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# Halogen Chemistry on Catalytic Surfaces

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**Abstract:** Halogens are key building blocks for the manufacture of high-value products such as chemicals, plastics, and pharmaceuticals. The catalytic oxidation of HCl and HBr is an attractive route to recover chlorine and bromine in order to ensure the sustainability of the production processes. Very few materials withstand the high corrosiveness and the strong exothermicity of the reactions and among them RuO<sub>2</sub> and CeO<sub>2</sub>-based catalysts have been successfully applied in HCl oxidation. The search for efficient systems for HBr oxidation was initiated by extrapolating the results of HCl oxidation based on the chemical similarity of these reactions. Interestingly, despite its inactivity in HCl oxidation, TiO<sub>2</sub> was found to be an outstanding HBr oxidation catalyst, which highlighted that the latter reaction is more complex than previously assumed. Herein, we discuss the results of recent comparative studies of HCl and HBr oxidation on both rutile-type (RuO<sub>2</sub>, IrO<sub>2</sub>, and TiO<sub>2</sub>) and ceria-based catalysts using a combination of advanced experimental and theoretical methods to provide deeper molecular-level understanding of the reactions. This knowledge aids the design of the next-generation catalysts for halogen recycling.

**Keywords:** Ceria-zirconia · Hydrogen halides · Oxidation · Prompt gamma activation analysis · Rutile-type oxides.

## Introduction

Halogens are widely applied as reactive intermediates in the synthesis of various commodities in the chemical, pharmaceutical, and plastics industry.<sup>[1]</sup> However, about half of the halogens are reduced to undesired hydrogen halides and halide salts. The copious formation of HCl or HBr by-products is a serious challenge, since options to deal with this waste stream such as marketing or neutralization are unattractive.<sup>[1]</sup> The recovery of Cl<sub>2</sub> and Br<sub>2</sub> from HCl and HBr has been recognized as the most appealing route in order to maintain an economically feasible and environmentally friendly process design. Amongst the available options, catalytic oxidation has been shown to be the most waste- and cost-efficient method to achieve this.<sup>[1,2]</sup>

The study of HCl oxidation dates back to the 1860s, when Henry Deacon invent-

ed the process to recover chlorine for the Leblanc process.<sup>[1a,b]</sup> The corrosiveness and the high exothermicity of the reaction was detrimental to the CuCl<sub>2</sub>-based catalyst, which suffered from volatilization of its active phase. The Deacon process was eventually abandoned in the 1890s due to substitution of the Leblanc process by the Solvay process.<sup>[1a,b]</sup> Still, various companies and researchers attempted throughout the 20<sup>th</sup> century to improve the Cu-based catalysts or to identify new systems.<sup>[1a,b]</sup> At the turn of the millennium, RuO<sub>2</sub>-based catalysts, developed independently by Sumitomo Chemicals and Bayer MaterialScience, were implemented as the new generation of highly active and stable HCl oxidation catalysts for chlorine recycling within the manufacture of polyurethanes and polycarbonates.<sup>[1a]</sup> In the continuous search for more alternative catalysts, other metal oxides such as CeO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, and CuCrO<sub>2</sub>, have been discovered.<sup>[3]</sup> In particular, ceria has received considerable attention, which culminated in the formulation of a technical CeO<sub>2</sub>/ZrO<sub>2</sub> catalyst with stable performance in pilot studies.<sup>[4]</sup>

The development of an analogue catalytic HBr oxidation process was first attempted in the 1930s by George Hooker, who adopted the original Deacon concept.<sup>[5]</sup> HBr oxidation has been investigated by different companies in the past decades, but the implementation was inhibited due to the difficulties of identifying stable catalysts and a safe process.<sup>[2b]</sup> Research in bromine recovery was re-

vised when the increased production of unconventional natural gas prompted the potential use of Br<sub>2</sub> to functionalize the inert alkanes into alkyl bromides for further conversion into fuels and chemicals.<sup>[1c,2a]</sup> The search for a cost-efficient bromine recovery process logically led to the investigation of HCl oxidation catalysts for HBr oxidation. CeO<sub>2</sub>-based and rutile-type (*i.e.* RuO<sub>2</sub> and IrO<sub>2</sub>) materials have been shown to catalyze HBr oxidation, corroborating the anticipated chemical similarities of both reactions.<sup>[6]</sup> However, the unexpected activity of TiO<sub>2</sub> in HBr oxidation, despite its inactivity in HCl oxidation, underlined that the mechanism of HBr oxidation has features distinct from that of HCl oxidation.<sup>[7]</sup> To close this gap in understanding, dedicated studies are needed to rationalize the relationship between the state of the surface and the apparent performance over both rutile-type and ceria-based catalysts in HBr oxidation.

In this article, we discuss the strategy for an integrated approach to halogen chemistry and present advanced methods, *i.e.* temporal analysis of products (TAP) and prompt gamma activation analysis (PGAA), as key techniques to experimentally analyze mechanistic aspects and the state of the catalyst surface under working conditions. We outline the interplay between the surface chemistry and the performance in HCl and HBr oxidation over rutile-type and ceria-based catalysts. We highlight the necessity to individually optimize the catalyst formulation for either HCl or HBr oxidation.

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## Integrated Approach to Halogen Chemistry

Throughout the research on HCl and HBr oxidation, the study of the surface chemistry under working conditions has been hampered by the corrosiveness of the reactants. Mechanistic studies mostly emphasized on *ex situ* characterization such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM), as well as molecular modeling.<sup>[8]</sup> Further, ultra-high vacuum (UHV) methods, such as the high-resolution core-level shift, enables the study of surface processes under reaction atmosphere over single RuO<sub>2</sub> crystals.<sup>[9]</sup> However, to connect the molecular-level studies on model surfaces to the apparent performance of real-life catalysts the pressure and materials gaps have to be closed.<sup>[10]</sup> For this purpose, an integrated approach was developed by combining different characterization techniques (Fig. 1a). The key methods of this strategy are theoretical studies using density functional theory (DFT), transient mechanistic studies using temporal analysis of products (TAP),<sup>[11]</sup> and the quantification of the halogen uptake under working conditions with *operando* prompt gamma activation analysis (PGAA),<sup>[4,8c,12]</sup>

TAP is a highly advanced technique to study mechanisms of experimentally demanding reactions over industrially relevant catalysts.<sup>[10]</sup> Small amounts (10<sup>6</sup> molecules) of the reactants are pulsed over the catalyst bed and are analyzed by quadrupole mass spectroscopy (QMS) as shown in Fig. 1b. The reactants can be pulsed individually, simultaneously, or in pump-probe fashion, *i.e.* with distinct time delay between individual reactant pulses. Key advantages of TAP comprise (i) a millisecond time resolution, (ii) the use of practical catalysts, (iii) excellent temperature control, and (iv) safe operation. These aspects

make TAP a unique technology to bridge the pressure and material gap between UHV and real-life catalytic conditions.<sup>[10]</sup>

PGAA has been shown to be a direct and reliable method to determine the elemental composition of the catalysts under reaction conditions.<sup>[4,8c,12]</sup> The working principle is based on radiative neutron capture, or (*n, γ*) reaction upon irradiation of the sample with cold neutrons (Fig. 1c). The nuclei capture the neutrons and promptly emit typically 2 to 4 gamma rays in a cascade before returning to the ground state. The gamma radiation is characteristic, *i.e.* the energy values of the gamma rays identify the nuclide, and their intensities are proportional to the number of atoms present in the analyzed volume. The sensitivity and the detection limit of PGAA differ from element to element, and depend on the partial gamma-ray production cross-section, the detector efficiency and the level of the baseline at the analytical line. The dynamic range of the method is limited by either the too low sensitivity, such as for oxygen, or by the too high counting rate that overloads the counting system, *e.g.* with iridium.<sup>[13]</sup>

## Surface Chemistry and Performance of Rutile-type Catalysts for Halogen Production

RuO<sub>2</sub>-based materials are the current state-of-the-art catalysts for HCl oxidation and have received widespread attention amongst researchers, who aimed to understand the reaction mechanism and to lower the amount of precious ruthenium required in the catalyst composition.<sup>[14]</sup> Besides RuO<sub>2</sub>, also IrO<sub>2</sub> was discovered to be active in HCl oxidation.<sup>[15]</sup> Both metal oxides comprise a dense rutile-type structure that inhibits the penetration of chlorine atoms into the subsurface layers. IrO<sub>2</sub> operates, however, at much higher temperature compared to RuO<sub>2</sub> due to its larger chlorine

evolution barrier. With respect to the catalyst scale up, both metal oxides can be dispersed in the form of small nano layers or clusters on TiO<sub>2</sub>-rutile, which is due to lattice matching (RuO<sub>2</sub>) or electronic effects (IrO<sub>2</sub>). Owing to their robustness in HCl oxidation, both catalysts were considered potential candidates for a stable oxidation of HBr. In fact, the comparison of their activities in HCl and HBr oxidation revealed that they oxidize HBr at much lower temperature (Fig. 2a).<sup>[6]</sup> The activity of TiO<sub>2</sub> for HBr oxidation<sup>[7]</sup> was not expected due to the inactivity in HCl oxidation which led to the commonly accepted theory that TiO<sub>2</sub> cannot catalyze hydrogen halide oxidation due to its inability to adsorb and dissociate molecular oxygen.<sup>[16]</sup>

In-depth studies were undertaken to assess and compare the rutile-type catalysts in HCl and HBr oxidation. Despite its stability in HCl oxidation, RuO<sub>2</sub> brominates in contrast to TiO<sub>2</sub>, which led to changes in the crystallinity observed by HRTEM and supported by *ab initio* thermodynamics, suggesting that the replacement of lattice oxygen is more exothermic in RuO<sub>2</sub> than TiO<sub>2</sub>, facilitating a strong bromination of the surface and subsurface (Fig. 2b).<sup>[17]</sup>

To shed light on the reaction mechanism, the surface of TiO<sub>2</sub> was studied with XPS, which evidenced the formation of Ti<sup>3+</sup> sites during the HBr oxidation;<sup>[7]</sup> an indication of the formation of surface defects. Theoretical calculations on this defect formation ultimately proposed that the replacement of the bridge oxygen with a bromine atom is a self-doping mechanism that eventually enables the adsorption of molecular oxygen due to the smaller energetic barrier to transfer the electrons from the bromide to the oxygen (Fig. 2c).<sup>[7]</sup> In contrast to that, the energetic barrier of the chlorine doped surface is too large to enable the activation of molecular oxygen on the surface.

DFT indicated that the reaction mech-

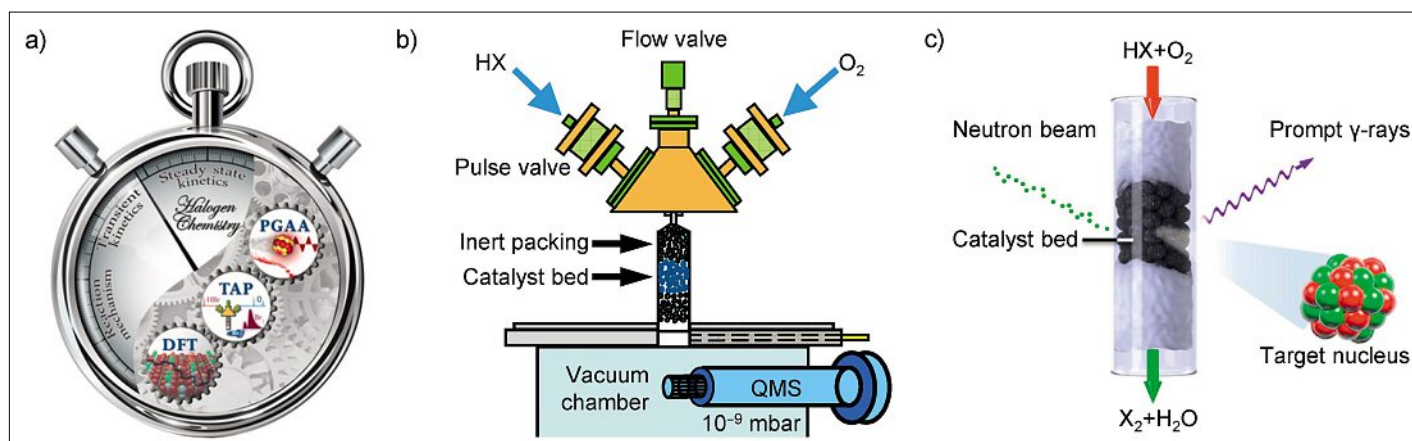


Fig. 1. The synchronization of advanced techniques bridges the pressure and materials gap between molecular studies and catalytic evaluation under working conditions (a). Transient mechanistic studies on real-life catalysts are conducted using TAP at millisecond time resolution (b). The uptake of halogens on the catalysts under working conditions is quantified using PGAA (c).

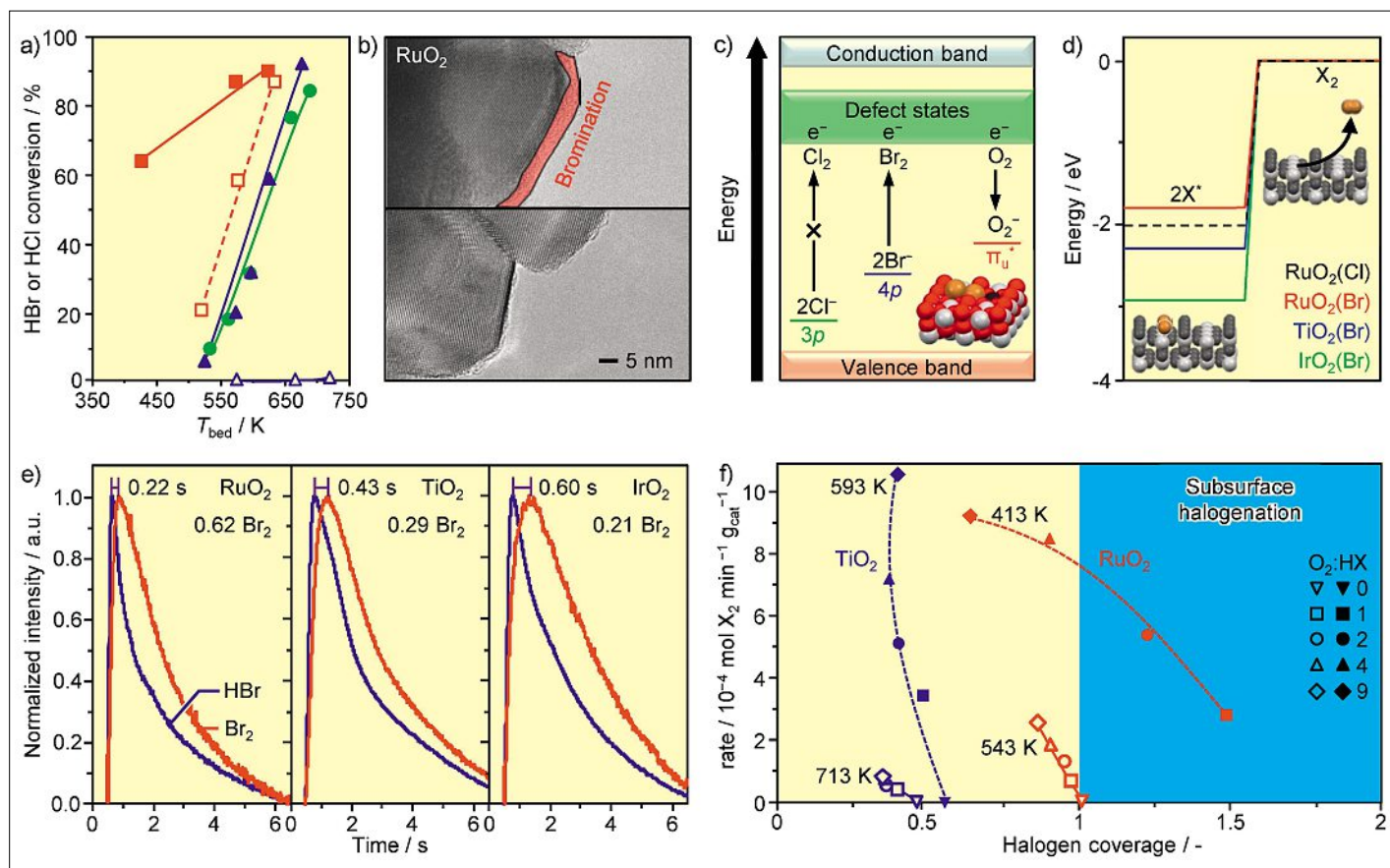


Fig. 2. Activity versus temperature for RuO<sub>2</sub> (red), IrO<sub>2</sub> (green) and TiO<sub>2</sub> (blue) in HCl (dashed line) and HBr (solid lines) oxidation (a). HRTEM micrographs of RuO<sub>2</sub> (b) treated in HBr (top) and HCl (bottom). Illustration of the band gap of the semiconductor TiO<sub>2</sub> (c). DFT calculation for the halogen evolution on halogenated rutile-type surfaces (d). Normalized HBr and Br<sub>2</sub> responses after simultaneous HBr and O<sub>2</sub> pulsing for rutile-type catalysts (e). Activity versus halogen coverage over TiO<sub>2</sub> and RuO<sub>2</sub> in HCl (open symbols) and HBr (solid symbols) oxidation at different oxygen partial pressures (f).

anism follows the same path with bromine evolution as the most energy demanding step (Fig. 2d).<sup>[7]</sup> The calculations were corroborated by TAP studies, which showed that the bromine evolution from the surface is the slowest step. Furthermore, the time delay between the HBr and the Br<sub>2</sub> pulse increases in the order: RuO<sub>2</sub> < TiO<sub>2</sub> < IrO<sub>2</sub>, which is in agreement with the increase in the calculated energy barriers (Fig. 2e)<sup>[17]</sup> This also supports that bromine evolution is easier on TiO<sub>2</sub> than IrO<sub>2</sub> and explains that the apparently similar activity of both catalysts in HBr oxidation results from a compensation effect between the surface coverage and the reaction kinetics.<sup>[7,17]</sup>

The quantitative determination of the halogen uptake under working conditions using PGAA demonstrates that RuO<sub>2</sub> suffers from extensive subsurface bromination, at low O<sub>2</sub>:HBr ratios and temperatures, which agrees with the microscopic studies and *ab initio* thermodynamics. TiO<sub>2</sub> exhibits inherently low halogen coverage (30–50%) at all conditions due to its unique defect-driven mechanism (Fig. 2f).<sup>[17]</sup> In HCl oxidation, TiO<sub>2</sub> is inactive and the chlorination of the active RuO<sub>2</sub> is limited to the surface. Correlating the halogen uptake to the apparent performance ev-

idenced the completely different behavior of the rutile materials under working conditions, which points to the need for further optimization of the stability of RuO<sub>2</sub> if an application at low reaction temperatures is desired. One way could be the formulation of mixed Ru-Ti oxides to decrease the surface bromination and inhibit the penetration of bromine into the subsurface.

### Stability and Activity of Mixed Ce-Zr Oxides in HCl and HBr Oxidation

Similar stability issues, as seen for RuO<sub>2</sub> in HBr oxidation, were already known from the case of CeO<sub>2</sub> in HCl oxidation.<sup>[3a]</sup> CeO<sub>2</sub> suffers from subsurface chlorination under harsh reaction conditions as evidenced by *operando* PGAA, forming stable and inactive cerium chloride.<sup>[12]</sup> In an attempt to stabilize the CeO<sub>2</sub> different support materials were investigated, which led to the discovery of the supported CeO<sub>2</sub>/ZrO<sub>2</sub> systems.<sup>[4]</sup> It was shown that the ZrO<sub>2</sub> support reduced the chlorine uptake and increased the activity of CeO<sub>2</sub> significantly, which was suggested to be linked to stabilization of CeO<sub>2</sub> nanostruc-

tures and the formation of Ce-Zr mixed oxides.<sup>[4]</sup> The formation of mixed Ce-Zr oxides positively affects the performance in HCl oxidation due to improved redox properties and higher thermal stability.<sup>[13]</sup> However, the impact of the catalyst's morphology, *i.e.* how well Ce and Zr have to be intermixed at an atomic or particle level to achieve these properties, was unknown.

To study the impact of zirconia on the performance of ceria, different ceria-zirconia mixed oxides were prepared exhibiting distinct morphologies that are either homogeneous or non-homogeneous mixed Ce-Zr oxides as shown by energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. 3a). The catalytic performance in HCl oxidation of both materials is very comparable.<sup>[13]</sup> However, in HBr oxidation distinctions became evident as the catalytic activity of non-homogeneous materials dropped more strongly within 40 h compared to the homogeneous mixed oxide (Fig. 3b).

PGAA studies on the different mixed Ce-Zr oxides indicated that CeO<sub>2</sub>-based catalysts are more prone to bromination than chlorination (Fig. 3c,d), which is detrimental to their stability. The chlorine uptake under different reaction conditions

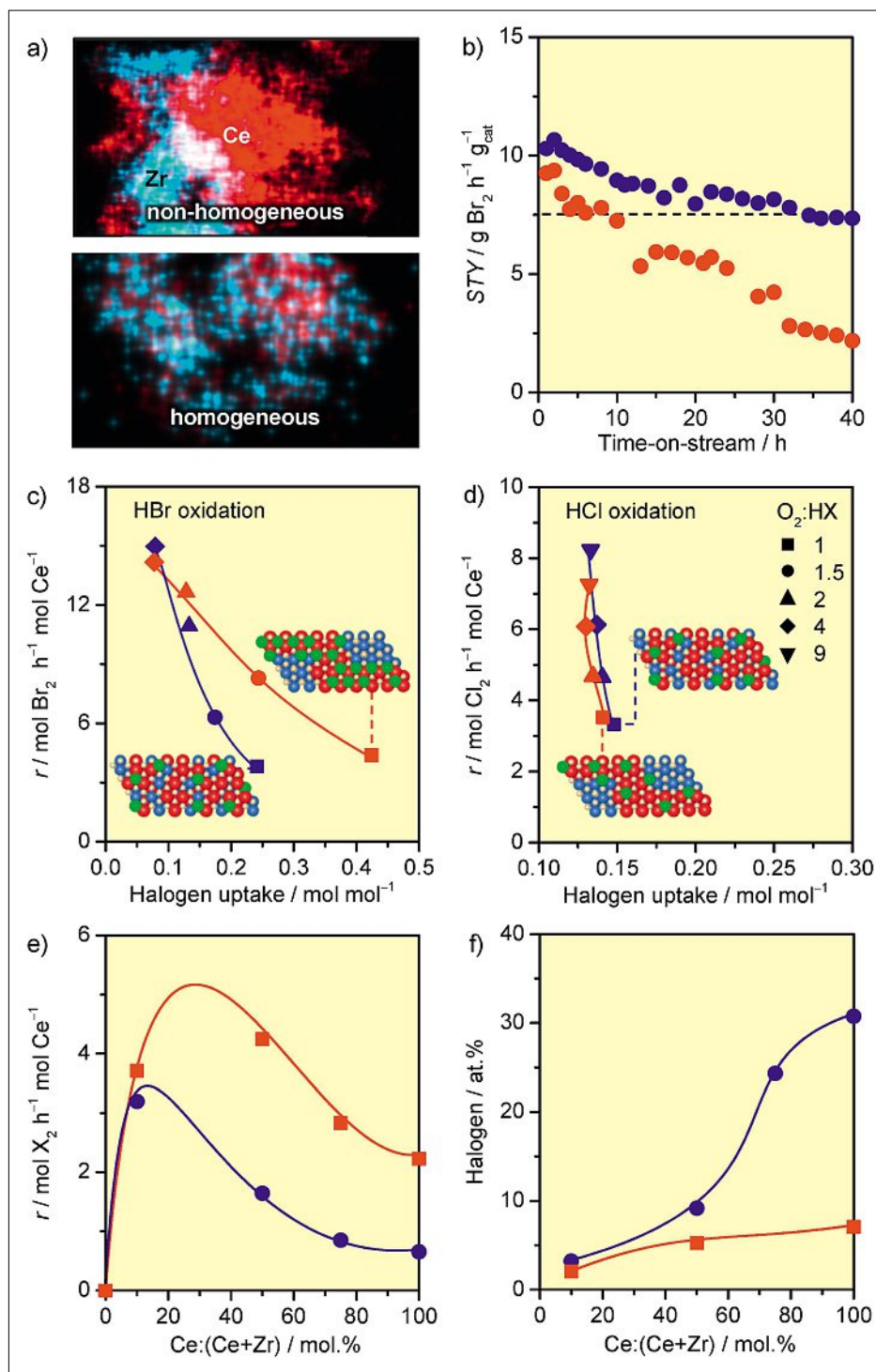


Fig. 3. EDS mapping of different mixed Ce-Zr oxides (a). Activity versus time on stream (b) and halogen uptake at different oxygen partial pressures (c,d) for homogeneous (blue) and non-homogeneous (red) mixed Ce-Zr oxides. Activity (e) and halogen content (f) versus Ce content of the homogeneous catalysts in HCl (red) and HBr (blue) oxidation.

was comparable over both materials and did not significantly change when reducing oxygen partial pressures. The bromine uptake of the non-homogeneous sample was up to 50% higher compared to the homogeneous counterpart (Fig. 3c).<sup>[13]</sup> This indicates that the stability can be optimized by the atomic-level intermixing of the Ce and Zr phases apart from tuning the reaction conditions.

In order to assess the influence of the

composition of the homogeneous ceria-zirconia solid solution on the catalytic performance, CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides with variable Zr content were tested in HCl and HBr oxidation.<sup>[13]</sup> The highest reaction rate over ceria-zirconia in both HBr and HCl oxidation was achieved with Zr contents between ca. 90 and 70 mol.% (Fig. 3e) at which point the halogen content reaches a minimum (Fig. 3f). For pure CeO<sub>2</sub> (i.e. 100 mol.%), the bromine content is about

four times higher than that of chlorine, due to the stronger tendency for bromination than chlorination. As the bromine content is higher than that of chlorine, the optimum for the HBr oxidation seems to have further shifted towards a higher Zr content (Fig. 3e), which underlines the distinctions in the optimal design of Ce-Zr catalysts for application in either HCl or HBr oxidation. In this respect, the Ce:Zr ratio is the key optimization parameter to tune the stability of the CeO<sub>2</sub>-based catalysts.

## Conclusions

The study of catalytic hydrogen halide oxidation is experimentally challenging, which presents significant demands for the mechanistic analysis and characterization of catalysts under working conditions. The combination of advanced techniques such as TAP and *operando* PGAA with theoretical calculations comprise an optimal approach to understand halogen chemistry on catalytic materials. This strategy enabled the rationalization of the exceptional activity of TiO<sub>2</sub> and the stability issues of RuO<sub>2</sub>- and CeO<sub>2</sub>-based catalysts in HBr oxidation. The comparison between HBr and HCl oxidation indicated that the catalyst design criteria applied in HCl oxidation cannot be directly extrapolated to the recycling of Br<sub>2</sub>. Thus, catalyst design should be tailored for each reaction. The investigation showed that the halogen coverage under working conditions is the best parameter to assess the catalytic performance, which also highlights the significance of PGAA for this research. The surface halogenation can be tuned by optimizing the reaction conditions or the catalyst formulation which provides the foundation for future work on developing more stable and active catalysts not only for halogen recovery, but also for other halogen-based reactions such as the oxyhalogenation of hydrocarbons.

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