Structure of Flame-Made Mixed Metal-Oxide Based Catalysts

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“No bird soars too high if he soars with his own wings.”
(William Blake)
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Mixed metal-oxide based catalysts constitute a large fraction of today’s heterogeneous catalysts. Especially supported transition metal oxides like V$_2$O$_5$, have proven to be very attractive materials for all kinds of catalytic applications including selective catalytic reduction (SCR), selective partial oxidations, total oxidations and oxidative dehydrogenations. Although vanadia-based catalysts are industrially applied for several decades now and extensive research has been carried out, the key parameters and properties of the active species leading to high activity and selectivity are not completely understood. In order to advance this knowledge and understand the main species of the active site involved in the catalytic reaction, model catalysts of high purity and reproducibility have to be synthesized and characterized.

Typically these materials are synthesized with classic wet-chemistry synthesis methods (sol-gel hydrolysis, wet-impregnation, precipitation) involving several process steps which often take days to collect the final catalysts. Control and reproducibility in these methods can be very limited. In this work the application of flame spray pyrolysis (FSP) as powerful tool for the single-step synthesis of mixed metal-oxide catalysts with high purity and reproducibility was explored. Special focus was placed but not limited on vanadia-based supported catalysts and the characterization of the material properties like specific surface area, crystallinity, reducibility and the VO$_x$ species structure,
which constitute the active sites. Furthermore the influence of said structure on
the catalytic behavior in different catalytic applications was analyzed. In case of
supported noble metal catalysts emphasis was put on tuning the surface ionicity
of the support and analyzing its influence on the catalytic performance.

In chapter 1 gives an overview of the synthesis of mixed metal oxide
catalysts with special focus on the vanadia-based catalysts. The classic
“monolayer theory” for the VO\textsubscript{x} species structure representing the results of
conventionally made materials is briefly discussed. An overview about current
advances in using flame processes, including vapor- and liquid-fed flames, for
the synthesis of vanadia-based mixed-metal oxides are presented, focusing of the
structure and dispersion of the VO\textsubscript{x} species made by these methods and the
influence of these structures on the catalytic performance. Additionally a brief
overview of other flame-made mixed metal oxide catalysts including also
supported noble metal catalysts is given. Finally, based on the research
experience collected over the past decade an attempt is made to assess the
potential and limitations of flame synthesis for catalytic mixed-metal oxide
materials and future challenges in research are identified.

In chapter 2 V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts made by FSP are explored. Such flame-
made catalysts showed unique characteristics and the synthesis method allows
precise control of the catalysts morphology. Properties like specific surface,
crystallinity, V dispersion and VO\textsubscript{x} species structure could be tailored by the
synthesis parameters such as choice of precursor concentration, liquid and gas
feed rates resulting in low and high enthalpy flames. Due to the significant
difference of the boiling and melting points of the TiO\textsubscript{2} (support) and V\textsubscript{2}O\textsubscript{5},
titania particles formed first in the flame and vanadia subsequently condensed
on the TiO\textsubscript{2} surface. The extremely high cooling rates in the flame favored high
V dispersion resulting in dominantly amorphous mono- and oligomeric VO\textsubscript{x}
species even at high V surface coverage (>8 V nm\textsuperscript{2}). This was never achieved for
conventional wet-chemistry derived catalysts which showed always the presence
of crystalline V\textsubscript{2}O\textsubscript{5} at such high V loading. These amorphous species were stable
up to temperatures of 450°C and surface densities of 27 V nm\textsuperscript{2}. The catalysts
were deposited directly from the aerosol onto ceramic foam substrates for the
catalytic evaluation in the selective partial oxidation of o-xylene to phthalic
anhydride. The activity of both flame-made and wet-impregnated catalysts seemed to depend only on the available V surface sites scaling only with the V surface density and specific surface area. The structure of these species, however, had almost no influence on the o-xylene conversion. In case of selectivity, however, a strong dependency on the structure (amorphous vs. crystalline) was found. Catalysts exhibiting only amorphous mono- and oligomeric VO\textsubscript{x} species showed significantly higher selectivity than catalysts exhibiting V\textsubscript{2}O\textsubscript{5} crystallites.

FSP was used to prepare V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts of constant surface area with varying vanadia loading (3-30 wt.%) and tested in the removal of volatile organic compounds, namely the total oxidation of chlorobenzene (chapter 3). XPS analysis proved the high V dispersion achieved in the flame compared to wet-impregnated materials and corroborated the results from Raman analysis. In contrast to the partial oxidation reaction, activity in the total oxidation seemed to be influenced by both, amount and structure of the VO\textsubscript{x} species. Increasing the vanadia content increased the conversion at given reaction temperature with a maximum around 12 V nm\textsuperscript{2} and 16 V nm\textsuperscript{2} for the flame- and classic wet-impregnated catalysts, respectively. Compared to wet-impregnated catalysts, the FSP-made V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} with higher V dispersion showed always lower catalytic activity at similar composition. It was proposed that for the total oxidation of chlorobenzene the presence of oligomeric VO\textsubscript{x} species, namely the V-O-V bonds, still in the vicinity of the TiO\textsubscript{2} support are beneficial for activity and could be the most active VO\textsubscript{x} species. Catalysts with high V dispersion and dominantly monomeric species as well as catalysts with high V surface density (>16 V nm\textsuperscript{2}) showed inferior catalytic performance. The presence of crystalline V\textsubscript{2}O\textsubscript{5} seemed to have no negative effect on the catalytic activity. For the first time it was shown that V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts with V surface densities even beyond the monolayer can be very active in the total oxidation of chlorobenzene.

Additionally FSP was applied for the synthesis of V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts for the application in the oxidative dehydrogenation of propane (chapter 4). Similar as for the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts exceptional high V dispersion compared to conventional preparation techniques was achieved. The as-prepared catalysts showed dominantly monomeric species on the silica surface up to V surface
density of 4.6 V nm\(^{-2}\). These species were stable under reaction conditions up to 2 V nm\(^{-2}\). At higher V surface density the structure of the VO\(_x\) species changed during reaction forming more and more crystalline V\(_2\)O\(_5\). The activity of the flame-made V\(_2\)O\(_5\)/SiO\(_2\) strongly depended on the vanadium loading reaching a conversion maximum at 4.6 V nm\(^{-2}\). For the ODH reaction monomeric species showed the highest selectivity to propylene while the presence of crystalline V\(_2\)O\(_5\) favored the total oxidation products CO\(_x\). Nevertheless, highest propylene yield were found for catalysts containing both, monomeric and crystalline species underscoring the unique catalytic performance of such flame-derived catalysts.

In light of the possible application in the ODH reaction flame-made V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts were briefly explored in chapter 5 with the same synthesis method. Similar to the silica and titania supported materials the structure of the VO\(_x\) species depended on the vanadia loading and surface area of the support. Catalysts containing more than 10 wt.% V\(_2\)O\(_5\) showed a diminishing of the alumina crystallinity. Raman analysis of the catalyst containing 30 wt.% V\(_2\)O\(_5\) showed indications of a AlVO\(_4\) phase not detected by XRD. In contrast to silica and titania, alumina seems to favor the formation of a solid solution at high vanadia contents.

Finally, in chapter 6 the versatility of flame spray pyrolysis for the synthesis of tailor-made mixed metal-oxides was shown for supported noble metal catalysts. The surface acid/base properties of Pt/Al\(_2\)O\(_3\) catalysts were tailored by doping either with SiO\(_2\) (0-100 wt.%) or Cs\(_2\)O (0-10 wt.%) directly in the flame. Up to 50 wt.% SiO\(_2\) the BET surface areas could be kept constant while defined control of the Pt particle size was not achieved due to the increasing Pt particle size with increasing silica content. Highest acidity was achieved for the catalysts containing 22-30 wt.% SiO\(_2\) as evidenced by TPD of NH\(_3\). These SiO\(_2\)-doped catalysts were highly active in the hydrogenation of acetophenone. The strong influence of the support acidity on the properties of the Pt-H system were evidenced by the significant increase of the hydrogenolysis byproducts with increasing SiO\(_2\)-content by more than 20-fold. The addition of Cs\(_2\)O had significant influence on the specific surface area and resulted in a surface enrichment of the Cs at the Al\(_2\)O\(_3\) surface. Accordingly support ionicity
was strongly influenced already a very low Cs$_2$O content increasing surface basicity with increasing Cs loading. The unique surface properties had strong influence: Only 0.25 wt.% Cs$_2$O blocked the hydrogenolysis of 1-phenylethanol to ethylbenzene.

The development of new catalysts with tailor-made properties requires the basic understanding of the influence of the different structures of active species and support compositions in certain catalytic applications. Flame synthesis and especially flame spray pyrolysis has been proven to advance this knowledge by providing easy accessible model catalysts of high purity and reproducibility with good catalytic performance. Additionally this synthesis method is easy scalable and allows material production not only in the lab scale but also in pilot or industrial scale, important for future application of such flame-derived catalysts in industry.
Zusammenfassung

Mischoxid basierte Katalysatoren stellen einen beträchtigen Anteil heutzutage eingesetzter heterogener Katalysatoren dar. Besonders geträgerte Oxide der Übergangsmetalle wie zum Beispiel V₂O₅ haben sich als äußerst attraktive Materialien für die unterschiedlichsten katalytischen Anwendungen (z.B. selektive katalytische Reduktion (SCR), selektive partielle Oxidation, oxidative Dehydrierung etc.) erwiesen. Speziell die Vanadiumoxid basierten Katalysatoren sind schon seit Jahrzehnten im industriellen Einsatz und die wissenschaftliche Forschung hat sich intensiv mit diesen Materialien auseinandergesetzt. Dennoch sind bis heute die entscheidenden Parameter und Eigenschaften der aktiven Spezies zum Erreichen der höchsten Aktivität und Selektivität noch nicht ausreichend verstanden. Um dieses Wissen weiter voranzutreiben und ein besseres Verständnis über die aktive Spezies während der katalytischen Reaktion zu erlangen, werden umfassend charakterisierte Modell-Katalysatoren von hoher Reinheit und guter Reproduzierbarkeit benötigt.

Klassischerweise werden solche Materialien mit konventionellen Nass-Chemie Synthesemethoden (Sol-Gel Hydrolyse, Nass-Imprägnierung, Fällung) hergestellt. Diese Methoden beinhalten mehrere Prozessschritte und die Herstellung dauert oft mehrere Stunden oder gar Tage, wobei die Kontrolle über die Eigenschaften und die Reproduzierbarkeit oft zu wünschen übriglässt.
In dieser Arbeit wurde die Flammen-Sprüh-Pyrolyse (FSP) als vielseitige Synthesemethode für die Herstellung von Mischoxid-Katalysatoren von hoher Reinheit und Reproduzierbarkeit angewendet und untersucht. Dabei wurde der Fokus speziell auf V$_2$O$_5$-basierte geträgerte Katalysatoren und deren Charakterisierung in Bezug auf spezifische Oberfläche, Kristallinität und Struktur der VO$_x$ Spezies, welche das aktive Zentrum in der Katalyse bilden, gelegt. Die flammen-synthetisierten Katalysatoren wurden hinsichtlich ihres katalytischen Verhaltens untersucht. Im Falle von geträgerten Edelmetall Katalysatoren wurde der Schwerpunkt auf das Einstellen der Oberflächenacidität des Trägeroxids und deren Einfluss auf die Katalyse analysiert.

Im ersten Kapitel dieser Arbeit wird die klassische “Monolagen-Theorie” und Struktur der VO$_x$ Spezies basierend auf konventionell hergestellten Katalysatoren kurz erläutert. In einem Überblick werden die aktuellsten Fortschritte im Bereich der Flammensynthese von V$_2$O$_5$-basierten Mischoxidkatalysatoren diskutiert. Dabei wird spezielles Augenmerk auf die Vanadium Dispersion sowie Struktur der VO$_x$ Spezies gelegt und der Einfluss auf die Katalyse aufgezeigt. Desweiteren wird ein allgemeiner Überblick über mittels Flammensynthese hergestellt Mischoxid basierte Katalysatoren gegeben, inklusive geträgerten Edelmetallkatalysatoren. Abschließend wird versucht das Potential und die Limitationen der Flammen-Synthese herauszuarbeiten und ein kurzer Ausblick auf die zukünftigen Herausforderungen gegeben.

Die durch die Flammen-Sprüh-Pyrolyse hergestellten V$_2$O$_5$/TiO$_2$ Katalysatoren zeigten einzigartige Charakteristika und die Flammensynthese erlaubte hervorragende Kontrolle der Partikelmorphologie. Eigenschaften wie zum Beispiel spezifische Oberfläche, Kristallinität, Vanadium Dispersion und Struktur der VO$_x$ Spezies konnten durch die Wahl der Syntheseparameter (z.B. Precursorkonzentration, Gas- und Flüssigkeitsförderrate) eingestellt werden. Auf Grund der deutlich höheren Siede- und Schmelztemperatur des Trägeroxids (TiO$_2$) im Vergleich zum Vanadiumoxid bildeten sich die Titandioxidpartikel zuerst in der Flamme während das VO$_x$ erst später durch Kondensation auf der TiO$_2$ Oberfläche bildete. Die sehr hohen Abkühlraten in
der Flammen führten zu einer hohen Vanadium Dispersion in überwiegend amorphen mono- oder oligomerischen VO\textsubscript{x} Strukturen auch für sehr hohe Vanadium Oberflächenbeladung (>8 \text{ V nm}^{-2}). Eine solch hohe Beladung ohne die Präsenz von kristallinem V\textsubscript{2}O\textsubscript{5} wurde bisher durch die konventionellen Synthesemethoden nicht erreicht. Diese amorphen Strukturen waren thermisch bis zu 450\textdegree{C} und einer Beladung von 27 \text{ V nm}^{-2} stabil. Die V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} Katalysatoren wurden für die katalytischen Tests in der selektiven partiellen Oxidation von \textit{o}-Xylol direkt aus dem Aerosol auf keramische Schwämme abgeschieden. Die Aktivität der flammensynthetisierten als auch der nass-imprägnierten Referenzkatalysatoren hing nur von der Anzahl der zugänglichen Vanadium Zentren basierend auf der Beladung und vorhandenen spezifischen Oberfläche ab. Die Struktur der VO\textsubscript{x} Spezies, jedoch, schien keinen entscheidenden Einfluss auf den Umsatz von \textit{o}-Xylol zu haben. Im Falle der Selektivität zu Phthalsäureanhydrid hingegen, war eine deutliche Abhängigkeit von der VO\textsubscript{x} Spezies zu erkennen: Katalysatoren mit amorphen Strukturen zeigten deutlich höhere Selektivitäten bei mittleren Umsätzen als jene die kristallines V\textsubscript{2}O\textsubscript{5} aufwiesen.

Des Weiteren wurde die Flammen-Sprüh-Pyrolyse für die Herstellung V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} Katalysatoren mit konstanter spezifischer Oberfläche und variierendem V\textsubscript{2}O\textsubscript{5} Gehalt (3-30 Gew.\%) verwendet. Die Katalysatoren wurden in der Totaloxidation volatiler organischer Verbindungen, namentlich Chlorobenzol, getestet. Analyse mittels XPS bestätigte die sehr hohe Vanadium Dispersion, die im Vergleich zu den imprägnierten Referenzkatalysatoren durch die Synthese via FSP erreicht wurde und bestätigte somit die Ergebnisse der Ramananalysen. Im Gegensatz zu der Verwendung in der partiellen Oxidierung schien die Aktivität in der Totaloxidation von Chlorobenzol von der Menge aktiver Spezies als auch deren Struktur abzuhängen. Eine Erhöhung des V\textsubscript{2}O\textsubscript{5} Gehalts führte zu einer höheren Aktivität bei gleicher Reaktionstemperatur und erreichte eine Maximum bei ungefähr 12 \text{ V nm}^{-2} und 16 \text{ V nm}^{-2} für die Referenz- bzw. flammensynthetisierten Katalysatoren. Im Vergleich zu den nass-imprägnierten Katalysatoren zeigten die FSP Katalysatoren mit deutlich höherer Vanadium Dispersion geringere katalytische Aktivität bei vergleichbarer
Zusammenfassung


Die Flammen-Sprüh-Pyrolyse wurde ebenfalls für die Synthese von V$_2$O$_5$/SiO$_2$ Katalysatoren verwendet, welche in der oxidativen Dehydrierung (ODH) von Propan zu Propen getestet wurden. Ähnlich wie bei den V$_2$O$_5$/TiO$_2$ Katalysatoren wurden auch für die Silica getragenen Materialien im Vergleich zu klassischen Katalysatoren außergewöhnlich hohe Vanadium Dispersionen erreicht. Die unbehandelten gebrauchsfertigen Katalysatoren zeigten hauptsächlich monomere VO$_x$ Strukturen bis zu einer Beladung von 4.6 V nm$^{-2}$. Die monomeren Spezies waren unter Reaktionsbedingungen bis zu einer Temperatur von 600°C und einer Beladung von 2 V nm$^{-2}$ stabil. Höhere Beladungen führten zu einer Umstrukturierung von amorphen VO$_x$ zu kristallinem V$_2$O$_5$. Die Aktivität der flammensynthetisierten Katalysatoren hing stark von der V$_2$O$_5$ Beladung ab und zeigte ein Maximum bei 4.6 V nm$^{-2}$. In der ODH Reaktion wurden die höchsten Selektivitäten für Katalysatoren mit überwiegend monomeren VO$_x$ Spezies erhalten, während Proben mit kristallinen V$_2$O$_5$ Anteilen mehr CO$_x$ produzierten. Trotzdem wurde die höchste Propenausbeute für Katalysatoren erreicht, die sowohl monomere als auch V$_2$O$_5$ Kristallite enthielten.

Im Zusammenhang mit einer möglichen Anwendung in der ODH Reaktion wurden auch V$_2$O$_5$/Al$_2$O$_3$ Katalysatoren hergestellt und physiochemisch charakterisiert. Im Gegensatz zu den SiO$_2$ oder TiO$_2$ getragten Materialien bildete sich bei hohen Vanadium Gehalten (>20 wt.%)
eine $\text{VALO}_4$ Mischphase, die allerdings amorph ist und nicht im XRD detektiert werden konnte. Bei kleinen Gehalten konnten die amorphen $\text{VO}_x$ Spezies bis 500 °C stabilisiert werden.

Abschließend wurde die Vielseitigkeit der Flammen-Sprüh-Pyrolyse für die Herstellung maßgeschneiderter Mischoxide als Träger für Edelmetall Katalysatoren am Beispiel von $\text{Pt/Al}_2\text{O}_3$ gezeigt. Dabei wurden die Säure/Base Eigenschaften der Trägeroberfläche gezielt durch direkte Zugabe von $\text{SiO}_2$ (0-100 Gew.%) oder $\text{Cs}_2\text{O}$ (0-10 Gew.%) in der Flamme beeinflusst. Bis zu einem Anteil von 50 Gew.% $\text{SiO}_2$ konnte die spezifische Oberfläche konstant gehalten werden, allerdings war ein Kontrolle der Pt Partikelgröße nicht möglich, da die Metallpartikel mit zunehmenden Silicaanteil größer wurden. Die höchste Oberflächenacidität wurde mittels temperaturprogrammierter $\text{NH}_3$ Desorption für eine $\text{SiO}_2/\text{Al}_2\text{O}_3$ Zusammensetzung von ca. 30/70 (Gew.%) gemessen. Diese flammen-synthetisierten Katalysatoren waren äußerst aktiv in der Hydrierung von Acetophenon. Der starke Einfluss der Oberflächenacidität auf die Eigenschaften des Pt-H System wurde durch den mehr als 20-fachen Anstieg der Nebenprodukte der Hydrogenolyse bewiesen. Die Zugabe von $\text{Cs}_2\text{O}$ hingegen hatte eine Anreicherung von Cs an der Partikeloberfläche und einem daraus resultierend starken Anstieg der spezifischen Oberfläche des Alumina-Trägers zur Folge. Dementsprechend wurde die Basizität bereits bei sehr geringen Mengen von $\text{Cs}_2\text{O}$ stark beeinflusst und erhöhte sich mit zunehmenden $\text{Cs}_2\text{O}$ Anteil. Diese einzigartigen Oberflächeneigenschaften hatten einen starken Einfluss auf die Katalyse: Nur 0.25 Gew.% $\text{Cs}_2\text{O}$ reichten aus, um die Hydrogenolyse von 1-Phenylethanol zu Ethylbezol zu unterbinden.

Die Entwicklung neuartiger Katalysatoren mit maßgeschneiderten Eigenschaften erfordert grundlegendes Verständnis der Wechselwirkungen verschiedener Strukturen der aktiven Spezies sowie Zusammensetzung des Mischoxids in der jeweiligen katalytischen Anwendung. Die Flammen-Synthese und die Flammen-Sprüh-Pyrolyse im Besonderen haben gezeigt, dass dieses fundamentale Wissen durch die Herstellung leicht zugänglicher Modell-Katalysatoren von hoher Reinheit und Reproduzierbarkeit mit guten
katalytischen Eigenschaften erweitert werden kann. Die Flammen-Sprüh-Pyrolyse ist eine einfach skalierbare Synthesemethode und erlaubt die Herstellung von Mischoxiden nicht nur im Labor- sondern auch im Industriemaßstab, ein wichtiger Faktor für die zukünftige industrielle Anwendung solcher flammensynthetisierter Katalysatoren.
CHAPTER 1

Overview: Flame aerosol synthesis of mixed-metal-oxide catalysts with unprecedented structural and catalytic properties

Abstract

In the past two decades flame aerosol synthesis of novel materials has experienced significant growth in both, industry and academia. Recent research is focused on the development of new materials in the nano size-range to be used in various applications such as catalysts, gas sensors, pigments, and batteries. Several studies indicate that this scalable synthesis method can result in novel and metastable phases of mixed metal oxides of high purity which may not be easy accessible by conventional wet- or solid-state processes. Especially for catalytic applications this synthesis method is emerging as an attractive fast and single-step production route for high surface area materials.

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often with unprecedented structural and catalytic properties. The large variety of possible organometallic precursors especially for the liquid-fed aerosol flame synthesis makes this technique very versatile for catalyst synthesis.

Using the example of the widely used vanadia-based mixed oxide catalysts, we analyse the structural and catalytic properties of flame-derived catalysts and compare them to corresponding catalysts prepared by classical wet-chemistry methods. The often unique structural properties along with their control at proper synthesis conditions and their influence on catalyst performance in selected reactions are discussed. Additionally we give an overview of other recent flame-made mixed metal oxide based catalysts and make an attempt to assess the potential and limitations of flame synthesis for the preparation of catalytic mixed metal oxide materials, and finally we identify future challenges in research.

1.1 Introduction

Mixed metal oxides play an important role in heterogeneous catalysis. Many of nowadays industrially used catalysts contain two or more metal oxide components as support, promoter or catalytically active species. Traditionally these catalysts are prepared using wet-chemical methods among which classic impregnation, (co-)precipitation [1, 2], and sol-gel synthesis [3] and hydrothermal synthesis [4], are some of the most prominent. These methods, however, involve several consecutive time-consuming steps (Fig. 1.1), which often render it difficult to control the final catalyst properties. Particularly the necessity of a calcination step during which the materials are exposed for relatively long time to high temperatures (400 to 600°C) often favor low dispersion of the active sites and undesired segregation phenomena. In the past two decades flame synthesis has emerged as a very powerful method for the synthesis of ceramic nanoparticles with unique structural properties. This development has been covered in several reviews [5-7]. Flame synthesis offers the possibility to prepare catalytically active materials randomly mixed on the nano- and even atomic-scale in a single step (Fig. 1.1) [8]. The high temperatures and fast cooling rates associated with oxidation/combustion of gaseous or liquid precursors, can provide novel
mixed metal oxide compositions [9, 10], combined with high purity [11, 12] and unique bulk structural [13, 14] and surface properties [15], not easy accessible through conventional wet-phase synthesis methods. Already in 1984 Ulrich [16] pointed out the potential of flame technology for catalysis because of the intrinsic high specific surface area of combustion-precipitated materials.

Fig. 1.1 Comparison of conventional wet-chemistry and aerosol synthesis of vanadia-based catalysts. The classic syntheses routes by (co-)precipitation or impregnation afford several process steps and often take days before the final catalyst is available. In contrast catalyst syntheses by flames are done with only one, short process step and the final catalytic material or even the ready to use catalyst (via direct deposition) is available within minutes.
This triggered several studies on the use of various flame processes for synthesis of solid catalysts which were reviewed in 2006 by Strobel et al. [8] Johanessen et al. [17] showed the possibility of using this technology for coating microreactors directly with flame-made particles and Phillips et al. [18] highlighted the potential of plasma aerosol reactors in catalysis as they share a number of similarities with flame reactors. Besides being continuous and fast, flame aerosol synthesis bears considerable potential for developing catalysts with strikingly different structural and thus catalytic properties. However, the exploitation of these attractive features of flame synthesis requires proper control of the synthesis parameters such as composition of solvents (enthalpy density) and precursors, metal concentration in the liquid precursor solution, flame parameters (liquid and gas feed rates) and reactor configuration as well as their effect on the final structural properties of as-prepared materials.

Here, we review the structural and catalytic properties of various aerosol-made metal oxide-based catalysts with a special focus on the well-known and widely applied vanadia-based mixed oxides. Latest research results on catalysts prepared by laser aerosol synthesis [19], hot-wall reactors [20], vapor-fed counter-[21, 22] or co-flow flame reactors [23] as well as liquid-fed flame reactors [24] will be considered and their structural and catalytic properties compared to corresponding materials prepared by classical wet-chemistry methods.

Special emphasis will be given to the discussion of the control and effect of different processes (vapor- or liquid-fed flames) and synthesis parameters (e.g. solvent selection, liquid- or gas feed rate) on the final properties (e.g. specific surface area, structure, phase composition, and dispersion of active sites) of as-prepared catalysts. In addition to the vanadia-based mixed oxides, other flame-derived catalytic mixed metal oxides are considered covering a broad spectrum of compositions (e.g. Cu/ZnO/Al₂O₃, MgAl₂₋ₓMₓO₄ (M=Mn, Fe, Co), Pt/SiO₂/Al₂O₃ etc.) and catalytic applications. Finally, we make an attempt to assess the potential and limitations of flame aerosol methods for the synthesis of these materials and identify future challenges.
1.2 Flame synthesis of vanadia-based catalysts

Catalysts made up of vanadia supported on or mixed with other metal oxides are applied in various important reactions, including e.g. the selective catalytic reduction (SCR) of NO\textsubscript{x} [25, 26], the partial oxidation of o-xylene to phthalic anhydride [27, 28], dehydrogenation of propane [29-31] and the oxidative destruction of volatile organic compounds (VOC) [32, 33]. The present knowledge on vanadia-based mixed oxide has been exclusively gathered from corresponding wet-chemistry derived materials. Rigorously one can distinguish between metal oxide supported vanadia catalysts (e.g. V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}) and vanadia-based mixed oxides where vanadia is randomly mixed with other metal oxides (e.g. VOPO\textsubscript{4}). Depending on the desired catalytic application, the properties of vanadia containing catalysts vary in the structure and surface density of VO\textsubscript{x} species. These properties are affected by the vanadia loading and the chemical and structural properties of the associated metal oxides (e.g. Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, TiO\textsubscript{2}, ZrO\textsubscript{2}). For wet-chemistry derived catalysts it is commonly agreed [27, 34] that vanadium oxide can be present on the support oxide in three different forms [28] (Fig. 1.2): monomeric VO\textsubscript{x} species at low loadings (typical <2.3 V nm\textsuperscript{-2}), amorphous di- or oligomeric form at medium loadings (1 - 8 V nm\textsuperscript{-2}), and crystalline domains or V\textsubscript{2}O\textsubscript{5} crystals at high loadings (> 8 – 10 V nm\textsuperscript{-2}).

The latter loading marks the transition from the so called “(sub-) monolayer” to “bulk” vanadia catalysts with e.g. supporting oxides TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. Exceeding this V surface density, the so-called “theoretical monolayer”, usually leads to formation of crystalline [28] V\textsubscript{2}O\textsubscript{5} irrespective of the preparation method, e.g. impregnation [27], atomic layer deposition (ALD) [35, 36], sputter deposition [37], and even vapor-fed flame synthesis [23]. Silica-supported vanadia catalysts show this transition from amorphous to crystalline V\textsubscript{2}O\textsubscript{5} already at a V surface density [38] of around 2 V nm\textsuperscript{-2} or even lower for mesoporous supports [31, 39].

Figure 1.2 illustrates the preferential structure of the VO\textsubscript{x} species achieved with different flame aerosol reactors. The structure of VO\textsubscript{x} species (mono- or oligomeric vanadates and V\textsubscript{2}O\textsubscript{5} crystals), and thus the catalytic performance of supported vanadia catalysts, can be influenced by the
preparation conditions such as flame characteristics, vanadia content, and nature and textural properties of the support [30, 40]. Table 1.1 provides an overview of vanadia-based catalytic materials prepared in flames and related processes. Details on their synthesis and structural properties as well as their catalytic application are specified.

Fig. 1.2 Possible structures of the VOₓ species reported for V₂O₅/TiO₂ catalysts prepared with different synthesis techniques depending on the V surface density expressed as V nm⁻². The theoretical monolayer [28] indicates the V surface density (usually around 8 V nm⁻²) at which the transition of amorphous to crystalline V₂O₅ is observed for catalysts made by-impregnation [27], atomic layer deposition [35, 36], or sputter deposition [37]. Silica supported catalysts show this transition already at a much lower surface density of around 2.3 V nm⁻², for molecular sieve like materials sometimes even lower [31, 39].
A good dispersion and accessibility of the mono- or polymeric VO\textsubscript{x} species is considered to be important for high activity, while usually crystalline species are assumed to be less active [34]. This belief generated numerous studies dealing with sub-monolayer catalysts for all sorts of oxidation or oxidative dehydrogenation reactions [26, 31, 32, 34, 39, 41-48]. Such catalysts are mainly produced with conventional multiple-step wet-chemistry methods. However, particularly for vanadia loadings exceeding the classic “monolayer” V surface density (>8 V nm\textsuperscript{-2}), the control over the structure of VO\textsubscript{x} species is demanding.

Aerosol flame synthesis (AFS), classified according to the state of the precursor fed to the flame in vapor-fed (VAFS) and liquid-fed AFS (LAFS) [49] is a relatively novel synthesis method for vanadia-based catalysts. In Fig. 1.3 the possible particle formation processes occurring during flame synthesis based on the selected method, VAFS or LAFS, are shown. While in VAFS particle formation occurs by nucleation from the gas-phase, in LAFS particles are formed by either droplet-to-particle or gas-to-particle routes depending on the synthesis parameters (Fig. 1.3) [49]. VAFS reactors were used for the production of metal oxide particles first [16], but are limited to vaporizable precursors [5]. The use of liquid precursors [50, 51] opened the field for a significantly larger variety of possible metal oxides and mixtures.

1.2.1 Vapor-fed aerosol synthesis (VAFS)

The first attempts were made with laser aerosol synthesis of V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} materials in 1992 by Musci et al. [19] (Table 1.1, entry 1). A gaseous reactant stream was loaded with Ti- and V-alkoxide precursor vapors and was ignited by a laser source (Fig. 1.2). Depending on process conditions, monodispersed, non-aggregated, monocrystalline V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} powders with anatase structure and vanadia loadings ranging from 0 to 14 wt.%, and surface areas in the range of 80 to 230 m\textsuperscript{2}g\textsuperscript{-1} (0 to 8 V nm\textsuperscript{-2}) could be produced. Anatase TiO\textsubscript{2} was made when choosing the correct sensitizer (SF\textsubscript{6} instead of C\textsubscript{2}H\textsubscript{4}) for energy transfer from the laser to the gas stream favoring homogeneous nucleation [19]. Higher vanadia loadings resulted in the segregation of separate V\textsubscript{2}O\textsubscript{5} needle-like particles.
Fig. 1.3 Schematic of the possible catalysts formation routes and designated intermediate steps during FASP, FSP and VAFS. Catalysts nucleated from the gas phase (VAFS and FSP) show dominantly VO\textsubscript{x} surface species and no solid solution of the vanadia in the support oxide as the support oxides usually nucleate first in the flame due to the higher melting point followed subsequent condensation of the vanadia on the surface resulting in small nano-sized particles with high VO\textsubscript{x} dispersion. In FASP instead (and partly in FSP) mainly solid solutions or even hollow or porous particles might be formed which are significantly larger than achieved with FSP or VASF. (adapted from Ref [8])
From electrical conductivity measurements showing the presence of V\(^{4+}\), it was concluded that V atoms were incorporated into the TiO\(_2\) lattice. IR analysis, however, showed similar spectra as for impregnated TiO\(_2\) made by laser-assisted synthesis, indicating similar nature of VO\(_x\) surface species in V\(_2\)O\(_5\)/TiO\(_2\) made by laser-pyrolysis and wet-impregnated samples [19]. Unfortunately, no catalytic data were reported for these materials.

Miquel et al. [21, 22] studied the vanadium mixed oxide systems of V\(_2\)O\(_5\)/TiO\(_2\) and V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) in a counterflow diffusion burner (Fig. 1.2) using VOCl\(_3\), TiCl\(_4\) and Al(CH\(_3\))\(_3\) as precursors added to the fuel (H\(_2\)) stream. In the V\(_2\)O\(_5\)/TiO\(_2\) system (Table 1.1, entry 2) spherical particles (40-70 nm in diameter) were collected in the stagnation plane with 26-47 m\(^2\)g\(^{-1}\) specific surface area (16-53 wt.% V\(_2\)O\(_5\)). The titania was mostly made up of rutile in contrast to the material prepared by laser pyrolysis [19]. Using chloride precursors probably facilitated the early formation of rutile in the reducing environment of H\(_2\) due to the acidic environment induced by the formation of HCl during oxidation [52] The addition of the lowest amount of VOCl\(_3\) (V:Ti = 0.5:3, 16 wt.% V\(_2\)O\(_5\)) to the feed induced a further reduction of the anatase phase. No indications of crystalline V\(_2\)O\(_5\) were found by XRD despite the high V surface density of 22 V nm\(^{-2}\). At higher vanadia loadings crystalline V\(_2\)O\(_5\) was detected. It was concluded that formation of V\(_2\)O\(_5\)/TiO\(_2\) occurs via heterogeneous nucleation resulting in a uniform mixture of both oxides [21]. For V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) (Table 1.1, entry 3), core-shell alumina-vanadia particles were formed with 50-90 m\(^2\)g\(^{-1}\) specific surface area (23-64 wt.% V\(_2\)O\(_5\)). Low V concentrations (23 wt.% V\(_2\)O\(_5\), 12 V nm\(^{-2}\)) resulted in XRD amorphous VO\(_x\) species, whereas higher ones caused the formation of V\(_2\)O\(_5\) crystals. Mixed vanadium phosphorous oxide (VPO) particles [53] (Table 1.1, entry 4) were made similarly [21, 22]. VPO formed mixed nanostructured chains (with primary particles ~5-10 nm in diameter) in the early stages of the flame. As these chains travelled through the hottest part of the flame they collapsed by sintering and coalescence into spherical particles of ~35 nm in diameter. For all three catalyst systems [21, 22, 54], however, no catalytic data were presented.
While vapor-fed flame reactors were used for synthesis of Al₂O₃, SiO₂ or TiO₂ as catalyst supports or photocatalysts (TiO₂) [8], it took half a decade before this approach was used for vanadia-based catalysts. Stark et al. [23] (Table 1.1, entries 6 and 7) used a vapor-fed, co-flow diffusion flame reactor (Fig. 1.2) to produce V₂O₅/TiO₂ and SiO₂-doped V₂O₅/TiO₂ catalysts (0-10 wt.% V₂O₅) for the selective catalytic reduction (SCR) of NO with NH₃ from V-isopropoxide and Ti-tetra-isopropoxide oxidation. These catalysts synthesized powders consisted of nonporous, spherical particles with 23-120 m²g⁻¹ surface area depending on the flame parameters. High O₂ flow rates, resulting in aerosol dilution and cooling of the flame, increased the surface area due to shorter residence time in the hot temperature zone, leading to decreased particle sintering and smaller primary particle sizes [5], while increasing the vanadia content up to 10 wt.% at constant O₂ flow rate had no significant effect on the surface area. As particle formation took place at fuel lean conditions [55], anatase was the dominant crystal phase in all samples (rutile < 10 wt.%%) and no crystalline V₂O₅ was detected by XRD. Raman analysis showed primarily monomeric and oligomeric VOₓ species at low V₂O₅ loadings (<5 wt.%, <4 V nm⁻²), while at 10 wt.% vanadia crystalline V₂O₅ was detected, even at the relatively low V surface density of 6 V nm⁻² (< “monolayer” coverage). In the flame, VOₓ species were formed mainly on the supporting oxide surface due to the lower boiling point of V₂O₅ compared to that of the oxide supports, as confirmed by XPS analysis showing V enrichment on the surface. Therefore it is expected that the vanadia condenses on top of the support TiO₂ particles later downstream in the flame when the formation process of the support oxide has been finished [23]. Adding low amounts of SiO₂ (3, 6 wt.%) resulted in segregated silica domains not affecting the V₂O₅/TiO₂ structure but decreasing the catalytic activity [23]. Increasing vanadia contents as well as higher surface area increased the activity for the NO reduction by SCR [23]. A unique property of the flame-made catalysts was the strong influence of preparation parameters on the N₂O selectivity. Increasing the V surface density afforded high (up to 60% for 10 wt.% V₂O₅, 28 V nm⁻²) N₂O selectivity. On the other hand increasing the oxygen feed, the N₂O selectivity could be reduced even for high vanadia contents [23]. Lowest
N₂O selectivity (<1%) was achieved for catalysts exhibiting 6 V nm⁻² independent of the flame parameters used. This flame process for synthesis of V₂O₅/TiO₂ could be scaled up to a production rate of 200 g h⁻¹ using a hydrogen flame without losing the high anatase content (>90 wt.%) and the high catalytic activity compared to wet-impregnated catalysts of similar composition [56] (Table 1.1, entry 7).

Kumar et al. [57] prepared V₂O₅/TiO₂ and V₂O₅/WO₃/TiO₂ catalysts by oxidation of a aerosolized (1.5 L min⁻¹ N₂) precursor solution with vanadium oxytriethoxide, titanium tetra-isopropoxide, and tungsten ethoxide also in a co-flow diffusion flame for the gas-phase oxidation of methanol (Table 1.1, entry 8). The synthesis parameters were kept constant and only the influence of the vanadia loading (1-5 wt.%) was investigated. These flame-made V₂O₅/TiO₂ particles had 43-58 m²g⁻¹ surface area corresponding to a V surface density of 1.1-8 V nm⁻² and an anatase content of about 80 wt.%. Compared to pure TiO₂ (rutile content 14 wt.%), the rutile content was increased slightly by the addition of vanadia. No crystalline V₂O₅ was observed indicating good dispersion of the VOₓ species. Doping with tungsten preserved the initial anatase content but had otherwise no significant effect on the catalyst structure [57]. With increasing vanadia content, higher catalytic activity was achieved with maximum conversion at the highest V surface density of 8 V nm⁻² (equal to a "theoretical monolayer"). Overall the activity of flame-made catalysts was higher (<8 V nm⁻²) or equal to standard wet-impregnated catalysts of similar composition. This superior performance was attributed to the higher dispersion of VOₓ species in the flame-made catalysts compared to wet-impregnated samples [57]. The addition of WO₃ had no beneficial effect on the light-off temperature for the total oxidation of methanol but stabilized the catalysts against sintering.

1.2.2 Liquid-fed aerosol synthesis

The need of volatile precursors limits the accessible compositions of mixed metal oxide particles made in vapor-fed flame reactors. This disadvantage can be eliminated by liquid-fed aerosol reactors, the so-called spray pyrolysis, flame-assisted spray pyrolysis (FASP) and flame spray
pyrolysis (FSP, Fig. 1.2), giving access to almost the whole periodic table for possible catalyst components [49].

FSP is a one-step process that is highly suitable for synthesis of tailor-made mixed metal oxide catalysts [8]. The FASP was introduced by Marshal et al. in 1971 for the synthesis of ZnO [50]. FSP was introduced in 1977 by Sokolowski et al. [51] for the synthesis of Al₂O₃. It should be noted that these technologies are routinely used in the manufacturing of carbon black by the so-called furnace process [5].

1.2.2.1 Spray Pyrolysis

Spray pyrolysis in a hot wall reactor involves pyrolysis of flowing precursor aerosol (ammonium metavanadate) droplets in an electrically heated tube (Table 1.1, entry 5) [20]. The as-prepared material consisted mainly of VOPO₄·nH₂O, which was converted into water-free, crystalline VPO structures upon thermal post treatment or during reaction [20]. Dominantly large and hollow particles were observed with a low surface area (<10 m²g⁻¹) hinting to droplet-to-particle formation as the main synthesis route (Fig. 1.3). These catalysts were tested for the oxidation of butane to maleic anhydride, revealing a strong influence of the synthesis temperature applied in the spray pyrolysis on the catalytic performance. Catalysts made at higher temperatures were more active due to their higher crystallinity [20]. These catalysts showed superior yield of maleic anhydride based on catalyst weight compared to catalysts prepared by wet-chemistry methods.

1.2.2.2 Catalysts made by gas-to-particle conversion

Jossen et al. [58] (Table 1.1, entry 9) synthesized WO₃/TiO₂ based SCR catalysts doped by vanadia (0-2 wt.%) and silica (0-5 wt.%) by FSP of titanium tri-isopropoxide, tungsten ethoxide, vanadium isopropoxide and tetraethyl-orthosilicate (TEOS) dissolved in toluene. Due to the use of high combustion enthalpy solvents and high dispersion at the FSP nozzle tip, these nonporous particles were formed by nucleation from the gas phase (gas-to-particle conversion) and had higher surface area (around 100 m²g⁻¹) compared to VAFS-made materials (40 to 60 m²g⁻¹) of comparable composition [57], and
showed nonporous particles as evidenced by TEM [58]. Silica doping enhanced drastically the thermal stability of V$_2$O$_5$/WO$_3$/TiO$_2$ catalysts, conserving 90% of the initial surface area even after calcination at 700 °C for 20h. Additionally the anatase content was preserved above 95 wt.% for all compositions, higher than for vapor-fed flame-made catalysts (80 to 85 wt.% anatase).[57] No crystalline V$_2$O$_5$ was found despite the high calcination temperature (700 °C) and the vanadia accessibility was very good. At low vanadia content (0.9 wt.%) the catalytic activity improved with increasing silica content at constant reaction temperature. For catalysts with higher V$_2$O$_5$ loadings (2 wt.%) doped with SiO$_2$, the NO conversion increased with increasing reaction temperature up to (320 °C) without loss of surface area or undesirable transformation to crystalline V$_2$O$_5$ [58].

Pure V$_2$O$_5$/TiO$_2$ prepared by FSP and directly deposited on mullite foams, resulted in ready-to-use catalysts for the selective partial oxidation of o-xylene to phthalic anhydride (Table 1.1, entry 10) [24]. Figure 1.4 shows a schematic of the experimental set up for the manufacturing of these catalysts. Titanium tetra-isopropoxide and vanadium isopropoxide dissolved in xylene and acetonitrile were used [24] as precursors for FSP synthesis of nonporous particles of V$_2$O$_5$/TiO$_2$ (Fig. 1.4a). The surface area (53-90 m$^2$/g), anatase content (>98 wt.%), and the dominantly monomeric vanadia species, even at high V surface density (12 V nm$^{-2}$, > ”theoretical monolayer”) on titania were thermally stable up to 450°C. The catalytic activity increased with larger surface area. These V$_2$O$_5$/TiO$_2$ coated ceramic foams (Fig. 1.4b) showed superior catalytic activity and selectivity at high o-xylene conversions than the corresponding wet-made V$_2$O$_5$/TiO$_2$ catalysts. This was partially attributed to the high porosity=(98%) [59] of the deposited V$_2$O$_5$/TiO$_2$ particle layer (Fig. 1.4c,d) [24] facilitating enhanced intraparticle mass transfer and thus preventing mass transfer limitations as occurring in pelletized catalysts of similar composition but smaller pore sizes [24].

With the FSP method, V$_2$O$_5$/TiO$_2$ (0-40 wt.% V$_2$O$_5$) catalysts with significant differences in particle structure and VO$_x$ species composition than wet-chemistry derived materials can be produced [60] (Table 1.1, entry 11).
Fig. 1.4 Schematic of the set-up for direct deposition of flame-made V$_2$O$_5$/TiO$_2$ catalysts onto ceramic foam substrates. The high porosity of the coating layer facilitates improved mass transfer of the reactants to the active site and alleviates possible mass transfer limitation in the active layer. Deposited mass and layer morphology could be controlled and the ready-to-use catalysts were successfully tested in the selective partial oxidation of o-xylene to phthalic anhydride (adapted from Ref. [24]).

By properly adjusting the synthesis parameters such as gas and liquid feed rates, precursor, solvent and metal concentration, FSP allows tailoring the final catalyst morphology and structure of the active species. Such FSP-made V$_2$O$_5$/TiO$_2$ catalysts showed a good dispersion of vanadia while retaining the amorphous VO$_x$-species up to a V surface density of 27 V nm$^{-2}$ (10 wt.% V$_2$O$_5$) where wet-impregnated catalysts normally exhibit dominantly crystalline [60] V$_2$O$_5$. Note that V$_2$O$_5$/TiO$_2$ catalysts of comparable composition prepared by VFAS show crystalline [23] V$_2$O$_5$ already at a V surface density as low as 6.6 V nm$^{-2}$.

The higher temperatures and cooling rates during LFAS compared to that during VFAS favor higher dispersion of V on the TiO$_2$ support surface [24, 60].
These highly dispersed VO\(_x\) species were stable up to 450 °C even at high V surface density (>8 V nm\(^2\), up to 27 V nm\(^2\)). High vanadia contents (40 wt.%) and low surface area (47 m\(^2\)g\(^{-1}\)), however, resulted in segregation of single crystalline V\(_2\)O\(_5\) particles as illustrated in Fig. 1.5. Elemental mapping by electron energy loss spectroscopy revealed the presence of separate V\(_2\)O\(_5\) particles (arrows in Fig. 1.5c). Nevertheless the presence of V was detected for all particles (Fig. 1.5b,c) indicating a good dispersion of V on the TiO\(_2\) support surfaces and not solely vanadia segregation.

![Fig. 1.5 TEM image (a) of 40 wt.% V\(_2\)O\(_5\)/TiO\(_2\) catalysts and the corresponding EELS mapping of Ti (b) and V (c). Arrows indicated segregated V\(_2\)O\(_5\) crystals.](image)

The structure of the VO\(_x\) species had a strong influence on the selectivity in the oxidation of o-xylene, favoring amorphous species for high selectivity to phthalic anhydride. The activity of the flame-made catalysts was directly proportional to the specific surface area and therefore to the number of exposed vanadium sites but showed no dependency on VO\(_x\) species composition (amorphous or crystalline) as observed with wet-impregnated catalysts [60]. FSP has been shown to be a versatile, and highly reproducible method for preparing V\(_2\)O\(_5\)/TiO\(_2\) catalysts with a wide range of surface area and VO\(_x\) species composition which may not be accessible by wet-chemistry routes [8, 60], laser induced pyrolysis [19], and even vapor-fed flame synthesis [21-23, 56].

Vanadia-titania catalysts made by FSP were also tested in the total oxidation of chlorobenzene and compared to corresponding wet-impregnated catalysts [61] (Table 1.1, entry 15).
Table 1.1 Overview of vanadium-based catalytic materials made in flames and related processes, and details on their synthesis method, physical properties and catalytic application.

<table>
<thead>
<tr>
<th>Entry</th>
<th>produced catalysts</th>
<th>type of reactor</th>
<th>flame temp in °C</th>
<th>BET surface area in m² g⁻¹</th>
<th>V₂O₅ content in wt.%</th>
<th>theor. V₂O₅ surface density in V nm²</th>
<th>V₂O₅ structure</th>
<th>tested reaction</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V₂O₅/TiO₂</td>
<td>laser induced pyrolysis</td>
<td>N/A.</td>
<td>80-230</td>
<td>0-14</td>
<td>≈3.3-7.7</td>
<td>amorph</td>
<td>N/A</td>
<td>Musci et al. 1992 [19]</td>
</tr>
<tr>
<td>2</td>
<td>V₂O₅/TiO₂</td>
<td>counterflow diffusion flame</td>
<td>≈2000</td>
<td>47.1</td>
<td>16</td>
<td>22</td>
<td>amorph (XRD)</td>
<td>N/A</td>
<td>Miquel et al. 1993 [21,22]</td>
</tr>
<tr>
<td>3</td>
<td>V₂O₅/Al₂O₃</td>
<td>&quot;</td>
<td>≈2000</td>
<td>86.6</td>
<td>23</td>
<td>12</td>
<td>amorph (XRD)</td>
<td>N/A</td>
<td>Miquel et al. 1993 [21,22]</td>
</tr>
<tr>
<td>5</td>
<td>VPO</td>
<td>spray pyrolysis</td>
<td>700</td>
<td>&lt;10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Oxidation of butane</td>
<td>Michalakos et al. 1995[20]</td>
</tr>
<tr>
<td>6</td>
<td>V₂O₅/TiO₂ and SiO₂-doped \ V₂O₅/TiO₂</td>
<td>coflow diffusion flame</td>
<td>≈1800</td>
<td>88</td>
<td>2</td>
<td>1.5</td>
<td>amorph</td>
<td>SCR</td>
<td>Stark et al. 2001 [23]</td>
</tr>
<tr>
<td>7</td>
<td>V₂O₅/TiO₂</td>
<td>&quot;</td>
<td>n.n.</td>
<td>25-55</td>
<td>7.5-10</td>
<td>12-19.8</td>
<td>n.n.</td>
<td>SCR</td>
<td>Stark et al. 2002 [56]</td>
</tr>
<tr>
<td>8</td>
<td>V₂O₅/TiO₂ and V₂O₅/WO₃/TiO₂</td>
<td>coflow diffusion flame</td>
<td>n.n.</td>
<td>43-58</td>
<td>1-5</td>
<td>1.1-8</td>
<td>amorph</td>
<td>Oxidation of methanol</td>
<td>Kumar et. Al. 2006 [57]</td>
</tr>
<tr>
<td>9</td>
<td>V₂O₅/WO₃/TiO₂</td>
<td>flame spray pyrolysis</td>
<td>≈2200</td>
<td>≈100</td>
<td>0.9-2</td>
<td>&lt; 1.4</td>
<td>amorph</td>
<td>SCR</td>
<td>Jossen et al. 2007 [58]</td>
</tr>
<tr>
<td>Entry</td>
<td>produced catalysts</td>
<td>type of reactor</td>
<td>flame temp in °C</td>
<td>BET surface area in m²/g</td>
<td>V₂O₅ content in wt. %</td>
<td>theor. V surface density in V nm²</td>
<td>V₂O₅ structure</td>
<td>tested reaction</td>
<td>reference</td>
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</tr>
<tr>
<td>9</td>
<td>V₂O₅/WO₃/TiO₂</td>
<td>flame spray pyrolysis</td>
<td>≈2200</td>
<td>=100</td>
<td>0.9-2</td>
<td>&lt; 1.4</td>
<td>amorph</td>
<td>SCR</td>
<td>Jossen et al. 2007 [58]</td>
</tr>
<tr>
<td>10</td>
<td>V₂O₅/TiO₂</td>
<td>&quot;</td>
<td>≈2200</td>
<td>53</td>
<td>10</td>
<td>12</td>
<td>amorph</td>
<td>partial oxidation of o-xylene</td>
<td>Schimmoeller et al. 2006 [24]</td>
</tr>
<tr>
<td>11</td>
<td>V₂O₅/TiO₂</td>
<td>&quot;</td>
<td>≈2200</td>
<td>24-93</td>
<td>0-15</td>
<td>0-27</td>
<td>amorph</td>
<td>partial oxidation of o-xylene</td>
<td>Schimmoeller et al. 2008 [60]</td>
</tr>
<tr>
<td>12</td>
<td>V₂O₅/SiO₂</td>
<td>&quot;</td>
<td>N/A</td>
<td>41</td>
<td>5</td>
<td>70</td>
<td>amorph</td>
<td>dehydrogenation of propane</td>
<td>Rossetti et al. 2008 [72]</td>
</tr>
<tr>
<td>13</td>
<td>V₂O₅/Al₂O₃</td>
<td>&quot;</td>
<td>N/A</td>
<td>19</td>
<td>10</td>
<td>35</td>
<td>crystalline</td>
<td>dehydrogenation of propane</td>
<td>Rossetti et al. 2009 [79]</td>
</tr>
<tr>
<td>14</td>
<td>V₂O₅/TiO₂</td>
<td>&quot;</td>
<td>≈1500</td>
<td>58-98</td>
<td>0-3</td>
<td>&lt; 2.8</td>
<td>amorph</td>
<td>methylene blue degradation</td>
<td>Tian et al. 2009 [67]</td>
</tr>
<tr>
<td>15</td>
<td>V₂O₅/TiO₂</td>
<td>flame spray pyrolysis</td>
<td>≈2200</td>
<td>≈50</td>
<td>0.13-5</td>
<td>2.3-16.2</td>
<td>amorph</td>
<td>total oxidation of chloro-benzene</td>
<td>Schimmoeller et al. 2010 [61]</td>
</tr>
<tr>
<td>16</td>
<td>V₂O₅/SiO₂</td>
<td>&quot;</td>
<td>≈2200</td>
<td>119-334</td>
<td>0-20</td>
<td>0.6-4.6</td>
<td>amorph</td>
<td>oxidative dehydrogenation of propane</td>
<td>Schimmoeller et al. 2010 [65]</td>
</tr>
</tbody>
</table>
The FSP-derived catalysts contained up to 30 wt.% $\text{V}_2\text{O}_5$ (33 V nm$^{-2}$) and the FSP synthesis parameters (liquid and gas feed rates) were adjusted to keep the overall surface area at around 50 m$^2$g$^{-1}$. Interestingly, high vanadia loadings showed the presence of VO$_2$ rather than $\text{V}_2\text{O}_5$ corroborating that FSP is capable to form $\text{V}_2\text{O}_5$/TiO$_2$ catalysts with unique VO$_x$ species. Raman- and X-ray photoelectron (XPS) spectroscopy proved the higher V dispersion of the flame-made catalysts compared to their wet impregnated counterparts. The catalytic activity increased with higher V surface density even above the so called “theoretical monolayer” (Fig. 1.2) independent of the preparation method. Highest activity, however, was observed for the wet-impregnated catalyst with a V surface density of around 16 V nm$^{-2}$ which corresponds to two times the “monolayer” coverage [61]. In this reaction, flame-made catalysts with higher dispersion of the surface VO$_x$ species and dominantly isolated monomeric species showed lower catalytic activity than the wet-impregnated ones with oligomeric or crystalline vanadia [61]. In fact the presence of a high amount of oligomeric species was shown to be beneficial for the catalyst activity when compared to materials [33, 41, 62, 63] with mainly monomeric isolated species (Fig. 1.6). The V-O-V bond is probably the most active one when it is in close proximity to TiO$_2$ as in the case of dimeric or oligomeric VO$_x$ species (Fig. 1.2). Additionally the presence of crystalline VO$_x$ species does not necessarily result in a lower catalytic activity of $\text{V}_2\text{O}_5$/TiO$_2$. The structure of the most active VO$_x$ species may vary depending on the type of catalytic reaction: Isolated monomeric species in the partial oxidation of o-xylene [24, 60, 64], or dehydrogenation of propane [31, 65] and oligomeric or even crystalline $\text{V}_2\text{O}_5$ in the oxidation of chlorobenzene [61, 66].

Tian et al. [67] used FSP in an attempt to advance the visible light activity of TiO$_2$ by doping with V in the range of 0 to 3 wt.% (Table 1.1, entry 14). Titanium tetrabutoxide and vanadium diacetylacetone dissolved in ethanol were used as precursors. The pressure drop over the nozzle tip was adjusted to 1.2 bar. This resulted in surface areas ranging from 98 (pure TiO$_2$) to 58 m$^2$g$^{-1}$ (2.8 wt.% $\text{V}_2\text{O}_5$) while keeping the fraction of anatase (86.5-89.5 wt.%) almost constant. TEM analysis showed nonporous, dominantly spherical particles with a broad size distribution (5-30 nm). EPR analysis
indicated the presence of $V^{4+}$ species which was interpreted as incorporation of V ions into the crystal lattice of TiO$_2$.

![Comparison of conversion of chlorobenzene at 250°C achieved by wet impregnated (WI) and flame-made $V_2O_5/TiO_2$ catalysts synthesized by flame spray pyrolysis (FSP). Exceeding the “theoretical monolayer” still caused an increase in the catalytic activity. In general the flame-made catalysts showed lower performance compared to wet-impregnated ones with lower V dispersion [61].](image)

This incorporation of the V atoms in the TiO$_2$ matrix seems to be in contrast to previous studies on vanadia/titania catalysts prepared by vapor-fed [23, 56, 57] flame synthesis and FSP [24, 58, 60, 61]. Increasing the V content resulted in higher absorption in the visible light spectra. The highest photocatalytic activity under visible light, however, was measured for the catalyst containing 0.6 wt.% V. No significant improvement compared to pure TiO$_2$ was achieved under UV light irradiation [67].
Recently, \( V_2O_5/SiO_2 \) \((0 – 50 \text{ wt.\% } V_2O_3)\) catalysts made by flame spray pyrolysis were tested in the oxidative dehydrogenation of propane [65] (Table 1.1, entry 16). Using high enthalpy solvents (xylene and 2-ethylhexanoic acid) and a high pressure drop (\( \Delta p = 1.6 \text{ bar} \)) over the nozzle tip, the surface area of as-prepared catalysts depended on the vanadia content and showed a maximum around 330 \( m^2g^{-1} \) for catalysts with \(<3.3 \text{ V nm}^2 \) V surface density \((<15 \text{ wt.\% } V_2O_3)\). These flame-made catalysts showed unique properties in terms of V dispersion as observed for \( V_2O_5/TiO_2 \) catalysts made by FSP [24, 60]. Such silica-supported vanadia catalysts exhibited dominantly isolated tetrahedrally coordinated VO\textsubscript{x} species (like Ti-doped SiO\textsubscript{2} epoxidation catalysts)[68] up to a relatively high V surface density of 3.3 \( V \text{ nm}^2 \) (Fig. 1.2), as confirmed by Raman and \( ^{51}\text{V} \text{ MAS-NMR} \) analysis (Fig. 1.7) [65]. The VO\textsubscript{x} species were highly stable up to 500 °C as evidenced by in-situ Raman spectroscopy. Higher vanadia contents (up to 30 wt.\% \( V_2O_3 \)) resulted in small \( V_2O_5 \) crystallites not detectable by XRD, but no indication of inaccessible V sites in the silica bulk framework was found. This is in contrast to \( V_2O_5/SiO_2 \) catalysts prepared by sol-gel process where inaccessible V sites in tetrahedral coordination were observed [69-71]. Further increase of the vanadia loading caused formation of separate, crystalline \( V_2O_5 \) particles in the flame, as detected by XRD and corroborated by TEM, a behavior similar to flame-made \( V_2O_5/TiO_2 \) with high (40 wt.\%) vanadia loading [60]. FSP-made \( V_2O_5/SiO_2 \) catalysts with similar amorphous VO\textsubscript{x} species showed comparable reduction behavior with reduction peak temperatures around 590 °C, while catalysts with crystalline \( V_2O_5 \) fractions required higher temperatures for reduction. The catalytic activity depended on the V surface density and increased with reaction temperature and \( V_2O_5 \) loading despite the presence of crystalline \( V_2O_5 \) domains at high loadings [65]. Low loaded \((<15 \text{ wt.\% } V_2O_3)\) catalysts showed very stable and high (40 to 55\%) propene selectivity at moderate propane conversion, while higher V surface density \((>3.3 \text{ V nm}^2)\) resulted in higher conversion but lower propene selectivity. Despite the presence of crystalline \( V_2O_5 \), the highest propene yield was measured for the catalyst containing 15 wt.\% \( V_2O_5 \) and a surface density of 3.3 \( V \text{ nm}^2 \) [65].
Fig. 1.7 $^{51}$V MAS NMR spectra of a 15 wt.% $V_2O_5/SiO_2$ catalyst (3.3 $V \text{nm}^{-2}$) [65] under dehydrated conditions (dehydrated at 500°C for 2h in vacuum). For low V surface density ($<4.6 \text{ Vnm}^2$) only isolated tetrahedral V sites were detected. Higher loadings, however showed the presence of V-O-V species which can be attributed to crystalline $V_2O_5$. Symbol * indicates the sidebands of the isotropic shifts at -714 ppm (V-O-Si). Experimental conditions: single pulse length: $\pi/8$, relaxation delay: 0.5 s, spinning rate: ca. 10 kHz.

1.2.2.3 Catalysts made by droplet-to-particle conversion

Rossetti et al. [72] prepared $V_2O_5/SiO_2$ catalysts for the oxidative dehydrogenation of propane to propene by flame spray-assisted pyrolysis of vanadium (IV) oxy-acetylacetonate and tetraethyl-orthosilicate (TEOS) in relative low (0.1-0.2M) concentration. (Table 1.1, entry 12). Compared to other flame-made silicas using vapor-fed [5] or FSP [73] reactors, very low surface area SiO$_2$ (14 m$^2$g$^{-1}$) was produced. This may be attributed to the use of
low enthalpy (1400-1530 kJ mol\(^{-1}\)) solvents (ethanol and carboxylic acid) \[74, 75\] and a low pressure drop (\(\Delta p=0.4\) bar) over the nozzle tip of the dispersion oxygen, resulting in a low dispersion of the liquid with a broad droplet size distribution \[73, 76, 77\]. These conditions may favor particle formation by droplet-to-particle (intra-particle) conversion (Fig. 1.3) \[8, 78\], resulting in significantly lower surface area and partly macro-porous particles. Interestingly, the addition of V increased the surface area of the final powder product significantly up to 80 m\(^2\)g\(^{-1}\) (28 wt.\%) before decreasing to 46 m\(^2\)g\(^{-1}\) at 50 wt.% V\(_2\)O\(_5\). From EPR, Raman and XRD analyses it was concluded that the vanadium was partly incorporated in the bulk silica matrix and TPO measurements indicated that less than 2 V nm\(^{-2}\) were accessible on the surface. For the highest content (50 wt.% V\(_2\)O\(_5\)) separate crystalline V\(_2\)O\(_5\) domains were detected by XRD \[72\]. High selectivities were measured for the flame-made catalysts only in anaerobic (absence of O\(_2\)) tests while co-feeding of propane and O\(_2\) resulted in propene selectivities around 20%. Best catalytic results were obtained for the 10 wt.% V\(_2\)O\(_5\)/SiO\(_2\) catalyst with up to 80% propene selectivity at 10% conversion of propane under anaerobic conditions. This high selectivity was attributed to the presence of isolated monomeric VO\(_x\) surface species in the low vanadia loading catalysts. Higher V\(_2\)O\(_5\) contents resulted in significantly lower propene selectivity (<20 %) and undesirable high selectivity to CO\(_x\).

V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts prepared by flame-assisted spray pyrolysis were also applied for the oxidative dehydrogenation of propane \[79\] (Table 1.1, entry 13). Again, low pressure drop and low enthalpy solvent resulted in powders with low surface area (20-27 m\(^2\)g\(^{-1}\)) perhaps by droplet-to-particle conversion. The powders showed a rather broad particle size distribution with sizes spreading over an order of magnitude. The surface area was 80% lower than that of FSP-derived alumina \[80\] for which high enthalpy precursors and higher pressure drop were applied. Doping with V did not increase the surface area significantly as for V\(_2\)O\(_5\)/SiO\(_2\) \[72\]. However, a slightly narrower particle size distribution was noticeable. XRD showed crystalline V-containing structures (mainly V\(_2\)O\(_5\) or AlVO\(_4\)) for all vanadia loadings indicating a lower surface and bulk dispersion compared to the V\(_2\)O\(_5\)/SiO\(_2\) catalysts which was
evidenced by Raman spectroscopy. Increasing the V loading increased the catalytic activity while selectivity decreased in the co-feed mode of the reactants propane and O₂. These V₂O₅/Al₂O₃ catalysts showed, however, inferior catalytic performance compared to similarly prepared V₂O₅/SiO₂ [72].

1.3 Flame synthesis of other mixed metal oxides

Beside the vanadia-based catalysts focused in this review, there are a number of other mixed oxide-based catalysts which have been prepared in flames, including perovskites [74, 75, 81, 82], which were already covered in an earlier review [8] and are therefore not discussed here. Progress in the flame synthesis of supported noble metal (e.g. Pt, Pd, Rh, Ag, Au) catalysts has been reviewed recently by Strobel and Pratsinis [83] and will therefore only briefly be considered here. An overview of the various mixed metal oxide catalysts prepared by flame processes along with their catalytic applications is given in Table 1.2.

1.3.1 Vapor-fed aerosol flame synthesis (VAFS)

Due to particularly the limited availability of vaporizable metal precursors such mixed metal oxide catalysts were prepared mostly by LFAS (FSP and FASP). The exceptions are doped titania-based photocatalysts [84-86], TiO₂/SiO₂ [68] and Cu/ZnO/Al₂O₃ [87] which were prepared by vapor-fed flame synthesis (VAFS).

1.3.1.1 TiO₂-based photocatalysts

Strobel et al. [8] in their review already covered most of the VAFS-made photocatalysts including mainly single-oxides such as TiO₂[84, 85, 88, 89] ZrO₂ [88], GeO₂ [88], SnO₂ [88]. Additionally the aforementioned review contains a brief overview of mixed metal oxides such as Si-doped [84, 85] TiO₂ and Fe, Zn, Cr, and bimetal (Fe+Zn) doped [86] TiO₂. The latter material has been studied extensively by Park et al. [90, 91]. By mixing titanium-tetraisopropoxide and the volatile acetylacetonates of Fe, Zn, and Cr in solution the liquid precursor was vaporized and then supplied with the aid of N₂ to the flame. The nominal dopant concentration was set to 1 wt.%.
Nanoparticles with surface areas in the range of $13$ (Fe) to $17 \text{ m}^2\text{g}^{-1}$ (Cr) with spherical primary particles around $45 \text{ nm}$ were achieved. Doping with both Fe and Zn resulted in similar surface areas comparable to that of pure TiO$_2$ ($20 \text{ m}^2\text{g}^{-1}$). X-ray fluorescence spectroscopy indicated for the bimetal doped samples a significant deviation from the nominal Fe/Zn ratio up to $15$ times larger. The authors attributed this difference to a Zn loss during preparation, but it seems likely that the different vapor pressures of TTIP and acetylacetonates used as precursors may have resulted in unpredictable dopant concentrations in the precursor stream therefore affecting the composition of the final powder product. Separate vaporizers for the different precursors seem to be mandatory for proper control of the final material composition [12, 23, 68]. While Zn and Cr doping significantly increased the anatase to rutile ratio of initially 75:25 for pure TiO$_2$ to almost $100 \text{ wt.\%}$ anatase, doping with Fe had no influence on said ratio [90, 91]. Incorporation of bimetals (Zn+Fe) initiated the formation of uniform particles with an anatase/rutile ratio of 60/40. These samples showed highest photocatalytic activity in the total oxidation of 2-propanol compared to the pure and monometal-doped materials which was even higher than for the commercially applied P-25 TiO$_2$. The presented results, however, should be looked at with care as the preparation method used seems to be rather unpredictable concerning the nominal and actual loadings of the different dopants in the TiO$_2$ catalyst.

1.3.1.2 TiO$_2$/SiO$_2$ epoxidation catalysts

As mentioned above, TiO$_2$/SiO$_2$ epoxidation catalysts constitute an exception of the mainly by LFAS synthesized catalytic materials. Stark et al. [68] prepared such catalysts applying a diffusion burner and titanium-tetraisopropoxide and hexamethyldisiloxane as titanium and silicon precursors, respectively. Depending on the methane:oxygen ratio in the diffusion flame the synthesized powders consisted of agglomerates of small primary particles (10-20 nm) ($\text{CH}_4:\text{O}_2 = 1:20$) or larger spherical particles ($\text{CH}_4:\text{O}_2 = 1:4$). High titania dispersion was achieved for powders containing up to $3.2 \text{ wt\%}$ TiO$_2$. The powders prepared with high O$_2$ feed showed improved efficiency with respect to peroxide and olefin consumption in the
epoxidation of 2-cyclohexenol with tert.-butylhydroperoxide compared to corresponding aerogels.

Fig. 1.8 Reaction scheme (a) of epoxidation of 2-cyclohexenol with tert.-butylhydroperoxide (TBHP) as oxidant. The selectivity of epoxide formation related to TBHP consumption (b) and alkene consumption (c) for transition metal-doped titania–silica. All metals lead to considerable peroxide decomposition. Cr doping reduced the peroxide selectivity by 20% at only 30 ppm Cr. The high sensitivity of the epoxidation to impurities underlines the importance of clean catalyst preparation. Doping with Cr and Co reduce the efficiency of the alkene usage, while incorporation of Mn and Fe does not lead to significant loss of alkene reactant at dopant levels of up to 2000 ppm. Cr exhibits the strongest effect, as it leaches into the reaction mixture, converting most of the substrate to the corresponding ketone (adapted from Ref.[12]).
This behavior was attributed to a more dehydrated state of the surface of the flame-made material, leading to lower Brønsted acidity and higher hydrophobicity [68, 92]. XANES studies confirmed the high dispersion of the Ti on the silica surface and the preferential tetrahedral coordination of these sites achieved with flame synthesis [93]. In a subsequent study it was shown that flame synthesis is very suitable to prepare materials where trace amounts of components have to be controlled [12]. This has been demonstrated by preparing titania/silica catalysts with trace amounts (ppm range) of Cr, Mn, Co and Fe. The trace amounts of transition metal impurities had a strong effect on the performance of titania-silica based epoxidation catalysts (Fig. 1.8).

1.3.1.3 Cu/ZnO/Al₂O₃

A ternary catalyst for methanol synthesis made from the volatile precursors consisting of the acetylacetonates of Cu, Zn and Al was prepared in a vapor-fed flame reactor by Jensen et al. [87] (Table 1.2, entry 3). Two main compositions were studied with an atomic ratio Cu:Zn:Al of 50:50:0 and 45:45:10 using either a H₂ or CH₄ flame which was optionally quenched with air 12.5 mm downstream the flame arrestor. The latter composition showed the best catalytic activity in methanol synthesis from CO, CO₂ and H₂ and better long term stability compared to the binary CuO/ZnO system [87]. Fuel variation did not cause any significant difference in the crystallinity of the quenched 45:45:10 samples as analyzed by XRD although flame peak temperatures differed by 400°C (CH₄ > H₂). Surface area was smaller for the CH₄ flame (93 m²g⁻¹) than for the H₂ flame (123 m²g⁻¹) due the different flame temperatures. For the binary system change of the flame synthesis parameters had a pronounced effect on both crystallinity and surface area: The low temperature, quenched H₂ flame yielded higher surface area (113 m²g⁻¹) but no crystalline CuO phase in the XRD, while the unquenched CH₄ flame resulted in large primary particles (surface area = 66 m²g⁻¹) and segregated, crystalline CuO [87]. Based on calculated ternary phase distribution at equilibrium it was concluded that first ZnAl₂O₄ nucleates and forms aggregates on which later segregated CuO and ZnO particles condense, nucleate and grow on the
preformed surface [87]. Despite the difference in surface area, Cu dispersion was similar for both flames in the ternary and binary system corroborating that the Cu₂O forms late in the flame. It was concluded that the intimate contact between ZnO and CuO particles achieved in the ternary system is the reason for the higher activity. The authors pointed out that by variation of the flame synthesis conditions optimization of the material may be possible as those can have a significant effect on the surface area, structure and phase composition.

*Table 1.2 Overview over mixed metal-oxide catalysts made by flame synthesis*

<table>
<thead>
<tr>
<th>Entry</th>
<th>produced catalysts (^a)</th>
<th>solvent/fuel</th>
<th>BET surface area in m(^2)g(^{-1})</th>
<th>tested reaction</th>
<th>Ref.</th>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SiO₂/TiO₂</td>
<td>CH(_4)</td>
<td>50 – 300</td>
<td>epoxidation of cyclohexanol</td>
<td>[12, 68, 92, 93]</td>
</tr>
<tr>
<td>2</td>
<td>Cr, Fe, Zn/TiO₂</td>
<td>“</td>
<td>13 – 20</td>
<td>total oxidation of 2-propanol</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu/ZnO/Al₂O₃</td>
<td>“</td>
<td>66 – 195</td>
<td>methanol synthesis</td>
<td>[87]</td>
</tr>
<tr>
<td><strong>FASP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>MoO₃/TiO₂</td>
<td>ethanol</td>
<td>33</td>
<td>photocatalysis</td>
<td>[94]</td>
</tr>
<tr>
<td><strong>FSP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CeₓZr(_{1-x})O₂ (Si, Al)</td>
<td>2-ethylhexanoic acid + toluene, lauric- + acetic acid</td>
<td>90 – 150</td>
<td>dynamic oxygen exchange (TWCs)</td>
<td>[95-97]</td>
</tr>
<tr>
<td>6</td>
<td>Al₂O₃/CeₓZr(_{1-x})O₂</td>
<td>ethanol</td>
<td>32 – 66</td>
<td>NO(_x) reduction</td>
<td>[13]</td>
</tr>
<tr>
<td>7</td>
<td>NiₓAl(_{1-x})O(_y)</td>
<td>“</td>
<td>45 – 69</td>
<td>NO(_x) reduction</td>
<td>[13]</td>
</tr>
<tr>
<td>8</td>
<td>CoₓAl(_{1-x})O(_y)</td>
<td>“</td>
<td>26 – 53</td>
<td>NO(_x) reduction</td>
<td>[13]</td>
</tr>
<tr>
<td>Entry</td>
<td>produced catalysts</td>
<td>solvent/fuel</td>
<td>BET surface area in m²·g⁻¹</td>
<td>tested reaction</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------</td>
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<td>-----------------------------</td>
<td>-----------------</td>
<td>------</td>
</tr>
<tr>
<td>9</td>
<td>ZnO/SiO₂</td>
<td>methanol + aceton</td>
<td>42 – 82</td>
<td>propene carbonate synthesis</td>
<td>[98]</td>
</tr>
<tr>
<td>10</td>
<td>MgAl₂₋ₓMₓO₄ (M=Mn, Fe, CO)</td>
<td>acetic acid + methanol</td>
<td>130 – 213</td>
<td>methane combustion</td>
<td>[99]</td>
</tr>
<tr>
<td>11</td>
<td>Pd/MgAl₂O₄</td>
<td>“</td>
<td>223</td>
<td>“</td>
<td>[100]</td>
</tr>
<tr>
<td>12</td>
<td>Pd/La₂O₃/Al₂O₃</td>
<td>“</td>
<td>120</td>
<td>“</td>
<td>[101]</td>
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<td>13</td>
<td>Fe/TiO₂</td>
<td>xylene + acetonitrile</td>
<td>86 – 100</td>
<td>photocatalysis</td>
<td>[102]</td>
</tr>
<tr>
<td>14</td>
<td>Cu/CeO₂</td>
<td>xylene</td>
<td>70 – 120</td>
<td>CO oxidation</td>
<td>[103]</td>
</tr>
<tr>
<td>15</td>
<td>Cu/CeₓZr₁₋ₓO₂</td>
<td>“</td>
<td>68 – 88</td>
<td>NO reduction by CO</td>
<td>[104]</td>
</tr>
<tr>
<td>16</td>
<td>La/Cu/ZnO</td>
<td>“</td>
<td>67 – 80</td>
<td>water-gas shift</td>
<td>[105]</td>
</tr>
<tr>
<td>17</td>
<td>Rh/CeₓZr₁₋ₓO₂</td>
<td>“</td>
<td>105</td>
<td>syngas production</td>
<td>[106]</td>
</tr>
<tr>
<td>18</td>
<td>Au/CuₓMgₓAlₓOₓ</td>
<td>acetic acid + methanol</td>
<td>81 – 110</td>
<td>aerobic oxidation of alcohols</td>
<td>[107]</td>
</tr>
<tr>
<td>19</td>
<td>Pt/CeₓZr₁₋ₓO₂</td>
<td>2-ethylhexanoic acid</td>
<td>78 – 98</td>
<td>dynamic oxygen exchange (TWCs)</td>
<td>[108]</td>
</tr>
<tr>
<td>20</td>
<td>Pt/Ba/CeₓZr₁₋ₓO₂</td>
<td>2-ethylhexanoic acid + toluene</td>
<td>90</td>
<td>NOₓ storage-reduction</td>
<td>[109]</td>
</tr>
<tr>
<td>21</td>
<td>Pt/MgAl₂O₄</td>
<td>acetic acid + methanol</td>
<td>226</td>
<td>“</td>
<td>[110]</td>
</tr>
<tr>
<td>22</td>
<td>Pt/Ba/Al₂O₃</td>
<td>diethylene glycol monobutyl ether + acetic anhydride</td>
<td>≈140</td>
<td>“</td>
<td>[111, 112]</td>
</tr>
<tr>
<td>23</td>
<td>Pt/K/Al₂O₃</td>
<td>“</td>
<td>146</td>
<td>“</td>
<td>[113]</td>
</tr>
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1.3.2 Liquid-fed aerosol flame synthesis (LAFS)

1.3.2.1 Mixed-metal-oxide RedOx catalysts

Ceria-based catalysts constitute an important class of catalysts due to their unique ability to store and release oxygen, the most prominent application being the automotive three-way catalyst. Flame spray pyrolysis has been successfully applied for the synthesis of highly thermally stable ceria nanoparticles with surface areas up to 250 m$^2$g$^{-1}$ [78]. Doping of ceria by Zr further stabilizes the flame-made ceria [96, 97] (Table 1.2, entry 5). Interestingly, doping of Ce$_{0.5}$Zr$_{0.5}$O$_2$ with small amounts of Si maximized the oxygen exchange capacity, while a similar effect was not observed when doping with Al (Fig. 1.9) even though the performance of flame-derived catalysts was superior to that of corresponding wet-made ones [95].

Kydd et al. [103] prepared Cu/CeO$_2$ catalysts (Table 1.2, entry 14) for CO oxidation by flame spray pyrolysis using copper 2-ethylhexanoate and cerium 2-ethylhexanoate mixed with a high enthalpy solvent (xylene) as Cu and Ce source, respectively. The Cu loading was varied from 0-12 wt.%.
Depending on Cu content, the specific surface area of the catalysts increased from 70 to 105 m²g⁻¹ with decreasing Cu content. The catalysts was made up of highly dispersed isolated Cu monomers at low, and dimer species at high loadings (up to 8 wt.%). Higher Cu contents resulted in segregated Cu-rich domains visible by TEM, while XRD gave no indication of separate Cu or CuO crystals. These catalysts showed good activity for the preferential CO oxidation (PROX), the dimeric Cu species being more active than the monomeric ones. The superior catalytic performance was explained by the increased bond ionicity at the catalyst surface induced by the Cu dimers [103].

\[ \text{Fig. 1.9 Dependence of the oxygen exchange capacity at 700 °C on the silica (triangles) and alumina (circles) dopant content for flame-made (full symbols) and impregnated precipitated (open symbols) Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \text{ samples [95].} \]

Cu/CeₓZr₁₋ₓO₂ catalysts (Table 1.2, entry 15) for NO reduction with different Ce/Zr ratios were prepared by Zhang et al. [104] with similar precursors and flame parameters as used by Kydd et al. [103] The catalysts containing 4 wt.% Cu had surface areas in the range of 68 – 88 m²g⁻¹. Doping
CeO\textsubscript{2} with zirconium resulted in solid solutions (Ce:Zr = 25:75) that stabilized Cu\textsuperscript{+} species on the particle surface. Additionally the presence of copper and the Zr\textsuperscript{4+} doping strongly enhanced reactive lattice oxygen and site reducibility compared to pure CeO\textsubscript{2} catalysts. These mixed metal oxides showed promising catalytic activity (40\% yield of N\textsubscript{2}) in the reduction of NO by CO already at very low temperature (150 °C). With increasing reaction temperature the N\textsubscript{2} yield increased reaching 100\% at 350 °C [104].

Weidenhof et al. [13] examined different compositions of Al\textsubscript{2}O\textsubscript{3}/Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2}, Ni\textsubscript{x}Al\textsubscript{1-x}O\textsubscript{y}, ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} and Co\textsubscript{x}Al\textsubscript{1-x}O\textsubscript{y} (Table 1.2, entries 6-9) made by FSP from ethanol-based precursor solutions for NO\textsubscript{x} reduction. These materials were prepared using ethanol precursor solutions of the corresponding metals and had surface areas in the range of 30 to 69 m\textsuperscript{2}g\textsuperscript{-1}. The Al\textsubscript{2}O\textsubscript{3}/Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} samples had a surface area around 42 m\textsuperscript{2}g\textsuperscript{-1} which is significantly smaller than that of FSP-derived [95] catalysts of comparable composition (75 – 95 m\textsuperscript{2}g\textsuperscript{-1}) synthesized by using high enthalpy solvents 2-ethylhexanoic acid and toluene. High-throughput screening identified certain Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}/Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} compositions as active catalysts for NO\textsubscript{x} reduction and propane/propene oxidation offering activities comparable to conventional Pt/Al\textsubscript{2}O\textsubscript{3} catalysts [13].

La-doped Cu/ZnO catalysts (Table 1.2, entry 16) were prepared by Kam et al. [105] and tested in the low-temperature water-gas shift reaction. While keeping the Cu content constant (37 wt.\%) the La loading was increased up to 11 wt.\% and the ZnO content varied accordingly. Addition of 2.3 wt.\% La had a positive effect on the catalyst activity and reduced the apparent activation energy compared to an undoped Cu/ZnO system. Moreover, the addition of La resulted in a higher catalyst stability indicated by a markedly decreased deactivation [105] as with alumina supported Pt catalysts for methane oxidation [101].

Ramin et al. [98] applied FSP for the preparation of ZnO/SiO\textsubscript{2} and MO\textsubscript{x}/ZnO (M=Li, Mg, Ca, Sr, and Ba) based catalysts (Table 1.2, entry 9) suitable for the solventless propene carbonate synthesis in dense carbon dioxide. Both xerogel synthesis and one-step flame spray pyrolysis, which could be performed without any work-up procedure, were shown to be well-
suited methods for synthesis of high surface area materials. A wide range of catalyst compositions including undoped and doped (P, Mg, Sr) ZnO/SiO$_2$ and even Zn precursor dispersions on preformed colloidal silica particles were investigated. Specific surface areas ranged from 283 to 480 m$^2$/g for the undoped and doped flame-made ZnO/SiO$_2$ catalysts depending on the composition and the ZnO particle size was in the range of 5-10 nm. At similar composition comparable surface areas were achieved in another study [118] on pure ZnO/SiO$_2$ composite particles while the ZnO crystal size was smaller (<3 nm) even at much higher Zn content [118, 119]. In case of the preformed SiO$_2$ colloids surface areas around 60 m$^2$/g were achieved [98] but the ZnO crystal size was significantly smaller (<3 nm), similar to those mentioned before [119]. For the doped ZnO materials surface areas in the range of 40 (Sr-doped) to 80 m$^2$/g-l (Ba-doped) were achieved comparable to pure FSP-made ZnO [118, 119]. All materials showed good catalytic performance but the ZnO-SiO$_2$ system based on pyrolyzing the precursor with the preformed colloidal silica and the pure and doped ZnO materials afforded the best yields of propene carbonate. It was concluded that small ZnO clusters either decorated on silica colloids or as single ZnO particles are beneficial for the catalytic activity [98]. In general, this “suspension” approach may be interesting to avoid substantial incorporation of the catalytically active transition metal into the support (in this case SiO$_2$) matrix during flame synthesis. Both from the catalytic results as well as from the spectroscopic studies the authors concluded that not single Zn sites but rather ZnO clusters were the most active sites for this reaction.

Cu-Mg-Al mixed oxides of different ratios prepared by FSP were used as support material for colloidal Au catalysts [107] (Table 1.2, entry 18). Direct admixing of the gold precursor to the flame was unsuccessful due to the high sintering rate of the gold constituent. Therefore the Au nanoparticles (6-9 nm) were deposited onto the flame-made supports (surface area in the range of 80 to 110 m$^2$/g) in a separate step using a colloidal route (Fig. 1.10). The as-prepared catalysts were tested in the aerobic liquid-phase oxidation of 1-phenylethanol to phenyl–methyl ketone affording turnover frequencies (TOFs) up to 1300 h$^{-1}$. The catalytic activity strongly depended on the support
Flame synthesis of other mixed metal oxides composition, with Cu and Mg being crucial components. Best results were achieved with a ternary oxide consisting of Cu, Mg and Al with molar ratio of 5:1:2. Extension of the catalytic tests to various structurally different alcohols indicated that the ternary mixed-oxide-supported gold catalyst has excellent catalytic properties in the aerobic oxidation of a broad range of structurally different alcohols, affording selectivities >98% [107].

Fig. 1.10 left: structural properties of ternary mixed oxide Cu₅Mg₁Al₂Oₓ as observed by TEM; right: HAADF-STEM investigation of corresponding gold-loaded catalyst Au/Cu₅Mg₁Al₂Oₓ. Au particles in the size range of 6–9 nm are discernible. Au particles are bright in the HAADF-STEM image (Z contrast). (images taken with permission from Ref. [107])

1.3.2.2 Metal-oxide doped TiO₂-based photocatalysts

LAFS-made (FASP) single oxide ZnO [120] and TiO₂ [121] photocatalysts as well as doped ones made by FSP Pt/TiO₂ [122] and MoO₃/TiO₂ [94] were already reviewed [8]. Theo et al. [102] prepared Fe-doped TiO₂ by FSP as visible light active photocatalyst (Table 1.2, entry 13) by combustion of a xylene/acetonitrile mixture containing titanium-tetra-isopropoxide and Fe naphthenate. In contrast to Mo-doping[94] the short residence times in the flame accompanied by rapid quenching afforded homogeneously distributed Fe within the TiO₂ matrix up to Fe/Ti ratios of 0.05. These solid solution materials with a surface area around 99 m²g⁻¹
showed superior catalytic performance for the mineralization of oxalic acid under visible light irradiation compared to pure TiO$_2$ and the commercial Degussa P25 [102]. The formation of a solid solution and the trend of increasing photocatalytic activity under visible light irradiation was reported for flame-made V-doped TiO$_2$ catalysts [67] (see section 1.3.1) [102]. Additionally, these flame-made particles showed a unique Fe leaching behavior of Fe(II) ions into the reaction mixture which, however, re-adsorbed on the particle surface at the end of the reaction and therefore exhibited reproducible reaction rates even after 5 cycles demonstrating the recyclability of such FSP-made catalysts [102].

1.3.2.3 Spinel-type oxidation catalysts

Spinels find use in many applications and are especially interesting for catalysis due to their (electro)chemical properties. NiMn$_2$O$_4$ spinels [82] were made in 1994 by flame-assisted spray pyrolysis (FASP). By combustion of Ni acetylacetonate and Mn acetylacetonate dissolved in toluene high surface area materials (170 m$^2$g$^{-1}$) were achieved. While using a solution of NiCO$_3$ and MnCO$_3$ in the low enthalpy solvent acetic acid resulted in a low surface area of 49 m$^2$g$^{-1}$, indicating a difference in the particle formation mechanism: gas-to-particle vs. droplet-to-particle conversion for high and low enthalpy precursor solution, respectively (Fig. 1.3). No catalytic results, however, were presented. These were the only flame-aerosol derived spinel-type materials for potential catalytic application reported until 2006 [8].

Recently, van Vegten et al. [100] prepared spinel (MgAl$_2$O$_4$) supported Pd catalysts for methane combustion by single step flame spray pyrolysis (Table 1.2, entry 11). These catalysts showed good thermal stability when compared to TiO$_2$-, CeO$_2$- or ZrO$_2$-supported Pd catalysts by retaining ca. 25% of their initial surface area (223 m$^2$g$^{-1}$) after calcination at 1050 °C for 3h. However, this is significantly less than that of pure and La-doped Pd/Al$_2$O$_3$ catalysts prepared by FSP for which more than 80% of their initial surface area ($\approx$ 130 m$^2$g$^{-1}$) could be conserved after calcination at 1100 °C for 4 hours in air [101]. During methane oxidation, the spinel supported catalysts showed
intermediate light-off temperatures ($T_{50\%} = 410 ^\circ C$ for 1st cycle) but 100% methane conversion was only achieved by alumina supported catalysts [100].

In a subsequent study [99] spinel-like oxides without a noble metal constituent (Table 1.2, entry 10) with the formula $\text{MgAl}_{2-x}\text{M}_x\text{O}_4$ ($x = 0.1, 0.5, 1$ and 2, $M = \text{Mn}, \text{Fe} \text{ or Co}$) were prepared by FSP using a mixture of acetic acid and methanol as solvent/fuel. The as-prepared non-porous mixed oxide powders exhibited high surface area ($120 - 195 \text{ m}^2\text{g}^{-1}$) and appeared single phase by X-ray diffraction. However, XPS indicated some surface enrichment of the transition metal, that depended on its composition ($\text{Mn}, \text{Fe} \text{ or Co}$). Additionally the doping of the $\text{MgAl}_2\text{O}_4$ with $\text{Mn}, \text{Fe} \text{ or Co}$ resulted, independent of the doping content, in lower surface area ($< 190 \text{ m}^2\text{g}^{-1}$) compared to either the pure spinel without [99] or with Pd [100] having surface areas of 213 or 223 $\text{ m}^2 \text{g}^{-1}$, respectively. The materials were tested for methane combustion and the activity increased in the order $\text{Fe} < \text{Co} < \text{Mn}$. Aluminum free spinels ($x = 2$) possessed good initial activity, but the low thermal stability of these materials significantly reduces their catalytic applicability. By introducing Al ($x = 0.1, 0.5$ and 1), the initial activity decreased, but a concurrent increase in thermal stability resulted in materials with almost similar ($\text{Fe}, \text{Co}$) or even superior ($\text{Mn}$) catalytic activity compared to the aluminum-free samples after conditioning [99] prior to the catalytic test for 1h at 200 $^\circ C$ in a He stream with 1 vol.% CH$_4$ and 4 vol.% O$_2$.

1.3.2.4 Mo-based metathesis catalysts

Recently ternary mixed oxides consisting of a mixed silica/alumina support and MoO$_x$ as active species have been synthesized by FSP and tested in the self metathesis of propane [117] (Table 1.2, entry 28). Mo 2-ethylhexanoate, hexamethyldisiloxane and aluminium acetylacetonate (dissolved in 2 ethylhexanoic acid and acetonitrile) were used as Mo, Si and Al precursor, respectively, and mixed with xylene. The support composition was kept constant at 30/70 silica to alumina to achieve high surface acidity [15] and MoO$_3$ content was varied between 0 and 15 wt.%. Such flame-made catalysts showed a highly dispersed Mo oxide phase deposited on the support surface up to loadings of 3 wt.% MoO$_3$ ($<1 \text{ Mo nm}^2$). Increasing the loading to
5 wt.% caused segregation of very small (1 - 3 nm) MoO$_3$ clusters/particles on the silica/alumina surface. In contrast to vanadia-based catalysts the dispersion achieved for Mo by the FSP method is not significantly higher than that of corresponding wet-chemistry derived materials, e.g. wet-impregnated systems [123] or catalyst prepared by thermal spreading [124]. Further increase (up to 15 wt.%) resulted in separate crystalline MoO$_3$ particles ($\approx$20 nm) detectable by XRD [117]. The latter material showed only poor activity in the metathesis reaction due to the presence of crystalline MoO$_x$ species. The low loading catalysts, however, were active in the metathesis of propene, affording TOF of up to 73 mmol$_{\text{propene}}$ mol$_{\text{Mo}}^{-1}$ s$^{-1}$ (1 wt.% MoO$_3$, 0.3 Mo nm$^{-2}$), seven times higher as the highest turnover frequency reported for Mo-based metathesis catalysts so far. The metathesis activity appeared to be directly linked to the degree of the MoO$_x$ dispersion decreasing with increasing fraction of polymerized Mo species [117].

1.3.2.5 Supported noble metal catalysts

The noble metal component of flame-made catalysts is usually well-dispersed and exists as small metal or metal oxide particles depending on the intrinsic properties of the metal and the support. Important characteristics of the dispersed metal which are affected by the support are thermal stability, dispersion and oxidation state. All these properties are influenced by the flame synthesis conditions. Until today, only a few studies have been reported about the single step flame synthesis of mixed oxide-supported noble metal catalysts, while several reports exist on single oxide supported noble metal systems [83], including bimetallic Pd-Pt alloys supported on Al$_2$O$_3$ [125]. Examples of mixed oxide supported systems include Pt/ Ce$_x$Zr$_{1-x}$O$_2$ as three way catalysts [108], Pd/La-Al$_2$O$_3$ for catalytic combustion [101], Rh/Ce$_x$Zr$_{1-x}$O$_2$ for syngas production [106], and Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ [109] and Pt/Ba/Al$_2$O$_3$ [111, 112] for NO$_x$ storage-reduction (NSR). These catalytic materials have been discussed already in terms of catalytic performance in the recent general reviews on supported noble metal catalysts [83] and aerosol synthesis of catalysts [8] and will be summarized here only briefly with focus on the structural properties
and synthesis set-up. Emphasis is given to the most recent studies on mixed metal oxide supported noble metal catalysts.

1.3.2.5.1 NO\textsubscript{x} storage-reduction catalysts

For the NSR catalysts containing a Ba compound as a storage component, the use of a single flame set up proved to be unfavorable because co-feeding the metal precursors to the same flame resulted in the formation of inactive amorphous BaAl\textsubscript{1-x}O\textsubscript{y} species [112] (Table 1.2, entry 22). Therefore a two-nozzle flame spray pyrolysis (FSP) process has been developed for the one-step preparation of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} (Fig. 1.11). The use of two separate nozzles, one as aluminum and the other as a barium/platinum source, resulted in individual Al\textsubscript{2}O\textsubscript{3} and monoclinic BaCO\textsubscript{3} nanoparticles, exhibiting good NO\textsubscript{x} storage activity [111, 112]. Increasing the inter-nozzle distance resulted in late mixing of the two flame products and increased the amount of crystalline BaCO\textsubscript{3}. The structural properties and NSR activities of these catalysts were compared to corresponding standard Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalysts prepared conventionally via wet impregnation [126]. The structural differences of the BaCO\textsubscript{3} storage phase in flame-made and conventionally prepared catalysts affected strongly their NO\textsubscript{x} storage efficiency. In contrast to the conventionally prepared catalysts where at higher Ba loadings a less active BaCO\textsubscript{3} phase (HT-BaCO\textsubscript{3}) dominated, this phase was absent in the flame-made catalysts and thus led to improved NO\textsubscript{x} storage potential of these catalysts at higher Ba loadings.

Generally, the use of a two-nozzle FSP set-up allows better control of the degree of intermixing of the different components in the flame and optimizing the flame conditions for particle formation. It also offers the possibility for preferential deposition of the noble metal, either on the support (e.g. alumina), directly on the storage component (e.g. BaCO\textsubscript{3}) or on both components [111]. This promising concept was later also used successfully for the synthesis of Pt/K/Al\textsubscript{2}O\textsubscript{3} [113] and Pt/Ba/CeO\textsubscript{2} NSR catalysts [114] (Table 1.2, entries 23, 24), where the active Pt was deposited preferentially on the storage component (K and Ba) or the support (Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}). This control of the spatial distribution of particular components adds another powerful facet to the flame synthesis of complex catalyst materials and greatly extents the scope of catalysts which can be prepared by flame aerosol technology.
Fig. 1.11 Photo and schematic of the two-nozzle set-up for the preferential noble metal deposition for NO\textsubscript{x}-storage-reduction catalysts. By variation of the metal containing liquid precursors the noble metal can be either deposited on the support (e.g. Al\textsubscript{2}O\textsubscript{3} or CeO\textsubscript{2}, left) or on the storage component (e.g. BaCO\textsubscript{3} or K\textsubscript{2}CO\textsubscript{3}, right) or on both components [111-114].

\( M = \text{Ba or K} \)
Recently, Roy et al. [110] successfully prepared an NSR catalyst (Table 1.2, entry 21) using single-step flame spray pyrolysis. Instead of using Ba as the storage component, the authors based their catalyst on MgAl₂O₄ spinel-based oxide, which served as support as well as storage component. The catalyst consisting of nano-sized Pt dispersed on MgAl₂O₄ spinel showed superior dynamic performance in NOₓ storage-reduction at short regeneration times (<30 s) compared to a standard 1%Pt–20%Ba/Al₂O₃ reference catalyst. However, the better NSR performance at short regeneration times of Pt/MgAl₂O₄ was limited to the use of hydrogen and H₂–CO mixtures as reductants, with other reductants, CO or C₃H₆, the NSR performance was similar for both catalysts. XRD and time-resolved in-situ DRIFT investigations indicated that during the storage period bulk nitrate species were formed on Pt–Ba/Al₂O₃, whereas on the spinel-based Pt/MgAl₂O₄ catalyst predominantly NOₓ is stored on the particle surface. The superior dynamic performance of the spinel-based Pt/MgAl₂O₄ was attributed to the different adsorbed NOₓ species and their different stability under regeneration conditions. Pt/MgAl₂O₄ also showed higher thermal stability up to 800 °C and lower stability of sulfur-containing species [110].

1.3.2.5.2 Hydrogenation and oxidation catalysts

A largely unexplored field in flame synthesis of catalytic materials with great potential is the direct addition of dopants (promoters) to the flame feed. Basic and acidic supports play a key role in various catalytic reactions [127-129] Doping the main support oxide with different alkali metal oxides results in an increase of basicity [130] while doping alumina with silicon increases surface acidity [131, 132]. The effect of the support material on the catalytic properties of noble metal particles is still a matter of intense research [133-136].

Recently, Schimmoeller et al. [15] showed that FSP is a highly versatile and reproducible synthesis method to fine tune the acid/base properties of 4.75 wt.% Pt/Al₂O₃ catalysts (Table 1.2, entries 25, 26). Doping the support with SiO₂ or Cs₂O allowed increasing surface acidity or basicity, respectively. Up to 50 wt.% SiO₂ the specific surface areas could be kept in a narrow range (141±15 m²g⁻¹) similar to pure FSP-made Pt/Al₂O₃ [80], while higher SiO₂
content increased the surface area and led to lower crystallinity similar to flame-made Ta2O5/SiO2 mixed oxides [137]. Platinum dispersion and particle size at low SiO2 support content was comparable to earlier studies [80] with similar Pt loading, but increased with increasing silica content. The catalysts containing 22-30 wt.% SiO2 were the most acidic as evidenced by TPD of NH3 (Fig. 1.12a). This contrasts the behavior of wet-chemistry derived Al2O3-SiO2 systems, where the highest acidity is observed at much higher silica content.

The catalysts were tested in the hydrogenation of acetophenone. The SiO2-doped catalysts were highly active and the selectivity to the hydrogenolysis byproducts increased with increasing SiO2 content by more than 20-fold. This behavior was attributed to the effect of support acidity on the properties of the Pt-H system. On the other hand, addition of Cs2O increased the surface basicity, as evidenced by TPD of CO2. Cs2O was probably enriched at the Al2O3 surface, stabilizing the high Pt dispersion of flame-made Pt/Al2O3 [15, 80] and strongly influenced the acid/base properties and thus the catalytic performance already at very low cesium oxide loadings [15]. It was later shown [115] that in such tailored flame-made catalysts the electronic properties of Pt are indeed changed, leading to different adsorption and interaction of the reaction components on the metal surface and thus significant differences in the catalytic behavior depending on the surface iconicity [15, 115]. The catalytic performance of the SiO2-doped Pt/Al2O3 catalysts showed a clear dependency on the support acidity and exhibited outstanding enantiomeric excess in the enantioselective hydrogenation of activated ketones (Fig. 1.12b) outperforming the wet-impregnated reference catalyst [115]. While for pure Pt/Al2O3 only a higher activity (TOF) and slightly lower selectivities compared to a wet-made reference catalyst in the hydrogenation of ethyl pyruvate were measured[80], Si-doped catalysts showed both, higher activity and selectivity (ee), compared to pure Pt/Al2O3 and the commercial reference catalysts achieving ee under optimized conditions of up to 94% [115].

Later it was shown by multinuclear solid-state NMR that flame-derived alumina-silica mixed oxides have tunable Brønsted acidities ranging from moderate to zeolitic acid strength, depending on the aluminum content.
Surface acidity, accessibility and local structure of Brønsted acid sites have been analysed and the relationship between Brønsted acidity and the local aluminum-silicon coordination has been elucidated [138].

Beier et al. [116] prepared Ag catalysts supported on a CeO₂/SiO₂ mixed oxide by FSP (Table 1.2, entry 27). Even though the ceria was present in segregated domains the effect of the Ce-doping was profound: By adding only 10 wt.% CeO₂ to the support the Ag particle size could be stabilized at significantly smaller size compared to Ag supported on pure SiO₂ which showed noble metal particles in the size of up to 50 nm. Such Ce-doped flame-made catalysts exhibited superior catalytic activity compared to wet-impregnated silver catalysts, affording turnover frequencies up to 2000 h⁻¹ in the side-chain oxidation of p-xylene, toluene or ethylbenzene [116]. In addition, the flame-synthesized catalysts were significantly less prone to leaching compared to the impregnated catalyst of similar composition.
1.4 Potential and limitations of flame methods

From the previous chapters it emerges that flame synthesis gives access to materials which are often structurally different than corresponding materials prepared by conventional wet-chemistry methods. Although, the application of vapor-fed flames is somewhat limited by the restricted availability of volatile metal precursors and the narrow concentration range of the metal, these shortcomings can be alleviated by the use of liquid-fed flame synthesis. The latter method offers significantly higher flexibility in the selection of the type of metal precursor and opens almost the whole periodic table for possible material compositions provided suitable organometallic or water soluble precursors are available [6, 8, 49]. Figure 1.13 gives an overview of the different synthesis parameters influencing the particle formation and therefore determining the final material’s characteristics. The various possibilities for adjusting these parameters enable the synthesis of tailor-made mixed metal oxide catalysts with various compositions and structures, rendering flame synthesis, and especially LAFS, an attractive process for catalyst synthesis.

Starting from the selection of the flame process, VAFS or LAFL (FASP or FSP), the possible particle formation routes (gas-to-particle or droplet-to-particle) as described in Fig. 1.3 can be controlled.

This basic selection can already result in different structures of the same material composition and therefore lead to greatly different performance of as-prepared catalysts. As shown for the vanadia-based catalysts (section 1.2), V dispersion and structure of VO$_x$ species strongly depend on the choice of synthesis route (VAFS or FASP and FSP within LAFS). Colder flames, as encountered in VAFS favor formation of crystalline V$_2$O$_5$ due to the longer residence time in the hot temperature zone allowing the vanadia to form the thermodynamically stable crystalline V$_2$O$_5$ phase at higher loadings [23, 56]. In contrast, catalysts made by LAFL, that is in flames with much higher turbulence and shorter residence time, showed unique amorphous and dominantly mono- or oligomeric VO$_x$ species even at very high V surface density [24, 60]. exceeding the so called “theoretical monolayer”. By changing the pressure drop ($\Delta p$) across the nozzle tip for the dispersion gas, switching between FSP (high $\Delta p$) and FASP (low $\Delta p$) allows controlling the final particle
morphology using the same or a similar set-up [73, 77]. Choosing FSP as synthesis route, results in non-porous powders with high surface area and high V dispersion on the support surface by homogeneous nucleation during gas-to-particle conversion [24, 58, 60, 61]. Using a low temperature flame can result in macroporous particles of low surface area and incorporation of the active vanadia species in the bulk [72, 79] by droplet-to-particle conversion (Fig. 1.3).

With respect to noble metal catalysts, FSP allows not only control of support morphology and dispersion of the metal particles [83] but also the tailoring of the support properties by additional dopants and promoters which can be easily added to the precursor solution, as exemplarily demonstrated for acid-base properties [15]. This tailoring of acid-base properties is of course not limited to supported noble metal catalysts but can also be applied for a large variety of other mixed metal oxide supported catalysts. Additionally, the metal concentration in the precursor solution can be adjusted in a broader range and more easily as it is generally possible for vapor-fed flames.

Due to the liquid state of the precursor solution, the choice of the solvent/fuel becomes an important parameter. By variation and/or combination of different organic solvents the flame enthalpy, directly influencing the temperature profile in the flame, can be altered and therefore affects particle formation.

For example high enthalpy solvents (e.g. xylene or 2-ethylhexanoic acid) can promote particle formation via the gas-to-particle route (Fig. 1.3) by providing enough combustion enthalpy to fully evaporate the metal precursor as shown for $\text{V}_2\text{O}_5/\text{SiO}_2$ [65], while the use of low enthalpy solvents (e.g. ethanol or acetic acid) can facilitate the droplet-to-particle route [72] or result even in hollow, inhomogeneous particles as in the case of $\text{Bi}_2\text{O}_3$ [139].

Not only the combustion enthalpy of the solvent can affect the final particle morphology but also the nature (alcohol, carboxylic acid, benzenes etc.) of the solvent and difference in boiling points in solvent mixtures can have a strong influence on the elemental distribution within the mixed oxide or on the homogeneity of the particle size distribution.[140] This can significantly affect the material properties (e.g. thermal stability) as observed for the Zr-doped ceria system[96] or for perovskite catalysts [74, 75].
Two important parameters for controlling the particle morphology, especially the surface area, are the liquid (precursor) feed rate and the corresponding feed rate of the dispersion gas [5, 7, 49, 55]. Both parameters have direct influence on the flame temperature, particle concentration within the flame and residence time of the particles in the hot temperature zone directly affecting the final particle size. High liquid feed rate increases nucleation and coagulation rate and favors particle growth by sintering while high dispersion gas flow rates decrease flame temperature (shorter residence times in hot temperature zone) and particle concentration reducing the overall particle growth due to faster cooling and less sintering [76]. The latter can be additionally suppressed by subsequent quenching of the flame to control particle growth of the metal oxide (support or full catalyst) as well as the noble metal, as shown for Pt/TiO$_2$ catalysts [137] by shorter residence times in the high temperature zone. So far only a few studies [23, 24, 60, 61, 77, 80, 101, 122] have investigated the influence of those two flame parameters on the structural properties of the catalyst, especially the active component. Downstream quenching [137, 141, 142] offers additionally the opportunity to introduce reactive gases such as CO or NH$_3$ into the aerosol which may affect the surface properties (oxidation state, acid-base properties) of the preformed particles.

Another advantage of the FSP technique is the possibility to achieve dense, almost hermetic, coatings in the same process step by addition of a coating precursor (e.g. Si) downstream of the particle producing flame [143]. By this approach it is possible to coat for example superparamagnetic FeO$_3$ particles with silica [144]. Such materials possess a virtually inert surface on which all kinds of desired catalytically active groups can be grafted. These superparamagnetic particles can be easily separated from a liquid media reaction system by applying an external magnetic field, an attractive concept for fine chemistry reactions involving immobilized homogeneous catalysts.

Reproducibility and purity of the final product are, especially for catalytic materials, an important factor. Already trace amounts of impurities can alter the catalyst performance significantly [12].
Fig. 1.13 Schematic of the parameters influencing material properties made by flame synthesis.
Flame synthesis offers high control of the product purity [5, 11] and provides a fast single-step synthesis tool with outstanding reproducibility at reasonable production rates.

Moreover the combination of flame synthesis and the direct deposition technique of mixed metal oxides, already applied for gas sensors[59] and on different substrates, e.g. ceramic foams [24, 60], stainless steel tubes [145] or micro-reactors [17] opens various possibilities for coating preformed structures with catalytic components. With this technique also ready-to-use catalyst with high porosity of the deposited layer, avoiding the usual mass transfer limitations of pelletized catalysts can be produced in only short process times and with high reproducibility [24, 60].

Due to the relative fast synthesis times with reasonable production rate (lab-scale ca. 5 – 50 g h⁻¹) for different material compositions, flame synthesis is predestinated for high throughput studies for mixed metal oxide catalysts reducing the overall synthesis and research time [146, 147].

Micro- and mesoporous materials constitute an important class of catalysts and supports. Flame synthesis dominantly results in non-porous particles of nanometer size. The synthesis of molecular sieve type materials with well-defined pore structure has not been achieved yet by flame synthesis. In fact Si-based materials have so far shown only amorphous bulk structure with no long range ordering of the constituents [65, 68, 73, 148]. Already the addition of 10 to 15 wt.% SiO₂ was enough to diminish the crystallinity of alumina almost completely while the addition of Cs₂O did not influence the alumina crystallinity even though the particle size was significantly reduced [15]. Therefore flame-synthesis of ordered micro- or mesoporous materials still remains a challenge.

Another challenge is related to materials/catalysts which need high crystallinity to achieve good catalytic performance. The very short residence times at high temperatures and the fast cooling rates due to quenching in the flame [76] sometimes do not allow enough time for complete crystallization as for example observed for BiVO₄ [149]. This leads to a high fraction of amorphous materials without any defined structure (texture) which might be both an advantage as well as a disadvantage depending on the material
conclusion and need for well-defined crystal structures as for example in the case of the V-Mo-M-O (M=Te, Sb) system [150-153] or even more complex systems like polyoxometalates [154] in Keggin-type [155] structures. For such materials new approaches in the FSP set-up are necessary in order to achieve the desired crystal phase. Such approaches may include increasing the combustion enthalpy [156] to increase the flame temperature, the enclosure of the flame [157] to increase the particle residence time at high temperatures, or the use of flame assisted spray pyrolysis (FASP) as tool for further increasing flame temperatures by decoupling the spray and the ignition point while using a high enthalpy fuel (e.g. acetylene) feeding the supporting flame [158].

Considering the previously described ability and potential of flame synthesis to make noble metal supported catalysts, it should be noted that supported gold catalysts have been a big challenge for direct flame synthesis. So far all supported gold catalysts directly made by flame synthesis suffered from low gold dispersion even at low Au loading due to substantial particle growth of gold (low melting point, weak metal-support interactions) in the flame. Presently the only possibility for reaching high gold dispersion seems to be the deposition of the gold particles in a preceding extra step, as shown by Haider and Baiker [107] who applied subsequent deposition-precipitation with colloidal Au particles to prepare highly dispersed Au supported on FSP-derived ternary Cu-Mg-Al mixed oxides for the aerobic oxidation of alcohols. This combined synthesis method may in some cases be favorable when high dispersion of a metal with low melting point is demanded, as in case of supported gold catalysts.

1.5 Concluding remarks and outlook

Flame synthesis represents an attractive complementary catalyst preparation method to provide materials with properties differing considerably from those prepared by classical methods. The flame aerosol process is continuous and fast and availability and accessibility of process parameters allow the preparation of a wide spectrum of catalytic materials ranging from single metal oxides to mixed metal oxides and metal salts as well as supported metal systems and even metal powders [159, 160]. Generally, as-prepared
Chapter 1: Flame aerosol synthesis of mixed-metal-oxide catalysts

materials do not need a high temperature calcination step prior to catalytic application as required for their wet-chemistry derived counterparts.

An important requirement for the beneficial use of flame synthesis is a thorough understanding of the interdependences of the various process parameters and their impact on the final properties of the produced powders. Although great progress has been made in developing this knowledge in the past decade, considerable further research efforts are needed for a systematic design and scale-up of flame-made materials. On the other hand, flame synthesis fills important gaps in the tool box of methods for the production of catalyst materials. In general flame-made catalysts are non-porous and often of controlled crystallinity with the beneficial effect of high thermal stability due to the high temperature characteristics of the process. Flame-synthesis has proven to give access to unique structures, e.g. with high surface densities of the active species [60, 65], controllable surface iconicity [15, 115] or even novel crystal phases [10] not accessible by conventional wet-chemistry methods. Such specific material properties paired with the proven scalability and continuous production with high reproducibility make flame techniques a promising tool for the optimization of conventional catalysts and the development of new catalytic materials with unique properties which are so far not commonly accessible by conventional synthesis methods.

Future research should not only focus on the material synthesis but also on a proper understanding of the chemical and physical processes occurring in the flame and their role in determining the final materials properties. This understanding will trigger a further optimization of the configuration of flame reactors and extend the scope of materials which can be made. The ultimate goal will be the rational design of catalyst materials with specific properties and their production with high rate in a single step. In specific cases this goal has been reached (e.g. TiO₂) but there is still much more flame synthesis can offer for the production of catalysts. The potential of flame synthesis has by far not been exploited yet and compared to the experience existing for wet-chemistry based synthesis processes, the knowledge accumulated so far is rather modest. Nevertheless, many studies have demonstrated that flame synthesis can offer opportunities which are unique in the sense that they are
not easy accessible by other traditional catalyst preparation methods and therefore it can be expected that the use of flame methods for the production of catalyst materials will increase in the future.

1.6 References


CHAPTER 2

Structure of flame-made vanadia/titania and catalytic behavior in the partial oxidation of \textit{o}-xylene

Abstract

Vanadia/titania particles with a specific surface area (SSA) up to 195 m$^2$g$^{-1}$ and a V$_2$O$_5$ content up to 40 wt.% or V-coverage up to 59 V nm$^{-2}$ were prepared by flame spray pyrolysis (FSP) using various conditions. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature programmed reduction, \textit{in situ} Raman spectroscopy and tested for partial oxidation of \textit{o}-xylene. Depending on vanadia content, monomeric, polymeric and crystalline vanadia species were formed on TiO$_2$ support particles by FSP. Increasing the high temperature particle residence time and concentration (production rate) during FSP reduced the SSA and increased the vanadia coverage of TiO$_2$ beyond a theoretical “monolayer” (> 8-10 V nm$^2$)

\footnote{Part of this chapter is published in \textit{J. Catal., 256}, (2008) p74}
while retaining amorphous (mono- and polymeric) VO\textsubscript{x} surface species. Controlling liquid precursor and dispersion gas feed rates, precursor concentration and V\textsubscript{2}O\textsubscript{5} content allowed tailoring SSA and the population of the different VO\textsubscript{x}-species in these vanadia/titania mixed oxides. For comparison, vanadia/titania catalysts containing 10 wt.% V\textsubscript{2}O\textsubscript{5} with comparable SSA and V-coverage were prepared by impregnation resulting in typical amorphous (< 10 V nm\textsuperscript{-2}) and crystalline (> 10 V nm\textsuperscript{-2}) VO\textsubscript{x}-species. Catalysts containing 7, 10 and 20 wt.% V\textsubscript{2}O\textsubscript{5} were deposited directly from the flame on ceramic foams that were tested for the partial oxidation of o-xylene to phthalic anhydride. The global activity of flame-made and conventionally impregnated catalysts depended mainly on SSA and vanadia loading (number of V-surface sites), while the amorphous or crystalline nature of the VO\textsubscript{x}-species seemed to be less critical. In contrast, selectivity to phthalic anhydride was significantly affected by the nature of the VO\textsubscript{x}-species: amorphous species exhibited higher selectivity for conversion below 90 % than catalysts containing crystalline V\textsubscript{2}O\textsubscript{5}.

2.1 Introduction

Supported vanadia catalysts are used for a variety of reactions, including selective catalytic reduction (SCR) of NO\textsubscript{x} [1, 2], oxidative destruction of volatile organic compounds (VOC) [1, 3], dehydrogenation of propane [4] or partial oxidation of o-xylene to phthalic anhydride (PA) [5] which is the focus of this study. Strong surface interactions between vanadia and titania result in amorphous mono-, di- and polymeric VO\textsubscript{x}-species which can be formed at sub-"monolayer" (<8-10 V nm\textsuperscript{2}) coverage [6]. Exceeding that V-coverage leads to crystalline V\textsubscript{2}O\textsubscript{5} [5] regardless of preparation method, e.g. classic impregnation [7], atomic layer deposition (ALD) [8] and even vapor-fed flame synthesis [9]. Crystalline V\textsubscript{2}O\textsubscript{5} has a detrimental effect on activity and selectivity [10, 11]. Recently V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts prepared by flame spray pyrolysis (FSP) showed a good dispersion of vanadia while retaining the amorphous VO\textsubscript{x}-species up to a V-coverage of 12 V nm\textsuperscript{2} [12]. This catalyst with a specific surface area (SSA) of 53 m\textsuperscript{2}g\textsuperscript{-1} showed higher selectivity at a given conversion than a sub-"monolayer" (7 V nm\textsuperscript{2}) catalyst with higher SSA (93 m\textsuperscript{2}g\textsuperscript{-1}) prepared also by
FSP. These results encouraged us to systematically study the effect of V$_2$O$_5$ content, SSA and nature of VO$_x$-species in vanadia/titania catalysts for the partial oxidation of o-xylene.

The contributions of different VO$_x$-species to the catalytic performance of vanadia-based catalysts has been debated for some time: For low loadings (up to 2-3 V nm$^{-2}$), strongly bound monomeric VO$_x$ groups with three V-O bonds to the support and a terminal partly hydrated V=O bond are formed at ambient conditions [13]. At V-coverages higher than about 3 V nm$^{-2}$, some V-O-support bridges rearrange themselves into V-O-V bridges [5, 6, 8] increasing the degree of polymerization. These still amorphous vanadia species turn into crystalline ones when the V-coverage exceeds about 8 V nm$^{-2}$ [5]. Many researchers claim that amorphous monomeric VO$_x$-species with terminal V=O bonds are the most active species for reactant adsorption and C-H bond breaking, particularly when compared to crystalline V$_2$O$_5$ [10, 14-16]. In contrast, Gervasini et al. [8] found higher catalytic activity for polymeric rather than monomeric VO$_x$-species in partial oxidation of o-xylene to PA. Weckhuysen and Keller [17] stated that the V-O-support bond is important in methanol oxidation, a model reaction for V$_2$O$_5$/TiO$_2$ catalysts. Recently, density functional theory (DFT) showed that the oxygen atom in the V-O-Ti bond is the most reactive towards H adsorption [18], the limiting step of the oxidation reaction, because of the high stability of terminal V=O bonds.

The influence of amorphous mono- or polymeric and crystalline VO$_x$-species on PA selectivity is still not clear. Pure crystalline V$_2$O$_5$ catalysts with high SSA (25 m$^2$g$^{-1}$) exhibited higher selectivity and activity than corresponding catalysts with low SSA (1.8 m$^2$g$^{-1}$) at constant residence times [19]. In contrast, Bond [14] stated that crystalline V$_2$O$_5$ does not affect catalytic activity and selectivity and the latter is influenced mainly by SSA. Sub-"monolayer" (<8 - 10 V nm$^{-2}$) V$_2$O$_5$/TiO$_2$ catalysts prepared by ALD and classic impregnation showed that the higher selectivity during partial oxidation of o-xylene can be attributed to polymeric VO$_x$-species rather than to monomeric species [8]. In industry, however, o-xylene catalysts have low SSA (7 - 30 m$^2$g$^{-1}$) with high vanadia loadings of 5 - 15 wt.%, preferably around 7 -
10 wt.% [14, 20, 21] exceeding the “monolayer” coverage often by a factor of >5 (V-coverage > 50 V nm⁻²).

Here we prepared vanadia/titania catalysts with high V-coverage and amorphous VOₓ-species by FSP and investigated the influence of FSP variables like precursor concentration, liquid feed-rate and V₂O₅ content on the structural and catalytic properties of vanadia/titania mixed oxides. The catalytic materials were directly deposited onto ceramic foam carrier structures and the effect of SSA and nature of VOₓ-species on activity and selectivity for the partial oxidation of o-xylene was investigated. Emphasis was placed on the elucidation of the crucial preparation variables determining the structural properties of the catalysts and on understanding how amorphous or crystalline VOₓ-species at high V-coverage affect the catalytic performance. For comparison, catalysts with comparable SSA and V₂O₅ content were prepared by impregnation.

2.2 Experimental

2.2.1 Catalyst Preparation

Nanostructured vanadia/titania particles were made by FSP [22] of appropriate precursor solutions [12], resulting in titanium metal concentrations of 0.1 to 3.4 M and a nominal V₂O₅ content of 0 to 40 wt.%. Two FSP conditions were used, one with low enthalpy (LE: 5 mL min⁻¹ liquid and 5 L min⁻¹ O₂) and one with high enthalpy (HE: 8 mL min⁻¹ liquid and 3 L min⁻¹ O₂). FSP-made particles were directly deposited onto ceramic foam substrates for catalytic examination [12]. Particles that were not deposited onto the ceramic foam substrates were collected on glass microfibre filters (Whatman GF/D, 257 mm in diameter) by a vacuum pump (Busch SV 1025 B) for subsequent analysis. The pressure drop over foam and filter was adjusted to 80 mbar to achieve evenly distributed V₂O₅/TiO₂ coatings on the foam carrier [12]. The deposition time was in the range of 20 - 300 s.

For comparison, 10 wt.% vanadia/titania reference catalysts were prepared by standard impregnation [23] of commercially available TiO₂ (TiO₂, >99.5 wt.% anatase, Millennium PC50 (45 m²g⁻¹) and PC100 (82 m²g⁻¹)).
Vanadia (Fluka, purity >99%) was dissolved in deionized water containing oxalic acid (Fluka, purity >99%, molar ratio V$_2$O$_5$:oxalic acid = 1:4). and an appropriate amount of titania was added to the solution. The suspension was mixed for several hours at 80 °C and water was evaporated. The material was dried at 65 °C in air over night, crushed, fractionated (0.114 to 0.5 mm) and finally calcined in air (1h, 450 °C, 1 °C min$^{-1}$).

2.2.2 Catalyst Characterization

The SSA (m$^2$ g$^{-1}$) of the flame made powders was determined by nitrogen adsorption (Pan Gas, >99.999%) using the BET method and a Micromeritics Tristar 3000 instrument. SSAs of the powders could be reproduced within 2.4%. X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer (step size of 0.03°, scan speed of 0.60° min$^{-1}$, Cu K$_\alpha$ radiation). Weight content and crystal size of titania phases were obtained by Topas 2.0 software (Model AXS 2000, Bruker) as described in [12]. Temperature programmed reduction (TPR) experiments were carried out on a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector by flowing 5 vol% H$_2$ in Ar (Pan Gas, >99.999%, 20 mL min$^{-1}$) through the sample [12]. TEM analysis was performed with a CM30ST microscope (Philips; LaB$_6$ cathode, operated at 300 kV, point resolution < 2 Å) [12].

Raman spectroscopy was performed with a Renishaw InVia Reflex Raman system equipped with a 514 nm diode (Ar-ion laser, 25 mW) laser as excitation source focused in a microscope (Leica, magnification x5). The spectra were recorded under dehydrated conditions for 20 – 65 s and 10-25 accumulations to obtain sufficient signal-to-noise ratio and collected on a CCD camera after being diffracted by a prism (1800 lines per millimeter) using 1.25 mW laser energy to avoid thermal alteration [24, 25]. The procedure was as follows: Samples were placed in a special in situ cell equipped with a quartz window. The samples were heated stepwise (50 ºC steps, 10 ºC min$^{-1}$) up to 350 ºC while flushing with synthetic air (PanGas, 99.999%, 25 mL min$^{-1}$). Spectra were recorded at different temperatures (100, 200, 250, 300 and 350 ºC) and after cooling down the cell. Spectra labeled hydrated were taken before heating. The spectra did not change from 350 ºC to ambient
temperatures but showed better signal-to-noise ratio. Therefore all shown Raman spectra are reported after dehydration and cooling down the \textit{in situ} cell to 20 °C unless otherwise stated.

Samples are labeled as xVy-z, where x, y, z denote V$_2$O$_5$ content (wt.%), SSA (m$^2$ g$^{-1}$) and V-atom coverage (# nm$^{-2}$) respectively (Table 2.1). One as-prepared catalyst (10V24-7) was subjected to an additional heat treatment between 350 and 600 °C for 5h (5 °C min$^{-1}$ heating rate) in air in an oven (Carbolite, CWF 1300).

\subsection*{2.2.3 Catalytic Tests}

Partial oxidation of \textit{o}-xylene was performed in an isothermal, plug-flow fixed-bed reactor [12]. All gases (N$_2$, >99.996\%, and O$_2$, >99.95\%, Air Liquide) and liquid \textit{o}-xylene (>99.0\%, Fluka) were fed by mass-flow controllers (Bronkhorst). Temperature and inlet pressure were kept constant at 367 °C and 1.3 bar, respectively. The molar fractions of \textit{o}-xylene and oxygen in the reactor feed were 0.005 and 0.2, respectively. Total gas-flows ranged from 120 to 600 mL min$^{-1}$ at standard conditions. Modified residence times ($\tau_{\text{mod}}$, g$_{\text{cat}}$ s cm$^{-3}$) were defined as the mass of vanadia/titania in the reactor divided by the total gas-flow rate under reaction conditions [12]. Analysis of all organic species was performed on-line by GC (HP 6890, capillary column: HP-5, 50 m long, 0.32 mm in diameter and 0.25 μm film thickness) while CO/CO$_2$ were measured by non-dispersive IR spectroscopy (ABB; AO2020, Uras14). The carbon balance closed to ± 5% and was additionally monitored by the CO$_x$ contents after catalytic combustion of organic species in a final total oxidation reactor [26]. Weisz numbers were found to be smaller than 0.6 for all catalysts indicating that intraparticle mass transfer limitations can be excluded [12].
2.3 Results and Discussion

2.3.1 Influence of preparation variables on structural properties of catalysts

Figure 2.1 shows the influence of TTIP concentration in the FSP precursor solution on the SSA of 10 wt.% V₂O₅ containing TiO₂ particles made by the low (LE, triangles) and high (HE, circles) enthalpy FSP processes. The highest SSA (195 m² g⁻¹) was obtained using the LE-FSP and a low Ti concentration (0.1 M, production rate 2.6 g h⁻¹). Increasing TTIP concentration up to 1 M resulted in a steep drop of SSA to 70 m² g⁻¹ which leveled off at around 53 m² g⁻¹ (d₅₀ ≈ 28 nm) at higher concentrations (2 - 3.4 M) [12].

![Figure 2.1 Influence of TTIP precursor concentration (and flame enthalpy) in the FSP precursor liquid feed on the specific surface area (SSA, open symbols) and particle diameter (filled symbols) of 10 wt.% V₂O₅/TiO₂ catalysts. Low enthalpy (LE) FSP corresponds to 5 mL min⁻¹ precursor liquid and 5 L min⁻¹ O₂ dispersion flow while high enthalpy (HE) corresponds to 8 mL min⁻¹ liquid on 3 L min⁻¹ O₂ flow.](image-url)
This is attributed to faster particle growth at higher particle concentrations and longer high temperature particle residence time in the flame favoring particle coagulation and coalescence, reducing the overall specific surface area in the flame as it has been seen for flame-made materials [22, 27]. At about 2 M TTIP in the LE-FSP solution, primary particles of 28 nm average diameter were formed. Their characteristic sintering time might be too long [28] compared to their high temperature residence time in the flame so further increase of TTIP and, subsequently, particle concentration did not increase the particle size resulting in similar SSAs [29].

For the high enthalpy FSP (HE-FSP), the SSA of the powder was reduced further compared to the LE-FSP in agreement with FSP-made CeO$_2$ [22]. Thus controlling the production parameters like precursor concentration, liquid feed rates and dispersion gas feed rate allowed tailoring the characteristics of the catalysts [30]. The SSA decreased from 93 to 73 m$^2$ g$^{-1}$ when increasing the V$_2$O$_5$ content from 1 to 20 wt.% and dropped to 47 m$^2$ g$^{-1}$ for 40 wt.% V$_2$O$_5$ content. As a previous study of flame-made V$_2$O$_5$/TiO$_2$ catalysts has shown [9], the vanadia forms a shell-like structure onto a TiO$_2$ core rather than a solid solution of V atoms in the TiO$_2$ matrix in a flame therefore increasing the VO$_x$ surface population density with decreasing SSA.

Figure 2.2 shows XRD patterns of the 1 – 40 wt.% V$_2$O$_5$-containing TiO$_2$ particles produced by LE-FSP and a 24 m$^2$ g$^{-1}$ 10 wt.% V$_2$O$_5$ containing TiO$_2$ catalyst made by HE-FSP. Line broadening of the XRD patterns indicates anatase crystals of 17 – 37 nm in close agreement to the calculated BET-diameter (Fig. 2.1) hinting at the presence of monocrystalline grains or primary TiO$_2$ particles. At 7 wt.% vanadia weak reflections corresponding to crystalline VO$_2$(B) (diamonds) appeared. Quantification of this phase was not possible as pure TiO$_2$ showed small and broad diffractions at these angles (14.2°, 28.4°, 33.4°) which can be attributed to a high pressure phase TiO$_2$(B) that has similar lattice structure and cell size [31]. Nevertheless, the increase of peak intensities at these angles with increasing V$_2$O$_5$ content may indicate the presence of a small fraction of crystalline VO$_2$(B), at least for V$_2$O$_5$ contents above 7 wt.% for the LE-FSP-made catalysts. The patterns of as-prepared 20 wt.% V$_2$O$_5$/TiO$_2$ catalyst showed high anatase content without any crystalline
V$_2$O$_5$ structure despite the relatively high V-coverage (19 V nm$^{-2}$) but for 40 wt.% V$_2$O$_5$-content, crystalline V$_2$O$_5$ was detected (circles). TEM and EELS analysis (not shown) indicated separate V$_2$O$_5$ particles suggesting that at higher V-contents, at least, a fraction of the vanadia nucleates homogeneously as individual particles in addition to that condensing heterogeneously on the earlier formed TiO$_2$ [9].

**Fig. 2.2** XRD patterns (Cu K$_{\alpha}$) of the 0 – 40 wt.% V$_2$O$_5$ containing TiO$_2$ catalysts produced by low enthalpy FSP with 0 to high V-coverage (0 - 59 V nm$^{-2}$) as well as the XRD of the 10 wt.% low SSA catalyst produced by high enthalpy FSP (HE-FSP).

Despite the high V-coverage of 16 and 27 V nm$^{-2}$, XRD patterns of the HE-FSP catalysts showed no diffraction lines attributed to crystalline VO$_2$ or V$_2$O$_5$ (Fig. 2.3 top) while a high anatase fraction (>98 wt.%) was observed with comparable crystallite sizes to the BET-diameter indicating monocrystalline
### Table 2.1 Symbols, preparation conditions, BET, TPR results, $k_m$, and $S_{PA,o}$ at $X_o = 0.6$ for all tested V$_2$O$_5$/TiO$_2$ catalysts from different preparation methods. Number in parenthesis indicate the initial SSA of the commercial TiO$_2$ support.

<table>
<thead>
<tr>
<th>Sample</th>
<th>symbol</th>
<th>V$_2$O$_5$ content (wt.%)</th>
<th>precursor TTIP concentration (mol L$^{-1}$)</th>
<th>SSA ($m^2$ g$^{-1}$)</th>
<th>V-coverage (# nm$^{-2}$)</th>
<th>dominant VO$_x$-species$^c$</th>
<th>TPR $T_{max}$ (°C)</th>
<th>AOS</th>
<th>$k_m$ $^{d)}$ (cm$^3$ s$^{-1}$ g$_{cat}$$^{-1}$)</th>
<th>$S_{PA,o}$ at $X_o = 0.6$ (-)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7V95-5</td>
<td>-</td>
<td>7</td>
<td>0.67</td>
<td>95</td>
<td>5</td>
<td>amorphous</td>
<td>490</td>
<td>3.2</td>
<td>239.8</td>
<td>0.47</td>
<td>this work</td>
</tr>
<tr>
<td>10V93-7</td>
<td>▼</td>
<td>10</td>
<td>0.67</td>
<td>93</td>
<td>7</td>
<td>amorphous</td>
<td>495</td>
<td>3.5</td>
<td>251.7</td>
<td>0.43</td>
<td>[12]</td>
</tr>
<tr>
<td>20V73-19</td>
<td>□</td>
<td>20</td>
<td>0.67</td>
<td>73</td>
<td>19</td>
<td>amorphous/crystalline</td>
<td>536</td>
<td>3.3</td>
<td>214.4</td>
<td>0.34</td>
<td>this work</td>
</tr>
<tr>
<td>10V53-12</td>
<td>⬤</td>
<td>10</td>
<td>3.4</td>
<td>53</td>
<td>12</td>
<td>amorphous</td>
<td>520</td>
<td>3.6</td>
<td>120.4</td>
<td>0.47</td>
<td>[12]</td>
</tr>
<tr>
<td>10V40-16 HE-FSP</td>
<td>△</td>
<td>10</td>
<td>0.67</td>
<td>40</td>
<td>16</td>
<td>amorphous</td>
<td>533</td>
<td>3.3</td>
<td>102.7</td>
<td>0.55</td>
<td>this work</td>
</tr>
<tr>
<td>10V24-27 HE-FSP</td>
<td>◊</td>
<td>10</td>
<td>3.4</td>
<td>24</td>
<td>27</td>
<td>amorphous</td>
<td>497, 558</td>
<td>3.5</td>
<td>62.4</td>
<td>0.59</td>
<td>“”</td>
</tr>
<tr>
<td>10V65-08 imp</td>
<td>●</td>
<td>10</td>
<td>-</td>
<td>65 (82) $^a$</td>
<td>8 $^b$</td>
<td>amorphous</td>
<td>510</td>
<td>3.0</td>
<td>206.7</td>
<td>0.46</td>
<td>“”</td>
</tr>
<tr>
<td>10V40-16 imp</td>
<td>▲</td>
<td>10</td>
<td>-</td>
<td>40 (45) $^a$</td>
<td>16 $^b$</td>
<td>crystalline</td>
<td>527</td>
<td>3.2</td>
<td>114.8</td>
<td>0.48</td>
<td>“”</td>
</tr>
<tr>
<td>10V9-74 imp</td>
<td>●</td>
<td>10</td>
<td>-</td>
<td>9 (9) $^a$</td>
<td>74 $^b$</td>
<td>crystalline</td>
<td>546, 694</td>
<td>3.6</td>
<td>14.0</td>
<td>0.52</td>
<td>[12]</td>
</tr>
</tbody>
</table>

$^a)$ initial SSA for the impregnated catalysts
$^b)$ calculated for the initial SSA before impregnation
$^c)$ based on Raman analysis in Fig. 3, 4 and 5.
$^d)$ calculated for first order reaction kinetics up to a $X_o = 0.6$ consistent with experimental data till this $X_o$. 

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**Chapter 2: Structure of flame-made vanadia/titania**

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**Table 2.1** Symbols, preparation conditions, BET, TPR results, $k_m$, and $S_{PA,o}$ at $X_o = 0.6$ for all tested V$_2$O$_5$/TiO$_2$ catalysts from different preparation methods. Number in parenthesis indicate the initial SSA of the commercial TiO$_2$ support.
particles as well. The XRD patterns (not shown) of impregnated catalysts (10 wt.% $\text{V}_2\text{O}_5$-content) showed no diffraction lines due to crystalline vanadia for both high (65 m² g⁻¹, 8 V nm⁻²) and low SSA (40 m² g⁻¹, 16 V nm⁻²) samples and the initial anatase weight fraction was preserved.

Figure Fig. 2.3 shows Raman spectra of dehydrated $\text{V}_2\text{O}_5$/TiO₂ catalysts made by LE-FSP. The two overtone bands (514 and 638 cm⁻¹) corresponding to anatase TiO₂ were clearly visible for all flame-made catalysts. The band around 800 cm⁻¹ stems from the Si-O-Si vibration of the quartz window used in the *in situ* cell. At very low V-coverage (1 V nm⁻², 1V93-1), the V=O stretching band at 1032 cm⁻¹ attributed to monomeric VOₓ [13] was detected. With increasing V-coverage up to 15 wt.% $\text{V}_2\text{O}_5$ a band around 920-940 cm⁻¹ appeared which is attributed to the V-O-V bridges of the polymeric VOₓ-species [6, 17, 32-35]. These bands (1032 and 940 cm⁻¹) allow no conclusion on the ratio between mono- and polymeric species as they hardly change in intensity with increasing $\text{V}_2\text{O}_5$-content. The frequently observed characteristic behavior that upon increasing V-coverage first the monomeric, then polymeric (decreasing monomeric) VOₓ-species and finally crystalline $\text{V}_2\text{O}_5$, form, seems also to be valid for flame-made $\text{V}_2\text{O}_5$/TiO₂ catalysts. The 1V93-1 sample showed no indication of monomeric but clear bands of polymeric (940 cm⁻¹) VOₓ-species under ambient (hydrated) conditions (not shown here).

For higher V-contents (15V77-13) Raman bands of amorphous mono- and polymeric VOₓ-species still are dominant. For the 20V73-19 catalyst features of amorphous VOₓ-species still are detected but additional Raman shifts (708 and 998 cm⁻¹) attributed to crystalline $\text{V}_2\text{O}_5$ are visible whose presence was not detected by XRD (Fig. 2.2). This corroborates the relative small size of crystalline $\text{V}_2\text{O}_5$ clusters in flame-made catalysts even at relative high V-coverage. Doubling the $\text{V}_2\text{O}_5$ content (40 wt.%) resulted in dominantly crystalline Raman bands consistent with XRD (Fig. 2.2) and TEM / EELS analysis (not shown). The dominant Raman shifts and scattering arising from the TiO₂ support and additional overlap with $\text{V}_2\text{O}_5$ bands prevented detection of discrete major VO₂ bands expected at 191, 258 and 335 cm⁻¹ [36] and could therefore not clarify the origin of the XRD patterns attributed to either VO₂(B) or TiO₂(B), respectively.
Fig. 2.3 Raman spectra of the FSP-made 0–40 wt.% V$_2$O$_5$ containing TiO$_2$ catalysts made by LE-FSP recorded (514 nm) after dehydrating the sample at 350 ° (by flowing 25 mL min$^{-1}$ synthetic air).

Figure 2.4 shows Raman spectra (solid line) of both dehydrated HE-FSP-made 10V40-16 and impregnated (10V65-9 imp, 10V40-16 imp) V$_2$O$_5$/TiO$_2$. The flame-made catalyst exhibited a clear band at 1033 cm$^{-1}$ that corresponds to monomeric VO$_x$-species [13] as well as the band at 940 cm$^{-1}$ confirming the presence of amorphous polymeric VO$_x$-species [32] stemming from the higher V-coverage (16 V nm$^{-2}$) of HE-FSP-made particles. Missing bands at 703 and 998 cm$^{-1}$ indicated the absence of any crystalline V$_2$O$_5$ species despite the relatively high V-coverage. This is in contrast to the classic “monolayer”
model for impregnated catalysts [5] and vapor-fed flame-made 10 wt.% V₂O₅/TiO₂ with slower gas velocities and longer high temperature particle residence times [9].

![Raman spectra](image)

*Fig. 2.4 Raman spectra of the 10 wt.% V₂O₅ HE-FSP- and impregnated catalysts recorded (514 nm) after dehydrating the sample at 350 ° (by flowing 25 mL min⁻¹ synthetic air). The spectra of the 10V40-16 HE-FSP are shown also under ambient (hydrated) conditions (dotted line).*

Note the missing band at 940 cm⁻¹ for the hydrated sample (dotted line) and higher intensity around 800 cm⁻¹ which might indicate the addition of polymeric VOₓ-species as observed under ambient conditions (not shown) to the signal arising from the quartz window as discussed in Fig. 2.3.

Raman spectra of the impregnated high SSA V₂O₅/TiO₂ (10V65-8 imp) showed weaker intensities for the monomeric and polymeric VOₓ-species (Fig. 2.4) compared to the FSP-made catalysts. For the impregnated low SSA catalyst (10V40-16 imp) only monomeric and almost no intensities of bands indicative of polymeric VOₓ-species were detected. Instead, crystalline V₂O₅ Raman bands at 703 and 998 cm⁻¹ were observed in contrast to the HE-FSP-made catalyst with comparable SSA and V-coverage (10V40-16 HE-FSP).
Crystalline V$_2$O$_5$ particles were again too small to be detected by XRD but their presence is consistent with impregnated catalysts having >8 or 10 V nm$^2$ [5, 25].

![Raman spectra of low SSA, high “monolayer” coverage 10V24-27 V$_2$O$_5$-containing TiO$_2$ HE-FSP-made catalyst sintered at 350 – 600 °C for 5 hours in air, recorded (514 nm) before (dotted line) and after dehydrating the sample at 350 ° (by flowing 25 mL min$^{-1}$ synthetic air).](image)

*Fig. 2.5 Raman spectra of of low SSA, high “monolayer” coverage 10V24-27 V$_2$O$_5$-containing TiO$_2$ HE-FSP-made catalyst sintered at 350 – 600 °C for 5 hours in air, recorded (514 nm) before (dotted line) and after dehydrating the sample at 350 ° (by flowing 25 mL min$^{-1}$ synthetic air).*

Figure 2.5 shows Raman spectra of the catalyst with the lowest SSA and highest V-atom coverage (10V24-27 HE-FSP). The dehydrated sample showed similar mono- and polymeric bands as the HE-FSP-made 40 m$^2$ g$^{-1}$ catalyst (Fig. 2.4). Again no bands corresponding to crystalline V$_2$O$_5$ could be detected despite the relative high V-coverage, 27 V nm$^2$. Apparently high cooling rates, up to $10^6$ °C s$^{-1}$ [37] and short high temperature residence times favor formation of a thin layer of amorphous VO$_x$ rather than crystalline V$_2$O$_5$. Additionally V$_2$O$_5$ is very volatile ($T_{\text{melt}} \approx 670°$C) compared to TiO$_2$ ($T_{\text{melt}} \approx 1800°$C) so it should condense on the TiO$_2$ surface late in the flame [9].
reducing the high temperature residence time of the mixed V$_2$O$_5$/TiO$_2$ particles so that the development of crystalline layers is prevented.

![TEM images](image)

Fig. 2.6 TEM images of (a) pure FSP-made TiO$_2$ (98 m$^2$/g$^1$, 0.67M TTIP, LE-FSP), (b) 20 wt.% V$_2$O$_5$/TiO$_2$ (20V73-19, 0.67M TTIP, LE-FSP) and (c) 10 wt.% V$_2$O$_5$/TiO$_2$ (10V24-27 HE-FSP, 3.4M TTIP) catalysts.

Figure 2.6 shows typical TEM images of these particles. Pure TiO$_2$ produced at 5 mL min$^-1$ (LE-FSP) and a precursor concentration of 0.67 M (Fig. 2.6a) showed predominantly spherical particles with a low degree of aggregation. Adding 20 wt.% V$_2$O$_5$ did not affect the particle shape and aggregation state at all even though particle size increased by 25%. Even the HE-FSP-made 10V24-27 catalyst exhibited no significant structural changes, except for the larger particle size. This indicates that the structure of TiO$_2$ particles is not affected by adding V$_2$O$_5$ and the formation of the TiO$_2$ is completed before the condensation of V$_2$O$_5$ on the particle surface in agreement with other flame-made V$_2$O$_5$/TiO$_2$ catalysts [9, 12].

As the 10V24-27 HE-FSP-made catalyst exhibited the highest theoretical “monolayer” coverage of the tested catalysts, it is most sensitive to any heat treatment, e.g., during reaction or post treatment (e.g. calcination). To characterize the stability of the detected amorphous VO$_x$-species in the as-prepared sample, it was annealed in air at different temperatures (Fig. 2.5). At 450 °C, which significantly exceeds the o-xylene reaction temperature (ca. 370 °C) and is similar to the calcination temperature of impregnated catalysts, no changes in the bands attributed to amorphous VO$_x$-species at 940 and 1032 cm$^-1$ were observed corroborating the stability of such species in FSP-made catalysts. Bands corresponding to crystalline V$_2$O$_5$ are detected after
annealing at 500 °C in agreement with results of sintered FSP-made high SSA (10V93-7) catalyst [12]. All bands (mono-, di- and polymeric) attributed to amorphous VO₅ₓ-species were still visible in contrast to the 10V93-7 catalyst.

At 600 °C the bands due to monomeric species disappeared but amorphous polymeric VO₅ₓ-species were retained and the crystalline bands became more distinct. Additionally the anatase (638 cm⁻¹) to rutile (608 cm⁻¹) phase transformation started in agreement with the XRD results. This is in contrast to the 10V93-7 catalyst with higher SSA where this transformation had been completed at this temperature [12]. At the same time the SSA of the catalyst was reduced from 22 m² g⁻¹ to 7 m² g⁻¹. Therefore low SSA catalysts made by HE-FSP are more stable in terms of VO₅ₓ-species, particle size and anatase to rutile transformation upon heat treatment compared to high SSA catalysts made by the LE-FSP as larger initial TiO₂ particle sizes lead to slower sintering and phase transformation than smaller ones [28, 38].

**Fig. 2.7 (a)** Temperature programmed reduction (TPR) profiles of the FSP-made V₂O₅/TiO₂ catalysts shown in Fig. 2.2 as well as pure V₂O₅ made by LE-FSP. (b) TPR profiles of 10 wt.% V₂O₅ containing FSP- and impregnated catalysts of similar SSA.

Figure 2.7a shows the TCD signals measured during TPR of the 0 – 100 wt.% V₂O₅ containing TiO₂ catalysts. At low V-coverage (1 V-atom nm⁻²) the maximum reduction peak temperature (T max) is around 500 °C. Increasing the V₂O₅ content from 1 to 7 wt.% reduced the T max to 490 °C (5 V nm⁻²) indicating
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a higher overall reducibility of the VO\textsubscript{x}-species present at this V-coverage. This corroborates the Raman results under ambient conditions which showed polymeric VO\textsubscript{x}-species at low coverage (1 V-atom nm\textsuperscript{-2}) and easily reducible monomeric species for contents 5 – 15 wt.%. Further increase of the V\textsubscript{2}O\textsubscript{5} content increased T\textsubscript{max} up to 595 °C for the 40 wt.% with 59 V nm\textsuperscript{-2} indicating lower reducibility of the high coverage VO\textsubscript{x}-species.

However, part of this shift in the peak temperature has to be attributed to the increasing amount of reducible species, as parametric sensitivity studies of TPR indicate [39]. All catalysts up to 20 wt.% V\textsubscript{2}O\textsubscript{5} showed only slightly asymmetric reduction peaks whereas the 40 wt.% V\textsubscript{2}O\textsubscript{5} sample showed a clear shoulder around 565 °C indicating a stepwise reduction or different reducibility of the corresponding VO\textsubscript{x}-species. The TPR of the pure FSP-made V\textsubscript{2}O\textsubscript{5} showed the two characteristic reduction peaks of crystalline vanadia around 650 - 750 °C.

Figure 2.7b compares TPR results from as-prepared 10 wt.% V\textsubscript{2}O\textsubscript{5} containing TiO\textsubscript{2} HE-FSP-made and impregnated low SSA catalysts. With increasing V-coverage the maximum reduction temperature for the 10V40-16 catalyst was shifted to 533 °C with a shoulder around 495 °C stemming from the higher amount of polymeric VO\textsubscript{x}-species. For lower SSA (24 m\textsuperscript{2} g\textsuperscript{-1}) and high V-coverage (10V24-27) a split of the reduction profile into two distinct peaks at T\textsubscript{max} = 497 and 558 °C was observed further indicating reduction of different VO\textsubscript{x}-species consistent with the Raman analysis of Fig. 2.4.

The impregnated 10V40-16 catalysts containing crystalline vanadia (Fig. 2.4) showed similar reduction temperatures as the FSP-made catalysts of comparable SSA and V\textsubscript{2}O\textsubscript{5} content that contained only amorphous VO\textsubscript{x}-species. This showed that the reduction temperature was not significantly influenced by the nature of VO\textsubscript{x}-species at this V-coverage and small V\textsubscript{2}O\textsubscript{5} cluster sizes. During reduction, the consumed H\textsubscript{2} was comparable for all FSP-made samples and the calculated average oxidation state (AOS) was in the range of 3.2 to 3.5 for all catalysts (Table 2.1). The H\textsubscript{2} consumption of impregnated catalysts was slightly higher and resulting AOS (≈ 3.0) were accordingly lower than the ones of FSP-made samples (Table 2.1).
2.3.2 Catalytic Performance

Table 2.1 summarizes the characteristics of all catalysts investigated in this work together with some samples reported earlier [12] for reference. This selection allows for the identification of the influence of vanadia content, type of VOx-species, SSA and preparation route on the catalytic performance in the selective oxidation of o-xylene to phthalic anhydride. All catalysts showed no external or internal mass transfer limitations due to relatively high gas velocity and the high porosity of the deposited active layer on the ceramic foam carriers [12].

![Conversion of o-xylene as a function of the modified residence time at a reaction temperature of 367°C for all tested catalysts (molar fraction of o-xylene = 0.005).](image)

Figure 2.8 shows the o-xylene conversion $X_o$, as a function of modified residence time of LE-FSP-made V$_2$O$_5$/TiO$_2$ directly deposited on foams and containing 7 and 20 wt.% V$_2$O$_5$. While the 7V95-5 (circles) showed comparable $X_o$ at given residence times as a 10 wt.% containing catalysts (10V93-7, Table 2.1) in the previous study [12], slightly lower values were measured for
the 20V73-19 catalyst (triangles). This may either be due to the lower SSA or to the presence of crystalline $V_2O_5$ in the 20V73-19 catalyst (Fig. 2.3) lowering its activity. Samples 10V65-8 imp (filled diamonds) and 10V24-27 HE-FSP (open diamonds) catalysts revealed the highest and lowest conversions of the here tested 10 wt.% containing $V_2O_5$ catalysts, respectively.

Flame-made and impregnated 10V40-16 catalysts (triangles) of similar SSA showed intermediate conversions. Even though the latter two catalysts were prepared by different methods, contained different VO$_x$-species (Fig. 2.4) and exhibited slightly different AOS (Table 2.1), they showed the same $X_o$. Samples 10V65-8 imp (filled diamonds) and 10V24-27 HE-FSP (open diamonds) catalysts revealed the highest and lowest conversions of the here tested 10 wt.% containing $V_2O_5$ catalysts, respectively. Flame-made and impregnated 10V40-16 catalysts (triangles) of similar SSA showed intermediate conversions. Even though the latter two catalysts were prepared by different methods, contained different VO$_x$-species (Fig. 2.4) and exhibited slightly different AOS (Table 2.1), they showed the same $X_o$. Similar conclusions can be drawn for the 20V73-19 LE-FSP and 10V65-8 imp catalysts despite the difference in VO$_x$-species population (Fig. 2.3 and Fig. 2.4). Thus, the nature of the VO$_x$-species does not determine the $X_o$ provided that the surface V-coverage amounts to at least 8 V-atoms per nm$^2$.

Figure 2.9 shows that catalyst activity is clearly related to SSA: First order reaction kinetics for the calculation of the rate constant $k_i$ was assumed, even though the partial oxidation of o-xylene does not strictly follow 1$^{st}$ order kinetics [40, 41]. If one, however, only considers the conversion up to $X_o = 0.6$, the data fit reasonably well ($R^2 = 0.9$) first order reaction kinetics in the ln(1-$X_o$) vs. $\tau_{mod}$ diagram and give a good estimate of the reaction rate constant. The calculated rate constant is shown as a function of SSA for catalysts made here and in [12] (Table 2.1). In Fig. 2.9a, $k_m$ is related to the mass of catalyst ($V_2O_5/TiO_2$) in the reactor and shows that the catalyst activity correlates well ($R^2 = 0.97$) with its SSA as observed for pure $V_2O_5$ [19]. So with increasing SSA, the activity increased linearly regardless of catalyst synthesis route, $V_2O_5$-content (V-coverage) or VO$_x$-species.
As both, $k_m$ and SSA are scaled by the mass as well as the number of V-surface sites is proportional to SSA, our results corroborate the conclusion that only surface species regardless of their type (mono- or polymeric, amorphous or crystalline) are responsible for the activity of such V$_2$O$_5$/TiO$_2$ catalysts. In addition, the km dependency on the SSA may support the contention of Weckhuysen and co-workers [17] and Calatayud et al. [18] claiming that the oxygen in the V-O-Ti bond is the most active one in V$_2$O$_5$/TiO$_2$ catalysts. With decreasing SSA, less V-O-support groups are available. When at the same time the V-coverage is raised, such bonds are covered and may not be accessible for reaction.

Fig. 2.9 Comparison of the calculated rate constants (1st order) for o-xylene conversion based on the catalyst mass (a, $k_m$) and on the amount of active species (b, $k_V$, mol V) for the catalysts prepared with different production rates and preparation methods in dependency of the SSA.

In contrast, when the rate constant is related to the molar amount of V ($k_V$, Fig. 2.9b) nominally present in the catalysts and assumed to be the only active species, a difference between catalysts with variable vanadia content becomes apparent. This would be in contrast to the above statement that only surface VO$_x$-species are important. The catalyst with the lowest coverage (7V95-5 LE-FSP, open circles, Fig. 2.9b) showed the highest activity. Further increase of the V coverage, while retaining the high SSA (10V93-7 LE-FSP, inverted triangle), reduces the activity of the catalyst. The V-based activity is
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reduced even more (∼30 %) for the 20 wt.% V₂O₅-containing catalyst (19 V nm², squares). For all catalysts, however, with 10 wt.% vanadia, the kV correlates very well with SSA, irrespective of the preparation method or the type of VOₓ-species present. Keeping in mind that the highest activity was observed for low V coverage regardless of rate constant scaling it becomes evident that the active VOₓ-species for the partial oxidation of α-xylene can form already at V-coverage as low as 5 V-atoms per nm². At comparable SSA, a further increase in V-coverage has no effect on the catalyst activity. This is in agreement with both, the above mentioned hypothesis by Weckhuysen and Calatayud and with the accepted “theory of towers” of Bond and co-workers [42] stating that the V₂O₅ layer grows in tower-like structures on TiO₂. A correlation of the activity of V₂O₅/TiO₂ catalysts with the amount of V is not conclusive because the role of the bridging O-atoms is not taken into account. The activity predominantly depends on the SSA.

Figure 2.10 shows that the selectivity to phthalic anhydride (S_PA,₀) increases for all catalysts with increasing α-xylene conversion [12]. The PA is mainly formed as a consecutive product via the main intermediates tolualdehyde and phthalide (inset Fig. 2.10). The maximum S_PA,₀ was observed above 90 - 95 % conversion (X₀) indicating the high stability of PA against its consecutive oxidation to COₓ as has been observed with V₂O₅/TiO₂ prepared by conventional methods [43].

Figure 2.10a shows that increasing the V content of low enthalpy (LE) FSP-made catalysts lowers the S_PA,₀ for X₀ < 0.95. The S_PA,₀ is higher for 7V95-5 (circles) than for 20V73-19 (squares) as well as for the 10V93-7 (triangle) catalyst even though in the latter case both catalysts have almost the same SSA. Thus, in contrast to activity (Fig. 2.8 and 2.9), the selectivity is affected by the type or content of vanadia. This is further supported by Fig. 2.10b showing catalysts with the same vanadia content (10 wt.%) but prepared by different methods: Flame-made catalysts (10V40-16 and 10V24-27), are more selective than those prepared by impregnation (10V65-8 imp and 10V40-16 imp) at X₀ < 0.9.
Fig. 2.10 Phthalic anhydride (PA) selectivity, $S_{PA,o}$ as a function of o-xylene conversion, $X_o$, for 7, 10 and 20 wt.% V$_2$O$_5$ containing (a) low enthalpy FSP- made catalysts. Inset shows simplified reaction diagram. (b) high enthalpy (HE) FSP- (open symbols) and impregnated (filled symbols) catalysts at 367 °C reaction temperature and 0.005 molar fraction o-xylene in the feed.
For impregnated catalysts, SSA has no significant effect on $S_{PA,o}$. In contrast, all flame-made catalysts containing 10 wt.% vanadia including 10V93-7LEF (Fig. 2.10a) show decreasing $S_{PA,o}$ (up to $X_o$ of at least 70 %) at increasing SSA. Finally, 10V40-16 imp and 10V40-16 HEF exhibit the same SSA, but the latter flame-made catalyst, exhibiting amorphous vanadia only (Fig. 2.4), yields significantly higher $S_{PA,o}$ than the former impregnated one.

With Fig. 2.11, the effect of the type of VO$_x$-species on the PA selectivity can be inspected in more detail. Here, $S_{PA,o}$ at 50% $o$-xylene conversion are plotted versus SSA, and two trend lines combine the data of catalyst samples with or without crystalline V$_2$O$_5$, respectively, as detected by XRD (Fig. 2.2) and Raman spectroscopy (Fig. 2.3, 2.4 and 2.5). At comparable SSA and, accordingly, comparable catalytic activity, the presence of crystalline V$_2$O$_5$ has a detrimental effect on the $S_{PA,o}$ at intermediate $X_o$ [14] consistent with the $S_{PA,o}$ at $X_o = 0.6$ reported in Table 2.1.

This means that among the numerous species present on the TiO$_2$ surface, amorphous monomeric and polymeric ones play the key role for obtaining high PA selectivities. Nevertheless, catalysts are more selective when SSA decreases regardless of the VO$_x$-species present [12]. Both findings are also supported by the selectivities to side products obtained over all tested materials. Higher SSAs and/or crystalline V$_2$O$_5$ promote formation of $o$-toluolaldehyde and phthalide (not shown). The CO$_x$ selectivity was almost constant for all tested catalysts (around 30%) over the whole $X_o$ range except for the 10V24-27 HE-FSP catalyst (20-25%). Although at $X_o = 90 – 95$ % all $S_{PA,o}$ become very similar so that the dependency between catalyst properties and $S_{PA,o}$ cannot be clearly discerned anymore, the most selective catalysts at almost full $o$-xylene conversions have high to moderate activity (SSA) and contain no crystalline V$_2$O$_5$ with exception of the 20V73-19 LE-FSP. The position of the 10V53-12 (butterfly) a bit away from the amorphous trendline is not entirely clear. It could be attributed to its slightly higher VO$_2$ content as indicated by the highest oxidation state of all samples (Table 2.1).
Fig. 2.11 Comparison of the PA selectivity at $X_0 = 0.5$ for the tested catalysts prepared with different preparation methods as function of the SSA. Same symbols as in Fig. 2.9.

From the present study it emerges that FSP facilitates the preparation of mixed vanadia/titania catalysts with maximum content of dispersed amorphous VO$_x$ and prevention of the formation of crystalline V$_2$O$_5$ especially for catalysts with moderate SSA and V-coverage above 8 - 10 V nm$^2$. As a result, FSP-made catalysts 10V40-16 and 10V24-27 exhibiting a high V-coverage of 16 and 27 V nm$^2$, respectively, resulted in the highest PA selectivity ($S_{PA,0} = 67 - 69\%$). This superior performance was observed both, at intermediate conversion levels and at o-xylene conversions greater than 90%.

2.4 Conclusions

Vanadia/titania nanostructured particles of various SSA (24 - 195 m$^2$/g) and V-coverage (5 - 59 V nm$^2$) containing predominantly amorphous VO$_x$-species below 30 V nm$^2$ have been prepared by flame spray pyrolysis (FSP). The influence of preparation method (flame or impregnation), SSA, V-content
and nature of VO\textsubscript{x}-species (mono-, polymeric and crystalline) on partial oxidation of \textit{o}-xylene to phthalic anhydride (PA) has been elucidated.

The major difference between flame-made and impregnated V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} particles lies in the state of VO\textsubscript{x}. As impregnated catalysts are calcined for long times to assure a stable catalyst, the VO\textsubscript{x} has enough time to form a thermodynamically stable crystalline phase. In corresponding FSP-made catalysts, the high temperature residence time is too short for development of crystalline V\textsubscript{2}O\textsubscript{5}, and especially at low (1 – 15 wt.%) V-contents so amorphous VO\textsubscript{x}-species are formed. These species, however, are stable even after similar heat treatment as for the impregnated catalysts during calcination. It is worth noting that FSP reactors reach much higher maximum temperature and cooling rates [37] than conventional vapor-fed ones [9]. This might be the reason that V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} particles made in the latter reactors formed crystalline V\textsubscript{2}O\textsubscript{5} in contrast to those made at FSP reactors here and in previous studies [12].

The catalyst activity strongly depended on SSA and therefore on the amount of surface V sites regardless of preparation method, V-coverage and nature of VO\textsubscript{x}-species. Impregnated V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} containing crystalline V\textsubscript{2}O\textsubscript{5} catalysts showed inferior selectivity for PA (S\textsubscript{PA,o}) compared to FSP-made ones of similar composition and SSA. In general, higher activity was accompanied by lower S\textsubscript{PA,o} for \textit{o}-xylene conversion (X\textsubscript{o}) < 90%. High V\textsubscript{2}O\textsubscript{5} contents (20% w/w) and SSA showed drastically lower S\textsubscript{PA,o} at X\textsubscript{o} < 95% while comparable S\textsubscript{PA,o} was obtained near full conversion. The S\textsubscript{PA,o} at X\textsubscript{o} = 50% decreased linearly with increasing SSA for both amorphous and crystalline VO\textsubscript{x}-species. However, catalysts containing amorphous VO\textsubscript{x}-species showed significantly higher selectivity than catalysts with crystalline vanadia. The most selective catalysts for X\textsubscript{o} < 90% had intermediate to low SSA and a high fraction of amorphous VO\textsubscript{x}-species. FSP has been shown to be a versatile method for the preparation of catalysts with a wide SSA range and controllable nature of VO\textsubscript{x}-species which may not be achievable by classical wet-chemistry routes [30].
2.5 References


CHAPTER 3

Flame-made vs. wet-impregnated vanadia/titania in the total oxidation of chlorobenzene: possible role of VO_x species

Abstract

Vanadia/titania particles with a specific surface area (SSA) around 50 m^2g^-1 and a V_2O_5 content up to 30 wt.% (corresponding to a V surface density up to 33 V nm^-2) were prepared by flame spray pyrolysis as well as by classic wet impregnation. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature programmed reduction, Raman spectroscopy, X-ray photoelectron spectroscopy and tested in the total oxidation of chlorobenzene. Depending on vanadia content, monomeric, polymeric and crystalline vanadia species were formed. The dispersion of the VO_x species was

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in general higher for flame-made catalysts. While the classic wet-impregnated catalysts already showed crystalline V$_2$O$_5$ when the V surface density reaches 8 V nm$^{-2}$, the flame-made ones exhibited only amorphous VO$_x$ species up to 16 V nm$^{-2}$. The activity of flame-made and wet-impregnated catalysts increased with increasing V$_2$O$_5$ loading and therefore depended on the VO$_x$ species structure: catalysts exceeding a V surface density of 8 V nm$^{-2}$ containing high amounts of amorphous polymeric and/or crystalline VO$_x$ species showed significantly higher activity than catalysts with lower V surface density. Wet-impregnated catalysts with numerous V-O-V bonds as involved in polymeric and crystalline VO$_x$ species showed superior activity than FSP-made ones of similar composition. This contribution proposes a discussion aiming at understanding the role played by the different types of VO$_x$ species in the total oxidation of volatile organic compounds on the example of chlorobenzene.

### 3.1 Introduction

Supported vanadia catalysts are used for a variety of reactions, including selective catalytic reduction (SCR) of NO$_x$ with NH$_3$ [1], oxidative destruction of volatile organic compounds (VOC) [2] or partial oxidation of o-xylene to phthalic anhydride [3]. Strong surface interactions between vanadia and titania result in amorphous monomeric (isolated) or di- and polymeric VO$_x$ species which can be formed at sub-"monolayer" (<8-10 V nm$^{-2}$) coverage [4]. Exceeding this V surface density leads usually to crystalline V$_2$O$_5$ regardless of the preparation method [5-7]. Crystalline V$_2$O$_5$ is considered to have detrimental effects on catalytic activity, supported by activity data of vanadia-based catalysts for both, the total oxidation of chlorobenzene [8] and the SCR reaction [8-9] where the highest turn over frequency was measured for a V surface density <8 V nm$^{-2}$. Accordingly most of the tested vanadia based catalysts deal with so called “sub-monolayer” catalysts [10-12]. In a recent review [13] on classic “sub-monolayer” wet-impregnated V$_2$O$_5$/TiO$_2$ catalysts for the total oxidation of VOC model molecules (e.g benzene, chlorobenzene and furane) it was concluded that the best catalytic performance are achieved with highly dispersed, amorphous VO$_x$ species. However, recent results on V$_2$O$_5$/TiO$_2$ catalysts prepared by nonhydrolytic sol-gel provided strong
Experimental evidence that isolated VO\textsubscript{x} species are less active than oligomeric species [14]. Also, one recent publication [15] reported decreasing reaction temperatures at 50% conversion for a V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst with V surface density up to 16 V nm\textsuperscript{-2} (2 “monolayer”) indicating that more research on high loading (surface density) catalysts is necessary.

Recently V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts prepared by flame spray pyrolysis (FSP) showed a good dispersion of vanadia while retaining the amorphous VO\textsubscript{x}-species up to a V surface density of 27 V nm\textsuperscript{-2} [16]. These species had a strong influence on the selectivity in the selective oxidation of o-xylene, favoring amorphous species for high selectivity. Activity, however, was directly proportional to the SSA and therefore to the exposed vanadium sites but showed no dependency on the different VO\textsubscript{x} species present [16]. This fast one-step synthesis technique allows now to tailor such V-based catalysts with specific VO\textsubscript{x} structure and high dispersion even at high V surface density and therefore systematic studies of the influence of amorphous vs. crystalline VO\textsubscript{x} species can be done by comparison of such flame-made V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts with high amorphous VO\textsubscript{x} content vs. classic wet-impregnated materials with high amount of crystalline V\textsubscript{2}O\textsubscript{5} at high V surface density.

In here we test such flame-made catalysts in the abatement of chlorinated volatile organic compounds, namely chlorobenzene and study the influence of vanadia content and of the nature of VO\textsubscript{x}-species on the activity in the total oxidation. These flame-made catalysts are compared to classic wet-impregnated catalysts of similar composition.

### 3.2 Experimental

#### 3.1.1 Catalyst Preparation

Nanostructured vanadia/titania particles were made by FSP of appropriate precursor solutions [17]. Xylene (Fluka, >98.5%) and acetonitrile (Fluka, >99.5%) solvents were mixed (11:5 by volume) with appropriate amounts of titanium tetraisopropoxide (TTIP, Aldrich >97%) and vanadium oxo-triisopropoxide (Strem Chemicals, >98%), resulting in titanium metal concentrations of 0.67 M and a nominal V\textsubscript{2}O\textsubscript{5} content of 2.3 to 30% (w/w).
This precursor solution was fed (8 mL min⁻¹) by a syringe pump (Inotec, IER-560) through the FSP nozzle and dispersed by O₂ (4 or 5 L min⁻¹, PanGas, 99.5%) into a fine spray that was ignited and sustained by a premixed CH₄/O₂ flame. Particles were collected on glass microfibre filters (Whatman GF/D, 257 mm in diameter) by a vacuum pump (Busch SV 1025 B) for subsequent analysis. Details on the synthesis are described elsewhere [16, 18].

For comparison, vanadia/titania reference catalysts were prepared by standard wet impregnation of commercially available TiO₂ (TiO₂, >85 wt.% anatase, Degussa P25 (49 m²g⁻¹)). The precursor NH₄VO₃ (Vel, >99%) was dissolved in distilled water and complexed with oxalic acid (Aldrich, >99%, molar ratio vanadium:oxalic acid = 1:2). An appropriate amount of titania was then added to the solution. The suspension was mixed for 2 h at room temperature and water was evaporated in a rotary evaporator under reduce pressure at 40°C. The material was dried over night in an oven at 110°C, crushed, fractionated (0.114 to 0.5 mm) and finally calcined in air in a muffle furnace (20h, 400°C). Samples made by flame spray pyrolysis and wet-impregnation are labeled as FSP-x and WI-x, respectively, where x denotes the V₂O₅ content in wt.% (Table 3.1).

3.1.2 Catalyst Characterization

The SSA (m² g⁻¹) of the powder was determined by nitrogen adsorption (Pan Gas, >99.999%) at 77 K by the Brunauer-Emmett-Teller (BET) method with a Micromeritics Tristar 3000 (five point-isotherm, 0.05<p/p₀<0.25). Accounting for the V₂O₅ content powder density, the average particle size (d_BET) was calculated assuming spherical particles [18]. X-ray diffraction (XRD) was measured on a Bruker D8 Advance diffractometer (step size of 0.03°, scan speed of 0.60° min⁻¹, Cu Kα radiation). Weight content and crystal size of titania phases were obtained by Topas 2.0 software (Model AXS 2000, Bruker) [18].

Temperature programmed reduction (TPR) was used for determination of the average oxidation state after reduction (AOS) and reducibility of vanadia. Experiments were carried out on a Micromeritics Autochem II 2920 equipped
with a TCD-detector by flowing 5 wt.% H\textsubscript{2} in Ar (Pan Gas, >99.999\%, 20 mL min\textsuperscript{-1}) through the sample [18].

Raman spectroscopy was performed with a Renishaw InVia Reflex Raman system equipped with a 514 nm diode (Ar-ion laser, 25 mW) laser as excitation source focused in a microscope (Leica, magnification x50). The spectra were recorded under dehydrated conditions in an in-situ cell following the procedure described in [16].

X-ray photoelectron spectroscopy (XPS) was performed on a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments. The analysis chamber was operated under ultrahigh vacuum with a pressure close to 5x10\textsuperscript{-9} Torr and the sample was irradiated with a monochromatic Al K\alpha (1486.6 eV) radiation (10 kV; 22 mA). Details of the exact settings and peak analysis can be found elsewhere [10].

3.1.3 Catalytic Evaluation

The catalytic tests were performed in a metallic fixed-bed reactor operating at atmospheric pressure. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200-315 µm and diluted in 800 mg glass spheres checked to be inactive. The gas stream contained 100 ppm of chlorobenzene (mixture in He; Praxair), 20 vol.% O\textsubscript{2} (Praxair; 99.995 \%) and He (Praxair; 99.996 \%) as diluting gas to obtain 200 mL min\textsuperscript{-1} (VVH = 37000h\textsuperscript{-1}). The reaction was run from 100 to 400°C. More details on the operating conditions can be found elsewhere [2].

3.3 Results

3.1.4 Characterization of structural properties of catalysts

Table 3.1 shows the structural characterization data of all tested catalysts. For FSP-made catalysts (2.3 – 13.5 wt.% V\textsubscript{2}O\textsubscript{5}) the SSA of \( \approx 55 \text{ m}^2 \text{ g}^{-1} \) (\( \text{d}_{\text{BET}} \approx 28 \text{ nm} \)) is almost constant, independent of the vanadia loading. At 17.5 wt.% the produced particles slightly decreased in SSA (49 \text{ m}^2 \text{ g}^{-1}) probably due
to the slightly increased production rate (higher V$_2$O$_5$ content) resulting in higher particle concentrations favoring coagulation and sintering.

Table 3.1 Vanadia content, BET and TPR results for all tested V$_2$O$_5$/TiO$_2$ catalysts from different preparation methods.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>nominal V$_2$O$_5$ content a in wt.%</th>
<th>SSA in m$^2$ g$^{-1}$</th>
<th>V surface density b in V nm$^{-2}$</th>
<th>AOS c</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSP-2.3</td>
<td>2.3</td>
<td>52.6</td>
<td>2.9</td>
<td>3.4</td>
</tr>
<tr>
<td>FSP-4.5</td>
<td>4.5</td>
<td>56.2</td>
<td>5.3</td>
<td>3.4</td>
</tr>
<tr>
<td>FSP-8.5</td>
<td>8.5</td>
<td>55.6</td>
<td>10.1</td>
<td>3.8</td>
</tr>
<tr>
<td>FSP-13.5</td>
<td>13.5</td>
<td>55.1</td>
<td>16.2</td>
<td>3.6</td>
</tr>
<tr>
<td>FSP-17.5</td>
<td>17.5</td>
<td>49</td>
<td>23.5</td>
<td>3.6</td>
</tr>
<tr>
<td>FSP-30</td>
<td>30</td>
<td>60</td>
<td>32.8</td>
<td>4.1</td>
</tr>
<tr>
<td>WI-2.3</td>
<td>2.3 (1.94)</td>
<td>48</td>
<td>3.1</td>
<td>3.4</td>
</tr>
<tr>
<td>WI-4.3</td>
<td>4.3 (4.55)</td>
<td>46.2</td>
<td>5.9</td>
<td>3.7</td>
</tr>
<tr>
<td>WI-8.2</td>
<td>8.2 (7.92)</td>
<td>45.6</td>
<td>11.4</td>
<td>3.8</td>
</tr>
<tr>
<td>WI-13.2</td>
<td>13.2 (13.22)</td>
<td>44.9</td>
<td>18</td>
<td>3.7</td>
</tr>
<tr>
<td>WI-19.5</td>
<td>19.5</td>
<td>36</td>
<td>26.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>

a) number in brackets state the real wt.% V$_2$O$_5$ measured by ICP-MS analysis
b) calculated for the initial SSA (48 m$^2$ g$^{-1}$) before impregnation and measured V$_2$O$_5$ content by ICP for WI catalysts
c) oxidation state after reduction, assuming V$^{+5}$ before reduction

To avoid further decrease of the SSA at higher vanadia contents [16] the dispersion gas feed rate was increased from 4 to 5 L min$^{-1}$ oxygen for the 30 wt.% V$_2$O$_5$ catalysts resulting in higher cooling rates. This slowed down coagulation and sintering causing a higher SSA of 60 m$^2$ g$^{-1}$. For the wet-impregnated (WI) catalyst the initial SSA (48 m$^2$ g$^{-1}$) slightly decreased to
Results

46 m²g⁻¹ with increasing the vanadia content from 2.3 to 13.2 wt.% during the impregnation and calcination procedure. The V surface density was calculated based on the final SSA of the flame-made catalysts and on the initial SSA of the P25 support for the wet-impregnated. The values of the V surface density (V nm⁻²) for FSP and WI are fairly comparable (Average oxidation states (AOS) after reduction of both, flame-made and WI catalysts, were in the range of 3.4 to 3.8 after reduction and comparable at given content, indicating almost similar reducibility of the present VOₓ species. Low loadings, however, showed a slightly higher reducibility than high loadings indicated by the lower AOS. Reported values for the FSP-made catalysts are similar to the ones observed in previous studies [16, 18].

XRD of the flame-made V₂O₅/TiO₂ analysis showed more than 98 wt.% anatase with respect to the TiO₂ phase and no crystalline V₂O₅ up to 13.2 wt.% (16.2 V nm⁻², not shown) in agreement with previous studies [16]. Broad XRD reflections indicating nanosized anatase crystals of ≈32 nm which correspond well to the calculated average BET-diameter and indicate thus the predominance of monocrystalline non porous particles [16]. Only at very high loadings of 30 wt.% crystalline V₂O₅ was detected by XRD (Fig. 3.1) contributing a fraction of 2 wt.% and a calculated crystal size of 14 nm. Diffraction lines, however, attributed to crystalline VO₂ (*, θ = 14.2, 28.4, 33.4, 43.7°) were detected already at 17.5 wt.% and got more pronounced in the 30 wt.% sample resulting in approximately 10 wt.% VO₂ (12 nm) in the latter sample. VO₂ formation in FSP-made V₂O₅/TiO₂ was reported before and is due to the very high cooling rates in the flame, allowing the formation of thermodynamically less stable crystal phases [16].

Increasing, however, the flame enthalpies by increasing the liquid feed rate (similar to the one used in this study) and decreasing dispersion gas (3 L min⁻¹) induced the disappearance of VO₂ in those catalysts reported before [16] due to longer residence time in the hot temperature range. Apparently with 4 and 5 L min⁻¹ dispersion gas it was not possible to extend the residence time in the hot temperature zone long enough in order to prevent VO₂ formation.
In case of the WI catalysts crystalline vanadia was detected for loadings \( \geq 8.2 \text{ wt.}\% \) (\( \geq 11.4 \text{ V nm}^{-2} \), Fig. 3.1) following the classic “monolayer” theory of wet-made \( \text{V}_2\text{O}_5/\text{TiO}_2 \) catalysts [3]. The crystalline \( \text{V}_2\text{O}_5 \) content increased from 3.3 wt.% (WI-8.2), 6.6 wt.% (WI-13.2) to 12.5 wt.% for the highest vanadia content (WI-19.5) as determined by TOPAS 2.0 software indicating that half or more of the nominal content is present as crystalline \( \text{V}_2\text{O}_5 \). The initial anatase weight fraction (85 wt.\%) of the P25 was preserved for all catalysts.

![XRD diffraction patterns of the high V surface density FSP- and WI catalysts.](image)

* Fig. 3.1 XRD diffraction patterns of the high V surface density FSP- and WI catalysts.

The structure of the present \( \text{VO}_x \)-species was analyzed by Raman spectroscopy under dehydrated conditions at 300°C. The FSP-made catalysts showed no indication of crystalline \( \text{V}_2\text{O}_5 \) species up to 17.5 wt.% loading (23.5 V nm\(^{-2}\), not shown), more than 2 times the theoretical “monolayer”, in agreement with previous studies [16, 18]. Only peaks at 1033 cm\(^{-1}\) attributed to V=O stretching modes of monomeric (isolated) \( \text{VO}_x \) species [19] and the broad band around 920 cm\(^{-1}\) of V-O-V bridges indicating polymeric \( \text{VO}_x \) species were detected [20-22]. Due to the high cooling rates in the flame and extremely
short residence times in the hot temperature zone, FSP-made \( \text{V}_2\text{O}_5/\text{TiO}_2 \) exhibit a high amount of stable, amorphous VO\(_x\) species at very high vanadium surface density \([16]\). At 30 wt.% vanadia loading (33 V nm\(^{-2}\), Fig. 3.2) crystalline \( \text{V}_2\text{O}_5 \) was formed as indicated by the peak at 998 cm\(^{-1}\) \([23]\) in agreement with XRD analysis (Fig. 3.1).

Due to the dominant Raman shifts and scattering arising from the TiO\(_2\) support and additional overlapping with \( \text{V}_2\text{O}_5 \) bands, detection of discrete major VO\(_2\) bands expected at 191, 258 and 335 cm\(^{-1}\) \([24]\) was not possible for the FSP-17.5 and FSP-30 samples.

*Fig. 3.2 Raman spectra of the WI catalysts and the FSP-30 catalyst. WI catalysts show the on-set for crystalline \( \text{V}_2\text{O}_5 \) already at low V surface density of 6 V nm\(^{-2}\) (WI-4.3). FSP-made \( \text{V}_2\text{O}_5/\text{TiO}_2 \) showed crystalline bands only for the FSP-30. Spectra were recorded under dehydrated conditions at 300°C.*
The wet-impregnated catalyst (Fig. 3.2), on the other hand, showed already traces of crystalline V$_2$O$_5$ at relative low (4.5 wt.%) vanadia loadings (< 5.9 V nm$^{-2}$), namely below the theoretical “monolayer”, indicated by the small peak at 998 cm$^{-1}$ which got more intense at higher V$_2$O$_5$ loadings. Thus the on-set of crystalline formation is reached at much lower V coverage for the wet-impregnated catalysts compared to the FSP-made ones. Usually such low contents don’t necessarily lead to a formation of crystalline species [3].

This indicates that the dispersion of the VO$_x$ species on catalysts obtained by the herein used wet-impregnation procedure is less homogeneous. This could probably be attributed to the relative low calcination temperature of 400°C. At higher loadings (≥ 8.5 wt.%) the Raman results for the WI catalysts are in agreement with XRD analysis (Fig. 3.1) as clear crystalline V$_2$O$_5$ bands are detected at 998 and 699 cm$^{-1}$.

All catalysts were analyzed by XPS in order to determine the V atomic surface concentration. In Fig. 3.3 the V/V+Ti ratio of both, FSP-made and wet-impregnated catalysts is shown in dependence of the V surface coverage. Up to 6 V nm$^{-2}$ FSP-made and WI catalysts show similar surface concentration of vanadium. Considering the synthesis of the WI catalysts and the fact that vanadium has almost no solubility in TiO$_2$ after treatment at 400°C [25] the XPS results corroborate, that for the flame-made catalysts vanadia is located dominantly on the titania surface. The TiO$_2$ nucleates first in the flame and then the VO$_x$ species condensate on top of it creating a core (TiO$_2$) shell (VO$_x$) type structure as stated already earlier [16, 18, 26-27]. Above 6 V nm$^{-2}$ the slope decreases. At the same time the surface concentration of the wet-impregnated catalysts is slightly lower compared to the FSP-made ones indicating a better dispersion of the V for the flame-made samples at such high contents [28]. Around 13.5 wt.% (16 V nm$^{-2}$) the increase in the surface ratio is noticeable leveling off. At 30 wt.% a significant increase in the surface concentration can be seen again due to the formation of VO$_2$ and V$_2$O$_5$ crystals likely grown in a more tower like structure [29], covering a large part of the surface of TiO$_2$ and thus dominating the XPS signal.
3.1.5 Catalytic Performance

Temperature dependency of the conversion of chlorobenzene ($X_{Clbz}$) (light-off curves) for the FSP-made and WI catalysts tested is shown in Fig. 3.4 and Fig. 3.5, respectively. For both preparation methods the conversion at a given temperature ($>200$ °C) increases with increasing vanadia content of the catalysts, indicating a higher activity of the catalysts with higher V$_2$O$_5$ content. This relation between the vanadia content and the activity was already reported for classic SCR reactions [11] with comparable catalyst systems and for VOC abatement with V$_2$O$_5$/Al$_2$O$_3$ catalysts [30]. The investigated vanadia content however is usually very low and the surface coverage does not exceed 8-10 V atoms per nm$^2$ constituting the class of so-called “sub-monolayer” catalysts. Recently V$_2$O$_5$/TiO$_2$ catalysts with $>10$ V nm$^2$ were reported for the total oxidation of chlorobenzene showing a maximum in activity for 16 V nm$^2$.
surface density [15]. A similar V surface density was reported for highly active 
$V_2O_5/TiO_2$ catalysts in the oxidative dehydrogenation of propane [31].

The WI catalysts steadily increase in activity with increasing vanadia content reaching a maximum around 18 V nm$^{-2}$ (WI-13.2, Fig. 3.5), namely more than 2 times the “theoretical monolayer”, before the activity decreases at higher loading (WI-19.5, Fig. 3.5), consistent with a former study [15]. The flame-made FSP-8.5 and FSP-13.2 catalysts on the other hand, follow the same trend but exhibit the activity maximum at lower loadings (FSP-8.5) before it decreases at higher loadings. Overall, the best catalytic activity was measured for the WI-13.2 catalyst with high amounts of polymeric/crystalline $V_2O_5$ species as confirmed by XRD (Fig. 3.1) and Raman (Fig. 3.2), reaching almost full conversion (98.5%) at 250°C.
Looking at the results presented in this study, several explanations can be considered: For both the wet-impregnated and flame-made catalysts, the samples with low V$_2$O$_5$ loading (< 4.3 wt.%), corresponding to dominantly monomeric VO$_x$ species as confirmed by Raman analysis, show inferior activity compared to the ones at higher V surface density (Fig. 3.4 and 3.5). Obviously the increasing amount of di-, polymeric and/or crystalline V-O-V bonds formed at higher loadings induce a higher activity in the total oxidation of chlorobenzene rather than well spread isolated VO$_x$ species as in the SCR reaction reported by Krishnamoorthy et al. [8]. Recently it was shown that in the total oxidation of benzene on nonhydrolytic solgel catalysts indeed the polymeric VO$_x$ species are more active than isolated monomeric species [14]. Krishnamoorthy et al. studied low surface coverage (< 8 V nm$^{-2}$) V$_2$O$_5$/TiO$_2$ catalysts in the total oxidation of chlorobenzene, too [8]. Interestingly no
correlation between V surface density and TOF was observed. Light off curves, however, showed increasing activity with increasing vanadia loading indicating that probably the amount of the increasing di- or polymeric VO\textsubscript{x} species is likely responsible for the increase in activity. In fact, several authors have reported high activity at relatively high (>8 V nm\textsuperscript{-2}) V surface density for different reactions including oxidative dehydrogenation of propane [31], oxidation of toluene to benzaldehyde [32] and oxidation of o-xylene [33].

At first glance all herein presented results seem to indicate towards the polymeric and crystalline V\textsubscript{2}O\textsubscript{5} species containing dominantly V-O-V bonds as an active species for the total oxidation of chlorobenzene. Indeed neither a high amount of well dispersed amorphous (monomeric) VO\textsubscript{x} species (Fig. 3.3) nor the presence of crystalline VO\textsubscript{2} (Fig. 3.1, FSP-17.5 and FSP-30) have a positive effect on activity (Fig. 3.4) for the flame-made catalysts when compared to the WI ones (Fig. 3.5). The latter show always a superior activity at comparable catalyst composition. The only (measured) difference in this study is the presence and amount of crystalline V\textsubscript{2}O\textsubscript{5} for FSP-made vs. wet-impregnated catalysts (Fig. 3.1 and 3.2) and higher VO\textsubscript{x} species dispersion of the flame-made catalysts (Fig. 3.3). Additionally the available surface area and therefore number of V surface sites cannot be called for explaining the differences in activity, as all catalysts have almost the same SSA. This is in contrast to studies on selective oxidation of o-xylene where the activity depended mainly on the SSA (available V sites) and not on the structure of those VO\textsubscript{x} sites [16].

On the other hand crystalline species have been always considered to be less active than mono- or polymeric VO\textsubscript{x} species. The herein presented results could indeed suggest that the difference in activity of the WI compared to the FSP catalysts is related to an actual difference in the amount of di- and polymeric VO\textsubscript{x} species in relation to the amount of crystalline species present on the surface of the TiO\textsubscript{2}. The higher dispersion and lower activity, however, of the FSP catalysts, due to the surface growth of VO\textsubscript{x} on single TiO\textsubscript{2} particles in the flame confirmed by Raman [16] and XPS (Fig. 3.3), corroborate a higher amount of less active mono- and dimeric species for the FSP catalysts compared to the wet-impregnated ones. With increasing vanadia loading
(> 16 \( \text{V nm}^{-2} \) or 2 “theoretical monolayers”) the flame-made catalysts show no enhancement in the activity anymore (Fig. 3.4) since the additionally formed V-O-V bonds are not close enough to the TiO\(_2\) support. While on the WI samples due to the lower dispersion more 2D polymeric VO\(_x\) species, V-O-V bonds influenced by the TiO\(_2\), could have formed already at low V surface density (WI-4.3, 6 \( \text{V nm}^{-2} \)) and additional TiO\(_2\) surface becomes available favoring the formation of 2D polymeric structures in close proximity of the titania at high loadings up to 18 \( \text{V nm}^{-2} \) which in turn increases the activity (Fig. 3.5).

In other words, the most active species could be those involved in V-O-V bonds that are directly connected to the support or not too distant from a V-O-Ti bond. The active V-O-V bonds would thus be those keeping a sufficient interaction with the support. This explanation would hence suggest a lower activity of the monomeric and isolated species, which consist only in V-O-Ti bonds (and not of V-O-V), and the big crystals, for which a big part of the V-O-V bonds are too far away from the support, to be influenced positively. In the opposite, the more active species would correspond to the polymeric species, namely those containing V-O-V bonds and sitting directly on the support, preferably as a 2D structure, but could also include the small amorphous 3D structures and the crystals little enough to keep a good interaction with the support.

The link between this interpretation and the catalytic results is quite clear. The catalysts with the lowest loading of vanadia, whatever the kind of synthesis, have only or essentially monomeric species and are the least active ones. In the same way, the highest loading of vanadia (FSP-30 and WI-19.5) lead to the biggest crystals observed in this study and showed a lower activity as compared to the most active catalysts which are those with an intermediate loading of vanadia (WI-13.2 and FSP-8.5). These intermediate samples contain essentially polymeric species and small 3D structures (amorphous bodies or little crystals) which are probably equally responsible of this high activity.
3.5 Conclusions

$\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with different vanadia loadings and comparable SSA were prepared by flame spray pyrolysis and classic wet-impregnation synthesis. For the first time vanadia/titania catalysts exceeding a V surface density of $8 \text{ V nm}^{-2}$ (sub-"monolayer") were evaluated in detail for the total oxidation of chlorobenzene. The flame-made catalysts showed in contrast to the wet-impregnated catalysts no indication of crystalline $\text{V}_2\text{O}_5$ species even at high ($>8 \text{ V nm}^{-2}$) V surface density. $\text{VO}_x$ species dispersion was found to be better for the FSP-made catalysts especially for $>6 \text{ V nm}^{-2}$. Activity in the catalytic total combustion of chlorobenzene increased with increasing vanadia loading at constant SSA independent of the preparation method, indicating an activity dependency on the structure and amount of $\text{VO}_x$ species present on the TiO$_2$ surface. Indeed V-O-V bonds in close proximity of the titania could be considered as the most active species. In contrast to earlier studies, higher loadings leading to polymeric and/or crystalline $\text{VO}_x$ species seem to be beneficial in the abatement of chlorinated VOCs. Additionally the beneficial role of the TiO$_2$ support for the catalytic activity up to a critical V surface density of around $18 \text{ V nm}^{-2}$ can be concluded.

This study exemplifies again that, even though $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts have a long history, the active species as well as catalytic mechanisms which are responsible for good catalytic performance of such catalysts are yet not completely understood. Further research is necessary in which effects like surface acidity, average oxidation state and possible vanadia crystal size effects should be analyzed in more detail.

3.6 References


CHAPTER 4

Structure of flame-made vanadia/silica and catalytic behavior in the oxidative dehydrogenation of propane

Abstract

Vanadia/silica particles with a specific surface area up to 330 m²g⁻¹ and a V₂O₅ content up to 50 wt.% or V surface density up to 27.6 V nm⁻² were prepared by flame spray pyrolysis. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature programmed reduction, Raman spectroscopy, and ⁵¹V MAS NMR, and tested in the oxidative dehydrogenation (ODH) of propane. Depending on vanadia content, different vanadia species were formed. The as-prepared flame-made catalysts showed dominantly isolated monomeric VOₓ surface species for V-loadings exceeding

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¹Part of this chapter were published in Journal of Catalysis, 274 (2010) p64
even the typical “monolayer coverage” (2 V nm\(^{-2}\)) of classic wet-impregnated materials. The stability of these VO\(_x\) species depended on temperature and V surface density. Catalysts with 3.3 V nm\(^{-2}\) were stable up to 500 °C and those with 2 V nm\(^{-2}\) up to 600°C. Catalysts loaded with 3 to 25 wt.% V\(_2\)O\(_5\) were tested for the ODH of propane. Catalysts containing \(\geq 15\) wt.% V\(_2\)O\(_5\) showed structural rearrangement of the VO\(_x\) species during the catalytic tests inducing a transition from monomeric to crystalline vanadia. The turnover frequency of flame-made catalysts decreased with increasing vanadia loading, indicating a higher activity of monomeric VO\(_x\) species compared to crystalline V\(_2\)O\(_5\). The conversion (global activity), however, showed a maximum for the 20 wt.% V\(_2\)O\(_5\)/SiO\(_2\) (4.6 V nm\(^{-2}\)) catalyst. The selectivity to propene depended mainly on propane conversion and only to a lesser extent on the structure of the VO\(_x\) species. Highest selectivity (55%) was achieved for the low loaded catalysts. With increasing vanadia loading formation to CO\(_x\) increased and the product ratio of CO\(_2\)/CO decreased. Highest propene yield was measured for catalysts with relative high V surface density containing both monomeric VO\(_x\) and crystalline V\(_2\)O\(_5\). Flame-spray-pyrolysis proved to be a very versatile method for synthesis of V\(_2\)O\(_5\)/SiO\(_2\) catalysts with high dispersion of isolated VO\(_x\) species at high surface density.

### 4.1 Introduction

Propene is one of the most important feedstock in the chemical industry as it is used for the synthesis of various chemical intermediates and major processes such as polypropene (PP) synthesis. Polypropene is used for the production of diverse products, ranging from solvents to plastics. At the present time, steam cracking, fluid-catalytic-cracking and catalytic dehydrogenations are the main processes to gain olefins from natural feedstock oil [1]. Increasing oil prices and growing PP market (4-5% per year) spur the development of a less energy-intensive process for the propene production [2]. One of the promising processes is the oxidative dehydrogenation (ODH) of propane to propene. This process will allow to use propane of natural gas stocks, in a range of 2-5% [3], as a feedstock for the propene/PP production.
Catalyst based on supported vanadia showed promising results for the ODH reaction. It is commonly agreed that vanadium oxide can be present on the support oxide in three distinct forms, i.e. as monomeric VO$_x$-species at low loadings (typical < 2.3 V nm$^{-2}$), in oligomeric form at medium loadings (2.3 - 7.5 V nm$^{-2}$), and as V$_2$O$_5$ crystals at high loadings (> 8 V nm$^{-2}$) [4-7]. The composition of VO$_x$ species and thus the catalytic behavior of supported vanadia catalysts is influenced by the specific surface area (SSA), V$_2$O$_5$ content, the composition of the support [6, 8-10], and also by the synthesis method [11-13]. For SiO$_2$-supported catalysts the transition from amorphous monomeric to crystalline vanadia occurs already at low V surface densities around 2 V nm$^{-2}$ [10] or even lower [2, 14], without exhibiting any oligomeric VO$_x$ species in the transition range.

The activity of vanadia species in the ODH reaction can depend significantly on the supporting oxide [6, 10]. The role of the structure of the VO$_x$ species on the support surface on activity and selectivity is still debated and not completely resolved. Khodakov et al. [6] stated that oligomeric VO$_x$ species or even small V$_2$O$_5$ crystallites are more active and selective than isolated monomeric sites independent of the supporting oxide (TiO$_2$, SiO$_2$, Al$_2$O$_3$, ZrO$_2$, HfO$_2$). Tian et al. [10] stated that the relative rate of propene formation does not depend on the nature of the support (SiO$_2$, Al$_2$O$_3$, ZrO$_2$), or V surface density and structure (mono- and oligomeric), in agreement with previous studies [15]. For silica-supported vanadia-based catalysts, however, several authors reported turn-over-frequencies that differ up to one order of magnitude depending on V surface density. Monomeric VO$_x$ species were identified as the most active and selective V sites in the ODH of propane [2, 14, 16-18].

Most of these catalysts were prepared using classic, multiple-step, wet-phase processes (e.g. impregnation) of the corresponding non- or mesoporous support. Good accessibility of the VO$_x$ species is important for high activity and selectivity. The dispersion and structure of the VO$_x$ species and thus their catalytic performance not only depend on the composition of the supporting oxide but also on the catalyst synthesis method, like vapor-fed flame synthesis [19], flame-spray pyrolysis [11, 13], sputter deposition [20] or atomic
layer deposition [12]. Especially the wet-chemistry synthesis routes sometimes show broad variation in the structure of the VO$_x$ species depending on the synthesis conditions.

A highly reproducible synthesis method leading to easy accessible model catalysts of high purity is flame spray pyrolysis (FSP), a one-step process suitable for producing mixed metal-oxide catalysts with excellent control of particle morphology and reproducibility [13, 21-23]. In the FSP process the VO$_x$ is formed on the oxide support surface due to the lower melting point (~700°C) of V$_2$O$_5$ compared to the oxide supports (melting point usually > 1000°C). The vanadia layer is formed when the flame temperature is low enough for it to condense out in vapor-fed [13, 19] and liquid-fed flame synthesis [13]. With this process, catalysts with significant differences in particle structure and VO$_x$ species composition can be produced. FSP-made V$_2$O$_5$/TiO$_2$ catalysts exhibit monomeric and oligomeric VO$_x$ species at high V surface densities where the corresponding wet-made catalysts form crystalline VO$_x$ species [13]. Recently V$_2$O$_5$/SiO$_2$ catalysts were prepared by flame pyrolysis [11] that showed a relative low surface area (<80 m$^2$g$^{-1}$) for flame-made silica supported materials [24-25] and a high V dispersion in the bulk of the particles which can probably be traced to their use of low enthalpy solvents and low dispersion of the liquid precursor that may have resulted in catalysts by droplet to particle formation rather than nucleation from the gas phase [23]. Only 30% of the nominal V atoms were accessible for the reaction. Particularly, the low vanadia content catalysts showed almost no selectivity to propene [11]. The aim of the present work was to explore the potential of flame spray pyrolysis for synthesis of nonporous, nanostructured V$_2$O$_5$/SiO$_2$ catalysts for the oxidative dehydrogenation of propane (ODH). A focal point was the effect of FSP synthesis on the structural properties of V$_2$O$_5$/SiO$_2$ catalysts and catalytic performance. For this purpose, catalysts with different V-loadings were prepared, characterized with various physicochemical techniques, and tested in ODH.
4.2 Experimental

4.2.1 Catalyst Preparation

Nanostructured vanadia/silica particles were made by FSP of appropriate precursor solutions [13, 26]. For the vanadium precursor, ammonium metavanadate (Sigma-Aldrich, 99%) was mixed with 2-ethylhexanoic acid (2-EHA, Riedel-de Haën, >99 %) and acetic anhydride (Riedel-de Haën, >99%) in a ratio of 2:1 under stirring and heating it to 100°C for several hours resulting in a metal concentration of 0.5 M. Then appropriate amounts of hexamethyldisiloxane (Aldrich, >98%) and the vanadium precursor were mixed based on the nominal weight content vanadia in the catalyst (0-50 wt.%) with xylene (Riedel-de Haën, >96 %) and 2-EHA (Riedel-de Haën, >99 %) in a ratio of 1:1 resulting in a total metal concentration of 0.75 M. The use of solvents (xylene, 2-EHA) with significantly higher combustion enthalpy (≈4600 kJ mol⁻¹) ensured high enthalpy density in the flame and particle formation via nucleation from the gas phase [27-28]. Moreover the O₂ pressure drop was adjusted to 1.7 bar for high dispersion of the liquid precursor spray and the flow rates (enthalpy) of the pilot flame was tripled (CH₄: 1.5 L min⁻¹, O₂: 3.3 L min⁻¹) compared to Rossetti et al. [11]. Solubility and stability of the metal precursors were no problem for the whole investigated range of vanadia contents.

This precursor solution was fed by a syringe pump (Inotec, IER-560) through the FSP nozzle and dispersed by O₂ (PanGas, 99.95%, 5 L min⁻¹) into a fine spray that was ignited and sustained by a premixed CH₄/O₂ flame. Additional 5 L min⁻¹ of sheath O₂ was fed in the reactor to ensure complete combustion. A detailed description of the laboratory scale FSP reactor can be found elsewhere [26]. The powders were collected with the aid of a vacuum pump (Busch SV 1050 B) on a glass microfiber filter (Whatman GF/D, 257 mm in diameter).
4.2.2 **Catalyst Characterization**

The specific surface area (SSA, m$^2$g$^{-1}$) of the powder was determined by nitrogen adsorption (Pan Gas, >99.999%) at 77 K using the Brunauer-Emmett-Teller (BET) method (Micromeritics Tristar 3000) with a five point-isotherm (0.05<p/p$_0$<0.25). Accounting for the V$_2$O$_5$ content in the powder density, the average particle size ($d_{BET}$) was calculated assuming spherical particles. Full BET adsorption-desorption isotherms were measured on the same instrument. X-ray diffraction (XRD) was measured on a Bruker D8 Advance diffractometer (step size of 0.03°, scan speed of 0.60° min$^{-1}$, Cu Kα radiation).

Temperature programmed reduction (TPR) was used for determination of the average oxidation state (AOS) after reduction and reducibility of vanadia. Experiments were carried out on a Micromeritics Autochem II 2920 equipped with a TCD-detector by flowing 5 vol.% H$_2$ in Ar (Pan Gas, >99.999%, 10 mL min$^{-1}$) through the sample. The temperature was increased from 50 to 950 °C at 10 °C min$^{-1}$. Prior to this analysis the sample was oxidized in flowing oxygen (PanGas, >99.999%, 20 mL min$^{-1}$) at 500 °C for 30 min to assure complete oxidation of vanadium species.

Raman spectroscopy was performed (Renishaw InVia Reflex Raman) with a 514 nm diode (Ar-ion laser, 25 mW) laser as excitation source focused with a microscope (Leica, magnification x5). For the dehydrated Raman analysis an *in-situ* cell equipped with a quartz window was used [13]. The samples were pressed into tablets and placed in the cell, then directly heated up to 500 °C under flowing synthetic air (PanGas, 99.999%, 40 mL min$^{-1}$). The spectra were recorded at 500 °C for 40 s and 20 accumulations to obtain sufficient signal-to-noise ratio and collected on a CCD camera after being diffracted by a prism (1800 lines per millimeter) using 12.5 mW laser energy.

The $^{51}$V MAS NMR experiments were performed at room temperature on a Bruker MSL-400 spectrometer at a resonance frequency of 105.25 MHz using a 4 mm MAS NMR probe. NMR measurements were done on as-prepared (hydrated) and on dehydrated samples. In the latter case the catalysts were treated in a furnace at 500 °C (10 K min$^{-1}$) for 2 h under vacuum, subsequently transferred without any contact to air into a glove box purged with dry N$_2$ and filled into the 4 mm MAS rotor. In the experiments, a single pulse length of
\(\pi/8\) and a relaxation delay of 0.5 s, and a spinning rate of ca. 12.5 kHz were used. The \(^{51}\text{V}\) chemical shift was referenced to vanadium trichloride oxide (VOCl\(_3\)). The NMR data were processed with the Bruker software WINNMR. Anisotropic shift values were obtained from the simulated MAS NMR spectra with the Bruker WINFIT software.

For transmission electron microscopy (TEM), the material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. The investigations were performed on a Tecnai F30 microscope (field emission cathode, operated at 300 kV).

Samples are designated as \(x\text{V-Si}\), where \(x\) denotes the \(\text{V}_2\text{O}_5\) content in wt.% (Table 4.1). An as-prepared catalyst (3V-Si) was subjected to an additional heat treatment between 400 and 600 °C for 5h (5 °C min\(^{-1}\) heating rate) in air in an oven (Carbolite, CWF 1300).

### 4.2.3 Catalytic Tests

Oxidative dehydrogenation of propane was performed on a lab-scale test plant (Celpat GmbH) in an isothermal, plug-flow fixed-bed reactor (i. d. 15 mm). All gases (\(\text{N}_2, >99.996\%\), \(\text{O}_2, >99.95\%\), and \(\text{C}_3\text{H}_8, >99.5\%\)) were fed by mass-flow controllers (Brooks). The temperature was varied in the range of 400 to 550 °C at atmospheric pressure. The molar fractions of propane and oxygen in the reactor feed were 0.2. Total gas-flows ranged from 125 to 200 mL min\(^{-1}\) at standard conditions, resulting in a gas hourly space velocity (GHSV) in the range of 37'500-60'000 L kg\(_{\text{cat}}^{-1}\) h\(^{-1}\). Analysis of all organic species was performed on-line by GC (Agilent, HP-PLOT-Q column, 30 m long, 0.32 mm in diameter and 0.2 \(\mu\)m thick) using \(\text{CH}_4\) as internal standard while \(\text{CO}/\text{CO}_2\) were measured by non-dispersive IR spectroscopy (ABB, Ureas). While the overall carbon balance (educts vs. products) was greater than 98%, the carbon balance of only the converted propane was closed to 92± 5% by summation of the products (\(\text{C}_3\text{H}_6, \text{C}_3\text{H}_4\text{O}, \text{C}_2\text{H}_4, \text{C}_2\text{H}_4\text{O}, \text{CO}, \text{CO}_2\)). TGA analysis of the spent catalysts showed no significant loss due to carbon burn off, while Raman showed trace amounts of carbon indicated by a band around 1600 cm\(^{-1}\) for some catalysts which could be responsible for the variation in the carbon balance.
For the catalytic tests the flame-made V$_2$O$_5$/SiO$_2$ catalysts were pressed (2t), crushed and fractioned (315-450 µm). 200 mg of catalyst was diluted with 20 g of SiC (<300 µm) resulting in a catalyst bed length of 60 mm to ensure good temperature control in the catalytic bed during the experiments. Reaction temperature was measured 10 mm after beginning of the catalyst bed by means of a thermocouple in the axial center of the reactor. Each catalyst was heated to 500 °C in flowing N$_2$/O$_2$ (150 ml min$^{-1}$, 4:1 by volume), kept there for 1h and then cooled down to 400 °C prior to the catalytic measurements.

4.3 **Results and Discussion**

4.3.1 **Catalyst preparation and structural properties**

A pronounced color change of the synthesized powders was observed when removing the powder collection filter from the set-up. Being almost completely white on the still warm filter for low V$_2$O$_5$ contents (<10 wt.%), the color of the powders quickly changed to slight yellow or orange when exposed to the ambient atmosphere. Higher loadings showed more intense colors already on the filter. Subsequent exposure (days) of the powders to ambient air induced further color change from yellow/orange to green/brown. The color change was reversible upon heat treatment resulting in almost white to orange powders under dehydrated conditions. This color change is attributed to a change of coordination from tetrahedral to a highly distorted VO$_6$ environment upon hydration [29]. This indicates that all samples exhibit highly dispersed and reactive VO$_x$ surface species which react with the ambient moisture forming hydrated vanadia species [30-32].

*Nitrogen Adsorption*

Nanosized catalyst particles with specific surface areas in the range of 119 - 333 m$^2$g$^{-1}$ (Table 4.1) were made by FSP. Only slight variation of the surface area (± 10 m$^2$g$^{-1}$) was observed for three different charges of the same sample composition (10V-Si, 20V-Si) underscoring the good reproducibility of the FSP synthesis.
Table 4.1 Chemical and textural properties of flame-made V$_2$O$_5$/SiO$_2$ catalysts: Composition, BET surface area (SSA), V surface density, temperature of maximal reduction rate (TPR T$_{\text{max}}$), and average oxidation state (AOS).

<table>
<thead>
<tr>
<th>Sample</th>
<th>V$_2$O$_5$ content (wt.%)</th>
<th>SiO$_2$ content (wt.%)</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
<th>VO$_x$-density (#V nm$^{-2}$)</th>
<th>TPR T$_{\text{max}}$ (°C)</th>
<th>AOS$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0V-Si</td>
<td>0</td>
<td>100</td>
<td>292</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3V-Si</td>
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<td>97</td>
<td>334</td>
<td>0.6</td>
<td>587</td>
<td>3.8</td>
</tr>
<tr>
<td>5V-Si</td>
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<td>331</td>
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<td>594</td>
<td>3.8</td>
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<tr>
<td>10V-Si</td>
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<td>332</td>
<td>2.0</td>
<td>592</td>
<td>3.6</td>
</tr>
<tr>
<td>15V-Si</td>
<td>15</td>
<td>85</td>
<td>300</td>
<td>3.3</td>
<td>587</td>
<td>3.5</td>
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<td>238</td>
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</tr>
<tr>
<td>30V-Si</td>
<td>30</td>
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<td>208</td>
<td>11.4</td>
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<td>n.m.</td>
</tr>
<tr>
<td>40V-Si</td>
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<td>60</td>
<td>168</td>
<td>15.6</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>50V-Si</td>
<td>50</td>
<td>50</td>
<td>119</td>
<td>27.6</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

$^a$ oxidation state after reduction, assuming V$^{+5}$ before reduction

An increase in surface area was noticed for catalysts with low (1-10 wt.%) V$_2$O$_5$ contents. After passing the maximum (333 m$^2$g$^{-1}$) at 10 wt.%, the surface area steadily decreased reaching a value (119 m$^2$g$^{-1}$) for 50 wt.% V$_2$O$_5$/SiO$_2$ significantly lower than for pure FSP-made SiO$_2$ (292 m$^2$ g$^{-1}$). This is attributed to the presence of separate V$_2$O$_5$ crystals with significant larger particle size which reduce the overall surface area. A similar trend with an SSA maximum at low dopant content (around 5-10 wt.%) was observed already previously for FSP-made Ta$_2$O$_5$/SiO$_2$ [33], Cs$_2$O/Pt/Al$_2$O$_3$ [22] and ZnO-containing SiO$_2$ [34]. In these studies [22, 33] it was shown by means of NH$_3$ TPD experiments that the particle surface is indeed enriched with the doping metal-oxide and significantly different from pure FSP-made silica [33] or alumina [22], respectively. Therefore the increase in SSA with increasing vanadia content up to 10 wt.% V$_2$O$_5$ could be related to a possible influence of
the vanadium constituent on the SiO$_2$ sintering rate. Probably the presence of highly dispersed V atoms on the silica surface reduces particle sintering rate which results in smaller primary particles and therefore higher SSA. Rossetti et al. [11] also found a maximum in SSA even though particles were formed by a different formation mechanism. The highest SSA was measured for 28 wt.% V$_2$O$_5$ and generally the catalysts had significantly lower surface areas (<80 m$^2$g$^{-1}$) at similar composition compared to the FSP-made catalysts reported here. For a flame based process with relative low precursor concentration (0.2 M) low surface areas in the range of 14 (pure SiO$_2$) to 80 m$^2$g$^{-1}$ (28 wt.% V$_2$O$_5$) were achieved by using tetraethoxysilane (TEOS) as Si precursor. In other studies specific surface areas for flame-made SiO$_2$ were in the range of 300 m$^2$g$^{-1}$ for both vapor fed diffusion flame [19] and liquid fed flame spray pyrolysis [33] using TEOS as Si precursor. This difference can mainly be attributed to the use of low enthalpy (1400-1530 kJ mol$^{-1}$) solvents (ethanol and propionic acid) for the precursors and the very low pressure drop (0.4 bar) over the dispersion nozzle used by Rossetti et al. [11]. The low enthalpy density in the precursor and the reduced enthalpy of the pilot flame igniting the spray facilitates the droplet-to-particle formation route instead of complete combustion of the precursor and particle nucleation from the gas phase [23] which usually results in a more homogeneous particle size distribution with small primary particles [27]. Additionally the low pressure drop of the O$_2$ dispersion gas, resulting in subsonic gas flow at the nozzle tip, induced a poor dispersion of the liquid favoring inhomogeneous particle formation and low SSA powders [21, 35].

Nitrogen adsorption-desorption isotherms of the pure SiO$_2$, 5V-Si and 50V-Si are shown in Fig. 4.1 as representative examples. They reveal the typical hysteresis characteristics of non-porous flame-made materials independent of the vanadia loading and catalyst particle size [26, 36]. Clearly the increase of the SSA at low vanadia contents (Table 4.1) is not related to any porosity of the catalyst particles but to the decrease in SiO$_2$ primary particle size during the particle formation process (coagulation and sintering) by addition of V$_2$O$_5$. This corroborates the already discussed gas-to-particle formation route of the catalysts presented here. Note that in the materials
prepared with the flame conditions used by Rossetti et al. up to 44% (pure SiO₂) and 33% (10 wt. V₂O₅/SiO₂) of the measured BET surface area was attributed to the presence of micropores [11].

![Nitrogen adsorption-desorption isotherms](image)

**Fig. 4.1** Nitrogen adsorption-desorption isotherms of pure FSP-made SiO₂, and the 5V-Si and 50V-Si catalysts.

**X-ray diffraction**

XRD for the as-prepared V₂O₅/SiO₂ catalyst (Fig. 4.2) revealed the typical hump observed for amorphous flame-made silica and no indications of V₂O₅ crystals or solid solutions up to a vanadia loading as high as 30 wt.% (9.5 V nm²). This stands in contrast to flame-made V₂O₅/SiO₂ [11], which showed already at 28 wt.% vanadia loading crystalline V₂O₅ domains in the XRD, and corroborates the different particle formation routes in the flame which can be explained by the different process conditions. The use of high enthalpy solvents and high dispersion of the liquid induce particle nucleation
from the gas phase favoring first the nucleation of SiO$_2$ because of the high boiling point temperature compared to V$_2$O$_5$. Therefore VO$_x$ condensation on the already formed silica surface is expected which will result in an enrichment of V at the support surface rather than forming a solid solution, as already observed for flame-made TiO$_2$ supported V$_2$O$_5$ catalysts before [13, 19].

![XRD pattern of flame-made V$_2$O$_5$/SiO$_2$ samples containing 0-50 wt.% V$_2$O$_5$. Circles indicate the peaks of crystalline V$_2$O$_5$.](image)

Additionally the big difference in ionic radii of V$^{5+}$ (54 Å) and Si$^{4+}$ (40 Å) make an incorporation of V atoms into the amorphous tetrahedral SiO$_2$ structure or even substitution of Si atoms very unlikely. To the best of our knowledge no reports exist on vanadia/silica catalysts stating the formation of a solid solution of vanadium in the silica matrix. On the other hand several studies report the formation of solid solutions with either TiO$_2$, ZrO$_2$ or CeO$_2$ but not with SiO$_2$ for V$_2$O$_5$/TiO$_2$-SiO$_2$ [37], V$_2$O$_5$/ZrO$_2$-SiO$_2$ [38] and V$_2$O$_5$/Ce$_x$Zr-SiO$_2$ [39] systems, respectively. Therefore the formation of a solid
solution seemed rather unlikely. At higher V loadings (>30 wt.% V₂O₅) clear reflections arising from crystalline V₂O₅ (circles, Fig. 4.2) were detected around 2θ = 14.5, 20.3, 26.1, 30.9 and 34.3°, indicating the formation of separate vanadia crystals at such high loadings (>9.5 V nm²) and reducing the overall SSA (Table 4.1). A similar trend was observed for Ta₂O₅/SiO₂ particles made by flame spray pyrolysis at 45 wt.% of Ta₂O₅ [33].

TEM

The sample containing 10 wt.% V₂O₅ (Fig. 4.3a) showed the typical nonporous, highly aggregated and fractal structure of flame-made SiO₂ based mixed oxides [33]. The EDX halo (Fig. 3a inset) clearly indicates the presence of only amorphous material as no diffraction pattern is visible. At higher loadings (50 wt.% V₂O₅, Fig. 3b) clear crystal planes are discernible indicating the presence of crystalline domains and therefore corroborating the results of XRD (Fig. 4.2) which verified the presence of V₂O₅ crystals at these high vanadia loadings.

![TEM images of the 10 wt.% (a) and 50 wt.% V₂O₅/SiO₂ samples. Only amorphous particles are detected for the 10V-Si catalysts while the 50V-Si sample clearly shows the presence of crystalline domains (EDX inset) which can be attributed to crystalline V₂O₅ with lattice fringes of ca. 6.5 Å.](image)

Interlattice distances were found to be ca. 6.5 Å and therefore resemble the (010) crystal plane of pure V₂O₅ indicating that the crystal is not distorted by Ti atoms in interstitial positions. These crystalline domains were
surrounded or could possibly even be covered by amorphous silica. Due to the higher vanadium content in the precursor solution nucleation and particle formation of vanadia could happen earlier in the flame and thereby allowing the silica to cover the V₂O₅ in the sintering step. Similar morphology of segregated crystal domains at high dopant contents has been observed before for FSP-made Ta₂O₅/SiO₂ [33] and TiO₂/SiO₂ made in diffusion flame [40].

Temperature programmed reduction

TCD signals measured during TPR of the 3-50 wt% V₂O₅/SiO₂ and pure flame-made V₂O₅ are shown in Fig. 4.4. At very low V-coverage (0.6-1.0 V nm⁻², up to 5 wt.%) the reduction peak was broad and became sharper for higher V₂O₅ contents. The maximum reduction peak temperature (T_max, Table 4.1) for catalysts of 3-20 wt.% vanadia content was rather constant in the range of 587-596 °C, indicating an almost comparable reducibility of the VOₓ species present in this range of vanadia loading. Increasing the V₂O₅ content to 25 wt% increased the T_max to 609 °C and a distinct shoulder appeared in the reduction profile. Clear assignment of VOₓ species based on the maximum reduction peak and comparison to literature is rather difficult as the peak position can substantially be influenced by the experimental conditions applied [41-42]. All measurements were done with a constant amount of reducible species (V) to exclude a shift due to the measurement parameters and not to the different structure of VOₓ species [42]. Therefore we consider any significant shift to higher reduction temperatures at increasing vanadia loadings as indicative of a structural difference in the VOₓ surface species. The relative stable peak temperature for the catalysts ≤ 20 wt.% V₂O₅ is indicative of a rather similar V dispersion in all these samples. Due to the absence of any other reduction peak at lower temperature the observed peak temperatures likely indicate dominantly isolated tetrahedral VOₓ species although they appeared at higher temperature than for wet-chemistry derived materials [14, 18, 43]. The shift in T_max (Table 4.1, Fig. 4.4) at higher loadings could be attributed to the presence of crystalline V₂O₅ domains.

For sol-gel prepared particles of comparable composition and V surface density a similar behavior of the shift in the reduction peak temperature was reported and was attributed to the presence of V₂O₅ domains [18]. Additionally
the shoulder visible in the reduction profile of the >25 wt.% V$_2$O$_5$ catalysts can be interpreted as a sign of stepwise reduction of different VO$_x$ species [44] indicating different reducibility of the corresponding species, as already observed for FSP-made V$_2$O$_5$/TiO$_2$ [13, 26].

![Fig. 4.4 H$_2$ reduction profiles of flame-made V$_2$O$_5$/SiO$_2$ in the range of 3 to 50 wt.% vanadia content.](image)

The average oxidation state (AOS) after reduction (Table 4.1) decreased from 3.8 at low ($\leq$1 V nm$^{-2}$) to 3.6 at higher V surface density ($\geq$2 V nm$^{-2}$) indicating a slightly stronger reduction of the VO$_x$ species present at high
loadings. Comparable results were observed for the AOS of sol-gel made and impregnated catalysts [14, 18].

Due to the presence of catalytically less favorable crystalline V$_2$O$_5$ in samples containing >30 wt.%, as confirmed by XRD (Fig. 4.2) and TEM (Fig. 4.3), the following characterization was focused on the catalysts containing 3 to 25 wt.% vanadia. These catalysts were considered to be the most interesting for the catalytic tests.

![Raman Spectra](image)

**Fig. 4.5** Raman spectra of dehydrated 3V-Si catalyst: in as-prepared state and after calcination at 400 and 600 °C. Only Raman bands assigned to monomeric VO$_x$ species were detected. Spectra were recorded at room temperature after calcination in air (5K min$^{-1}$, 5h) and dehydration at 300 °C in synthetic air.

**Raman Spectroscopy**

For characterization of the VO$_x$ species, Raman spectroscopy was performed under dehydrated conditions for the flame-made V$_2$O$_5$/SiO$_2$ catalysts. For high V-contents (>25 wt.% V$_2$O$_5$, not shown) dominantly
crystalline V$_2$O$_5$ even for the XRD amorphous as-prepared 30V-Si catalysts were detected. In Fig. 4.5 the Raman spectra of the low V surface density (0.6 V nm$^{-1}$) calcined (400-600 °C) and dehydrated 3V-Si catalyst are shown. Dehydration temperature was set to relative low temperature (300 °C) to avoid any alteration of the sample during dehydration. The spectra of the as-prepared catalyst showed a band at 1034 cm$^{-1}$ which can be attributed to the symmetric stretching mode of V=O bonds indicating the presence of isolated monomeric VO$_x$ species in tetrahedral coordination [45-47].

Upon calcination at 600 °C in air the signal of the monomeric band became more prominent. This is probably related to the fact that dehydration temperatures for V$_2$O$_5$/SiO$_2$ need to be significantly higher than those of e.g. V$_2$O$_5$/TiO$_2$ for which temperatures up to 300°C were sufficient for complete dehydration [13]. Flame-made SiO$_2$ is known to be hydrophilic with a high stability of chemisorbed OH groups even at high temperatures (>300 °C) [48]. Therefore the additional heat treatment by calcination at 400 °C and higher caused a more effective dehydration of the sample resulting in higher intensity of the monomeric VO$_x$ band. No additional bands, possibly indicating other VO$_x$ species (oligomeric or crystalline), were detected corroborating our reduction peak assignment in the TPR analysis (Fig. 4.4). The heat treatment had only small influence on the surface area of this sample which dropped from 333 to around 320 m$^2$g$^{-1}$, corroborating the high stability of these flame-made V$_2$O$_5$/SiO$_2$ catalysts, not only in terms of VO$_x$ species structure but also particle morphology.

Based on these findings, the dehydration temperature in the in-situ cell for the following Raman measurements was set to 500 °C to assure complete dehydration. In Fig. 4.6 representative spectra recorded at 500 °C over a period of 72h are shown for selected V$_2$O$_5$/SiO$_2$ catalysts. It should be noted that a slight shift ($\approx$5 cm$^{-1}$) of the detected bands to lower wave numbers was observed for the spectra recorded at 500°C compared to those cooled down to room temperature after dehydration (not shown).

The 5V-Si (Fig. 6a) and 15V-Si (Fig. 4.6b) show the band located at 1034 cm$^{-1}$ but no band at 993 cm$^{-1}$ indicating the absence of crystalline V$_2$O$_5$ [47] and corroborating the results of XRD analysis (Fig. 4.2). Even after 72h at
500 °C the structure of the VO$_x$ species didn’t change, further supporting the excellent stability of monomeric VO$_x$ species in flame-made V$_2$O$_5$/SiO$_2$. Note that the 15V-Si catalyst exhibited a V surface density of 3.3 V nm$^{-2}$ which exceeds the “theoretical monolayer” coverage of classical wet-impregnated V$_2$O$_5$/SiO$_2$ systems. The classical catalyst systems show crystalline V$_2$O$_5$ at significantly lower V surface density: usually below 2.3 V nm$^{-2}$ [4-7] or as low as 1.3 for zeolithe type materials [2, 14]. Clearly the presence of highly stable (up to 500 °C), exclusively amorphous monomeric VO$_x$ species at such high loadings is a unique characteristic of FSP-made V$_2$O$_5$/SiO$_2$ catalysts.

Fig. 4.6 Long term in-situ Raman spectra recorded at 500 °C in synthetic air for 72h for the
The observed bands around 603 and 802 cm\(^{-1}\) originate from the SiO\(_2\) support and were identified as Si-O-Si stretching modes [5, 45]. The intensity of these bands constantly decreased with increasing V\(_2\)O\(_5\) content of the catalysts, indicating the covering of these SiO\(_2\) species by surface VO\(_x\) species. A broad band around 915 cm\(^{-1}\) was discernible for both the 5V-Si and 15V-Si catalysts, which was not observed for the 3V-Si catalysts (Fig. 4.5). This band is usually attributed to V-O-V vibrations [14, 47] which would indicate the rather atypical presence of small amounts of oligomeric VO\(_x\) species on SiO\(_2\) even at this low V surface density (1-3.3 V nm\(^{-2}\)). Recently, however, this assignment was challenged by several other EXAFS and Raman studies [7, 49-50] (and references therein) attributing this band clearly to symmetric V-Si-O vibrations. Additionally the shoulder at around 1060 cm\(^{-1}\), visible for catalysts 3, 5, 10 and 15V-Si, is attributed to the corresponding asymmetric vibrations of these V-Si-O bands [7, 49-50]. Therefore bands around 915, 1034 and 1065 cm\(^{-1}\) in the flame-made V\(_2\)O\(_5\)/SiO\(_2\) catalysts are assigned accordingly and the presence of dominantly isolated monomeric VO\(_x\) species in tetrahedral coordination on the silica surface up to a V surface density of 3.3 V nm\(^{-2}\) and 500°C is assumed. These observations further support the role of V-species on altering the surface of SiO\(_2\) and delaying its sintering especially at low vanadia contents.

Upon increasing the vanadia content to 20 wt.\% (Fig. 4.6c) the bands at 993 and 695 cm\(^{-1}\) indicating crystalline V\(_2\)O\(_5\) became apparent. Showing only a small peak after 1h at 500 °C the intensity of the bands progressively increased with time, indicating the transformation of amorphous VO\(_x\) species into crystalline domains under these conditions. Additionally vanishing of the V-O-Si bands at 910 cm\(^{-1}\) at 24h at 500°C was observed, indicating a decrease of the fraction of V-O-Si bonds and corroborating the transformation of monomeric VO\(_x\) species into crystalline V\(_2\)O\(_5\). The band of the monomeric VO\(_x\) species, however, was still dominant although Raman spectroscopy is more sensitive for crystalline metal oxides [51] corroborating a high amount of monomeric VO\(_x\) species and only trace amounts of crystalline V\(_2\)O\(_5\) even at such high vanadia loading (4.6 V nm\(^{-2}\)). This is different for the 25V-Si catalysts shown in Fig. 4.6d. Here the crystalline bands at 528, 695 and 998 cm\(^{-1}\) are dominat
features. The increase in intensity of the 993 cm\(^{-1}\) band relative to the monomeric band at 1034 cm\(^{-1}\) with longer exposure time at high temperature indicates a change of the VO\(_x\) species structure on the particle surface, forming more and more crystalline V\(_2\)O\(_5\). Nevertheless a small peak at 1034 cm\(^{-1}\) is visible and suggests the presence of monomeric VO\(_x\) species even at high VO\(_x\) density (6.9 V nm\(^{-2}\)).

\[\text{spent 10V-Si} \]
\[\text{spent 15V-Si} \]
\[\text{spent 20V-Si} \]

\[1200 1100 1000 900 800 700 600 500\]
\[\text{Raman shift, cm}^{-1}\]

\text{Fig. 4.7 Raman spectra of the spent 10V-Si, 15V-Si and 20V-Si catalysts dehydrated at 500 °C. Only Raman bands assigned to amorphous VO\(_x\) species were detected for the 10 wt.%V\(_2\)O\(_3\)/SiO\(_2\) catalysts, while dominantly crystalline V\(_2\)O\(_5\) was detected in the catalyst containing 15 or 20 wt.% vanadia after the catalytic tests.}

It should be noted that spectra of hydrated samples for both, the as-prepared 20V-Si and 25V-Si catalysts (not shown) did not show any bands related to crystalline V\(_2\)O\(_5\) in agreement with the XRD results (Fig. 4.2). Therefore it can be concluded that the crystalline V\(_2\)O\(_5\) detected with Raman at 500 °C (Fig. 4.6c+d) was formed during dehydration treatment.
Figure 4.7 depicts Raman spectra of the 10V-Si, 15V-Si and 20V-Si catalysts dehydrated at 500 °C after their use in catalytic tests for >24h on stream at 550 °C. Note that after exposure to reaction conditions the 10V-Si showed only bands due to amorphous monomeric VO\(_x\) similar to the as-prepared state (not shown), whereas in 15V-Si and 20V-Si crystalline V\(_2\)O\(_5\) prevailed. For latter compositions clear structural changes in the VO\(_x\) species occurring under reaction conditions can be observed when compared to the as-prepared sample (Fig. 4.6b +c). Raman bands of the amorphous monomeric VO\(_x\) species are significantly lower in intensity while the band at 998 cm\(^{-2}\) representing crystalline V\(_2\)O\(_5\) increased in intensity indicating a transition from amorphous to crystalline vanadia during reaction for these two catalysts.

Nevertheless a small peak at 1037 cm\(^{-1}\) can be observed for the 15V-Si catalyst corroborating still the presence of monomeric VO\(_x\) species even under reaction conditions whereas for the 20V-Si catalyst the monomeric band is hardly visible and crystalline V\(_2\)O\(_5\) seems to be dominating.

**Table 4.2 Chemical shift parameters of the flame-made V\(_2\)O\(_5\)/SiO\(_2\) catalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isotropic chemical shift (\delta_{iso}) (ppm)(^{a)})</th>
<th>Anisotropic chemical shift tensor(^{b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta_{11}) (ppm)</td>
<td>(\delta_{22}) (ppm)</td>
</tr>
<tr>
<td>All hydrated</td>
<td>-580 ± 10</td>
<td>-101 ± 10</td>
</tr>
<tr>
<td>3V-Si</td>
<td>-715 (V-O-Si)</td>
<td>-485</td>
</tr>
<tr>
<td>10V-Si</td>
<td>-712 (V-O-Si)</td>
<td>-487</td>
</tr>
<tr>
<td>20V-Si</td>
<td>-615 (V-O-V)</td>
<td>-125</td>
</tr>
<tr>
<td>25V-Si</td>
<td>-616 (V-O-V)</td>
<td>-127</td>
</tr>
</tbody>
</table>

\(^{a)}\) The values obtained from measured MAS NMR spectrum.

\(^{b)}\) The values obtained from simulated MAS NMR spectrum.

**NMR analysis**

Additional to Raman spectroscopy selected catalysts were characterized by \(^{51}\)V MAS NMR to gain more information about the structure of the VO\(_x\) species present at different V surface density. The chemical shift parameters of
the catalysts under hydrated and dehydrated conditions are summarized in Table 4.2.

\[ \delta_{51\text{V}}, \text{ppm} \]

**Fig. 4.8** $^{51}\text{V}$ MAS NMR spectra of the 3V-Si and 25V-Si catalysts under hydrated conditions.

In Fig. 4.8 the $^{51}\text{V}$ MAS NMR spectra under hydrated conditions of the 3V-Si and 25V-Si catalysts are presented. Both spectra show an isotropic chemical shift at around -580 ppm with the components of an anisotropic chemical shift tensor at -101, -427, and -1244 ppm, according to the simulation of $^{51}\text{V}$ MAS NMR spectra. An isotropic chemical shift in the range of -570-590 ppm was observed for other silica supported vanadia catalysts [32, 52] and V-silicalites [30] before. This peak resembles quite closely the environment of crystalline $\text{V}_2\text{O}_5$ but can clearly be assigned to $\text{V}^{5+}$ five-coordinated hydrated tetrahedral surface species [32, 52]. A close inspection of the 25V-Si spectra reveals a slightly asymmetric peak width in the high field indicating the
Results and Discussion

The presence of a second V species in this sample with an isotropic chemical shift around -610 ppm. This signal can be attributed to distorted octahedral environment of crystalline V₂O₅ [53] corroborating the results from Raman analysis (Fig. 6d). A distinct peak, however, was not detected which is likely due to the lower sensitivity of NMR for crystalline V₂O₅ compared to Raman [32] and the dominant peak of the hydrated tetrahedral VOₓ species.

Additionally the absence of any peak feature of four coordinated tetrahedral VO₄ species in the range of -700 ppm in the hydrated state proofs the high dispersion, accessibility and reactivity of the V surface sites in the flame-made V₂O₅/SiO₂ catalysts in contrast to sol-gel derived materials where inaccessible V site in tetrahedral coordination were found [30-32].

It should be noted that the V⁵¹ MAS NMR spectra under hydrated conditions of all V₂O₅/SiO₂ catalysts in a broad range of V surface densities (0.6 to 6.9 V nm⁻²) were similar and no significant difference could be observed. Additionally all anisotropic chemical shift tensors are close to axial.

This, however, is completely different for the dehydrated case shown in Fig. 4.9 and Table 4.2. At low V surface density (<6.6 V nm⁻²) the only isotropic shift is detected around -715 ppm. This peak shift upon dehydration was observed for various V₂O₅/SiO₂ made by different synthesis methods before and clearly shows the presence of isolated four-coordinated dehydrated V⁵⁺ species with V=O and three V-O-Si bonds to the support [30, 52]. This data supports the assignments of the 915 cm⁻¹ (and 1060 cm⁻¹) shift in the Raman spectra (Fig. 6) to the V-O-Si bridging bonds rather than to oligomeric V-O-V species which were not detected by NMR. The spectra of the 15V-Si catalysts (not shown) were similar to the one obtained for the 10V-Si sample which corroborates the results from Raman and TPR analysis and confirms the high V dispersion for the as-prepared V₂O₅/SiO₂ catalysts made by FSP. The NMR spectrum of the 20V-Si catalyst instead, shows a narrow peak at -615 ppm in the dehydrated state. This peak indicates the presence of V-O-V bonds of crystalline V₂O₅ [53-54] in agreement with Raman analysis (Fig. 4.6c). Additionally comparable to the low V surface density catalysts a clear peak at -692 ppm was detected and attributed, though slightly shifted to higher chemical shifts, to the presence of distorted tetrahedral surface V sites. Despite
the high V surface density of 4.6 V nm\(^2\) a significant amount of monomeric VO\(_x\) species seemed to be present on the catalyst surface, corroborating the Raman results shown in Fig. 4.6c.

![Fig. 4.9 \(^{51}\text{V} \text{MAS NMR spectra of the 3V-, 10V-, 20V- and 25V-Si catalysts under dehydrated conditions. Symbols, and * indicate the sidebands of the isotropic shifts at -616 ppm (V-O-V) and -690 or -711 ppm (V-O-Si), respectively.}]

Further increase of the vanadia loading (25V-Si) resulted in an enhanced intensity of the -616 ppm peak compared to the -691 ppm peak indicating the
presence of dominantly crystalline V$_2$O$_5$ and lower fraction of monomeric species compared to the 20V-Si, as already observed in the Raman analysis (Fig. 4.6d).

### 4.3.2 Catalytic performance

The activity of selected V$_2$O$_5$/SiO$_2$ catalysts was tested under steady state conditions at 400-550 °C with a constant gas hourly space velocity (GHSV, 45’000 L kg$^{-1}$ cat$^{-1}$ h$^{-1}$) and propane/oxygen/nitrogen ratio (1:1:3). In Fig. 4.10 the C$_3$H$_8$ conversion ($X_{C_3H_8}$) is plotted as a function of the reaction temperature.

![Graph](image)

*Fig. 4.10 Propane conversion for all tested V$_2$O$_5$/SiO$_2$ catalysts with variation of reaction temperature. Reaction conditions: $m_{\text{cat}} = 0.2$ g, GHSV = 45'000 L g$^{-1}$ cat$^{-1}$ h$^{-1}$, C$_3$H$_8$:O$_2$:N$_2$ = 1:1:3.*

Pure FSP-made SiO$_2$ (filled circles) showed only minor catalytic activity while doping the silica with V resulted in an increase of the conversion of propane. Therefore catalytic activity and conversion of the flame-made V$_2$O$_5$/SiO$_2$ catalysts strongly depended on the V surface density and increased
with temperature. Increasing the vanadia content from 3 (0.6 V nm\(^{-2}\), 3V-Si) to 20 wt.% (4.6 V nm\(^{-2}\), 20V-Si) caused a 4-5 times higher propane conversion at given reaction temperature.

The significant increase in conversion with V-loading can be attributed to the presence of a high concentration of isolated tetrahedral VO\(_x\) species completely accessible to the reactants on the catalyst surface. Interestingly this increase seems to be only little dependent on the structure of the VO\(_x\) species. Catalysts containing >10 wt.% V\(_2\)O\(_5\) showed the presence of crystalline V\(_2\)O\(_5\) (Fig. 4.6c, 4.7 and 4.9) which apparently had no detrimental effect on the activity. This is in contrast to V-SBA-15 [14] or impregnated mesocellular silica foams (MCF) [2], where already the appearance of crystalline VO\(_x\) species caused a decrease in propane conversion at a surface density of around 1.2-1.6 V nm\(^{-2}\). This corroborates the extremely high dispersion of VO\(_x\) species of FSP-made V\(_2\)O\(_5\)/SiO\(_2\) catalysts even at high V surface density, making these catalysts very attractive for the oxidative dehydrogenation of propane.

Only when the vanadia loading was increased further (6.9 V nm\(^{-2}\), 25V-Si) and crystalline V\(_2\)O\(_5\) became the dominating VO\(_x\) species (Fig. 6d), for which a considerable amount of vanadium is not accessible to the reactants, a lower propane conversion (Fig. 4.10) was observed. This is illustrated in more detail in Fig. 4.11 which compares the turnover frequency (TOF, squares) and propane conversion (triangles) at constant reaction temperature (550 °C) and GHSV (45’000 L kg\(_{cat}\)\(^{-1}\)h\(^{-1}\)) as function of the V surface density.

A clear conversion maximum around 4.6 V nm\(^{-2}\) (20 wt.% V\(_2\)O\(_5\)) could be observed indicating that not all vanadia was accessible (active) beyond this loading due to an increased fraction of crystalline vanadia (Fig. 4.6 and 4.8). The TOF of propene production strongly decreased with increasing vanadia loading. The decrease followed an almost exponential decay with a strong decrease up to 2 V nm\(^{-2}\) (10 wt.% V\(_2\)O\(_5\)) (close to the “theoretical monolayer”) and reached an almost asymptotic value for catalysts with >3 V nm\(^{-2}\). A similar trend at low V surface density was observed for vanadia-based MCF [2] and SBA-15 [14] catalysts. The latter, however, showed a drop in TOF over one order of magnitude when increasing the V surface density from 0.2 to 2.4 V nm\(^{-2}\) suggesting a low dispersion in these catalysts, and corroborating the
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high accessibility of VO$_x$ species in flame-made V$_2$O$_5$/SiO$_2$. The most active VO$_x$ species of flame-made V$_2$O$_5$/SiO$_2$ seems to be the isolated tetrahedral sites, dominantly present in the low V surface density (≤2 V nm$^{-2}$) catalysts in agreement with other studies [2, 14, 16-18].

Fig. 4.11 Variation of the turnover frequencies (TOF, cubes) and propane conversion ($X_{\text{C}_3\text{H}_8}$, triangles) with the V surface densities. Reaction conditions: $m_{\text{cat}} = 0.2$ g, GHSV = 45'000 L g$^{-1}$ h$^{-1}$, $T_{\text{reaction}} = 550$ °C, C$_3$H$_8$/O$_2$/N$_2 = 1:1:3$.

Not only activity, also selectivity to the corresponding light olefins is of high importance for ODH catalysts. Usually selectivity to propene is strongly related to conversion. When looking at the selectivity with increasing reaction temperature the following was observed: The two low V surface density flame-made V$_2$O$_5$/SiO$_2$ catalysts (3V-Si and 5V-Si) with a high fraction of isolated VO$_x$ species showed a rather constant selectivity of around 55% and 45%, respectively, independent of the reaction temperature and conversion change. A similar trend was observed for 10V-Si (2 V nm$^{-2}$) up to a reaction temperature of 525 °C before a drop (40 to 32%) in propene selectivity occurred. This contrasts the behavior of conventional mesoporous [17] and
flame pyrolyzed [11] V$_2$O$_5$/SiO$_2$ catalysts which showed a strong dependency of the propene selectivity on the reaction temperature at comparable vanadia V surface density or vanadia loading, respectively. For higher vanadia contents (15-25 wt.%) all catalysts showed a steadily decreasing selectivity with increasing reaction temperature.

The influence of the conversion on the selectivity is additionally illustrated in Fig. 4.12a. Low V surface density catalysts 3V-Si and 5V-Si showing the lowest propane conversion, afforded the highest propene selectivities. With increasing the V loading and thus activity, propene selectivity decreased even for catalysts containing exclusively isolated VO$_x$ species (3V-, 5V- and 10V-Si) corroborating, that these species are probably active for both the dehydrogenation step as well as the further oxidation of propene to CO$_x$ depending on the distances of the active sites [15].

Fig. 4.12 Propylene selectivity as function of propane conversion on flame-made V$_2$O$_5$/SiO$_2$ catalysts for (a) constant GHSV (45'000 L g$_{cat}$^{-1} h$^{-1}$) and (b) with variation of GHSV (37'500-60'000 L g$_{cat}$^{-1} h$^{-1}$). Reaction conditions: m$_{cat}$ = 0.2 g, T$_{reaction}$ = 550 °C, C$_3$H$_8$:O$_2$:N$_2$ = 1:1:3.

Focusing on the 3, 5, 10 and 25V-Si catalysts an almost linear decrease of the propene selectivity with increasing conversion could be observed. Starting from 55% at 7% conversion (3V-Si) the propene selectivity decreased to 20% for a conversion of 22.5% (25V-Si). Clearly the catalysts 15V-Si and 20V-Si showed significant difference of this dependency with higher conversions
Results and Discussion

(>25%) but similar or increasing propene selectivity up to 28% (20V-Si). This behavior may be related to the observed structural rearrangement of the amorphous VOₙ species into V₂O₅ crystallites upon heating to temperatures ≥500 °C during the catalytic tests (Fig. 4.6c and 4.7) while retaining a considerable fraction of monomeric VOₙ species.

In order to investigate the dependency of the propene selectivity on the propane conversion in more detail a different set of experiments with variation of the GHSV (from 37'500 to 60'000 L kg⁻¹cat⁻¹h⁻¹) were performed. In Table 4.3 the product distribution for the shortest contact time, which resulted in the highest propene yield for the tested catalysts, is shown.

Table 4.3 Conversion and selectivity of the flame-made V₂O₅/SiO₂ catalysts in the oxidative dehydrogenation of propane at 550 °C.a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C₃H₈ conv. (%)</th>
<th>Selectivity (%)</th>
<th>CO₂/CO</th>
<th>TOF x 10⁻¹ (µmol-C₃H₆ V⁻¹s⁻¹)</th>
<th>STY C₃H₆ b) (kg kg⁻¹catalyst⁻¹h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0V-Si</td>
<td>3.7</td>
<td>40.4</td>
<td>2.2</td>
<td>36.0</td>
<td>5.9</td>
</tr>
<tr>
<td>3V-Si</td>
<td>8.5</td>
<td>50.0</td>
<td>2</td>
<td>2.4</td>
<td>34.6</td>
</tr>
<tr>
<td>5V-Si</td>
<td>11.5</td>
<td>43.4</td>
<td>1.7</td>
<td>3.0</td>
<td>29.0</td>
</tr>
<tr>
<td>10V-Si</td>
<td>16.6</td>
<td>34.0</td>
<td>1.2</td>
<td>3.3</td>
<td>25.6</td>
</tr>
<tr>
<td>15V-Si</td>
<td>23.7</td>
<td>33.2</td>
<td>1.0</td>
<td>4.3</td>
<td>26.4</td>
</tr>
<tr>
<td>20V-Si</td>
<td>19</td>
<td>31.2</td>
<td>1.3</td>
<td>4.3</td>
<td>21.9</td>
</tr>
<tr>
<td>25V-Si</td>
<td>20.2</td>
<td>25.0</td>
<td>0.7</td>
<td>3.2</td>
<td>24.1</td>
</tr>
</tbody>
</table>

a) Reaction conditions: mcat = 0.2 g, GHSV = 60,000 L kg⁻¹cat⁻¹h⁻¹, C₃H₈:O₂:N₂ = 1:1:3
b) rate of formation of propylene per unit mass of catalyst per time, STY C₃H₆ (space-time yield)

It can be noticed that flame-made V₂O₅/SiO₂ resulted in the formation of an appreciable amount of acrolein almost independent of the vanadia loading. Similar catalytic behavior has been reported for vanadia-based catalysts on mesoporous silica SBA-15 [14]. In the latter study, however, only catalysts with low vanadia loading (<1 V nm⁻¹) exhibiting almost exclusively isolated tetrahedral VOₙ species showed the formation of oxygenated products. This could be considered as indication for the high VOₙ dispersion with a significant amount of monomeric species of FSP-made V₂O₅/SiO₂ even at high vanadia loadings. It is notable that with increasing vanadia content the ratio of
CO₂/CO decreased (Table 4.3). This tendency was valid for the whole range of propane conversion investigated. Apparently the increase in V surface density and the presence of crystalline VOₓ species in flame-made V₂O₅/SiO₂ favor the formation of CO rather than CO₂ at high conversion as has been observed for other flame-made V₂O₅/SiO₂ catalysts before [11].

As can be seen in Fig. 4.12b, the selectivity vs. conversion with variation of the contact time followed the same trend as observed in Fig. 4.12a: increasing propane conversion lead to lower propene selectivity. Only minor influence, however, was observed for both the low V surface density catalysts 3V-Si and 5V-Si. For higher vanadia loadings (> 10 wt.% V₂O₅) the propane conversion and propene selectivity changed significantly with variation of the GHSV. While the 10V-Si and 25V-Si catalysts showed an almost linear dependency of the propene selectivity, again the catalysts 15V-Si and 20V-Si showed a considerable deviation from this behavior as discussed earlier.

![Propylene selectivity as function of V surface density and GHSV of flame-made V₂O₅/SiO₂ catalysts. Reaction conditions: m_cat = 0.2 g, T_reaction = 550 °C, C₃H₈/O₂:N₂ = 1:1:3.](image)
 Apparently the presence of some small crystalline V\textsubscript{2}O\textsubscript{5} domains had virtually no influence on the propene selectivity. Additionally to the observed conversion dependency, Fig. 4.12 indicates that the selectivity depends also on the vanadia loading.

This is illustrated in Fig. 4.13 in more detail. Low V surface density catalysts (3V-Si and 5V-Si) show the higher propene selectivity almost independent of the GHSV. Increasing the vanadia loading reduced the propene selectivity to around 20\% for the catalyst with the highest V surface density and crystalline V\textsubscript{2}O\textsubscript{5} present. At intermediate V surface densities (10 to 20 wt.% V\textsubscript{2}O\textsubscript{5}), however, a clear dependency of the propene selectivity on the GHSV could be observed. Shorter contact times resulted in only a minor decrease (3\% for the 15V-Si and 7\% for the 20V-Si) in propane conversion but a significant increase in propene selectivity by 10 and 14\% (absolute) for the 15V-Si and 20V-Si catalysts, respectively. Although these catalysts contained a significant amount of crystalline V\textsubscript{2}O\textsubscript{5} (Fig. 4.6c and 4.7) they showed the best catalytic performance as indicated by the highest space time yield (STY\textsubscript{C\textsubscript{3}H\textsubscript{6}} in kg kg\textsubscript{cat}\textsuperscript{-1}h\textsuperscript{-1}, Table 4.3) of all tested flame-made V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts. The STY was always close to or above 1 which is significantly higher than that of impregnated V catalysts supported on mesoporous MCM-41 [18], but lower than those on MCF supported catalysts [2]. For an industrially interesting application of such catalysts, the STY should be at least 1 kg propene per kg\textsubscript{cat}\textsuperscript{1}h\textsuperscript{-1} [55], corroborating further the possible potential of such flame-made V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts in an industrial process.

### 4.4 Conclusions

Here one-step flame spray pyrolysis was applied as fast and highly reproducible synthesis method for nonporous nanosized V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalyst for the oxidative dehydrogenation of propane. The BET surface area of as-prepared catalysts depended on the V\textsubscript{2}O\textsubscript{5} content, resulting in up to 330 m\textsuperscript{2}g\textsuperscript{-1} for catalysts with <3.3 V nm\textsuperscript{-1} V surface density (<15 wt.% V\textsubscript{2}O\textsubscript{5}). Such flame-made catalysts showed unique properties in terms of V dispersion exhibiting dominantly isolated tetrahedral coordinated VO\textsubscript{x} species up to a relative high V surface density of 3.3 V nm\textsuperscript{-2}, as confirmed by Raman and NMR analysis.
This is to the best of our knowledge the highest V surface density reported for exclusively isolated VO\textsubscript{x} species on any SiO\textsubscript{2} support so far. The VO\textsubscript{x} species were highly stable up to 500 °C as determined by \textit{in-situ} Raman spectroscopy. Higher contents (up to 30 wt.% V\textsubscript{2}O\textsubscript{5}) resulted in the presence of small V\textsubscript{2}O\textsubscript{5} crystallites not detectable by XRD and no indications of inaccessible V sites in the silica bulk framework was found. Further increase of the vanadia loading caused formation of separate V\textsubscript{2}O\textsubscript{5} particles in the flame, as detected by XRD and evidenced by TEM. FSP-made V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts showed a similar reducibility for vanadia loadings of 3 - 15 wt.% V\textsubscript{2}O\textsubscript{5} with reduction peak temperature around 590 °C, while higher contents needed higher temperatures for reduction.

The catalytic activity strongly depended on the amount of vanadia on the SiO\textsubscript{2} surface and increased with reaction temperature and V\textsubscript{2}O\textsubscript{5} loading despite the presence of crystalline V\textsubscript{2}O\textsubscript{5} domains at relative high V surface density (3.3-4.6 V nm\textsuperscript{-2}). Low V surface density (<3.3 V nm\textsuperscript{-2}) catalysts showed very stable and high propene selectivity (40 to 55%) at intermediate propane conversion, while higher contents resulted in higher conversion but lower propene selectivity. Catalysts exhibiting V surface densities higher than 2 V nm\textsuperscript{-2} showed structural rearrangement of the present VO\textsubscript{x} species during the catalytic tests, forming an increased amount of crystalline V\textsubscript{2}O\textsubscript{5} domains. Despite the presence of the latter, the highest propene yield was measured for the catalyst containing 15 wt.% V\textsubscript{2}O\textsubscript{5} or 3.3 V nm\textsuperscript{-2}. Based on the presented results the most promising catalysts under conditions applied should have an intermediate to high V surface density around 3 V nm\textsuperscript{-2}. Best performance is expected at short contact times (GHSV >50'000) and moderate to high reaction temperatures (500–550°C). The reasonably high space time yield achieved (1.8 kg\textsubscript{C\textsubscript{3}H\textsubscript{6}} kg\textsubscript{cat} \textsuperscript{-1}h\textsuperscript{-1}) indicates the potential of such flame-made catalysts for the oxidative dehydrogenation of propane. Further optimization of the ODH with these flame-derived V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts seems feasible.

4.5 References

References


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CHAPTER 5

Structure of flame-made V$_2$O$_5$/Al$_2$O$_3$ catalysts

Abstract
Vanadia/alumina particles with a specific surface area (SSA) up to 160 m$^2$g$^{-1}$ and a V$_2$O$_5$ content up to 30 wt.% or V surface density up to 16 V nm$^{-2}$ were prepared by flame spray pyrolysis. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature programmed reduction, Raman spectroscopy and TEM analysis. Up to 15 wt.% the addition of V$_2$O$_5$ had no influence on the catalysts specific surface area while further increase resulted in a slight SSA reduction. No indications of crystalline phases besides γ-alumina were found by XRD. Catalysts containing more than 10 wt.% V$_2$O$_5$ showed a diminishing of the alumina crystallinity. Depending on vanadia content, different vanadia species were formed. These flame-made catalysts exhibited dominantly amorphous monomeric VO$_x$ surface species at low (<4 V nm$^{-2}$) V surface density. Higher loadings showed the presence of oligomeric species and were stable up to
500 °C for 72h. Raman analysis of the catalyst containing 30 wt.% V₂O₅ showed indications of an AlVO₄ phase not detected by XRD. Reducibility of the VOₓ species increased with increasing vanadia loading and showed a maximum for intermediate V surface density (6.6 V nm⁻²) indicated by the shift of the maximum reduction peak temperature.

5.1 Introduction

Catalyst based on supported vanadium oxide show promising results for the ODH [1]. V₂O₅ based metal oxide catalysts are also widely applied in other catalytic reactions, e.g. reduction of NOₓ [2], synthesis of phthalic anhydride from o-xylene [3] and numerous other applications as oxidation catalysts [4].

Depending on the desired reaction, the properties of the catalyst can be adapted by the metal oxide support (e.g. Al₂O₃, SiO₂, ZrO₂, etc) the present state and structure of the VOₓ species on the surface. The composition of VOₓ species (monovanadates, polyvanadates and vanadia crystals), and thus the catalytic behavior of supported vanadia catalysts, is influenced by the specific surface area (SSA), V₂O₅ content and the composition of the support [5-6]. These catalysts are mainly produced with classic multiple-step wet phase processes (e.g. wet-impregnation) often limiting the controllability of the structure of the active site and exhibiting a poor reproducibility.

Another synthesis method is flame spray pyrolysis process (FSP), a one-step process that has been intensively studied in the last years and is a suitable technique for producing mixed metal oxide catalysts [7]. In the FSP process the VOₓ is formed on the oxide support surface due to the lower melting point (~700°C) of V₂O₅ compared to the oxide supports (melting point usually > 1300°C) the vanadia layer is formed when the coagulation process of the support oxide is finished [8]. With this process, catalysts with significant differences in particle structure and VOₓ-species composition can be produced. FSP-made catalysts exhibited monovanadate and polyvanadate VOₓ species for high surface vanadia coverage when wet-made ones would have already turned to crystalline VOₓ species [9]. Recently V₂O₅/Al₂O₃ catalysts in the range of 0-50 wt.% vanadia were prepared by flame pyrolysis and tested in the ODH reaction [10]. These catalysts exhibited very low specific surface areas around
22 m²g⁻¹ independent of the vanadia loading. Already 10 wt.% loading showed V₂O₅ phase segregation. This can likely be attributed the to droplet-to-particle formation mechanism favored by the choice of synthesis parameters in this study. The use of low enthalpy solvents and low pressure drop of the dispersion gas above the nozzle resulted in a large droplet size and nucleation of the oxides from the liquid rather than from the gas-phase [10].

Here V₂O₅/Al₂O₃ catalysts with 3-30 wt.% V₂O₅ and high specific surface area made by flame spray pyrolysis are presented and characterized with respect to particle morphology and structure of the VOₓ species.

5.2 Experimental

5.2.1 Catalyst Preparation

Nanostructured vanadia/alumina particles were made by FSP of appropriate precursor solutions. For the vanadium precursor ammonium metavanadate (Sigma-Aldrich, 99%) was mixed with 2-ethylhexanoic acid (2-EHA, Riedel-de Haën, >99 %) and acetic anhydride (Riedel-de Haën, >99%) in a ratio of 2:1 under stirring and heating it to 100°C for several hours resulting in a metal concentration of 0.5M.

For the aluminum precursor (0.4M) appropriate amounts of aluminium acetyl acetonate (Aldrich, 99%) was dissolved in 2-EHA (Riedel-de Haën, >99 %) and acetonitril (Sigma-Aldrich, >99.5%, 2:1 by volume) under stirring for 12h. The Al and V precursors were mixed based on the nominal weight content vanadia in the catalyst (0 - 30 wt.%) with xylene (Riedel-de Haën, >96 %) resulting in a total metal concentration of 0.4 mol L⁻¹.

This precursor solution was fed by a syringe pump (Inotec, IER-560) through the FSP nozzle and dispersed by O₂ (PanGas, 99.95%, 5 L min⁻¹) into a fine spray that was ignited and sustained by a premixed CH₄/O₂ flame. Additional 5 L min⁻¹ of sheath O₂ were fed in the reactor to ensure complete combustion. A detailed description of the laboratory scale FSP reactor can be found elsewhere [9]. The powders were collected with the aid of a vacuum pump (Busch SV 1050 B) on a glass microfiber filter (Whatman GF/D, 257 mm in diameter).
5.2.2 Catalyst Characterization

The SSA (m² g⁻¹) of the powder was determined by nitrogen adsorption (Pan Gas, >99.999%) at 77 K by the Brunauer-Emmett-Teller (BET) method with a Micromeritics Tristar 3000 (five point-isotherm, 0.05<p/p₀<0.25). Accounting for the V₂O₅ content powder density, the average particle size (d_BET) was calculated assuming spherical particles.

X-ray diffraction (XRD) was measured on a Bruker D8 Advance diffractometer (step size of 0.03°, scan speed of 0.60° min⁻¹, Cu Kα radiation).

Temperature programmed reduction (TPR) was used for determination of the average oxidation state after reduction (AOS) and reducibility of vanadia. Experiments were carried out on a Micromeritics Autochem II 2920 equipped with a TCD-detector by flowing 5 vol.% H₂ in Ar (Pan Gas, >99.999%, 10 mL min⁻¹) through the sample. The temperature was increased from 50 to 950 °C at 10 °C min⁻¹. Prior to this analysis the sample was oxidized in flowing oxygen (PanGas, >99.999%, 20 mL min⁻¹) at 300 °C for 30 min to assure complete oxidation of vanadia.

Raman spectroscopy was performed with a Renishaw InVia Reflex Raman system equipped with a 514 nm diode (Ar-ion laser, 25 mW) laser as excitation source focused in a microscope (Leica, magnification x5). For the dehydrated Raman analysis an in-situ cell equipped with a quartz window was used [9]. The samples were pressed into tablets and placed in the cell, then directly heated up to 500°C under flowing synthetic air (PanGas, 99.999%, 40 mL min⁻¹). The spectra were recorded for 40 s and 20 accumulations to obtain sufficient signal-to-noise ratio and collected on a CCD camera after being diffracted by a prism (1800 lines per millimeter) using 12.5 mW laser energy.

For transmission electron microscopy (TEM), the material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. The investigations were performed on a Tecnai F30 microscope (field emission cathode, operated at 300 kV).

Samples are labeled as xV-y, where x and y denote V₂O₅ content (wt.%) and support metal (Al) for the metal oxide support, respectively (Table 5.1).
Table 5.1 Chemical and textural properties of flame-made V$_2$O$_5$/SiO$_2$ catalysts: Composition, BET surface area (SSA), V surface density, temperature of maximal reduction rate (TPR Tmax), and average oxidation state (AOS).

<table>
<thead>
<tr>
<th>Sample</th>
<th>V$_2$O$_5$ content (wt.%)</th>
<th>support content (wt.%)</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
<th>V-coverage (# nm$^{-2}$)</th>
<th>TPR Tmax (°C)</th>
<th>AOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>3V-Al</td>
<td>3</td>
<td>97</td>
<td>159</td>
<td>1.2</td>
<td>550.1</td>
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<td>5V-Al</td>
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<td>2.0</td>
<td>530.6</td>
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<td>70</td>
<td>125</td>
<td>15.9</td>
<td>573.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>

5.3 Results and Discussion

The one-step flame synthesis of V$_2$O$_5$/Al$_2$O$_3$ by flame spray pyrolysis (FSP) resulted in nanosized catalyst particles with specific BET surface areas in the range of 125 to 165 m$^2$g$^{-1}$ (Table 5.1). For the V$_2$O$_5$/Al$_2$O$_3$ catalysts the effect of V addition is not as pronounced as in the case of V$_2$O$_5$/SiO$_2$ (see Chapter 4) and the surface area shows only slight variation for catalysts containing < 15 wt.% V$_2$O$_5$. Higher loadings induce a slight decrease of SSA resulting in 125 m$^2$g$^{-1}$ for the 30V-Al sample, lower than the SSA of pure FSP-made Al$_2$O$_3$ (155 m$^2$g$^{-1}$, not shown). This is, however, significantly larger as for flame-pyrolyzed V$_2$O$_5$/Al$_2$O$_3$ catalysts which showed low SSAs in the range of 20-25 m$^2$g$^{-1}$ due to the droplet-to-particle conversion [10] while the herein used flame-spray-pyrolysis synthesis parameters resulted in gas-to-particle formation [7].

The XRD pattern of V$_2$O$_5$/Al$_2$O$_3$ catalysts in the range of 5-30 wt.% V$_2$O$_5$ are collected in Fig. 5.1. No indication for crystalline V$_2$O$_5$ or a solid solution (e.g. AlVO$_4$) was observed up to 30 wt.% V$_2$O$_5$ (15.9 V nm$^{-2}$). Up to 10 wt.% the typical $\gamma$-alumina diffraction pattern was observed [11], which does not significantly differ from pure FSP-made alumina.
Doping with additional V$_2$O$_5$ resulted in an overall decrease of the crystallinity indicated by the vanishing of the alumina reflections at 2$\Theta$ = 19.3, 31.6, 61.0, and 66.7°. The change in the degree of crystallinity has already been reported for flame-made SiO$_2$-doped Pt/Al$_2$O$_3$ [12], which was attributed to the incorporation of SiO$_2$ into the crystalline alumina framework favored by the similar melting temperatures of SiO$_2$ (1710 °C) and Al$_2$O$_3$ (2050 °C) and simultaneous nucleation. Here, however, the melting temperature of V$_2$O$_5$ is substantially lower (≈790 °C) compared to alumina (≈2054 °C) and therefore an enrichment on the support surface as VO$_x$ species could be expected rather than forming a solid solution. The formation of dominantly VO$_x$ surface species was observed for flame-made V$_2$O$_5$/TiO$_2$ [8-9] and V$_2$O$_5$/SiO$_2$ (chapter 4) before.
The sample containing 1 wt.% V$_2$O$_5$ (Fig. 5.2a) showed the typical nonporous, dominantly non agglomerated, spherical shaped structure of flame-made Al$_2$O$_3$ based mixed oxides [11]. The EDX diffraction pattern (Fig. 5.2a inset) clearly indicates the presence of crystalline material. With increasing vanadia loading the formation of sintering necks can be observed (Fig. 5.2b +c). Additionally the intensity of the EDX (insets) diffraction pattern is vanishing corroborating the results from XRD (Fig. 5.1).

For characterization of the present VO$_x$ species on the catalysts Raman spectroscopy was performed under dehydrated conditions after heating the sample to 500 °C. The corresponding dehydrated spectra after 72h at 500°C are shown in Fig. 5.3. At low loading and V surface density (<10 wt.% V$_2$O$_5$, <4.1 V nm$^{-2}$) a clear Raman band around 1024 cm$^{-1}$ is detected along with a rather broad band around 910 cm$^{-1}$ indicative of the V=O and V-O-Al stretching modes of monomeric VO$_x$ species [13-14]. At higher contents (>15 wt.% V$_2$O$_5$) the monomeric peak becomes less pronounced and is only visible as shoulder. This indicates the vanishing of monomeric species at this V surface density.

Additionally a broad band around 780 cm$^{-1}$ is visible starting for catalysts containing >5 wt.% V$_2$O$_5$ or >2 V nm$^{-2}$. This band can be attributed to the stretching modes of V-O-V bonds [15] indicating the presence of oligomeric VO$_x$ species in agreement with the classic monolayer theory [5-6].

In case of the 30V-Al catalysts small peaks located at 984 and 947 cm$^{-1}$ are visible which can be attributed to the presence of an AlVO$_4$ phase [16].
which was not detected by XRD (Fig. 5.1). The comparable size of the ionic radii of Al$^{3+}$ and V$^{5+}$ could have favored the formation of such a solid solution or separate mixed oxide phase. This is in contrast to V$_2$O$_5$/TiO$_2$ [8-9] and V$_2$O$_5$/SiO$_2$ (see chapter 4) catalysts for which no indications of a solid solution phase even at high V$_2$O$_5$ loading and surface density were found. It should be noted that all catalysts didn’t show any significant rearrangement of the VO$_x$ species during 72h of dehydration at 500 °C in contrast to V$_2$O$_5$/SiO$_2$ (see chapter 4).

![Raman spectra of V$_2$O$_5$/Al$_2$O$_3$ catalysts containing 3-30 wt.% V$_2$O$_5$. Spectra were recorded after 72h under dehydrated conditions at 500 °C in synthetic air.](image)

Fig. 5.3 Raman spectra of V$_2$O$_5$/Al$_2$O$_3$ catalysts containing 3-30 wt.% V$_2$O$_5$. Spectra were recorded after 72h under dehydrated conditions at 500 °C in synthetic air.
In Fig. 5.4 the TCD signals of the 3 - 30 wt% $V_2O_5/Al_2O_3$ samples during TPR analysis are presented. All measurements were done with a constant amount of reducible species (V) to exclude a shift due to the measurement parameters and not to the different structure of VO$_x$ species [17]. Therefore any shift to higher reduction temperatures at increasing vanadia loadings is considered as indicative of a structural difference in the VO$_x$ surface species.

![Graph showing TCD signals](image)

*Fig. 5.4* $H_2$ reduction patterns of flame-made $V_2O_5/Al_2O_3$ in the range of 3 to 30 wt.% vanadia content.

No distinct reduction peaks at high temperatures (>650°C) indicative of $V_2O_5$ are visible confirming the XRD results (Fig. 5.1) that no $V_2O_5$ crystals are present until 30 wt% vanadia loading. The reduction peak maximum ($T_{max}$, Table 5.1) for the $V_2O_5/Al_2O_3$ catalysts shift as function of the surface VO$_x$ density from 550.1°C for the low V surface density (3V-Al, 0.6 V nm$^{-1}$) to lower temperatures (down to 503°C) for intermediate loadings (2-6.6 V nm$^{-1}$) before the temperature increases again up to 573°C for the 30V-Al catalyst.
This suggests that the present polymeric species as confirmed by Raman (Fig. 5.3) of the higher vanadia contents are more easily reduced than the monomeric ones as indicated by the minimum of $T_{\text{max}}$ for the 10V-Al (503.3°C) and 15V-Al (504.5°C) catalyst. It should be noted that V$_2$O$_5$/Al$_2$O$_3$ catalysts made by impregnation showed a similar trend [13, 16, 18-19]. Starting from an average oxidation state (AOS) around V$^{+4}$ after reduction for the low VO$_x$ surface density (3V-Al and 5V-Al, Table 5.1) the AOS decreases to 3.5 at 30 wt% V$_2$O$_5$ (16 V nm$^{-2}$). This corroborates the results of the Raman analysis (Fig. 5.3) that a low loadings ($\leq$ 5 wt.%) dominantly monomeric VO$_x$ surface species are present which are stabilized in the V$^{+4}$ oxidation state on the Al$_2$O$_3$ [18] while at higher loadings the presence of more easily reduced polymeric VO$_x$ is suggested due to the lower final AOS. Reddy and Varma [18] reported AOS values in the range of 4.5-4.7 for impregnated V$_2$O$_5$/Al$_2$O$_3$ catalysts for a surface V density in a similar range as in this study. Lemonidou et al. [1], however, reduced an impregnated V$_2$O$_5$/Al$_2$O$_3$ catalyst (1.3 V nm$^{-2}$), comparable to the 3V-Al sample, to an AOS of 3.15 at significant higher reduction peak temperature ($T_{\text{max}}$=585°C).

5.4 Conclusions

By applying flame-spray-pyrolysis for the synthesis of V$_2$O$_5$/Al$_2$O$_3$ catalysts nonporous, nanostructured powders of high specific surface area were achieved. The vanadia doping had only minor influence on the particle structure up to a loading of 15 wt.% V$_2$O$_5$. Higher contents, contents diminished the crystallinity of the alumina support and reduced the SSA. Raman measurements showed a high V dispersion with dominantly monomeric VO$_x$ species at V surface densities up to 6.6 V nm$^{-2}$, still less than the theoretical monolayer loading. Increasing the vanadia loading resulted in the formation of oligomeric VO$_x$ species, and finally in segregation of partly crystalline AlVO$_4$ solid solution domains for 30 wt.% containing V$_2$O$_5$/Al$_2$O$_3$ catalysts. Apparently the V dispersion achieved for the V$_2$O$_5$/Al$_2$O$_3$ catalysts is significantly lower compared to V$_2$O$_5$/SiO$_2$ (see chapter 4) or V$_2$O$_5$/TiO$_2$ [9, 20] catalysts made by FSP. The reducibility of the different catalysts was measured by TPR. Catalysts with dominantly monomeric VO$_x$ species were
more difficult to reduce than oligomeric VO\textsubscript{x} species indicated by the higher reduction peak temperature of former species.

5.5 References


CHAPTER 6

Fine tuning the surface acid/base properties of single step flame-made Pt/alumina

Abstract

The acid/base properties of Pt/Al₂O₃ were modified by doping the support with SiO₂ or Cs₂O and the catalysts were prepared by flame spray pyrolysis in a rapid, single step process with excellent reproducibility. The catalysts contained 4.7 wt.% Pt and the support composition varied in the range 0-100 wt.% SiO₂ or 0-10 wt.% Cs₂O. Up to 50 wt.% SiO₂ the BET surface areas could be kept in a narrow range (141±15 m²g⁻¹), while higher SiO₂ content increased the surface area and diminished the crystallinity of the support. CO chemisorption and XRD showed a positive correlation between the SiO₂ content and the size of the dominantly spherical Pt particles. The catalysts containing 22-30 wt.% SiO₂ were the most acidic as evidenced by

TPD of NH$_3$. In the hydrogenation of acetophenone the SiO$_2$-doped catalysts were highly active and the selectivity to the hydrogenolysis byproducts increased with increasing SiO$_2$-content by more than 20-fold. This is a confirmation of the effect of support acidity on the properties of the Pt-H system. On the other hand, addition of Cs$_2$O barely affected the Pt particle size and TPD of CO$_2$ confirmed the increase of surface basicity with increasing Cs$_2$O content. Cs$_2$O was probably enriched at the Al$_2$O$_3$ surface and strongly influenced the acid/base properties and thus the catalytic performance already at very low concentrations. Only 0.25 wt.% Cs$_2$O blocked the hydrogenolysis of 1-phenylethanol to ethylbenzene.

### 6.1 Introduction

Supported platinum catalysts are widely used in many chemical reactions, such as hydrogenation, oxidation, and reforming. For all these applications different catalyst characteristics, uniquely tailored to the specific reaction, are desired [1]. A great effort has been expended to control and fine tune Pt-based catalytic materials by various classic wet-phase methods to fulfill these special needs. Among these methods the synthesis of the support via the sol-gel technique [2] and subsequent wet impregnation with a Pt salt or complex is one of the common approaches. These conventional methods, however, allow only limited control over the physical properties of the materials, the reproducibility may be difficult to achieve, and the whole procedure often takes days before the final catalyst can be used.

Flame spray pyrolysis (FSP) instead offers the possibility to synthesize catalytically active metal- and metal oxide nanoparticles in only one, short process step. In addition to this technical advantage, the method may provide novel compositions of mixed metal oxides, combined with high purity and unique structural properties not easy accessible through conventional wet-phase techniques [3-5]. Supported noble metal catalysts were made in flames and their properties and applications have been reviewed recently [6]. In particular, FSP allows tailoring the properties of Pt/Al$_2$O$_3$ in terms of BET surface area and Pt dispersion, and these catalysts showed excellent performance in the enantioselective hydrogenation of ketones superior to those
of commercially available catalysts [7]. In general, flame synthesis is a highly suitable method to control material morphology [8] and various physical properties of catalysts [4].

Basic and acidic supports play a key role in various catalytic transformations [9-11]. Doping alumina with silica is a known procedure to increase the surface acidity of alumina [12-13], whereas Cs₂O [14] and other alkali metal oxides strongly increase the basicity. The effect of support on the catalytic properties of noble metal particles is well established [15-18] and several concepts have been forwarded to rationalize the physico-chemical nature of metal-support interactions. Electronic modification of supported noble metal particles via the acidity and basicity of the support and the influence of support on the properties of chemisorbed hydrogen have been studied extensively by the group of Koningsberger [14, 19-21]. They proposed that the interaction between the metal nanoparticle and the support results in a shift in the metal valence orbitals and proved by DFT calculations that the Pt-H and Pt-O bond strengths vary strongly with the acid/base properties of the support.

Hydrogenation of aromatic ketones to the corresponding alcohols is a facile reaction on supported Pd and Pt, while hydrogenolysis of the C-O bond necessitates acidic media or acidic surface sites [22]. The rate of hydrogenolysis is highly sensitive to the charging of the active metal [15-18] and the extent of hydrogenolysis as a side reaction during hydrogenation can be used as a reliable indication to surface acidic or basic sites. An example is the hydrogenolysis of the C-O bond during acetophenone hydrogenation. On Pt/SiO₂ under ambient conditions in cyclohexane the hydrogenolysis takes place on the Pt surface, where the C-OH or C=O bond is broken [23-24]. Pd supported on (acidic) zeolite catalyzes the direct hydrogenolysis of the carbonyl group to a methylene group at elevated temperature (120°C), but the contribution of this elementary step to the formation of ethylbenzene is negligible on Pd/Al₂O₃ [25].

Here we report FSP synthesis of 4.7 wt.% Pt/Al₂O₃ catalysts where the support composition was modified in a broad range by addition of Si- or Cs-oxides. The catalysts were characterized by nitrogen physisorption, electron
microscopy, XRD, CO chemisorption, and temperature programmed desorption (TPD) of \( \text{NH}_3 \) and \( \text{CO}_2 \). The control of the acid/base properties of Pt by the support was confirmed in the hydrogenation-hydrogenolysis of acetophenone as a test reaction.

### 6.2 Experimental

#### 6.2.1 Catalyst preparation

Aluminum tri-sec-butoxide (Aldrich, >98%), hexamethyldisiloxane (HMDSO, Fluka, >98%), and cesium acetylacetonate (Fluka) dissolved in 2-ethylhexanoic acid (Aldrich, >98%, 0.5M) were used as aluminum, silicon, and cesium precursors, respectively. The appropriate precursor amounts were mixed with diethyleneglycol-monobutylether (Fluka, >98%) and acetic anhydride (Aldrich, >98%) 1:1 by volume. The total support metal (Al + Si or Cs) concentration was kept constant at 0.6 M in these solutions. The nominal SiO\(_2\) weight fraction in the product powder ranged from 0 to 100 wt.\%, whereas the nominal Cs\(_2\)O fraction was in the range 0 - 10 wt.\%. As Pt precursor platinum(II)-bis(acetylacetonate) (Pt-70, Johnson Matthey) was added to the support solution to reach a nominal 4.7 wt.\% Pt loading in the final powder product. The Pt/Al\(_2\)O\(_3\)-SiO\(_2\) and Pt/Al\(_2\)O\(_3\)-Cs\(_2\)O powders were produced in a laboratory scale FSP reactor described elsewhere [26]. The production rate ranged from 11 g/h for pure SiO\(_2\) to 18.5 g/h for pure Al\(_2\)O\(_3\) and to 21.6 g h\(^{-1}\) for 10 wt.% Cs\(_2\)O/Al\(_2\)O\(_3\). The powders were collected with the aid of a vacuum pump (Busch SV 1025 B) on a glass microfiber filter (Whatman GF/D, 257 mm in diameter).

#### 6.2.2 Catalyst characterization

Nitrogen adsorption-desorption isotherms of the catalyst were determined at 77K and specific surface areas were derived using the BET method (Micrometerics Tristar 3000, 5-point isotherm, 0.05 < \( \frac{p}{p_0} \) < 0.25). X-ray diffraction (XRD) was measured on a Bruker D8 Advance diffractometer (step size of 0.02°, scan speed of 0.03° min\(^{-1}\), Cu K\(_{\alpha}\) radiation).
Pt metal dispersion was determined by CO-pulse chemisorption on a Micromeritics Autochem II 2920 unit. Off-gas was analyzed via a mass spectrometer (Pfeiffer Vacuum, Thermostat) to derive the amount of chemisorbed CO [27]. Prior to the measurement, all samples were freshly reduced for 30 min at 400 °C (after heating up at a rate of 10 °C min⁻¹) under flowing hydrogen (5 mol.% in Ar, 20 ml min⁻¹) and then flushed with He (20 ml min⁻¹) at 400 °C for 30 min before cooling down under He to 40°C. For the SiO₂-doped samples pulses of 0.5 ml (10 mol% CO in He) were injected into a He flow of 50 ml min⁻¹. Cs₂O-doped samples were tested in 5 % H₂/Ar (PanGas, 50 ml min⁻¹) atmosphere in which the CO pulses were injected [27].

The stoichiometry factor CO/Pt (Table 1) was determined by the ratio of linear to bridged CO adsorption modes. The diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) study was carried out at 297 K with an EQUINOX 55 spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled HgCdTe detector. Multiple samples (max. 5), separated by quartz wool, were placed without dilution in a plug-flow DRIFTS cell, allowing identical experimental conditions for all samples. The off-gas of the cell was analyzed by a mass spectrometer. Spectra were collected by averaging 200 scans at 4 cm⁻¹ resolution. The standard reductive treatment procedure mentioned above was used to reduce the catalysts in flowing 20 vol.% H₂/He (40 ml/min). CO adsorption was monitored over 60 min in flowing 10 vol.% CO/He (40 ml/min), followed by flowing He (40 ml/min) for 30 min. The peak areas were determined after deconvolution of the spectra.

Surface acidity for the SiO₂-doped samples was measured by temperature-programmed desorption (TPD) of NH₃ (Micromeritics Autochem II 2920). The sample (ca. 200 mg) was pressed (2 t), crushed, and placed in a U-shaped glass tube, heated to 400 °C (10 °C min⁻¹) in 5 mol.% H₂/Ar (PanGas), and then kept at this temperature for 30 min to achieve full reduction. After reduction the sample was flushed with He (PanGas, >99.999%) for 30 min, cooled down to 50 °C, flushed with 10 mol.% NH₃/Ar (PanGas) for 90 min, then purged with He (PanGas, >99.999%) for 120 min, and finally heated to 900 °C at a rate of 10 °C min⁻¹. Evolving gases were monitored using a mass spectrometer (Pfeiffer Vacuum, Thermostat, SEM and emission mode, signal m/z = 15).
The stronger signals m/z = 16, 17, and 18 could not be used due to overlapping with desorbing H₂O [28]. The basicity of the Cs₂O-containing samples was probed by TPD of CO₂ in the same apparatus using a method analogous to that described above; the signal m/z = 44 was used for evaluation.

For transmission electron microscopy (TEM), the material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. The investigations were performed on a Tecnai F30 microscope (field emission cathode, operated at 300 kV). Scanning transmission electron microscopy (STEM) images, obtained with a high-angle annular dark field (HAADF) detector, show the metal particles with bright contrast (Z contrast). In the STEM image, certain areas were selected for a qualitative analysis by energy dispersive X-ray spectroscopy (EDXS; detector (EDAX) attached to the Tecnai F30 microscope). The surface weighted mean Pt particle size dₛ was calculated based on a minimum of 500 particles, using the following equation:

\[ d_s = \frac{\sum n_i d_i}{\sum n_i d_i^2} \]  

were nᵢ is the number of particles with diameter dᵢ.

### 6.2.3 Chemoselective hydrogenation

Acetophenone (Acros, 98%, extra pure) was carefully distilled in vacuum before use. Other chemicals were used as received: bicyclohexyl (Fluka, ≥ 99%), n-hexane (Scharlau, HPLC grade), and a 5 wt.% Pt/Al₂O₃ (Engelhard 4759) as reference catalyst.

All catalysts were reduced at elevated temperature in a fixed-bed reactor prior to use. According to the standard procedure, the catalyst was heated under flowing nitrogen up to 400°C in 30 min, followed by a reduction in flowing hydrogen for 60 min at the same temperature, and finally cooling down in hydrogen in 30 min. At the end, the freshly reduced catalyst was purged with nitrogen for 10 min at room temperature to remove the excess of hydrogen and then transferred immediately to the autoclave.

The reactions were carried out at 3 bar in a 25 ml stainless steel Parr autoclave equipped with a 16 ml glass liner and a PTFE cover, and a magnetic stirrer. The autoclave was equipped also with a valve for sample collection or
substrate addition. The Pt/substrate molar ratio was kept constant at 1/101. The proper amount of catalyst containing 4.9 µmol Pt, 0.5 mmol substrate, and 6 ml solvent (n-hexane) were stirred magnetically (1000 rpm) at 20°C for 180 min. The pressure was held at a constant value with a constant pressure regulator valve. The conversion and product composition were determined by GC analysis, using a Thermo Quest Trace 2000 gas chromatograph and a HP-FFAP (Agilent HP-FFAP 30 m × 0.32 mm × 0.25 µm) capillary column. Bicyclohexyl was used as internal standard (0.1 mmol).

6.3 Results and discussion

6.3.1 Catalyst synthesis by flame spray pyrolysis (FSP)

Different particle morphologies and catalyst characteristics can be achieved by changing the FSP synthesis parameters [4]. The focus of this study was to investigate the influence of acid/base properties on the performance of Pt/Al₂O₃ based catalysts in hydrogenation reactions. Therefore, a synthesis procedure resulting in a preferably narrow Pt particle size distribution with an intermediate size range was necessary to minimize the effect of Pt particle size on the reactions studied. In a preliminary series of experiments some 4.7 wt.% Pt/Al₂O₃ (Pt/Al) catalysts were synthesized to clarify the influence of some key parameters, such as the types of precursors, the metal concentrations in the precursor solution, the liquid feed rate, and the dispersion gas feed rate on the Pt particle size distribution. Using aluminum acetate as precursor generally resulted in higher BET surface area of the support, as did higher dispersion gas rate and lower liquid feed rate consistent with the current understanding of FSP synthesis of materials [4,7]. But at the same time the Pt particle size distribution became rather broad, which may obscure the interpretation of acid/base effects. The best results in terms of narrow Pt particle size distribution and sufficiently high support surface area were achieved at 5 mL min⁻¹ of liquid precursor feed rate and 5 L min⁻¹ of O₂ dispersion gas. Chemical and textural properties as well as the designations used for the different catalysts are given in Table 6.1. The catalysts are designated as Pt/Al-
xSi and Pt/Al-xCs, where x is the content in wt.% of SiO$_2$ and Cs$_2$O, respectively. Catalyst characterization

Table 6.1 Chemical and textural properties of 4.7 wt% Pt/Al$_2$O$_3$-SiO$_2$ and 4.7 wt% Pt/Al$_2$O$_3$-Cs$_2$O catalysts (composition, BET surface area, stoichiometry factor of CO chemisorption, and Pt dispersion).

<table>
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<th>Catalyst$^a)$</th>
<th>SiO$_2$ content wt.%</th>
<th>Cs$_2$O content wt.%</th>
<th>Al$_2$O$_3$ content wt.%</th>
<th>Stoichiometry factor$^b)$</th>
<th>Pt dispersion %</th>
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</table>

$^a)$ Catalysts are designated as Pt/Al-xSi and Pt/Al-xCs, where x is the content in wt.% of SiO$_2$ and Cs$_2$O, respectively.

$^b)$ Determined by DRIFT measurement of CO adsorption and used for the calculation of Pt dispersion.

Nitrogen adsorption

The one-step flame synthesis of SiO$_2$-and Cs$_2$O-doped Pt/Al$_2$O$_3$ resulted in nanosized catalyst particles with specific BET surface areas in the range 126 - 233 m$^2$g$^{-1}$ for the SiO$_2$- and up to 257 m$^2$g$^{-1}$ for the Cs$_2$O-doped samples.

In Fig. 6.1a the surface area is shown as function of the SiO$_2$ content. The minor variation of the surface area ($\pm 4$ m$^2$g$^{-1}$) from four different charges of the
same sample composition (Pt/Al-5Si and Pt/Al-30Si) underscores the good reproducibility of the synthesis method. The surface area of undoped 4.7 wt.% Pt/Al₂O₃ (PtAl) was 138 m²g⁻¹, higher than that reported (112 m²g⁻¹) when higher combustion enthalpies were used [7]. There is a positive correlation between the surface area and the SiO₂ content, except the initial region till 10 wt.%. A similar trend was observed for flame-made SiO₂-doped ceria/zirconia [29], which was attributed to incorporation of SiO₂ into the existing crystalline framework. Analogously, we expect that SiO₂ enters into the alumina framework here.

A general trend of increasing surface area with increasing SiO₂ content was observed already in flame-made Ta₂O₅/SiO₂ mixed oxides [30]. Note that in the range of generally used noble metal loadings, the Pt content does not significantly influence the surface area of flame-made Pt/Al₂O₃ catalysts [7].

In case of the Cs₂O-doped samples the opposite trend is seen in Fig. 6.1b: the surface areas increased rapidly to a maximum of 257 m²g⁻¹ at only 3 wt.% Cs₂O before the slow decrease at higher dopant content. Addition of Cs₂O to the precursor solution has a direct influence on the particle formation in the flame. Ionic additives, especially alkali metals, are known to affect aerosol coagulation already at very low concentrations [31] by enhancing the particle charge and therefore reducing the particle coagulation rate and product
particle size, in this case the alumina. Additionally, the melting point of Cs$_2$O of 490 °C is lower than that of alumina (2050 °C) and it is therefore expected that Cs enriches on the Al$_2$O$_3$ surface rather than forming solid solutions or taking interstitial positions in the alumina crystal lattice. This is similar to V$_2$O$_5$ depositing predominantly on the surface of TiO$_2$ made in flames [26, 32]. This may drastically alter the sintering rate of particles and their final specific surface area. A similar behavior was reported for flame-made Ta$_2$O$_5$/SiO$_2$ mixed oxides at low Ta$_2$O$_5$ loadings [30].

![Nebulized nitrogen adsorption-desorption isotherms of the Pt/Al, Pt/Al-30Si and Pt/Si samples](image)

Fig. 6.2 Nitrogen adsorption-desorption isotherms of the Pt/Al, Pt/Al-30Si and Pt/Si catalysts.

Nitrogen adsorption-desorption isotherms of the Pt/Al, Pt/Al-30Si, and Pt/Si samples are depicted in Fig. 6.2 as representative examples. They reveal the typical hysteresis characteristics of non porous flame-made materials [7, 33], independent of the oxide composition and catalyst particle size. The
reference catalyst E4759 exhibits small mesopores with an average pore size around 8 nm [7].

Electron microscopy

Typical STEM and TEM images of the catalysts are shown in Fig. 6.3. The 4.7 wt.% Pt/Al₂O₃ (Pt/Al, Fig. 6.3a) contained Pt particles (bright spots, verified by EDX, not shown) with a rather broad size distribution in the range 1 - 10 nm, with the majority of the Pt particles being below 3 nm. HRTEM analysis (Fig. 6.3b) revealed more or less spherical Pt particles. By increasing the SiO₂ content to 30 wt.% the fraction of very small Pt particles vanished and the average Pt particle size increased (Fig. 6.3c). The particle shape, however, did not change noticeably (Fig. 6.3d). The Al₂O₃ particles are rather spherical with a diameter of 10 to 20 nm judging from the TEM analysis (Fig. 6.3e). TEM images of Pt/Al-30Si in Fig. 6.3e show amorphous (inset Fig. 6.3e) spherical particles without any distinct silica segregation or shell-like coating, as observed in FSP-made Si-doped ceria/zirconia [29], indicating a rather good mixing of alumina and silica in the particles. The Pt particle size distribution in the Pt/Al-30Si catalyst is shown in Fig. 6.3f as an example. The majority of the particles are in the range 3-6 nm and the contribution of the extreme fractions of 1 nm or 10-11 nm particles is only about 0.5-1.3 %. The biggest Pt particle sizes, up to 50 nm, were observed in Pt/Si and in the absence of alumina the support possessed an extended structure of irregular shape instead of the spherical particles seen in Fig. 6.3. In addition, analysis of the high silica-content samples (not shown) uncovered that the increasing fraction of the big Pt particles is seemingly not well stabilized by the relatively small particles of the support. Furthermore, such large Pt particles may arise by droplet-to-particle-conversion (e.g. Pt precipitation in the solution droplets [26]) or by simultaneous formation Pt and support particles during FSP.

The microscopic characterization of Cs₂O-doped catalysts is illustrated by the STEM images of Pt/Al-3Cs (Fig. 6.4a) and Pt/Al-10Cs (Fig. 6.4b). The Pt particle size distributions are comparable to that of non doped 4.7 wt.% Pt/Al₂O₃ (Pt/Al, Fig. 6.3a).
Fig. 6.3 STEM and HRTEM images of the Pt/Al (a, b) and the Pt/Al-30Si (c, d) catalysts, and a typical TEM image of the Pt/Al-30Si (e) sample. All catalysts have been pre-reduced in hydrogen at 400°C. (f) shows the Pt particle size distribution of $N_{\text{total}}$ measured particles with the geometric standard deviation ($\sigma_{g,V}$) and average surface diameter ($d_s$) obtained from STEM micrographs of Pt/Al-30Si.
The majority of the Pt particles were below 3 nm, independent of the Cs$_2$O content, and only very few Pt particles bigger than 10 nm could be detected. In order to gain spatial resolution of the Cs distribution, areas 1, 2 and 3 in the Pt/Al-10Cs catalyst were analyzed by EDXS (Fig. 6.4c). Due to the relative low concentration of Cs in the sample, it was difficult to detect any Cs in the samples. However, areas 2 and 3 that contain no Pt particles showed clearly the presence of Cs, whereas in the smaller Pt-containing area 1 no Cs could be detected. This is an indication that there is no preferential location of Cs$_2$O around the Pt particles.

![Fig. 6.4 STEM images of the Pt/Al-3Cs (a) and Pt/Al-10Cs (b) catalyst. All catalysts have been pre-reduced in hydrogen at 400°C. (c) shows three regions of Pt/Al-10Cs examined with EDXS for clarifying the spatial distribution of Cs in the sample.](image)

**X-ray diffraction**

The XRD patterns of the Pt/Al-Si series are collected in Fig. 6.5a. For Pt/Al the typical $\gamma$-alumina diffraction pattern was observed [7], which does not significantly differ from the diffraction pattern of flame-made Al$_2$O$_3$ (Fig. 6.5b). Only the reflection around $2\Theta = 39.0^\circ$ shows higher intensity, which is due to the presence of Pt crystals. Doping with silica resulted in a decrease of the overall crystallinity indicated by the vanishing of the alumina reflections at $2\Theta = 19.3$, 31.6, 61.0, and 66.7$^\circ$. This structural change is in good agreement with the electron microscopic results (vide supra).

The change in the degree of crystallinity has already been reported for flame-made Si-doped ZnO [34] or Ta$_2$O$_5$/SiO$_2$ [28]. Starting at 15 wt.% SiO$_2$ a shift of the main diffraction peaks can be seen. This is due to the vanishing of the alumina reflections and appearing the diffraction peaks of metallic Pt.
Additionally, the typical hump for amorphous flame-made silica in the region of 15 to 35° becomes apparent. The closeness of the melting temperatures of SiO₂ (1710 °C) and Al₂O₃ (2050 °C) favors their simultaneous nucleation and high degree of atomic mixing in the flame leading to a good homogeneity in the mixed oxides [8]. The proximity of the alumina (022) and (004) reflections (2Θ = 39.2 and 46.05 °) to those of Pt (111) and (002) (2Θ = 39.7 and 46.2 °), respectively, hinders determination of the Pt crystallite size up to 15 wt.% SiO₂ content. In the range 22.5 - 50 wt.% SiO₂ the average Pt crystallite size was ≈ 9 ± 1 nm and increased rapidly above this SiO₂ content (Fig. 6.6).

![X-ray diffraction patterns of some Pt/Al-Si (a) and Pt/Al-Cs (b) catalysts.](image)

Cs₂O-doping had no significant influence on the crystallinity of alumina in the whole range investigated (Fig. 6.5b), despite its big influence on the BET surface area (Fig. 6.1b). No additional reflection indicative of a spinel phase is seen. The line broadening with increasing Cs₂O content is due to the smaller crystallite size and it is indicative of the probable effect of Cs₂O on particle coalescence. Although the intense reflections at 2Θ = 39.7 corroborate the presence of some Pt crystals bigger than 3 nm, determination of the average Pt crystal size was not possible due to the overlapping reflections of alumina and Pt.
CO chemisorption

The Pt dispersion and particle size were determined by CO chemisorption. As illustrated in Table 6.1, there is a clear trend of decreasing dispersion with increasing Si content. The dispersion of Pt/Al is remarkably higher (60 %) than that of other flame-made Pt/alumina catalysts reported before (32% dispersion at best [7]), which difference is mainly attributed to the different precursor, solvent, and stoichiometry factor used in this study.

![Graph showing the variation of Pt particle size with SiO₂ content](image)

Fig. 6.6 Average Pt particle size (○) determined by CO chemisorption and Pt crystallite size (♦) determined by XRD for the Pt/Al₂O₃-SiO₂ catalysts.

The average Pt particle size derived from the Pt dispersion for the Si-doped catalysts is shown in Fig. 6.6. The average Pt particle size of about 4.5 nm for the Pt/Al-30Si catalyst is only slightly bigger than the mean Pt size calculated from the STEM analysis (dₜ, Fig. 6.3f). The bigger the size of Pt particles, the smaller is the deviation between the average particle size determined by CO chemisorption and the crystallite size obtained from the
XRD analysis (Fig. 6.6). The positive correlation between the Pt particle size and the Si content corroborates the results of the STEM analysis shown in Fig. 6.3. Note that contrary to the present study of Pt/Al₂O₃-SiO₂ catalysts, a change in the BET surface area of flame-made particles usually does not lead to a significant change of the metal dispersion for Pt/Al₂O₃ [7].

Fig. 6.7 Variation of the average Pt particle size in the Pt/Al₂O₃-Cs₂O catalysts determined by CO chemisorption.

In the series of base-promoted catalysts, increasing the Cs₂O content resulted in higher BET surface areas (Fig. 6.1) but the Pt dispersion (Table 6.1) and the average Pt particle size (Fig. 6.7) remained in a relatively narrow range. Hence, in contrast to Si-doping, independent control of the support composition and Pt particle size was possible by Cs₂O-doping in the composition range investigated.
Temperature programmed desorption (TPD)

The acid/base properties of the catalysts were investigated by temperature programmed desorption (TPD) of NH$_3$ and CO$_2$ for the SiO$_2$- and Cs$_2$O-doped samples, respectively. The NH$_3$ desorption patterns for the SiO$_2$-doped catalysts are shown in Fig. 6.8. Pure Al$_2$O$_3$, Pt/Al, and the reference Pt/Al$_2$O$_3$ catalyst E4759 had similar acidity with desorption peaks between 90 and 350 °C and the maxima at 139 - 143 °C (Fig. 6.8b). The acidity changed considerably by doping with SiO$_2$ as the peak maxima and the tails of the desorption peaks (> 400 °C) were shifted to higher temperatures. The strongest acidity was measured at 22.5 - 30 wt.% SiO$_2$; above this range the acidity decreased again. The peak maximum at 140 °C for the Pt/Si sample with a narrow desorption peak in the range of 90 to 190 °C is comparable to that of flame-made SiO$_2$ [28].

![Fig. 6.8 TPD patterns of NH$_3$ (a) and the corresponding maximum desorption peak temperatures (b) for the Pt/Al$_2$O$_3$-SiO$_2$ catalysts.](image)

Note that the maximum acidity of SiO$_2$-Al$_2$O$_3$ mixed oxides prepared by wet-chemical methods is usually located in the silica-rich region at around 75 - 85 wt.% SiO$_2$ [13, 35-36]. The maximum in the alumina-rich range seems to be
a unique property of the flame-made catalysts. Extensive characterization of (amorphous) silica-alumina with various spectroscopic methods in the past years has revealed two types of Al coordination: tetrahedral (AlO$_4$) and octahedral (AlO$_6$) [37]. The ratio of the two species is a function of the Al content and the pretreatment temperature [38]. It was proposed that the acidic surface silanol groups are closely located to tetrahedral Al sites [39].

A comparison of Fig. 6.6 and Fig. 6.8 shows that the shift in the support acidity cannot explain the enhancement of Pt particle size with the SiO$_2$ content. Most probably, this effect is related to the surface properties of the silica rich (amorphous) support, which cannot sufficiently stabilize the Pt particles against growing in the flame.

![Graph showing influence of Cs$_2$O doping of Pt/Al$_2$O$_3$ (Pt/Al) on the position of the maximum temperature of the CO$_2$ desorption peak.](image)

*Fig. 6.9 Influence of Cs$_2$O doping of Pt/Al$_2$O$_3$ (Pt/Al) on the position of the maximum temperature of the CO$_2$ desorption peak.*
Results and discussion

The TPD peak maxima of CO₂ from the Cs₂O-doped catalysts are shown in Fig. 6.9. The values for Pt/Al and pure alumina are in the range reported for alumina prepared by wet-chemical methods [12]. With increasing Cs₂O content the maximum desorption temperature increased up to 127 °C at 10 wt.% Cs₂O content in the support, that confirms the enhanced basicity of these samples and is consistent with the literature [13]. Additionally, a longer desorption tail at higher temperatures (not shown) was observed.

The fact that small amounts of Cs₂O (<0.5 mol.%) enhance the CO₂ desorption temperature, and also the BET surface area (Fig. 6.1), corroborates our interpretation that Cs₂O is located mostly on the particle surface and thereby strongly influences the acid/base properties of the catalyst. Note again that the enhanced basicity has barely any influence on Pt particle size during catalyst synthesis (Fig. 6.7).

Scheme 1 Reaction pathway of the hydrogenation of acetophenone (APh) on Pt, based on the products detected by GC analysis.

6.3.2 Catalytic hydrogenation

The TPD of NH₃ and CO₂ confirmed the expectation that doping of Pt/Al₂O₃ with SiO₂ or Cs₂O increases the acidity and basicity of the catalysts, respectively. The shifts in the desorption peaks are, however, related to the characteristics of the two-component supports rather than to those of the Pt
particles. Additionally, we used the chemoselective hydrogenation of acetophenone (APh) as a test reaction to prove that the change in the support acidity-basicity controls the characteristics of the Pt-H system in hydrogenation and hydrogenolysis reactions [14].

Although acetophenone is the simplest aromatic ketone, the reaction pathway shown in Scheme 1 contains five products formed by the transformation of the two functional groups [25, 40-42]. The primary products are 1-phenylethanol (PhE) by hydrogenation of the C=O bond and cyclohexyl methyl ketone (CMK) by saturation of the aromatic ring.

![Fig. 6.10 Reaction time necessary to achieve 50% conversion of acetophenone using Pt/Al-Si (a) and Pt/Al-Cs (b) catalysts. The reference Pt/Al₂O₃ catalyst E4759 is marked by a filled square.](image)

At ambient temperature the carbonyl reduction is significantly faster on Pt and PhE is the main product. (Note that the one-step hydrogenolysis of APh to ethylbenzene (EB) and the routes via styrene and an enol intermediate are usually not considered as a significant route on Pt under mild conditions.) At higher conversion of APh, both intermediates PhE and CMK are further hydrogenated to the saturated alcohol 1-cyclohexylethanol (CE). In addition, hydrogenolysis of PhE and CMK gives EB and ethylcyclohexane (EC), respectively. There is a considerable difference in the reactivity of the aromatic and aliphatic alcohols towards hydrogenolysis: PhE is transformed to EB, but the saturated hydrocarbon EC is formed directly from the ketone CMK and
not from the saturated alcohol CE [24]. An additional route to EC is the saturation of the aromatic ring of EB.

Hydrogenation of acetophenone was studied over the whole series of Pt/SiO$_2$-Al$_2$O$_3$ catalysts except the Pt/SiO$_2$ (Pt/Si) sample that showed too low activity under the conditions applied (3 bar, 20°C). The selectivities were determined at 50% conversion of acetophenone to obtain comparable results.

The time to achieve 50% conversion increased monotonously with the Si content (Fig. 6.10a). The TOF related to the number of surface Pt atoms was 0.15 s$^{-1}$ on Pt/Al and 0.13 - 0.22 s$^{-1}$ on the Si-doped catalysts. The short reaction times, and the higher TOFs compared to the reference catalyst E4759 (0.10 s$^{-1}$), confirm that highly active multi-component catalysts could be prepared by the single step flame spray synthesis.

The selectivity towards 1-phenylethanol at 50% conversion of acetophenone varied in the narrow range 76 - 82% for all catalysts. The selectivities to C-O bond hydrogenolysis products (the sum of EB and EC) and phenyl ring hydrogenation products (the sum of CMK, CE, and EC) are illustrated in Fig. 6.11. Increasing the SiO$_2$ content up to 30 wt.% enhanced

![Fig. 6.11 Influence of Si-doping on the hydrogenation of APh: (a) Selectivity to CO bond hydrogenolysis to produce EB + EC, and (b) Selectivity to phenyl ring hydrogenation to give CE + EC + CMK (see reaction pathway in Scheme 1). Data refer to 50% conversion of APh; filled symbols represent the performance of the reference Pt/Al$_2$O$_3$ catalyst E4759.](image-url)
the (very low) selectivity of Pt/Al (0.15%) to hydrogenolysis products by more than 20-fold; further addition of SiO₂ had only minor effect (Fig. 6.11a).

The selectivity to phenyl ring hydrogenation also increased by Si-doping but only at low SiO₂ content (5 - 22.5 wt.%, Fig. 6.11b).

The effect of Cs₂O-doping on the acetophenone hydrogenation activity and selectivity of Pt/Al₂O₃ is the opposite to that of Si-doping. The activity increased already at low Cs₂O content (Fig. 6.10b). Addition of Cs₂O diminished the selectivity to hydrogenation of the aromatic ring (S_{CE+EC+CMK}) and improved the selectivity to the main product 1-phenylethanol up to 97 mol.% at 50% conversion of APh (Fig. 6.12).

![Graph showing selectivity to 1-phenylethanol and sum of cyclohexyl methyl ketone, 1-cyclohexylethanol, and ethylcyclohexane.](Fig. 6.12 Hydrogenation of acetophenone on Pt/Al-Cs catalysts: the selectivity to 1-phenylethanol (carbonyl hydrogenation, ●), and to the sum of cyclohexyl methyl ketone, 1-cyclohexylethanol, and ethylcyclohexane (phenyl ring hydrogenation, □). The selectivities are determined at 50% conversion.)

It is known that a basic support or introduction of a basic additive diminishes the rate of aromatic hydrogenation [18] and increases the selectivity of acetophenone hydrogenation toward 1-phenylethanol over
supported Pd and Pt catalyst [25, 43-47]. The effect of Cs₂O on the hydrogenolysis of the CO bond was even stronger: only 0.25 wt.% Cs₂O hindered the hydrogenolysis of 1-phenylethanol to ethylbenzene. The catalytic results are in good agreement with the enhancement of the basicity of Pt/Al-Cs catalysts already at low Cs₂O content (Fig. 6.9).

Recycling experiments have been carried out to get further information on the location of Cs₂O in the catalyst. The Pt/Al-0.25Cs and Pt/Al-5Cs catalysts were filtered off after the first use, washed with 50 ml n-hexane solvent, stored under vacuum over night at 30°C, and then reused without any further treatment. In the second hydrogenation of acetophenone the selectivities to 1-phenylethanol decreased from 83.9% to 82.0% and from 91.1% to 89.3%, respectively. According to Fig. 6.12, the probable explanation is that small amounts of Cs₂O were dissolved by the product 1-phenylethanol, resulting in lower selectivities to 1-phenylethanol in the second use. These experiments corroborate our interpretation that Cs₂O is (mainly) located on the outer surface of the catalyst particles.

6.4 Conclusions

Flame spray pyrolysis was applied to prepare in a single step two series of SiO₂- and Cs₂O-doped Pt/Al₂O₃ catalysts with excellent reproducibility. Silicon seemed to be incorporated into the bulk of alumina in the non-porous matrix, reducing the alumina crystallinity till the Si-rich samples became amorphous. Cesium was located at or close to the surface and exerted a strong influence on the catalyst properties already at low Cs₂O-contents.

For Si-doped Pt/Al₂O₃ independent control of catalyst composition and Pt particle size was not possible. The synthesis conditions optimized for this series seem to be good in the alumina-rich region, while at higher SiO₂ content (> 50 wt.%) the support cannot limit the growth of Pt particles in the flame. Variation of the SiO₂ content in the support in the whole concentration range revealed a maximum in acidity at 22.5 - 30 wt.%, as determined by temperature programmed desorption of ammonia.

Very low contents of Cs₂O (<0.5 wt.%) resulted in a remarkable increase of the catalyst surface area while the average Pt particle size could be kept
constant at around 2 nm. The basicity of the catalysts increased rapidly with Cs$_2$O-doping, as confirmed by the temperature programmed desorption of carbon dioxide.

The catalysts were highly active in the hydrogenation of acetophenone at near to ambient conditions; their activity was comparable or higher than that of the reference Pt/Al$_2$O$_3$ (E4759), which is commonly used in the hydrogenation of various ketones. A correlation between the support acidity/basicity and the electronic properties of Pt, or more precisely the characteristics of the Pt-H system, was found in the chemoselective hydrogenation of acetophenone. By changing the amount of dopants it was possible to tune systematically the selectivity toward carbonyl group or phenyl ring hydrogenation, or toward hydrogenolysis of the C-O bond.

The results confirm that flame spray pyrolysis is a highly suitable method for synthesis of tailor-made, multi-component hydrogenation catalysts and the reproducibility of the catalyst synthesis route is excellent.

6.5 References


CHAPTER 7

Outlook and Research Recommendations

In this work it was shown that flame spray pyrolysis (FSP) is a powerful tool for the synthesis of mixed metal-oxide catalysts. Vanadia based metal-oxide supported catalysts made by FSP showed unique characteristics not achievable with classic wet-chemistry methods and the synthesis method allows precise control of the catalysts morphology. Properties like specific surface, crystallinity, V dispersion, VO_x species structure could be tailored by the synthesis parameters such as choice of metal precursor, solvent, dispersion gas pressure drop, liquid and gas feed rate. It was shown that the V dispersion and therefore the transition from amorphous to crystalline VO_x not only depend on vanadia loading and available SSA but also on the synthesis method (flame-synthesis vs. classic wet-chemistry) and therefore the term "monolayer catalyst" should be reconsidered and maybe not used anymore. Clearly the transition from amorphous VO_x species to crystalline V_2O_5 is not limited anymore solely by loading or surface area but rather limited by the synthesis method. Future discussions for supported vanadia-based catalysts should focus on only the vanadium surface density (in V nm^2) as parameter to
compare and classify different catalysts as this value is independent of the supporting material and synthesis method. Additionally it has been shown in this study that the structure of the VO\textsubscript{x} species plays an important role in the catalytic performance, too. And not every catalytic application needs a high V dispersion with dominantly monomeric VO\textsubscript{x} species.

Although vanadia-based catalysts are industrially applied for several decades now and extensive research has been carried out, key parameters and properties of the active species leading to high activity and selectivity are under debate. In this work it was shown that due to the controllable structure of the VO\textsubscript{x} species in FSP-made V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts more information about the active sites resulting in high activity and selectivity can be obtained and that those species are different for different kinds of catalytic reactions. While monomeric VO\textsubscript{x} species showed high selectivity in the oxidative dehydrogenation of propane, selectivity to phthalic anhydride in the partial oxidation of o-xylene was favored by amorphous oligomeric VO\textsubscript{x} species and the activity in the total oxidation of volatile organic compounds seems to be favored by high V surface density catalysts exhibiting dominantly oligomeric species or even small V\textsubscript{2}O\textsubscript{5} crystallites. Therefore the synthesis and use of FSP-made model catalysts for the determination and evaluation of certain material compositions could provide additional fundamental understanding of the role of the active site as well as the structural properties in the corresponding catalytic application.

In here classic supporting oxides like TiO\textsubscript{2} and SiO\textsubscript{2} were investigated. The composition of the supporting oxide, however, can have substantial influence on the V dispersion, corresponding VO\textsubscript{x} structure and therefore finally on the catalytic behavior of such catalysts. Studying for example zirconia, ceria, and magnesia supported vanadium catalysts could advance the fundamental knowledge about the interaction of active site with the support and the influence of the support properties on the catalytic performance. FSP is based on a liquid precursor giving access to almost the whole periodic table for possible metal precursors and therefore the addition of a ternary or quaternary metal oxide as dopant to tailor the active site or support properties is easily and with high reproducibility possible [1, 2]. It is well know that
doping the catalysts with additional alkaline earth metals like Cs or K can influence the catalytic performance substantially [3, 4]. Future research should focus on the preparation of such doped mixed metal-oxide catalysts and the influence of these dopants on the structure of the active site, surface properties, overall particle morphology and of course the catalytic performance.

With respect to supported noble metal catalysts FSP allows not only control of the dispersion of the metal particles but also tailoring the support properties like surface ionicity. It was shown that the acid/base surface properties of flame-made supports can significantly differ from classic wet-chemistry derived materials at similar composition. not every time successful compositions from classic wet-chemistry can be transferred to flame-made materials one to one. The tuning of this property had pronounced influence on the final catalytic performance of such doped Pt/Al₂O₃ catalysts [5]. Future research should focus on tuning the support properties with different or additional dopants some already used so far in classic wet-made materials but not confined to those. Exploring different compositions or combinations via flame synthesis could advance current understanding and create additional knowledge on specific support systems and their influence on the active site and therefore on the catalytic behavior. Additionally the research should focus on exploring different noble metals (e.g. Ru, Rh and Ir) besides platinum or palladium as possible new active catalysts.

It has been shown that flame-derived materials can have significant differences in the surface properties that materials made by classic wet-chemistry methods. Already addition of trace amounts of certain metal can alter the surface properties and particle morphology substantially. These unique properties of FSP-made mixed-metal oxides need to be explored in more detail. Additionally the use of such flame-made materials as support for classic catalyst synthesis by e.g. wet-impregnation could result in completely different characteristics in both structure of the active site and catalytic behavior compared to classic supports made by wet methods (e.g. sol-gel).

Replacing often expensive homogeneous single-use catalysts, often containing alkaline earth, alkali, transition or noble metal complexes, with recyclable heterogeneous catalysts becomes more and more of greater interest.
The gained knowledge about the synthesis of vanadia based catalysts can now be transferred to similar supported catalyst systems based for example on tungsten-, molybdenum- or manganese-oxide catalysts for different catalytic applications in bulk (e.g. exhaust gas treatment, selective oxidations, dehydrogenation, etc.) and fine (e.g. alkene metathesis, enantioselective hydrogenation etc.) chemistry processes alike.

Catalysis for a sustainable world seems to be a worthwhile goal for the future. In order to achieve this goal the development of new catalysts with tailor-made properties requires the basic understanding of the influence of the different structures of active species and support compositions in certain catalytic applications. This knowledge will make it possible to synthesize such new materials which finally can compete in the market and possibly rationalize new reactor and feedstock concepts. Flame synthesis and especially flame spray pyrolysis has been proven to advance this knowledge by providing easy accessible model catalysts of high purity and reproducibility. Additionally this synthesis method is easy scalable and allows material production not only in the lab scale but also in pilot or industrial scale, important for future application of such flame-derived catalysts in industry.

References

The flame spray pyrolysis (FSP) reactor

The herein used FSP reactor was developed and build at the Particle Technology Laboratory at ETH Zürich in 2002 and reported frist by Mädler et al [1]. Since then only minor modifications (i.e circular flamelet, sheath gas outlet) have been done and numerous studies on different kind of material compositions have been carried out, most of them summarized in this thesis and the following reviews by Strobel et al. [2-3]. Teoh et al just recently reviewed flame spray pyrolysis in general [4]. Additional to the group at ETH Chiarello et al. in Italy have studied the influence of different flame parameters [5] and solvent composition [6-7] on the particle characteristics.

The different steps in particle formation during flame spray pyrolysis (i.e. precursor dispersion, combustion, nucleation, coagulation, sintering and agglomeration) as depicted in Fig. A.1 and how these can be influenced has been discussed in more detail in chapter 1 (see also Fig. 1.3).
In a typical experiment the precursor solution was fed in the FSP reactor (Fig. A.1) being a concentric two-phase nozzle with a capillary (inner diameter of 0.42 mm) through which the liquid precursor was fed by a syringe pump (Inotec, IER-560). Through the 1st annulus (inner/outer diameter: 0.71/0.95 mm) dispersion gas (O₂, Pan Gas, 99.95 %) was fed with a pressure drop of 1.5 to 1.7 bar. The resulting spray was ignited and sustained by a circular premixed flame (inner diameter 6 mm, slit width 10 µm) of CH₄ (1.5 L min⁻¹, Pan Gas 99.5 %) and O₂ (3.2 L min⁻¹). The liquid and dispersion gas feed rate were adjusted accordingly. Additionally a sheath gas flow of 5 L min⁻¹ O₂ was applied through a metal ring (11 mm i.d., 18 mm o.d.) with 32 holes (0.8 mm i.d.) to ensure complete combustion of the precursor. The powders were
collected with the aid of a vacuum pump (Busch SV 1050 B) on a glass microfiber filter (Whatman GF/D, 257 mm in diameter).

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Curriculum Vitae

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List of Publications

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