Catalytic Processes for Natural Gas Valorization via Bromine Chemistry

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Summary

Catalytic alkane functionalization into bromoalkanes and their subsequent conversion into liquid fuels and chemicals presents an attractive technology for valorizing abundant and low-cost natural gas feedstocks. The industrial implementation of this route is contingent on the full recovery of hydrogen bromide (HBr), which is the end form of the halogen after the activation and upgrading steps. Catalytic oxidation of HBr into bromine (Br₂) and catalytic oxybromination of methane (CH₄) into bromomethane (CH₃Br) and dibromomethane (CH₂Br₂) are two processes indicating great potential to close the halogen cycle. However, the practical application of these pathways has been impeded by (i) insufficient activity and/or fast deactivation of HBr oxidation catalysts under realistic process conditions and (ii) limited CH₄ oxybromination selectivity to CH₃Br and CH₂Br₂.

This thesis contributes to the fundamental understanding of CH₄ oxybromination, provides guidelines for designing catalysts for this complex reaction scheme, and discovers new families of catalytic materials enabling the efficient bromine looping via both CH₄ oxybromination and HBr oxidation. The first insights into the chemistry of CH₄ oxybromination were gathered by investigating the activities and product distributions of different bulk oxide and phosphate catalysts and comparing those with the activities of these solids in the oxidation of HBr, CH₄, CH₃Br, and CH₂Br₂, the reaction steps that were suggested as participants in the overall mechanism. It was shown that the highest selectivity and yields to bromomethanes were attained over those structurally-stable catalysts that feature both a high activity in HBr oxidation and low propensity to combust CH₄ and brominated products. Along with the steady-state kinetics assessment, which implied substantial similarities between CH₄ oxybromination and non-catalytic CH₄ bromination, this observation suggests that the surface-catalyzed production of Br₂ and gas-phase bromination of CH₄ lead to C-Br bond formation. To address the impact of the hydrogen halide type on the oxyhalogenation, the same series of oxide and phosphate catalysts was further evaluated in CH₄ oxychlorination performance. The kinetic fingerprints have revealed that CH₄ activation by hydrogen chloride (HCl) and O₂ also involves the cooperation between the surface-catalyzed and gas-phase reactions. However, in contrast to oxybromination in which halogenation of CH₄ is proposed to control the activity, chlorine evolution appears to be a rate-determining step in oxychlorination. This induces stark activity and selectivity differences between the two halides. In particular, while the oxybromination over mildly oxidizing catalysts favors the production of bromomethanes, the oxychlorination
over these solids results in a highly selective production of CO, thereby providing a novel route for upgrading natural gas into this well-established platform chemical.

In view of halomethanes production, the use of HBr as the halogenating agent enables broader possibilities to enhance the selectivity. To this end, three strategies are devised in this thesis.

The first is based on using catalytic materials with redox active metal centers embedded in a matrix featuring a mild combustion propensity and a high structural stability in oxybromination. This led to the development of vanadium phosphate \((\text{VO}_2\text{P}_2\text{O}_7, \text{VPO})\), lanthanum vanadate \((\text{LaV}_{0.5}\text{O}_{2.75})\), and particularly europium oxybromide \((\text{EuOBr})\) catalysts, that have demonstrated both an outstanding selectivity to bromomethanes (up to 96%) and stable behavior. In addition to its exceptional performance in oxybromination, EuOBr has been shown as a unique catalytic material for HBr oxidation, enabling a high activity and outstanding stability using a stoichiometric feed composition. The specific activity was further enhanced and robustness preserved upon preparing a supported EuOBr/\(\text{Al}_2\text{O}_3\) catalyst with 9 wt.% europium loading, demonstrating its realistic practical potential.

The second strategy to enhance the selectivity and yield of \(\text{CH}_3\text{Br}\) and \(\text{CH}_2\text{Br}_2\) exploits the oxybromination under an increased partial pressure of HBr, resulting in a reduced combustion propensity of the catalyst surface due to an increase in the coverage of bromine. This approach was found particularly effective in the case of catalysts with strongly oxidizing action such as ceria \((\text{CeO}_2)\).

In the third strategy, the redox properties of \(\text{CeO}_2\) are tuned by supporting its nanocrystals over suitable carriers using low oxide loadings (0.5-2 wt.%). In particular, basic MgO support promotes the bromination in the surface region of the catalyst. This minimizes the production of \(\text{CO}_2\) under the stoichiometric feed, and eventually results in significantly higher selectivity to bromomethanes compared to the bulk \(\text{CeO}_2\), which offers attractive opportunities in view of potential catalyst scale-up into technical material.

The structure-performance relationships developed and steady-state kinetics acquired over different catalyst families hinted that C-H bond activation in oxybromination proceeds in the gas phase via homolytic dissociation mediated by free radicals. However, due to their short lifetimes and corrosive reaction environment, the direct detection of these highly reactive intermediates has been the long-standing challenge in oxyhalogenation. This thesis has demonstrated that \textit{operando} photoelectron photoion coincidence spectroscopy presents a powerful method to accomplish this goal. Namely, not only this method has provided the
evidence for the formation of methyl (CH₃●) and bromine (Br●) radicals over the benchmark EuOBr and VPO catalysts, but it also uncovered a strong correlation between the concentrations of the radicals and the production of bromomethanes. In addition, complemented with operando prompt gamma activation analysis that revealed extremely low coverage of bromine on VPO, it also provided unequivocal proof of the mechanism comprising surface-catalyzed oxidation of HBr generating Br● and Br₂ that then induce the gas-phase bromination of CH₄ as rationalized by molecular modeling.

The aforementioned concepts and findings provide the basis for efficient halogen looping in bromine-mediated natural gas upgrading and give momentum to the future developments in the halogen-based functionalization of alkanes.
Zusammenfassung


Diese Arbeit trägt zum grundlegenden Verständnis der CH4-Oxybromierung bei, zeigt Richtlinien für das Design von Katalysatoren für dieses komplexe Reaktionsschema auf und behandelt neue Katalysatorfamilien, die einen effizienten Bromkreislauf sowohl über CH4-Oxybromierung als auch über HBr-Oxidation ermöglichen. Die ersten Einblicke in die Chemie der CH4-Oxybromierung wurden durch den Vergleich der Aktivitäten und Selektivitäten verschiedener Oxid- und Phosphatkatalysatoren in dieser Reaktion mit deren Aktivität und Selektivität in der Oxidation von HBr, CH4, CH3Br und CH2Br2 gewonnen, da dies die ursprünglich vorgeschlagenen Teilreaktionen des Gesamtmechanismus sind. Es wurde gezeigt, dass die höchste Selektivität und Ausbeute an Brommethan mit strukturstabilen Katalysatoren erreicht werden kann, die sowohl eine hohe Aktivität in der HBr-Oxidation als auch eine geringe Neigung zur Verbrennung von Kohlenwasserstoffen und bromierten Produkten aufweisen. Zusammen mit einer Steady-State-Kinetik Analyse, die wesentliche Ähnlichkeiten zwischen CH4-Oxybromierung und nichtkatalytischer CH4-Bromierung impliziert, legt diese Beobachtung nahe, dass die oberflächenkatalysierte Produktion von Br2 und die Gasphasen-Bromierung von CH4 zur Bildung von C-Br-Bindungen führt. Um den Einfluss des Halogenwasserstofftyps auf die Oxyhalogenierung zu untersuchen, wurden die gleichen Oxid- und Phosphatkatalysatoren auf ihr Potenzial in der CH4-Oxychlorierung untersucht. Die kinetischen Fingerabdrücke zeigten, dass die CH4-Aktivierung durch Chlorwasserstoff (HCl) und O2 auch das Zusammenspiel zwischen der oberflächenkatalysierten Reaktion und der
Gasphasenreaktion beinhaltet. Im Gegensatz zur Oxybromierung, bei der die Halogenierung von \( \text{CH}_4 \) die Aktivität kontrolliert, scheint die Chlorentwicklung jedoch ein reaktionsratenbestimmender Schritt bei der Oxychlorierung zu sein. Dies verursacht gravierende Aktivitäts- und Selektivitätsunterschiede zwischen den zwei Halogeniden. Während die Oxybromierung über leicht oxidierenden Katalysatoren die Herstellung von Brommethanen begünstigt, führt die Oxychlorierung über diesen Materialien zu einer hochselektiven CO-Produktion, wodurch ein neuer Weg für die Veredelung von Erdgas durch diese etablierte Plattformchemikalie geschaffen wird.

Im Hinblick auf die Herstellung von Halometanen eröffnet die Verwendung von HBr als Halogenierungsmittel breitere Möglichkeiten zur Erhöhung der Selektivität. Zu diesem Zweck sind in dieser Arbeit drei Strategien entwickelt worden.

Die Erste basierte auf der Verwendung katalytischer Materialien mit in einer Matrix eingebetteten redoxaktiven Metallzentren, welche eine geringe Verbrennungsneigung und eine hohe strukturelle Stabilität in der Oxybromierung aufweisen. Dies führte zur Entwicklung von Vanadiumphosphat \((\text{VO})_2\text{P}_2\text{O}_7\), Lanthanvanadat \((\text{LaV}_{0.5}\text{O}_{2.75})\) und insbesondere Europiumoxybromid \((\text{EuOBr})\)-Katalysatoren, die sowohl eine hervorragende Selektivität für Brommethan (bis zu 96%), als auch gute Stabilität aufweisen. Zusätzlich zu seiner aussergewöhnlichen Leistungsfähigkeit in der Oxybromierung stellte sich \text{EuOBr} als herausragender Katalysator für die HBr-Oxidation heraus, da hohe Aktivität und hervorragende Stabilität bei niedrigen Temperaturen unter Verwendung von stöchiometrischen Edukteinsätzen erzielt werden konnten. Die Selektivität und Stabilität konnte noch weiter durch Aufbringung der aktiven \text{EuOBr} Phase (9 Gew.\% Metallanteil) auf ein \text{Al}_2\text{O}_3 Trägermaterial verbessert werden.

Die zweite Strategie zur Erhöhung der Selektivität und Ausbeute von \text{CH}_3\text{Br} und \text{CH}_2\text{Br}_2 nutzte die Oxybromierung unter erhöhtem Partialdruck von HBr, welches zu einer verringerten Verbrennungsneigung des Katalysators aufgrund einer Zunahme der Bromierung des Materials führte. Dieser Ansatz erwies sich als besonders effektiv bei stark oxidierend wirkenden Katalysatoren wie Ceroxid \((\text{CeO}_2)\).

Bei der dritten Strategie wurden die Redoxeigenschaften von \text{CeO}_2 verändert, indem dessen Nanokristalle auf geeignete Träger mit geringem Sauerstoffanteil (0,5-2 Gew.\%) aufgetragen wurden. Insbesondere basisches MgO unterstützt die Bromierung im Oberflächenbereich des Katalysators. Dies minimierte die Produktion von \text{CO}_2 unter stöchiometrischer Reaktantenzufuhr und führte schließlich zu einer signifikant erhöhten Selektivität für
Brommethane im Vergleich zu purem-CeO$_2$, was attraktive Möglichkeiten im Hinblick auf ein mögliches Upscaling des Katalysators im technischen Massstab bietet.

Author Contributions

During the work on this Thesis, the collaboration with experts from different fields was developed. In view of experiments, Vladimir Paunović synthesized and evaluated catalytic materials and was actively involved in their characterization by different methods. Guido Zichittella contributed to the catalyst preparation and evaluation in methane oxyhalogenation presented in Chapter 3, while Dr. Ronghe Lin contributed to the testing and characterization of HBr oxidation catalysts, which are discussed in Chapter 6. The electron microscopy analysis of the catalyst specimens was performed by Dr. Frank Krumeich in Chapters 2 and 4, and by Dr. Sharon Mitchell in Chapters 5 and 6. Dr. Roland Hauert and Dr. René Verel performed the X-ray photoelectron and solid state nuclear magnetic resonance spectroscopy measurements, respectively. Dr. Andras Bodi and Dr. Patrick Hemberger contributed to mechanistic study of methane oxybromination by Photoelectron Photoion Coincidence Spectroscopy, which is presented in Chapter 7, and Prof. Dr. Núria López performed the molecular level modeling of the reaction network. Their input on the interpretation of different results was essential to gather the comprehensive understanding of halogen-mediated upgrading of natural gas.
Chapter 1

Introduction

The prosperity of modern society strongly depends on the continuous supply of energy, and of chemicals and materials such as fertilizers, polymers, and pharmaceuticals, which are essential to sustain the growing world population and living standards.\textsuperscript{[1,2]} Since the dawn of the industrial era in the 18\textsuperscript{th} century, fossil resources comprising coal, oil, and natural gas have been driving the world economy, satisfying most of the energy demand and providing the main building blocks for the manufacture of fuels and base chemicals. Nonetheless, their finite reserves limit global development. On the other hand, technologies enabling the utilization of renewable resources such as solar energy, biomass, water, and carbon dioxide (CO\textsubscript{2}) for the production of energy and chemicals are still in an early developmental stage, and will likely require a long period of time to fit the demand. Moreover, the global potential of biomass is insufficient to sustain the production of chemicals and fuels due to the finite availability of arable land, competition with food crops, and low carbon-weight content.\textsuperscript{[3,4]} The most obvious solution to bridge the gap between the limited resources and growing societal needs is to maximize the use of the remaining fossil carbon reserves through technological advancement. Given the large reserves and potential to lower the CO\textsubscript{2} footprint, the valorization of natural gas into readily transportable liquid fuels and chemicals is recognized as one of the major strategies to accomplish this goal providing transitional feedstock towards renewable future.\textsuperscript{[5]}

1.1. Natural Gas: Status, Perspectives, and Challenges

Natural gas is particularly rich in methane (CH\textsubscript{4}, 75-99 mol.\%), although the content of ethane (C\textsubscript{2}H\textsubscript{6}, 1-15 mol.\%) and propane (C\textsubscript{3}H\textsubscript{8}, 1-10 mol.\%) is significant (Figure 1.1, left).\textsuperscript{[6,7]} Higher hydrocarbons, hydrogen (H\textsubscript{2}), helium (He), and impurities such as moisture (H\textsubscript{2}O), hydrogen sulfide (H\textsubscript{2}S), carbon oxides (CO, CO\textsubscript{2}), oxygen (O\textsubscript{2}), and nitrogen (N\textsubscript{2}), are typically present in low quantities. Nonetheless, the purification of the main alkane components is much less demanding compared to the purification of crude oil.\textsuperscript{[7]} Natural gas occurs naturally in
geological formations that are classified into two main categories, conventional or unconventional (Figure 1.1, bottom). Conventional gas is either associated with oil (associated gas) or accumulated in readily accessible rock formations (nonassociated gas), from which it is recovered by the well-established vertical drilling technology. Unconventional gas is trapped inside the pores of surface coal deposits (coalbed methane), deep and low-permeable rocks (shale and tight gas), or ice-like cages of water molecules formed under the low-temperature and/or high-pressure conditions experienced in permafrost areas and deep marine environments (methane hydrates). As a consequence, more sophisticated extraction technologies based on the vertical drilling in the case of coalbed methane, horizontal drilling and hydraulic fracturing of shale deposits, and depressurization or injection of heat, CO₂, or chemicals into the hydrates reservoirs are required. The proven recoverable reserves of conventional and unconventional gas were
estimated at ca. 200 trillion m³ worldwide at the end of 2016, which at the present state of consumption are sufficient for ca. 50 years, rivalling the remaining reserves of crude oil (Figure 1.1, right).\textsuperscript{[15,16]} Notably, recoverable reserves have increased by 18% since 2006, and 28% since 1996, which is primarily driven by breakthroughs in the extraction from gas shales. In this context, future developments toward tapping hydrate deposits, which the most conservative assessments predict to contain ca. 440 trillion m³ of gas, while the more optimistic estimates suggest up to two orders of magnitude higher quantities, may unlock the supply of this feedstock for over 200 years (Figure 1.1, right).\textsuperscript{[17–19]}

The ample reserves of natural gas complemented by the exceptionally high hydrogen to carbon ratio and up to one order of magnitude lower price compared to crude oil\textsuperscript{[20,21]} offer an attractive solution to the global thirst for energy, fuels, and chemicals.\textsuperscript{[5,22–31]} Most of the global gas production (ca. 90%) is nowadays used for heating, electricity generation, and transportation, which is also stimulated by the reduced environmental footprint of its combustion compared to coal and oil.\textsuperscript{[7,25,32]} In contrast, only a small portion (< 8%) is utilized as a raw material for the production of chemicals most commonly ammonia (NH₃), methanol (CH₃OH), dimethyl ether (CH₃OCH₃), liquid fuels, and hydrogen cyanide (HCN). The current situation reflects the unique inertness of C-H bonds in CH₄,\textsuperscript{[25,32]} which exhibit the highest bond energy (440 kJ mol\textsuperscript{−1}) among all alkanes and low polarity.\textsuperscript{[22,25,27]} Consequently, its functionalization via electrophilic hydride abstraction imposes a high activation barrier due to the low stability of the methyl cation, while the high energy of the C-H σ* orbital hinders a nucleophilic attack on the carbon atom. The alternative homolytic C-H bond scission is impeded due to the low stability of the methyl radical (CH₃•), although this is the most facile activation pathway.\textsuperscript{[25]} For these reasons, reactive chemical reagents and/or harsh reaction conditions are typically required to activate CH₄.

1.2. Catalytic Technologies for Natural Gas Upgrading

Except for HCN synthesis,\textsuperscript{[33]} commercial technologies for CH₄ upgrading involve its steam or autothermal reforming over nickel-based catalysts (Figure 1.2, left). These yield a mixture of CO and H₂, known as syngas,\textsuperscript{[32,34]} which is transformed into CH₃OH over Cu/ZnO/Al₂O₃ catalysts,\textsuperscript{[35,36]} or higher hydrocarbons via Fischer-Tropsch synthesis over iron- and cobalt-based
Catalytic materials.\textsuperscript{[37]} This gas mixture is also used in hydroformylation processes and as a H\textsubscript{2} pool for ammonia synthesis.\textsuperscript{[38,39]} The syngas route provides a high single-pass yield (ca. 40-80\%) on a carbon basis.\textsuperscript{[40–42]} Nonetheless, the extremely high temperatures (1073-2273 K) required to produce CO and H\textsubscript{2} result in high capital expenditures and low thermal efficiency (ca. 50\%) compared to conventional petroleum refineries (> 90\%), which diminish the cost advantage of natural gas over oil.\textsuperscript{[40,42]} Given the maturity of syngas technologies, the only strategy to improve the process economy and preserve the competitiveness rests on the construction of megaplants.\textsuperscript{[40,41]} However, this contrasts the world-wide distribution of natural gas (Figure 1.1, middle), since a significant portion of the proven reserves (30-80\%) includes small and scattered wells, which are far from the main consumption centers.\textsuperscript{[19,24,43–46]} The transport of gas to the centralized chemical plants using pipelines or in the liquefied formed is only economical for the large reservoir capacities or short distances to the market.\textsuperscript{[47]} In the absence of cost-efficient alternatives, this stranded gas is often reinjected back into the reservoirs, or flared in order to reduce the direct atmospheric emissions of CH\textsubscript{4}, since the latter exhibits a greenhouse effect ca. 28 times stronger than that of CO\textsubscript{2} over a hundred-year horizon.\textsuperscript{[22,25,26,29,32]} Shockingly, the current amount of flared natural gas (ca. 3.5\%) is comparable to the fraction that is used for commodities production (vide supra).\textsuperscript{[48]} To harvest this abundant, essentially free feedstock and

**Figure 1.2.** Commercial (left) and alternative (right) catalytic routes for methane valorization.
counteract this wasteful practice new technologies are required enabling the cost-effective on-site transformation into readily transportable chemicals and liquid fuels.[5,22–31]

One of the main pitfalls of syngas generation originates from the approach of completely dissociating the strong C-H bonds in CH$_4$, which are later reestablished upon the synthesis of the final products (e.g., CH$_3$OH). Thus, it is proposed that future catalytic processes for natural gas valorization should pursue the direct functionalization of CH$_4$ into platform molecules such as CH$_3$OH,[31,42,49,50] methyl halides (CH$_3$X, X = Cl, Br),[5,29,51] olefins,[23,30,52–56] or aromatics (Figure 1.2, right).[30,55–57] In this context, (i) a high selectivity to desired product(s) (> 90%), (ii) a high space-time yield ($STY \geq 10^{-6}$ mol s$^{-1}$ cm$^{-3}$), (iii) low operating temperatures (preferably ≤ 523 K), and (iv) minimal number of process steps are required in order to minimize the separation train, process emissions, reactor size and cost, energy inputs, and heat management.[42] Besides, (v) the use of air as the ultimate oxidant is preferred due to the high price of an O$_2$-production plant or alternative oxidants. The principal challenge of direct activation comes from the higher activity of the desired intermediates compared to CH$_4$, which drives the reaction towards the thermodynamically most stable products such as CO$_2$ or carbon (coke), resulting in selectivity losses.[25]

Over the past decades several heterogeneously catalyzed processes targeting the one-step functionalization of CH$_4$ have been intensively studied (Figure 1.2).[5,22–31,42] Non-oxidative routes enable the conversion of CH$_4$ into aromatics, olefins, and H$_2$, which is free of CO$_2$ production.[30,55–57] Like syngas-based routes, however, these transformations are endothermic and require high temperatures to achieve desirable reaction rates. Besides, the porous catalysts applied deactivate rapidly due to coking, requiring frequent oxidative regeneration.[30,56,57] On the other hand, the exothermic nature of oxidative routes offers advantages both in terms of the ease of conversion and the potential to reuse the reaction heat within the process. The oxidative coupling of CH$_4$ into C$_2$H$_4$ is one of the most studied catalytic reactions given the large market size of the latter intermediate.[23,28,53,54,58,59] It proceeds by the formation of methyl radicals (CH$_3^\cdot$) through a hydrogen abstraction by the surface oxygen species, followed by their quenching into C$_2$H$_6$ in the gas phase, and subsequent dehydrogenation of the latter by a catalyst or CH$_3^\cdot$.[23,52,60] Kinetic analysis suggests that this mechanism limits a single-pass yield to around 30% due to the higher propensity of the catalysts to dissociate the weaker C-H bonds
of C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} compared to CH\textsubscript{4}, which favors the production of CO\textsubscript{x} at higher conversion levels.\[63] As a matter of fact, after four decades of intense research and hundreds of catalysts investigated, the yield (<30\%) and the selectivity (70-85\%) to C\textsubscript{2} products (comprising a molar C\textsubscript{2}H\textsubscript{4}:C\textsubscript{2}H\textsubscript{6} ratio of ca. 5-40) are still below the industrially attractive thresholds of 30\% and 90\%, respectively.\[28,53,54] In addition, catalyst deactivation due to sintering, coking, and leaching of the active phase constitutes an additional challenge for this technology.\[59\

The selective oxidation of CH\textsubscript{4} into CH\textsubscript{3}OH or formaldehyde (CH\textsubscript{2}O) is often regarded as a “dream reaction”, owing to severe constraints for its practical accomplishment. The attractive yield and selectivity to CH\textsubscript{3}OH are achieved using homogeneous mercury and platinum complexes in concentrated sulfuric acid, followed by the hydrolysis of the intermediate methyl bisulfate.\[42,50,62] However, low space-time yields, the expensive re-oxidation of byproduct sulfur dioxide, and the challenging catalyst separation hamper the industrialization.\[25] The more preferred oxidation of CH\textsubscript{4} over heterogeneous catalysts has failed to provide yields of CH\textsubscript{3}OH and CH\textsubscript{2}O higher than ca. 1\% and ca. 7\%, respectively, while maintaining the selectivity > 30\% due to a much faster deep oxidation of these products into CO\textsubscript{x}.\[25,28,31] A higher selectivity to CH\textsubscript{3}OH has been recently achieved over copper and iron clusters confined in the zeolite pores, which are operated in a quasi-catalytic cyclic process, involving the oxidation of the active sites in the first step, followed by CH\textsubscript{4} oxidation and CH\textsubscript{3}OH extraction in the subsequent steps.\[63,64] Nonetheless, this concept results in extremely low space-time yield, which makes it far away from an industrial reality.

Halogenation or oxyhalogenation of CH\textsubscript{4} into CH\textsubscript{3}X (X = F, Cl, Br, I) show great potential to mitigate the selectivity challenges encountered in oxidative routes while preserving high space-time yields.\[5,29] CH\textsubscript{3}X can be converted into a wide spectrum of liquid products such as alcohols, ethers, olefins, or gasolines using conceptually similar catalytic pathways as those practiced in methanol upgrading, which generally involve the elimination of halogen in the form of hydrogen halide (HX).\[5,29,51,65–68] The recovery of HX via catalytic oxidation or oxyhalogenation ultimately allows for the use of oxygen or air as actual oxidants of CH\textsubscript{4}.\[5,29,69,70] Among the halogens, chlorine (Cl\textsubscript{2}) and bromine (Br\textsubscript{2}) are the most suitable for practical implementation, since the reaction of CH\textsubscript{4} with fluorine (F\textsubscript{2}) is extremely vigorous and even explosive, while the activation with iodine (I\textsubscript{2}) is thermodynamically limited.\[66,71] Although less
abundant and more expensive than Cl₂, Br₂ shows distinctive advantages in view of the higher attainable selectivity to CH₃X, and lower C-Br and H-Br bond energies compared to those of chlorine, which facilitate halogen elimination as well is the re-oxidation of hydrogen bromide (HBr), respectively.[29,72,73] Besides, provided it is possible to achieve 100% recovery, the halogen price plays a marginal role in the overall economics.

1.3. Bromine-Mediated Natural Gas Upgrading

Although the discovery of alkane bromination cannot be precisely located, it likely occurred soon after Dumas described the chlorination of CH₄ in 1840,[74] since the literature of the first half of 20th century already reports these processes as well-known chemical transformations. For example, in 1918, Spelling disclosed an improved method for the halogenation of CH₄ and other light alkanes using chlorine or bromine.[75] The first patents presenting the conversion of halomethanes into different commodity chemicals were filed between the 1920s and 1940s.[65,70] Since the 1970s, several new concepts such as the conversion of CH₃X into higher hydrocarbons over zeolite catalysts,[77] electrophilic CH₄ halogenation,[78] and CH₄-to-CH₃OH conversion using FeBr₃,[79] have been developed. Interest in alkane valorization using bromine chemistry was reignited in the early 2000s in response to the shale gas “revolution”. A series of patents was filed,[80–82] and a joint venture aiming to build the first facility exploiting Br₂ for the conversion of natural gas was announced. Only recently, CH₄-to-aromatics technology employing Br₂ as the active agent was proven at the demonstration plant and is now offered for commercialization.[83]

The backbone steps of the bromine-mediated CH₄ upgrading comprise: (i) CH₄ bromination into CH₃Br and byproduct dibromomethane (CH₂Br₂),[51,66,78] (ii) reforming of CH₂Br₂ into CH₃Br,[84,85] and (iii) elimination of bromine from CH₃Br to yield higher hydrocarbons or oxygenates (Figure 1.3).[51,67,71,80–82,86–92] The bromination of CH₄ is typically conducted non-catalytically, i.e., in an empty reactor using contact times in the range of 1-60 s at 673-873 K and < 4 bar.[66,71,81] The reaction proceeds via a radical-chain pathway, wherein in the first fast and kinetically-controlled phase, the dissociation of Br₂ generates bromine radicals (Br•), which abstract hydrogen atom from CH₄ yielding HBr and CH₃•.[84,85] The latter intermediates react with Br₂ forming CH₂Br and regenerating Br•. As the reactivity in bromination increases in the order CH₄ < CH₃Br < CH₂Br₂ < CHBr₃, this reaction phase leads to
a complete bromine consumption, low CH₄ conversion, and high selectivity to polybromomethanes (CH₄ₓBrₓ, x > 1). Nonetheless, in contrast to their chlorinated counterparts, CH₄ₓBrₓ can brominate CH₄ in a second slower and thermodynamically controlled phase, which is known as reproportionation. At sufficiently long residence times (up to 60 s), the conversion of CH₄ and the selectivity to CH₃Br reach up to 73.5% and 69.5%, respectively, with CH₂Br₂ as the only byproduct.[84] Further selectivity enhancements are accomplished by conducting the reaction under CH₄ excess (a molar CH₄:Br₂ ratio of 2-10).[66,82] The bromination of CH₄ can also be performed catalytically over superacid catalysts. These enable the polarization of a Br₂ molecule, which permits activation of the C-H bond via electrophilic attack, leading to the formation of five-coordinate carbonium ions.[51,78] In contrast to the radical pathway, an increased degree of bromine substitution decreases the electron density of the remaining C-H bonds and sterically hinders electrophilic insertion. This explains the almost complete selectivity

Figure 1.3. Possible process scheme for natural gas upgrading via bromine chemistry.
Introduction
to CH$_3$Br (up to 99%) over several catalytic systems comprising supported precious metals,$^{[51]}$ oxyhalides,$^{[78]}$ and sulfated zirconium and niobium catalysts,$^{[80,94]}$ which typically operate at lower temperatures (473-613 K) compared to the non-catalytic bromination. Nonetheless, the reported space-time yields of catalytic processes are relatively low and no information is available on their long-term stability.

The reforming of CH$_2$Br$_2$ into CH$_3$Br comprises an intermediate step (Figure 1.3), which not only increases the yield of monosubstituted product, but also extends the lifetime of the coupling catalysts applied downstream, since polybrominated hydrocarbons are the main precursors of coke formation.$^{[66,71,85,91,95,96]}$ The reproportionation of CH$_2$Br$_2$ using an excess of CH$_4$ or other light alkanes that are recycled from the coupling reactor presents the main reforming route described in patent literature.$^{[71,84,91,95]}$ It is typically arranged as the non-catalytic process, taking place in the last section of the bromination reactor or in a separate reactor. Attempts to promote this reaction using heterogeneous systems suffered from limited catalyst lifetime due to coking.$^{[95]}$ The hydrodebromination of CH$_2$Br$_2$ represents an alternative process that has been recently studied over silica supported ruthenium, platinum, palladium, silver, and gold, as well as palladium on carbon.$^{[85]}$ A substantial selectivity to CH$_3$Br was achieved over ruthenium-based catalyst, while palladium on carbon displayed the highest activity and the possibility to generate higher hydrocarbons such as olefins.

The valorization of CH$_3$Br can be accomplished via (i) coupling into olefins, higher paraffins, and aromatics,$^{[66,86-92,97]}$ (ii) hydrolysis into CH$_3$OH or CH$_3$OCH$_3$,$^{[51,98-100]}$ or (iii) carbonylation into acetic acid (Figure 1.3).$^{[67,101]}$ CH$_3$Br coupling is typically performed over zeolite catalysts based on ZSM-5 and SAPO-34 frameworks, which provide the highest reaction rates and favor the production of light (C2-C3) olefins. In its essence, the reaction closely resembles the much more studied CH$_3$OH-to-hydrocarbons processes and is hypothesized to involve a similar mechanism.$^{[86,97]}$ Just like in CH$_3$OH coupling, the zeolite catalysts face the problem of coke formation and consequential deactivation, which is particularly pronounced in the presence of polybrominated compounds.$^{[66,71,85,91,95,96]}$ Although the combustion of the carbonaceous deposits restores the original activity,$^{[86]}$ coking has a negative impact on the overall carbon efficiency. Reforming of CH$_2$Br$_2$ and modification of ZSM-5 zeolites with magnesium oxide or desilication with fluorine anions are found effective in extending operation, which can exceed 400 h on
In addition to zeolites, CH$_3$Br can be coupled into C2-C5 alkanes using liquid AlBr$_3$ at ca. 473 K and < 20 bar.\[^{[87]}\] The main advantage of this approach relates to the simple separation of the catalyst and products from the carbonaceous deposits, which can be recovered by hydrogenation.

The hydrolysis of CH$_3$Br into CH$_3$OH and CH$_3$OCH$_3$ can be accomplished in the gas phase over bare \(\gamma\)-Al$_2$O$_3$ or basic metals supported on \(\gamma\)-Al$_2$O$_3$ using an excess of steam, or in the liquid phase over a homogeneous RuCl$_3$-based catalyst.\[^{[51,98]}\] The former approach results in low conversions and suffers from catalyst deactivation, while the tedious separation of products in the latter route makes it less suitable for the practical implementation. CH$_3$Br can be hydrolyzed into oxygenates by reacting with basic oxides, which are then transformed into the respective bromides, or using a poly(4-vinylpyridine) solution.\[^{[80,99,100]}\] These so-called cataloreactant systems result in the formation of CO$_2$ and necessitate the regeneration of the catalyst by oxidation in a separate step. CH$_3$Br can be carbonylated using homogenous RhCl$_3$-PPh$_3$-KI catalytic system.\[^{[67,101]}\] Thereby the excellent yields of acetic acid (> 99%) can be obtained.

### 1.4. Bromine Recovery in Natural Gas Upgrading

As detailed above, CH$_4$ bromination, CH$_2$Br$_2$ reforming, and CH$_3$Br upgrading generate HBr as a stoichiometric byproduct (Figure 1.3), which needs to be recovered using inexpensive O$_2$ or air in order to close the bromine loop.\[^{[69,70]}\] To this end, several technologies have been investigated, but none of them has yet been commercialized. The electrolysis of HBr in liquid or gas phase, provides significant Br$_2$ yields at high current efficiencies, and also allows for H$_2$ evolution, which can be employed in hydrodebromination.\[^{[101-106]}\] Despite these advantages, the high costs compared to alternative processes limit the broad application of this route.\[^{[107]}\]

Cataloreactants comprise metal oxides (MO$_x$, e.g., NiO, CuO, MgO, and CaO) or aqueous suspensions of metal hydroxides (M(OH)$_2$, e.g., Fe(OH)$_3$ and Cu(OH)$_2$) which react with HBr to form (oxy)bromides (MO$_{x-y/2}$Br$_y$), enabling the separation of the halogen from unconverted alkanes, bromoalkanes, and different coupling products.\[^{[71,80,91,108]}\] Oxidation of MO$_{x-y/2}$Br$_y$ by O$_2$ or air in a separate step generates Br$_2$ and recovers MO$_x$ or M(OH)$_2$. Although conceptually simple, cataloreactants typically suffer from limited cyclability and short lifetimes due to the sintering and/or volatilization of MO$_{x-y/2}$Br$_y$, which additionally complicates the control of this
non-stationary process. In this context, HBr oxidation over heterogeneous catalysts represents a more attractive technology enabling continuous and energy-efficient bromine looping.\cite{69,70,107,109,110} As noted in the first patent on this process filed by Hooker in 1937,\cite{109} catalytic HBr oxidation resembles the industrially applied Deacon process (HCl oxidation), but without the thermodynamic limitations, permitting 100% HBr recycling. This patent also presents the first examples of catalysts containing oxides and salts of cupper, cerium, nickel, cobalt, manganese, thorium, or mixtures thereof supported on carriers such as pumice, quartz, or ceramics. Since then, different catalytic materials comprising transition metals such as ruthenium, platinum, palladium, iron, chromium, and vanadium have been investigated, although the main focus was on cupper- and cerium-based systems.\cite{107,110–117} The recent advances in Deacon chemistry led to the discovery of RuO$_2$/TiO$_2$, U$_2$O$_3$/ZrO$_2$, CeO$_2$/ZrO$_2$, and IrO$_2$/TiO$_2$,\cite{118–121} which also display remarkable activity in HBr oxidation.\cite{69,122} In particular, RuO$_2$/TiO$_2$ exhibits the highest reaction rate at temperatures as low as 473 K. However, the implementation of the leading catalytic materials is hampered by their deactivation when the reaction is performed at low temperatures (< 573 K) and under (close to) stoichiometric molar O$_2$:HBr ratio (O$_2$:HBr = 0.25) in the inlet feed, which is caused by the progressive incorporation of bromine in their subsurface structure.\cite{122,123} On the other hand, the latter conditions, which allow for the use of air as an oxygen source and to minimize the construction costs, are essential for industrialization. Besides, lower reaction temperatures contribute to improved process control and safety. Prior to this thesis, TiO$_2$ was the only catalyst known to be inherently resistant against the bromination due to a unique self-doping mechanism.\cite{70,123} However, it exhibits a rather low activity in the preferred low-temperature window.

Compared to previously discussed technologies, CH$_4$ oxybromination into CH$_3$Br and CH$_2$Br$_2$ (Figure 1.3) combines HBr recovery and CH$_4$ bromination in a single step.\cite{29} Moreover, in contrast to bromination, wherein 50% of bromine atoms ends up as HBr, oxybromination theoretically allows for 100% bromine incorporation into the halogenated products. Hence, this reaction, which is conceptually analogous to ethylene oxychlorination, the process used to recycle waste HCl streams in the polyvinyl chloride industry,\cite{124} provides a basis for highly desired process intensification. In spite of its great potential, only a few catalytic materials such as oxides of ruthenium, rhodium, vanadium, tungsten, barium, molybdenum, and cerium, as well as
Chapter 1

Iron phosphate (FePO₄) have been investigated. Similar to HBr oxidation, the oxybromination catalysts need to fulfill stringent stability criteria. Besides, the presence of O₂ in the reaction feed provokes the side combustion reactions, which lead to undesired selectivity loss of bromomethanes through the formation of COₓ. Thereby, the design of novel catalytic systems which could overcome the above stated challenges is additionally impeded by the absence of the mechanistic understanding of this reaction.

The catalytic oxidation of HCl and HBr has been intensively studied by the group of Prof. Dr. Javier Pérez-Ramírez during the last decade, with particular focus on the development of stable and active materials and their mechanistic understanding. This thesis expands the research in the area of HBr oxidation and opens the field of catalyst design for CH₄ oxybromination, which are the pillars of bromine-mediated natural gas upgrading.

1.5. Aim of the Thesis

This thesis aims to develop catalytic materials for the efficient recovery of bromine in the context of natural gas valorization. The comprehensive characterization and kinetic evaluation of different catalyst families, as well as the detection of the main intermediates and reaction pathways by using advanced operando methods and molecular modeling contribute to fundamental understanding of CH₄ oxybromination. This allows the derivation of structure-performance relationships to guide the design of the optimal catalytic material, providing a high yield to bromomethanes. This work also addresses the impact of the hydrogen halide type on activity and selectivity patterns in catalytic oxyhalogenation. Another focal point comprises the extrapolation of the hitherto established activity and stability descriptors to the discovery of a catalyst enabling the low-temperature oxidation of HBr using a stoichiometric reaction feed. Finally, the findings accomplished within this work are expected to provide the background for the practical implementation of these processes.

1.6. Outline of the Thesis

The achievements of this thesis are presented in six Chapters (Chapters 2-7) followed by the Conclusions and Outlook (Chapter 8).
Chapter 2 provides a systematic study of various oxide and phosphate catalysts in CH$_4$ oxybromination in relation with their activity in the oxidation of HBr, CH$_4$, CH$_3$Br, and CH$_2$Br$_2$, which are proposed to contribute to the catalytic cycle, enabling the derivation of criteria for their optimal performance in the former reaction. The latter are adequately met by vanadium phosphate (VPO), which is found to exhibit a highly selective and stable production of bromomethanes. Its kinetic fingerprint suggests that the formation of the C-Br bond may proceed via gas-phase reaction pathways.

Chapter 3 compares CH$_4$ oxybromination and oxychlorination over the set of catalysts introduced in Chapter 2, highlighting mechanistic similarities and distinctions between the two reactions. The activity and the selectivity in oxyhalogenation are found to strongly depend on the hydrogen halide type and for certain catalysts on its partial pressure, which may lead to a complete switch in the product distribution. Specifically, it is demonstrated that the use of HCl instead of HBr over VPO offers a highly selective route for the production of CO, a key platform for commodities production. Nevertheless, in terms of maximum attainable selectivity to halomethanes, the use of HBr is more advantageous over most of the studied materials.

Chapter 4 develops composition-structure-performance relationships for CH$_4$ oxybromination over lanthanum vanadates, LaV$_x$O$_{2.5x+1.5}$, which display stable behavior in the compositional range of $0.2 \leq x \leq 1$. The selectivity to bromomethanes of stoichiometric LaVO$_4$ ($x = 1$) can be substantially enhanced when a certain excess of lanthanum is used ($x < 1$). This is due to the synergetic interaction of LaVO$_4$ with LaOBr nanocrystals, which are formed by the partial bromination of La$_2$O$_3$ during the reaction. LaV$_{0.5}$O$_{2.75}$ yields the optimum performance which ranks it among the best reported oxybromination catalysts.

Chapter 5 demonstrates an effective strategy to tailor the oxidizing potential of CeO$_2$ by nanostructuring this phase over appropriate carriers, hence boosting the selectivity and yield to bromomethanes. The product distribution is shown to be strongly dependent on the carrier type, which not only affects the dispersion, structure, and redox properties of the active phase, but also displays a variable degree of inertness in the undesired oxidation of bromomethanes. The use of a basic MgO support stabilizes CeO$_2$ nanoparticles and minimizes their combustion activity by favoring the surface-confined bromination, thereby significantly enhancing the selectivity to CH$_3$Br and CH$_2$Br$_2$ compared to bulk CeO$_2$. 
Chapter 1

Chapter 6 introduces europium oxybromide, EuOBr, as a unique active phase enabling unparalleled selectivity to CH$_3$Br in CH$_4$ oxybromination and stable oxidation of HBr at low temperatures using a stoichiometric feed mixture. To maximize the utilization of the EuOBr phase in bromine recovery processes, strategies to support it over technical bodies are devised, demonstrating its realistic potential for sustainable bromine looping in natural gas upgrading.

Chapter 7 elucidates the mechanism of CH$_4$ oxybromination over VPO and EuOBr catalysts. Operando photoelectron photoion coincidence spectroscopy with synchrotron radiation is implemented to yield key evidence on the formation of gaseous CH$_3^\cdot$ and Br$_2^\cdot$ radicals over the catalysts, and the strong correlation between the radicals concentration and the yield of bromomethanes. Operando prompt gamma activation analysis indicates the extremely low bromine coverage, implying a low probability of the catalytic CH$_4$ bromination. These results complemented with the steady-state kinetic analysis and molecular modeling elucidate the surface-catalyzed generation of Br$^\cdot$ and Br$_2$ followed by the gas-phase CH$_4$ bromination as the main reaction pathway.

Chapter 8 summarizes the major findings and concepts introduced in this thesis, discusses their relevance, and outlines the future research directions in the field of halogen-mediated natural gas upgrading.

*Each chapter in this thesis was written based on one or more separate publications and can be read independently. Accordingly, some overlap cannot be avoided.*
Chapter 2
Catalytic Oxybromination for Natural Gas Upgrading

2.1. Introduction

The emerging conventional and unconventional natural gas reserves, which contain copious amounts of methane (CH₄, 75-99 mol.%), but also of ethane (C₂H₆, 1-15 mol.%) and propane (C₃H₈, 1-10 mol.%), offer an exciting potential as a feedstock for value-added chemicals and fuels.[5,6,25,66,80,87,108,131,132] However, currently less than 10% of the global natural gas production is used for the manufacture of commodities and the rest is burned for heating, transport, and electricity generation purposes.[5,25] This reflects the inadequacy of state-of-the-art technologies for natural gas upgrading, inevitably intermediated by energy- and capital-intensive reforming processes.[5,25] Thus, more-efficient methods that allow a selective one-step functionalization of the rather inert C-H bonds in CH₄ and other alkanes have been recognized as important goals in catalysis research. As noted in Chapter 1, among various strategies proposed, halogen-based processes are particularly attractive as they enable a homolytic C-H bond scission in the gas phase to proceed in a selective fashion under relatively mild conditions ($T < 800 \text{ K, } P \approx 1 \text{ bar}$).[5,36,133] Bromination is preferred over chlorination as it provides a high selectivity for monohaloalkanes (also referred to as alkyl halides) and facile halogen elimination because of the weaker C-Br bond (284.9 kJ mol⁻¹) compared with the C-Cl bond (338.9 kJ mol⁻¹).[5] Notably, the bromination of alkane to give bromoalkane, and the subsequent dehydrobromination of the latter to give a wide range of valuable products release HBr. The efficient recovery of bromine from the byproduct HBr is a decisive factor to realize this approach on an industrial scale. The gas-phase oxidation of HBr over the recently developed RuO₂-, IrO₂-, CeO₂- or TiO₂-based systems, which generally proceeds at much lower temperatures compared with those of HCl oxidation, can be implemented as a separate step to close the bromine cycle.[60,70] However, the integration of the alkane functionalization with the HBr recovery in a single-step process via an oxybromination reaction is
conceptually a more advanced strategy, as it enables process intensification and a theoretical 100% halogen atom efficiency.\cite{67,89,125,127,134} In fact, the oxyhalogenation of light alkanes, which has a long history dating back to the first half of the 20th century,\cite{65} has been forecast as the most cost-effective technology for natural gas upgrading.\cite{5} Different materials, such as noble Ru- and Rh-based catalysts, as well as non-noble FePO$_4$ and CeO$_2$ systems, have been reported to catalyze the oxybromination of CH$_4$, which is typically claimed to proceed as a heterogeneously catalyzed reaction.\cite{67,89,125,127,134} Besides the polybromination that leads to CH$_2$Br$_2$ formation, CO$_2$ generation is the main challenge in this reaction because it eventually limits the yield of the brominated products.

The present Chapter aims to develop an oxybromination process for the selective functionalization of CH$_4$, through symbiosis between heterogeneously catalyzed HBr oxidation and gas-phase alkane bromination, sustained by bromine pool that is, in turn, regenerated on the catalyst surface by molecular oxygen (O$_2$). The C-H bond scission is thus decoupled from the highly reactive oxygen species on the catalyst, which would generally promote the undesired deeper oxidation of alkane and brominated products. The key to accomplish this microlevel spatiotemporal management of the complex heterogeneous gas-phase network is to find a catalyst that is able to oxidize HBr, but is inert with respect to the C-H bonds of the carbon-containing molecules. Owing to their stability and operational window, which generally coincides with that of the gas-phase alkane bromination, the above-mentioned HBr oxidation catalysts are interesting candidates to investigate in the oxybromination reaction,\cite{69,70} although their strong oxidizing character is likely to cause substantial combustion. These undesired oxidation reactions can be suppressed by applying the concept of redox-site isolation through dispersion in a quasi-inert matrix, such as phosphates, and thereby enabling better control of the surface-active oxygen species, as well as fine tuning of the redox and acid-base properties.\cite{135,136} The phosphate incorporation also ensures that the redox centers are more stable under the highly corrosive oxybromination conditions,\cite{137} and the involvement of lattice oxygen (the Mars-van Krevelen mechanism) makes the oxidation less severe.\cite{135,136}

Here the catalytic activity of different oxides and phosphates in the oxybromination of CH$_4$ was investigated systematically and a set of new active oxybromination catalysts identified. Vanadium phosphate (VPO) was observed to be the best, with an operating temperature approximately
100 K lower than those of previous reports.[67,89,125,127,134] Performance differences among various catalysts were related to their activities in the oxidation of HBr, CH₄, and bromomethanes (CH₃Br and CH₂Br₂), which are proposed to constitute the key descriptors of the oxybromination potential. The mechanism of CH₄ oxybromination over VPO, which involves heterogeneous HBr oxidation coupled with gas-phase CH₄ bromination, was supported experimentally and, based on that, feed-optimization strategies to maximize the CH₃Br selectivity and productivity are discussed. Finally, the oxybromination of the more-activated light alkanes, such as C₂H₆ and C₃H₈, over VPO was investigated.

2.2. Experimental

2.2.1. Catalyst Preparation

TiO₂ (Aldrich, rutile nanopowder, 99.5%) and Cu₃(PO₄)₂ (ABCR, 98%), RuO₂ (Sigma Aldrich, 99.9%) and CeO₂ (Sigma Aldrich, 99.9%) were calcined at 823, 723 and 1173 K, respectively, in static air with a heating rate of 5 K min⁻¹ for 5 h. VPO was prepared via an organic route.[136] A suspension of V₂O₅ (15 g; Aldrich, ≥ 99.6%) in isobutanol (90 cm³; Acros, > 99%) and benzyl alcohol (60 cm³; Sigma Aldrich, > 99%) was refluxed for 3 h. After cooling to room temperature, H₃PO₄ (Sigma Aldrich, ≥ 85%) was added to set the molar P:V ratio to 1.2 and the mixture was then refluxed for another 16 h. The resulting slurry was separated by filtration, washed with isobutanol and methanol (Fluka, ≥ 99.9%), dried in vacuum (50 mbar) at 373 K for 16 h and finally activated in flowing air (100 cm³ min⁻¹) at 823 K (heated at 5 K min⁻¹) for 5 h. FePO₄ was prepared by mixing the Fe(NO₃)₃·9H₂O (13.38 g; Sigma Aldrich, ≥ 98%) and (NH₄)H₂PO₄ (3.81 g; Acros, > 99%) in deionized water for 2 h, then dried in vacuum (50 mbar) at 363 K for 16 h and calcined in flowing air (100 cm³ min⁻¹) at 873 K (5 K min⁻¹) for 5 h. CrPO₄ was synthesized by mixing aqueous CrCl₃·6H₂O (0.09 M, 1 dm³; Aldrich, ≥ 98%) and KH₂PO₄ (0.09 M, 1 dm³; Fluka, ≥ 99.5%) in deionized water with NaCH₃COO·3H₂O (0.1 M; Acros, > 99%) for 6 h. The precipitate was recovered by filtration, washed with water, dried in vacuum (50 mbar) at 363 K for 3 h, and finally calcined in flowing air (100 cm³ min⁻¹) at 1273 K (20 K min⁻¹) for 3 h. The preparation of the other metal phosphates, CePO₄, LaPO₄, TiP₂O₇, Mn₃(PO₄)₂, CoPO₄, Ni₃(PO₄)₂, and Zn₃(PO₄)₂, studied in this work is provided in the Annex of Chapter 2.
2.2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) measurements were carried out with a PANalytical X’Pert PRO-MPD diffractometer. Data were recorded in the 10-70° 2θ range with an angular step size of 0.017° and a counting time of 0.26 seconds per step. N₂ sorption at 77 K was performed using a Quantachrome Quadrosorb-SI analyzer. Prior to the measurement, the solid was evacuated to 50 mbar at 573 K for 12 h. Temperature programmed reduction with hydrogen (H₂-TPR) was measured using a Micromeritics Autochem 2920 unit. The sieved sample (40 mg) was loaded into a U-shaped quartz microreactor and pretreated in He (20 cm³ min⁻¹) at 473 K for 30 min. The analysis was carried out in 5 vol.% H₂ in Ar (20 cm³ min⁻¹), ramping the temperature from 473 to 1203 K at 10 K min⁻¹. The magic-angle spinning nuclear magnetic resonance phosphorous-31 (³¹P MAS NMR) spectra were acquired at a spinning speed of 80 kHz by using a Bruker Avance 400 NMR spectrometer at 400 MHz and 9.4 T. The spectra were recorded by using 512 accumulations at pulses of 8 ms and a relaxation time of 1 s, with 85% H₃PO₄ as a reference. High-resolution transmission electron microscopy (HRTEM) measurements were performed using a FEI Tecnai F30 ST microscope with field emission gun operated at 300 kV.

2.2.3. Catalyst Testing

CH₄, C₂H₆, and C₃H₈ oxybromination, CH₄ bromination, CH₄, CH₂Br, CH₂Br₂, and HBr oxidation were performed at ambient pressure in a continuous-flow fixed-bed reactor setup, which is described in Appendix A. The catalyst was loaded in a quartz reactor (internal diameter, \(d_c = 16\) mm, except for HBr oxidation, \(d_c = 8\) mm) between the two plugs of quartz wool to form a fixed-bed the volume of which was in the range of \(V_{bed} = 0.5-2\) cm³. Non-catalytic gas-phase CH₄ bromination was performed over the bed of quartz particles (\(d_p = 0.4-0.6\) mm, \(V_{bed} = 2.0\) cm³). In alkane oxybromination, CH₄ bromination, and CH₄ oxidation the post-catalyst zone was filled with quartz beads (Sigma-Aldrich, \(d_p = 0.6\) mm) to minimize its volume and the possible occurrence of the gas-phase reactions in this reactor section. Prior to testing, the catalyst bed was heated in a He flow to the desired temperature (\(T = 393-813\) K) and allowed to stabilize for at least 30 min before the reaction mixture was fed. The catalyst weight (\(W_{cat}\)), total flow rate (\(F_T\)), and feed
mixture applied in the tests are summarized in Table 2.1. Quantification of reactants and products, determination of conversion, selectivity, yield, and space-time yield as well as the evaluation of carbon and bromine mass balance was conducted using the same protocol as detailed in Appendix A.

### Table 2.1. Conditions applied in the reactions studied.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(W_{\text{cat}}) / g</th>
<th>(F_{Ta}^a) / cm(^2) min(^{-1})</th>
<th>Feed composition / vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Alkane</td>
<td>HBr</td>
</tr>
<tr>
<td>(\text{CH}_4) oxybromination</td>
<td>1.0</td>
<td>4.5</td>
<td>3</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_6) oxybromination</td>
<td>1.0</td>
<td>4.5</td>
<td>3</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_8) oxybromination</td>
<td>1.0</td>
<td>4.5</td>
<td>3</td>
</tr>
<tr>
<td>(\text{CH}_4) bromination</td>
<td>1.0</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>(\text{CH}_4) oxidation</td>
<td>1.0</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>(\text{CH}_3\text{Br}) oxidation</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\text{CH}_3\text{Br}_2) oxidation</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HBr oxidation</td>
<td>0.25</td>
<td>167</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Flow units correspond to standard temperature (273 K) and pressure (1 bar) conditions. \(^b\) Internal standard. \(^c\) Carrier gas.

2.3. Results and Discussion

#### 2.3.1. Oxybromination over Oxide and Phosphate Catalysts

The concept of oxybromination based on in situ coupling of the catalyzed HBr oxidation with the non-catalyzed gas-phase bromination was first approached by evaluating the representative HBr oxidation catalysts, TiO\(_2\), RuO\(_2\), and CeO\(_2\), in the oxybromination of \(\text{CH}_4\). The catalytic tests revealed a substantial productivity of \(\text{CH}_3\text{Br}\) and \(\text{CH}_2\text{Br}_2\) over these materials, being significantly higher than the “background” activity of the empty quartz microreactor (Figure 2.1). The highest yields of the brominated compounds were observed over CeO\(_2\), which was previously reported to be an efficient oxybromination catalyst. \(\text{CH}_2\text{Br}_2\) generation is a common challenge in both the bromination and oxybromination of \(\text{CH}_4\), particularly if the mixture of bromomethanes is coupled to the higher hydrocarbons, with which \(\text{CH}_2\text{Br}_2\) is known to favor aromatics formation, and
eventually it promotes catalyst deactivation because of fouling. Different strategies to convert CH₂Br₂ into CH₃Br and higher hydrocarbons via disproportionation or catalytic hydrodebromination processes make this product yet to be utilized. Nevertheless, the selectivity for the bromomethanes over the studied oxides was seriously conflicted by CO₂ generation, especially over RuO₂ and CeO₂. Although the CO₂ formation might appear as an inherent drawback of the oxybromination approach, a substantial carbon loss also occurs in the O₂-free bromination of CH₄ in the form of coke deposition, which gives rise to a semicontinuous reactor operation. Among the two carbon oxides, CO₂ is easier to separate, but the possibility to exploit CO as a carbonylation reagent in a Monsanto-like process to yield acetic acid from CH₃Br increases the overall efficiency of the carbon-atom utilization. Thus, although a high yield of CH₃Br is of prime interest, it is in the first place necessary to suppress the undesirable CO₂ formation, which is the only product of no practical use in the halogen-mediated light-alkane upgrading chain. This is not possible over the above-mentioned oxide catalysts because of their strong oxidizing character, which relates to the high mobility of the surface oxygen atoms, as well
as to the high concentration of the basic oxygen sites.\textsuperscript{[139-141]} The latter favors nucleophilic attack on the brominated compounds, and ultimately results in overoxidation and combustion.

To mitigate these, metal phosphates (Figure 2.1) are promising candidates with which to reconceive the mild oxidation potential with a reduced oxygen basicity and high stability under the corrosive reaction environment.\textsuperscript{[127,135,136,142-146]} The oxybromination tests performed over many phosphates show that, besides the previously reported FePO$_4$ catalyst,\textsuperscript{[127]} Cu$_3$(PO$_4$)$_2$, CrPO$_4$, and VPO are highly active in this reaction. In fact, VPO provided the highest yield of the brominated compounds with negligible CO$_2$ productivity and thus emerged as the best catalyst among all the investigated systems. XRD analysis of the VPO sample (Figure B.1) evidenced the substantial bulk changes of the catalyst structure, which primarily involve the reduction of the initial V(V) into V(IV) phases, although no changes in the catalyst performance could be observed (Figure 2.2). The operational window of all the active catalysts, including those that were previously reported to catalyze this reaction, was advantageously shifted to temperatures at least 100 K lower than those in the earlier works on CH$_4$ oxybromination.\textsuperscript{[67,89,125,127,134]} This marked increase in activity is attributed to the absence of water inhibition when using dry HBr instead of its aqueous solution. The latter is commonly used in the studies reported to date.

### 2.3.2. Evolution of the VPO Structure in the Oxybromination of Methane

The VPO catalyst was evaluated in a long run followed by ex situ characterization of the samples recovered at different times to gain insights into structural alterations of the starting phase. Importantly, the conversion of CH$_4$ as well as the product distribution remained unchanged over 100 h on stream (Figure 2.2a). However, XRD analysis of the samples collected after quenching the reaction at 5, 15 and 40 h indicated a progressive transformation of the initial vanadium oxyphosphate (VOPO$_4$) phases into a reduced vanadium pyrophosphate ((VO)$_2$P$_2$O$_7$) form (Figure 2.2b) and equilibration of the bulk-phase composition within the first 15 h of the reaction. The reduction of V$^{5+}$ into V$^{4+}$ was also evidenced by a H$_2$-TPR (Figure 2.2c) and $^{31}$P MAS NMR spectroscopy (Figure B.2). The low-temperature peaks in the H$_2$-TPR profiles positioned at about 780 and 845 K are attributed to the reduction of V$^{5+}$ species into V$^{4+}$ and V$^{3+}$, respectively.\textsuperscript{[147]} These peaks gradually vanished over the reaction time and were almost undetectable in the 40 h sample. Similarly, the strong signals located at around $\delta = 0$ ppm in the
31P NMR spectra, which are characteristic of the V5+ states in VOPO4 phases,\cite{148,149} were substantially reduced over time (Figure B.2). Nevertheless, 31P MAS NMR spectra demonstrated the presence of a small amount of V5+ even after 40 h on stream. An increase in crystallinity over reaction time was observed from XRD (Figure 2.2b), 31P MAS NMR spectroscopy, and HRTEM (Figure B.3) analyzes and is corroborated by a decrease of the specific surface area of the used catalyst samples (Figure 2.2b). Moreover, HRTEM evidenced a transformation of the needle-like (fresh) particles into cuboids (40 h) and the continuous presence of the amorphous layer on the surface of the crystalline grains. This layer was also observed in the n-butane oxidation to give maleic anhydride over VPO catalysts and is thought to be crucial for its performance in this reaction.\cite{150}

### 2.3.3. Performance Descriptors for the Oxybromination Catalysts

To rationalize the performance differences of various catalyst classes, we studied their behaviour in the reactions that are proposed to constitute the key descriptors for the ultimate product distribution in the oxybromination of CH₄ (Figure 2.3). These include HBr oxidation, which is essential to enable a continuous (re)generation of bromine (Br₂) along the catalyst bed, and the
Combustion of the brominated products (CH$_3$Br and CH$_2$Br$_2$) and CH$_4$, which are responsible for the loss in the overall selectivity for the bromomethanes. Temperatures at which 40% ($T_{40}$) of HBr, CH$_3$Br and CH$_2$Br$_2$, or 2% ($T_2$) of CH$_4$ are converted were taken as a relative measure of the catalyst's activity in the corresponding oxidation reactions (activity profiles are shown at the respective corners of the pyramid). Oxidation of HBr (HBr:O$_2$:He = 10:20:70) was conducted using $F_T$ = 166 cm$^3$ min$^{-1}$ and $W_{\text{cat}}$ = 0.25 g at $P$ = 1 bar. Oxidation of CH$_3$Br (CH$_3$Br:O$_2$:Ar:He = 1:1.5:3:94.5), CH$_2$Br$_2$ (CH$_2$Br$_2$:O$_2$:Ar:He = 1:1.5:3:94.5), and CH$_4$ (CH$_4$:O$_2$:Ar:He = 4.5:1.5:3:89.5) were performed using $F_T$ = 100 cm$^3$ min$^{-1}$ and $W_{\text{cat}}$ = 1.0 g at $P$ = 1.4 bar.

2.3.4. Insights into the Mechanism of Methane Oxybromination over VPO

The study of the performance descriptors (vide supra) evidenced that the oxidation of CH$_4$ over VPO and FePO$_4$ under conditions similar to those applied in the oxybromination reaction is rather unique...
slow (Figure 2.3). This points to a high activation barrier for the catalytic C-H bond scission and hints that the gas-phase bromination is a likely pathway for C-Br bond formation in the oxybromination reaction. To verify this aspect, the following experiments were conducted. First, gas-phase bromination was performed over a bed of inert quartz particles that had a volume typical of a catalyst bed in the oxybromination of CH$_4$ (Figure 2.4a). The results demonstrated that the onset temperature of 675 K, the trends in CH$_4$ conversion and the distribution of brominated products in the bromination reaction (Figure 2.4a) are in a good agreement with those in the oxybromination reaction (Figure 2.4a). The only exception was CO formation in the latter process.

Figure 2.4. Heterogeneous gas-phase reaction pathways and improvement of the CH$_3$Br productivity by optimizing reaction conditions. (a) CH$_4$ conversion and product selectivity versus temperature in the gas-phase CH$_4$ bromination follow similar trends as in the oxybromination of CH$_4$ over VPO. (b) HBr conversion and yields of Br$_2$ and bromocarbons (carbon-based) versus temperature in the oxybromination of CH$_4$ over VPO indicate the Br$_2$ consumption in the gas-phase bromination, which ultimately results in a formal decrease of the HBr conversion. (c) CH$_3$Br selectivity versus space-time yield of CH$_3$Br production for two CH$_4$ concentrations, total pressure and temperature over VPO shows that an excess of CH$_4$ in the inlet feed is crucial to reach a high selectivity for CH$_3$Br. (d) The single-pass carbon yields of products and space-time yield of CH$_3$Br versus total reactant concentrations at a fixed CH$_4$:HBr:O$_2$:Ar:He = 4.5:3:1.5:3:88 over VPO demonstrate the rather stable product distribution and the scalability of the oxybromination processes over the VPO catalyst. Bromination of CH$_4$ (CH$_4$:Br$_2$:O$_2$:Ar:He = 4.5:1.5:0.1:1.5:3:91(89.5)) was performed using $F_T = 100$ cm$^3$ min$^{-1}$ at $P = 1.55$ bar. Oxybromination of CH$_4$ (CH$_4$:HBr:O$_2$:Ar:He = 4.5-18:3-12:1.5-6:3:88-61) was conducted using $F_T = 100$ cm$^3$ min$^{-1}$ and $W_{cat} = 1.0$ g at $P = 1.4$ bar.

The addition of molecular O$_2$ to the bromination mixture (Figure 2.4a) did not change the product...
yields, except that some CO was observed at 745 K, which testifies to the absence of any inhibition by \( \text{O}_2 \). This pronounced difference in CO productivity suggests that its formation in the oxybromination reaction probably originates from the combustion of brominated products on the catalysts, which is also reflected by lower \( T_{40} \) values for \( \text{CH}_3\text{Br} \) and \( \text{CH}_2\text{Br}_2 \) combustion over catalysts compared with that over inert SiC particles (Figure 2.3). Second, the quantification of the \( \text{Br}_2 \) during the oxybromination over VPO showed that this was the main product observed at low temperatures (ca. 88% yield at 90% HBr conversion, Figure 2.4b), which suggests the bromine desorption occurs at low temperatures. With a rise in bed temperature, the increasing production of the bromomethanes is accompanied by a decreasing \( \text{Br}_2 \) yield and HBr conversion, which illustrates that the uptake of the evolved \( \text{Br}_2 \) by \( \text{CH}_4 \) in the gas phase results in HBr liberation. These results suggest that the formation of C-Br bonds in \( \text{CH}_4 \) oxybromination originates from a gas-phase reaction between \( \text{CH}_4 \) and \( \text{Br}_2 \). To comprehend whether the gas-phase free-radical chain reactions can be unfolded in our experimental conditions, we simulated the bromination of \( \text{CH}_4 \) under conditions comparable to those applied in the oxybromination (Figure B.4). This revealed that significant \( \text{CH}_4 \) conversion and yields of brominated products can be attained at the residence times estimated for the void volume between the catalyst particles. Based on this consideration, a simplified reaction mechanism is proposed for VPO. The bromine that is formed by the catalytic HBr oxidation (Equation 2.1) initiates the gas-phase bromination (Equation 2.2) and polybromination (Equation 2.3) reactions, liberating the HBr, which is continuously recycled on the catalyst surface (Equation 2.1). The functionalized bromomethanes are more prone to oxidize than \( \text{CH}_4 \) (Equation 2.4), which leads to CO\(_2\) formation that predominantly occurs on the catalyst surface.

\[
2\text{HBr} + 0.5\text{O}_2 \rightarrow \text{Br}_2 + \text{H}_2\text{O} \quad (2.1)
\]

\[
\text{CH}_4 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr} \quad (2.2)
\]

\[
\text{CH}_3\text{Br} + \text{Br}_2 \rightarrow \text{CH}_2\text{Br}_2 + \text{HBr} \quad (2.3)
\]

\[
\text{CH}_{1-x}\text{Br}_y + 0.5(2 + x - y)\text{O}_2 \rightarrow \text{CO}_2 + y\text{HBr} + (2 - y)\text{H}_2\text{O} \quad (2.4)
\]
2.3.5. Improved Productivity by Optimizing the Operating Conditions

Having rationalized the performance of the best catalyst, VPO, and understood the different pathways of oxybromination, our next step was to improve the CH₃Br selectivity by engineering the feed compositions and reaction conditions. The partial pressure of O₂ is critical as it is expected to promote the undesired oxybromination reactions. Moreover, it was demonstrated that the present O₂ content is sufficient to attain high HBr conversions (Figure 2.4b). Based on our findings that the gas-phase CH₄ bromination is the principal pathway of CH₄ activation over the VPO catalyst and on the well-known kinetics of the bromination reaction,[80,91,93,131] a CH₄-rich feed is expected to enhance the selectivity towards CH₃Br as it reduces polybromination. Indeed, an increase of the CH₄ concentration in the inlet feed from about 4.5 to 10 vol.% brought an increase of about double the CH₃Br productivity and a 10% increase in its selectivity at 753 K (Figure 2.4c). By decreasing the temperature to 693 K, the space-time yield (STY) of CH₃Br at 10 vol.% of CH₄ in the inlet feed was similar to that obtained with a 4.5 vol.% CH₄ feed content at a temperature 60 K higher. Importantly, the selectivity for CH₃Br reached 91%, with about 5% and 4% selectivity for CO and CH₂Br₂, respectively. An increase in the total pressure from 1.4 to 1.8 bar led to an increase in the CH₄ conversion. Nevertheless, the Pareto-like dependence of the selectivity for CH₃Br on CH₄ was preserved. To verify further the applicability of the VPO under realistic reactant-rich feeds, its performance was evaluated at increasing partial pressures of the reactants with their molar ratio kept constant (Figure 2.4d). The small alterations in the product distribution at similar CH₄ conversions that were observed demonstrate the scalability of the catalyst performance and, consequentially, a strong enhancement of the space-time yield of CH₃Br.

2.3.6. Extrapolation to Other Light Alkanes

The applicability of the VPO catalyst to the functionalization of the other two representative alkane candidates, C₂H₆ and C₃H₈, was explored further (Figure 2.5). The onset temperature of the oxybromination reaction decreased in the order CH₄ > C₂H₆ > C₃H₈, in line with increase in their C-H bond strengths.[151] In the case of CH₄ (Figure 2.5a), a high selectivity for CH₃Br (> 92%) can be achieved at low conversions (< 7%). However, a further increase in the conversion, was inevitably coupled with a loss in the selectivity for CH₃Br (vide supra) because of the formation of CH₂Br₂ and CO. Likewise, in the oxybromination of C₂H₆, bromoethane (C₂H₅Br) was the
principal product in the lower temperature window (83% selectivity, 8% conversion) but, in contrast to CH\textsubscript{4}, no polybrominated ethanes could be detected at the reactor outlet (Figure 2.5b). This might be a result of their susceptibility to cracking and/or combustion, which could also explain the equimolar production of CO and CH\textsubscript{4} at higher conversions, at which the

![Figure 2.5](image-url)

**Figure 2.5.** The performance of VPO in the oxybromination of (a) CH\textsubscript{4}, (b) C\textsubscript{2}H\textsubscript{6}, and (c) C\textsubscript{3}H\textsubscript{8}. The alkane conversion as a function of temperature shows that the temperature onset of the oxybromination reaction decreases in the order CH\textsubscript{4} > C\textsubscript{2}H\textsubscript{6} > C\textsubscript{3}H\textsubscript{8}, which is in line with a decrease in the C-H bond strength. C\textsubscript{2}H\textsubscript{5}Br is the principal product observed in the oxybromination of C\textsubscript{2}H\textsubscript{6} at low reaction temperatures but, in contrast to CH\textsubscript{4}, no polybromoethanes are observed, probably because of their higher propensity to cracking. At higher temperatures, the dehydrobromination pathway is opened, which results in significant C\textsubscript{2}H\textsubscript{4} production, with negligible selectivity for CO\textsubscript{2}. Differently, C\textsubscript{3}H\textsubscript{8} oxybromination causes significant cracking and coking, probably because of the activation of C\textsubscript{3}H\textsubscript{8} on the catalyst surface. Conditions: alkane:HBr:O\textsubscript{2}:Ar:He = 4.5:3:1.5:3:88, \(F_T = 100\ \text{cm}^3\ \text{min}^{-1}\), \(W_{\text{cat}} = 1.0 \text{ g}\), and \(P = 1.4\ \text{bar}\).
polybromination is more favored. Notably, the selectivity for the latter C1 products slightly decreased at a higher temperature. Instead, a drop in selectivity for C₂H₅Br was progressively compensated with ethylene (C₂H₄) formation. This suggests the in situ dehydrobromination of the former, which can be promoted over phosphate catalysts. The productivity of C₂H₄ (67% selectivity, 42% conversion) was higher than that observed in the oxidative dehydrogenation of C₂H₆ over VPO conducted under comparable conditions (Figure B.5), and those previously reported for the best-performing VPO systems in oxidative dehydrogenation. The rate of double-bond formation in the case of C₃H₈ was also higher than that recorded in the oxidative dehydrobromination performed under similar conditions (Figure 2.5c). Nonetheless, given the even weaker C-C bonds in propyl radicals, cracking reactions were more pronounced than those of C₂H₆, which resulted in C₂H₅Br being a dominant product in the lower temperature window, and no bromopropanes could be detected. Moreover, at higher temperatures, coking was evident from a substantial deviation in the carbon balance (vide infra, 10% at 693 K) and visually confirmed by the dark deposits on the catalyst bed and reactor wall. The results for C₂H₆ and C₃H₈ suggest that the reaction network is even more complex than that of CH₄, probably induced by the higher affinity of higher alkanes and the corresponding bromoalkanes to the catalyst surface. Although challenging in terms of the catalyst and process design, these results testify to a bright perspective for the oxybromination approach to functionalize light alkanes.

2.4. Conclusions

The efforts to design a catalyst that allows a selective one-step CH₄ functionalization via oxybromination chemistry resulted in the identification of VPO, which provided the highest yields of the bromomethanes along with negligible CO₂ production. The catalyst demonstrated a stable operation over 100 h on stream, despite the restructuring of its bulk, which equilibrated within the first 15 h of the reaction. The outstanding performance of VPO is rationalized by its high activity in the HBr oxidation and low propensity to oxidize CH₄ and brominated compounds. Based on the mechanistic understanding of the reaction that comprises synergetic cooperation between the heterogeneous HBr oxidation and the gas-phase CH₄ bromination, the productivity of CH₃Br over a VPO catalyst was enhanced further by optimizing the reaction conditions, whereby a selectivity for CH₃Br of above 90% was attained by increasing the feed partial pressure of CH₄. The
oxybromination of C$_2$H$_6$ and C$_3$H$_8$ over VPO indicated a more-complex reaction network that comprised dehydrobromination and cracking of the brominated compounds. In the case of C$_2$H$_6$, high yields of C$_2$H$_4$ could be achieved with only marginal CO$_2$ formation. These findings constitute an important step and provide a comprehensive background for the design of an efficient process to valorize the abundant and readily available natural gas reserves.
Chapter 3

Impact of the Hydrogen Halide Type on Methane Oxyhalogenation

3.1. Introduction

The selective activation of the inert C-H bonds in methane (CH\(_4\)), being the principal component of natural gas, is one of the key challenges in catalysis research. With its abundant reserves, CH\(_4\) offers a huge potential as a feedstock for the manufacture of chemicals and fuels.\[5,23,25,34\] Nevertheless, over 30% of the world’s natural gas is trapped in small basins and/remote areas, whose valorization via syngas using existing steam reforming technology is not economical due to its high energy and capital demands.\[5,24,43\] Consequently, less than 10% of the global annual gas production is currently used for the manufacture of commodities, while ca. 3.5%, a share which is worth ca. 13 billion USD, is flared at oil and gas fields or refineries.\[24,43,48,154\]

Over the last decades, various CH\(_4\) activation routes such as partial oxidation,\[1,155\] oxidative coupling,\[53,156\] aromatization,\[55,157\] selective oxidation into methanol,\[63,64,158,159\] and (oxy)halogenation\[68,78,84,89,96,101,108,127,131,160-166\] have been studied as alternative approaches to steam reforming. Among those, halogen-mediated CH\(_4\) functionalization is of particular interest since halogens, such as chlorine (Cl\(_2\)) and bromine (Br\(_2\)), readily react with CH\(_4\) under moderate reaction conditions (~1 bar, < 800 K) in the presence or absence of a catalyst, yielding halomethane (CH\(_3\)X, X = Cl, Br).\[5\] The latter, isostructural with methanol, are versatile platform molecules and can be readily transformed into a wide spectrum of chemicals and fuels by halogen elimination in the form of hydrogen halide (HX).\[5,106\] Nevertheless, the real-life implementation of the direct halogenation route necessitates the closing of the halogen cycle by converting HX, liberated in both the halogenation and subsequent elimination step, to X\(_2\), e.g., via catalytic oxidation.\[5,69,70,118\] On the other hand, catalytic oxyhalogenation, involving the reaction of methane with HX and oxygen, enables the integration of methane functionalization with HX recovery in a single step.\[5\] Still, critical challenges will have to be overcome in order to bring this concept from
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the laboratory to the industrial scale. Particularly, the presence of oxygen (O\textsubscript{2}) in the feed leads to the formation of carbon oxides, which might be further promoted due to an enhanced oxygen vacancy formation in the presence of halogens\textsuperscript{[167]} thus decreasing the selectivity to CH\textsubscript{3}X. In addition, an HX atmosphere is detrimental to the stability of a great number of materials. Cu-based catalysts, inherited from the Deacon process and widely applied in ethylene oxychlorination\textsuperscript{[168,169]} were the first materials studied in CH\textsubscript{4} oxychlorination. Although these catalysts exhibit a noticeable productivity of CH\textsubscript{3}Cl (Y = 16%, S = 85%), their instability has limited the practical implementation\textsuperscript{[165]} Continuous research to find an optimal oxyhalogenation catalyst led to the discovery of promising systems, comprising LaOCl for CH\textsubscript{4} oxychlorination\textsuperscript{[165]} Ru- and Rh-containing materials\textsuperscript{[101]}, FePO\textsubscript{4}\textsuperscript{[127]} as well as TiO\textsubscript{2} and vanadyl pyrophosphate ((VO\textsubscript{2})P\textsubscript{2}O\textsubscript{7}, VPO) described in Chapter 2 for CH\textsubscript{4} oxybromination, and CeO\textsubscript{2}-based catalysts for both CH\textsubscript{4} oxybromination and oxychlorination\textsuperscript{[80]} where the last two materials provided the highest yields of CH\textsubscript{3}Br (Y = 16%, S = 64%) and CH\textsubscript{3}Cl (Y = 17%, S = 74%), respectively. Nevertheless, these studies were confined to a single type of HX and/or a single catalyst family and were investigated in a relatively narrow kinetic regime. This not only limits the realistic comparison of the catalyst performance but also hampers the understanding of the role of HX in oxyhalogenation chemistry.

In this Chapter, CH\textsubscript{4} oxybromination and oxychlorination are compared over different catalyst families, characterized by diverse oxidizing properties, in a broad range of temperatures (600-873 K) and HX concentrations (0-15 vol.%) to determine the dependence of product distribution on the nature of catalyst and the type of HX and its partial pressure. These results were understood by an investigation of the related oxidation and gas-phase halogenation reactions, which also enabled us to gain insights into the mechanism of CH\textsubscript{4} oxyhalogenation. Finally, these findings were summarized vis-à-vis for CH\textsubscript{4} oxybromination and oxychlorination in the form of extracted kinetic parameters, providing an overview of the oxyhalogenation performance of different materials as a function of HX.
3.2. Experimental

3.2.1. Catalyst Preparation

RuO$_2$ was obtained by calcination of anhydrous RuCl$_3$ (ABCR, 99.9%) at 823 K in static air, while commercial CeO$_2$ (Sigma-Aldrich, nanopowder, 99.9%) and TiO$_2$ (Sigma-Aldrich, rutile nanopowder, 99.5%) were calcined at 1173 and 873 K, respectively, in static air prior to their use in the catalytic tests. Vanadyl pyrophosphate ((VO)$_2$P$_2$O$_7$, VPO) was prepared by refluxing a suspension of V$_2$O$_5$ (Sigma-Aldrich, 99.5%) in isobutyl alcohol (Acros Organics, 99%) and benzyl alcohol (Sigma-Aldrich, 99%) for 3 h with a molar V$_2$O$_5$:C$_4$H$_{10}$O:C$_7$H$_8$O ratio of 1:12:6.5. After the mixture was cooled to room temperature, H$_3$PO$_4$ (Sigma-Aldrich, 85%) was added to attain a molar P:V ratio of 1.2, and the mixture was then refluxed for another 16 h. The resulting solid was recovered by filtration, washed with isobutyl alcohol and methanol (Fluka, 99.9%), dried at 373 K under vacuum (50 mbar) for 12 h, and thermally activated at 823 K in flowing N$_2$. FePO$_4$ was synthesized by mixing Fe(NO$_3$)$_3$·9H$_2$O (Sigma-Aldrich, 99%) and NH$_4$H$_2$PO$_4$ (Acros Organics, 99%) in a molar P:Fe ratio of 1 in deionized water for 2 h, followed by drying at 373 K under vacuum (50 mbar) for 12 h and calcination at 873 K in flowing air. The supported copper-based catalyst (Cu-K-La-X) containing 7 wt.% Cu, 2 wt.% K, and 2 wt.% La was prepared by sequential incipient wetness impregnation of precalcined (673 K in static air) $\gamma$-Al$_2$O$_3$ (Alfa Aesar, 160 m$^2$ g$^{-1}$) with an aqueous solution of CuCl$_2$·2H$_2$O (Sigma-Aldrich, 99.99%), KCl (Acros Organics, 99%), and LaCl$_3$·7H$_2$O (ABCR, 99.99%), respectively. After each impregnation step, the impregnate was dried at 373 K under vacuum (50 mbar) for 12 h. The thermal treatment for all catalysts was performed using a heating rate of 5 K min$^{-1}$ and a holding time of 5 h.

3.2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) was measured using a PANalytical X’Pert PRO-MPD diffractometer and Cu Kα radiation ($\lambda = 0.154$ nm). The data was recorded in the 10-70° 2θ range with an angular step size of 0.017° and a counting time of 0.26 s per step. N$_2$ sorption at 77 K was measured in a Quantachrome Quadrasorb-SI analyzer. Prior to the measurements, the sample was outgassed to 50 mbar at 573 K for 12 h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the total surface area, $S_{\text{BET}}$, in m$^2$ g$^{-1}$. X-ray fluorescence (XRF) was performed using an EDAX Orbis Micro-XRF analyzer equipped with a Rh source operated at a voltage of 30 kV.
and a current of 500 μA. Temperature-programmed reduction with hydrogen (H$_2$-TPR) was performed using a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector coupled to a MKS Cirrus 2 mass spectrometer. The powder sample (0.01 g for RuO$_2$ and 0.25 g for all other catalysts) was loaded into a U-shaped quartz microreactor, pretreated in He (20 cm$^3$ min$^{-1}$) at 673 K for 2 h, and cooled to room temperature followed by ramping the temperature at 10 K min$^{-1}$ up to 1273 K in 5 vol.% H$_2$ in N$_2$ (20 cm$^3$ min$^{-1}$). The $^{31}$P nuclear magnetic spectra were acquired using the spin-echo mapping$^{[170]}$ or variable offset cumulative spectrum (VOCS) method$^{[171]}$ on a bruker avance IIIHD spectrometer equipped with a 9.4 T Magnet (162.2 MHz $^{31}$P Larmor frequency). The sample was loaded into 3.2 mm rotors and measured using a 3.2 mm double resonance magic-angle spinning (MAS) probe in static mode. For each sample, 7 experiments with a variation of the carrier frequency from 0 to 6000 ppm in 1000 ppm steps were combined. For each offset of the carrier frequency the tuning and matching of the probe was checked and adjusted. The individual experiments used a $\pi$/2-$\tau$-$\pi$-acquire spin-echo sequence with a 16 step phase cycle. The $\pi$/2 pulse was set to 1.0 μs and the delay $\tau$ to 20 μs. A total of 512 scans were acquired with a recycle delay of 0.2 s. The possibility of saturation was tested by repeating a number of experiments with a recycle delay of 2.0 s. No difference between experiments with 0.2 s or 2.0 s recycle delay was observed. The full-echo time domain signals were processed and combined to a final skyline type spectrum using custom written Matlab scripts incorporating functions of the MatNMR toolbox.$^{[172]}$ X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electronics Quantum 2000 spectrometer using monochromatic Al K$_\alpha$ radiation generated from an electron beam operated at 15 kV and equipped with a hemispherical capacitor electron-energy analyzer. The powdered sample was analyzed at an electron takeoff angle of 45° and a pass energy of 46.95 eV. Partial compensation of surface charging during spectral acquisition was obtained by the simultaneous operation of electron and argon ion neutralizers. Elemental concentrations expressed in atomic percent were determined using the measured photoelectron peak areas after Shirley background subtraction and the built-in sensitivity factors for calculation.
3.2.3. Catalyst Testing

All of the catalytic tests were performed at ambient pressure in a continuous-flow fixed-bed reactor setup, which is described in Appendix A. The catalyst ($W_{\text{cat}} = 1.0 \, \text{g}$, particle size, $d_p = 0.4\text{-}0.6 \, \text{mm}$) was intimately mixed quartz particles ($d_p = 0.2\text{-}0.3 \, \text{mm}$) to ensure a constant bed volume ($V_{\text{bed}} = 1.8 \, \text{cm}^3$) and loaded in a quartz reactor (internal diameter, $d_r = 8 \, \text{mm}$). In CH$_4$ oxyhalogenation, CH$_4$ halogenation, and CH$_4$ oxidation the post-reactor zone was filled with quartz beads (Sigma-Aldrich, $d_p = 0.6 \, \text{mm}$) to minimize its volume and the possible occurrence of the gas-phase reactions in this reactor section. Prior to the tests, the catalyst was heated in a He flow until the desired bed temperature ($T = 423\text{-}895 \, \text{K}$) and then stabilized for 30 min under these conditions before the reaction mixture was admitted. Unless otherwise stated, the volumetric flow of $F_T = 100 \, \text{cm}^3 \, \text{min}^{-1}$ (corresponding to the space velocity of $F_T/W_{\text{cat}} = 100 \, \text{cm}^3 \, \text{min}^{-1} \, \text{gcat}^{-1}$) was used in all tests, wherein the flow units correspond to standard temperature and pressure (STP) conditions, i.e., 273 K and 1 bar. Reactions and feed compositions studied in this work are summarized in Table 3.1. Quantification of reactants and products, determination of conversion, selectivity, yield, and reaction rate, as well as the evaluation of carbon and halogen mass balance was conducted using the same protocol as detailed in Appendix A.

**Table 3.1.** Conditions applied in the reactions studied.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Concentration / vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_4$</td>
</tr>
<tr>
<td>CH$_4$ oxyhalogenation</td>
<td>6</td>
</tr>
<tr>
<td>CH$_4$ chlorination</td>
<td>6</td>
</tr>
<tr>
<td>CH$_4$ bromination</td>
<td>6</td>
</tr>
<tr>
<td>CH$_4$ oxidation</td>
<td>6</td>
</tr>
<tr>
<td>CH$_3$X oxidation</td>
<td>0</td>
</tr>
<tr>
<td>CH$_2$X$_2$ oxidation</td>
<td>0</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>0</td>
</tr>
<tr>
<td>HX oxidation</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Internal standard. $^b$ Carrier gas.
Chapter 3

3.3. Results and Discussion

3.3.1. Oxyhalogenation over Different Catalysts

CH₄ oxychlorination and oxybromination were studied under variable temperature (600-900 K, Figure 3.1) and feed HX concentration (3-15 vol.%, Figure 3.2) over different catalyst families: namely, RuO₂, CeO₂, VPO, TiO₂, and FePO₄, as well as Cu-K-La-X, which is one of the benchmark oxychlorination catalysts. The choice of these systems was based on their diverse oxidizing characters, as inferred from their H₂-TPR profiles (Figure B.6). The comparison of the catalytic activity in CH₄ oxychlorination and oxybromination, as well as between different catalysts in the same reaction, can be achieved on different basis, generally involving the ranking of reaction rates, which can be expressed with respect to the surface area of a catalyst, its weight, its volume, or its classification on the basis of the activation barriers. The advantages and disadvantages of the different approaches are discussed in more detail in the Annex of this Chapter.

Herein, catalytic activities are compared on the basis of the relative position of the light-off curves of methane conversion versus temperature. These were obtained by performing the two reactions over a constant catalyst weight (1 g) and reaction volume (1.8 cm³), allowing the normalization of the reaction rate to catalyst weight and reaction volume. This widely accepted approach in catalysis, also applied in previous study on oxyhalogenation, is found to be particularly suitable, as it enables the comparison of the kinetics of different (partially) catalytic and noncatalytic reactions (vide infra), while still providing a differentiation of the single catalyst performance in two oxyhalogenation reactions, which are the primary focus of our study. On the basis of this criterion, the overall activity ranking, RuO₂ > Cu-K-La-X > CeO₂ > VPO > TiO₂ > FePO₄ (Figure 3.1, left column), is similar in the two reactions. Still for RuO₂ and Cu-K-La-X catalysts, the light-off curves are shifted to higher temperatures in CH₄ oxybromination by ca. 100 K in comparison to those in oxychlorination, while they remained mostly identical for CeO₂ and VPO, and evidenced a reversed order over the least active TiO₂ and FePO₄ systems.

The product distribution patterns revealed that in general the selectivity to desired CH₃X decreased, while that to CO₂ increased with temperature. Despite being the most active catalyst, RuO₂ led to a pronounced formation of CO₂ in both CH₄ oxybromination ($S$(CO₂) ≤ 84%) and oxychlorination ($S$(CO₂) ≤ 77%) over the entire temperature range investigated. Likewise, although
Figure 3.1. Conversion and product selectivity versus temperature in CH₄ oxybromination (open symbols) and oxychlorination (solid symbols) over the catalysts. Conditions: CH₄:HX:O₂:Ar:He = 6:6:3:4.5:80.5, $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, and $P = 1 \text{ bar}$. 
Figure 3.2. Conversion and product selectivity versus feed HX concentration in CH₄ oxybromination (open symbols) and oxychlorination (solid symbols) over the catalysts. Conditions: CH₄:HX:O₂:Ar:He = 6:3-15:3:4.5:83.5-71.5, \( F_T/ W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1} \), and \( P = 1 \text{ bar} \).
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Cu-K-La-X achieved a high selectivity to chloromethanes ($S(\text{CH}_3\text{Cl} + \text{CH}_2\text{Cl}_2) \leq 90\%$) in CH$_4$ oxychlorination, it led to a marked CO$_2$ generation in CH$_4$ oxybromination ($S(\text{CO}_2) \leq 60\%$). In addition, this catalyst suffered from severe metal leaching from the support in both reactions, as observed in the form of the deposits on the reactor wall. These results are in line with previous studies on this material reporting the volatilization of copper phases in the oxychlorination of methane.$^{[165]}$ Nevertheless, the performance of Cu-based catalysts is still presented here as an archetypical oxyhalogenation catalyst. The third most active catalyst, CeO$_2$, led to the highest selectivity to chloromethanes ($\leq 90\%$) but displayed considerable CO$_2$ formation in CH$_4$ oxybromination ($S(\text{CO}_2) \leq 50\%$), which makes it less selective to bromomethane production ($S(\text{CH}_3\text{Br} + \text{CH}_2\text{Br}_2) \leq 47\%$). VPO and TiO$_2$, being mildly oxidizing systems, provided selectivity to bromomethanes up to 84 and 75%, respectively. However, in CH$_4$ oxychlorination, they both evidenced inferior selectivity to chloromethanes and instead showed a highly selective production of CO ($S(\text{CO})$ up to 96% and 90%, respectively), which is still a valuable chemical intermediate.$^{[174]}$ FePO$_4$, exhibited high selectivity to the desired halomethanes in both CH$_4$ oxychlorination, in which it was investigated for the first time, and CH$_4$ oxybromination (especially below 800 K). Still, to achieve reasonable conversion levels, this catalyst needs to be operated at high temperature, which compromises the CH$_3$X production with CO formation. Overall, CeO$_2$ is the most promising candidate for CH$_3$Cl formation, while VPO and TiO$_2$ are suitable for bromomethane production.

The catalysts were further evaluated at variable HX concentrations (3-15 vol.%) in order to investigate the effect of HX on their catalytic performance (Figure 3.2). RuO$_2$ displayed a decrease in CH$_4$ conversion with an increase in feed HX content in both CH$_4$ oxybromination and oxychlorination, whose effect was more pronounced in the latter reaction. In contrast, the activity of FePO$_4$ was markedly promoted at higher concentrations of both HCl and HBr. The promotion of activity was also observed over Cu-K-La-X and TiO$_2$ in CH$_4$ oxychlorination, while in case of the other materials, CH$_4$ conversion was essentially unaffected by the variations in HX concentrations. Interestingly, the product distribution was significantly altered over Cu-K-La-X, CeO$_2$, and RuO$_2$ at higher inlet HX contents, especially when HBr was used. In particular, the selectivity to CH$_3$Br increased from 30, 40, and 25% to 50, 80, and 85%, respectively, with a corresponding drop in CO$_2$ selectivity. On the other hand, this effect was less pronounced in CH$_4$
oxychlorination, especially over CeO₂, showing almost no change in the selectivity to CH₃Cl and a mild increase in selectivity to CH₂Cl₂. Likewise, over VPO and TiO₂, the selectivity to halomethanes was only slightly altered.

All investigated materials were characterized by means of XRD and N₂ sorption in their fresh form and after the use in CH₄ oxybromination and oxychlorination tests. The diffractograms of the used samples evidenced no structural changes in comparison to their fresh analogues (Figure B.8), thus testifying to their robustness under oxyhalogenation conditions. The specific surface area of the sample after use in CH₄ oxybromination or oxychlorination was generally decreased in comparison to the fresh materials, which indicates a certain degree of sintering (Table B.2). The only exception was the Cu-based catalyst, which showed a dramatic change in phase composition and a significant increase in the surface area, indicating the volatilization of the deposited phase from the pores of the support.

3.3.2. Relationships between Oxyhalogenation, HX Oxidation, and Halogenation

To understand the performance differences among various catalyst families, the temperature at which ca. 15% conversion of CH₄ is achieved, $T_{15}(\text{CH}_4)$, is taken as a relative measure of their oxyhalogenation activity (Figure 3.3). The $T_{15}(\text{CH}_4)$ values reflect the overall reactivity trends as derived by the light-off curves (vide supra). In addition, $T_{15}(\text{CH}_4)$ in CH₄ oxychlorination ranges from 630 to 860 K, whereas it falls in a narrower temperature range (690-780 K) in CH₄ oxybromination. To shed light on these differences, the performance of the catalysts in CH₄ oxidation was evaluated under conditions comparable to those of CH₄ oxyhalogenation (Figure 3.3). Interestingly, the light-off curves in the former reaction were shifted to higher temperatures in comparison to the corresponding profiles in CH₄ oxidation (Figure 3.4a), with RuO₂ being the only exception. This result indicates the promotion of the CH₄ conversion in the presence of HX, particularly over mild oxidants such as VPO and TiO₂, which are scarcely able to activate CH₄ unless a halogen source is present, and is in good agreement with the recent theoretical work of Metiu et al.,[175] who proposed the enhancement of CH₄ activation on CeO₂ surfaces in the presence of HX and X₂. To further elucidate the origin of the catalytic activity in the oxyhalogenation reactions, we have evaluated the representative materials in HCl and HBr oxidation (Figure 3.4b). In line with previous studies,[60] catalysts displayed HCl oxidation activity...
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Figure 3.3. Temperature required to attain 15% conversion ($T_{15}$) in CH$_4$ oxybromination (open bars) and CH$_4$ oxychlorination (solid bars) over the catalysts. The inset exemplifies the determination of $T_{15}$ in CH$_4$ oxybromination and oxychlorination for RuO$_2$. Conditions as reported in the caption of Figure 3.1.

at higher temperatures in comparison to HBr oxidation. Interestingly, the catalyst rankings in HX oxidation coincided with those in CH$_4$ oxyhalogenation, with RuO$_2$ being the most active and FePO$_4$ the least active. Moreover, the $T_{15}$(CH$_4$) value in CH$_4$ oxyhalogenation correlates linearly with the $T_{15}$(HX) value in HX oxidation (Figure 3.5a), particularly in CH$_4$ oxychlorination, suggesting that the oxyhalogenation activity is controlled by the catalyst ability to activate HX. This correlation between the HX oxidation and oxyhalogenation activity is also observed if the catalyst activities are expressed on the basis of surface area (Figure B.9). In the case of HCl, this behavior is not only limited to a selected methane or HX conversion level but also preserved over a wide temperature range. To demonstrate this, the apparent activation energies for CH$_4$ conversion in oxychlorination, $E_a$(CH$_4$), and for HCl oxidation, $E_a$(HX), were determined (Figure B.10, Table B.3). The strong linear dependence between these two parameters indicates that the correlation between the CH$_4$ oxychlorination and HCl oxidation is preserved over a broad temperature range (Figure 3.5b). Nevertheless, no clear dependence between the apparent activation energies of CH$_4$ oxybromination and HBr oxidation was observed (Figure 3.5b). These differences might be explained by considering the role of gas-phase CH$_4$ halogenation in controlling the reactivity, as put forward in Chapter 2. CH$_4$ chlorination occurs at temperatures lower (ca. 573-673 K) than those for bromination (ca. 693-793 K). Thus, if the halogenation is controlling the overall reaction rate, the X$_2$ evolved from the catalyst surface could only react
when the temperature is sufficiently high for the homolytic C–H activation. Accordingly, the temperature dependence of the gas-phase CH₄ halogenation was studied (Figure 3.4c) under conditions equivalent to those for CH₄ oxyhalogenation. By extraction of the $T_{15}(\text{CH}_4)$ value from the CH₄ halogenation experiments, it can be observed that the distribution of $T_{15}(\text{CH}_4)$ in both CH₄ oxybromination and oxychlorination falls in the region where the respective gas-phase halogenation is significant (Figure 3.5a). This supports the previous hypothesis that the oxyhalogenation reaction might proceed through a heterogeneous-gas-phase mechanism. At first glance, CH₄ oxybromination over RuO₂ might appear exceptional, as its $T_{15}(\text{CH}_4)$ value is significantly lower in comparison to the corresponding value in the gas-phase bromination. Still, a high activity of this catalyst in CH₄ oxidation (Figure 3.4a) suggests that a significant part of CH₄ oxidation versus temperature in (a) CH₄ oxidation (CH₄:O₂:Ar:He = 6:3:4.5:86.5) and (b) HCl (solid symbols) and HBr (open symbols) oxidation (HX:O₂:Ar:He = 6:3:4.5:86.5) over the catalysts. (c) Conversion and product selectivity versus temperature in CH₄ bromination (open symbols, CH₄:Br₂:Ar:He = 6:2.7:4.5:86.8) and chlorination (solid symbols, CH₄:Cl₂:Ar:He = 6:1.8:0:4.5:87.7). Other conditions: $F_T/W$ = 100 cm³ min⁻¹ g⁻¹ cat⁻¹ and $P = 1$ bar.

\[ \text{Figure 3.4.} \] Conversion versus temperature in (a) CH₄ oxidation (CH₄:O₂:Ar:He = 6:3:4.5:86.5) and (b) HCl (solid symbols) and HBr (open symbols) oxidation (HX:O₂:Ar:He = 6:3:4.5:86.5) over the catalysts. (c) Conversion and product selectivity versus temperature in CH₄ bromination (open symbols, CH₄:Br₂:Ar:He = 6:2.7:4.5:86.8) and chlorination (solid symbols, CH₄:Cl₂:Ar:He = 6:1.8:0:4.5:87.7). Other conditions: $F_T/W$ = 100 cm³ min⁻¹ g⁻¹ cat⁻¹ and $P = 1$ bar.
conversion in CH₄ oxybromination might stem from its direct oxidation. This is further corroborated by the product distribution in CH₄ oxybromination (Figure 3.6), wherein RuO₂ leads to CO₂ as a dominant product in the low-temperature range (ca. 85% selectivity at 15% CH₄ conversion), while production of CH₃Br starts to be significant only in the temperature window of the gas-phase bromination (Figure 3.1). In addition, a comparison of the catalyst activity in CH₄ oxybromination and oxychlorination unequivocally shows that, although the Br₂ evolution is expected to be more facile than that of Cl₂ (Figure 3.5a), CH₃Br formation over RuO₂ requires higher temperatures in comparison to CH₃Cl production in congeneric oxychlorination (Figure 3.1). The same reasoning holds for Cu-La-K-X and CeO₂. The T₁₅(CH₄) values of these catalysts in oxybromination are much closer to the T₁₅(CH₄) value in the bromination reaction, in line with their lower activity in CH₄ oxidation in comparison to RuO₂ (Figure 3.4a). On the other hand, the T₁₅(CH₄) values observed for VPO, TiO₂, and particularly FePO₄ in oxychlorination appear to be lower than the corresponding T₁₅(HX) values, which might indicate a marked role of the catalyst in CH₄ activation. To elucidate this important point, the rates of CH₄ oxychlorination, CH₄, and HCl oxidation are compared over the broader temperature window (Figure 3.8, vide infra, Figure B.12). From this representation it can be observed that (i) CH₄ oxidation over TiO₂ and particularly VPO proceeds at significantly higher temperatures in comparison to CH₄
oxychlorination, suggesting the low propensity of these two catalysts to activate CH$_4$ in a temperature window of the oxychlorination reaction, and (ii) the rate of CH$_4$ oxychlorination over VPO and TiO$_2$ is comparable to the rate of HCl oxidation, particularly at lower conversion levels. In addition, both VPO and TiO$_2$ favor CO production (Figure 3.1), whereby HCl is continuously regenerated along the catalyst bed. This suggests a higher effective concentration of this reactant in oxychlorination in comparison to sole HCl oxidation, which might contribute to the slightly higher rate of the former reaction with respect to the latter reaction. In contrast, the activity of FePO$_4$ in CH$_4$ oxychlorination and CH$_4$ oxidation is significantly higher than that in HCl oxidation, indicating a low Cl$_2$ evolution under oxychlorination conditions. Moreover, this catalyst requires the highest operating temperature in oxychlorination. On the basis of these considerations, a gradual transition from mostly gas-phase to heterogeneous C-Cl bond formation on going from VPO to FePO$_4$ can be proposed. It is interesting to note that by switching the halogen source from HCl to HBr the variance of the distribution of the $T_{15}$(CH$_4$) values is reduced significantly (Figure 3.5a) between the two reactions. This difference might originate from a change in the rate-determining step (rds) of the reaction. In essence, the reaction rate in CH$_4$ oxychlorination could be primarily determined by the evolution of Cl$_2$ from the catalyst surface, which is proved to be the most energy demanding step in the Deacon reaction.$^{[118,119,176,177]}$ This not only rationalizes the strong correlation between $T_{15}$(CH$_4$) and $T_{15}$(HCl) (Figure 3.5a) but also explains why this is preserved over a wide temperature range (Figure 3.5a). In contrast, in CH$_4$ oxybromination the rate-determining step might be the reaction between the evolved Br$_2$ with CH$_4$ in the gas phase. This can describe (i) the decrease in activity in CH$_4$ oxybromination of the highly active HBr oxidation catalysts, such as RuO$_2$ and CeO$_2$ in comparison to the respective HCl-driven reactions, (ii) the narrow distribution of the $T_{15}$(CH$_4$) in CH$_4$ oxybromination, centered in the region of $T_{15}$(CH$_4$) for gas-phase bromination observed for all catalysts, except for RuO$_2$, and (iii) the absence of correlation between $E_a$(CH$_4$) and $E_a$(HBr).

### 3.3.3. Rationalization of Selectivity Patterns

Product selectivity is another important aspect of the oxyhalogenation performance, which for a given catalyst depends on reactor geometry, space velocity, feed composition, degree of conversion, and reaction temperature.$^{[173]}$ However, these cannot all be fixed simultaneously, since
conversion is also a function of the remaining parameters. Herein, we fixed all the parameters except for the temperature, which was varied so to achieve the constant level of methane conversion of ca. 15% at which selectivity to halomethanes, CO, and CO₂ in CH₄ oxybromination and oxychlorination were compared (Figure 3.6). RuO₂ led to a pronounced CO₂ formation in both CH₄ oxybromination and oxychlorination, in line with its highest reducibility as is evident from its H₂-TPR profile (Figure B.6). However, it is interesting to note that, in contrast to the other catalysts, the selectivity to CH₃Br in CH₄ oxybromination over RuO₂ was enhanced at higher temperatures (Figure 3.1). This apparently contradictory result might be explained by the high activity of RuO₂ in CH₄ (Figure 3.4a) and HBr (Figure 3.4b) oxidation, generally proceeding at temperatures which are substantially lower in comparison to CH₄ oxybromination. On the basis of this, CO₂ and Br₂ are the principal reaction products (along with H₂O) in the lower temperature regime of CH₄ oxybromination, while O₂ consumption is almost quantitative, in good agreement with our experimental observations. At higher temperatures, the generated Br₂ reacts with CH₄, thus increasing the yield of CH₃Br, while the yield of CO₂ is almost constant (Figure B.13), ultimately resulting in an increased selectivity toward CH₃Br. Nevertheless, the inevitable CO₂ formation caused by the marked propensity of this catalyst to combust CH₄ as well as bromo compounds hampers the achievement of 100% selectivity to CH₃Br (Figure 3.1).

On the other hand, Cu-K-La-X and CeO₂ were more selective to CH₃X in CH₄ oxychlorination than in CH₄ oxybromination due to the pronounced deep oxidation to CO₂ in the latter reaction.

**Figure 3.6.** Product selectivity at ca. 15% conversion in CH₄ oxybromination (open bars) and oxychlorination (solid bars) over the catalysts.
In contrast, TiO₂ and VPO attained high selectivity to CH₃Br in CH₄ oxybromination, while they produce CO in CH₄ oxychlorination. Interestingly, the FePO₄ catalyst exhibited a high selectivity to CH₃X in both CH₄ oxybromination and oxychlorination.

To rationalize the observed selectivity patterns, the rate of CH₄ oxyhalogenation was compared with that of CH₄, HX, and CH₂X₂ oxidation over the representative catalysts CeO₂, VPO, and FePO₄, showing three different product distribution trends (Figure 3.7). In the case of CeO₂, the rate of HX oxidation is significantly higher in comparison to the rate of CH₄ oxychlorination, which is greater than the rate of CH₂Cl₂ and CH₄ oxidation. From this activity order, it follows that in CH₄ oxychlorination over CeO₂ the chloromethanes are formed at a higher rate than they are consumed in the corresponding oxidation reactions, in good agreement with the relatively high selectivity to CH₃X in both CH₄ oxybromination and oxychlorination.

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bromomethanes in over VPO and FePO$_4$, since the rate of HBr oxidation is significantly higher than the rate of CH$_4$ oxybromination, which is almost comparable to the rate of CH$_2$Br$_2$ oxidation. On the other hand, the rate of CH$_4$ oxybromination over CeO$_2$ is significantly lower than the rate of CH$_2$Br$_2$ oxidation, suggesting that bromomethanes, once produced, readily undergo oxidation, thus resulting in a limited selectivity to these products. Nevertheless, the rate of HBr oxidation is still higher than the rate of CH$_2$Br$_2$ oxidation, indicating that competition between these two reactions might be exploited to suppress the CO$_x$ formation (Figure 3.2). In the case of VPO, the kinetics of HCl oxidation is comparable to that of CH$_2$Cl$_2$ oxidation in the low reaction rate regime, while CH$_2$Cl$_2$ oxidation is slightly faster than the rate of oxychlorination, which might explain the low selectivity to chloromethanes and the high selectivity to CO. As already discussed in section 3.3.2, FePO$_4$ exhibits somewhat exceptional performance in CH$_4$ oxychlorination in comparison to the other catalysts, since the rate of HCl oxidation is significantly lower than the rate of CH$_4$ oxychlorination, suggesting that the latter reaction over this catalyst likely involves surface participation in activating CH$_4$. Similar to CH$_4$ oxybromination, the rate of CH$_2$Cl$_2$ oxidation is comparable to or lower than the rate of CH$_4$ oxychlorination, in line with the low CO$_x$ evolution over this catalyst.

These contrasting behaviors of the catalysts in two reactions have been further assessed by considering the effect of HX on the product distribution and the catalyst activity. For this purpose,
the partial reaction orders for CH$_4$ conversion ($n$(CH$_4$)), and for CO ($n$(CO)) and CO$_2$ ($n$(CO$_2$)) production with respect to the variation of feed HX concentration were determined (Figure 3.8 and Figures A.10 and A.11 and Table B.3). The positive, zero, or negative values of these parameters express a positive, null, or negative effect, respectively, on CH$_4$ conversion and CO$_2$ formation. On consideration of first the role of feed HX content on the activity, RuO$_2$ appears to be adversely affected in both reactions, with $n$(CH$_4$) = $-0.67$ in CH$_4$ oxychlorination and $-0.90$ in oxybromination. Higher deactivation in the case of CH$_4$ oxybromination than of oxychlorination is in line with the more vigorous surface halogenation by HBr in comparison to HCl, which might lead to subsurface bromination forming inactive bromide phases, as recently found in congeneric HX oxidation.$^{[122,123]}$ Cu-La-K-X and CeO$_2$ exhibited slightly negative $n$(CH$_4$) values in CH$_4$ oxybromination, while they showed activity promotion, particularly in the case of Cu-La-K-X, in CH$_4$ oxychlorination. More interestingly, VPO, TiO$_2$, and FePO$_4$ displayed positive values of $n$(CH$_4$) at higher HX content, with FePO$_4$ showing the highest promotion effect, in both CH$_4$ oxychlorination and oxybromination.

Second, considering the suppression of CO$_x$, the CO formation in CH$_4$ oxychlorination is essentially unaltered by the variation of the inlet HCl content, except over FePO$_4$ and Cu-K-La-X, which displayed positive $n$(CO) values of 0.43 and 0.81, respectively. A marked suppression of CO$_2$ formation upon an increase in the content of HX in the feed was observed over RuO$_2$ (Figure 3.2). This effect was particularly pronounced in CH$_4$ oxybromination, which hints that an operation of this catalyst under high HBr concentration at high temperatures might compensate the inhibition effect of HBr on the methane conversion, while preserving a high selectivity to bromomethanes. Nevertheless, an excursion to higher temperature enhances the combustion despite the high HBr concentration and promotes the formation of CH$_2$Br$_2$ at the expense of CH$_3$Br (Figure B.14). In CH$_4$ oxybromination, CeO$_2$ showed the strong promotion in CO formation on exposure to an increased HBr concentration, whereas the opposite behavior was observed over VPO ($n$(CO) = $-0.45$) and TiO$_2$ ($n$(CO) = $-0.2$). High HX content brought a reduction in the formation of CO$_2$ over CeO$_2$. Herein, a switch from the stoichiometric 6 to 15 vol.% HX led to a marked increase in productivity of chloromethanes (from ca. 23% yield at 73% total selectivity to ca. 27% total yield at 82% selectivity) and bromomethanes (from ca. 11% total yield at 57% selectivity to ca. 20% total yield at 98% selectivity), respectively, at unaltered CH$_4$ conversion. To the best of
knowledge, these are the highest values reported in the literature to date.\textsuperscript{[68,89,101,127,165]} In the case of oxybromination over CeO\textsubscript{2}, only trace amounts of O\textsubscript{2} were detected at the reactor outlet when the HBr content was increased from 6 to 15 vol.\%, while the conversion of HBr formally decreased from 90\% (6 vol.\% HBr) to 75\% (15 vol.\% HBr). The latter value is close to the theoretical maximum of 80\% calculated from the stoichiometry of HBr oxidation. These results imply that the suppression of CO\textsubscript{x} formation might come from the significantly faster kinetics of HBr oxidation in comparison to the bromomethane oxidation (Figure 3.7), which leads to a fast depletion of oxygen in the system. Moreover, an excess of HBr might favor the bromination of CeO\textsubscript{2}, thus lessening its reducibility. To elucidate these effects, CeO\textsubscript{2}, used in CH\textsubscript{4} oxybromination and oxychlorination, was characterized in more detail. The XRD analysis of the samples after testing under low (6 vol.\%) and high (15 vol.\%) HX contents revealed no alterations of bulk structure in comparison to its fresh analogue (Figure B.15), discarding any role of bulk on selectivity reforms. Thus, the used CeO\textsubscript{2} was analyzed by means of XPS (Figure B.15 and Table 3.2), which demonstrated that the Cl:Ce ratios in the surface region after exposure to 6 vol.\% and 15 vol.\% HCl were essentially identical, in good agreement with the less pronounced improvement of chloromethane selectivity at high HCl content (vide supra). In contrast, an exposure to 15 vol.\% HBr was necessary to achieve comparable surface Br:Ce ratios, correlating well with the significant increase in the selectivity to bromocarbons observed under these conditions (vide supra). A lower Br:Ce in comparison to Cl:Ce under stoichiometric feed composition indicates that the Br\textsubscript{2} evolution from the catalyst surface is more facile in comparison

<table>
<thead>
<tr>
<th>Sample</th>
<th>Br:Ce / mol mol(^{-1})</th>
<th>Cl:Ce / mol mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>oxybromination 6 vol.% HBr</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>oxybromination 15 vol.% HBr</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>oxychlorination 6 vol.% HCl</td>
<td>0</td>
<td>0.14</td>
</tr>
<tr>
<td>oxychlorination 15 vol.% HCl</td>
<td>0</td>
<td>0.14</td>
</tr>
</tbody>
</table>
to that of Cl₂ under oxyhalogenation conditions (> 733 K, Figure 3.5), in line with the HX oxidation studies reported previously.\cite{69,122,123}

To further substantiate the suppression of the combustion reactions upon HX addition, we have studied the oxidation of CH₂X₂ and CO in the presence (6 vol.%) or absence of HX over CeO₂. The effect of halogen coadsorption is evidenced in CH₂Cl₂ oxidation (Figure 3.9a), which generally yielded CO and CO₂ as the main products with traces of CHCl₃. An addition of HCl to the feed brought to a significant suppression of CO₂ formation and a redirection of the reaction toward the formation of CHCl₃, especially at lower temperatures. Nevertheless, the effect of HCl was gradually decreasing at higher temperatures until the end of CHCl₃ formation, which might be related to the evolution of the protective surface halogen coverage, as was demonstrated in congeneric HCl oxidation.\cite{119} However, the formation of CO₂ was still suppressed under these conditions (S(CO₂) ≤ 20%). This is further corroborated by the great inhibitory effect of HCl on the oxidation of CO (Figure 3.8b), also in accordance with previous studies in Deacon chemistry.\cite{178} In the case of CH₂Br₂ oxidation, the addition of HBr led to a significant increase of the light-off temperature (Figure B.16), which is in good agreement with the strongly suppressed combustion at high HBr contents. In contrast to CH₂Cl₂ oxidation, no polybrominated products could be observed. The conversion of HBr under these conditions was > 99%, suggesting that suppression of oxidation might partially arise from the competition of the two reactions for the available oxygen in the feed. Nevertheless, the concentration of O₂ remains high even after full HBr conversion, as inferred from ca. 60% CH₂Br₂ conversion observed at the highest temperature applied (660 K) in the cofeeding test (Figure B.16). Hence, a 4-fold decrease in CH₂Br₂ conversion (from 80% in the absence of HBr
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to 19\% at 6 vol.\% HBr) at ca. 620 K indicates that the inhibition effect of HBr on the CH$_2$Br$_2$
oxidation activity is primarily caused by the decrease in the catalyst’s reducibility.

As has been previously discussed, a drop in the selectivity to halocarbons when the CH$_4$
conversion is increased at higher temperatures was a common feature for all the catalysts, except
for RuO$_2$ in CH$_4$ oxybromination. The decrease in the selectivity might be caused by the additional
enhancement of the combustion reactions at increased temperature, which was used here to
promote the methane conversion. To examine this effect, the product distribution in the
oxyhalogenation was evaluated at constant conversion level that was adjusted by varying both the
temperature and space velocity ($F_T/W_{cat}$). As exemplified over CeO$_2$ (Figure B.17), a low space
velocity favors the oxidation of CH$_4$ and halocarbons despite the lower temperatures. These results
suggest that high temperature itself is not detrimental for the selectivity to halocarbons.

3.3.4. Selective Production of Carbon Monoxide via Methane Oxychlorination

As discussed above, CH$_4$ oxychlorination over TiO$_2$ and particularly VPO provides a high
selectivity to CO, with unprecedentedly suppressed CO$_2$ formation and low residual amounts of
chloromethanes. In particular, 33\% yield and 96\% selectivity for CO are achieved over VPO at
836 K. Besides, only trace amounts of H$_2$ are detected, while the effective HCl conversion is $\leq$ 1.5\% (Table B.4), which suggests that the biggest part of HCl is recycled in situ in a single reactor pass.

These findings hint at the extra potential of oxychlorination as an effective one-step route to
exploit the natural gas feedstock for on-purpose production of CO, a key building block in the
manufacture of numerous commodities (Figure 3.10a),\cite{174} which is currently obtained by the highly
endergonic steam reforming and coal gasification processes. Nonetheless, this application of the
oxyhalogenation reaction has not been considered to date, probably due to the fact that CO was
never produced at a selectivity exceeding 50\%.\cite{68,127,165}

The negligible CH$_4$ conversion over both VPO and TiO$_2$ in the direct oxidation (Figure 3.4a), at
temperatures which are significantly higher compared to those applied in the oxychlorination
reaction, and an increase in CH$_4$ conversion upon increasing the inlet HCl concentration
(Figure 3.2), demonstrates the pivotal role of HCl in activating methane and corroborates the
oxidation of halomethanes as the principal source of CO over these two catalysts. The higher
activity of VPO in CO production is in line with its higher propensity of this catalyst to evolve
Cl\(_2\) (Figure 3.4b), and thus the enhanced production of the precursor chloromethanes. In good agreement with the oxychlorination tests, CO is produced with very high selectivity (> 99%) in both CH\(_3\)Cl and CH\(_2\)Cl\(_2\) oxidation over VPO (Figure 3.10a,b), while in the case of TiO\(_2\), the selectivity to CO observed in the oxidation of CH\(_3\)Cl (ca. 90%) is lower than that obtained in the oxidation of CH\(_2\)Cl\(_2\) (> 99%).

The exceptional CO production via methane oxychlorination over VPO is shown to be stable during 100 h on-stream test (Figure 3.11a). Similar to the stability test conducted in CH\(_4\) oxybromination in Chapter 2, XRD analysis of the fresh and used VPO samples recovered after different time-on-stream durations (Figure B.18) indicated the equilibration of the starting (VO)\(_2\)P\(_2\)O\(_7\) structure within the first 1 h of operation, which remains unaltered over the whole evaluated period of time. \(^{31}\)P nuclear magnetic resonance by spin-echo mapping (Figure 3.10b) showed a major peak centered at around 2500 ppm, which is characteristic for a (VO)\(_2\)P\(_2\)O\(_7\) phase (Figure 3.11b).\(^{170}\) This peak is slightly broader in the case of the fresh catalyst sample, but shows no significant changes among the used catalyst, in line with XRD data. No peaks ascribed to V\(^{3+}\):
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phases (located at ca. 4700 ppm) could be observed, while a small peak located around 0 ppm, which is more pronounced in the case of used catalyst samples, indicates the presence of V$^{5+}$ sites. This is further corroborated by temperature-programmed reduction with H$_2$ and X-ray photoelectron spectroscopy (Figure B.18, Table B.5), which also point to the presence of V$^{5+}$ sites in the surface region of all catalyst samples.

The unique performance of VPO opens a way for the development of a novel process for natural gas upgrading by exploiting CO as a versatile platform molecule. In particular, if coupled with the well-established production of formic acid, a valued chemical and highly prospective energy carrier,$^{[180-182]}$ it could provide an effective means of bringing carbon, hydrogen, and/or energy equivalents of stranded methane reserves to the market in a liquid form. Alternatively, the on-site water-gas shift reaction of the CO-H$_2$O mixture could generate hydrogen.$^{[183]}$ In this way, traditional syngas-to-chemicals transformations, such as methanol production or Fischer-Tropsch (F-T) hydrocarbon synthesis, can be practiced by circumventing steam-reforming (1073-1273 K, 20-30 bar) or auto-reforming ($>2273$ K, $<100$ bar) processes, which are the most energy- and capital-demanding steps of the commercial syngas generation technologies.$^{[23,25,184]}$ Moreover, H$_2$ derived from renewable sources, such as photocatalytic water splitting or biomass reforming,$^{[185]}$ might also be utilized.

Figure 3.11. (a) CH$_4$ conversion of and product selectivity versus time-on-stream (tos) in CH$_4$ oxychlorination over VPO. (b) $^{31}$P nuclear magnetic resonance spectra by spin-echo mapping of fresh and used VPO after the different time on stream. Conditions: CH$_4$:HCl:O$_2$:Ar:He = 6:6:3:4.5:80.5, $F_T/W_{cat} = 100$ cm$^3$ min$^{-1}$ g$^{-1}$, $T = 803$ K, and $P = 1$ bar.
3.3.5. Overview of the Catalytic Potential in Methane Oxyhalogenation

To systematically analyze the complex oxyhalogenation chemistry, which involves multivariable dependence and multiobjective performance classification, kinetics parameters were extracted from the above discussion and presented in an integrated manner for CH₄ oxychlorination and CH₄ oxybromination (Figure 3.12). The upper half of the radar charts classifies materials on the basis of their activity and tendency toward deep oxidation. Thus, the systems exhibiting high activity (low $T_{15}$, high $E_a(CH_4)$) for CH₄ conversion, which is even promoted by the HX addition ($n(CH_4) > 0$), and low propensity to CO₂ formation (low $S(CO_2)$, $n(CO_2) < 0$) approach the periphery of the plot and are regarded as good oxyhalogenation catalysts. Given the complexity of the oxyhalogenation process, the activation barriers extracted from the temperature variation experiments likely lump together the contributions from the different heterogeneous and/or gas-phase reaction steps that might vary among various oxyhalogenation catalysts. Since the determined activation barriers do not necessarily reflect the intrinsic catalyst propensity to facilitate the halomethane formation, these are not used as criteria for ranking their performance. Instead, the activity of the catalysts is primarily related to the temperature window of their operation, here presented by $T_{15}(CH_4)$, while the apparent activation energy is considered as a kinetic parameter reflecting the increment in the reaction rate upon a change in temperature. Since higher values of the latter parameter indicate a steeper increase in reaction rate with temperature, they are perceived as advantageous. In this respect, RuO₂, which suffers from HX poisoning and shows high CO₂ production in both CH₄ oxybromination and oxychlorination, can be considered as a suboptimal catalyst since its coordinates approach the center in both radar plots. On the other hand, CeO₂ and particularly Cu-K-La-X showed opposite trends in CH₄ oxybromination and oxychlorination, as their calculated parameters lie in the outer annulus for the former reaction and in the inner part for the latter case. Although the results in CH₄ oxychlorination might appear promising, the instability of the Cu-based catalyst makes it unattractive for potential industrial application. Mild oxidants, such as TiO₂, FePO₄, and VPO, placing themselves toward outer edge of the plot in the oxybromination reaction, are more effective in CH₄ oxybromination than in oxychlorination. In addition, their activity is promoted at increased HBr content.

This analysis is further expanded at the bottom half of the radar plots, which classifies materials on the basis of their ability to produce the desired CH₃X (high $S(CH_3X)$, low $S(CO)$, $n(CO) < 0$)
Figure 3.12. Overview of the catalytic descriptors in (a) CH\textsubscript{4} oxybromination and (b) CH\textsubscript{4} oxychlorination, extracted from the experimental program (Figure 3.1 and Figure 3.2). The upper half of the radar charts classifies a material as a good oxyhalogenation catalyst if it combines high activity (low $T_{15}$, high $E_a(\text{CH}_4)$, $n(\text{CH}_4) > 0$) and low propensity to CO\textsubscript{2} formation (low $S(\text{CO}_2)$, $n(\text{CO}_2) < 0$) even increased by inlet HX addition, which will be displayed centrifugally in this part of the plot. The bottom half, instead, classifies materials for their ability to produce CH\textsubscript{3}X (high $S(\text{CH}_3X)$), if they lie on the outer annulus of the plot, or as CO generators (high $S(\text{CO})$ and $n(\text{CO})$), if they converge to the center of the chart.
if they lie on the outer annulus of the plot. Thus, it can be seen that CeO$_2$ and FePO$_4$ are centrifugally displayed in the bottom part of the CH$_4$ oxychlorination radar, since they act as the most effective CH$_3$Cl producers, both reaching a $S$(CH$_3$Cl) of 75%, and display positive sensitivity to HCl. Still, CeO$_2$ offers the advantage of lower operating temperature over FePO$_4$.

The same pattern obtained in the catalyst classification from the top part of the radar charts is also observed in the bottom section, with less reducible catalysts being more effective CH$_3$Br producers. In particular, VPO and FePO$_4$ showed the highest $S$(CH$_3$Br) values, which can be increased at higher HBr contents ($n$(CO) $< 0$). This exceptional performance makes them effective CH$_4$ oxybromination catalysts.

VPO and TiO$_2$, displayed in the center of the bottom CH$_4$ oxychlorination radar, exhibit the unique possibility of selectively producing CO ($S$(CO) = 95 and 78%) via oxychlorination chemistry that could not be obtained over any other investigated material and under any conditions when HBr was used as halogenating agent, which points to the complexity of oxyhalogenation chemistry, dependent not only on the nature of the catalyst but also on the type of HX and operating conditions.

### 3.4. Conclusions

In this Chapter, analogies and differences between CH$_4$ oxychlorination and oxybromination were assessed through the steady-state catalytic evaluation of different materials under variable conditions coupled with selected characterization techniques. On the basis of these, the relationships among the oxyhalogenation, gas-phase halogenation, and HX and CH$_4$ oxidation were established for the first time over a diverse set of materials, suggesting that the activity in the oxyhalogenation reaction depends on (i) the ability of a catalyst to oxidize HX and (ii) the inherent propensity of the thus produced molecular halogen to react with CH$_4$ in the gas phase. The performance of FePO$_4$ was somewhat exceptional to this rule, as its CH$_4$ oxychlorination activity substantially exceeds that in HCl oxidation, which might suggest the active participation of the catalytic surface in C-Cl bond formation. In terms of product distribution, it was found to be dependent not only on the nature of the catalyst but also on the type of HX, as well as its partial pressure. Thereby, four different classes of catalysts were observed: (i) RuO$_2$ favoring combustion in both oxybromination and oxychlorination, (ii) CeO$_2$ and Cu-K-La-X, which are effective
chloromethane producers, while in oxybromination they lead to CO$_2$ formation, (iii) VPO and TiO$_2$, which are selective to bromomethanes but in oxychlorination they bring selective CO formation, and (iv) FePO$_4$ showing a high selectivity to halomethanes in both CH$_4$ oxybromination and oxychlorination. These selectivity patterns are explained by the differences in reaction rates among oxyhalogenation, CH$_2$X$_2$ oxidation, and HX oxidation. A high selectivity to halomethanes is achieved if the rate of oxyhalogenation is greater than or comparable to the rate of CH$_2$X$_2$ oxidation, while the rate of HX oxidation should be higher than the rate of CH$_2$X$_2$ oxidation.

Regarding the impact of HX concentration on the product distribution, it is here shown that the selectivity to halocarbons over the first and second classes of catalysts can be boosted if these are operated under high HX concentration. This enhancement was especially pronounced over CeO$_2$, resulting in the highest reported yields of chloro- and bromocarbons (ca. 27% and 20%, respectively), which might be related to the (i) faster kinetics of the HX oxidation step in comparison to halocarbon combustion and (ii) an enhanced reduction of the surface of the catalyst.

These experimental findings shed light on the great diversity of oxyhalogenation chemistry. Nevertheless, a comprehensive understanding of the phenomena presented here should be related to the intrinsic properties of the materials, which is essential for rational catalyst design and necessitates the application of advanced operando characterization techniques and theoretical modeling.
Chapter 4

Lanthanum Vanadate Catalysts for Methane Oxybromination

4.1. Introduction

The development of catalytic processes enabling the efficient transformation of methane (CH$_4$) into valued chemicals and liquid fuels is one of the major directions in catalysis research.[5,25,27-29,186] The interest is driven by the large amounts of stranded natural gas (> 30% of proven reserves), which although providing a low-cost and long-lasting alternative to diminishing oil, cannot be utilized due to the high transport expenses and substantial capital expenditures of the commercial syngas-based plants that are only economical at large-scale. Bromine-mediated functionalization of CH$_4$ into bromomethanes, viz., bromomethane (CH$_3$Br) and dibromomethane (CH$_2$Br$_2$), constitutes a promising technology to valorize the stranded natural gas using small-scale processes amenable to decentralization. CH$_3$Br has similar upgrading routes as methanol, which offers numerous possibilities for the production of commodities such as olefins, higher paraffins, aromatics over zeolites, while CH$_2$Br$_2$ can be reformed into CH$_3$Br via catalytic hydodebromination or reproportionation processes.[8,29,84,88-90] Catalytic oxybromination of CH$_4$ is an integral process of this technology which combines CH$_4$ activation into bromomethanes with the recovery of hydrogen bromide (HBr) that is released as the end form of halogen after upgrading steps.[29,89] It allows to close the bromine loop in which oxygen (O$_2$) acts as the ultimate oxidant of CH$_4$, and is hence of great significance for the practical implementation of this technology.[89] Nonetheless, the potential industrialization of oxybromination is contingent on the development of the cost-effective materials displaying a high structural stability under the corrosive reaction atmosphere and finely tuned redox properties in order to achieve a high yield of bromomethanes with minimized selectivity losses through undesired combustion reactions. In this context the isolation of redox active metal centres in the matrixes which are relatively inert to oxidation constitutes an attractive approach to enhance the selectivity to bromomethanes, as exemplified by FePO$_4$ and VOPO$_4$ in Chapter 2,
and EuOBr in Chapter 6. The latter catalyst combines the highest selectivity to bromomethanes (92-98%) with minimal production of carbon oxides (selectivity to CO₂ 2-8%) at 15-31% of CH₄ conversion, and the remarkable stability. However, a design of new catalysts comprising more affordable rare-earth element, such as La, would be very desirable in view of high europium price. In fact, lanthanum (oxy)chlorides were found as the outstanding catalysts in congeneric oxychlorination of CH₄, which is proposed to proceed by the redox cycling of adsorbed chlorine species without changes in the oxidation state of La³⁺ ion. Nonetheless, owing to the growing evidences that CH₄ oxybromination involves the surface-catalyzed HBr oxidation followed by the CH₄ bromination in gas-phase, the lack of redox ability of La³⁺ ion might cause a low activity of the respective lanthanum (oxy)bromides.

In this context, an appealing strategy to enhance the performance comprises the formation of the mixed oxides of La₂O₃ with a redox active component such as vanadium oxide. The lanthanum orthovanadate (LaVO₄) belongs to the class of rare-earth orthovanadates (REVO₄), which gained a significant interest in light emitting devices and various catalytic applications, due to their high thermal stability and interesting optical, electric, and redox properties. The activity of these materials in oxidation reactions originates from V⁵⁺/V⁴⁺ redox couple and with it associated oxygen vacancy formation. RE-O-V structural motives are proposed to decrease the oxygen mobility compared to the pure V₂O₅, which is the essence of their application in selective oxidation. Besides, the structural and redox properties of REVO₄ can be potentially tailored by controlling the molar V:RE ratio, which has been rarely investigated.

In this Chapter, a series of lanthanum vanadate catalysts (LaVₓO₂.₅ₓ+₁.₅) with molar V:La ratio in the range x = 0-1.2 are prepared using citrate method and studied in CH₄ oxybromination. Complemented with the comprehensive materials characterization with X-ray diffraction, electron microscopy, Raman, ⁵¹V magic angle spinning nuclear magnetic resonance, and X-ray photoelectron spectroscopies, we assess the structure-performance relationships as a function of vanadium content in the catalyst. Finally, we attain the material which is among the best reported oxybromination catalysts.
4.2. Experimental

4.2.1. Catalyst Preparation

A series of lanthanum vanadium oxides, LaV$_x$O$_{2.5x+1.5}$, with molar V:La ratios in the range of $x = 0-1.2$ were syntheitized using the citrate method.[195] Briefly, 0.3 M solutions of La(NO$_3$)$_3$·6H$_2$O (Aldrich, > 99.8%) and NH$_4$VO$_3$ (Aldrich, > 99%) were prepared by dissolving the respective salts in deionized water, followed by the addition of citric acid (Aldrich, > 99%) to adjust the molar citric acid:metal ratio to 3. The vanadium content in the oxide was varied by mixing the appropriate volume (0-120 cm$^3$) of NH$_4$VO$_3$ solution with 100 cm$^3$ of La(NO$_3$)$_3$ solution. The mixture was magnetically stirred (500 rpm) for 30 min and then dried in a two-step temperature program comprising heating at 433 K for 5 h and 473 K for another 5 h. The resulting sponge-like solids were finally decomposed into oxides by calcination in static air at 973 K for 5 h. All thermal treatments were conducted using a heating rate of 5 K min$^{-1}$.

4.2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) was measured using a PANalytical X’Pert PRO-MPD diffractometer with Bragg-Brentano geometry by applying Cu-K$\alpha$ radiation ($\lambda$ = 1.54060 Å). The data were recorded in the 10-70° 2$\theta$ range with an angular step size of 0.017° and a counting time of 2.04 s per step. N$_2$ sorption at 77 K was performed using a Micromeritics TriStar analyzer. Prior to the measurement, the sample (0.3 g) was evacuated to 50 mbar at 573 K for 12 h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area, $S_{BET}$.

The content of vanadium and lanthanum in the solid was measured by X-ray fluorescence (XRF) using an EDAX Orbis Micro-XRF analyzer equipped with a Rh source operated at a voltage of 30 kV and a current of 500 μA. Temperature-programmed reduction with hydrogen (H$_2$-TPR) was conducted in a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector. The sample (0.15 g) was loaded in an U-shaped quartz reactor between two plugs of quartz wool and pretreated in He (20 cm$^3$ min$^{-1}$) at 573 K for 1 h. H$_2$-TPR was then performed in 5 vol.% H$_2$ in N$_2$ (20 cm$^3$ min$^{-1}$) by increasing the temperature in the range of 573-1150 K at 10 K min$^{-1}$. High-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and elemental mapping with
energy-dispersive X-ray spectroscopy (EDXS) were conducted on a FEI Talos microscope operated at 200 kV. The sample was dispersed as a dry powder onto lacy carbon-coated nickel grid. Fast Fourier transform images of the selected regions of HRTEM micrographs were generated using ImageJ software. The particle size distribution was determined by examining over 50 nanoparticles. Raman spectroscopy was performed on a WITec CRM200 confocal Raman system using a 532 nm laser with 20 mW power, a 100× objective lens with numerical aperture NA = 0.9 (Nikon Plan), and a fiber-coupled grating spectrometer (2400 lines per mm), giving a spectral sampling resolution of 0.7 cm⁻¹. Solid-state ⁵¹V magic angle spinning nuclear magnetic resonance (⁵¹V MAS NMR) spectroscopy was carried out in a Bruker Avance IIIHD spectrometer equipped with a 9.4 T magnet (105.2 MHz ⁵¹V Larmor frequency). The sample was loaded into 3.2 mm rotor and measured using a 3.2 mm double resonance MAS probe. The specimen was rotated around the magic angle at a rate of 16.00 kHz and the signal was acquired using a single pulse excitation experiment with a very short pulse duration of 0.3 s in order to achieve the required excitation bandwidth over the whole spectral range. A total of 1024 scans with a recycle delay of 1 s were recorded. The data were processed by shifting the free induction decay to the first rotor echo prior to Fourier transform so as to avoid a rolling baseline and a large first-order phase correction. X-ray photoelectron spectroscopy (XPS) was measured in a Physical Electronics Quantum 2000 spectrometer using monochromatic Al-Kα radiation, generated from an electron beam operated at 15 kV, and equipped with a hemispherical capacitor electron-energy analyzer. The solid was analyzed at an electron take-off angle of 45° and a pass energy of 46.95 eV. In order to suppress sample charging during analysis, an electron and an ion neutralizer were operated simultaneously. Remaining charging effects were corrected by referencing all spectra to adventitious carbon (C 1s at 284.8 eV). The elemental concentrations were quantified based on the measured photoelectron peak areas (La 3d, V 2p, Br 3d) after Shirley background subtraction using PHI-MultiPak software and the built-in relative sensitivity factors, which are corrected for the system transmission function.

4.2.3. Catalyst Testing

CH₄ oxybromination, and CO, CH₃Br, CH₂Br₂, and HBr oxidation were performed at ambient pressure in a continuous-flow fixed-bed reactor setup, which is described in Appendix A. The
catalyst (catalyst weight, \( W_{\text{cat}} = 1 \, \text{g} \) and particle size, \( d_p = 0.4-0.6 \, \text{mm} \)) was intimately mixed with inert quartz particles (Thommen-Furler, \( d_p = 0.2-0.3 \, \text{mm} \)) and loaded in a quartz reactor between the two plugs of quartz wool (\( V_{\text{bed}} = 2 \, \text{cm}^3 \)). The post-catalyst zone was filled with quartz beads (Sigma-Aldrich, \( d_p = 0.6 \, \text{mm} \)) to minimize the contributions of the gas-phase reactions. The effect of the volume after the catalyst bed on the oxybromination performance was studied in quartz reactors with constant size of the catalyst zone (\( d_r = 4 \, \text{mm} \), \( W_{\text{cat}} = 0.1 \, \text{g} \), \( d_p = 0.3-0.4 \, \text{mm} \),) and different size of the post-catalyst zone. The bed was heated to the desired temperature (753-813 K) under He flow and was left to stabilize for at least 30 min under these conditions prior to admitting the reaction mixture. Unless otherwise stated, the catalytic runs were conducted using a molar ratio of \( \text{CH}_4: \text{HBr}: \text{O}_2: \text{Ar}: \text{He} = 6:6:3:4.5:80.5 \) and the total gas flow of \( F_T = 100 \, \text{cm}^3 \, \text{min}^{-1} \), wherein the flow units correspond to standard temperature and pressure (STP) conditions, i.e., 273 K and 1 bar.

Analysis of reactants and products, determination of conversion, selectivity, yield, and reaction rate, as well as the evaluation of carbon and bromine mass balance was conducted using the protocol described in Appendix A. The reaction rate normalized per content of vanadium, \( r_{V, \text{mol}} \) was determined using the Equation 4.1,

\[
r_{V, \text{mol}} = \frac{n(\text{CH}_4)_{\text{inlet}} - n(\text{CH}_4)_{\text{outlet}}}{N(V)}, \, \text{mol}_{\text{CH}_4} \, \text{s}^{-1} \, \text{mol}^{-1}_V
\]

where \( n(\text{CH}_4)_{\text{inlet}} \) and \( n(\text{CH}_4)_{\text{outlet}} \) are the respective molar flows of \( \text{CH}_4 \) at the reactor inlet and outlet and \( N(V) \) is the molar content of vanadium in the catalyst.

### 4.3. Results and Discussion

#### 4.3.1. Characterization of the Fresh Catalysts

The textural and structural properties of the lanthanum vanadate catalysts, \( \text{LaV}_x\text{O}_{2.5x+1.5} \), with a molar \( \text{V}:\text{La} \) ratio in the range of \( x = 0-1.2 \), were assessed by \( \text{N}_2 \) sorption (Figure 4.1), X-ray diffraction (Figure 4.2), and Raman spectroscopy (Figure 4.3). Specific surface areas \( (S_{\text{BET}}) \) were in the range of 2-35 m\(^2\) g\(^{-1}\), whereby the lowest values of 5 and 2 m\(^2\) g\(^{-1}\) were attained in the materials with boundary contents of vanadium i.e., \( \text{La}_2\text{O}_3 \) \((x = 0)\) and \( \text{LaV}_1.2\text{O}_{4.5} \) \((x = 1.2)\), respectively. The diffractograms of \( \text{La}_2\text{O}_3 \) and stoichiometric \( \text{LaVO}_4 \) \((x = 1)\) exhibited sharp
reflections, matching the reference patterns of hexagonal lanthanum oxide (h-La2O3) and monoclinic lanthanum orthovanadate (m-LaVO4). The monoclinic phase is thermodynamically preferred over the tetragonal in the case of LaVO4, as it provides a higher coordination number for the lanthanum ion (9 versus 8), which has the smallest diameter among the rare-earth elements.[201] Sub-stoichiometric LaV0.2xO2.5x+1.5 with 0.2 ≤ x < 1 featured the diffraction lines of both h-La2O3 and m-LaVO4, whereby the contribution of the latter phase increased with an increase in V:La ratio. The over-stoichiometric LaV1.2O4.5 showed only the reflections of m-LaVO4. It is put forward that the excess of vanadium is in the form of amorphous vanadium oxide species (vide infra).

The observations from XRD analyses were complemented by Raman spectroscopy (Figure 4.3). Pure lanthanum oxide displayed three strong bands centered at 104, 188, and 404 cm⁻¹, which can be ascribed to h-La2O3,[202] while the low-frequency bands of lanthanum vanadate catalyst at 309, 329, 348, 374, and 397 cm⁻¹, and the high-frequency band at 860 cm⁻¹ match the Raman-active modes of m-LaVO4 that are ascribed to La-O bond vibrations and internal vibrations within the VO₄³⁻ group, respectively.[32,34,35,190,203-204] Consistent with XRD, the LaV0.25x+1.5 samples with V:La ratios in the range of 0.2 ≤ x < 1 showed the features of both m-LaVO4 and h-La2O3. Herein, h-La2O3 peaks decreased in their intensity at higher vanadium contents and were almost indistinctive in LaV0.5O2.75, whereas the bands of m-LaVO4 became sharper and more intense. The Raman spectrum of LaV1.2O4.5 catalyst displayed high-intensity peaks at ca. 99 and 140 cm⁻¹,
Figure 4.2. X-ray diffractograms of the catalysts in fresh form and after equilibration in CH$_4$ oxybromination for different times. Reference patterns identified with their ICDD-PDF numbers are provided as vertical lines below the measured diffractograms. Inset bars denote the percentage of $m$-LaVO$_4$ (gray) and $t$-LaOBr (orange) phases estimated from the relative ratio of their 120 and 102 reflections, respectively. Equilibration conditions as reported in the caption of Figure 4.1.
Figure 4.3. Raman spectra of the catalysts in fresh form and after equilibration in CH₄ oxybromination for different times. Equilibration conditions as reported in the caption of Figure 4.1.
substantial broadening in the spectral range of 250-450 cm$^{-1}$, and the new peak at ca. 992 cm$^{-1}$, which are indicative of the presence of amorphous V$_2$O$_5$.$^{[205,206]}$

Owing to the fact that the XRD and Raman analyses suggest that vanadium is present only in the form of $m$-LaVO$_4$ in the stoichiometric and the sub-stoichiometric catalysts, $^{51}$V MAS NMR spectroscopy was used to further assess the potential differences in the electronic and geometric

![Figure 4.4. $^{51}$V MAS NMR spectra of LaV$_{0.5}$O$_2$ and LaVO$_4$ in fresh form and after equilibration in CH$_4$ oxybromination for different times. The insets present the spinning sidebands (left) and the centerband (right) of the measured (solid line) and the simulated (dashed line) spectra. Equilibration conditions as reported in the caption of Figure 4.1.](image)
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state of vanadium ions (Figure 4.4). The spectra displayed no substantial differences as shown for LaVO₄ and LaV₀.₅O₂.₇₅. Their features resembled to those previously reported for LaVO₄ and can be very accurately simulated by using published values for the quadrupole coupling constant and quadrupolar asymmetry parameter of this material.[²⁰⁷,²⁰⁸] The quadrupole interaction is a direct probe of the electric field gradient at the location of the $^{51}$V nucleus and is therefore reflects the structure at a molecular level. The similarity between simulated and experimental spectrum was especially good for the spectrum of the stoichiometric LaVO₄, where both the line shape of the centerband as well as the fine structure of the spinning sidebands is reproduced. The fact that the spectrum can be simulated with a single value for the quadrupolar parameters indicates that there is very little variation of the structure around the vanadium centers. The slight differences between the spectra can be phenomenologically explained as the higher broadening of LaVO₄ compared to LaV₀.₅O₂.₇₅, which can be tentatively related to an increasing amount of variation of the local structure in sub-stoichiometric compared to stoichiometric oxides.

4.3.2. Catalytic Performance in Methane Oxybromination

The stability of $\text{LaV}_x\text{O}_{2.5x+1.5}$ catalysts in CH₄ oxybromination was assessed, as it is the one of the major challenges in the catalyst development (Figure 4.5). Several attempts to perform the reaction over La₂O₃ led to a gradual pressure build-up until the flow of gas mixture was almost completely obstructed and reaction had to be stopped after just 1 h on-stream. Inspection of the recovered catalyst bed revealed severe particle agglomeration (Figure 4.5, left inset). In the case of the over-stoichiometric $\text{LaV}_{1.2}\text{O}_{4.5}$, fast deactivation took place, with > 50% of its original activity lost within 20 h on stream. The catalyst bed (Figure 4.5, right inset) displayed two distinct layers, namely white (top) and dark (bottom), with the relative fraction of the top section increasing over time. In contrast to the aforementioned catalysts, the performance of the stoichiometric LaVO₄ as well as the sub-stoichiometric LaV₀.₂O₂ and LaV₀.₇O₃.₂₅ was stable for 20 h on stream, whereas the stability test over LaV₀.₅O₂.₇₅, was successfully extended to 60 h. Besides, no signs of sticking or color change could be observed (Figure 4.5, middle inset).

Given their stability, $\text{LaV}_x\text{O}_{2.5x+1.5}$ catalysts within the compositional window of $0.2 \leq x \leq 1$ were further evaluated in CH₄ oxybromination in order to determine their inherent activity (Figure 4.6) and selectivity-conversion patterns (Figure 4.7). The tests were conducted over the
catalysts equilibrated in CH$_4$ oxybromination for 20 h under the identical conditions to those applied in Figure 4.5 (vide supra). The specific reaction rates normalized per catalyst weight determined at low CH$_4$ conversions (ca. 5%) increased with vanadium content in the catalyst. Nonetheless, the rates normalized per content of vanadium followed the opposite trend, implying the better utilization of the former metal in the sub-stoichiometric oxides compared to the stoichiometric LaVO$_4$. Stoichiometric LaVO$_4$ as well as the sub-stoichiometric LaV$_{0.7}$O$_{4.25}$ exhibited the high selectivity to bromomethanes (ca. 91-85%) in the low-conversion regime (9-15%).
Nonetheless, a substantial CO\textsubscript{x} production (15-27% selectivity) occurred over these catalysts at >20% conversion. In contrast, LaV\textsubscript{0.2}O\textsubscript{5} displayed a relatively low CO\textsubscript{x} production (ca. 5-9% selectivity) at CH\textsubscript{4} conversions of ca. 7-20%. However, its activity was the lowest among the investigated catalysts. LaV\textsubscript{0.5}O\textsubscript{2.75} displayed optimized performance, preserving the relatively high activity that is comparable to LaV\textsubscript{0.7}O\textsubscript{3.25} and LaVO\textsubscript{4}, high selectivity to bromomethanes (ca. 95-90%), and low selectivity to CO\textsubscript{x} (ca. 5-10%) in the broad conversion range of 7-25%. The comparison of the product distribution over different lanthanum vanadate catalysts at ca. 20% conversion of CH\textsubscript{4}, which is achieved by adjusting the space velocity at $T = 793$ K (Figure 4.7c) leads to a very similar selectivity-conversion dependence as observed by the temperature variation at constant space velocity presented in Figure 4.7a. The activity and the product distribution patterns of the optimal LaV\textsubscript{0.5}O\textsubscript{2.75} catalyst were further evaluated at different space velocities and inlet concentrations of HBr, CH\textsubscript{4}, and O\textsubscript{2} (Figure 4.7b). As expected, higher space velocities impact positively on the selectivity to bromomethanes at the expense of a lower conversion of CH\textsubscript{4}, ultimately resulting in a similar selectivity-conversion dependence as observed by the temperature variation (Figure 4.7a). Similarly, a decrease in the O\textsubscript{2} feed content curbs the combustion, but also decreases the conversion. High concentrations of CH\textsubscript{4} lead to slightly lower conversions of this reactant, resulting in an increase of the reaction rate, which is in line with the first order dependence with respect to this reactant (vide infra). Nonetheless, the higher rates of
Figure 4.7. Product selectivity versus conversion in CH₄ oxybromination over (a) LaVₓO₂.₅ₓ₊₁.₅ catalysts at various temperatures (CH₄:HBr:O₂:Ar:He = 6:6:3.5:80.5, Fₑ/Wₑ = 100 cm³ min⁻¹ g⁻¹) and (b) LaV₀.₅O₂.₇₅ at 793 K and various space velocities (CH₄:HBr:O₂:Ar:He = 6:6:3.5:80.5, T = 793 K). The product distribution over LaVₓO₂.₅ₓ₊₁.₅ catalysts at similar level of CH₄ conversion, which is achieved by adjusting the space velocity (CH₄:HBr:O₂:Ar:He = 6:6:3.5:80.5, T = 793 K). The product distribution over LaVO₄ and LaV₀.₅O₂.₇₅ with respect to EuOBr at similar level of CH₄ conversion. Prior to the tests, the catalysts were equilibrated in CH₄ oxybromination as reported in the caption of Figure 4.5. All the tests were conducted at P = 1 bar.
bromomethanes formation are likely promoting their subsequent deep oxidation, which might explain a relatively small drop in their selectivity (ca. 5%) observed at high CH₄ contents. Increasing the inlet concentrations of HBr further minimizes formation the formation of CO₂ at unchanged methane conversion, enabling to achieve the selectivity to bromomethanes of up to 96%. The latter effect can be rationalized by the increased coverage of bromine which reduces the oxidizing potential of the catalyst surface as discussed in Chapter 3. In overall, the selectivity to bromomethanes attainable over LaV₀.5O₂.75 are comparable to the best reported oxybromination catalyst, EuOBr (Figure 4.7d), which is presented in Chapter 6.
The previous Chapters have highlighted that CH$_4$ oxybromination over different catalytic materials might proceed via the synergetic interplay between the surface-catalyzed HBr oxidation and CH$_4$ bromination in the gas phase. The investigation of the reaction kinetics strongly suggests that this is likely the principal pathway of methane oxybromination over LaV$_{0.5}$O$_{2.75}$. Specifically, the increase in bromomethanes production upon increasing the temperature led to a drop in the bromine yield, suggesting that the latter product might react with CH$_4$ (Figure 4.8a). In addition, larger volumes of the void zone after the catalyst bed which provide longer times for the gas-phase reactions to take place, led to the increase of the yield of bromomethanes at the extent of a decreased Br$_2$ yield (Figure 4.8b), confirming the active role of the gas-phase bromination. Besides, the apparent activation energy of oxybromination of ca. 120-130 kJ mol$^{-1}$ (Figure 4.8c) as well as the apparent reaction order with respect to CH$_4$ of ca. 1 (Figure 4.8d), are very similar to the values of the respective parameters reported for the non-catalytic CH$_4$ bromination.$^{[83,84]}$ Consistently, the reaction displays a small positive reaction order with respect to HBr of ca. 0.2, suggesting its facile activation, which along with the previous kinetic fingerprints supports that methane activation by the gas-phase bromination plays an important role in the oxybromination over lanthanum vanadates.

4.3.3. Characterization of the Equilibrated Catalysts

The stark performance differences between the LaV$_{x}$O$_{2.5x+1.5}$ catalysts in terms of stability and product selectivity were rationalized by an in-depth characterization of the materials recovered after different times in CH$_4$ oxybromination. Bulk V:La molar ratio was unaltered after 20 h on stream in all the samples except for LaV$_{1.2}$O$_{4.5}$ (Figure 4.1). In the case of the latter material, the top part of the catalyst bed (Figure 4.5, right inset) showed a decrease of molar V:La ratio from 1.2 to 1, which corresponds to the stoichiometry of $m$-LaVO$_4$ phase, while the bottom part exhibited a similar vanadium content as in the fresh catalyst. XRD diffractograms of both bed sections displayed only the reflections of $m$-LaVO$_4$ and were in this regard identical to the fresh material (Figure 4.2). Nonetheless, while the Raman spectrum of the top bed section matched that of stoichiometric LaVO$_4$ (Figure 4.3), the bottom part preserved the features of the fresh catalyst where free vanadium oxide was detected. The H$_2$-TPR profile of the catalyst recovered from the top bed section exhibited no characteristic reduction peaks of V$_2$O$_5$ at ca. 840 K and 870 K.$^{[209]}$
which were observable in of the fresh material (Figure 4.9). These results indicate volatilization of $V_2O_5$ as the main cause of LaV$_{1.2}O_{4.5}$ deactivation, the structure of which thereby converges into the stoichiometric LaVO$_4$. This is expected from the propensity of $V_2O_5$ to form vanadium (oxy)bromides with the boiling points that are below the reaction temperature.\[210\]

The XRD patterns of the La$_2$O$_3$ retrieved after the reactor obstruction indicated its conversion into tetragonal lanthanum oxybromide ($t$-LaOBr), with no observable reflections of La$_2$O$_3$ or fully brominated LaBr$_3$ (Figure 4.2). Consistently, the Raman spectra of the used catalyst displayed bands at 110, 126, 133, 188, 329, and 428 cm$^{-1}$ (Figure 4.3), which are all characteristic of $t$-LaOBr.\[211,212\] It is put forward that bromination of La$_2$O$_3$ into LaOBr under the reaction environment comprising moisture and HBr leads to the formation of interparticle bridges and subsequent agglomeration, ultimately resulting in their sticking and reactor blockage.

Notably, the XRD patterns (Figure 4.2), Raman (Figure 4.3) and $^{51}$V MAS NMR (Figure 4.4) spectra of the equilibrated LaVO$_4$ catalyst confirmed that the originally present $m$-LaVO$_4$ phase
was intact after CH₄ oxybromination. In line with this result and observed transformation of La₂O₃ into LaOBr, the equilibrated LaV₁.₀₂O₂, LaV₁.₅₀₂.₇₅, and LaVO₄ exhibit the contributions of both m-LaVO₄ and t-LaOBr. As indicated in the bar insets of Figure 4.2, the fraction of t-LaOBr phase increases with a decrease in vanadium content. Besides, the portion of this phase in the catalysts stabilized for 20 h was higher compared to 5 h, and closely matched the phase composition that is expected based on the stoichiometry of starting material under the assumption that all La₂O₃ is transformed into LaOBr. The total surface area, S_BET, of the equilibrated LaVO₄ and LaV₁.₅₀₂.₇₅ catalysts exhibited slight changes with respect to the fresh materials. In contrast, the S_BET values of LaV₁.₀₂O₂ and particularly LaV₀.₇₀₃.₂₅ decreased substantially after the 20 h test. Notably, the drop in LaV₀.₇₀₃.₂₅ occurred already during the first hour of operation (Figure 4.1).
implying a relatively fast initial equilibration of the catalyst. Complementary characterization of the used catalysts reveal that these textural changes are primarily associated with the transformation of \( h-La_2O_3 \) into \( t-LaOBr \) – both phases display a marginal contribution to the activity compared to \( m-LaVO_4 \). Moreover, the kinetic fingerprints of \( CH_4 \) oxybromination shown in Figure 4.8 give strong hints of the interplay between the surface catalyzed HBr oxidation generating \( Br_2 \), which activates methane in the gas phase (the latter seems to be the rate-determining step). All these arguments account for the limited impact of the surface area of the materials on the overall activity and explain the stable catalytic behavior of \( LaV_{0.2}O_2 \) and \( LaV_{0.7}O_{3.25} \) shown in Figure 4.5.

The equilibrated \( LaV_{x}O_{2.5x+1.5} \) catalysts with \( 0.2 \leq x \leq 1 \) displayed qualitatively similar \( H_2\)-TPR profiles which comprise a broad and low-intensity peak in \( H_2 \) consumption in the temperature range of 750-900 K, and strongly pronounced high-temperature peak at \( > 900 \) K (Figure 4.9), which is comparable to the previous reports on the reduction of rare-earth orthovanadates.\[^{[195]}\]

Total \( H_2 \) consumption increased and the position of the high-temperature peak maxima was shifted to higher temperatures at progressively higher vanadium content in the catalyst. This is consistent with an increased fraction of the redox-active \( m-LaVO_4 \) phase, which necessitates longer times, i.e., higher temperatures to complete the reduction at given reaction rate.

The morphology of the equilibrated \( LaV_{0.2}O_2 \), \( LaV_{0.5}O_{2.75} \), and \( LaVO_4 \) was studied in more detail by HAADF-STEM and HRTEM (Figure 4.10). The micrographs indicated a high crystallinity of these materials, which comprised 20-100 nm particles, with an average particle diameter in the range of 40-50 nm. EDXS spectra and respective elemental maps evidenced an inverse relationship between the intensity of the bromine signal and the vanadium content in the samples (Figure 4.10). In particular, the signal of halogen was almost no detectable in \( LaVO_4 \) (Figure 4.10d), implying its stability against bulk bromination. Moreover, EDXS maps of \( LaV_{0.2}O_2 \) and \( LaV_{0.5}O_{2.75} \) (Figure 4.10a-c) demonstrated an uneven bromine distribution as well as the confinement of its signal to the regions wherein the vanadium signal exhibits a low intensity. It can be therefore inferred that bromine uptake is primarily related to the bromination of \( h-La_2O_3 \) nanocrystals leading to their transformation into \( t-LaOBr \). This is further corroborated by the analysis of the interplanar distances in HRTEM micrographs, which revealed the sole presence of \( m-LaVO_4 \) nanoparticles in \( LaVO_4 \) (Figure 4.10d), and \( m-LaVO_4 \) and \( t-LaOBr \) nanoparticles in
LaV$_{0.2}$O$_2$ and LaV$_{0.5}$O$_{2.75}$ catalysts (Figure 4.10a-c). HRTEM also suggests a high degree of interaction between $m$-LaVO$_4$ and $t$-LaOBr nanoparticles in the latter materials. This can rationalize the stable performance of the sub-stoichiometric oxides in which $m$-LaVO$_4$ acts as a spacer preventing the sticking of $t$-LaOBr nanoparticles. Consistent with the Raman spectra of
lanthanum vanadates equilibrated over 20 h and LaV_{0.5}O_{2.75} used over 60 h (Figure 4.3), which indicate the absence of the bands at ca. 1287 and 1587 cm^{-1} that are characteristic for the carbonaceous deposits.\textsuperscript{[213]} the HRTEM analysis also corroborates the absence of the catalyst coking.

Having understood the bulk structure of the LaV_{x}O_{2.5x+1.5} catalysts at 0.2 ≤ x ≤ 1, their surface properties were also assessed their by XPS (Figure 4.11) as these are particularly relevant for their catalytic behavior. The binding energies of V 2p (517.1 eV), O 1s (530.0 eV), and La 3d (851.6 and 834.8 eV) levels in LaVO_{4} (Figure 4.11a) were comparable to previous reports in the literature.\textsuperscript{[194]} Thereby, V 2p core level spectra indicated that surface vanadium is mostly present in the V\textsuperscript{5+} state, which displays binding energies in the range of 516.9-517.7 eV.\textsuperscript{[214]} Consistently, the O 1s peak corresponds to the energy level that is characteristic of VO\textsuperscript{2−} group.\textsuperscript{[194]} In line with the bromine maps illustrated in Figure 4.10, the Br 3d peak located between 188.2 and 182 eV, became more prominent with a decrease in vanadium content (Figure 4.11a), whereas the O 1s core level in the spectra of LaV_{0.2}O_{2} and LaV_{0.5}O_{2.75} catalysts displayed a shoulder at a lower binding energy, which can be ascribed to t-LaOBr (see Chapter 6). A decrease in vanadium content led to a gradual shift of the V 2p and O 1s peak to a higher binding energy in LaV_{x}O_{2.5x+1.5}. Besides, the Br 3d core level of LaV_{0.5}O_{2.75} was shifted to a lower binding energy. This hints at the field effect of the surface bromine of the LaOBr phase, which displays an electron withdrawing effect, and thus impacts on the Fermi level of vanadium and oxygen in LaVO\textsubscript{4}.

XPS also evidenced the differences in the surface composition among the stabilized catalysts (Figure 4.11b). Surface molar V:La ratio is slightly lower than the one in the catalyst bulk, but directly correlates with the latter. Consistent with the low propensity of m-LaVO\textsubscript{4} to brominate, Br:La ratio is reversely proportional to the bulk vanadium content of the catalyst. Moreover, the difference in the surface vanadium and bromine concentrations of LaVO\textsubscript{4} catalysts equilibrated for 5, 20, and 60 h were rather low (Figure 4.11b), which is an indicator of the catalyst stability against excessive bromination.

4.3.4. Structure-Performance Relationships

The structure-performance relationships of LaV_{x}O_{2.5x+1.5} catalysts are summarized in (Figure 4.12) as a function of the molar V:La ratio. The partial bromination of the pure La_{2}O_{3}
Lanthanum Vanadate Catalysts for Methane Oxybromination

(x = 0) into t-LaOBr under the reaction atmosphere causes particle sticking and agglomeration, which ultimately results in the reactor blockage. On the opposite end, the over-stoichiometric catalysts exhibit deactivation due to the loss of V₂O₅ species, which are prone to form volatile brominated compounds. In contrast to these boundary compositions, the stoichiometric LaVO₄ and the sub-stoichiometric catalysts with vanadium content in the range of 0.2 ≤ x ≤ 1 display stable performance. This is ascribed to the structural integrity of m-LaVO₄ phase that is resistant against bulk bromination and vanadium losses under the corrosive oxybromination feed. Furthermore, m-LaVO₄ prevents interconnecting of t-LaOBr nanoparticles in the sub-stoichiometric catalysts, securing the stable operation. LaVO₄ exhibits substantial activity and
selectivity to bromomethanes. Nonetheless, a synergetic interaction between \( m \)-LaVO\(_4\) and redox-inactive \( t \)-LaOBr nanocrystals in the sub-stoichiometric systems enables to tune their oxidizing potential by adjusting the V:La ratio, which determines the relative content of two phases and the surface concentration of vanadium. Besides, it impacts on bromine content at the catalysts’ surface, which likely further reduces the oxidizing propensity as discussed on Chapter 3. As a consequence, the lower vanadium content enhances the selectivity to bromomethanes at the expense of a lower catalytic activity. Owning to these counteracting effects, optimal performance is achieved over LaV\(_{0.5}\)O\(_{2.75}\), i.e., a catalyst with an intermediate vanadium content.

### 4.4. Conclusions

The results presented in this Chapter highlight the tuneability of lanthanum vanadate catalysts, LaV\(_{2.5x+1.5}\), enabling to tailor their redox properties and performance in CH\(_4\) oxybromination by adjusting the content of vanadium. In particular, the stoichiometric \((x = 1)\) and the sub-stoichiometric catalyst compositions with molar V:La ratio in the range of \(0.2 \leq x < 1\) exhibit stable behaviour in contrast to the severe particle sticking of LaOBr in catalysts with \(x < 0.2\), and volatilization of free V\(_2\)O\(_5\) in over-stoichiometric materials with \(x > 1\), leading to their deactivation. The stoichiometric catalyst \((x = 1)\) comprising LaVO\(_4\) nanocrystals is highly active and rather selective to bromomethanes. Further selectivity enhancement can be achieved by decreasing the molar V:La ratio from stoichiometric to sub-stoichiometric, i.e., \(x < 1\). This leads to an additional LaOBr phase that is obtained by the partial bromination of the excess La\(_2\)O\(_3\) under the reaction conditions. The synergetic interaction between LaOBr and LaVO\(_4\) nanocrystals prevents the particle agglomeration and moderates the oxidizing potential of the latter, which curtails the undesired oxidation of bromomethanes into carbon oxides. Up to 96% selectivity to bromomethanes at 15-25% CH\(_4\) conversion can be attained over LaV\(_{0.5}\)O\(_{2.75}\) catalyst, which ranks it among the best oxybromination systems.
Chapter 5

Nanostructured Ceria Catalysts for Methane Oxybromination

5.1. Introduction

An amount of natural gas equivalent to about 18% of the US annual needs and worth ca. 13 billion USD is lost every year by flaring at far-flung fields (comprising > 30% of known reserves) due to a lack of technologies enabling its economical on-site processing or transport to the centralized megaplants.[5,7,25,28,43,48,215] Among various routes that circumvent energy and capital intensive syngas generation,[55,58,60,63,64,216,217] the bromine-mediated upgrading of methane (CH₄) emerged as an attractive technology to valorize this stranded natural gas,[5,7,66,71,84,86,89] which has been demonstrated at plant scale.[83] It is based on the selective bromination of CH₄ to methyl bromide (CH₃Br), the latter serving as a platform for the production of alcohols, ethers, gasolines, and aromatics via catalytic pathways similar to those of methanol. The feasibility of this technology relies on the efficient recovery of hydrogen bromide (HBr), which is formed in stoichiometric quantities in the bromination and subsequent CH₃Br upgrading steps.[5,7,89,69] Compared to the reaction of CH₄ with molecular bromine (Br₂), oxybromination enables process intensification by using HBr and oxygen (O₂) to convert CH₄ into CH₃Br.[25,64] Dibromomethane (CH₂Br₂) is the only polybrominated byproduct in this reaction, which can be transformed to CH₃Br via reproportionation or hydrodebromination.[71,84,85] Still, the presence of O₂ in the reaction medium promotes combustion reactions, which is the main challenge for the implementation of CH₄ oxybromination.

As shown in Chapters 2 and 3, catalysts like (VO)₂P₂O₇ and FePO₄ exhibit promising selectivity to CH₃Br in CH₄ oxybromination and relatively low selectivity to COₓ (S(CH₃Br) = 81-64%, S(COₓ) ≤ 15 % at CH₄ conversions of X(CH₄) = 14-30%). In contrast, although CeO₂ would be an attractive candidate in view of its abundance and stability,[119,218-220] tests over the bulk phase evidenced significant combustion under equivalent conditions (S(COₓ) = 30-45% at
X(CH\textsubscript{4}) = 15-30\%). Interestingly, similar to some other processes catalyzed by CeO\textsubscript{2}, the performance of this material in CH\textsubscript{4} oxybromination was shown to be structure sensitive.\cite{89} Substantially enhanced selectivity to CH\textsubscript{3}Br was achieved by tailoring the nanocrystal morphology (up to S(CH\textsubscript{3}Br) = 75\% at X(CH\textsubscript{4}) = 18\% over nanocubes), which was further improved by the addition of NiO\textsubscript{x} (S(CH\textsubscript{3}Br) = 82\% at X(CH\textsubscript{4}) = 22\%). Nonetheless, the formation of CO\textsubscript{x} over nanocrystalline CeO\textsubscript{2} remained significant (S(CO\textsubscript{x}) \geq 17\%).

In view of strong hints that the formation of the C-Br bond in CH\textsubscript{4} oxybromination results from the gas-phase reaction of CH\textsubscript{4} with bromine species generated over the catalyst, selectivity losses can be primarily associated with the surface catalyzed combustion of CH\textsubscript{4}, CH\textsubscript{3}Br, and CH\textsubscript{2}Br\textsubscript{2}. This can be approached by controlling (i) the reaction conditions or (ii) the catalyst properties, which are interlinked. Indeed, as shown in Chapter 3, the production of CO\textsubscript{x} over CeO\textsubscript{2} could be curbed by operating under a large excess of HBr (S(CO\textsubscript{x}) = 2\% at X(CH\textsubscript{4}) = 20\%), which was ascribed to the controlled surface reduction due to bromination of the outward catalyst structure under reaction conditions. Another well-known strategy that allows tailoring of the geometric and electronic properties of CeO\textsubscript{2} catalysts comprises the dispersion over a suitable carrier.\cite{219,226-233} However, despite constituting a pivotal step towards catalyst scale-up, the impact of supporting CeO\textsubscript{2} on the performance in CH\textsubscript{4} oxybromination has not been studied previously.

In this Chapter, CeO\textsubscript{2} catalysts supported over commonly applied supports (SiO\textsubscript{2}, SiC, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, MgO) using different synthesis methods and a relatively low active phase loading (\leq 2 wt.\% CeO\textsubscript{2}) are investigated in methane oxybromination. Their performance is correlated to the catalyst structure, its oxidizing potential, and propensity to brominate, as well as to the activity of the support in side combustion reactions. It is shown that nanostructured CeO\textsubscript{2} catalysts on suitable carriers display substantially enhanced selectivity to CH\textsubscript{3}Br and CH\textsubscript{2}Br\textsubscript{2} due to a suppressed CO\textsubscript{x} production.

5.2. Experimental

5.2.1. Catalyst Preparation

Bulk CeO\textsubscript{2} (Sigma-Aldrich, nanopowder, 99.9\%) was calcined at 973 K for 5 h in static air (heating rate 5 K min\textsuperscript{-1}) prior to the catalytic tests. If not stated otherwise, MgO (ca. 20 nm, Strem Chemicals, \geq 99\%), SiO\textsubscript{2} (20-60 \textmu m, Evonik, AEROPERL\textsuperscript{®} 300/30, \geq 99.0\%),
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SiC (< 100 nm, Sigma-Aldrich, ≥ 99%), ZrO2 (≤ 60 μm, Alfa-Aesar, 99%), and γ-Al2O3 (5-100 μm, Sasol, PURALOX® SCFa 140, ≥ 98%) were calcined using the same protocol as that for CeO2 and stored under vacuum (50 mbar) at 373 K prior to their use as supports in the catalyst preparation.

Dry impregnation was used as a standard method to prepare CeO2 catalysts supported over various carriers. Herein, Ce(NO3)3·6H2O (Aldrich, 99.9%) was dissolved in a volume of deionized water equal to the pore volume of the carrier in appropriate amounts to achieve 2 wt.% loading of CeO2. The precursor solutions were added dropwise to the carrier and the resulting materials were periodically mixed at room temperature for 1 h, then dried under vacuum (50 mbar) at 373 K for 12 h, and finally calcined in static air at 973 K for 5 h (heating rate 5 K min⁻¹). These catalysts were referred to as CeO2/S, where S denotes the carrier.

Using an analogous protocol, a set of MgO-supported catalysts were prepared with reduced CeO2 loading (0.1 and 0.5 wt.%, referred to as CeO2/MgO-0.1 and CeO2/MgO-0.5, respectively). A second series of catalysts with a CeO2 loading of 0.5 wt.% were synthesized varying the temperature of the final calcination step (973, 1173, or 1373 K, denoted as CeO2/MgO-0.5-973, CeO2/MgO-0.5-1173, CeO2/MgO-0.5-1373, respectively). In this case, the MgO carrier was calcined at 1373 K prior to use.

MgO-supported CeO2 (2 wt.%) catalysts were also prepared by mechanochemical synthesis, coprecipitation, and hydrothermal synthesis. Mechanochemical synthesis was performed by introducing Ce(NO3)3·6H2O on the MgO carrier by impregnation. The resulting materials was transferred to a stainless steel jar (50 cm³), filled with 12 stainless steel balls (d_ball = 10 mm, W_ball = 7.8 g) and ground in a planetary ball mill (Retch PM 200) for 4 h (500 rpm). Coprecipitation was conducted starting from a solution containing 0.006 M Ce(NO3)3·6H2O and 1.2 M Mg(NO3)2·6H2O, which was prepared by dissolving the metal salts in deionized water (200 cm³). Hydrogen peroxide (53 cm³, Aldrich, 35 wt.%) was then added and the solution was stirred (500 rpm) for 1 h. Subsequently, aqueous ammonium hydroxide (Merck, 25 wt.%) was added dropwise until reaching a pH of 10, and the resulting slurry was aged for 2 h under stirring. The solids were recovered by filtration and washed with deionized water. For hydrothermal synthesis, MgO was suspended in a 6 M solution of NaOH (Fisher Chemicals, 99%) in deionized water (40 cm³). A 0.4 M solution of Ce(NO3)3·6H2O in deionized water (1.8 cm³) was mixed with this slurry, stirred (500 rpm) for 2 h, then transferred into a Teflon-lined autoclave (50 cm³), and...
hydrothermally treated at 453 K for 24 h. The solid was collected by filtration and washed with deionized water. The materials recovered after mechanochemical synthesis, coprecipitation, and hydrothermal synthesis were dried and calcined as described above for dry impregnation. The resulting catalysts were denoted as CeO$_2$/MgO-m, CeO$_2$/MgO-c, and CeO$_2$/MgO-h, respectively.

5.2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) was measured using a PANalytical X’Pert PRO-MPD diffractometer with Bragg-Brentano geometry by applying Cu-K$_\alpha$ radiation ($\lambda = 1.54060$ Å). The data were recorded in the 10-70° 2$\theta$ range with an angular step size of 0.017° and a counting time of 2.04 s per step. The average size of CeO$_2$ crystallites was estimated from the broadening of the [111] reflection of CeO$_2$ by using Scherrer equation with a dimensionless shape factor of $K = 0.9$. N$_2$ sorption at 77 K was performed using a Micromeritics TriStar analyzer. The solid was evacuated to 50 mbar at 573 K for 12 h prior to the measurement. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area, $S_{\text{BET}}$. The total pore volume, $V_{\text{pore}}$, was determined from the amount of N$_2$ adsorbed at a relative pressure of $p/p_0 = 0.98$. The total cerium content in the catalyst was quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Horiba Ultima 2 instrument equipped with photomultiplier tube detection. High-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and elemental mapping with energy-dispersive X-ray spectroscopy (EDXS) were conducted on a FEI Talos microscope operated at 200 kV. The sample was dispersed as dry powders onto lacy carbon coated nickel grids. The average size of the CeO$_2$ nanoparticles was calculated by examining over 50 of them. Fast Fourier transforms of selected areas of HRTEM images were calculated using ImageJ software. Raman spectroscopy was performed on a WITec CRM200 confocal system using a 532 nm laser with 20 mW power, a 100× objective lens with numerical aperture NA = 0.9 (Nikon Plan) and a fiber-coupled grating spectrometer (2400 lines per mm), giving a spectral sampling resolution of 0.7 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS) was performed on a Physical Electronics Quantum 2000 spectrometer using monochromatic Al-K$_\alpha$ radiation, generated from an electron beam operated at 15 kV, and equipped with a hemispherical capacitor electron-energy analyzer. The sample was analyzed at an electron take-off angle of 45° and a pass energy of 46.95 eV. In
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In order to suppress sample charging during analysis an electron and an ion neutralizer were operated simultaneously. Remaining charging effects were corrected by referencing all spectra to adventitious carbon (C 1s at 284.5 eV). The elemental concentrations were quantified based on the measured photoelectron peak areas (Br 3d, Ce 3d) after Shirley background subtraction using PHI-MultiPak software and the built-in relative sensitivity factors, which are corrected for the system transmission function. The fractions of different oxidation states of cerium were estimated by deconvolution of the Ce 3d peak.

5.2.3. Catalyst Testing

CH₄ oxybromination, and CO, CH₃Br, CH₂Br₂, and HBr oxidation were performed at ambient pressure in a continuous-flow fixed-bed reactor setup, which is described in Appendix A. The catalyst (particle size, \(d_p = 0.4-0.6\) mm) was well mixed with quartz particles (Thommen-Furler, \(d_p = 0.2-0.3\) mm) to ensure a constant bed volume \(V_{\text{bed}} = 2\) cm³ and loaded in a quartz reactor (internal diameter, \(d_r = 8\) mm). Prior to testing, the catalyst bed was heated in a He flow to the desired temperature \(T = 423-823\) K and allowed to stabilize for at least 30 min before the reaction mixture was fed. In CH₄ oxybromination and CH₄ oxidation the post-catalyst zone was filled with quartz beads (Sigma-Aldrich, \(d_p = 0.6\) mm) to minimize its volume and the possible occurrence of the gas-phase reactions in this reactor section. The catalyst weight \(W_{\text{cat}}\), total flow rate \(F_T\), and feed mixture applied in the tests are summarized in Table 5.1. Analysis of reactants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(W_{\text{cat}})/ g</th>
<th>(F_T)/ cm³ min⁻¹</th>
<th>Feed composition / vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₄</td>
</tr>
<tr>
<td>CH₄ oxybromination</td>
<td>1.0</td>
<td>100-200</td>
<td>3-20</td>
</tr>
<tr>
<td>CH₄ oxidation</td>
<td>1.0</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>CH₃Br oxidation</td>
<td>0.2</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>CH₂Br₂ oxidation</td>
<td>0.2</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>0.2</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>HBr oxidation</td>
<td>0.5</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

*a All tests were conducted at \(P = 1\) bar.\(^b\) Flow units correspond to standard temperature (273 K) and pressure (1 bar) conditions. \(^c\) Ar (4.5 vol.%) was added as an internal standard to all the reaction mixtures, except for HBr oxidation. He was used as the balance gas.

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and products, determination of conversion, selectivity, yield, and reaction rate, as well as the evaluation of carbon and bromine mass balance was conducted using the protocol described in Appendix A.

5.3. Results and Discussion

5.3.1. Characterization of Fresh Catalysts

To study the effect of dispersing ceria on the performance in CH₄ oxybromination, the first task was to assess the impact of the carrier. For this purpose, supported catalysts containing equivalent amounts of CeO₂ (2 wt.%) were prepared by dry impregnation applying five representative supports (leading to samples coded CeO₂/S, where S = MgO, SiO₂, SiC, Al₂O₃, or ZrO₂). Analysis by X-ray diffraction (XRD) pointed towards differences in the dispersion of CeO₂ depending on the carrier applied (Figure 5.1). In particular, while broad weak reflections, characteristic of the presence of cubic CeO₂ nanocrystals with an estimated average size of ca. 4-9 nm (Table 5.2) were visible in CeO₂/MgO, CeO₂/SiO₂, and CeO₂/SiC, they were absent in the diffractograms of CeO₂/Al₂O₃, and CeO₂/ZrO₂. Consistently, examination by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) coupled with elemental mapping confirmed the presence of CeO₂ nanoparticles decorating the surface of the MgO, SiO₂, and SiC carriers (Figure 5.2), contrasting the near atomic dispersion of the active phase on Al₂O₃ or ZrO₂. Subtle differences could be noted in the average size and morphology of the supported CeO₂ nanoparticles (Table 5.2), appearing bigger on MgO (ca. 6 nm) and SiC (ca. 9 nm) compared to SiO₂ (ca. 4 nm), which is likely related to the high surface area of the latter, and presenting a higher aspect ratio on MgO with respect to the spherical-like particles observed on SiO₂ and SiC (Figure 5.3, Figure B.19). High-resolution transmission electron microscopy (HRTEM) revealed that the CeO₂ nanoparticles dominantly expose the {111} facets with a d-spacing of 0.31 nm, in line with their higher thermodynamic stability.[89,224,225] In line with XRD and electron microscopy analysis, the Raman spectra of bulk CeO₂, CeO₂/MgO, CeO₂/SiO₂, and CeO₂/SiC (Figure 5.4) displayed a peak located at 461-464 cm⁻¹, which is ascribed to the F₂g mode of nanocrystalline fluorite structure of CeO₂.[228,229,231,234] Contrastingly, the spectra of CeO₂/ZrO₂, which shows only the bands ascribed to the monoclinic ZrO₂ support, and CeO₂/Al₂O₃, which shows no Raman active bands in the
Figure 5.1. X-ray diffractograms of bulk and supported CeO$_2$ catalysts in fresh form (blue) and after equilibration in CH$_4$ oxybromination (red). Reference patterns are shown as vertical lines below the measured diffractograms and are identified with their ICDD-PDF numbers. The insets show magnification of the 2θ regions where the main CeO$_2$ reflections are expected. Equilibration conditions: CH$_4$:HBr:O$_2$:Ar:He = 6:6:3:4.5:80.5, $F_T/W_{cat} = 100$ cm$^3$ min$^{-1}$ g$_{cat}^{-1}$, $T = 773$ K, $P = 1$ bar, and $tos = 5$ h.
Table 5.2. Characterization data of the samples.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CeO₂ nominal / wt.%</th>
<th>CeO₂ bulk / wt.%</th>
<th>CeO₂ crystallite size&lt;sup&gt;a&lt;/sup&gt; / nm</th>
<th>CeO₂ crystallite size&lt;sup&gt;b&lt;/sup&gt; / nm</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; / m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>V&lt;sub&gt;pore&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; / cm&lt;sup&gt;3&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>100</td>
<td>-</td>
<td>fresh used</td>
<td>fresh used</td>
<td>49</td>
<td>38</td>
</tr>
<tr>
<td>CeO₂/ZrO₂</td>
<td>2</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>41 (41)</td>
<td>41</td>
</tr>
<tr>
<td>CeO₂/Al₂O₃</td>
<td>2</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>143 (143)</td>
<td>146</td>
</tr>
<tr>
<td>CeO₂/SiC</td>
<td>2</td>
<td>2.0</td>
<td>9</td>
<td>9</td>
<td>38 (36)</td>
<td>36</td>
</tr>
<tr>
<td>CeO₂/SiO₂</td>
<td>2</td>
<td>1.9</td>
<td>5</td>
<td>5</td>
<td>246 (241)</td>
<td>246</td>
</tr>
<tr>
<td>CeO₂/MgO</td>
<td>2</td>
<td>2.0</td>
<td>9</td>
<td>9</td>
<td>27 (29)</td>
<td>27</td>
</tr>
<tr>
<td>CeO₂/MgO-0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>48 (29)</td>
<td>30</td>
</tr>
<tr>
<td>CeO₂/MgO-0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>37 (29)</td>
<td>26</td>
</tr>
<tr>
<td>CeO₂/MgO-0.5-973</td>
<td>0.5</td>
<td>0.6</td>
<td>6</td>
<td>6</td>
<td>24 (28)</td>
<td>22</td>
</tr>
<tr>
<td>CeO₂/MgO-0.5-1173</td>
<td>0.5</td>
<td>0.6</td>
<td>10</td>
<td>10</td>
<td>24 (28)</td>
<td>21</td>
</tr>
<tr>
<td>CeO₂/MgO-0.5-1373</td>
<td>0.5</td>
<td>0.5</td>
<td>16</td>
<td>16</td>
<td>22 (28)</td>
<td>18</td>
</tr>
<tr>
<td>CeO₂/MgO-m</td>
<td>2</td>
<td>2.0</td>
<td>7</td>
<td>7</td>
<td>32 (29)</td>
<td>25</td>
</tr>
<tr>
<td>CeO₂/MgO-c</td>
<td>2</td>
<td>2.1</td>
<td>7</td>
<td>7</td>
<td>48</td>
<td>29</td>
</tr>
<tr>
<td>CeO₂/MgO-h</td>
<td>2</td>
<td>1.9</td>
<td>16</td>
<td>16</td>
<td>50 (29)</td>
<td>32</td>
</tr>
</tbody>
</table>

<sup>a</sup> Scherrer equation. <sup>b</sup> STEM. <sup>c</sup> Values in the brackets refer to the bare carrier.
Figure 5.2. High-angle annular dark field scanning transmission electron micrographs and corresponding elemental maps of (a,f) CeO$_2$/MgO, (b,g) CeO$_2$/SiO$_2$, (c,h) CeO$_2$/SiC, (d,i) CeO$_2$/ZrO$_2$, and (e,j) CeO$_2$/Al$_2$O$_3$ catalysts in fresh form (a-e) and after equilibration in methane oxybromination (f-j). Equilibration conditions as reported in the caption of Figure 5.1.
Figure 5.3. High-resolution transition electron micrographs of (a,b) CeO$_2$/MgO and (c,d) CeO$_2$/SiO$_2$ catalysts in fresh form (a,c) and after equilibration in CH$_4$ oxybromination (b,d). The insets show the fast Fourier transform of the boxed regions. Equilibration conditions as reported in the caption of Figure 5.1.
Figure 5.4. Raman spectra of bulk and supported CeO₂ catalysts in fresh form (blue) and after equilibration in CH₄ oxybromination (red). Equilibration conditions as reported in the caption of Figure 5.1.
spectral region of interest, are indicative of high ceria dispersion over these carriers and point to the possible formation of Ce₃Zr₄O₂ and CeAlO₃ (vide infra). The latter compound is known to exhibit no active peaks in the investigated spectral range. Bulk CeO₂ also exhibited a weak peak at 246 cm⁻¹, which is attributed to the second-order transverse acoustic mode (2TA). In the case of CeO₂/SiO₂, a low-intensity peak at 604 cm⁻¹ is ascribed to a defect induced mode of CeO₂. This mode has been correlated to the increased concentration of oxygen vacancies in silica-supported ceria catalysts. The feature at 144 cm⁻¹ in the spectrum of CeO₂/MgO likely originates from MgO support, while the peak located at 512 cm⁻¹ in the spectrum of CeO₂/SiC is related to Si-Si bonds in SiC.

To confirm the effect of supporting ceria nanostructures on the electronic properties of the active phase, the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS, Figure B.20). Both Ce³⁺ and Ce⁴⁺ species could be identified based on the satellite peaks observed around the 3d peaks of ceria. Analysis of the relative composition of these species indicated that CeO₂/MgO and CeO₂/SiC contained predominantly Ce⁴⁺ (> 93% Ce⁴⁺, < 7% Ce³⁺) consistent with the distribution expected for CeO₂ (Figure 5.5a). Comparatively, appreciable amounts of Ce³⁺ were observed for CeO₂/SiO₂ (ca. 33% Ce⁴⁺), and particularly CeO₂/ZrO₂ (ca. 45% Ce⁴⁺) and CeO₂/Al₂O₃ (ca. 52% Ce⁴⁺). Considering the high ceria dispersion observed in the latter materials, these results also suggest that a significant portion of cerium is likely present in the form of CeAlO₃ or Ce₃Zr₄O₂ solid solutions, respectively, due to the reaction with support, while the formation of CeO₂-silica compounds might also be possible in the case of CeO₂/SiO₂. In other words, the interaction of ceria with SiO₂, and particularly Al₂O₃ and ZrO₂ support appears to be stronger compared to MgO and SiC. It is noteworthy that the CeO₂/SiC catalyst exhibited a strong O 1s signal (Figure B.20), with a surface O:Si ratio of ca. 1.9, which is consistent with HRTEM observations (Figure B.19) suggesting the formation of a silica-like structure at the surface of SiC.

Different molecules such as H₂, CO, O₂, or CH₄ can be used to probe the reactivity of oxygen species in oxide-based catalysts by temperature-programmed reactions, which can be conducted in the form of transient (non-stationary) or steady state tests. The redox properties of the bulk and supported CeO₂ catalysts were here assessed using CO oxidation. This reaction is expected to proceed via a Mars-van Krevelen mechanism, in which CO reacts with surface bound oxygens of
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The rates of CO oxidation at 753 K (Figure 5.5b), which were extracted from the representative light-off curves (Figure B.21), decrease as follows: bulk CeO$_2$ $>\sim$ CeO$_2$/ZrO$_2$ $>\sim$ CeO$_2$/MgO $>\sim$ CeO$_2$/SiC $>\sim$ CeO$_2$/Al$_2$O$_3$ $>\sim$ CeO$_2$/SiO$_2$, indicating that the oxidizing potential of the supported catalysts is significantly (ca. 2–40 times) reduced compared to bulk CeO$_2$. This could benefit the performance in CH$_4$ oxybromination, since the strongly oxidizing character of bulk CeO$_2$ promotes combustion, resulting in a selectivity loss (Chapters 2 and 3). The activity of the catalysts in CO oxidation were also compared based on the apparent...
activation energy (Figure 5.5b), which was calculated from the linear region of Arrhenius plots that corresponds to 5-40% of CO conversion (Figure B.21). The values of this parameter were in the range of 40-100 kJ mol\(^{-1}\) and increased in the following order: \(\text{CeO}_2/\text{SiC} < \text{CeO}_2 \sim \text{CeO}_2/\text{ZrO}_2 \sim \text{CeO}_2/\text{MgO} < \text{CeO}_2/\text{Al}_2\text{O}_3 < \text{CeO}_2/\text{SiO}_2\), corroborating the previous observation that CO oxidation is particularly hampered over the fresh CeO\(_2/\text{Al}_2\text{O}_3\) and CeO\(_2/\text{SiO}_2\) catalysts.

5.3.2. Evaluation of Catalysts in Methane Oxybromination

The bulk and supported CeO\(_2\) catalysts were evaluated in CH\(_4\) oxybromination at three different temperatures (753, 773, and 793 K), using a stoichiometric ratio of reactants (CH\(_4\):HBr:O\(_2\) = 2:2:1) in the feed (Figure 5.6). The conversion of CH\(_4\) was in the range of 6-40%, which is comparable to those previously observed.\[^{89}\] The oxybromination activity decreased in the following order: CeO\(_2/\text{SiO}_2\) > CeO\(_2/\text{SiC}\) > CeO\(_2/\text{ZrO}_2\) > bulk CeO\(_2\) > CeO\(_2/\text{MgO}\) > CeO\(_2/\text{Al}_2\text{O}_3\), wherein the most active CeO\(_2/\text{SiO}_2\) catalyst displayed a 2-2.8 times higher activity compared to the least active CeO\(_2/\text{Al}_2\text{O}_3\). Nevertheless, the rates over the other supported catalysts, i.e., CeO\(_2/\text{SiC}\), CeO\(_2/\text{ZrO}_2\), and CeO\(_2/\text{MgO}\) showed much smaller differences (5-30%) and were comparable to those over bulk CeO\(_2\). Consistently, the apparent activation energies (Figure B.22), which ranged from 80-156 kJ mol\(^{-1}\), increased in a similar order: CeO\(_2/\text{SiO}_2\) (80 kJ mol\(^{-1}\)) \sim CeO\(_2/\text{ZrO}_2\) < CeO\(_2/\text{SiC}\) (100 kJ mol\(^{-1}\)) < CeO\(_2\) (110 kJ mol\(^{-1}\)) < CeO\(_2/\text{MgO}\) (120 kJ mol\(^{-1}\)) < CeO\(_2/\text{Al}_2\text{O}_3\) (156 kJ mol\(^{-1}\)).

As exemplified for several catalysts (Figure 5.6), the selectivity-conversion curves followed the same trend when the conversion was controlled by adjusting the reaction temperature or the space velocity. Supported CeO\(_2\) systems displayed remarkable differences in product distribution compared to bulk CeO\(_2\). Significantly enhanced selectivity to CH\(_3\)Br was observed over CeO\(_2/\text{MgO}\) (61-81%), CeO\(_2/\text{SiC}\) (56-73%), and CeO\(_2/\text{SiO}_2\) (52-71%) compared to CeO\(_2/\text{ZrO}_2\), which was similar to bulk CeO\(_2\) (ca. 40%), while the lowest selectivity to this product was obtained over CeO\(_2/\text{Al}_2\text{O}_3\) (28-35%). This could be linked to the selectivity to CO\(_x\), which increased in the opposite order: CeO\(_2/\text{MgO}\) (6-11%) < CeO\(_2/\text{SiC}\) (9-21%) < CeO\(_2/\text{SiO}_2\) (17-34%) < CeO\(_2/\text{ZrO}_2\) (ca. 50%) \sim bulk CeO\(_2\) < CeO\(_2/\text{Al}_2\text{O}_3\) (30-65%). The most prominent byproduct over the best-performing CeO\(_2/\text{MgO}\) catalyst was CH\(_2\)Br\(_2\), which although less valued than CH\(_3\)Br,
could be further valorized in bromine-mediated natural gas upgrading via reproporation or hydrodebromination.\cite{60,85,216} The yield of CH$_3$Br (≤ 18.7%), as well as the combined yield of CH$_3$Br and CH$_2$Br$_2$ (≤ 25.9%) are among the highest reported to date (Chapters 2 and 3).\cite{89} To confirm the catalyst stability, the activity of CeO$_2$/MgO was evaluated under more demanding conditions.

![Figure 5.6](image-url)
of moderate conversion and decreased oxygen content in the feed (Figure 5.7). Remarkably, the performance of this catalyst was stable over 80 h on stream.

5.3.3. Characterization of Used Catalysts

The structure, porosity, and electronic properties of the oxyhalogenation catalysts can be altered under reaction conditions. To determine the impact of the reaction environment on these properties, the bulk and supported CeO$_2$ catalysts were characterized after equilibration in CH$_4$ oxybromination at 773 K over 5 h. The specific surface areas and pore volumes of the supported catalysts were essentially unaltered after this test, confirming the stability of the respective carriers, while bulk CeO$_2$ experienced ca. 20% decrease (Table 5.2). The XRD patterns of the equilibrated catalysts resembled those of the respective fresh materials (Figure 5.1), demonstrating the absence of structural alterations, such as the formation of bromide phases, which is consistent with the previously reported stability of CeO$_2$ in this reaction (Chapter 3).[89] The HAADF-STEM micrographs of CeO$_2$/MgO catalyst evidenced an increased prevalence of rod-like CeO$_2$ nanoparticles (length: 5-12 nm, width: 2-3 nm) along the edges of MgO particles, although the average particle size assuming a spherical geometry was unaltered (ca. 6 nm, Figure 5.2f, Table 5.2). Comparatively, the size of CeO$_2$ nanoparticles in the equilibrated CeO$_2$/SiO$_2$ (Figure 5.2g) and CeO$_2$/SiC (Figure 5.2h) matched those of the respective fresh catalysts (Table 5.2). HRTEM analysis of CeO$_2$/MgO (Figure 5.3b) and CeO$_2$/SiO$_2$ (Figure 5.3d) demonstrated that the {111} type facets remain predominant, although {200} facets (with a 96
Nanostructured Ceria Catalysts for Methane Oxybromination

d-spacing of 0.27 nm) were also observable (Figure B.19).\cite{89,224,225} HAADF-STEM micrographs and elemental maps indicated that the dispersion of ceria in equilibrated CeO$_2$/ZrO$_2$ (Figure 5.2i) and CeO$_2$/Al$_2$O$_3$ (Figure 5.2j) remained close to atomic. Consistently, the Raman spectra of the equilibrated catalysts (Figure 5.4) displayed no significant differences compared to the fresh samples. The only exception was CeO$_2$/SiC, wherein the peak at 512 cm$^{-1}$ ascribed to Si-Si bond in SiC support vanished upon its exposure to the oxybromination, likely due to carrier oxidation into SiO$_2$. Elemental maps also suggest that a higher amount of bromine was taken up by the CeO$_2$/MgO and CeO$_2$/Al$_2$O$_3$ catalysts compared to the other materials (Figure 5.2). This was substantiated by the increased Br:Ce ratio evidenced by XPS in the surface of the equilibrated catalysts, which followed the trend: CeO$_2$/MgO > CeO$_2$/Al$_2$O$_3$ > CeO$_2$/ZrO$_2$ > CeO$_2$/SiO$_2$ > CeO$_2$/SiC (Figure 5.5a). Analysis of the Ce 3$d$ core level spectra of equilibrated CeO$_2$/MgO, CeO$_2$/SiC, CeO$_2$/ZrO$_2$, and CeO$_2$/SiC revealed a slightly lower fraction of Ce$^{4+}$ compared to the fresh catalysts, suggesting a partial reduction of ceria (Figure 5.5a, Figure B.20). In contrast, an increased fraction of Ce$^{4+}$ was observed for CeO$_2$/SiO$_2$. Since the bromination of CeO$_2$ is expected to induce reduction, i.e., a decrease in the fraction of Ce$^{4+}$ state, the increased bromine content of CeO$_2$/MgO is likely related to the bromination of the carrier, which could be expected due to its strong basic character. This was supported by the good correlation between the bromine and magnesium signals in the elemental maps (Figure 5.2f). Still, the surface Br:Mg ratio of ca. 0.03 determined from XPS was well below that expected for MgBr$_2$, indicating that the bromination of MgO is partial and/or constrained to the outermost layers of the carrier. Another interesting feature was the change of the redox properties of the catalysts after use in CH$_4$ oxybromination, as evidenced by the change in CO oxidation rates compared to the fresh catalysts (Figure 5.5b, Figure B.21). The equilibration of CeO$_2$/Al$_2$O$_3$, CeO$_2$/ZrO$_2$, CeO$_2$/SiC, and CeO$_2$/SiO$_2$ led to an increase in their CO oxidation activity, which was particularly pronounced for the latter two materials. It is hypothesized that CH$_4$ oxybromination induced decomposition of ceria-silica compounds that could be present in the fresh CeO$_2$/SiC and CeO$_2$/SiO$_2$ catalysts, yielding smaller ceria crystallites, which are more active in oxidation.\cite{227,239} This may also explain the noticeable increase in the Ce$^{4+}$ fraction in the equilibrated CeO$_2$/SiO$_2$ catalyst (Figure 5.5a). In contrast, CeO$_2$/MgO showed similar behavior to bulk CeO$_2$, both catalysts exhibiting a lower rate and higher apparent activation energy with respect to the fresh materials. The decreased oxidizing
potential of CeO$_2$/MgO could be related to the growth of the rod-like CeO$_2$ nanoparticles, which exhibited a slightly increased size compared to those present in the fresh catalyst. Nevertheless, these structural changes appear to be of a much lower magnitude compared to the more than 50% decrease in the CO oxidation rate. It seems more plausible that the reduction of the oxidizing propensity of the equilibrated CeO$_2$/MgO is related to its bromination, which as discussed above primarily occurs on the support. It might also be possible that CeO$_2$ nanoparticles are doped or decorated with MgO, which after being brominated reduces their ability to oxidize CO as well as bromomethanes.

5.3.4. Optimization of MgO-Supported CeO$_2$ Catalysts

Given the remarkable performance of CeO$_2$/MgO catalyst in CH$_4$ oxybromination, this system was chosen to evaluate the role of morphology of supported CeO$_2$ phase on its activity and product distribution. In this regard, the loading of CeO$_2$ and the synthesis method were adjusted to tailor the geometry of CeO$_2$ nanoparticles, and hence to determine their impact on the CH$_4$ oxybromination performance. As the CeO$_2$/MgO catalyst exhibited an activity comparable to that of bulk CeO$_2$ (Figure 5.6), the effect of reducing the CeO$_2$ loading to 0.5 and 0.1 wt.% (i.e., CeO$_2$/MgO-0.5 and CeO$_2$/MgO-0.1) and the contribution of the bare MgO carrier were evaluated in CH$_4$ oxybromination (Figure 5.8, left). Decreasing the content of the active phase led to the expected reduction in the rate of CH$_4$ oxybromination. Nevertheless, the activity of CeO$_2$/MgO-0.5 was only ca. 10% lower compared to that of CeO$_2$/MgO, while the product distribution was essentially unaffected. Inspection of the equilibrated CeO$_2$/MgO-0.5 catalyst revealed a similar size (ca. 6 nm), shape, and faceting of CeO$_2$ nanoparticles as observed in CeO$_2$/MgO (Figure 5.9a, Figure B.23, Table 5.2), although no rod-like nanostructures could be observed. In the case of CeO$_2$/MgO-0.1, the particles of CeO$_2$ could not be clearly distinguished (Figure B.24). Its activity was significantly lower and selectivity to CO$_x$ enhanced, and was in this regard more similar to the bare MgO. Although the latter carrier exhibited a relatively high selectivity to CH$_3$Br, it led to a more pronounced CO$_x$ production compared to CeO$_2$/MgO. Besides, activity of MgO and the yield of bromomethanes over this material are ca. 4-5 times lower compared to CeO$_2$/MgO, which preserves the high selectivity to bromomethanes and low selectivity to CO$_x$ at significantly higher
conversions. This result indicates that CeO₂ is primarily responsible for the activity of the supported catalysts.

To confirm the impact of the particle size on the performance of CeO₂ nanoparticles supported on MgO, catalysts with a CeO₂ loading of 0.5 wt.% were calcined at three different temperatures (973, 1173, and 1373 K). The resulting samples (i.e., CeO₂/MgO-0.5-973, CeO₂/MgO-0.5-1173, and CeO₂/MgO-0.5-1373) displayed comparable surface areas (Table 5.2), while the average size of
CeO$_2$ nanoparticles increased from ca. 6 to 15 nm with increasing calcination temperature (Figure B.24, Table 5.2). The rate of CH$_4$ oxybromination decreased with increasing the particle size (Figure 5.8, middle). Nevertheless, the selectivity-conversion patterns for these catalysts followed an almost identical trend as the one observed for CeO$_2$/MgO catalyst, suggesting the absence of a noticeable particle size effect on the product distribution in CH$_4$ oxybromination over this catalytic system.

Besides, to further probe the impact of the particle geometry and their interaction with the support on CH$_4$ oxybromination, supported CeO$_2$ catalysts (2 wt.%) were prepared by coprecipitation, mechanochemical, and hydrothermal synthesis (i.e., CeO$_2$/MgO-c, CeO$_2$/MgO-m, and CeO$_2$/MgO-h, respectively). The average size of the CeO$_2$ nanoparticles in these materials was similar to or slightly larger than that of CeO$_2$/MgO (Figure 5.9, Table 5.2). In the equilibrated CeO$_2$/MgO-c catalyst {111} fringes were prevalent, although the particles also exposed {200} facets, while CeO$_2$/MgO-h displayed CeO$_2$ nanocubes dominated by {200} facets. CeO$_2$/MgO-c exhibited the highest reaction rate (Figure 5.8, right), exceeding that of the reference CeO$_2$/MgO catalysts (Figure 5.8, left), at almost similar selectivity to bromomethanes. The activity and selectivity profiles of CeO$_2$/MgO-h and CeO$_2$/MgO-m catalysts were analogous to those of CeO$_2$/MgO. Overall, these results indicate that CeO$_2$ nanostructure has a minor effect on the product distribution over MgO supported CeO$_2$ catalysts. This contradicts previous findings of He et al. who reported the structure sensitive performance of CeO$_2$ in CH$_4$ oxybromination based on the study of well-defined nanocrystals of CeO$_2$, wherein the nanocubes, i.e., {200} facets were

Figure 5.9. High-resolution transition electron micrographs of (a) CeO$_2$/MgO-0.5, (b) CeO$_2$/MgO-c, and (c) CeO$_2$/MgO-h catalysts equilibrated under CH$_4$ oxybromination. The insets show the fast Fourier transform of the boxed regions. Equilibration conditions as reported in the caption of Figure 5.1.
found the most active and selective.[89] However, it has to be noted that the differences in product
distribution and particularly the reaction rates between the different CeO2 nanoparticles observed
by these authors were not so strongly pronounced (ca. ±10%).

Consistently, the CO oxidation activity of the various MgO-supported CeO2 catalysts was
almost identical after their equilibration in CH4 oxybromination, and substantially lower compared
to that of the fresh catalysts, for which significant differences in the redox properties could be
observed (Figure 5.10, Figure B.25). This result indicates that the different MgO supported
catalysts possess a very similar oxidizing potential under oxybromination environment, likely
caused by the catalyst bromination, which ultimately result in the very similar product
distribution.

5.3.5. Rationalization of the Product Distribution

Investigation of CH4 oxybromination over bulk catalytic systems in Chapters 2 and 3 suggested
that the formation of C-Br bonds might involve the gas-phase reaction of CH4 with Br2 that is
generated by the HBr oxidation on the catalysts (Figure 5.11). Several kinetic fingerprints, such
as (i) the occurrence of CH4 oxybromination in the temperature window (≥ 753 K) which coincides
with that of the non-catalyzed gas-phase bromination, (ii) comparable rates of CH4 oxybromination over bulk and supported CeO2 catalyst in spite of their markedly different redox
properties, (iii) selectivity to CH$_3$Br and CH$_2$Br$_2$ over the best performing CeO$_2$/MgO catalyst which is similar to those in the gas-phase bromination, and (iv) the absence of the sensitivity of the product distribution on the size and faceting of CeO$_2$ nanoparticles (Figure 5.8) give strong hints that this mechanism might also operate in the case of supported CeO$_2$ catalysts. To shed a light on the origin of CH$_4$ oxybromination activity, the equilibrated bulk and supported CeO$_2$ catalysts were also evaluated in CH$_4$ and HBr oxidation (Figure 5.12a, Figure B.26), which were applied as the probe reactions to access the catalyst ability to activate these reactants. Herein, the rates of CH$_4$ oxidation over bulk CeO$_2$ and CeO$_2$/ZrO$_2$ catalyst were ca. 2-3 times lower compared

Figure 5.11. Criteria for the design of supported CeO$_2$ catalyst for methane oxybromination and schematic representation of key parts of the reaction scheme.
Figure 5.12. (a) Rates of CH₄ oxybromination, CH₄ and CH₂Br₂ oxidation versus the rate of HBr oxidation at 753 K over the bulk and supported CeO₂ catalysts. (b) Rates of CH₄, CH₃Br, and CH₂Br₂ oxidation at 753 K over the bare MgO and Al₂O₃ supports and the supported CeO₂/MgO and CeO₂/Al₂O₃ catalysts. (c) Rate of CH₂Br₂ oxidation over the supported CeO₂ catalysts versus the rate of CH₂Br₂ oxidation over respective bare supports after equilibration in CH₄ oxybromination. The oxidation of CH₃Br (CH₃Br:O₂:Ar:He = 1:2:4:5:92.5) and CH₂Br₂ (CH₂Br₂:O₂:Ar:He = 1:2:4:5:92.5) were performed at $F_T/W_{cat} = 500 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$, and the oxidation of HBr (HBr:O₂:He = 6:3:91) and CH₄ (CH₄:O₂:Ar:He = 6:3:4:5:86.5) were studied at $F_T/W_{cat} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$ and $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$, respectively. CH₄ oxybromination was performed under the conditions reported in the caption of Figure 5.6. All tests were conducted at $P = 1 \text{ bar}$. 

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to those in CH₄ oxybromination (Figure 5.12a), implying that there could be a catalytic contribution in the latter reaction. This result also correlates with the strong oxidizing potential of the latter catalysts (Figure 5.5b). Nevertheless, a catalytic activation of CH₄ over these materials is likely contributing to a pronounced CO₂ evolution in CH₄ oxybromination (Figure 5.6). Contrarily, the rates of CH₄ oxidation over CeO₂/MgO, CeO₂/SiO₂, CeO₂/SiC, and CeO₂/Al₂O₃ were ca. 5-10 times lower compared to those in oxybromination (Figure 5.12a), suggesting that CH₄ activation over these catalysts is substantially impeded. In fact, this set of catalysts displayed a great selectivity enhancement in CH₄ oxybromination, with the exception of CeO₂/Al₂O₃ (Figure 5.6). On the other hand, the rates of HBr oxidation were > 8 times higher compared to those of oxybromination (Figure 5.12a), indicating the facile evolution of Br₂, which may enter the gas-phase bromination (Figure 5.11). The feasibility of the mechanism comprising heterogeneous HBr oxidation and gas-phase bromination of CH₄ was also probed by studying the reaction kinetics over the most selective CeO₂/MgO catalyst in more detail (Figure B.27). The apparent reaction order with respect to CH₄ of ca. 1 (Figure B.27) displayed by this catalyst was close to that observed in CH₄ bromination (ca. 1). The order with respect to HBr of ca. 0.2 (Figure B.27), which might appear in contrast to the known inhibition effect of this reactant on the gas-phase bromination, can be explained by the continuous oxidation of HBr into Br₂, to which the gas-phase bromination exhibits a positive reaction order (ca. 0.5).

In the above proposed mechanism the principal role of a catalyst is to oxidize HBr into Br₂ and to suppress a loss of selectivity to bromomethanes by suppressing the combustion reactions (Figure 5.11). The propensity of CeO₂ catalysts supported over different carriers to evolve CO₂ in CH₄ oxybromination (Figure 5.6) generally agreed with the order of catalysts activity in CO oxidation after the equilibration (Figure 5.5b). In agreement with our previous findings presented in previous Chapters, this result indicates that the product distribution is primarily determined by the redox properties of the catalyst (Figure 5.11). The exception to this rule was the CeO₂/Al₂O₃ catalyst, which although exhibiting a slightly higher CO oxidation activity compared to the best performing CeO₂/MgO catalyst (Figure 5.5b), displayed the lowest selectivity to bromocarbons in oxybromination. A possible explanation for this exceptional behavior might be the activity of the carrier in the undesired combustion reactions, comprising the oxidation of CH₄ or bromomethanes (CH₃Br and CH₂Br₂).
To assess the carrier contribution to the product distribution over the supported catalysts, CeO$_2$/MgO, CeO$_2$/Al$_2$O$_3$ and respective carriers MgO and Al$_2$O$_3$ were evaluated in CH$_4$, CH$_3$Br, and CH$_2$Br$_2$ oxidation (Figure B.28) under conditions closely matching those of CH$_4$ oxybromination. In both cases, the rate of CH$_4$ oxidation was negligible compared to the rate of bromomethanes oxidation (Figure 5.12b). Moreover, the activity of bulk and other supported CeO$_2$ catalysts in CH$_4$ oxidation is ca. 2-8 times lower than the rate of CH$_4$ oxybromination, while the rate of CH$_2$Br$_2$ oxidation is similar to or higher than the rate of oxybromination (Figure 5.12a). This indicates that a consecutive oxidation of bromomethanes has much higher impact on the formation of CO$_x$ than the oxidation of CH$_4$. Still, in the case of bulk CeO$_2$ and CeO$_2$/ZrO$_2$ catalysts, the contribution of CH$_4$ oxidation is likely higher compared to other materials. In agreement with the product distribution observed in oxybromination, MgO, and CeO$_2$/MgO exhibited substantially lower activity for bromomethanes oxidation compared to Al$_2$O$_3$ and CeO$_2$/Al$_2$O$_3$. Notably, the rate of CH$_2$Br$_2$ oxidation over Al$_2$O$_3$ was rather high and comprised ca. 85% of the activity of CeO$_2$/Al$_2$O$_3$ catalyst in this reaction, in line with previous reports of the high activity of this carrier in the oxidation of halocarbons.$^{[240,241]}$ The latter involves halogen displacement by hydroxyl groups, whereby the eliminated hydrogen halides are prone to react with Lewis acidic aluminum atoms. This mechanism is consistent with our observations that CO is the main product in CH$_4$ oxybromination, CH$_3$Br and CH$_2$Br$_2$ oxidation over both the CeO$_2$/Al$_2$O$_3$ catalyst and Al$_2$O$_3$ carrier, and with the increased surface Br:Ce ratio in the equilibrated CeO$_2$/Al$_2$O$_3$ catalyst (Figure 5.5a). Hence, a low selectivity to bromomethanes observed over CeO$_2$/Al$_2$O$_3$ catalyst is primarily caused by their combustion over the carrier (Figure 5.11).

Based on these results, CH$_2$Br$_2$ oxidation was chosen as a model reaction to assess the propensity of the other supported catalysts and carriers to combustion. Herein, ZrO$_2$ was also found to exhibit a relatively high activity (equivalent to ca. 20% of that of CeO$_2$/ZrO$_2$), which is in analogy to the Al$_2$O$_3$ carrier likely caused by the presence of basic OH groups and Lewis acidic zirconium ions.$^{[242]}$ In contrast, MgO, SiO$_2$, and SiC can be considered inert in CH$_2$Br$_2$ oxidation (Figure 5.12c). Nevertheless, CeO$_2$/SiO$_2$ and CeO$_2$/SiC catalysts were more active in combusting CH$_2$Br$_2$ than CeO$_2$/MgO, indicating that most CO$_x$ formation (ca. 70-90%) over the former catalysts results from the enhanced oxidizing potential of the active phase (Figure 5.5b). Finally, a comparison of CH$_4$ oxybromination, CH$_4$, CH$_2$Br$_2$, and HBr oxidation rates (Figure 5.12a), shows
that CeO$_2$/MgO exhibits the lowest activity in CH$_2$Br$_2$ oxidation, while preserving relatively high activity in HBr oxidation and CH$_4$ oxybromination, in good correspondence to the highest selectivity to bromocarbons observed over this catalysts (Figure 5.6). Figure 5.12a also demonstrates that catalyst must exhibit certain threshold activity in HBr oxidation in order to be sufficiently active in CH$_4$ oxybromination. The clear example for this is CeO$_2$/Al$_2$O$_3$ catalyst, which shows the lowest rate of HBr oxidation (Figure 5.12a) and is consequentially the least active in oxybromination (Figure 5.6). On the other hand, the high activity in HBr oxidation (e.g., bulk CeO$_2$ and CeO$_2$/ZrO$_2$) is correlated with the enhanced oxidation of bromomethanes. Therefore, a high oxybromination performance requires the balanced oxidizing potential, which is best-matched by CeO$_2$/MgO catalyst.

5.4. Conclusions

Supported CeO$_2$ catalysts were investigated in CH$_4$ oxybromination, revealing major differences in performance compared to the bulk material, especially in the product distribution. The latter was strongly dependent on the type of carrier, which both influenced the dispersion, structure, and redox properties of the active phase, and exhibited a variable degree of inertness with respect to the oxidation of bromomethanes. Supported CeO$_2$ catalysts displayed decreased oxidizing potential compared to the bulk phase, which was associated with an enhanced selectivity due to a reduced activity in side combustion reactions (Figure 5.11). This effect was least pronounced over CeO$_2$/ZrO$_2$, which exhibited similar performance to bulk CeO$_2$. Another influential factor was the carrier propensity to combust bromomethanes. The latter reactions were more pronounced over the ZrO$_2$ and particularly the Al$_2$O$_3$ supports, which was related to the presence of Lewis acidic metal ions and basic hydroxyl groups, and resulted selectivity losses over the respective supported catalysts (Figure 5.11). An optimal balance of redox properties and carrier inertness was observed over CeO$_2$/MgO catalyst (Figure 5.11), stabilizing CeO$_2$ in the form of nanoparticles (ca. 9 nm). This catalytic system provided the highest selectivity to CH$_3$Br (61-81%), which substantially exceeded that of bulk CeO$_2$ (ca. 40%) and rivalled those of the best previously reported oxybromination catalysts. Besides, the selectivity to CO$_2$ (6-10%) was drastically reduced and its performance was stable for over 80 h on stream. Importantly, the product distribution over the MgO-supported catalysts was almost unaffected by the changes in the loading, size, and faceting
of CeO$_2$ nanoparticles, which was in agreement with the similar oxidation potentials observed after equilibration of the latter catalysts, hinting at the adoption of a common surface structure. The findings are consistent with the mechanism comprising heterogeneous HBr oxidation into Br$_2$, followed by the reaction of the latter with CH$_4$ in the gas-phase. Thereby, supporting CeO$_2$ over suitable carriers provides an effective strategy to tailor its redox properties, and particularly the propensity to combustion, which is relevant in view of developing technical form catalyst for practical implementation of this technology.
Chapter 6

Europium Oxybromide Catalysts for Bromine Looping

6.1. Introduction

More than 30% of the known world’s natural gas reserves are located in remote and scattered wells.[24,43] This fact precludes their use as a long-lasting feedstock for the manufacture of chemicals and fuels due to the prohibitive shipping expenses to centralized megaplants.[5,29] Consequently, natural gas emitted from these wells is nowadays flared or vented, wasting ca. 3.5% of its global production, which is a fraction worth ca. 13 billion USD.[48,154] Among the various routes proposed to overcome the capital intensity of conventional syngas-based processes,[25,26,50,55,58,63,64,88] the bromine-mediated functionalization of methane (CH$_4$) into methyl bromide (CH$_3$Br), a versatile C1 platform molecule with similar upgrading paths to methanol, emerged as an economically attractive technology for the decentralized manufacture of readily transportable value-added chemicals and fuels in compact plants amenable to decentralization.[5,29,51,66,71,80,84,86,88,91,96,163] As shown in Figure 1.3, Chapter 1, key steps of the process,[5,29,66,71,80,84,86,88,91,96] which could also be applied to ethane and propane,[5,29] comprise (i) CH$_4$ bromination, which provides up to 95% selectivity to CH$_3$Br, (ii) reproporionation of the polybrominated byproducts into monobrominated alkanes and olefins by reaction with C1-C5 alkanes, (iii) coupling of CH$_3$Br and reproporation products into valuable hydrocarbons such as gasolines, olefins, and aromatics, and (iv) recycling of hydrogen bromide (HBr), which is generated in stoichiometric amounts in the bromination and coupling steps. The latter step closes the bromine loop and is vital to the feasibility of the entire technology, since the high price and low availability of this halogen necessitate its full recovery. The highly efficient carbon atom utilization enabled by developments in the bromination, reproporation, and coupling reactions, as well as advances in corrosion resistant construction materials led to a large-scale demonstration of the bromine-based process for the production of petrochemical-grade aromatics from CH$_4$, which is nowadays offered for
Nevertheless, little progress has been made towards sustainable bromine looping, which is commonly accomplished via cataloreactant processes or the catalytic HBr oxidation. The former approach relies on the absorption of HBr by an oxide or hydroxide, followed by its re-oxidation in a second step to evolve molecular bromine (Br$_2$). However, such a cyclic operation necessitates large reactors and is difficult to control due to the limited lifetime of the cataloreactants. Hence, it is highly desirable to develop a catalytic system for the continuous oxidation of HBr into bromine at relatively low temperatures ($T \leq 573$ K) and stoichiometric feed (O$_2$:HBr = 0.25). In addition to enhancing the overall space-time and energy efficiency of the process, this would enable the use of air as an oxygen (O$_2$) source, thereby substantially reducing production costs. Nevertheless, such an operating window remains highly challenging due to the extensive bromination of active catalysts like RuO$_2$ and CeO$_2$ even under significant O$_2$ excess, leading to severe deactivation.

Herein, europium oxybromide (EuOBr) is introduced as a unique catalytic material to close the bromine loop via HBr oxidation, permitting long lifetimes under realistic feed conditions at which any catalyst reported to date severely deactivates due to excessive bromination. Besides, EuOBr is shown to exhibit the unparalleled selectivity to CH$_3$Br in CH$_4$ oxybromination, an alternative route for bromine looping. This novel active phase is finely dispersed on appropriate carriers and scaled up to technical extrudates, enhancing the utilization of europium by over an order of magnitude while preserving the performance, demonstrating its realistic potential for practical implementation.

6.2. Experimental

6.2.1. Catalyst Preparation

Commercial lanthanum(III) oxide (La$_2$O$_3$, Alfa-Aesar, 99.99%), cerium(IV) oxide (CeO$_2$, Sigma-Aldrich, nanopowder, 99.9%), samarium(III) oxide (Sm$_2$O$_3$, ABCR, 99.9%), europium(III) oxide (Eu$_2$O$_3$, Sigma-Aldrich, 99.5%), gadolinium(III) oxide (Gd$_2$O$_3$, Alfa-Aesar, 99.99%), terbium(III) oxide (Tb$_2$O$_3$, Stream Chemicals, 99.9%), and dysprosium(III) oxide (Dy$_2$O$_3$, ABCR, 99.99%) were heated in flowing air at 973 K for 5 h prior to the catalytic tests. Commercial titanium(IV) oxide (TiO$_2$, Sigma-Aldrich, rutile nanopowder, 99.5%) was heated in static air at 873 K for 5 h. Europium oxybromide (EuOBr) studied in HBr oxidation and CH$_4$ oxybromination...
was prepared by exposing the calcined Eu$_2$O$_3$ (2.0 g) to an HBr-containing gas-mixture (molar ratio O$_2$:HBr:He = 9:4.5:86.5, total flow rate $F_T = 100$ cm$^3$ min$^{-1}$) at 623 K (HBr oxidation) or 773 K (CH$_4$ oxybromination) for 5 h. Vanadyl pyrophosphate ((VO)$_2$P$_2$O$_7$, VPO) was synthesized by refluxing a suspension of vanadium(V) oxide (15 g; V$_2$O$_5$, Aldrich, $\geq$ 99.6%) in isobutanol (90 cm$^3$; Acros, > 99%) and benzyl alcohol (60 cm$^3$; Sigma-Aldrich, > 99%) for 3 h. After cooling down to room temperature, the molar P:V ratio was set to 1.2 by adding H$_3$PO$_4$ (Sigma-Aldrich, $\geq$ 85%) and the mixture was then refluxed for another 16 h. The blue solid was recovered by filtration, washed with isobutanol and methanol (Fluka, $\geq$ 99.9%), dried under vacuum (50 mbar) at 373 K for 16 h, and finally heated in flowing N$_2$ (Pan Gas, purity 4.5) at 873 K for 5 h. Supported Eu-based catalysts denoted as EuOBr/SiO$_2$, EuOBr/Al$_2$O$_3$, EuOBr/ZrO$_2$, EuOBr/Al$_2$O$_3$-t, and EuOBr/ZrO$_2$-t were prepared by impregnating an aqueous solution of Eu(NO$_3$)$_3$·6H$_2$O (ABCR, 99.9%) on pre-calcined (static air, 973 K, 5 h) carriers comprising SiO$_2$ (20-60 µm, Evonik, AEROPERL® 300/30, $\geq$ 99.0%), $\gamma$-Al$_2$O$_3$ (5-100 µm, Sasol, PURALOX® SCFa 140, $\geq$ 98%), or ZrO$_2$ ($\leq$ 60 µm, Alfa-Aesar, 99%) powders and $\gamma$-Al$_2$O$_3$ (diameter: 3.2 mm, length: 3-4.5 mm, Saint-Gobain Norpro, SA6176) or ZrO$_2$ (diameter: 3.2 mm, length: 3-4.5 mm, Alfa-Aesar, 99%) extrudates, respectively. An appropriate amount of Eu(NO$_3$)$_3$·6H$_2$O was dissolved in a volume of deionized water equivalent to the pore volume of the support as determined from N$_2$ sorption, and the obtained solution was added dropwise to the carrier under continuous mixing. Unless otherwise stated, Eu content in supported catalysts was set to 9 wt.%.

After impregnation, the material was left for 1 h at room temperature, then dried under vacuum (50 mbar) at 373 K for 12 h, and calcined in flowing air at 973 K for 5 h. Prior to evaluation, the supported catalyst was subjected to the HBr-containing gas mixture following the same protocol as for the synthesis of the bulk EuOBr. All thermal treatments were conducted using a heating rate of 5 K min$^{-1}$.

6.2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) was measured using a PANalytical X’Pert PRO-MPD diffractometer by applying Cu-Kα radiation ($\lambda = 1.54060$ Å). The data was recorded in the 10-70° 2θ range with an angular step size of 0.017° and a counting time of 0.26 s per step. N$_2$ sorption at 77 K was performed using a Micromeritics TriStar analyzer. Prior to the measurement, the sample
was evacuated to 50 mbar at 573 K for 12 h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area, $S_{BET}$, in m$^2$ g$^{-1}$. The pore volume, $V_{\text{pore}}$, in cm$^3$ g$^{-1}$, was calculated from N$_2$ adsorption at relative pressure $p/p_0 = 0.98$. The content of europium in supported catalyst was quantified by X-ray fluorescence spectroscopy (XRF), using an Orbis Micro instrument equipped with a Rh source operated at 35 kV and 500 µA. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC 1 Star system connected to a Pfeiffer Vacuum Thermo-Star GDS 320 T1 mass spectrometer (MS). The solid (0.05 g) was pretreated in flowing air (45 cm$^3$ min$^{-1}$) at 393 K for 1 h. The analysis was carried out in the same medium (45 cm$^3$ min$^{-1}$), heating at a rate of 10 K min$^{-1}$ from 393 K to 1173 K for CeO$_2$ and to 1473 K for EuOBr. The evolution of bromine and water was monitored by MS, following the ions at a mass-to-charge ratio ($m/z$) of 81 and 18, respectively. Temperature-programmed reduction with hydrogen (H$_2$-TPR) was performed in a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector (TCD). The solid (0.10 g) was loaded into a U-shaped quartz micro-reactor, pretreated in He (20 cm$^3$ min$^{-1}$) at 423 K for 1 h, and cooled to 373 K. A mixture comprising 5 vol.% H$_2$ in N$_2$ (20 cm$^3$ min$^{-1}$) was then fed and the temperature was increased up to 1173 K at a rate of 10 K min$^{-1}$, while monitoring the H$_2$ consumption by using a TCD detector. High-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and elemental mapping with energy-dispersive X-ray spectroscopy (EDXS) were conducted on a FEI Talos microscope operated at 200 kV. All samples were dispersed as dry powders onto lacey carbon coated nickel grids. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electronics Quantum 2000 spectrometer using monochromatic Al-K$\alpha$ radiation, generated from an electron beam operated at 15 kV, and equipped with a hemispherical capacitor electron-energy analyzer. The solid was analyzed at the electron take-off angle of 45° and the pass energy of 46.95 eV. A compensation for sample charging was obtained by referencing the spectra to the C 1s at 284.5 eV. The elemental concentrations were quantified based on the measured photoelectron peak areas (Br 3$d$, Ce 3$d$, Eu 3$d$) after Shirley background subtraction using PHI-MultiPak software and the built-in relative sensitivity factors which are corrected for the system transmission function.
6.2.3. Catalyst Testing

HBr and CH₄ oxidation, CH₄ oxybromination, and CH₄ bromination were performed at ambient pressure in a continuous-flow fixed-bed reactor setup, which is described in Appendix A. The catalyst in form of particles (particle size, \(d_p = 0.4-0.6\) mm) or extrudates (diameter: \(3.2\) mm, length: \(3-4.5\) mm) was well mixed with quartz particles (Thommen-Furler, \(d_p = 0.2-0.3\) mm) to ensure a constant bed volume \(V_{\text{bed}} = 2\) cm³) and loaded in a quartz reactor (internal diameter, \(d_i = 8\) mm for particles and \(d_i = 17\) mm for extrudates). In CH₄ oxybromination, CH₄ bromination, and CH₄ oxidation the post-catalyst zone was filled with quartz beads (Sigma-Aldrich, \(d_p = 0.6\) mm) to minimize its volume and the possible occurrence of the gas-phase reactions in this reactor section. Prior to testing, the catalyst bed was heated in a He flow to the desired temperature \(T = 423-853\) K and allowed to stabilize for at least 30 min before the reaction mixture was fed. The catalyst weight \(W_{\text{cat}}\), total flow rate \(F_T\), and feed mixture applied in the tests are summarized in Table 6.1. Quantification of reactants and products, determination of conversion, selectivity, and yield, as well as the evaluation of carbon and bromine mass balance was conducted using the same protocol as detailed in Appendix A.

**Table 6.1. Conditions applied in the reactions studied.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(W_{\text{cat}} / \text{g})</th>
<th>(F_T^b / \text{cm}^3\text{ min}^{-1})</th>
<th>Feed compositionc / vol.%</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₄ HBr Br₂ O₂</td>
<td></td>
</tr>
<tr>
<td>HBr oxidation</td>
<td>0.5 (2.0)c</td>
<td>100</td>
<td>0 4.5 (10)d</td>
<td>0</td>
</tr>
<tr>
<td>CH₄ oxybromination</td>
<td>1.0 (0.5)c</td>
<td>50-200</td>
<td>3-19 3-12</td>
<td>0</td>
</tr>
<tr>
<td>CH₄ bromination</td>
<td>1.0</td>
<td>100</td>
<td>6 0 3</td>
<td>0</td>
</tr>
<tr>
<td>CH₄ oxidation</td>
<td>1.0</td>
<td>100</td>
<td>6 0 0 3</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) All tests were conducted at \(P = 1\) bar.\(b\) Flow units correspond to standard temperature (273 K) and pressure (1 bar) conditions. \(c\) Ar (4.5 vol.%) was added as an internal standard to all the reaction mixtures, except for HBr oxidation. He was used as the balance gas. \(d\) Values in brackets refer to tests performed over catalyst extrudates.
6.3. Results and Discussion

6.3.1. Performance of Europium Oxybromide in Hydrogen Bromide Oxidation

In our quest for a novel catalytically active phase enabling efficient bromine looping, we have investigated the performance of various rare-earth oxides comprising La₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃, and Dy₂O₃ in HBr oxidation. Catalysts based on lanthanide metals have been widely applied in numerous reactions, but apart from CeO₂, no member of this catalyst family has been investigated in HBr oxidation. Initial catalytic tests were conducted using an O₂-rich feed (O₂:HBr = 2), which favors the re-oxidation of the catalyst (Figure B.30). All of the catalysts were found to transform to the oxybromide phase under these conditions (Figure B.29). Consequently, the performance of the lanthanide oxybromide phases was considered henceforth. Comparatively, the highest rates of HBr oxidation in the low-temperature window (423-473 K) were observed over EuOBr, substantially exceeding those of the benchmark CeO₂ and TiO₂ catalysts (Figure 6.1a, Figure B.30), which is the first report on the application of EuOBr in catalysis. The light-off curve of LaOBr was shifted to ca. 150 K higher temperature compared to EuOBr. Besides, it suffered deactivation (Figure B.29). Other lanthanide oxybromides were all active at temperatures (T > 623 K), exceeding the preferred operating window.

The performance of EuOBr remained unaltered upon temperature cycling (Figure 6.1a), which simulates the likely spatial and temporal fluctuations in a reactor. In contrast, during the temperature-increasing part of cycle CeO₂ displayed a lower HBr conversion than during the temperature-decreasing part, indicating deactivation caused by a bromine uptake at low temperatures. On the other hand, TiO₂, which is the benchmark of the bromination-resistant catalysts (Figure B.31), was much less active compared to EuOBr. The stability of the latter material was also evidenced on cycling the feed concentration of O₂ (Figure 6.1b). Notably, the performance of EuOBr was only slightly affected by the O₂ concentration, showing no deactivation. Contrarily, the conversion of HBr over CeO₂ drops to almost zero under the preferred stoichiometric feed (O₂:HBr = 0.25), and is only partially restored upon returning to higher O₂ concentrations. The outstanding robustness of EuOBr was further demonstrated by its stable activity in a time-on-stream test under stoichiometric feed at 523 K (Figure 6.1c). Under the same conditions, the bromine production over CeO₂ almost completely ceased just after 6 h. The deactivation profiles of this material observed upon temperature and O₂ cycling, as well as with...
time-on-stream coincide with the behavior of other highly active catalysts in this reaction such as RuO$_2$.[122,123] The contrasting performance of EuOBr and CeO$_2$ was rationalized by in-depth characterization of the catalysts recovered after different time-on-stream in HBr oxidation. The
Figure 6.2. High-angle annular dark field scanning transmission electron micrographs (left) and energy-dispersive X-ray spectroscopy elemental maps (right) of EuOBr in (a) fresh form and (b) recovered after 20 h on stream, and CeO$_2$ recovered after (c) 1 h and (d) 6 h on-stream. Electron dispersive X-ray spectra of CeO$_2$ recovered after (e) 1 h and (f) 6 h on stream. Conditions: HBr:O$_2$:He = 4.5:1.13:94.37, $F_T/W_{\text{cat}} = 200$ cm$^3$ min$^{-1}$ g$_{\text{cat}}^{-1}$, $T = 523$ K, and $P = 1$ bar.
appearance of new reflections in the X-ray diffraction patterns of the used samples evidenced the chemical transformation of CeO$_2$ (Figure 6.1d, Figure B.32), which based on the increasing degree of bromination (vide infra) was tentatively ascribed to the formation of (oxy)bromide phases (Figure B.33). Besides, pronounced particle sintering was evidenced from a drop in surface area of the catalyst recovered after 6 h of reaction (13 m$^2$ g$^{-1}$) with respect to the fresh material (27 m$^2$ g$^{-1}$) which was also supported by electron microscopy examination (Figure 6.2). Remarkably, the bulk structure of EuOBr showed no significant change after 20 h of use (Figure 6.1d), whereby its surface area (19 m$^2$ g$^{-1}$) was slightly lower compared to the fresh catalyst (22 m$^2$ g$^{-1}$). The profound resistance of EuOBr to further bromination and the progressive uptake of bromine by CeO$_2$ were evidenced by the High-angle annular dark field microscopy complemented with elemental maps obtained using energy dispersive X-ray spectroscopy (Figure 6.2). The micrographs of EuOBr indicate that rod-like morphology and particle size of EuOBr are preserved under harsh reaction conditions, while elemental maps testify the uniform distribution of europium, bromine, and oxygen in fresh and used catalysts (Figure 6.2a,b). In contrast to this, CeO$_2$ undergoes substantial particle agglomeration (Figure 6.2c,d, left) in line with a drop in surface area. The catalyst exhibited a significant bromine uptake already after 1 h of operation (Figure 6.2c), which was increasing during reaction as inferred from the relative ratio of bromine and cerium peaks in X-ray spectra of 1 h and 6 h samples (Figure 6.2e,f), as well as thermogravimetric analysis (Figure B.33). Thereby, the catalyst recovered after 6 h on-stream showed significant depletion of oxygen and enrichment in bromine (Figure 6.2d). Inspection of the fresh and used CeO$_2$ by X-ray photoelectron spectroscopy revealed that the Ce 3$d$ spectrum of fresh CeO$_2$ comprises three pairs of spin-orbit doublets, which is characteristic of Ce$^{4+}$ state, while the used samples after 3 h exhibited only two pairs of doublets, which are typical of Ce$^{3+}$.[238] Besides, the XPS spectra testified the increase in bromine content in the surface region of this catalyst upon use (Figure 6.1e, Figure B.34) These results imply the progressive reduction of Ce$^{4+}$ into Ce$^{3+}$ due to catalyst bromination, ultimately resulting in its deactivation (Figure 6.1c). On the other hand, EuOBr displayed a constant Br:Eu ratio of ca. 0.7 in the surface region (Figure 6.1f, Figure B.34), confirming the ability of EuOBr to preserve an excess of oxygen under stoichiometric feed. The Eu 3$d$ core level spectra displays dominant peaks at binding energies of 1134 eV (3$d_{5/2}$) and 1164 eV (3$d_{3/2}$), which are ascribed to Eu$^{3+}$, with small contributions at 1128 eV (3$d_{5/2}$) and 1156 eV (3$d_{3/2}$), corresponding to Eu$^{2+}$,[246] suggesting the
Eu³⁺/Eu²⁺ redox couple to be responsible for the catalyst activity. In contrast to CeO₂, no signs of catalyst reduction could be observed, as the ratio of Eu²⁺/Eu³⁺ was unaltered during. Based on these results, the exceptional stability of EuOBr can be ascribed to the structural integrity of this phase, which is preserved in oxygen-rich and HBr-rich feed mixture.

6.3.2. Performance of Europium Oxybromide in Methane Oxybromination

Given the outstanding performance in HBr oxidation, EuOBr was further evaluated in CH₄ oxybromination, which comprises an alternative route to accomplish a continuous bromine looping by integrating HBr oxidation and CH₄ functionalization in a single step. Besides stability and activity constraints, another challenging aspect in the design of an oxybromination catalyst is to attain a high selectivity to CH₃Br by suppressing the side combustion reactions. The latter are avoided if CH₄ bromination and HBr oxidation are executed separately, which favors the two-step route over CH₃Br. Notably, the selectivity to CH₃Br over EuOBr (85-65% at 6-33% single-pass CH₄ conversion) substantially exceeded that of the benchmark (VO)₂P₂O₇ (VPO) and CeO₂ catalysts at comparable reaction rates in the broad range of conditions applied (Figure 6.3, Figure B.35).[89] EuOBr also provided the highest selectivity to CH₃Br (7-56%) and CH₂Br₂ (2-30%) on the basis of HBr (51-95% single-pass conversion), although the selectivity to bromine (17-90%) was significant (17-90%) (Figure B.36). Moreover, it exhibited a low formation of carbon oxides (COₓ), yielding Br₂ and dibromomethane (CH₂Br₂) as the dominant byproducts, which can be further upgraded via bromination and reproportionation, respectively.[5,29,71,84]

To rationalize the activity of EuOBr in CH₄ oxybromination, the catalyst was evaluated in CH₄ oxidation and bromination (Figure B.37), which were chosen as the test reactions to probe the catalyst ability to dissociate C-H and form C-Br bonds, respectively. The low activity of EuOBr in CH₄ combustion and absence of its catalytic effect in CH₄ bromination, suggest a low propensity of this material to activate this alkane. Besides, CH₄ oxybromination over EuOBr proceeds in the same temperature window (T > 733 K) as the non-catalytic gas-phase bromination of CH₄, whereby the two reactions exhibit very similar apparent activation energy (Figure B.37). It is thus proposed that similar to the catalysts presented in the previous Chapters, CH₄ oxybromination over EuOBr proceeds by the gas-phase reaction of CH₄ with bromine species that are (re)generated.
6.3.3. Supported EuOBr Catalysts for Bromine Looping

Having identified the outstanding properties of EuOBr in HBr oxidation and CH$_4$ oxybromination, the next step was to develop a technical catalyst based on this material. Besides reducing the price of a catalyst, the dispersion of an active phase over a suitable carrier can improve...
the intrinsic activity by ensuring both a high surface area and favorable electronic interaction. To study the potential impact of active phase dispersion, EuOBr was supported on three carriers: Al2O3, ZrO2, and SiO2 (9 wt.% europium loading) yielding catalysts denoted as EuOBr/Al2O3, EuOBr/ZrO2, and EuOBr/SiO2, respectively. These were evaluated in HBr oxidation revealing the following activity trend: EuOBr/Al2O3 > EuOBr/ZrO2 > EuOBr/SiO2 (Figure 6.4a). Notably, the conversion of HBr over EuOBr/Al2O3 substantially exceeded that of the bulk system in the low-temperature region, enabling over one order of magnitude higher rate of HBr oxidation per content of europium, while preserving its resistance against bromination (Figure B.38). The specific surface area of the best performing EuOBr/Al2O3 was intermediate between that of EuOBr/ZrO2 and EuOBr/SiO2 (Table B.7), suggesting that the observed activity trend is also affected by the specific interaction with the support. XRD patterns of fresh and used catalysts were identical to
Figure 6.5. Elemental maps of the (a) EuOBr/Al₂O₃, (b) EuOBr/ZrO₂, and (c) EuOBr/SiO₂ catalysts used in the HBr oxidation tests shown in Figure 6.4a. The signals used for detecting the elements are indicated in the representative X-ray spectra on the right. The similar morphology observed in the HAADF-STEM micrographs before and after elemental mapping confirms the stability of the samples under the electron beam.
those of the bare carriers, with no observable contributions from Eu₂O₃ and EuOBr phases (Figures B.39). Consistent with this result, HAADF-STEM micrographs and respective elemental maps (Figure 6.5) and HRTEM (Figure 6.6) of used catalysts also evidenced a fine dispersion of the active phase over the carriers. The relative ratio of Br and Eu signals in the elemental maps indicated a decrease in Br:Eu ratio in the order: EuOBr/Al₂O₃ > EuOBr/ZrO₂ >> EuOBr/SiO₂, which was also corroborated by the thermogravimetric analysis conducted under flowing air (Figure B.40). The latter demonstrated that the type of carrier has an important impact on the temperature of re-oxidation, with EuOBr/Al₂O₃ displaying a significant reduction compared to that predicted for the bulk EuOBr. In very good agreement with this observation, the position of the low-temperature reduction peak (520-700 K) in the temperature programmed reduction with H₂ indicated a decrease in the oxidizing potential of the catalysts in the order EuOBr/Al₂O₃ > EuOBr/ZrO₂ ~ EuOBr > EuOBr/SiO₂ (Figure B.41). The above-discussed results imply that the degree of bromination, ability to evolve Br₂, and reducibility of the supported catalysts, strongly correlate with the activity in HBr oxidation. This confirms the impact of the carrier identity on the susceptibility to bromination, whereby the supported systems with a bromine content close to that of the oxybromide display a higher activity in HBr oxidation. The outstanding performance of EuOBr/Al₂O₃ was thus rationalized by the ability of Al₂O₃ to stabilize
the brominated form the catalyst and to promote the bromine evolution with respect to the bulk system.

In the case of CH₄ oxybromination the supported systems led to an increased production of COₓ with respect to bulk EuOBr (Figure 6.3, Figure B.42). This was particularly pronounced over EuOBr/Al₂O₃, which could be attributed to its high oxidizing potential as well as the propensity of Al₂O₃ to combust halocarbons.[241] On the other hand, the enhanced COₓ formation over EuOBr/SiO₂ is consistent with the low degree of the catalyst bromination, which promotes combustion (Chapter 3). EuOBr/ZrO₂ shows balanced redox properties and a relatively high degree of bromination, providing the highest selectivity to CH₃Br among the supported systems, which is close to that of the bulk EuOBr and is also preserved at lower Eu loading (Figure B.43). Based on the relative performance of the supported systems, Al₂O₃ and ZrO₂ extrudates were chosen to prepare technical catalysts (i.e., EuOBr/Al₂O₃-t and EuOBr/ZrO₂-t), which were tested in the low-temperature HBr oxidation and CH₄ oxybromination under stoichiometric, and substoichiometric feeds, respectively. Their activity matched that of the supported systems in powder form and was stable for over 60 h of operation under these harsh conditions (Figure 6.4b,c), with no detectable loss of europium.

6.4. Conclusions

EuOBr was found to be an exceptional catalyst for HBr oxidation, enabling low-temperature operation under a stoichiometric feed, conditions inaccessible to existing systems. This was ascribed to the marked bromine evolution activity and inherent resistance to further bromination of the oxybromide phase. Moreover, this material provided a high selectivity to CH₃Br in CH₄ oxybromination, outperforming all previously reported catalysts. The substantially suppressed COₓ production over EuOBr opens the door for the development of catalytic systems that do not produce these side products. Thereby, the conversion of CH₂Br₂ via reproportionation could further enhance the overall selectivity to CH₃Br. To bridge the gap between the activity of EuOBr in bromine recovery processes and its high price, the impact of different carriers on its performance was investigated. Al₂O₃ and ZrO₂ were identified as the best supports for HBr oxidation and CH₄ oxybromination, respectively, enabling an order of magnitude improved utilization of europium compared to the bulk catalyst. Technical catalysts prepared using the latter supports displayed
robust performance demonstrating their realistic potential for application in bromine-based processes that can enable the decentralized valorization of stranded natural gas.
Chapter 7

Evidence of Radical Chemistry in Catalytic Methane Oxybromination

7.1. Introduction

Understanding the mechanisms of the heterogeneously-catalyzed functionalization of methane (CH\textsubscript{4}) and other light alkanes contained in natural gas goes well beyond a scientific curiosity, as it may unlock the transformation of this increasingly abundant, relatively cheap, and potentially renewable feedstock into commodities via highly efficient catalytic routes.\footnote{55,56,58,60,63,64,245,247-249} This challenging task requires sophisticated kinetics, spectroscopic, and theoretical approaches in order to uncover the reaction pathways, their elementary steps, and underlying reactive intermediates, with the ultimate aim of translating this information into the design of selective catalytic processes.\footnote{52,55,56,58,60,63,64,245,247-251} An additional level of complexity arises in reaction systems such as oxidative coupling,\footnote{52,56,68,250} oxidative dehydrogenation,\footnote{245,247} selective oxidation into alcohols and aldehydes,\footnote{49} transformation into olefins and aromatics,\footnote{55} or the reaction of CH\textsubscript{4} with ammonia,\footnote{251} wherein the species formed on the catalyst surface might enter gas-phase reactions leading to desired and undesired products. As put forward in the previous chapters, a mechanism involving interplay between surface-catalyzed and gas-phase reaction steps has been hypothesized for the catalytic oxybromination of CH\textsubscript{4} (Equations 7.1 and 7.2) into bromomethanes, viz., methyl bromide (CH\textsubscript{3}Br) and dibromomethane (CH\textsubscript{2}Br\textsubscript{2}), which comprise highly attractive platform molecules for the manufacture of valuable chemicals and fuels.\footnote{29,85}

\begin{align*}
\text{CH}_4 + \text{HBr} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CH}_3\text{Br} + \text{H}_2\text{O} \quad \text{(7.1)} \\
\text{CH}_4 + 2\text{HBr} + \text{O}_2 & \rightarrow \text{CH}_2\text{Br}_2 + 2\text{H}_2\text{O} \quad \text{(7.2)} \\
\text{CH}_4 + \text{Br}_2 & \rightarrow \text{CH}_3\text{Br} + \text{HBr} \quad \text{(7.3)} \\
\text{CH}_4 + 2\text{Br}_2 & \rightarrow \text{CH}_2\text{Br}_2 + 2\text{HBr} \quad \text{(7.4)}
\end{align*}
Among the bulk catalytic materials studied in this thesis, vanadyl pyrophosphate (\((\text{VO})_2\text{P}_2\text{O}_7, \text{VPO}\)) and particularly europium oxybromide (\(\text{EuOBr}\)) provided the highest selectivity to \(\text{CH}_3\text{Br}\) and \(\text{CH}_2\text{Br}_2\) with minimal production of undesired carbon oxides (\(\text{CO}_x\)). Steady-state reaction tests over multiple catalysts pointed out that \(\text{CH}_4\) oxybromination commonly occurs at similar temperatures (\(\ge 693 \text{ K}\)) as the non-catalyzed gas-phase bromination (Equations 7.3 and 7.4). Moreover, an increase in the production of bromomethanes in oxybromination was coupled to a drop in bromine (\(\text{Br}_2\)) evolution, which is the main reaction product at low temperatures. This led to the proposal that the reaction mechanism may synergistically involve the surface-catalyzed oxidation of hydrogen bromide (\(\text{HBr}\), Equation 7.5) into \(\text{Br}_2\) and \(\text{CH}_4\) bromination in the gas phase (Equations 7.3 and 7.4), which proceeds via methyl (\(\text{CH}_3^*\)) and bromine (\(\text{Br}^*\)) radicals.[84,93,94] However, this reaction pathway has not been evidenced yet. In this sense, a theoretical study on lanthanaum oxide surfaces suggested that the adsorption of \(\text{HBr}\) or \(\text{Br}_2\) in the presence of oxygen (\(\text{O}_2\)) might facilitate the surface-catalyzed activation of the C-H bond.[252] Hence, the key step to unequivocally unravel the mechanism of \(\text{CH}_4\) oxybromination comprises the detection of radical intermediates during the reaction (viz., under \textit{operando} conditions), which is highly challenging given their short lifetimes and extremely corrosive reaction environment.

Lunsford and coworkers pioneered the application of matrix isolation electron spin resonance spectroscopy (MIESR) to confirm the formation of alkyl radicals in catalytic processes such as oxidative coupling of \(\text{CH}_4\) and \(n\)-propene oxidation.[52,253] More recently, molecular beam mass spectrometry (MS) coupled with electron impact ionization (EI) was used to directly detect short-lived gaseous intermediates in the synthesis of hydrogen cyanide from \(\text{CH}_4\) and ammonia over a platinum catalyst.[254] However, a use of high ionization energy (ca. 70 eV) leads to significant fragmentation of molecular ions and limits the application of EI. In contrast, the photoionization of molecular beam by vacuum ultraviolet (VUV) synchrotron radiation enables fine tuning of the photon energy, which suppresses the fragmentation interferences and boosts the sensitivity.[250,254] VUV photoionization mass spectroscopy (VUV-PIMS) was successfully applied to trace transient gaseous intermediates formed in combustion[254] and heterogeneously-catalyzed reactions such as the activation of \(\text{CH}_4\),[55,250] oxidation of volatile organics,[253] and conversion of syngas.[256] Further advances have been achieved by the development of VUV photoelectron
Evidence of Radical Chemistry in Catalytic Methane Oxybromination

Photoion coincidence (PEPICO) spectroscopy based on mass analysis of photoions and kinetic energy analysis of photoelectrons in delayed coincidence, which besides the high energy resolution, high dynamic range, and fragment-free ionization, offers the possibility to measure photoion mass-selected (threshold) photoelectron spectra. This makes it a powerful tool for an isomer-specific detection of short-lived species such as radicals in complex gas-phase reactions, as demonstrated by the studies on non-catalytic (bi)molecular rearrangements, flame chemistry, and catalytic pyrolysis of biomass. Accordingly, PEPICO can be a decisive technique to interrogate the formation of gaseous intermediates in the heterogeneously-catalyzed halogen-based processes for C-H bond activation under operando conditions.

In this Chapter, the steady-state kinetic fingerprints of catalytic CH₄ oxybromination over VPO and EuOBr (Equations 7.1 and 7.2) and non-catalytic gas-phase bromination (Equations 7.3 and 7.4) are analyzed, evidencing the importance of gas-phase chemistry in the former reaction (Equations 7.1 and 7.2). Operando PEPICO spectroscopic experiments demonstrate for the first time the formation of CH₃● and Br● radicals in the oxybromination chemistry and verify their substantial role in CH₄ activation. Density functional theory (DFT) strengthens the understanding of the surface and gas-phase processes at a molecular level.

7.2. Experimental

7.2.1. Catalyst Preparation and Characterization

Vanadyl pyrophosphate ((VO)₂P₂O₇, VPO) and europium oxybromide (EuOBr) were synthetized as described in Chapter 3. Briefly, VPO was synthesized by refluxing a suspension of vanadium(V) oxide (V₂O₅, 15 g; Aldrich, ≥ 99.6%) in isobutanol (90 cm³; Acros, > 99%) and benzyl alcohol (60 cm³; Sigma-Aldrich, > 99%) for 3 h. After cooling down to room temperature, H₃PO₄ (Sigma-Aldrich, ≥ 85%) was added to achieve molar P:V ratio of 1.2 and the mixture was then refluxed for another 16 h. The blue solid was recovered by filtration, washed with isobutanol and methanol (Fluka, ≥ 99.9%). After drying under vacuum (50 mbar) at 373 K for 16 h, the material was heated in flowing N₂ (Pan Gas, purity 4.5) at 873 K for 5 h. EuOBr was prepared starting from europium(III) oxide (Eu₂O₃, 2 g; Sigma-Aldrich, 99.5%), which was calcined at 973 K for 5 h and then exposed to an HBr-containing gas mixture (HBr:O₂:He = 9:4.5:86.5, total flow rate F_T = 100 cm³ min⁻¹) at 773 K for 5 h. Powder X-ray diffraction (XRD) was measured in a
Chapter 7

PANalytical X’Pert PRO-MPD diffractometer operated in Bragg-Brentano geometry using Ni-filtrated Cu K\(\alpha\) radiation (\(\lambda = 1.54060 \text{ Å}\)). Data were recorded in 2\(\theta\) range of 10-70° with an angular step size of 0.017° and counting time set to 0.026 s per step. N\(_2\) isotherms at 77 K were measured in a Micromeritics TriStar analyzer, after evacuation of the samples at 573 K and 50 mbar for 12 h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area.

7.2.2. Catalyst Testing

\(\text{CH}_4\) oxybromination, \(\text{CH}_4\) bromination, and \(\text{CH}_4\) oxidation, and \(\text{CH}_3\text{Br}\) disproportionation experiments were performed in a continuous-flow reactor setup described in Appendix A. In \(\text{CH}_4\) oxybromination and \(\text{CH}_4\) oxidation, and \(\text{CH}_3\text{Br}\) disproportionation, the catalyst (catalyst weight, \(W_{\text{cat}} = 1 \text{ g}\) and particle size, \(d_p = 0.4-0.6 \text{ mm}\)) was mixed with inert quartz particles (Thommen-Furler, \(d_p = 0.2-0.3 \text{ mm}\)) and loaded in a quartz reactor (inner diameter, \(d_r = 8 \text{ mm}\)) between the two plugs of quartz wool in order to form a fixed bed of constant volume (\(V_{\text{bed}} = 2 \text{ cm}^3\)). The post-catalyst zone was filled with quartz beads (Sigma-Aldrich, \(d_p = 0.6 \text{ mm}\)) to minimize its volume. The influence of residence time on the \(\text{CH}_4\) conversion in oxybromination was studied by using a reduced amount of catalyst (\(W_{\text{cat}} = 0.012-0.05 \text{ g}\)) placed in the quartz reactor (\(d_r = 4 \text{ mm}\)). The effect of the volume after the catalyst bed on the oxybromination performance was studied in quartz reactors with constant size of the catalyst zone (\(W_{\text{cat}} = 0.07 \text{ g}, d_p = 0.3-0.4 \text{ mm}, d_r = 4 \text{ mm}\)) and different size of the post-catalyst zone. Non-catalytic gas-phase \(\text{CH}_4\) bromination was performed in an empty quartz reactor (\(V_r = 2.5 \text{ cm}^3\)). Prior to testing, the catalyst bed was heated in a He flow to the desired temperature (\(T = 423-873 \text{ K}\)) and allowed to stabilize for at least 30 min before the reaction mixture was fed. The catalyst weight (\(W_{\text{cat}}\)), total flow rate (\(F_T\)), and feed mixture applied in the tests are summarized in Table 7.1.

Quantification of reactants and products, determination of conversion, selectivity, yield, and reaction rate, as well as the evaluation of carbon and bromine mass balance was conducted using the same protocol as detailed in Appendix A.
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7.2.3. Operando Photoelectron Photoion Coincidence Spectroscopy

Photoelectron photoion coincidence (PEPICO) spectroscopy experiments during CH₄ oxybromination were performed using the PEPICO endstation at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source (Figure 7.1).[261,263,264] The gases: CH₄, HBr, O₂, and Ar, were supplied by a set of digital mass-flow controllers to a tubular reactor (d_r = 1 mm) made of SiC placed in the source chamber. VPO and EuOBr (W_cat = 0.05 g) were deposited on the inner walls of the reactor by wash-coating using catalyst suspension in ethanol (Merck, absolute), followed by drying in air at 573 K for 1 h. An empty SiC reactor used in a control experiment was only washed with pure ethanol and dried using the previous protocol. Two ring electrodes connected to a DC power supply (Voltcraft) were applied to heat the reactor resistively, and its temperature was monitored by a type C thermocouple attached to the outside reactor wall at the middle point between the electrodes. The temperature of the flowing gas was calibrated against that measured at the outside wall and applied heating power in an independent experiment, which showed that these deviations are in the range of ±30 K. This calibration was used to recalculate the reaction temperature in the oxybromination experiments. The pressures at the reactor inlet and in the source chamber surrounding its outlet were 0.2 bar and 2·10⁻⁸ bar, respectively, and the effective pressure in the reaction zone was estimated to be in the range of 1·4·10⁻² bar based on the previous reports and by taking into account the flow rate, temperature, and the reactor diameter applied in the experiments.[265] The central part of the molecular beam leaving the reactor was skimmed and fed in the analysis chamber operated at 2·10⁻⁹ bar. Synchrotron VUV radiation was used to

<table>
<thead>
<tr>
<th>Reaction</th>
<th>W_cat / g</th>
<th>F_T / cm³ min⁻¹</th>
<th>Feed composition / vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ oxybromination</td>
<td>0.012-1</td>
<td>100-200</td>
<td>3-20</td>
</tr>
<tr>
<td>CH₄ bromination</td>
<td>-</td>
<td>100</td>
<td>3-12</td>
</tr>
<tr>
<td>CH₄ oxidation</td>
<td>1.0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>CH₃Br disproportionation</td>
<td>1.0</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>

a All tests were conducted at P = 1 bar.b Flow units correspond to standard temperature (273 K) and pressure (1 bar) conditions. c Ar (4.5 vol.%) was added as an internal standard to all the reaction mixtures, except for HBr oxidation. He was used as the balance gas.
ionize the sample, as provided by a bending magnet, collimated by a mirror, dispersed by a 150 mm⁻¹ grating working in grazing incidence, and focused onto an exit slit in a rare gas filter by a second mirror. Higher grating orders in the 7-14 eV photon energy range are suppressed in the differentially pumped rare gas filter filled with 1·10⁻² bar of an Ar, Ne, and Kr mixture over an optical length of 10 cm or by using MgF₂ window. The photoions and photoelectrons are accelerated vertically in opposite directions by a constant field of 250 V cm⁻¹ and velocity map imaged onto two delay-line anode detectors (Roentdek, DLD40) in delayed coincidence. The signal of methyl radical (CH₃●) at m/z = 15 was recorded at a photon energy of 10 eV using MgF₂ filter to suppress radiation above 10 eV quantitatively. The CH₃Br mass spectral peak was recorded at a photon energy of 10.6 eV. CH₄, O₂, HBr, Br₂, and bromine radicals (Br●) were detected by recording the fragmentation-free mass spectrum at a photon energy of 13 eV. The false

**Figure 7.1.** PEPICO reactor setup for an *operando* detection of radicals in the catalytic oxybromination of CH₄. The reaction mixture is fed by a set of digital mass-flow controllers to the SiC reactor of small diameter (1.0 mm) placed in the source chamber. The reactor comprises an oxybromination catalyst deposited on its inner walls and is heated resistively, whereby the temperature is monitored by a thermocouple attached to its outside wall. The central part of the molecular beam escaping the reactor is selected by a skimmer and fed to the analysis chamber, wherein it is photoionized by monochromatic synchrotron radiation. Generated photoions and photoelectrons are accelerated in opposite directions by constant electric field and velocity map imaged by the two delay-line anode detectors in delayed coincidence.
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coincidence background was subtracted in the TOF mass spectra to obtain peak integrals. Photoion mass-selected threshold photoelectron spectra (ms-TPES) were obtained by subtracting the hot electron contribution using the procedure outlined in the literature.\[266\] The ratio of the molar fractions of CH₃●, x(CH₃●), and CH₃Br, x(CH₃Br), was calculated according to the Equation 7.6,  
\[
\frac{x(CH₃●)}{x(CH₃Br)} = \frac{A(CH₃●)}{A(CH₃Br)} \frac{\sigma(CH₃●)}{\sigma(CH₃Br)}
\]  
where A(CH₃●) and A(CH₃Br) are the respective integrated peak areas of CH₃● and CH₃Br recorded using a photon energy of 10.6 eV, and σ(CH₃●) and σ(CH₃Br) are the respective ionization cross sections of CH₃● and CH₃Br at this energy. The values of σ(CH₃●) of 6.3 Mb and σ(CH₃Br) of 20.2 Mb at 10.6 eV were determined from the literature.\[267,268\]

7.2.4. Operando Prompt Gamma Activation Analysis

The bromine content on the VPO catalyst during methane oxybromination was quantified using Prompt Gamma Activation Analysis (PGAA) at cold neutron beam line at the Budapest Neutron Center.\[123\] This technique, which is based on the capture of cold neutrons by the atomic nuclei and detection of the element-specific prompt gamma rays that are emitted upon their relaxation, has been previously used to precisely determine the uptake of halogen over catalysts in HCl and HBr oxidation.\[123\] The reactor setup was identical to that depicted in Figure A.1, except for the oven, which had three openings: front and back for the incoming and outcoming neutrons, respectively, and a side opening enabling the passage of the emitted prompt gamma photons to the detector based on Compton-suppressed high-purity germanium crystal.

7.2.5. Computational Details

The reaction profiles of both the heterogeneous and homogeneous reaction steps in the catalytic CH₄ oxybromination were calculated by means of Density Functional Theory (DFT) using the Vienna \textit{ab initio} Simulation Package (VASP) code,\[269,270\] and the Perdew-Burcke-Ernzerhof (PBE) functional, whereby the core electrons were represented by projector augmented wave pseudopotentials (PAW) and the valence electrons were expanded in plane waves with a cutoff
7.3. Results and Discussion

7.3.1. Evaluation of the Reaction Kinetics

Preliminary insights into the mechanism of CH₄ oxybromination were gained by studying the steady-state kinetics over the best-performing EuOBr and VPO catalysts (Figure 7.2), the structure of which was confirmed by X-ray diffraction analysis (Figure B.44). The kinetic fingerprints were thereby compared with those of the non-catalytic gas-phase bromination of CH₄ (Figure 7.2), as the latter reaction is known to proceed via homolytic scission of the C-H bonds by Br•,[84,93,96] which has been speculated as the pathway of CH₄ activation in catalytic oxybromination in Chapters 2-6. As shown in Figure 7.2a (top), the temperature at which CH₄ oxybromination is initiated (viz., light-off temperature) was very similar to that of CH₄ bromination. Besides, an increased yield of bromomethanes (CH₃Br and CH₂Br₂) in oxybromination correlated with a drop in Br₂ yield (Figure 7.2a, top), which hints that the latter product might react with CH₄ to generate the brominated hydrocarbons. Furthermore, the
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The conversion of CH₄, yield of Br₂, and selectivity to bromomethanes versus temperature in CH₄ oxybromination (CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5) over VPO (red) and EuOBr (blue) catalysts, and in non-catalytic gas-phase CH₄ bromination (MB, gray, CH₄:Br₂:Ar:He = 6:3:4.5:86.5). (b) The reaction rate versus the partial pressure of CH₄ (CH₄:HBr(Br₂):O₂:Ar:He = 3-20:6(3):3(0):4.5:83.5(86.5)-66.5(69.5)), HBr (CH₄:HBr:O₂:Ar:He = 6:3-12:3:4.5:83.5-74.5), O₂ (CH₄:HBr:O₂:Ar:He = 6:6:1.5-6:4.5:82-77.5), and Br₂ (CH₄:Br₂:Ar:He = 6:3-6:4.5:86.5-83.5) in CH₄ oxybromination (T = 773 K) over VPO (top) and EuOBr (middle), and non-catalytic gas-phase CH₄ bromination (bottom, T = 753 K). (c) Arrhenius plots of CH₄ oxybromination (MOB) and CH₄ oxidation (MO) over VPO (red) and EuOBr (blue) catalysts and non-catalytic gas-phase CH₄ bromination (MB, gray). (d) The yield of bromomethanes and Br₂ versus post-catalyst volume in CH₄ oxybromination (CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5, T = 773 K) over VPO (red) and EuOBr (blue). The apparent activation energies and the partial reaction orders are stated in the respective plots in (b) and (c). The catalytic oxybromination of CH₄ was performed using W_cat = 1.0 g and V_bed = 2.0 cm³ in the tests presented in (a), (b), and (c), and W_cat = 0.07 g, V_i = 0.1 cm³ in (d). The non-catalytic gas-phase bromination was studied using V_i = 3.1 cm³. All the tests were conducted using F_T = 100 cm³ min⁻¹ at P = 1 bar.

dependence of the selectivity to CH₃Br and CH₂Br₂ on the conversion of CH₄ in the oxybromination and the bromination followed a very similar trend (Figure 7.2a, bottom), which was particularly evident in the case of highly selective EuOBr catalyst. The lower selectivity to bromomethanes over VPO is caused by its higher propensity to oxidize them to CO₂.
An additional link between the oxybromination and the bromination is inferred from the similarity of their kinetic parameters. The apparent reaction orders of the non-catalytic bromination with respect to CH$_4$ of ca. 1 and Br$_2$ of ca. 0.5 are consistent with its well-established radical-chain mechanism (Figure 7.2b).\cite{84,93,96} The oxybromination displays relatively low positive orders with respect to HBr and O$_2$ of ca. 0.15-0.3, which suggest their fast activation, and the order of ca. 0.8 with respect to CH$_4$, which is comparable to that observed in CH$_4$ bromination. The apparent activation energies of CH$_4$ oxybromination over VPO (ca. 122 kJ mol$^{-1}$) and EuOBr (ca. 105 kJ mol$^{-1}$) catalysts also approach the value of this parameter in CH$_4$ bromination (ca. 120 kJ mol$^{-1}$, Figure 7.2c). In contrast, they are substantially different to the apparent activation barriers of CH$_4$ oxidation (ca. 64–72 kJ mol$^{-1}$, Figure 7.2c), which is used as a probe reaction to reflect the possibility of catalytic C-H bond scission. The oxidation yields CO and CO$_2$ as the only products, with no detectable partially oxidized intermediates, such as methanol (Figure B.45). Notably, EuOBr and VPO are one order of magnitude less reactive in CH$_4$ oxidation compared to oxybromination, which points to their low propensity to activate CH$_4$ (vide infra). In accordance with this result, the enlargement of the void zone after the catalyst bed (post-catalyst volume), which provides additional time for the gaseous intermediates to react and is hence used to verify the occurrence of the gas-phase reaction steps,\cite{275} led to a progressive increase in the yield of bromomethanes and a decrease in the yield of Br$_2$ (Figure 7.2d).

7.3.2. Detection of Free Radicals

The above-discussed kinetic fingerprints provide a strong hint that the mechanism of CH$_4$ oxybromination likely involves the surface-catalyzed HBr oxidation followed by the bromination of CH$_4$ in the gas phase. Nonetheless, it could only be verified through a detection of the key gaseous intermediates participating in the homolytic mechanism of C-H bond splitting. Catalytic oxybromination of CH$_4$ was therefore studied by depositing VPO and EuOBr catalysts on the walls of a tubular reactor placed in the source chamber of the PEPICO spectroscopy setup (Figure 7.1d),\cite{260} which comprises a powerful technique to isomer-selectively trace the formation of highly reactive gaseous species, such as radicals.\cite{257-262} This reactor configuration and gas-phase sampling setup minimized the quenching of the short-lived reaction intermediates that are desorbed from the catalyst surface or generated in the gas phase above the catalyst, by high dilution of the
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Figure 7.3. (a) The representative mass spectra of different reactant (gray), product (blue), and intermediate radical (red) species detected in CH₄ oxybromination over EuOBr (CH₄:HBr:O₂:Ar = 2:1:0.5, T = 970 K). (b) The photoionization yield and photoion mass-selected threshold photoelectron spectra (ms-TPES) of the \( m/z = 15 \) ion. (c) The velocity map images of room temperature (RT) background (left), ions detected at \( m/z = 15 \) corresponding to CH₃⁺ (middle), and ions detected at \( m/z = 79/81 \) corresponding to Br⁺ (right) allows for the differentiation between CH₃⁺ (blue) and Br⁺ (red) radicals escaping directly from the reactor and the scattered and thermalized ones (yellow) based on their position. (d) The normalized peak areas of the signals corresponding to CH₃⁺ (top), CH₃Br (middle), and Br₂ (bottom) in CH₄ oxybromination over VPO, EuOBr, and in an empty reactor at different temperatures and concentrations of reactants (CH₄:HBr:O₂:Ar = 2:0-2:0.3-0.5:19-21). Peak areas of various species were normalized with respect to acetone as an internal standard present at constant concentration in the chamber. All the tests were conducted using \( W_{cat} = 0.05 \) g and \( F_T = 23.5 \) cm³ min⁻¹.
feed and low pressure inside the reactor (ca. 1-4 · 10⁻² bar) and the source chamber surrounding its outlet (ca. 2·10⁻⁸ bar). The effluent reactor stream forms a molecular beam, which is skimmed and ionized by monochromatic VUV radiation, yielding photoelectrons and photoions that are detected in delayed coincidence.²⁵⁸,²⁶⁰ In line with the steady-state catalytic tests, mass spectra of the outlet reactor feed recorded using different ionization energies evidenced that besides the ions of respective reactants: CH₄ (m/z = 16), O₂ (m/z = 32), and HBr (m/z = 80/82), the ions of the oxybromination products: CH₃Br (m/z = 94/96) and Br₂ (m/z = 158/160/162) were also present (Figure 7.3a, Figures B.46 and B.47). CH₃⁺ (m/z = 15) and Br⁺ (m/z = 79/81) ions could be unambiguously related to the ionization of the corresponding CH₃• and Br• radicals using a photon energy of 10.0 eV and 13.6 eV, respectively (Figure 7.3a, Figures B.46 and B.47). Thereby, the photoionization energy at which the spectra of CH₃⁺ were recorded sits well below the threshold for dissociative photoionization of CH₄ (14.3 eV) and CH₃Br (12.8 eV) that could potentially yield ions at m/z = 15 upon VUV irradiation, corroborating that CH₃⁺ ions stem from CH₃•, which undergo ionization at 9.84 eV.²⁷⁶-²⁷⁸ This is firmly confirmed by the photoion mass-selected threshold photoelectron spectra (ms-TPES), which shows a peak at 9.84 eV (Figure 7.3b) in accordance with the reported ionization energy of CH₃•.²⁷⁸ Similarly to the detection of CH₃•, the VUV photon energy at which Br⁺ ions were observed is below the dissociative photoionization threshold of HBr (15 eV), Br₂ (13.8 eV), CH₃Br (14.8 eV), and CH₂Br₂ (15.5 eV).²⁷⁶,²⁷⁹,²⁸⁰ Hence, the ions at m/z = 79/81 could only stem from the direct photoionization of Br• which occurs already at 11.8 eV.²⁷⁶ Additional information can be gained by momentum imaging: as the gas sample leaves the reactor a molecular beam is formed, which travels with almost the speed of sound and the gaseous species exhibit a narrow speed distribution (blue and red spots in Figure 7.3c) perpendicular to the beam axis (i.e., along the x position, Figure 7.3c). In contrast, the ionized background gas features room temperature velocities in both x and y directions, which are imaged as almost circular spot (yellow room temperature background, Figure 7.3c). Dissociative ionization would directly lead to a broadening of the velocity distribution perpendicular to the beam axis (x position) due to the statistical release of excess energy as kinetic energy of the fragments. The CH₃⁺ and Br⁺ ions detected upon oxybromination show a narrow distribution along the x axis and are thus formed by direct ionization of CH₃• and Br• present in the beam.
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Besides the detection of $\text{CH}_3^\cdot$ and $\text{Br}^\cdot$ intermediates in $\text{CH}_4$ oxybromination, PEPICO spectroscopy also established the relationships between their production and the formation of the reaction products (Figure 7.3d, Figure B.49). The onset of $\text{CH}_4$ oxybromination in PEPICO spectroscopy experiments was ca. 150-200 K higher compared to the tests performed in the conventional reactor setup. This can be rationalized by the significantly shorter residence time in the former tests (ca. 0.0004 s)\textsuperscript{[265]} with respect to the fixed-bed reactor (ca. 0.4 s), which necessitates higher temperatures to achieve the specific reaction rate enabling to detect product formation, as also demonstrated by the experiments conducted at ambient pressure (Figure B.50). Besides, a lower reactor pressure (ca. 10-40 mbar compared to ca. 1 bar) requires higher temperatures to achieve similar collision frequencies in the gas phase. While the internal energy distributions are broadened and shifted up, 150-200 K difference only results in a minor change at the reaction energy profile and the system does not fly over the potential energy surface. The validity of the conclusion made from PEPICO spectroscopy was further corroborated by the similar trends in product distribution as observed from the steady-state experiments conducted at ambient pressure. $\text{Br}_2$ was the only product at low temperatures (Figure 7.3d), whereby its evolution was accompanied by the formation of $\text{Br}^\cdot$ (Figure B.49). The onset of $\text{CH}_3\text{Br}$ production was shifted to higher temperatures and was associated with the appearance of $\text{CH}_3^\cdot$. Furthermore, the formation of this product was strongly correlated to the relative concentration of $\text{CH}_3^\cdot$ and the ratio of the molar fractions of $\text{CH}_3^\cdot$ and $\text{CH}_3\text{Br}$ was estimated to be in the range of 0.5-1.5 based on their reported ionization cross sections.\textsuperscript{[267,268]} These observations were additionally corroborated by conducting a control experiment under identical feed composition in an empty reactor, which showed that the generation of $\text{CH}_3^\cdot$ proceeds at ca. 200 K higher temperatures compared to the catalytic process (Figure 7.3d, Figures B.48 and B.49). The concentration of $\text{CH}_3^\cdot$ was much lower and $\text{Br}^\cdot$ was hardly detectable. Notably, formation of $\text{CH}_3\text{Br}$ could not be detected, which confirms that the catalyst surface generates $\text{Br}^\cdot$, which initiate the formation of $\text{CH}_3^\cdot$, and hence the production of $\text{CH}_3\text{Br}$. Further insights into the origin of $\text{CH}_3^\cdot$ were obtained by varying the concentration of $\text{HBr}$ and $\text{O}_2$ in the feed (Figure 7.3d). In line with the positive reaction order with respect to $\text{HBr}$, higher concentration of this reactant enhanced the production of $\text{Br}_2$, $\text{Br}^\cdot$, and $\text{CH}_3\text{Br}$, although the concentration of $\text{CH}_3^\cdot$ remained almost unaltered. As exemplified for EuOBr, a decrease in $\text{O}_2$ content leads to a drop in production of $\text{CH}_3\text{Br}$, $\text{CH}_3^\cdot$, and $\text{Br}^\cdot$. The removal of
HBr from the feed, completely stopped the evolution of Br$^\bullet$ and CH$_3$$^\bullet$, and consequently the production of CH$_3$Br. Together with the strong correlation between the CH$_3$$^\bullet$ and CH$_3$Br formation, these results unequivocally demonstrate that the activation of CH$_4$ in the catalytic oxybromination involves gas-phase CH$_3$$^\bullet$ generation through hydrogen abstraction from CH$_4$ by reactive Br$^\bullet$, the formation of which remains still unaccounted for. Surface catalyzed oxidation of HBr and propagation step of the gas-phase CH$_4$ bromination might be the potential sources.

### 7.3.3. Rationalization of the Reaction Pathway

Density functional theory (DFT) calculations were employed to gather a comprehensive molecular level picture of the interplay between the surface-catalyzed HBr oxidation and CH$_4$ bromination in the gas-phase using VPO as a model catalytic system (Figure 7.4). The first step of HBr oxidation comprises dissociative O$_2$ adsorption, which is exothermic by $-0.36$ eV per oxygen atom adsorbed. In the next step, HBr is dissociatively adsorbed on VPO, yielding a surface bromine anion (Br$^*$) and a proton, which binds to the neighboring O$^*$. This is an acid-base reaction and is therefore exothermic by $-0.87$ or $-0.91$ eV depending on the final position of the proton. The second molecule of hydrogen bromide can then be adsorbed leaving a water molecule and the second Br$^*$ on the surface, which is exothermic by $-0.42$ eV. A desorption of the newly formed water molecule necessitates $1.31$ eV that is partially compensated by entropic contributions. Notably, elimination of adsorbed Br$^*$ from the surface can proceed via two pathways. The first involves the recombination of Br$^*$ to generate Br$_2$ in the gas phase, the energy barrier of which is $0.60$ eV. The second comprises desorption in the form of gas-phase radicals, Br$^\bullet$. This step can proceed after the adsorption of the first molecule of HBr and requires $1.30$ eV. Comparatively, the formation of bromine radicals on EuOBr is less energy demanding, $1.09$ eV. These results reveal the importance of the surface-catalyzed HBr oxidation in CH$_4$ oxybromination, enabling the generation of Br$_2$ and Br$^\bullet$, which are essential for CH$_4$ activation. Theory also predicts that these processes are barrierless at temperatures commonly used in oxybromination (ca. 753 K).

Once ejected from the catalyst surface, Br$_2$ and Br$^\bullet$ are interrelated by the gas-phase equilibria in which the former might dissociate into the latter, and vice versa (Figure 7.4).$^{[93,96]}$ The calculations show that Br$_2$ dissociation is endothermic by $2.56$ eV, which is higher compared to the experimentally determined value of $2.02$ eV.$^{[96]}$ This energy barrier can be partially overcome at the temperatures oxybromination is conducted, enabling homolytic Br$_2$ splitting to occur to a
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certain degree. $\text{Br}^\bullet$ produced by the catalyst surface or dissociation of $\text{Br}_2$ can abstract a hydrogen atom from $\text{CH}_4$, leading to the formation of $\text{CH}_3^\bullet$ (Figure 7.4). The computed energy barrier is 0.73 eV, and is comparable to the previously reported value of 0.78 eV.\(^{[96]}\) However, if the gas-phase thermal and entropic contributions are taken into account, this step requires 1.25 eV (i.e., 121 kJ mol\(^{-1}\)), which is comparable to the experimentally determined apparent activation energy of the catalytic $\text{CH}_4$ oxybromination and non-catalytic $\text{CH}_4$ bromination (Figure 7.1c). The high energy barrier of the gas-phase $\text{CH}_4$ activation compared to the barrierless evolution of $\text{Br}^\bullet$ rationalizes the appearance of $\text{Br}^\bullet$ at lower temperatures compared to $\text{CH}_3^\bullet$ (Figure B.49). It also

Figure 7.4. Reaction profile of the catalytic $\text{CH}_4$ oxybromination. The surface-catalyzed reaction steps (blue, counterclockwise direction), which comprise the oxidation of $\text{HBr}$ into $\text{Br}^\bullet$ and $\text{Br}_2$ and the gas-phase steps (red, counterclockwise direction), which comprise $\text{Br}_2$-$\text{Br}^\bullet$ equilibrium, generation of $\text{CH}_3^\bullet$, and formation of $\text{CH}_3\text{Br}$ are interrelated by the desorption of $\text{Br}^\bullet$ and $\text{Br}_2$, and regeneration of $\text{HBr}$. $\text{O}^\bullet$, $\text{OH}^\bullet$, $\text{H}_2\text{O}^\bullet$, and $\text{Br}^\bullet$ denote the adsorbed oxygen anion, hydroxyl group, water molecule and bromine anion, respectively, while $^\bullet$ denotes the free sites on the surface. Color code: V (dark gray), P (orange), O (red), Br (purple), C (light gray), and H (white).
implies that C-H scission is the rate-determining step of CH$_4$ oxybromination, in good agreement with close to the first order reaction with respect to CH$_4$. HBr produced in the previous step can regenerate Br$^\bullet$ by surface oxidation, while CH$_3^\bullet$ can enter a reaction with Br$_2$ forming CH$_3$Br and regenerating Br$^\bullet$. This step is reported to be exothermic by $-1.08$ eV and our calculations retrieve the same value.$^{[96]}$ The coupling of CH$_3^\bullet$ into ethane (C$_2$H$_6$) is also exothermic ($-4.10$ eV, Table B.8), but kinetically much less favored due to the substantially lower concentration of the short-lived radical intermediates compared to Br$_2$. This translates into a much higher frequency of CH$_3^\bullet$-Br$_2$ collisions, which explains the absence of C$_2$H$_6$ production in CH$_4$ oxybromination. The formation of CH$_2$Br$_2$ primarily proceeds via CH$_3$Br reaction with Br$^\bullet$ and Br$_2$, following an analogous pathway as described for CH$_4$. The bromination of CH$_3$Br by second CH$_3$Br molecule (viz., CH$_3$Br disproportionation) has a negligible contribution, as shown experimentally in Figure B.51.

The alternative reaction pathways comprising CH$_4$ activation by: (i) an adsorbed oxygen anion (O$^\bullet$), and (ii) an adsorbed bromine anion (Br$^\bullet$) on VPO have also been studied by DFT (Table B.8). Nonetheless, their energy barriers of 1.76 eV and 1.79 eV, respectively, exceed that for the gas-phase CH$_4$ bromination (1.25 eV), as well as the experimentally determined activation energy of CH$_4$ oxybromination (Figure 7.1c). The low propensity of CH$_4$ activation by surface O$^\bullet$ is additionally corroborated by the substantially lower rates of CH$_4$ oxidation compared to CH$_4$ oxybromination (Figure 7.1c). Similarly, the marginal contribution of surface C-H bond scission
Evidence of Radical Chemistry in Catalytic Methane Oxybromination

via Br\textsuperscript{•} can be deduced from the extremely low surface bromine coverage, $\theta_{Br} < 0.01$, over VPO during CH\textsubscript{4} oxybromination at ambient pressure, as determined by operando prompt gamma activation analysis (PGAA, Figure 7.5).

7.4. Conclusions

The detection of Br\textsuperscript{•} and CH\textsubscript{3}\textsuperscript{•} by PEPICO spectroscopy complemented with the steady state kinetics analysis and molecular-level reaction modeling by DFT revealed the mechanism of the catalytic CH\textsubscript{4} oxybromination, which comprises the synergetic interplay between the surface-catalyzed HBr oxidation and activation of CH\textsubscript{4} in the gas phase. Herein, the catalyst surface evolves Br\textsuperscript{•} and Br\textsubscript{2} into gas phase, which are the barrierless processes under typical reaction conditions, which is in good agreement with the observation of Br\textsubscript{2} and Br\textsuperscript{•} as the main product species at low reaction temperatures. In analogy to the non-catalytic CH\textsubscript{4} bromination, Br\textsuperscript{•} induces the homolytic scission of C-H bond in the gas-phase via hydrogen abstraction, yielding CH\textsubscript{3}\textsuperscript{•} and HBr, which can re-enter the oxidation step on the catalyst. The activation of CH\textsubscript{4} by Br\textsuperscript{•} constitutes the rate-determining step in both the catalytic CH\textsubscript{4} oxybromination and non-catalytic CH\textsubscript{4} bromination, which is consistent with substantial kinetics similarities between the two reactions such as comparable operating temperature, product distribution, reaction order with respect to CH\textsubscript{4}, and activation energy. The generated CH\textsubscript{3}\textsuperscript{•} can react with Br\textsubscript{2} producing CH\textsubscript{3}Br and regenerating Br\textsuperscript{•}, which can propagate the homolytic CH\textsubscript{4} activation in the previous step. The formation of CH\textsubscript{3}Br through CH\textsubscript{3}\textsuperscript{•} is supported by the strong correlation between the molar fractions of these species. In the overall process, the catalytic surface plays an essential role as it enables a continuous recovery of Br\textsuperscript{•} and Br\textsubscript{2} from HBr, suppressing the termination steps. These findings evidence the importance of the radical chemistry in heterogeneously catalyzed halogen-based processes for alkane activation and highlight the great potential of PEPICO spectroscopy to unravel the complex reaction networks involving short-lived gaseous intermediates, which can be detected in isotope specific manner. Unraveling the contributions from the surface-catalyzed and gas-phase reaction pathways has important practical implications for the perspective design of catalytic and reactor systems, as the latter have to provide the optimal balance between the desirable Br\textsuperscript{•} and Br\textsubscript{2} evolution, their maximized interaction with CH\textsubscript{4} in the
gas-phase, and minimized selectivity losses through the surface oxidation of bromomethanes and CH$_4$ to ensure a high process efficiency.
Chapter 8

Conclusions and Outlook

Bromine-mediated conversion of methane and other light alkanes into liquid fuels and chemicals constitutes an attractive technology for valorizing natural gas using intensified processes amenable to decentralization. Its practical implementation is tightly linked to the full recovery of HBr, which is the end form of the halogen after the activation and upgrading steps. This thesis contributes to the development of new catalyst families for selective methane oxybromination and HBr oxidation, two processes showing realistic potential for closing the bromine cycle.

8.1. Catalyst Design Strategies for Methane Oxybromination

Comparative studies of different bulk oxide and phosphate catalysts in methane oxybromination and oxidation of HBr, CH₄, CH₃Br, and CH₂Br₂ have revealed that the highest yields of bromomethanes are achieved with materials displaying high rates of bromine evolution and minimal propensity to combustion. This criterion precludes the application of most simple metal oxides, including those developed for HBr oxidation, due to their pronounced ability to activate oxygen and promote deep oxidation. In this thesis, three strategies were devised to attain superior oxybromination performance:

**Isolation of the redox-active metal centers in the matrixes** reduces the mobility of oxygen and ensures structural stability. This approach was first demonstrated via the discovery of vanadium phosphate (VPO) and lanthanum vanadate (LaVO₄) as selective and stable active phases in which the phosphate and lanthanum oxide domains reduce combustion and stabilize vanadium. The performance of LaVO₄ can be further enhanced by introducing an excess of La₂O₃, which transforms into LaOBr upon exposure to the reaction mixture. The latter irreducible phase moderates the oxidizing potential of LaVO₄, which slightly reduces the rate of oxybromination, but more significantly suppresses deep oxidation. The catalytic behavior of these substoichiometric oxides can be tuned by adjusting the molar V:La ratio, whereby the optimal catalyst was attained for the composition LaV₀.5O₂.75. The major accomplishment in this approach was the discovery of
europium oxybromide (EuOBr), which provides the highest selectivity and yields of bromomethanes among all the systems reported to date. The oxybromide structure, which displays a substantially reduced propensity to combust CH$_4$ and brominated products, is uniquely combined with mildly oxidizing Eu$^{3+}$/Eu$^{2+}$ centers, resulting in well-balanced redox behavior.

Feeding an excess of HBr inhibits combustion through “selective surface poisoning” by bromine. This effect was particularly pronounced over bulk CeO$_2$, leading to a very high selectivity to bromomethanes compared to substantial CO$_x$ evolution at a stoichiometric feed. The reaction rate was thereby unaltered.

Nanostructuring of CeO$_2$ through supporting on an appropriate carrier enables to tune its redox properties and catalyst susceptibility to bromination. The evaluation and extensive characterization of supported catalysts prepared using different carriers, synthesis methods, and low cerium loadings (0.1-2 wt.%) revealed that the carrier type greatly impacts the product distribution. It affects the oxidizing potential of the active phase and displays a different degree of inertness in the oxidation of CH$_3$Br and CH$_2$Br$_2$. The use of basic MgO support is particularly advantageous as it promotes the bromination in the surface region of the catalyst, which minimizes combustion and ultimately results in significant selectivity enhancement, offering attractive opportunities considering potential scale-up in the technical form.

8.2. Impact of the Hydrogen Halide on Methane Oxyhalogenation

Previous studies on methane oxyhalogenation focused on a single catalyst and/or hydrogen halide type, thus preventing conclusions on the differences in reaction chemistry induced by using HCl instead of HBr, and the potential advantages of one halide over the other. Analysis of the kinetic fingerprints of oxychlorination and oxybromination over the same series of bulk oxide and phosphate catalysts conducted in this thesis suggests that they follow a similar pathway comprising surface-catalyzed hydrogen halide oxidation into halogen, which reacts with methane in the gas phase. Due to the evolution of Cl$_2$, which is more energy demanding than that of Br$_2$ and the fact that CH$_4$ chlorination is more facile than bromination, oxychlorination activity is determined by the ability of the catalyst surface to produce halogen, whereas methane halogenation in the gas phase appears to control the rate of oxybromination. Consequentially, catalysts with strong oxidizing potential, such as ruthenium oxide (RuO$_2$) and CeO$_2$, which evolve chlorine at low
Conclusions and Outlook

temperatures, are more reactive in oxychlorination than in oxybromination. In addition, they exhibit a higher intrinsic selectivity to chloromethanes than to bromomethanes, likely due to more efficient “selective surface poisoning” by chlorine. Nevertheless, the production of CO$_2$ is still substantial with regard to the best developed oxybromination systems and is less affected by the partial pressure of HCl. In contrast, the oxychlorination light-off curves of catalysts with mild oxidizing potential, such as titanium oxide (TiO$_2$) and VPO, are shifted to higher temperatures due to hampered HCl oxidation. Under these conditions, the rate of CH$_3$Cl and CH$_2$Cl$_2$ formation is substantially lower with respect to their consecutive oxidation. As a result, oxychlorination over these materials enables selective CH$_4$ conversion into CO, which is the key building block used by the chemical industry.

8.3. New Catalysts for HBr Oxidation

Deactivation of highly active catalysts, such as CeO$_2$ and RuO$_2$, in low-temperature HBr oxidation performed using a (close to) stoichiometric O$_2$:HBr feed ratio is one of the major challenges for the implementation of this process. This is due to the thermodynamically favored substitution of subsurface oxygen atoms with bromine. The only exception to this trend is titanium oxide (TiO$_2$), which is only mildly active in the above-stated temperature window. Bearing in mind the resistance to bulk bromination as the main stability descriptor, the performances of rare earth oxybromides were systemically evaluated in this thesis, since their partially brominated structure was proposed to hamper the extensive halogen uptake. This led to the discovery of EuOBr as a unique catalytic material exhibiting a high structural integrity in O$_2$- and HBr-rich feed mixtures as well as outstanding activity, which is related to the redox active Eu$^{3+}$/Eu$^{2+}$ couple. This novel active phase was readily supported over commercially available oxide carriers using a simple dry impregnation method, enabling a near atomic dispersion at metal loadings of 9 wt.% The susceptibility of supported phase to bromination and its redox properties are strongly influenced by the support. In particular, the Al$_2$O$_3$ carrier stabilizes the brominated form of the catalyst, which displays an improved oxidizing potential compared to the bulk and other supported materials, enabling the significant activity enhancement. The robust performance of EuOBr/Al$_2$O$_3$ extrudates under practically relevant conditions was demonstrated, which establishes a new milestone in bromine-based technologies for light alkane valorization.
8.4. Mechanistic Understanding of Methane Oxybromination

Steady-state kinetic analyses of methane oxybromination over the multiple catalysts investigated in this thesis revealed substantial similarities in activity patterns, apparent activation energies, reaction orders, and product distributions between this reaction and non-catalytic bromination of methane, and strongly hint that \( \text{CH}_4 \) activation by \( \text{HBr} \) and \( \text{O}_2 \) is mediated by bromine (\( \text{Br}^* \)) and methyl (\( \text{CH}_3^* \)) radicals. The confirmation of such a mechanism is challenging due to the short lifetime of the radical intermediates and corrosive reaction feed, which limits experimental studies of reaction pathways by advanced spectroscopic methods. Operando photoelectron photoion coincidence (PEPICO) spectroscopy was introduced here as a powerful method for detecting the evolution of transient gaseous species in heterogeneously catalyzed processes for alkane functionalization using halogens or halides. In particular, it provided direct evidence of the formation of \( \text{CH}_3^* \) and \( \text{Br}^* \) in the gas phase over \( \text{EuOBr} \) and \( \text{VPO} \) catalysts and unequivocally showed the strong dependence of \( \text{CH}_3\text{Br} \) production on the concentration of \( \text{CH}_3^* \). The formation of \( \text{CH}_3^* \) was only observed in the presence of \( \text{HBr} \) and a catalytic material, indicating that \( \text{CH}_4 \) reacts with \( \text{Br}^* \) that is produced by the catalytic oxidation of hydrogen halide. This reaction pathway is further corroborated by the extremely low bromine coverage of \( \text{VPO} \) determined using operando prompt gamma activation analysis (PGAA), which suggests the low probability of surface-catalyzed bromination. The experimental observations are supported by molecular modeling, which predicts the barrierless desorption of \( \text{Br}^* \) and \( \text{Br}_2 \) from the catalyst under the typical reaction conditions and hydrogen abstraction by \( \text{Br}^* \) in the gas phase as the rate-determining step.

8.5. Outlook

The achievements in this thesis provide the basis for efficient bromine recovery in natural gas upgrading and outline directions for future advances in this technology. Aiming to attain higher efficiency in \( \text{CH}_4 \) valorization, further research efforts should focus on maximizing the selectivity and yield of \( \text{CH}_3\text{Br} \) with respect to \( \text{CH}_2\text{Br}_2 \), as the latter molecule displays a much higher propensity to form coke upon conversion into final products. To this end, progress in electrophilic C-H bond activation over bromination catalysts is sought in order to overcome the intrinsic...
selectivity limitations of the radical chain pathway. Despite the encouraging results presented by Olah et al. and Degirmenci et al.,[78,94] this concept is still confined to a narrow scope of catalytic materials and lacks detailed kinetic and stability assessments. Future research should therefore be directed toward more systematic evaluation and detailed characterization of different families of solid acid catalysts to identify suitable descriptors aiding catalyst design. In parallel to this long-term goal, efforts should be devoted to the development of CH₂Br₂ reforming technologies. Promising activity patterns in CH₂Br₂ dehydrodebromination over archetypical hydrogenation catalysts have recently been reported. Nevertheless, such aspects as the impact of catalyst composition and morphology on performance, as well as the reaction kinetics and mechanism, to date, have not been tackled. In this context, the toolboxes used to study hydrogenation and oxyhalogenation, comprising precise material synthesis, operando determination of halogen, hydrogen, and carbon uptake, and identification of reaction intermediates supported by molecular modeling, are necessary to uncover design rules for selective and stable catalyst behavior. Tightly linked with efforts to enhance the productivity of CH₃Br, the engineering of a zeolite-based catalyst for coupling into valuable products is also required. In this regard, the impact of the zeolite framework, promoters, Brønsted and Lewis type acidity, size, quality, and connectivity of hierarchical pore network, on activity, stability, and preference toward specific products needs to be addressed and complemented with assessment of the reaction mechanism, which is not yet well understood.

Another obvious research direction is the extrapolation of the concepts derived for methane oxybromination to oxyhalogenation of ethane and propane. Given the differences in activity patterns between methane oxychlorination and oxybromination, understanding the impact of the halogen/halide type on the reaction pathway(s) and consequential product distribution in the case of ethane and propane would be of substantive importance, particularly as recent reports highlight the oxychlorination of the latter alkanes as a highly efficient route for the production of olefins.[3] The catalysts and toolboxes, such as the combination of operando PEPICO spectroscopy, PGAA, and molecular modeling in unraveling the reaction mechanisms, which have been demonstrated in this thesis, offer great potential for deeper research into this area of chemistry.

The above-discussed research challenges are currently the topic of two PhD theses conducted under the supervision of Prof. Dr. Javier Pérez-Ramírez.
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Appendix A

Evaluation of Catalyst Performance

**Reactor Setup.** The catalytic as well as the non-catalyzed reactions were performed in a home-made continuous-flow microreactor setup (Figure A.1) comprising (1) a set of digital mass-flow controllers (Bronkhorst) for feeding gases (Table A.1) via (2) check valves and (3) two-way valves to a (4) a mixing unit connected to a pressure indicator (PI), (5) a syringe pump (Nexus 6000, Chemyx) with a water-cooled glass syringe (Hamilton, 1 cm³) for supplying liquids (Table A.1) to (6) a vaporizer operated at 343 K, (7) a three-way valve for directing the flow through (8) a bypass line, which allows to analyze the composition of the inlet feed, (9) a homemade electrical oven, which accommodates (10) a quartz microreactor (internal diameter, \( d_r \)) with (10a) standard catalyst loading (particle size, \( d_p \)) and post-catalyst zone filled with quartz beds (Sigma-Aldrich, \( d_o = 0.6 \) mm), or (10b,c) with low catalyst loading and (10b) small and (10c) big post-catalyst zone, or (10d) with void volume to perform homogeneous gas-phase reactions, a thermocouple (TI) fixed in a (11) coaxial quartz thermowell with a tip positioned in the center of (12) the catalyst bed (bed volume, \( V_{\text{bed}} \)), (13) heat tracing operated at 393 K for preventing the condensation of reactants and reaction products in the bypass line and down-stream tubing and valves, (14) a needle valve positioned after the reactor for adjusting the reaction pressure in the experiments performed above the ambient pressure (\( P > 1 \) bar), a set of three-way valves for directing the flow through: (15) Na₂CO₃ bed (\( d_p = 0.4-0.6 \) mm; Sigma-Aldrich, ≥ 99.5%) for absorbing HBr, (16) a gas chromatograph coupled to a mass spectrometer (GC-MS) for analyzing carbon-containing compounds, O₂, and Ar, (17) an impinging bottle filled with aqueous NaOH solution (1 M; ABCR, > 98%) and connected to (18) a gas bag (Tedlar) for collecting H₂ along with other non-condensable gases, (19) impinging bottles filled with aqueous H₂SO₄ solution (0.05 M; Merck) for absorbing HCl, (20) an impinging bottle filled with aqueous KI solution (0.1 M, Sigma-Aldrich, ≥ 99.5%) for absorbing Br₂ and Cl₂, and (17) impinging bottles filled with NaOH solution (1 M) for neutralizing the effluent gas stream.
Table A.1. Gases and liquids used in this thesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>20% in He, 5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>20% in He, 5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td>HBr</td>
<td>2.8</td>
<td>Air Liquide</td>
</tr>
<tr>
<td>HCl</td>
<td>2.8</td>
<td>Air Liquide</td>
</tr>
<tr>
<td>Cl₂</td>
<td>2.8</td>
<td>PanGas</td>
</tr>
<tr>
<td>O₂</td>
<td>5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>5 vol.% in He 5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>5 vol.% in He 5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td>CO</td>
<td>5 vol.% in He 5.0</td>
<td>Messer</td>
</tr>
<tr>
<td>Ar</td>
<td>5.0</td>
<td>PanGas</td>
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<tr>
<td>N₂</td>
<td>5.0</td>
<td>PanGas</td>
</tr>
<tr>
<td><strong>Liquids</strong></td>
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<td></td>
</tr>
<tr>
<td>Br₂</td>
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<tr>
<td>CH₂Br₂</td>
<td>99%</td>
<td>ABCR</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>99.5%</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

*Used as internal standard. † Used as carrier gas. ‡ Used as carrier gas in the experiments in which H₂ was quantified.

**Reactant and Product Analysis.** Carbon-containing compounds, O₂, and Ar were quantified on-line via a gas chromatograph equipped with a GS-Carbon PLOT column coupled to mass spectrometer (Figure A.1, position 15, GC-MS, Agilent GC 6890, Agilent MSD 5973N), using the program as described in Figure A.2. The content of H₂ was analyzed by injecting the content of the gas bag (Figure A.1, position 18) into a GC (SRI 8610C) equipped with HayeSep D and Molecular Sieve 13X packed columns and TCD detector. The GC is operated isothermally at 318 K.
Figure A.2. Temperature program of GC run (bottom) and retention times, $t_R$, of different reactants, products, and internal standard (top). He was used as carrier gas. The concentrations of Ar, O$_2$, and CO were determined using the respective ion chromatograms recorded at $m/z = 40, 32, \text{and } 28$, respectively, due to their identical retention times, whereas the other compounds were quantified using the total ion chromatographs. Other chromatographic conditions: $F_T(\text{He}) = 63.1 \text{ cm}^3 \text{ min}^{-1}$, split ratio: 50:1.

The concentration of reactant ($i$) or product ($j$) in the gas mixture was determined according to Equation A.1,

$$c(i, j) = A(i, j) \cdot k(i, j), \text{ mol}_{i,j} \text{ cm}^{-3}$$  \hspace{1cm} (A.1)

where $A(i, j)$ and $k(i, j)$ denote to the respective peak area and the calibration coefficient of reactant $i$ or product $j$. The molar flow of reactant ($i$) and product ($j$) at reactor inlet and outlet were calculated with Equations A.2 and A.3, respectively,

$$n(i)^{\text{inlet}} = c(i) \cdot F_T^{\text{inlet}}, \text{ mol}_i \text{ s}^{-1}$$  \hspace{1cm} (A.2)
Evaluation of Catalyst Performance

\[ n(i, j)_{\text{outlet}} = c(i, j)_{\text{outlet}} \cdot \frac{A(\text{Ar})_{\text{inlet}}}{A(\text{Ar})_{\text{outlet}}} \cdot F_{\text{inlet}}^{-1}, \text{ mol}_{i, j} \cdot s^{-1} \]  

(A.3)

where \( A(\text{Ar})_{\text{inlet}} \) and \( A(\text{Ar})_{\text{outlet}} \) denote the respective peak areas of Ar at the reactor inlet and outlet, and \( F_{\text{inlet}} \) stands for the total gas flow at the reactor inlet.

The content of HBr was determined by feeding the gas mixture through a Na\textsubscript{2}CO\textsubscript{3} bed (Figure A.1, position 15), which react according to Equation A.4,

\[ 2\text{HBr} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaBr} + \text{H}_2\text{O} + \text{CO}_2 \]  

(A.4)

The generated CO\textsubscript{2} was quantified by GC-MS (Figure A.1, position 16). The molar flow of HBr at the reactor outlet was then determined with Equation A.5,

\[ n(\text{HBr})_{\text{outlet}} = 2 \cdot (n(\text{CO}_2)_{\text{CS}} - n(\text{CO}_2)_{\text{RS}}), \text{ mol}_{\text{HBr}} \cdot s^{-1} \]  

(A.5)

where superscript CS (carbonated sample) refers to the sample which was admitted through a carbonated bed, and superscript RS (reaction sample) denotes the sample taken when bypassing the Na\textsubscript{2}CO\textsubscript{3} bed.

The content of HCl was measured by passing the outlet gas stream through an absorption tray comprising two impinging bottles filled with H\textsubscript{2}SO\textsubscript{4} solution (Figure A.1, position 19) to absorb HCl, while dissolution of Cl\textsubscript{2} is strongly suppressed in acidic media. The content of HCl was quantified by titration with a NaOH standard solution (0.05 M; Merck) according to Equation A.6,

\[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]  

(A.6)

The molar flow of HCl was calculated with Equation A.7,

\[ n(\text{HCl}) = \frac{c(\text{NaOH})}{t} \cdot \sum_{p=1}^{p=2} \left( V(\text{NaOH})_{p}^{\text{HCl+H}_2\text{SO}_4} - V(\text{NaOH})_{p}^{\text{H}_2\text{SO}_4} \right), \text{ mol}_{\text{HCl}} \cdot s^{-1} \]  

(A.7)

where \( c(\text{NaOH}) \) corresponds to the concentration of standard NaOH solution, \( t \) denotes the sampling time, and \( V(\text{NaOH})_{p}^{\text{HCl+H}_2\text{SO}_4} \) and \( V(\text{NaOH})_{p}^{\text{H}_2\text{SO}_4} \) represent the volumes of NaOH consumed for titration of H\textsubscript{2}SO\textsubscript{4} solution after and prior to passing the outlet gas stream in the first \( (p = 1) \) and the second impinging bottle \( (p = 2) \), respectively. In the experiments, the content
of HCl in the second bottle was close to 0, suggesting that it was mostly absorbed in the first bottle.

The content of molecular halogen ($X_2$, $X = Cl$, Br) was determined by iodometric titration of triiodide (Equation A.8), formed by the reaction of $X_2$ with aqueous KI solution (Figure A.1, position 20) according to Equation A.9, with a Na$_2$S$_2$O$_3$ solution (0.01 M; Aldrich).

\[ \Gamma_3 + 2S_2O_3^{2-} \rightarrow 3I^- + S_3O_6^{2-} \]  \hspace{1cm} (A.8)

\[ 3I^- + X_2 \rightarrow \Gamma_3 + 2X^- \]  \hspace{1cm} (A.9)

The molar flow of $X_2$ was calculated according to Equation A.10:

\[ n(X_2) = \frac{1}{2} \cdot \frac{c(Na_2S_2O_3)}{t} \cdot V(Na_2S_2O_3), \text{mol}_X \cdot s^{-1} \]  \hspace{1cm} (A.10)

where $c(Na_2S_2O_3)$ corresponds to the concentration of standard Na$_2$S$_2$O$_3$ solution, and $V(Na_2S_2O_3)$ represents its volume needed to titrate triiodide in the impinging bottle.

**Determination of Reaction Parameters and Mass Balances.**

The conversion of reactant $i$ was calculated according to Equation A.11,

\[ X(i) = \frac{n(i)^{\text{inlet}} - n(i)^{\text{outlet}}}{n(i)^{\text{inlet}}} \cdot 100, \% \]  \hspace{1cm} (A.11)

Specifically, the conversion of hydrogen halide (HX) in the respective HX oxidation reaction was calculated with Equation A.12,

\[ X(HX) = \frac{2 \cdot n(X_2)^{\text{outlet}}}{n(HX)^{\text{inlet}}} \cdot 100, \% \]  \hspace{1cm} (A.12)

The selectivity to product $j$ and the yield of product $j$ on the basis of carbon containing compound were determined using Equations A.13 and A.14, respectively,

\[ S(j) = \frac{N_c(j) \cdot n(j)^{\text{outlet}}}{\sum \limits_{\text{min}} N_c(j) \cdot n(j)^{\text{outlet}}} \cdot 100, \% \]  \hspace{1cm} (A.13)
Evaluation of Catalyst Performance

\[ Y(j) = \frac{X(i) \cdot S(j)}{100}, \% \]  
(A.14)

where \( N_C(i) \) denotes the number of carbon atoms of product \( j \).

The selectivity to product \( j \) and the yield of product \( j \) on the basis of HX were calculated using Equations A.15 and A.16, respectively,

\[ S(j) = \frac{N_X(j) \cdot n(j)_{\text{outlet}}}{\sum N_X(j) \cdot n(j)_{\text{outlet}}} \cdot 100, \% \]  
(A.15)

\[ Y(j) = \frac{X(HX) \cdot S(j)}{100}, \% \]  
(A.16)

where \( N_X(i) \) denotes the number of halogen atoms of product \( j \).

The space-time yield of product \( j \) was determined according to Equation A.17,

\[ STY(j) = \frac{n(j)_{\text{outlet}}}{W_{\text{cat}}} \cdot M(j), \text{ g s}^{-1} \text{ g}_{\text{cat}}^{-1} \]  
(A.17)

where \( W_{\text{cat}} \) denotes the catalyst weight and \( M(j) \) represents the molecular weight of product \( j \).

The reaction rates expressed with respect to the reactant \( i \) and normalized with respect to the catalyst weight \( (W_{\text{cat}}) \), its surface area \( (S_{\text{BET}}) \), or the reactor volume \( (V) \) were determined with Equations A.18, A.19, and A.20 respectively. In the case of catalytic reactions \( V \) corresponds to the \( V_{\text{bed}} \), whereas in the case of non-catalytic reactions performed in a void reactor volume, it corresponds to \( V_r \) (Figure A.1, positions 10a-b).

\[ r_W(i) = \frac{n(i)_{\text{inlet}} - n(i)_{\text{outlet}}}{W_{\text{cat}}}, \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1} \]  
(A.18)

\[ r_S(i) = \frac{n(i)_{\text{inlet}} - n(i)_{\text{outlet}}}{S_{\text{BET}}}, \text{ mol s}^{-1} \text{ m}_{\text{cat}}^{-2} \]  
(A.19)

\[ r_V(i) = \frac{n(i)_{\text{inlet}} - n(i)_{\text{outlet}}}{V}, \text{ mol s}^{-1} \text{ cm}^{-3} \]  
(A.20)
Appendix A

The errors of the carbon and halogen mass balances were determined using Equations A.21 and A.22.

\[
\varepsilon_C = \frac{\sum_{\text{inlet}} N_C(i) \cdot n(i)_{\text{inlet}} - \left( \sum_{\text{outlet}} N_C(i) \cdot n(i)_{\text{outlet}} + \sum_{\text{outlet}} N_C(j) \cdot n(j)_{\text{outlet}} \right)}{\sum_{\text{inlet}} N_C(i) \cdot n(i)_{\text{inlet}}} \cdot 100\% \tag{A.21}
\]

\[
\varepsilon_X = \frac{\sum_{\text{inlet}} N_X(i) \cdot n(i)_{\text{inlet}} - \left( \sum_{\text{outlet}} N_X(i) \cdot n(i)_{\text{outlet}} + \sum_{\text{outlet}} N_X(j) \cdot n(j)_{\text{outlet}} \right)}{\sum_{\text{inlet}} N_X(i) \cdot n(i)_{\text{inlet}}} \cdot 100\% \tag{A.22}
\]

The errors of mass balances were less than 5% in the experiments reported in this thesis.
Chapter 2

Catalyst preparation. CePO₄, LaPO₄, Mn₃(PO₄)₂, CoPO₄, Ni₃(PO₄)₂, and Zn₃(PO₄)₂ were prepared by precipitation. For the first two samples, 0.4 M solutions of Ce(NO₃)₃·6H₂O (Sigma Aldrich, 99.9%) and La(NO₃)₃·6H₂O (Sigma Aldrich, ≥ 99.0%), respectively, were mixed with a stoichiometric amount of 0.4 M H₃PO₄ solution (Sigma Aldrich, ≥ 85%) at room temperature. The latter four samples were obtained by mixing the 0.02 M solutions of MnCl₂·4H₂O (Sigma Aldrich, ≥ 99%), Co(NO₃)₂·6H₂O (Acros, 99%), Ni(NO₃)₂·6H₂O (Acros, 99%), and Zn(NO₃)₂·6H₂O (Sigma Aldrich, ≥ 98%), respectively, with a stoichiometric amount of 0.02 M solution of NaH₂PO₄ (Sigma Aldrich, ≥ 99.0%). All solutions were prepared in deionized water. The resulting suspensions were aged for 2 h at room temperature. The precipitates were then separated by filtration, extensively washed with deionized water, dried in vacuum (50 mbar) at 373 K for 24 h, and calcined in a static air at 823 K (5 K min⁻¹) for 5 h. Ti₂P₂O₇ was synthesized by reacting the TiO₂-rutile (Aldrich, nanopowder, 99.5%) with the H₃PO₄ in molar ratio Ti:P = 1:3 at room temperature. The resulting paste was mixed overnight at the room temperature and dried under static air at 523 K for 2 h. The thus obtained solid was washed with deionized water to remove unreacted phosphorous species and calcined at 823 K (5 K min⁻¹) for 5 h. The structures of the all above mentioned phosphate catalysts were confirmed by the XRD analysis.

Reactor modeling. The concentration profile of the reactants, intermediates, and products for the gas-phase bromination were modeled using a reaction network described with Equations B.1-5 with the kinetic and thermodynamic parameters reported by Ding et al. (ACS Catal. 2013, 3, 474-477)

\[
\text{Br}_2 + M \rightleftharpoons 2\text{Br}^\bullet + M
\]  

(B.1)
Appendix B

\[ \text{Br}^* + \text{CH}_4 \rightleftharpoons \text{CH}_3^* + \text{HBr} \]  \hspace{1cm} (B.2)

\[ \text{CH}_3^* + \text{Br}_2 \rightleftharpoons \text{CH}_3\text{Br} + \text{Br}^* \]  \hspace{1cm} (B.3)

\[ \text{CHBr}^* + \text{CH}_3\text{Br} \rightleftharpoons \text{CH}_2\text{Br}^* + \text{HBr} \]  \hspace{1cm} (B.4)

\[ \text{CH}_2\text{Br}^* + \text{Br}_2 \rightleftharpoons \text{CH}_2\text{Br}_2 + \text{Br}^* \]  \hspace{1cm} (B.5)

The simulations were conducted using MATLAB® assuming a homogeneous model with ideal plug-flow behavior under isothermal \((T = 753 \text{ K})\) and isochoric conditions \((P = 1.4 \text{ bar})\) for the inlet feed containing \(\text{CH}_4:\text{Br}_2:\text{Ar}:\text{He} = 4.5:1.5:3:91\).
Table B.1. Performance of the catalysts in the oxybromination of CH₄.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>X(CH₄) / %</th>
<th>S(CH₃Br) / %</th>
<th>S(CH₂Br₂) / %</th>
<th>S(CO) / %</th>
<th>S(CO₂) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8.0</td>
<td>82±3.4 (6.6)b</td>
<td>10±2 (0.8)</td>
<td>8±2.5 (0.6)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>CePO₄</td>
<td>9.5</td>
<td>70±2 (6.6)</td>
<td>7±1 (0.7)</td>
<td>22±2.1 (2.1)</td>
<td>1±0.2 (0.1)</td>
</tr>
<tr>
<td>LaPO₄</td>
<td>8.7</td>
<td>85±0.6 (7.4)</td>
<td>11.0±0.6 (1.0)</td>
<td>4±1 (0.3)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Ti₃P₂O₇</td>
<td>8.9</td>
<td>66±2 (5.9)</td>
<td>9±1.2 (0.8)</td>
<td>25±2 (2.2)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Mn₃(PO₄)₂</td>
<td>6.3</td>
<td>68±1.1 (4.3)</td>
<td>0 (0)</td>
<td>31±2 (1.9)</td>
<td>1±0.1 (0.1)</td>
</tr>
<tr>
<td>CoPO₄</td>
<td>8.4</td>
<td>73±2 (6.1)</td>
<td>9±1.3 (0.8)</td>
<td>18±3 (1.5)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Ni₃(PO₄)₂</td>
<td>10.8</td>
<td>74±2.1 (8.0)</td>
<td>9±1.5 (1.0)</td>
<td>12±4 (1.3)</td>
<td>5±0.9 (0.5)</td>
</tr>
<tr>
<td>Zn₃(PO₄)₂</td>
<td>8.2</td>
<td>84±3 (6.9)</td>
<td>5±1 (0.4)</td>
<td>11±2.5 (0.9)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Cu₃(PO₄)₂</td>
<td>27.0</td>
<td>57±2 (15.4)</td>
<td>16±1.7 (4.3)</td>
<td>4±0.5 (1.1)</td>
<td>23±1 (6.2)</td>
</tr>
<tr>
<td>CrPO₄</td>
<td>26.4</td>
<td>50±1.1 (13.2)</td>
<td>14.0±0.4 (3.7)</td>
<td>27±2 (7.1)</td>
<td>9±1 (2.4)</td>
</tr>
<tr>
<td>VPO</td>
<td>24.5</td>
<td>64±1.3 (15.7)</td>
<td>20.5±1 (5.0)</td>
<td>15±1 (3.7)</td>
<td>0.5±0.05 (0.1)</td>
</tr>
<tr>
<td>FePO₄</td>
<td>19.1</td>
<td>68±1.5 (13.0)</td>
<td>16.6±0.5 (3.2)</td>
<td>15±1.4 (2.9)</td>
<td>0.4±0.05 (0.1)</td>
</tr>
<tr>
<td>FePO₄/SiO₂</td>
<td>26.0</td>
<td>56.3±0.7 (14.6)</td>
<td>22.6±0.5 (5.9)</td>
<td>19.5±0.9 (5.1)</td>
<td>1.6±0.6 (0.4)</td>
</tr>
<tr>
<td>RuO₂</td>
<td>26.0</td>
<td>46.7±0.9 (12.1)</td>
<td>15.2±0.9 (4.0)</td>
<td>0 (0)</td>
<td>38.1±0.8 (9.9)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>25.0</td>
<td>49.1±0.3 (12.3)</td>
<td>13.6±0.6 (3.4)</td>
<td>32.6±0.6 (8.1)</td>
<td>4.7±0.1 (1.2)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>29.0</td>
<td>52±1.5 (15.1)</td>
<td>18.3±0.8 (5.3)</td>
<td>0 (0)</td>
<td>29.7±0.9 (8.6)</td>
</tr>
</tbody>
</table>

---

a Conditions: CH₄:HBr:O₂:Ar:He = 4.5:3.1:5:3:88, F_T = 100 cm³ min⁻¹, W_cat = 1.0 g, T = 753 K, and P = 1.4 bar. Data were collected after 1 h on stream over each catalyst. Conversion and selectivities are calculated as an average of minimum three measurements. The error in the reported conversion values was less than 2%.

b Single-pass carbon yields of reaction products in brackets.
Figure B.1. X-ray diffractograms and specific surface areas of the oxide and phosphate catalysts in fresh form and after CH$_4$ oxybromination. The crystalline phases identified in the samples are listed on the right panel and surface areas are indicated above the corresponding patterns.
Figure B.2. $^{31}$P MAS NMR spectra of the fresh and used VPO samples recovered after equilibration under CH$_4$ oxybromination conditions for a different time on stream. The $^{31}$P NMR signals which are located at around 0 ppm, correspond to the phosphorous atoms in close vicinity to the V$^{5+}$ states in the VPO phases (Frey et al., *Solid State Nucl. Magn. Reson.* 2009, 35, 130-137; Hutchings, *J. Mater. Chem.* 2004, 14, 3385-3395,) and were gradually vanishing over time. In contrary, the signal positioned at around $-175$ ppm, ascribed to the P surrounding a defect V$^{5+}$ states was gradually increasing over time. Nevertheless, the overall integral of the V$^{5+}$ was stabilized after 15 h on stream (see inset in the top left corner). The spinning side bands are denoted with ▼.
Figure B.3. High-resolution transmission electron micrographs of VPO samples before and after equilibration in CH₄ oxybromination for different times. Equilibration conditions: CH₄:HBr:O₂:Ar:He = 4.5:3:1.5:3:88, $F_T = 100 \text{ cm}^3 \text{ min}^{-1}$, $W_{\text{cat}} = 1.0 \text{ g}$, $T = 753 K$, and $P = 1.4 \text{ bar}$
Figure B.4. Simulation of the CH₄ bromination in a plug-flow reactor. (a) Simulation predicts relatively low conversion of CH₄ at short residence times up to ca. 0.4 s and a sharp increase in conversion from ca. 0.4 s till ca. 1 s. This residence time interval is comparable with the residence time estimated according to the void volume between the catalyst particles under typical oxybromination conditions (Vᵣ = 1-2 cm³, particle size = 0.4-0.6 mm, and bed porosity, ε = 0.4, T = 753 K), which is in the order of 0.4-0.5 s. The normalized concentration of the bromine radicals indicated by the dashed line suggests relatively high concentration of these reactive species already at very short residence times. (b) Simulation is made for the limiting case when the bromine dissociation (Equation B.1) is in equilibrium. It predicts even shorter residence time (ca. 0.5 s) is sufficient to reach ca. 22% of CH₄ conversion.

Figure B.5. Oxidative dehydrogenation of (a) C₂H₆ and (b) C₃H₈ over VPO catalyst. Conditions: alkane:O₂:Ar:He = 4.5:1.5:3:91, Fᵣ = 100 cm³ min⁻¹, W_cat = 1.0 g, and P = 1.4 bar.
Chapter 3

Comparison of the catalyst activities in CH₄ oxyhalogenation. The comparison of the catalytic activities can be achieved in several ways. Rigorously, turn-over frequency (TOF) is the recommended measure of the inherent catalytic activity (Derouane et al., in: Combinatorial Catalysis and High Throughput Catalyst Design and Testing, Springer-Science, Dodrecht, The Netherlands, 1999, pp. 61-98), which however necessitates the exact knowledge about the number of the active sites. A commonly used approximation of TOF is based on normalization of the reaction rate with respect to the surface area. If this approach is applied, the following order of activities in oxychlorination: RuO₂ > CeO₂ ~ Cu-K-La-X ~ FePO₄ > VPO > TiO₂, and oxybromination: RuO₂ ~ FePO₄ > CeO₂ VPO ~ TiO₂ > Cu-K-La-X (Figure B.7). Nevertheless, this expression of activity has a drawback as it implies the surface density of active sites for different types of materials (e.g., oxides and phosphates, or bulk and supported catalysts) to be the same, which is likely not the case. Therefore, the rate per surface area does not necessarily reflect TOF in its core definition, which might lead to some contradictory conclusions, such that supported Cu-based system exhibits a rather low activity, though it is widely accepted as a benchmark oxyhalogenation catalyst. On the other hand, any attempt to estimate the surface density of sites for a real-life, polycrystalline material will necessitate assumptions on the size, shape, or structure of individual particles, which in principle might introduce uncontrolled errors and possible misinterpretation of the results. Moreover, the overall oxyhalogenation performance is possibly affected by the gas-phase contributions, which would be incorrectly (and unfairly) ascribed to the surface sites. In an alternative approach, the activation barriers (Table B.3) can be used for ranking the catalyst activity, as these are considered as an inherent measure of the active site ability to promote the given reaction, so that highly active catalyst should exhibit the lowest activation barrier. An implementation of this criteria, gives the following order of activity in oxychlorination: VPO > TiO₂ > RuO₂ > FePO₄ > CeO₂ > Cu-K-La-X, and in oxybromination: RuO₂ > TiO₂ = CeO₂ > FePO₄ > VPO > Cu-K-La-X, which is different than the one based on surface- or weight/volume-normalized reaction rates. Nevertheless, the complexity of the oxyhalogenation process suggests the activation barriers extracted from the temperature variation
experiments likely include contributions from the different heterogeneous and/or homogenous reaction steps that might vary among various oxyhalogenation catalysts. As such, they do not necessarily reflect the intrinsic catalyst propensity to facilitate the halomethane formation, and are thus not considered as an appropriate measure of the catalyst performance. Given the above-mentioned challenges, the comparison of the catalytic activities per unit of weight/volume was used, which is a widely accepted approach in catalysis (He et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 2438-2442.), also applied in the previous studies on oxyhalogenation. Therefore, the catalytic tests were performed over a constant weight of a catalyst (1 g), which was mixed with quartz particles to ensure the constant reaction volume of 1.8 cm$^3$. Though it does not reflect the surface reactivity of different materials, we find it useful as it (i) provides information on the productivity per unit of space, which is highly relevant for potential reactor and process design, and (ii) enables the comparison of the kinetics of different (partially) catalytic and non-catalytic reactions (vide infra), since the rate of the latter is per definition space-dependent. Besides, the differences in the performance among distinct materials are not the primary focus of our study, but more the performance similarities and diversities of a single material in the two oxyhalogenation reactions. Since the measured surface area do not differ significantly among fresh and used samples of the same nature (Table B.2), the expression of reaction rate with respect to surface, weight, or volume, does not induce important implications for the discussion.
## Appendix B

**Table B.2.** Specific surface area of the samples in fresh form and after CH$_4$ oxybromination and oxychlorination.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ / m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>9</td>
</tr>
<tr>
<td>Cu-K-La-X</td>
<td>92</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>34</td>
</tr>
<tr>
<td>VPO</td>
<td>30</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>19</td>
</tr>
<tr>
<td>FePO$_4$</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table B.3.** Apparent activation energy, $E_a$(CH$_4$), and partial orders with respect to HX in CH$_4$ oxybromination and oxychlorination over the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
<th>$E_a$(CH$_4$)$^{a}$ / kJ mol$^{-1}$</th>
<th>$n$(CH$_4$)$^{b}$ /</th>
<th>$n$(CO)$^{b}$ /</th>
<th>$n$(CO$_2$)$^{b}$ /</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO$_2$</td>
<td>oxybromination</td>
<td>34</td>
<td>-0.90</td>
<td>-</td>
<td>-4.01</td>
</tr>
<tr>
<td></td>
<td>oxychlorination</td>
<td>86</td>
<td>-0.67</td>
<td>0.01</td>
<td>-1.30</td>
</tr>
<tr>
<td>Cu-K-La-X</td>
<td>oxybromination</td>
<td>133</td>
<td>-0.11</td>
<td>-1.07</td>
<td>-1.07</td>
</tr>
<tr>
<td></td>
<td>oxychlorination</td>
<td>134</td>
<td>0.48</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>oxybromination</td>
<td>71</td>
<td>0.23</td>
<td>-0.17</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>oxychlorination</td>
<td>111</td>
<td>0.08</td>
<td>-0.06</td>
<td>1.69</td>
</tr>
<tr>
<td>VPO</td>
<td>oxybromination</td>
<td>66</td>
<td>0.14</td>
<td>0.09</td>
<td>-0.28</td>
</tr>
<tr>
<td></td>
<td>oxychlorination</td>
<td>111</td>
<td>0.15</td>
<td>-0.41</td>
<td>-1.57</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>oxybromination</td>
<td>71</td>
<td>0.23</td>
<td>-0.17</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>oxychlorination</td>
<td>85</td>
<td>0.34</td>
<td>0.25</td>
<td>-1.70</td>
</tr>
<tr>
<td>FePO$_4$</td>
<td>oxybromination</td>
<td>83</td>
<td>0.41</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>oxychlorination</td>
<td>103</td>
<td>0.49</td>
<td>0.44</td>
<td>-</td>
</tr>
</tbody>
</table>

$^{a}$ Derived from Figure B.10.$^{b}$ Derived from Figure B.11.
Table B.4. HCl conversion and selectivity to Cl\textsubscript{2} and H\textsubscript{2} in CH\textsubscript{4} oxychlorination over VPO at different temperatures.

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$X$(HCl) / %</th>
<th>$S$(Cl\textsubscript{2}) / %</th>
<th>$S$(H\textsubscript{2}) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>762</td>
<td>1.5</td>
<td>16</td>
<td>0.05</td>
</tr>
<tr>
<td>777</td>
<td>1.3</td>
<td>&lt;6</td>
<td>0.04</td>
</tr>
<tr>
<td>800</td>
<td>1.4</td>
<td>&lt;6</td>
<td>0.04</td>
</tr>
<tr>
<td>818</td>
<td>1.2</td>
<td>&lt;6</td>
<td>0.05</td>
</tr>
<tr>
<td>836</td>
<td>1.2</td>
<td>&lt;6</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Figure B.6. Temperature-programmed reduction with H$_2$ of the fresh catalysts, classifying the reducibility property based on the onset of H$_2$ consumption.
Figure B.7. Normalization of the activity with respect to the surface area of the used catalyst (a) in CH₄ oxyhalogenation (CH₄:HX:O₂:Ar:He = 6:6:3:4.5:80.5) and (b) HX oxidation (HX:O₂:Ar:He = 6:3:4.5:86.5). Legend: X = Br, open symbols; X = Cl, solid symbols. Other conditions: $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$ and $P = 1 \text{ bar}$.
Figure B.8. X-ray diffractograms of the samples in fresh form and after CH₄ oxybromination and oxychlorination. The right panel provides the identified crystalline phases and ICDD-PDF numbers. Conditions as specified in the caption of Figure B.7.
Figure B.9. Temperature required to attain $0.5 \times 10^{-7} \text{ mol s}^{-1} \text{ mcat}^{-2}$ in CH$_4$ oxyhalogenation versus HX oxidation over the catalysts.

Figure B.10. Arrhenius plots for CH$_4$ conversion in oxybromination (open symbols) and oxychlorination (solid symbols) over the catalysts. The derived apparent activation energy ($E_a$(CH$_4$)) is indicated in Table B.3.
Figure B.11. Logarithm of CH₄ conversion (left), and CO (middle) and CO₂ (right) yields versus logarithm of feed HX concentration in CH₄ oxybromination (open symbols) and oxychlorination (solid symbols) over the catalysts. The derived apparent partial orders with respect to HX, n(CH₄), n(CO), and n(CO₂), are indicated in Table B.3. The values of n(CO) for RuO₂ in oxybromination and n(CO₂) for FePO₄ in oxychlorination and oxybromination could not be derived because these products were not detected.
Figure B.12. Reaction rate versus temperature in CH₄ oxyhalogenation (CH₄:HX:O₂:Ar:He = 6:6:3:4.5:80.5), HX (HX:O₂:Ar:He = 6:3:4.5:86.5) and CH₄ (CH₄:O₂:Ar:He = 6:0:3:4.5:86.5) oxidation over TiO₂. Legend: X = Br, open symbols; X = Cl, solid symbols. Other conditions: \( F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{g}_{cat}^{-1} \) and \( P = 1 \text{ bar} \).

Figure B.13. Product yield versus temperature in CH₄ oxybromination over RuO₂. Conditions: CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5, \( F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{g}_{cat}^{-1} \), and \( P = 1 \text{ bar} \).

Figure B.14. CH₄ conversion and product selectivity versus temperature in CH₄ oxybromination over RuO₂. Conditions: CH₄:HBr:O₂:Ar:He = 6:15:3:4.5:71.5, \( F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{g}_{cat}^{-1} \), and \( P = 1 \text{ bar} \).
Figure B.15. (a) X-ray diffractograms, and (b) Br 3d and (c) Cl 2p core level X-ray photoelectron spectra of the catalysts in fresh form (blue), and after the equilibration under 6 vol.% (CH₄:Hₓ:O₂:Ar:He = 6:6:3:4.5:80.5) and 15 vol.% (CH₄:Hₓ:O₂:Ar:He = 6:15:3:4.5:71.5) of Hₓ in the feed in CH₄ oxybromination (red, T = 760 K) and oxychlorination (green, T = 775 K). Equilibration conditions: $F_T/W_{cat} = 100$ cm$^3$ min$^{-1}$ g$^{-1}$, $P$ = 1 bar, and $t_{os} = 5$ h.

Figure B.16. Conversion and product selectivity versus temperature in CH₂Br₂ oxidation over CeO₂ in the absence (open symbols, CH₂Br₂:O₂:Ar:He = 1:3:4.5:91.5) and presence of HBr (solid symbols, CH₂Br₂:HBr:O₂:Ar:He = 1:6:3:4.5:85.5). Other conditions: $F_T/W_{cat} = 100$ cm$^3$ min$^{-1}$ g$^{-1}$ and $P = 1$ bar.
Figure B.17. Product selectivity at ca. 18% CH$_4$ conversion in CH$_4$ oxybromination (open bars) and oxychlorination (solid bars) at different space velocities over CeO$_2$. The corresponding reaction temperature is indicated on top of each bar. Other conditions: CH$_4$:HX:O$_2$:Ar:He = 6:6:3:4.5:80.5 and $P = 1$ bar.
Figure B.18. (a) X-ray diffractograms (b) temperature-programmed reduction with H\textsubscript{2} profiles, and (c) V 2p X-ray photoelectron core level spectra of VPO in fresh form and after CH\textsubscript{4} oxychlorination for different time-on-stream at 803 K. The diffractogram of the fresh sample indicates that it is mainly composed of two (VO)\textsubscript{2}P\textsubscript{2}O\textsubscript{7} phases. Exposure of the catalyst to the reaction mixture leads to its reconstruction into the originally present dominant (VO)\textsubscript{2}P\textsubscript{2}O\textsubscript{7} phase within the first hour. The latter phase is preserved during 103 h on stream. H\textsubscript{2}-reduction profiles of used catalysts are essentially identical, while fresh catalyst shows a slightly broader peak in the region of V\textsuperscript{4+} reduction, and a bit more pronounced V\textsuperscript{5+} reduction peak. They demonstrate V\textsuperscript{4+} to be the dominant oxidation state of V, although a small contribution from V\textsuperscript{5+} reduction can be observed.
**Table B.5.** Characterization data of VPO samples in fresh form and after CH$_4$ oxychlorination for different time-on-stream at 803 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ / m$^2$ g$^{-1}$</th>
<th>P:V$^a$ /</th>
<th>V oxidation state$^b$ /</th>
<th>V$^{5+}$ $^c$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>20</td>
<td>1.01</td>
<td>4.08</td>
<td>28</td>
</tr>
<tr>
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<td>23</td>
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<td>4.08</td>
<td>36</td>
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<td>23</td>
<td>1.01</td>
<td>4.15</td>
<td>39</td>
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<tr>
<td>10 h</td>
<td>23</td>
<td>1.01</td>
<td>4.07</td>
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</tr>
<tr>
<td>103 h</td>
<td>16</td>
<td>1.01</td>
<td>4.14</td>
<td>36</td>
</tr>
</tbody>
</table>

$^a$ Determined by XRF.

$^b$ Calculated based on O 1s and V 2p (3/2) core level binding energies (Figure B.18), using formula given by Coulston et al., (*J. Catal.* 1996, 163, 122-129). V oxidation state = 13.82 - 0.68·(Binding energy (O 1s) - Binding energy (V 2p (3/2))).

$^c$ Calculated based on deconvolution of V 2p (3/2) peak as shown in Figure B.18c.
Appendix B

Chapter 5

Figure B.19. High-resolution transmission electron micrographs of (a) fresh CeO$_2$/SiC and (b) CeO$_2$/MgO after equilibration in CH$_4$ oxybromination. The insets show the fast Fourier transform of the boxed regions. Equilibration conditions: CH$_4$:HBr:O$_2$:Ar:He = 6:6:3:4.5:80.5, $F_T/W_{\text{cat}} = 100$ cm$^3$ min$^{-1}$ g$^{-1}$, $T = 773$ K, $P = 1$ bar, and $t_{\text{os}} = 5$h.
Figure B.20. Core level X-ray photoelectron spectra of supported CeO$_2$ catalysts in fresh form (blue symbols) and after equilibration in CH$_4$ oxybromination (red symbols). Spectra of the bulk CeO$_2$ (green symbols) and of CeBr$_3$ (gray symbols) are provided for reference. The positions of the peaks which are characteristic of Ce$^{4+}$ (U, U", U"", V, V", V""") and Ce$^{3+}$ (U$_0$, U', V$_0$, V') oxidation states are indicated in the bottom left spectra. The solid lines behind the respective symbols represent the results obtained by spectral fitting. The dashed brown lines define the used background and the dashed green and gray lines.
filled with colored areas display the calculated contributions of Ce$^{4+}$ and Ce$^{3+}$ states. Equilibration conditions as reported in the caption of Figure B.19. Ceria gives a complex set of satellite peak pairs (U'' and V'', U''' and V''') around its 3d signals (U and V) associated with shake-up/shake-down. Each pair of satellite peak pairs have the same 18.3 eV separation and 2:3 peak area ratio as the main 3d signals. The sharp U''' peak at the high binding energy of ca. 916 eV is only associated with Ce$^{4+}$, and is useful for characterizing the oxidation state of cerium in the supported samples (Gore et al., J. Mater. Chem. A 2014, 2, 2363-2373). A more accurate quantitative separation of the Ce 3d signal into the relative Ce$^{3+}$ and Ce$^{4+}$ contribution can be obtained by spectral fitting using reference spectra acquired under the same conditions as used to analyze the different supported catalysts (Holgado et al., Appl. Surf. Sci. 2000, 161, 301-315). The latter procedure was adopted to estimate the ratio Ce$^{4+}$:(Ce$^{3+}$+Ce$^{4+}$) in the supported CeO$_2$ catalysts in their fresh form and after equilibration in CH$_4$. Herein, the spectra obtained from fresh CeO$_2$ and CeBr$_3$ (bottom) were used as a reference for Ce$^{4+}$ and Ce$^{3+}$ contributions, respectively. The spectrum of CeO$_2$ was reproduced by a set of seven Gauss peaks and the spectrum of CeBr$_3$ was reproduced by a set of five Gauss peaks. For each reference all the peaks have been locked in their relative positon, relative area, and FWHM (bottom). This allows compensating for different charging during analysis as well as for small peak broadening.
Figure B.21. (a) Conversion and rate of CO oxidation over bulk and supported CeO$_2$ catalysts in fresh form (open symbols) and after equilibration in CH$_4$ oxybromination (solid symbols), and (b) corresponding Arrhenius plots used to determine the apparent activation energy. Equilibration conditions as reported in the caption of Figure B.19. Conditions for CO oxidation: CO:O$_2$:Ar:He = 1.5:3:4.5:91, $F_T/W_{\text{cat}} = 500$ cm$^3$ min$^{-1}$ g$_{\text{cat}}^{-1}$, and $P = 1$ bar. The rates were calculated as the average reaction rate of an integral reactor (Equation A.18) and were primarily used as the parameter to establish the relative order of the catalyst activities in CH$_4$ oxybromination and different complementary reactions comprising the oxidation of CO, CH$_4$, HBr, CH$_3$Br, and CH$_2$Br$_2$. The rates reported in the Figure 5.5b were determined from the region of the respective light-off curves that corresponds to 5-40% of conversion. This approach, which was also applied in previous studies (Farra et al., ACS Catal. 2013, 3, 2256-2268) provides a compromise between (i) the errors in the analysis of reactants and products, which tend to propagate under differential reactor operation and relatively low product concentrations, (ii) linearity of the Arrhenius plots, and (iii) the axial concentration gradient, which is relatively similar for the different catalysts since the rates were estimated at comparable conversion levels.
Figure B.22. Arrhenius plots used to determine the apparent activation energy of CH\textsubscript{4} oxybromination over bulk and supported CeO\textsubscript{2} catalysts. Conditions: CH\textsubscript{4}:HBr:O\textsubscript{2}:Ar:He = 6:6:3:4.5:80.5, \(F_T/W_{\text{cat}} = 100 \text{ cm}^3 \text{ min}^{-1} g_{\text{cat}}^{-1}\), and \(P = 1\) bar. The reaction rates were calculated as reported in the caption of Figure B.21.
Figure B.23. X-ray diffractograms of the MgO-supported CeO$_2$ catalysts in fresh form (blue) and after equilibration in CH$_4$ oxybromination (red). Reference patterns shown as vertical lines below the measured diffractograms are identified with their ICDD-PDF numbers. The insets show the magnified parts of the diffractograms in which the main reflections of CeO$_2$ are expected to appear. Equilibration conditions as reported in the caption of Figure B.19.
Figure B.24. High-angle annular dark field scanning transmission electron micrographs of (a) CeO$_2$/MgO-0.1, (b) CeO$_2$/MgO-0.5, (c) CeO$_2$/MgO-0.5-973, and (d) CeO$_2$/MgO-0.5-1373 catalysts after equilibration in CH$_4$ oxybromination. Equilibration conditions as reported in the caption of Figure B.19.
Figure B.25. (a) Conversion and rate of CO oxidation over MgO-supported CeO$_2$ catalysts in the fresh form (open symbols) and after equilibration in CH$_4$ oxybromination (solid symbols), and (b) corresponding Arrhenius plots used to determine the apparent activation energy. Equilibration conditions as reported in the caption of Figure B.19. Conditions: CO:O$_2$:Ar:He = 1.5:3:4:5:91, $F_T/W_{cat} = 500$ cm$^3$ min$^{-1}$ g$_{cat}^{-1}$, and $P = 1$ bar. The reaction rates were calculated as reported in the caption of Figure B.21.
Figure B.26. Conversion and rate of (a) CH$_4$ oxidation ($\text{CH}_4$:O$_2$:Ar:He = 6:3:4.5:86.5, $F_T/W_{\text{cat}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$) and (b) HBr oxidation ($\text{HBr}$:O$_2$:He = 6:3:91, $F_T/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$) over bulk and supported CeO$_2$ catalysts after equilibration in CH$_4$ oxybromination. Equilibration conditions as reported in the caption of Figure B.19. All the tests were conducted at $P = 1 \text{ bar}$. The reaction rates were calculated as reported in the caption of Figure B.21.
Figure B.27. (a) Conversion of CH₄ and product selectivity and (b) rate of CH₄ oxybromination versus the feed concentrations of CH₄ (CH₄:HBr:O₂:Ar:He = 3-20:6:3:4.5:80.5-66.5), HBr (CH₄:HBr:O₂:Ar:He = 6:3-12:3:4.5:83.5-74.5), and O₂ (CH₄:HBr:O₂:Ar:He = 6:6:1.5-6:4.5:82-77.5) over CeO₂/MgO at different space velocities (Fₜ/Wₗcat = 100 or 150 cm³ min⁻¹ g⁻¹) and temperatures (T = 723-773 K). All the tests were performed at P = 1 bar. The apparent reaction orders with respect to CH₄, n(CH₄), HBr, n(HBr), and O₂, n(O₂), are reported in the corresponding plots in (b). The reaction rates were calculated as reported in the caption Figure B.21. In the experiments performed at T = 723 K, Fₜ/Wₗcat = 100 cm³ min⁻¹ g⁻¹, and 736 K, Fₜ/Wₗcat = 150 cm³ min⁻¹ g⁻¹ CH₄ conversion was in the range of 3-6%, at which the rate computed by Equation A.18 shows a small deviation from the initial rate.
Figure B.28. Conversion and reaction rate of CH$_2$Br$_2$ oxidation (CH$_2$Br$_2$:O$_2$:Ar:He = 1:2:4.5:92.5, \( \frac{F_{T}}{W_{\text{cat}}} = 500 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1} \)) over (a) bulk and supported CeO$_2$ catalysts, and (b) the carriers after equilibration in CH$_4$ oxybromination. Equilibration conditions as reported in the caption of Figure B.19. All the tests were conducted at \( P = 1 \text{ bar} \). The reaction rates were calculated as reported in the caption of Figure B.21.
# Chapter 6

Table B.6. Specific surface areas of the bulk catalysts in their fresh form and after the HBr oxidation and CH₄ oxybromination tests shown in Figure B.22, Figures 6.1a and 6.3.

<table>
<thead>
<tr>
<th>Catalystᵃ</th>
<th>$S_{\text{BET}}$ / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh</td>
</tr>
<tr>
<td>HBr oxidation</td>
<td></td>
</tr>
<tr>
<td>EuOBr</td>
<td>22</td>
</tr>
<tr>
<td>CeO₂</td>
<td>27</td>
</tr>
<tr>
<td>LaOBr</td>
<td>2</td>
</tr>
<tr>
<td>SmOBr</td>
<td>1</td>
</tr>
<tr>
<td>DyOBr</td>
<td>2</td>
</tr>
<tr>
<td>GdOBr</td>
<td>1</td>
</tr>
<tr>
<td>TbOBr</td>
<td>6</td>
</tr>
<tr>
<td>TiO₂</td>
<td>18</td>
</tr>
<tr>
<td>CH₄ oxybromination</td>
<td></td>
</tr>
<tr>
<td>EuOBr</td>
<td>6</td>
</tr>
<tr>
<td>CeO₂</td>
<td>22</td>
</tr>
<tr>
<td>VPO</td>
<td>28</td>
</tr>
</tbody>
</table>

ᵃ The pore volume of the bulk catalysts was lower than 0.14 cm³ g⁻¹.
Figure B.29. X-ray diffractograms of the catalysts in fresh form and after HBr oxidation tests presented in Figure B.30. Reference patterns shown as vertical lines below the measured diffractograms are identified on the right with their ICDD-PDF numbers.
Figure B.30. Catalytic performance of different lanthanide oxides and oxybromides in HBr oxidation. Conditions: HBr:O₂:He = 4.5:9:86.5, \( F_T/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1} \), and \( P = 1 \text{ bar} \). The tests were performed using an oxide as starting material and ramping from the highest to the lowest temperature. XRD analysis of the used samples (Figure B.29) revealed that all the oxides were transformed into the corresponding oxybromides, with the exception of CeO₂ which preserved the bulk oxide structure. The catalysts were thus named according to the dominant phase identified by XRD in the materials recovered after the temperature ramp, which is anticipated to be the active phase. Among the tested catalysts, EuOBr showed exceptionally high activity, exceeding that of the benchmark CeO₂ at low temperatures. The light-off curve of LaOBr was shifted to ca. 150 K higher temperature compared to EuOBr, while other oxybromides exhibited little activity in the preferred temperature window (≤ 573 K). The specific surface areas of these catalysts are ca. 2-10 times lower compared to EuOBr (Table B.6). Still, their initial activity (≤ 573 K) is ca. 20-100 times lower compared to the latter catalyst, indicating that the exceptional performance of EuOBr is not only the consequence of its higher surface area. It is interesting to note that some of the used materials (LaOBr, SmOBr, DyOBr, GdOBr) showed an increased surface area with respect to the fresh materials (Table B.6), suggesting the occurrence of restructuring on transformation from the oxide to the oxybromide phase. A short time-on-stream tests (HBr:O₂:He = 4.5:9:86.5, \( F_T/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1} \), \( P = 1 \text{ bar} \), \( T = 523 \text{ K} \) (EuOBr, CeO₂), 673 K (LaOBr), 723 K (SmOBr, DyOBr, GdOBr, TbOBr), \( tos = 8 \text{ h} \)) demonstrated stable catalytic performance of all the catalysts, except LaOBr (inset). The activity of the latter was substantially reduced after 8 h, indicative of catalyst instability even under O₂:HBr molar ratio of 2, i.e., 8 times higher O₂ excess with respect to the stoichiometric O₂:HBr molar ratio of 0.25.
Figure B.31. X-ray diffractograms of the TiO$_2$, EuOBr, CeO$_2$, and VPO catalysts in fresh form and after HBr oxidation and CH$_4$ oxybromination tests presented in Figures 6.1a and 6.3, respectively. Reference patterns shown as vertical lines below the measured diffractograms are identified on the right with their ICDD-PDF numbers.

Figure B.32. X-ray diffractograms of the CeO$_2$ catalysts in their fresh form and recovered after different time-on-stream in HBr oxidation. Conditions: HBr:O$_2$:He = 4.5:1.13:94.37, $F_T/W_{cat} = 200$ cm$^3$ min$^{-1}$ g$_{cat}^{-1}$, $T = 523$ K, and $P = 1$ bar. X-ray diffractograms of the CeO$_2$ catalysts in their fresh form and recovered after different time-on-stream in HBr oxidation. The results of the microscopy (Figure 6.2) and thermogravimetric analysis (Figure B.33) suggest the formation of new (oxy)bromide phases(s) of cerium during the reaction. This is also substantiated by the appearance of new peaks in the diffractograms of the used catalysts, which however did not match the reflections of any previously reported oxides or bromides of ceria.
Figure B.33. Thermogravimetric analysis (bottom) and the Br₂ evolution signals (top) over (a) CeO₂ and (b) EuOBr prior to (fresh) and after $n$ hours of HBr oxidation under a stoichiometric feed. Conditions: HBr:O₂:He = 4.5:1.13:94.37, $F_T/W_{cat} = 200$ cm$^3$ min$^{-1}$ g$^{-1}$, $T = 523$ K, $P = 1$ bar. Dashed lines indicate the theoretical weight loss for the transformations indicated. The weight loss of used CeO₂ demonstrates a time-progressive bromination of the catalyst, which results in a drop in the HBr conversion noticed in Figure 6.1c, suggesting an inherently low activity of the brominated ceria phases. In stark contrast to this, EuOBr exhibits a high activity in HBr oxidation, and high resistance to further bromination, as also corroborated by the identical thermogravimetric profiles of the catalysts after 6 h and 20 h on stream, the weight loss of which agrees with the theoretical value (29%) for the transformation of EuOBr into Eu₂O₃. The difference between the fresh and used samples likely results from the incomplete conversion to EuOBr during the pretreatment period, but has no impact on the catalyst activity. Notably, even under the HBr-free feed in which thermogravimetric analysis was performed, the transformation of EuOBr into Eu₂O₃ occurs at temperatures exceeding those applied in HBr oxidation (< 600 K) and CH₄ oxybromination (≤ 793 K), confirming the stability of this phase against reoxidation.
Figure B.34. O 1s (left) and Br 3d (right) X-ray core level spectra of EuOBr (top) and CeO$_2$ (bottom) prior to (fresh) and after $n$ hours of HBr oxidation under a stoichiometric feed. Conditions: HBr:O$_2$:He = 4.5:1.13:94.37, $F_T/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$, $T = 523 \text{ K}$, and $P = 1 \text{ bar}$. O 1s spectra of EuOBr exhibited two peaks at 528.9 eV and 531.8 eV, which can be ascribed to oxide-like species and oxygen atoms that are close to electronegative bromine atoms, respectively (Ai et al., Environ. Sci. Technol. 2009, 43, 4143-4150). After initial stabilization the shape of the O 1s spectra was essentially constant for the catalysts used for 1 h, 6 h, and 20 h, further corroborating the stability of the catalyst surface under the stoichiometric feed composition. Contrastingly, the O 1s peak in fresh CeO$_2$ (529 eV) decreased in intensity and was progressively shifted to higher binding energy (531.8 eV), which is similar to that of EuOBr. Simultaneously, the signal of Br 3d peak increases, testifying a severe bromination leading to catalyst deactivation.
Figure B.35. Conversion of and product selectivity on the basis of CH₄ in CH₄ oxybromination versus temperature (CH₄:HBr:O₂:Ar:He = 6:6.3:4.5:80.5, \( \frac{F_T}{W_{\text{cat}}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1} \)), O₂ concentration (CH₄:HBr:O₂:Ar:He = 6:6.15-6.45:82-77.5, \( \frac{F_T}{W_{\text{cat}}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}, T = 773 \text{ K} \)), HBr concentration (CH₄:HBr:O₂:Ar:He = 6:3-12:3.5-83.5-74.5, \( \frac{F_T}{W_{\text{cat}}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}, T = 773 \text{ K} \)), CH₄ concentration (CH₄:HBr:O₂:Ar:He = 3-19:6.3:4.5:80.5-73.5, \( \frac{F_T}{W_{\text{cat}}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}, T = 773 \text{ K} \)), and space velocity (CH₄:HBr:O₂:Ar:He = 6:6.3:4.5:80.5, \( T = 773 \text{ K} \)) over EuOBr, CeO₂, and VPO at \( P = 1 \text{ bar} \).
Figure B.36. Conversion and product selectivity on the basis of HBr in CH₄ oxybromination versus temperature (CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5, \( F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1} \)), CH₄ concentration (CH₄:HBr:O₂:Ar:He = 3-19:6:3:4.5:80.5-73.5, \( F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1} \), \( T = 773 \text{ K} \)), and space velocity (CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5, \( T = 773 \text{ K} \)) over EuOBr, CeO₂, and VPO at \( P = 1 \text{ bar} \).
Figure B.37. (a) Yield of Br2 on the basis of HBr and bromomethanes (CH3Br + CH2Br2) on the basis of CH4 versus temperature in CH4 oxybromination over EuOBr. (b) CH4 conversion versus temperature CH4 oxybromination and oxidation over EuOBr, and CH4 bromination over quartz. (c) Arrhenius plots used to derive the apparent activation energies, $E_a$, for CH4 oxybromination over EuOBr and for CH4 bromination over quartz. (d) Yield of bromomethanes in CH4 bromination at two different temperatures over quartz (open bars) and EuOBr (solid bars). CH4 oxybromination (CH4:HBr:O2:Ar:He = 6:6:3:4.5:80.5), oxidation (CH4:O2:Ar:He = 6:3:4.5:86.5), bromination (CH4:Br2:Ar:He = 6:3:4.5:86.5) were performed at $F_T/W_{cat} = 100$ cm$^3$ min$^{-1}$ g$^{-1}$ and $P = 1$ bar. Bromine was the main product in CH4 over EuOBr at lower reaction temperatures (ca. 730 K), which only yielded low amounts of bromomethanes (Figure B.36a). An increased production of bromomethanes upon increasing the reaction temperature (750-795 K) is coupled to a drop in the bromine yield (Figure B.37a) and HBr conversion (Figure B.37). Selectivity to Br2 and HBr conversion also decrease with an increase in CH4 concentration and a decrease in space-velocity, which favor the generation of bromomethanes (Figure B.37), suggesting that their formation might proceed by the reaction of CH4 with Br2 generated by heterogenous HBr oxidation. Moreover, the temperature region of CH4 oxybromination overlaps with that of the non-catalytic CH4 bromination over quartz particles (Figure B.37b) and the reactions have similar apparent activation energies (Figure B.37c). To elucidate the role of EuOBr in CH4 activation under oxybromination conditions, CH4 oxidation was studied over this catalyst using identical CH4:O2 ratio as the one applied in the former reaction (Figure B.37b). The much lower CH4 conversion in oxidation compared to oxybromination indicates the low propensity of EuOBr to activate C-H bonds in the temperature window of these reactions. This is further corroborated by conducting CH4 bromination over EuOBr and comparing the performance with the reaction over quartz particles (Figure B.37b). The two tests provided almost identical yields of bromomethanes, demonstrating that EuOBr has no particular advantage for CH4 activation by Br2 with respect to quartz. These results hint that the gas-phase reaction of CH4 with bromine species generated by catalytic HBr oxidation is likely the dominant pathway for C-Br bond formation in the oxybromination over EuOBr.
Table B.7. Specific surface areas and pore volumes of the supported Eu-based catalysts in their fresh form and after the HBr oxidation and CH₄ oxybromination tests.

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<th></th>
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<th>HBr oxidation</th>
<th>CH₄ oxybromination</th>
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<th>HBr oxidation</th>
<th>CH₄ oxybromination</th>
</tr>
</thead>
<tbody>
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<td>EuOBr/Al₂O₃</td>
<td>127</td>
<td>114</td>
<td>92</td>
<td>0.42</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>EuOBr/Al₂O₃-t</td>
<td>235</td>
<td>187</td>
<td>-</td>
<td>0.72</td>
<td>0.68</td>
<td>-</td>
</tr>
<tr>
<td>EuOBr/ZrO₂</td>
<td>29</td>
<td>25</td>
<td>24</td>
<td>0.19</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>EuOBr/ZrO₂-t</td>
<td>55</td>
<td>-</td>
<td>51</td>
<td>0.21</td>
<td>-</td>
<td>0.24</td>
</tr>
<tr>
<td>EuOBr/SiO₂</td>
<td>204</td>
<td>195</td>
<td>190</td>
<td>1</td>
<td>0.85</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Figure B.38. HBr conversion versus molar O₂:HBr ratio over EuOBr/Al₂O₃. Conditions: HBr:O₂:He = 4.5:1.3-9:94.37-86.5, $F_t/W_{cat} = 200$ cm³ min⁻¹ g⁻¹, $T = 523$ K, and $P = 1$ bar. The O₂ content was changed from the highest to the lowest value (down) and then increased back to the starting point (up). The test demonstrates that the robustness of bulk EuOBr is preserved in the supported catalytic system.
Figure B.39. X-ray diffractograms of $\gamma$-Al$_2$O$_3$, ZrO$_2$, and SiO$_2$ carriers, and EuOBr/Al$_2$O$_3$, EuOBr/ZrO$_2$, and EuOBr/SiO$_2$ catalysts in fresh form and after HBr oxidation shown in Figure 6.4a. Reference patterns shown as vertical lines below the measured diffractograms are identified on the right with their ICDD-PDF numbers.
Figure B.40. Thermogravimetric analysis of EuOBr/Al₂O₃, EuOBr/ZrO₂, and EuOBr/SiO₂ catalysts in fresh form and after the HBr oxidation tests presented in Figure 6.4a and Br₂ evolution signals evidenced for the used samples. The bottom plot was obtained by subtracting the weight loss profile of the precursor from that of the used catalyst to isolate the weight loss associated with the supported phase, assuming that the carrier is not affected by the reaction. The horizontal dashed line indicates the predicted weight loss upon complete transformation of the active phase to EuOBr. Only the EuOBr/Al₂O₃ displays a weight loss of similar magnitude, while the EuOBr/ZrO₂ catalyst shows a slightly lower weight loss. In contrast, the minimal weight loss observed in the case of EuOBr/SiO₂ suggests almost no bromination, which is in line with the EDXS mapping shown in Figure 6.5.
Figure B.41. Temperature-programmed reduction with hydrogen profiles of EuOBr/Al₂O₃, EuOBr/ZrO₂, and EuOBr/SiO₂ catalysts after the HBr oxidation tests presented in Figure 6.4a. The reduction profile of bulk EuOBr is shown for comparison. TCD signals are normalized with respect to the Eu content in the sample.

Figure B.42. CH₄ conversion and product selectivity versus temperature in CH₄ oxybromination over EuOBr/Al₂O₃, EuOBr/ZrO₂, and EuOBr/SiO₂ catalysts. Conditions: CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5, \( F_T/W_{\text{cat}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1} \), and \( P = 1 \text{ bar} \).
Figure B.43. CH₄ conversion and product selectivity versus temperature in CH₄ oxybromination over EuOBr/ZrO₂ catalyst for two Eu loadings of 9 wt.% and 4.5 wt.%. Conditions: CH₄:HBr:O₂:Ar:He = 6:6:3:4.5:80.5, \( \frac{F_T}{W_{cat}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1} \), and \( P = 1 \text{ bar} \). Decreasing the Eu content from 9 wt.% to 4.5 wt.% led to a very similar CH₄ conversion and selectivity to bromomethanes.
Chapter 7

Figure B.44. X-ray diffractograms and specific surface areas of the catalysts applied in the CH₄ oxybromination tests. Reference patterns identified with their ICDD-PDF numbers are provided as vertical lines below the measured diffractograms.

Figure B.45. CH₄ conversion and product selectivity in CH₄ oxidation over the catalysts. Conditions: CH₄:O₂:Ar:He = 6:3:4:5:86.5, $F_T/W_{cat} = 100$ cm$^3$ min$^{-1}$, and $P = 1$ bar.
Figure B.46. Mass spectra of reactant, product, and intermediate radical species detected at the outlet of the reactor in CH₄ oxybromination over VPO at different temperatures and concentrations of HBr and O₂. Conditions: CH₄:HBr:O₂:Ar = 2:0-2:0.3-0.5:19-21, \( F_T = 23.5 \text{ cm}^3 \text{ min}^{-1} \), \( W_{\text{cat}} = 0.05 \text{ g} \), and \( P = 1-4 \text{ kPa} \).
Figure B.47. Mass spectra of reactant, product, and intermediate radical species detected at the outlet of the reactor in CH₄ oxybromination over EuOBr at different temperatures and concentrations of HBr and O₂. Reaction conditions are equivalent to those reported in the caption of Figure B.46.
**Figure B.48.** Mass spectra of reactant, product, and intermediate radical species detected in CH₄ oxybromination performed using an empty reactor at different temperatures. Reaction conditions are equivalent to those reported in the caption of Figure B.46.
Figure B.49. Normalized peak areas of the signals corresponding to different reaction species observed in CH₄ oxybromination performed over the VPO and EuOBr catalysts, as well as in an empty reactor at different temperatures, concentrations of O₂ and HBr. Peak areas of various species presented in Figures B.46, B.47, and B.48 were normalized to constant integral intensity of ionizing radiation using acetone as an internal standard present at constant concentration in the chamber. The effect of slightly different expansion conditions and the photoionization cross sections were not taken into account. Reaction conditions are equivalent to those reported in the caption of Figure B.46.
Figure B.50. Conversion of CH$_4$ versus temperature in CH$_4$ oxybromination over the catalysts at different residence times. Shorter residence times progressively shift the temperature at which certain level of CH$_4$ conversion is achieved to higher values. This explains the higher temperature onset of this reaction under extremely short residence times applied in the PEPICO spectroscopy experiments. Conditions: CH$_4$:HBr:O$_2$:Ar:He = 6:6:3:4.5:80.5, $W_{\text{cat}}$ = 0.012-1 g, $F_T$ = 100-200 cm$^3$ min$^{-1}$, and $P$ = 1 bar.

Table B.8. Reaction energies and activation barriers of alternative reaction pathways during CH$_4$ oxybromination.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>$\Delta E$ / eV</th>
<th>$E_a$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl radical-methyl radical coupling</td>
<td>$2\text{CH}_3^* \rightarrow \text{C}_2\text{H}_6$</td>
<td>−4.10</td>
<td>0</td>
</tr>
<tr>
<td>Methyl radical-bromine coupling</td>
<td>$\text{CH}_3^* + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{Br}^*$</td>
<td>−1.08</td>
<td>0</td>
</tr>
<tr>
<td>Activation by surface bromine anion</td>
<td>$\text{CH}_4 + \text{Br}^* + \text{O}^* \rightarrow \text{CH}_3\text{O}^* + \text{OH}^*$</td>
<td>−0.07</td>
<td>1.76</td>
</tr>
<tr>
<td>Activation by surface oxygen anion</td>
<td>$\text{CH}_4 + 2\text{O}^* \rightarrow \text{CH}_3\text{O}^* + \text{OH}^*$</td>
<td>−0.94</td>
<td>1.79</td>
</tr>
</tbody>
</table>
Figure B.51. Rate of CH₄ oxybromination and CH₃Br disproportionation over VPO catalyst. CH₃Br disproportionation (2CH₃Br → CH₄ + CH₂Br₂) is shown to be >10 times slower compared to CH₄ oxybromination in which the rate-determining step is CH₄ bromination in the gas phase. Owning to the fact that CH₃Br is more reactive (ca. 10 times) in bromination compared to CH₄ (Kistiakowsky et al., J. Chem. Phys. 1944, 12, 469-478), the bromination of CH₃Br into CH₂Br₂ has a much higher contribution to the formation of CH₂Br₂ than the disproportionation route. Conditions: CH₄ oxybromination: CH₄:Br₂:O₂:Ar:He = 6:6:3:4.5:80.5, CH₃Br disproportionation: CH₃Br:Br₂:Ar:He = 1:3:4.5:91.5, W_cat = 1.0 g, and F_T = 100 cm³ min⁻¹. The tests were performed at P = 1 bar.
Appendix C

List of Publications and Presentations

Doctoral Publications

V. Paunović, P. Hemberger, A. Bodi, N. López, J. Pérez-Ramírez
Evidence of Radical Chemistry in Catalytic Methane Oxybromination
Nat. Catal. 2018, in press (Chapter 7)

V. Paunović, M. Artusi, R. Verel, F. Krumeich, R. Hauert, and J. Pérez-Ramírez
Lanthanum Vanadate Catalysts for Selective and Stable Methane Oxybromination

Activated TiC-SiC Composite for Natural Gas Upgrading via Catalytic Oxyhalogenation

V. Paunović, G. Zichittella, S. Mitchell, R. Hauert, J. Pérez-Ramírez
Selective Methane Oxybromination over Nanostructured Ceria Catalysts
ACS Catal. 2018, 8, 291-303 (Chapter 5)

G. Zichittella, N. Aellen, V. Paunović, A.P. Amrute, J. Pérez-Ramírez
Olefins from Natural Gas via Oxychlorination Catalysis
Angew. Chem. 2017, 129, 13858-13862

V. Paunović, R. Lin, M. Scharfe, A.P. Amrute, S. Mitchell, R. Hauert, J. Pérez-Ramírez
Europium Oxybromide Catalysts for Efficient Bromine Looping in Natural Gas Valorization
Angew. Chem. 2017, 129, 9923-9927 (Chapter 6)
Appendix C

G. Zichittella, V. Paunović, A.P. Amrute, J. Pérez-Ramírez
Catalytic Oxychlorination versus Oxybromination for Methane Functionalization
ACS Catal. 2017, 7, 1805-1817 (Chapter 3)

V. Paunović, G. Zichittella, R. Verel, A.P. Amrute, J. Pérez-Ramírez
Selective Production of Carbon Monoxide via Methane Oxychlorination over Vanadyl Pyrophosphate (Chapter 3)
Angew. Chem. Int. Ed. 2016, 55, 15619-15623 (hot paper, inside back cover, highlighted twice in Chemistry Views)
Angew. Chem. 2016, 128, 15848-15852

V. Paunović, G. Zichittella, M. Moser, A.P. Amrute, J. Pérez-Ramírez
Catalyst Design for Natural Gas Upgrading via Oxybromination Chemistry
Nat. Chem. 2016, 8, 803-809 (Chapter 2)

Interplay Between Surface Chemistry and Performance on Rutile-Type Catalysts for Halogen Production
Chem. Sci. 2016, 7, 2996-3005 (inside front cover)

M. Scharfe, P.A. Lira-Parada, V. Paunović, M. Moser, A.P. Amrute, J. Pérez-Ramírez
Oxychlorination-Dehydrochlorination Chemistry on Bifunctional Ceria Catalysts for Intensified Vinyl Chloride Production
Angew. Chem. Int. Ed. 2016, 55, 3068-3072
Angew. Chem. 2016, 128, 3120-3124

Presentations

V. Paunović, R. Lin, M. Scharfe, A.P. Amrute, S. Mitchell, R. Hauert, J. Pérez-Ramírez
Poster: Europium Oxybromide for Efficient Bromine Looping in Natural Gas Upgrading
Materials, Characterization, and Catalysis Workshop, Zurich, Switzerland, August 2018
V. Paunović, R. Lin, M. Scharfe, A.P. Amrute, S. Mitchell, R. Hauert, J. Pérez-Ramírez
Poster: Europium Oxybromide as an Integral Catalytic Platform for Bromine-Mediated Natural Gas Upgrading
**Fall Meeting NSCS**, Bern, Switzerland, August 2017

V. Paunović, G. Zichittella, A.P. Amrute, J. Pérez-Ramírez
Talk: HCl-Mediated Partial Oxidation of Methane for Selective CO Production
**Fall Meeting NSCS**, Zurich, Switzerland, September 2016.
*Winner of the Runner-Up Award*

V. Paunović, G. Zichittella, M. Moser, A.P. Amrute, J. Pérez-Ramírez
Talk: Catalyst Design for HBr-Mediated Natural Gas Upgrading
**16th International Congress on Catalysis**, Beijing, China, July 2016
*Winner of the Chemistry Travel Award*

V. Paunović, Z. Guo, G. Zichittella, J. Pérez-Ramírez
Poster: Novel Catalysts for the Oxybromination of Methane
**Fall Meeting NSCS**, Lausanne, Switzerland, September 2015

V. Paunović, J. Straus, M. Moser, I. Czekaj, Javier Pérez-Ramírez
Poster: Ethylene Oxychlorination over Deacon Catalysts
**Fall Meeting NSCS**, Zurich, Switzerland, August 2014
Appendix D

Curriculum Vitae

Name
Vladimir Paunović

Date of birth
March 6th, 1989

Place of birth
Užice, Serbia

Nationality
Serbia

Education

2014-2018
Doctoral studies under the supervision of Prof. Dr. Javier Pérez-Ramírez, Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

2012-2013
Master studies in Chemical Engineering, Faculty of Technology and Metallurgy, University of Belgrade, Serbia Master thesis: “Application of Nonlinear Frequency Response Analysis for Studying Enzymatic Processes: Enzymes Showing Direct Electron Transfer Mechanism. Case study: Hydrogenase” realized at Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany under the supervision of Prof. Dr. Menka Petkovska and Prof. Dr. Kai Sundmacher

2008-2012
Bachelor studies in Chemical Engineering, Faculty of Technology and Metallurgy, University of Belgrade, Serbia