Doctoral Thesis

Aerosol flame synthesis of supported metal particles and their catalytic applications

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AEROSOL FLAME SYNTHESIS OF SUPPORTED METAL PARTICLES AND THEIR CATALYTIC APPLICATIONS

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

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presented by

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Acknowledgements

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Summary

Flame synthesis of nanoparticles is a promising technology for the preparation of catalytic materials. In the introduction the progress in this field during the last two decades has been reviewed demonstrating the high potential of flame methods for synthesis of catalysts.

In this thesis, synthesis of catalytically active nanoparticles by flame spray pyrolysis (FSP) was explored. Emphasis was placed on various supported noble metal catalysts and their application in different catalytic processes. The focus of the research was on nanoparticle synthesis, characterization of the materials properties and evaluation of their behavior in catalytic applications.

In a first part, palladium supported on alumina was prepared by single step flame spray pyrolysis (FSP) and tested for the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone, an important intermediate for pharmaceuticals. The influence of flame process parameters on the structural properties and the catalytic performance was elucidated.
The catalysts were made up of small palladium particles (1 - 5 nm) attached to the surface of agglomerated, nonporous alumina particles (10 - 30 nm) and showed good catalytic performance in terms of activity as well as selectivity compared to reference catalysts prepared by conventional methods. Flame-made Pd/Al₂O₃ catalysts with different Pd particle size revealed a significant structure sensitivity of the reaction.

Furthermore, Pd-based flame-made materials were evaluated towards their thermal stability in the catalytic combustion of methane. The influence of lanthanum on the stability of the alumina support was investigated. The addition of La resulted in materials with excellent thermal stability as judged from the loss in specific surface area and the transformation of γ- into α-alumina. These catalysts were compared also to corresponding impregnated reference catalysts. Independent of preparation method, La content and specific surface area, both flame- and wet-made materials showed a similar deactivation behavior at high temperatures indicating a very low metal-support interaction after palladium sintering and restructuring. As the sintering of the palladium particles was the major influence for the deactivation, the Pd particles were stabilized by the addition of platinum. Flame-synthesis of bimetallic Pd-Pt/Al₂O₃ resulted in small alloyed Pd-Pt clusters (<5 nm) finely dispersed on the supporting alumina particles. The addition of very small amounts of platinum stabilized the Pd particles towards sintering and decreased catalyst deactivation during methane combustion at high temperatures.

In the last part a novel two-nozzle flame spray pyrolysis technique was developed for synthesis of Pt/Ba/Al₂O₃ catalysts that are used as NOₓ-
storage-reduction (NSR) materials for the abatement of NO\textsubscript{x} effluent from engines operating under lean conditions. The use of two separate nozzles, one for Al and one for Ba-Pt, allowed precise control of the structural properties of barium. The late mixing of the two flames forced mixing at the nanoscale rather than at the atomic scale between Al and Ba that resulted in higher amounts of individual, crystalline BaCO\textsubscript{3} particles. This metastable monoclinic BaCO\textsubscript{3} was also observed for pure flame-made BaCO\textsubscript{3}. In contrast to wet-chemical preparation methods of Ba-containing compounds on Al\textsubscript{2}O\textsubscript{3}, the flame-made BaCO\textsubscript{3} always decomposed at low temperatures up to Ba loadings of 30 wt\% compared to bulk BaCO\textsubscript{3}. These Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalysts were tested for their performance as NO\textsubscript{x}-storage-reduction materials. Compared to impregnated catalysts the absence of bulk-like BaCO\textsubscript{3} in the flame-made materials exhibited a faster NO\textsubscript{x} uptake and retained their NO\textsubscript{x} storage capacity also at higher Ba loadings.

The influence of support composition (Ce-Zr) on the thermal stability during NSR of Pt-Ba catalysts was investigated by further extending the two nozzle synthesis technique. These materials exhibited similar structural properties as Pt/Ba/Al\textsubscript{2}O\textsubscript{3} concerning mixing of support and BaCO\textsubscript{3} particles. The as prepared BaCO\textsubscript{3} decomposed at low temperatures and exhibited high NO\textsubscript{x} storage capacity. The formation of stable PtO\textsubscript{x} on Ce-rich supports reduced the activity of Pt for NO\textsubscript{x} reduction. After thermal deactivation of the catalysts through formation of inactive BaZrO\textsubscript{3} and BaCeO\textsubscript{3}, active BaCO\textsubscript{3} could be recovered in CO\textsubscript{2} containing atmosphere on Ce-rich supports.

Flame spray pyrolysis is a very suitable process for synthesis of various
supported noble metal catalysts. In general, flame-made catalysts are non-porous and of controlled crystallinity often possessing high thermal stability. Optimization of existing catalytic systems which are prepared by conventional techniques can only be one goal for flame aerosol techniques. As flame techniques can result in the formation of unique materials, it seems more promising to use them for development of novel catalytic materials which are not commonly used.
Zusammenfassung


In einem ersten Teil wurden Pd/Al$_2$O$_3$ Katalysatoren mittels einem einstufigen Flammen-Sprüh-Pyrolyse-Verfahren (FSP) hergestellt. Diese Materialien wurden getestet für die enatioselektive Hydrogenierung von 4-Methoxy-6-methyl-2-pyron. Untersucht wurde vor allem der Einfluss von verschiedenen Flammen-Parametern auf die strukturellen und den darausfolgenden katalytischen Eigenschaften. Die kleinen Palladium Partikel (1 - 5 nm) waren fein dispergiert auf der Oberfläche von agglomerierten, nicht-porösen Aluminuimoxid Partikeln (10 - 30 nm). Im Vergleich zu konventionell hergestellten Katalysatoren zeigten die Flam-
menmaterialen gute katalytische Eigenschaften bezüglich Aktivität und Selektivität. Durch die Flammensynthese von Pd/Al$_2$O$_3$ mit unterschiedlich grossen Palladium Partikeln konnte gezeigt werden, dass die katalytischen Leistung bei der untersuchten Reaktion stark von der Partikelgröße abhängt.


In einem letzten Teil wurde ein neuer sogenannter Zwei-Düsen Flam-
menschprüh-Prozess für die Herstellung von Pt/Ba/Al₂O₃ Katalysatoren entwickelt. Diese Materialen finden Verwendung als NOₓ-Speicher Katalysatoren, um die Abgase von Magermotoren zu reinigen. Die Verwendung von zwei separaten Düsen, eine für Al und eine für Ba, erlaubte eine präzise Kontrolle über das Mischverhalten von Barium und Aluminium. Ein späteres Durchmischen der beiden Flammen ergab einen höheren Gehalt an einzelnen, krystallinen BaCO₃ Partikeln. Dieses metastabile monokline BaCO₃ konnte auch in reiner Form mittels Flammensynthese hergestellt werden. Im Gegensatz zum Herstellungsverfahren in der Flüssigphase, zersetzte sich das in der Flamme hergestellte Bariumcarbonat auch bei hohen Ba-Gehalt ausschließlich bei tiefen Temperaturen. Diese Pt/Ba/Al₂O₃ Katalysatoren wurden als NOₓ-Speicher Materialien getestet. Im Vergleich zu imprägnierten Katalysatoren hatte das Fehlen von stabilem BaCO₃ in den Flammenpulvern sowohl eine schnellere Speicherung von NOₓ als auch eine höhere Speicherkapazität bei hohem Bariumgehalt zur Folge.

pazität und eine tiefe thermische Stabilität welche mit einer Zersetzung in BaCeO₃ oder BaZrO₃ einherging. Mit Cer im Trägermaterial und in CO₂-haltiger Athmosphäre konnte aktives BaCO₃ nach der thermische Zersetzung wieder zurückgebildet werden. Auf Ce-reichen Trägermaterialien bewirkte die hohe Stabilität von PtOₓ jedoch eine Deaktivierung des Platins bezüglich dessen NOₓ Reduktionsaktivität
Chapter 1

Introduction: Aerosol flame synthesis of catalysts

Abstract

A review of synthesis and performance of flame-made catalytic materials is presented. Emphasis is placed on flame technology for its dominance in aerosol manufacturing of materials of high purity with minimal liquid by-products. Flame aerosol processes are characterized in terms of the precursor state supplied to flame. During the last decade, a better understanding of aerosol and combustion synthesis of materials contributed essentially to one-step dry synthesis of catalysts that are prepared conventionally by multi-step wet-phase processes. This includes TiO₂-based photocatalysts, mixed oxides (e.g. V₂O₅/TiO₂, TiO₂/SiO₂, perovskites, etc.) as well as supported noble metals (e.g. Pt/TiO₂, Pd/Al₂O₃, Pt/CeO₂/ZrO₂, Pt/Ba/Al₂O₃). In general, highly

¹Part of this chapter will be published in Adv. Powder Technol. 2006
crystalline and nonporous nanoparticles are formed during flame synthesis resulting in materials with high thermal stability. Unique particle structures, only available through aerosol processes lead to improved performance in various catalytic applications.

1.1 Introduction

Heterogeneous catalysis occurs on the nanoscale by definition. The control and design of the nanostructure is crucial for catalytic materials with good performance [1]. This includes chemical and physical properties not only of the active site, where the reaction takes place, but also of the surrounding material, i.e. of the support for dispersed metal nanoparticles [2, 3]. Mechanical strength, thermal stability and porosity of the material are very important for catalytic applications. Flame synthesis of catalytically active nanoparticles can give access to novel structures and materials that are not available through conventional techniques [4, 5]. Today, mostly wet-phase techniques are used for the industrial manufacturing of catalysts: Incipient wetness impregnation, sol-gel, precipitation, grafting and solid-state reactions, just to name a few, are batch processes requiring several after-treatment steps, such as filtration, drying and calcination [1, 6, 7]. Figure 1.1 shows a schematic of wet and flame processes for synthesis of catalysts.

Flame technology is a scalable, continuous and well-established method for production of nanoparticles in large quantities. For decades it has been used for large scale manufacture of simple commodities, such as carbon black, pigmentary titania, waveguide preforms, fumed silica and
1.1 Introduction

Figure 1.1: Comparison of conventional wet-phase and flame methods for synthesis of catalysts illustrated for Pt/Al$_2$O$_3$. Flame synthesis allows preparation of the catalyst in one step [8], whereas the conventional route by precipitation and impregnation is a multi-step process [1].

Alumina [9–11]. Production rates of these materials can be in the order of 25 t/h and the corresponding reactors resemble best the rockets of a departing space shuttle [11]. Already since the seventies flammemade materials have been used as catalyst supports (i.e. Al$_2$O$_3$, SiO$_2$, TiO$_2$) [1, 7, 12] and as photocatalysts (mainly TiO$_2$) [13]. In fact, the most often applied TiO$_2$ photocatalyst is manufactured by aerosol flame synthesis and marketed by Degussa as P25. A decade later, Ulrich pro-
posed to use flames for production of more complex catalytic materials [9]. However, it took more than another decade until the first works on flame-made materials and their catalytic properties have been published [14–17]. Since then, flame synthesis of catalytic materials has attracted many researchers resulting in a rapid progress towards more sophisticated catalysts. In general, flame-made materials are nonporous with high external surface area that went through high temperatures and cooling rates resulting in some unique phases and good thermal stability and mass transfer during catalysis [8, 18].

Here, recent progress in flame synthesis of solid catalysts is presented along with the unique structural and catalytic properties of these materials. Other gas-phase processes for catalyst manufacture such as chemical vapor deposition (CVD) [19], plasma processing [20] as well as spray pyrolysis [21, 22] which was applied for synthesis of perovskite [23, 24], spinel [25] and noble metal [26–29] catalysts are beyond the scope of this paper and have been summarized elsewhere.

1.2 Flame Processes for Catalyst Preparation

Various aerosol reactors and methods have been developed for synthesis of a wide variety of metal and metal oxide particles. Compared to wet-chemical routes with various post-treatment steps such as filtration, washing, drying and calcination, gas phase processes allow the preparation of the desired material without any further post-processing. In this
review processes for aerosol flame synthesis (AFS) are classified first depending on the precursor state fed to the flame in vapor-fed AFS (VAFS) and liquid-fed AFS (LAfS). In the latter, if the liquid precursor solution drives the flame process (contributes more than 50% of the energy) it is called flame spray pyrolysis (FSP). If a non-combustible solution is fed into the flame then LAfS is called flame-assisted spray pyrolysis (FASP).

**Figure 1.2:** *Schematic of selected flame configurations used for synthesis of heterogeneous catalysts. A: Vapor-fed aerosol flame synthesis (VAFS), B: Flame-assisted spray pyrolysis (FASP), C: Flame spray pyrolysis (FSP).*

### 1.2.1 Vapor-fed aerosol flame synthesis (VAFS)

This is the most common industrial flame process for synthesis of various ceramic commodities, such as fumed silica, waveguide preforms, alumina and pigmentary titania [9–11]. In this process volatile metal precursors
Chapter 1 Introduction: Flame-made catalysts

(e.g. chlorides) are evaporated and fed into a flame that either supports the process (e.g. H$_2$/O$_2$ flame in fumed silica manufacture) or ignites the process as in pigmentary TiO$_2$ production (Fig. 1.2a). The metal precursor is converted into the metal oxide and starts to form particles by nucleation from the gas phase (Fig. 1.3). This is a simple and scalable process as industrial practice shows along with recent studies [30, 31]. However, a drawback is the need of volatile precursors, which limits the application of VAFS to a few products, where volatile precursors are available for a reasonable price, such as for SiO$_2$, TiO$_2$, Al$_2$O$_3$, V$_2$O$_5$, SnO$_2$ etc. [10, 11]. In the field of heterogeneous catalysts VAFS has been used for synthesis of TiO$_2$/SiO$_2$ [32], V$_2$O$_5$/TiO$_2$ [17, 33], Pt/TiO$_2$ [34] or Cu/ZnO/Al$_2$O$_3$ [35] (Table 1).

1.2.2 Flame-assisted Spray Pyrolysis (FASP)

In FASP a non-combustible liquid precursor is dispersed into fine droplets that are evaporated and pyrolyzed by an external flame as was first developed for synthesis of ZnO [36] and superconducting materials [37]. Instead of an electrically heated tube as in conventional spray pyrolysis [21, 22], an external hydrogen or hydrocarbon flame is used as energy source during FASP (Fig. 1.2b) [38]. In general, aqueous solutions of metal salts (i.e. nitrates) are spray in the external flame where the solvent evaporates from the droplets and metal precursors are converted in products. Supplying the energy by an external vapor flame allows much higher process temperatures and cooling rates compared to electrically heated hot-wall reactors where temperatures are usually rela-
tively low (< 2000 °C) and residence times longer (up to a few seconds). Depending on process conditions hollow/micron- or nano-sized particles are formed when the precursor reacts in the droplet or gas-phase, respectively (Fig. 1.3) [21, 22, 38]. Beside photocatalytic materials [39], mainly perovskite and spinel structures [14, 40] have been made by FASP (cf. Table 1).

1.2.3 Flame Spray Pyrolysis (FSP)

In FSP the metal precursor is a combustible liquid that is sprayed and ignited resulting in product nanoparticles. Although this method was developed as early as in 1977 by Sokolowski et al. for synthesis of Al₂O₃ [41], it took nearly two decades until other researchers used it for synthesis of nanoparticles [42–45]. The organic precursor solution is dispersed either ultrasonically [41, 44] or by gas convection through a nozzle [42, 43] forming a fine spray which is ignited (Fig. 1.2). The metal-precursors evaporate in this spray flame and are combusted. Particles are then formed by nucleation from the gas phase (Fig. 1.3). The process features short residence times (a few milliseconds) and high maximum process temperatures (up to 3000 K) [46]. The main advantage of FSP over FASP is the formation of generally homogeneous, nanosized particles through control of the precursor-solvent composition [47]. FSP has been used for synthesis of many different solid catalysts, such as Pt/Al₂O₃ [8], Pt/CeZrO₂ [48], various perovskites [15, 49], etc. (Table 1).
Figure 1.3: Schematic of particle formation processes occurring during spray pyrolysis, flame spray pyrolysis and aerosol flame synthesis. Two basic particle formation processes can be observed: particle formation in a droplet leading to large or hollow particles (mainly FASP and partly in FSP) and particle formation from the gas phase giving small nanosized particles (VAFS, FSP and partly FASP). More detailed particle formation mechanisms can be found elsewhere [38, 50].
Figure 1.4: Schematic of the direct deposition technique as used to coat flame generated particles onto a mullite foam. The deposited layer was extremely porous. These ready-to-use catalysts were successfully tested in the synthesis of phthalic anhydride (adapted from [51]).
1.2.4 Direct deposition

Instead of collecting the as-prepared powder from the gas phase by filtration, electrostatic precipitation or in a cyclone, gas-phase preparation methods offer the possibility to directly deposit catalytically active materials on a substrate. Hunt et al. prepared thin films by combusting organic precursor solutions [45]. Direct flame deposition of the particles results in nanoporous films. For application in catalysis, substrates of various geometries have been used, such as flat plates [52] tubes [53] or foams [51]. Cooling of the substrate enhances particle deposition by thermophoresis as observed for directly deposited Pt/SnO$_2$ particles, which were applied as porous gas sensing films [54]. Choy and Seh [55] used FASP for synthesis of Ni/Al$_2$O$_3$ directly deposited on a flat substrate resulting in homogeneous, porous coatings. Larger particles and lower porosity was observed for higher substrate temperatures. Unfortunately no catalytic tests were reported. Figure 1.4 depicts V$_2$O$_5$/TiO$_2$ nanoparticles were deposited directly after FSP synthesis on a mullite foam resulting in highly-porous, patchy catalysts layers of controlled structure [51]. This ready-to-use catalyst was successfully tested for synthesis of phthalic anhydride from o-xylene exhibiting better performance than flame- or wet-made catalyst pellets. Thybo et al. [56] deposited FSP-made Au/TiO$_2$ directly on a microreactor. The use of shadow masks allowed catalyst deposition in well defined patterns with good adhesion on various substrates. These catalysts were tested for CO oxidation after deposition into a microreactor channel.
1.3 Catalysts

Heterogeneous catalysis relies on different materials. Hardly any element of the periodic table has not yet been used either in the function of active species, supporting material, promoter, stabilizer, or additive. Various catalytic materials have been prepared by flame aerosol processes, such as metal oxides, mixed metal oxides and supported noble metals.

1.3.1 Photocatalysts

Beside ceramic supports photocatalysts are so far the only catalytic materials which are industrially produced by flame processes. The standard TiO$_2$ photocatalyst is sold commercially by Degussa as P25 [11, 74]. TiO$_2$ is one of the most often applied semiconductor photocatalysts as its redox potential lies within the band-gap energy [74–76]. Environmental cleanup of organic and inorganic pollutants in air and wastewater is the main application of photocatalysts [74–77].

Already in 1971 Formenti et al. [13] prepared various metal oxides by hydrolysis/combustion of the corresponding metal chlorides by VAFS in a oxy/hydrogen flame. Compared to other metal oxides (ZrO$_2$, GeO$_2$ or SnO$_2$) titania particles showed by far the highest activity for photooxidation of isobutene into acetone. The flame-made TiO$_2$ was also much more active than corresponding aero- or xerogels [13]. The influence of conventional SP and FASP for synthesis of TiO$_2$ particles on their photocatalytic activity was investigated and unraveling that FASP-made TiO$_2$ resulted in the highest performance [39]. VAFS-made titania particles
Table 1.1: Overview of catalytic materials made in flames and related processes and their evaluated catalytic application.

<table>
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<tr>
<th>Material</th>
<th>Catalytic application</th>
<th>Reference</th>
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<td><strong>Aerosol Flame Synthesis (VAFS)</strong></td>
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<tr>
<td>TiO₂</td>
<td>Photocatalysis</td>
<td>[13, 57–59]</td>
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<tr>
<td>TiO₂</td>
<td>Photocatalysis</td>
<td>[39]</td>
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<td>ZnO</td>
<td>Photocatalysis</td>
<td>[60]</td>
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<td>[61]</td>
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<td>Methane combustion</td>
<td>[14]</td>
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<tr>
<td>LaBO₃ (B = Co, Mn, Fe)</td>
<td>Methane combustion</td>
<td>[62, 63]</td>
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<td>SrTiO₃</td>
<td>Methane combustion</td>
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<td><strong>Flame Spray Pyrolysis (FSP)</strong></td>
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<td>LaCoO₃</td>
<td>Methane combustion</td>
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were studied for photodestruction of phenol [57, 78] and salicylic acid [57] confirming the superior performance of flame-made TiO$_2$ particles. Compared to pure anatase powders, the presence of small amounts of rutile resulted in more active catalysts [79]. The influence of particle size on photocatalytic properties was elucidated for flame-made TiO$_2$ particles in the range of 6 to 50 nm [57, 58, 78]. Varying the residence time of the particles in the hot flame zone during preparation allowed a precise control of TiO$_2$ particle size and crystallinity. For very small particles (< 14 nm) quantum size effects resulted in an increased band-gap energy [58]. Concerning the photocatalytic oxidation of phenol in aerated suspensions an optimum particle size between 20 and 40 nm was found [57, 58], whereas in non-aerated suspensions smaller particles exhibited the best performance [78]. Also for the decomposition of methylene blue on TiO$_2$ films smaller particles (15 nm) were more active [59]. These effects were attributed to decreased quantum efficiencies for smaller particles and less available surface area for oxidation reactions on larger particles [58]. Other factors affecting the photocatalytic activity are charge transfer efficiency, OH· generation or Ti$^{3+}$ defect sites as observed for different flame-made TiO$_2$ particles [80].

Various dopants have been added to flame-made TiO$_2$ particles to enhance the photocatalytic activity or shift its photocatalytic response into the visible light regime. This can be achieved by surface doping (supported metals or substitution of Ti in the crystal lattice. Si [57, 78], Fe and Zn [81] by VAFS as well as Pt [70] or Fe [82] by FSP and Mo by FASP [61] have been used as dopants for flame-made TiO$_2$. Titania particles doped with Cr, Fe, V or Zn were prepared by VAFS result-
ing in powders with rather low surface area (ca. 20 m$^2$/g) [81]. The addition of Zn together with Fe resulted in the highest activity in the photocatalytic oxidation of 2-propanol, which was even higher than for P25. For Pt/TiO$_2$ and MoO$_3$/TiO$_2$ adding dopant nearly doubled the photocatalytic activity compared to that of Degussa P25. For FSP-made Pt/TiO$_2$, a Pt content of 0.5 at% was optimal for the mineralization of sucrose [70] whereas for MoO$_3$/TiO$_2$ a MoO$_3$ content of 2.5 at% showed the highest activity for the decomposition of dichlorobenzene [61]. The addition of iron strongly enhanced the photocatalytic activity under visible light for mineralization of oxalic acid [82].

Beside TiO$_2$, ZnO-based catalysts are often applied in photocatalysis since ZnO exhibits a similar band-gap as TiO$_2$. Jang et al. prepared ZnO particles by conventional spray pyrolysis (SP) and FASP of aqueous Zn(NO$_3$)$_2$ solutions [60]. Similar to TiO$_2$ [39] FASP-made ZnO particles exhibited higher photocatalytic activity that was attributed to their morphologies. Nanosized ZnO particles (ca. 20 nm) with similar photocatalytic behavior as P25 were formed by FASP, whereas larger particles (ca. 1 µm) with low activity were formed by SP [38]. Height et al. reported an increased photodegradation of methylene blue for larger ZnO particles (32 nm) [73], whereas Jang et al. observed the best performance for small particles (18 nm) [60]. The photocatalytic activity of ZnO nanoparticles could be further improved by adding Ag clusters on the ZnO surface during FSP-synthesis [73].
1.3.2 Vanadia-based catalysts

Vanadia coated titania for selective catalytic reduction (SCR) of NO with NH$_3$ exhibits a V$_2$O$_5$-surface layer structure on TiO$_2$ as prepared by VAFS in opposed [33] or co-flow [17] diffusion flames. As V$_2$O$_5$ is more volatile than TiO$_2$, the latter particles are formed first and vanadia condenses on them further downstream forming a surface layer [17, 83]. Different flame parameters altered the specific surface area (SSA) from 20 to 120 m$^2$/g [17]. Using a counterflow diffusion flame resulted in SSA between 40 and 50 m$^2$/g for V$_2$O$_5$/TiO$_2$ and 80-90 m$^2$/g for V$_2$O$_5$/Al$_2$O$_3$ [33]. Higher SSA as well as higher vanadia loading resulted in higher activities for the selective catalytic reduction of NO by NH$_3$ [17]. The process for synthesis of V$_2$O$_5$/TiO$_2$ was scalable up to a production rate of 200 g/h without any loss in catalytic activity [84]. V$_2$O$_5$/TiO$_2$-based SCR catalysts were also prepared by FSP [66]. The addition of tungsten oxide and especially silica increased dramatically the thermal stability of the material concerning loss of specific surface area and prevented the transformation of anatase into rutile. The addition of a few wt% SiO$_2$ to the V$_2$O$_5$/W$_2$O$_3$/TiO$_2$ catalysts improved the activity in the SCR of NO by NH$_3$.

V$_2$O$_5$/TiO$_2$ as-prepared by flame spray pyrolysis and directly deposited on mullite foams were tested for the oxidation of o-xylene into phthalic anhydride [51]. Well-dispersed vanadia species on the TiO$_2$ particles and the absence of crystalline V$_2$O$_5$ resulted in a very high activity of these catalysts. Smaller particles with higher accessible surface area further increased the catalytic activity.
Vanadium phosphorous oxide (VPO) catalysts were prepared by spray pyrolysis [85] and VAFS in opposed jet diffusion flames [86]. For both processes, the as-prepared material consisted mainly of VOPO$_4$·nH$_2$O which could be converted into water free, crystalline VPO structures upon heating. However, small VPO nanoparticles were formed by VAFS [86], whereas larger and hollow particles were observed for VPO made by spray pyrolysis [85]. The SP-made catalysts were tested for the oxidation of butane into maleic anhydride, revealing a strong influence of the reactor temperature during SP on the catalytic performance [85]. However, no catalytic results were reported for the VAFS-made catalysts [86].

1.3.3 TiO$_2$/SiO$_2$ epoxidation catalysts

These catalysts were made by VAFS of titanium tetraisopropoxide and hexamethyldisiloxane with SSA in the range of 50 - 300 m$^2$/g [32]. With up to 3 wt% TiO$_2$ the titania was atomically dispersed over the surface of the SiO$_2$ particles. The absence of Ti-hydroxides and the formation of individual, tetrahedral TiO$_2$ sites [87] improved the activity and selectivity of these catalysts for epoxidation of 2-cyclohexenol by tert-butylhydroperoxide. The materials properties could be conserved during VAFS scale-up from 6 up to 500 g/h [88]. Impurities in the form of transition metals as they commonly occur during wet chemical processes can result in a dramatic loss in catalytic performance. The selectivity of these TiO$_2$/SiO$_2$ epoxidation catalysts was lowered by very small amounts (<50 ppm) of Fe, Cr, Co or Mn [89]. This demonstrates the advantage of flame processes concerning the preparation of high pu-
rity materials. Especially the VAFS process gives access to very pure materials as nonvolatile impurities are separated during evaporation of the metal precursors. This has been fully exploited in manufacture of optical fiber preforms [11].

1.3.4 Ceria-based catalysts

The unique ability of ceria to store and release $\text{O}_2$ makes automotive three-way catalysts (TWC) the most important application of ceria [90]. As ceria has to sustain high temperatures, its thermal stability is critical for TWCs. The addition of zirconia as a stabilizer strongly enhances the resistance of ceria against thermal deactivation [67]. However, different preparation techniques also affect the thermal stability of ceria. As flame processes generally form highly crystalline and nonporous nanoparticles, a high thermal stability of such materials can be expected making flame processes particularly attractive for synthesis of ceria-based catalysts. Hence, various (flame) spray pyrolysis methods have been applied for synthesis of ceria nanoparticles.

Depending on process conditions, especially temperature and precursor formulation, either hollow, micron- or nano-sized $\text{CeO}_2$ particles have been formed [91]. Emulsion combustion of aqueous emulsions in kerosene resulted in porous, micron-sized ceria particles [92]. Spray pyrolysis of aqueous Ce-nitrate solutions at low temperatures in a hot-wall reactor ($400 \, ^\circ\text{C}$) resulted in precipitation and conversion of the precursor at the droplet surface giving large, hollow particles (Fig. 1.2) [93]. In contrast, higher temperatures occurring during FSP of appropriate Ce-precursors
led to complete evaporation of the precursor and formation of nanosized particles with specific surface area up to 250 m$^2$/g [91, 94]. It should be noted however that appropriate precursors during FSP synthesis of CeO$_2$ resulted in the desired nanostructure [91]. These nanosized ceria particles exhibited good thermal stability compared to other preparation methods [91] and similar dynamic oxygen exchange capacity compared to precipitated CeO$_2$ [67]. Scale up of FSP for synthesis of ceria particles up to 500 g/h was achieved without loosing its high specific surface area [94].

Further stabilization for flame-made ceria is achieved by addition of Zr. Stark et al. demonstrated that solvent composition strongly affects mixing of FSP-made CeO$_2$ and ZrO$_2$ in the solid phase [47]. Low boiling solvents resulted in segregated ceria and zirconia phases [47, 95]. In contrast, high boiling precursor solvents led to homogeneous solid solutions of Ce$_x$Zr$_{1-x}$O$_2$ over the range of Ce:Zr ratios with surface areas around 150 m$^2$/g and very high thermal stability, which can be attributed to the nonporous characteristics and the high crystallinity of flame-made materials [47, 96]. However, these solid-solutions exhibited rather low oxygen exchange capacities compared to precipitated catalysts, which was attributed to their high crystallinity and low defect concentration [47]. Introducing artificial defects by doping ceria-zirconia with low amounts Si increased the oxygen storage capacity [68].
1.3.5 Perovskites

Perovskites are mixed oxides with general formula $\text{ABO}_3$, where for catalytic applications $A$ usually is a lanthanide ion and $B$ a transition metal ion, both of which can be partially substituted. Perovskites exhibiting high thermal stability materials are attractive for catalytic combustion of natural gas in turbines for electricity generation, a high temperature process. Two kinds of such catalysts are generally used and have been prepared by flame processes: perovskites [40] and supported noble metals as will be described later [18]. The cheaper perovskites generally show lower activity but better thermal stability compared to noble metal based catalysts, where severe sintering of noble metals results in their deactivation.

Traditional preparation methods such as calcination-milling or the sol-gel citrate (SGC) method are not suitable for synthesis of perovskites exhibiting both high surface area (as needed for high activity) and high thermal stability. In the last years, flame technology turned out to be promising for synthesis of perovskites of high surface area and thermal stability. The use of spray pyrolysis for synthesis of various hollow, micron-sized perovskites has been summarized earlier [23, 24]. Here we focus on flame-based processes for synthesis of perovskite catalysts.

In an earlier work Kriegel et al. [14] made perovskites by FASP of organic precursor solutions in a oxy/hydrogen flame. The as-prepared $\text{SrMnO}_3$ was more active for methane combustion than the corresponding material prepared by solid state reaction and showed a high surface area of $45 \text{ m}^2/\text{g}$. 
Synthesis of LaMnO$_3$ and LaCoO$_3$ based catalysts has been carried out by both FASP [16, 62–64] and FSP [49, 65]. The former generally resulted in non-porous particles with surface area between 20 and 30 m$^2$/g [16, 62], whereas 70 m$^2$/g were achieved by the latter [65]. The phase purity of the perovskite crystal structure was exceptionally high for all flame-derived materials.

Flame-made perovskites showed similar or even higher activity for the catalytic combustion of methane than corresponding catalysts made by conventional SGC and other methods [16, 63]. But the most notable improvement concerns the deactivation of the catalysts by sintering at high temperatures. Although the surface area was similar, the non-porous structure of flame-derived perovskites prevented their sintering and thus deactivation compared to SGC materials [40, 64]. The shorter residence times at high temperatures during FSP synthesis of LaCoO$_3$ resulted in the highest specific surface area (up to 70 m$^2$/g) and catalytic activity. However, materials with very high surface area sintered faster during reaction and thus a faster deactivation was observed [65]. The partial substitution of La by Ce improved the activity of LaCoO$_3$ catalysts [16, 64]. This was attributed to higher oxygen mobility in the crystal lattice with small amounts of Ce being present.

SrTiO$_3$-based perovskites were prepared by flame processes and tested for catalytic combustion of methane [49, 97]. Similar to the previously described LaCoO$_3$, the highest surface area for SrTiO$_3$ was achieved by FSP (110 m$^2$/g) [49] rather than FASP (12 m$^2$/g) [64]. Both preparation methods afforded highly crystalline materials with catalytic activity similar to SGC-derived materials. A partial substitution of Sr by
Ag strongly increased the activity and thermal stability for FSP-made SrTiO$_3$ [49]. Concerning deactivation at high temperatures, however, the highest stability was observed for FASP- and SGC-derived materials, whereas FSP-derived SrTiO$_3$ was less resistant.

It can be summarized that various highly crystalline perovskites can be prepared by flame-techniques in one step. In general, these materials exhibit high surface area and good activity for methane combustion. The absence of internal micro- or mesopores often leads to a high resistance against sintering at high temperatures and consequently lower deactivation of the catalysts.

![Figure 1.5](image.png)

**Figure 1.5:** Two nozzle flame synthesis of Pt/Ba/Al$_2$O$_3$ catalysts. Al$_2$O$_3$ and BaCO$_3$ particles are formed separately resulting in individual BaCO$_3$ and Al$_2$O$_3$ particles (see TEM picture on the right, Ba particles are colored in red) exhibiting good behavior as NO$_x$ storage reduction catalysts (adapted from [98]).
1.3.6 NO$_x$ storage reduction catalysts

NO$_x$ storage reduction (NSR) catalysts are applied for exhaust gas cleanup from engines operating under fuel-lean conditions. Typical NSR catalysts consisting of Pt and Ba supported on Al$_2$O$_3$ were prepared by FSP in one step [98]. Spraying all three components together resulted in amorphous barium species, which were not active for NO$_x$ storage. However, using a two nozzle process, one as aluminium and the other as barium/platinum source, allowed synthesis of individual Al$_2$O$_3$ and BaCO$_3$ particles as shown in figure 1.5. These materials exhibited a similar behaviour during NSR as impregnated catalysts [99]. At higher Ba loadings however, the flame-made catalysts showed faster and higher NO$_x$ uptake. This could be attributed to the unique formation of relatively unstable BaCO$_3$ in flame-made materials even at high Ba content.

1.3.7 Supported metal catalysts

Supported noble metals are widely used as catalysts in processes ranging from fine chemical synthesis to exhaust gas treatment and even oil refining. Small active metal clusters are generally dispersed on high surface area supports such as TiO$_2$, Al$_2$O$_3$, SiO$_2$. Various flame techniques have been applied for preparation of supported noble metal catalysts in one step though FSP is the dominant as it allows high throughput of the noble metal. The relatively high vapor pressure of noble metals compared to that of the supporting metal oxides allows the co-synthesis of support with the noble metal. In a first step, the support is formed and later downstream noble metal particles nucleate at lower temperatures either
1.3 Catalysts

Figure 1.6: Formation of nanoparticles in flames. After evaporation and combustion of the precursors, particle formation starts by nucleation from the gas phase. These particles coagulate and, depending on the temperature, sinter into larger particles or agglomerate. In the case of supported noble metal catalysts, noble metal particle formation starts after support formation by homogeneous nucleation from the gas phase and/or heterogeneous nucleation on the support.
heterogeneously on the support or homogeneously in the gas phase with later deposition on the support (Fig. 1.6).

**Figure 1.7:** Electron microscopy images of supported noble metals made by flame spray pyrolysis. A: Pd/Al$_2$O$_3$ [18], B: Pt/TiO$_2$ [70], C: Au/SiO$_2$ [100].

### 1.3.7.1 Platinum

Vapor-fed aerosol flame synthesis was used for preparation of Pt/TiO$_2$ [34]. Ti-isopropoxide and Pt-acetylacetonate were evaporated and burned in a premixed methane flame. The as-prepared material consisted of small Pt particles (<5 nm) supported on TiO$_2$ nanoparticles exhibiting similar performance in the oxidation of SO$_2$ as impregnated catalysts.
Figure 1.8: Behavior of flame-made and commercial Pt/Al₂O₃ catalysts containing 5 wt% Pt in the enantioselective hydrogenation of ethyl pyruvate. The non-porous structure of the flame-made catalyst resulted in a 5 times higher activity (adapted from [8]).

In contrast to the VAFS process, FSP allows much higher production rates for supported noble metal catalysts as liquid feeds can provide much higher throughputs. Pt/Al₂O₃ (1-7.5 wt% Pt) or Pt/TiO₂ (0.1-4 atom% Pt) made by FSP consisted of well dispersed Pt particles (<5 nm) on top of γ-Al₂O₃ or TiO₂ particles (Fig. 1.7) [8, 70]. By adjusting the precursor concentration and flame temperature profile, the specific surface area of both catalysts could be controlled between 70 and 150 m²/g. The platinum dispersion on both supports depended strongly on Pt content and support surface area resulting in an almost linear increase of Pt particle size with the Pt loading on Al₂O₃ or TiO₂. The
catalytic properties of flame-made Pt/Al₂O₃ were evaluated for enantioselective hydrogenation of ethyl pyruvate. The non-porous structure of the flame-made material resulted in little mass transfer limitations and thus much higher activity compared to commercial porous catalysts as shown in figure 1.8 [8].

High thermal stability and very small Pt clusters were observed for Pt supported on ceria/zirconia at low Pt loadings (< 2 wt%) [48]. As the Pt clusters were very small, Pt was mainly present in its oxidized form and hardly reduced up to 300 °C in 5% H₂. Compared to catalysts prepared by precipitation and impregnation the thermally more stable flame-made Pt/ceria-zirconia did not lose its low-temperature oxygen exchange capacity after high temperature treatment.

Rapid quenching of the flame was applied for Pt/TiO₂ to control the size of noble metal clusters independently of that of the TiO₂ support [101]. Two different quenching devices have been applied for FSP-made Pt/TiO₂: Cooling by a gas stream [101, 102] and by expansion of the flame gases into a supercritical nozzle similar as used for VAFS [103]. The extra quenching of the flame resulted in a steep drop of flame temperature [101]. Figure 1.9 shows specific surface area and corresponding Pt dispersion for Pt/TiO₂ prepared by FSP and a supercritical nozzle as a function of the burner-nozzle distance (BND). Quenching by this supercritical nozzle was more efficient as by a gas stream resulting in very high surface area at low BND. However, incomplete evaporation of Pt at early stages in the flame resulted in the formation of large residual particles beneath smaller particles which were formed through nucleation from the gas phase [101]. If the flame was quenched after complete evap-
oration of the Pt precursor smaller Pt clusters were formed compared to an unquenched flame. In this operation window the Pt particles size could be controlled without altering the surface area of the TiO$_2$ support.

![Graph showing Pt dispersion and specific surface area as a function of burner nozzle distance](image)

**Figure 1.9:** *Pt dispersion and specific surface area of 5wt% Pt on TiO$_2$ made by quenching the flame in a supercritical nozzle as a function of the burner nozzle distance (BND).*

1.3.7.2 **Palladium**

Figure 1.7A depicts similar structural properties for Pd/Al$_2$O$_3$ [69] as well as Pd supported on La stabilized Al$_2$O$_3$ [18]as for Pt/Al$_2$O$_3$. The Pd/Al$_2$O$_3$ catalysts were also evaluated for enantioselective hydrogenation and exhibited good selectivity and activity. The easy control of noble metal particle size was used to elucidate the structure sensitiv-
ity of the reaction [69]. Similar to Pt/ceria-zirconia [48], alumina based supports showed good thermal stability [18]. After annealing at 1100 °C flame-made Al$_2$O$_3$ retained 90 m$^2$/g compared to 57 m$^2$/g for a commercial alumina. Adding a few weight % of La increased even further the thermal stability of flame-made alumina. High thermal stability of γ-Al$_2$O$_3$ was also observed for hollow, La-doped alumina particles made by emulsion combustion [104]. In general, the high thermal stability of these materials concerning loss in specific surface area can be attributed to the absence of small pores, which makes them promising catalysts for high temperature processes. Consequently, flame-made Pd/La-Al$_2$O$_3$ was tested for catalytic combustion of methane, where the catalysts have to sustain temperatures up to 1000 °C. However, the deactivation of the catalyst was mainly caused by sintering of palladium with only marginal effects from the stability of the support, preparation method (impregnation, flame-synthesis) or La content.

1.3.7.3 Copper and Gold

Cu/ZnO/Al$_2$O$_3$, a typical catalysts for methanol synthesis, was prepared by VAFS [35]. The as-prepared material consisted of ZnAl$_2$O$_4$ with small ZnO and CuO crystallites on its surface. Upon reduction in hydrogen at 220 °C small Cu particles (10 nm) were formed. The use of hydrogen instead of methane as a fuel during VAFS nearly doubled the catalytic activity in methanol synthesis from syngas.

The FSP was applied for synthesis of Au supported on SiO$_2$ or TiO$_2$ [56, 100]. Here the gold clusters were larger (ca. 16 nm for 4 wt% Au on
TiO$_2$) compared to the previously described systems and Au particle size was independent of the support composition and its surface area (Fig. 1.7C). This indicates that Au particles probably form independently of the support by homogeneous nucleation or exhibits a high mobility on the support surface.

1.3.7.4 Bimetallic catalysts

Bimetallic Pd-Pt on Al$_2$O$_3$ and Au-Ag on SiO$_2$, TiO$_2$ or Fe$_2$O$_3$ were also prepared by FSP [71, 72]. For the Pd-Pt/Al$_2$O$_3$, STEM/EDX and EX-AFS analysis detected Pd and Pt in the same clusters and formation of Pd-Pt alloys upon reduction. Figure 1.10 shows an STEM image of this material with the corresponding EDX analysis of a single metal particle. The addition of Pt to Pd and vice versa increased the stability of the noble metal clusters against sintering at high temperatures resulting in an improved resistance against deactivation during catalytic combustion of methane [71].

Concerning the formation of small bimetallic clusters, similar observations were made for Au-Ag as used for selective CO oxidation. The catalyst consisted of small alloyed Au-Ag clusters (<10 nm) dispersed on titania, iron oxide or silica [72]. Alloy formation was also observed for unsupported Ag-Pd particles [105], whereas Pt-Ru was only partly alloyed [106]. It can be assumed, that simultaneous nucleation of noble metals in the gas phase or on the support and similar oxidation states lead to formation of bimetallic clusters. This makes flame technology a promising alternative to wet-phase processes for preparation of various
Figure 1.10: Electron microscopy image of bimetallic Pd-Pt on alumina. The inset shows EDX analysis of a single metal particle revealing the presence of Pt and Pd in the same particles (adapted from [71]).
bimetallic catalysts.

## 1.4 Concluding remarks

Concerning supported metal catalysts it can be summarized that FSP of supported noble metals generally results in well dispersed noble metal particles. It can be assumed, that noble metals form by heterogeneous nucleation on the support (Fig. 1.6). Their particle size strongly depends on the surface area of the support and the strength of the metal-support interaction. Stronger metal-support interactions result in less sintering of the noble metals on the surface of the support at the high temperatures during synthesis. That is for platinum, the highest dispersions were observed on ceria/zirconia [48] followed by titania [70] and alumina [8]. Beside the properties of the support, the ”nobleness” of the supported metal has a strong influence on the metal-support interactions. It can be assumed that partly oxidized noble metals, as observed for Pd, Pt and Ag [48, 71, 72], exhibit strong metal-support interactions preventing extensive sintering during the high temperature flame processes. As a result small particles (<5 nm) are formed. In contrast, more noble metals like gold form larger particles at similar loadings. This can be attributed to lower metal-support interactions as no oxides are formed [72] and to the relatively low melting point of this metal which enhances sintering on the support during flame synthesis.

Flame based aerosol techniques are suitable processes for synthesis of a wide variety of catalytic materials. Well known catalysts such as supported noble metals as well as novel materials that are not accessible
through conventional methods can readily be made in flames. In general, flame-made catalysts are non-porous and of controlled crystallinity often possessing high thermal stability. For some specific catalytic applications flame-made materials exhibit superior performance compared to conventionally prepared ones. Proven scalability and continuous production make flame processes attractive for industrial production of catalysts. Optimization of existing catalytic systems which are prepared by conventional techniques can only be one goal for flame aerosol techniques. As flame techniques can result in the formation of unique materials, it seems more promising to use them for development of novel catalytic materials which are not commonly used. This includes especially mixed oxides, where novel phases have already been reported [107], but also metal salts which have recently been prepared by flame synthesis [108–111]. These materials may exhibit improved and unexpected catalytic properties.

References


References


Chapter 1 Introduction: Flame-made catalysts


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References


Chapter 1 Introduction: Flame-made catalysts


Flame spray synthesis of Pd/Al$_2$O$_3$ catalysts and their behavior in enantioselective hydrogenation

Abstract

Flame spray pyrolysis (FSP) was used for the synthesis of alumina-supported palladium catalysts containing 1 - 7.5 wt% Pd. Precursor solutions of aluminium sec-butoxide and palladium acetylacetonate were sprayed and combusted, resulting in nanostructured materials that were characterized by high-resolution transmission electron microscopy, CO-pulse chemisorption, nitrogen adsorption and X-ray diffraction. Well-dispersed palladium particles (1-5 nm) were confined to the alumina surface. Palladium dispersion depended on the metal loading and decreased for higher amounts of Pd. The FSP-derived alumina-supported palladium catalysts were chirally modified with cinchonine and tested for the

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enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone. Rate and enantioselectivity decreased with higher Pd dispersion. A comparison of these catalysts to a corresponding commercial Pd/Al$_2$O$_3$ catalyst revealed lower reaction rate and enantioselectivity for the FSP-derived catalysts. However, hydrogen pretreatment of the flame-made catalysts at 500 °C improved rate and enantioselectivity strongly, whereas only a comparatively weak beneficial effect was observed with the corresponding wet-phase derived catalysts. Enantiomeric excess in the formation of (R)-4-methoxy-6-methyl-5,6-dihydro-2-pyrone reached 80 % for flame-made catalysts after pretreatment in hydrogen. Hydrogen pretreatment temperatures above 600 °C led to sintering of the Pd particles and drastic loss in activity and enantioselectivity.
2.1 Introduction

Most noble-metal-based catalysts consist of nanometer-sized metal particles dispersed on high-surface-area supports [1]. Flame synthesis is a relatively new method for the one-step production of supported noble metal catalysts and catalysts in general [2, 3]. Moser et al. [4] made noble metal nanoparticles supported on Al$_2$O$_3$ of low specific surface area (10 m$^2$g$^{-1}$) by a high temperature decomposition process. Johannessen and Koutsopoulos [5] prepared Pt/TiO$_2$ catalysts for SO$_2$ oxidation using a vapor-fed aerosol flame reactor. Since their platinum precursor showed very low volatility they operated at very low production rates (some mg/h). Very recently, Jensen et al. [6] reported the flame aerosol synthesis of Cu/ZnO/Al$_2$O$_3$ catalysts for methanol synthesis. In contrast to the aerosol route, flame spray pyrolysis offers the possibility to use nonvolatile precursors and was applied for synthesis of Pt/Al$_2$O$_3$ hydrogenation catalysts [7] at a considerably higher production rate of 15 g/h and Au supported on TiO$_2$ and SiO$_2$ [8].

Flame aerosol synthesis is used on large scale today to produce carbon black, fumed silica and titania pigments. Flame synthesis in general and especially flame spray pyrolysis is a fast, cost-effective and versatile process for the production of a wide variety of different nano-particles [9–11]. More specifically, in this process a flame is used to drive chemical reactions of precursor compounds, resulting in the formation of clusters, which grow to nanometer-sized products by coagulation and sintering [10].

In the field of fine chemical synthesis, palladium is one of the most ver-
statile and most widely applied catalytic metals [12]. Heterogeneous enantioselective hydrogenation over platinum catalysts, chirally modified by cinchona alkaloids and derivatives, has been intensively investigated and covered in several recent reviews [13–18]. Less effort was spent to the study of analogous palladium systems [16, 17]. Since the first report on the Pd-cinchona-catalyzed hydrogenation of a C=C bond in 1985 [19], systematic investigations focused on α,β-unsaturated acids and ketons. Enantiomeric excess (ee) is usually low or moderate with exception of the Pd-cinchona-catalyzed hydrogenation of hydroxy- and methoxymethylpyrone [20, 21]. Dihydropyriones are important chiral intermediates in the synthesis of biologically active compounds [22]. At present, the most widely used Pd catalysts for heterogeneous enantioselective hydrogenation are Pd/Al₂O₃ [23] and Pd/TiO₂ [20] but also Pd on Fe₂O₃ [24] and other materials [25] have been used.

Flame synthesis offers the possibility to synthesize nonporous catalysts with high specific surface area, providing high accessibility for reactants and chiral modifiers [7]. This prompted us to synthesize Pd/Al₂O₃ catalysts by flame spray pyrolysis and test them for the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone (Scheme 1). The catalytic behavior of the new flame-made catalysts will be compared to that of state-of-the-art reference catalysts.
Figure 2.1: Sketch of the flame spray pyrolysis unit. The liquid precursor mixture is rapidly dispersed by a gas stream and ignited by a premixed methane/oxygen flame. After evaporation and burning of the precursor, particles are formed by nucleation, condensation, coalescence and coagulation. The image shows a typical spray flame producing Pd/Al$_2$O$_3$ nanoparticles.
2.2 Experimental

2.2.1 Particle synthesis

Figure 2.1 shows the experimental setup for the synthesis of Pd/Al$_2$O$_3$ by flame spray pyrolysis. Precursor solutions were prepared by dissolving appropriate amounts of aluminium sec-butoxide (Al(s-BuO)$_3$, Aldrich, 97%) and palladium acetylacetonate (Pd(acac)$_2$, Strem, 99%) in xylene (Riedel deHaen, 96%)/acetonitrile (Fluka, 99.5%) mixtures (70:30 vol%). The aluminium concentration was always 0.675 M. In a typical run, the liquid precursor mixture was fed in the center of a methane/oxygen flame by a syringe pump (Inotech) and dispersed by oxygen (3 ml/min), forming a fine spray. The pressure drop at the capillary tip was kept constant at 1.5 bar by adjusting the orifice gap area at the nozzle. The spray flame was surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing, at a radius of 6 mm). The total gas flow rate through this premixed methane/oxygen supporting flame ring was 3.5 L/min with a fuel/oxygen ratio of 0.92. A sintered metal plate ring (8 mm wide, starting at a radius of 8 mm) provided an additional sheath flow surrounding the spray flame. Calibrated mass flow controllers (Bronkhorst) were used to monitor all gas flows. Product particles were collected on a glass fibre filter (Whatmann GF/A, 15 cm in diameter) with the aid of a vacuum pump.

For some catalysis experiments, the flame-made and reference catalysts were subjected to a heat pretreatment in flowing hydrogen. The samples, placed in a U-tube, were flushed by He (20 ml/min) for 20 min and then
pretreated by heating at 10 °C/min in flowing hydrogen (20 ml/ min) up to a certain temperature (100 - 800 °C) and kept constant at this temperature for 1 h.

As reference materials a 5 wt% Pd/TiO$_2$ prepared by wet-precipitation [20] and a commercial 5 wt% Pd/Al$_2$O$_3$ catalyst (Engelhard 40692) were used. Characteristic properties of these catalysts are listed in Table 1.

### 2.2.2 Catalyst characterization

The specific surface area (SSA) of the as-prepared powders was determined by nitrogen adsorption at 77 K using the BET method (Micromeritics Tristar). All samples were outgassed at 150 °C for 1 h prior to analysis. The pore size distribution was determined from the desorption branch of a fully recorded isotherm of the as-prepared powders (Micromeritics ASAP 2010 Multigas System). The powder X-ray diffraction pattern were recorded with a Bruker D8 advance diffractometer from 20° to 65°, step size 0.06°, at a scan speed of 0.72 °/min.

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 Tecanai 30F microscope (Philips; field emission cathode, operated at 300 kV). The high-resolution TEM (HRTEM) images were recorded on a slow-scan CCD camera. 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). The Sauter-mean diameter ($d_S$) of the Pd-particle size distribution as derived from
Figure 2.2: Hydrogenation of 4-methoxy-6-methyl-2-pyrone 1 over cinchona-modified palladium. 2: (R)-4-methoxy-6-methyl-5,6-dihydro-2-pyrone, 3: 4-methoxy-6-methyl-tetrahydro-2-pyrone

STEM-images was calculated according to

\[ d_S = \frac{\sum n_id_i^3}{\sum n_id_i^2}. \]

Palladium dispersion was determined by CO-pulse chemisorption at 35 °C using a He flow of 50 ml/min and pulses of 0.5 ml (10 %CO in He) on a Micromeritics Autochem II 2920 unit. Prior to experiment all samples were freshly reduced for 1 h at 250 °C under flowing hydrogen (20 ml/min) and then flushed by He (50 ml/min) at 260 °C for 90 min. In order to calculate the metal dispersion, an adsorption stoichiometry of Pd/CO = 1 was assumed [26].

2.2.3 Catalytic measurements

The hydrogenation reactions were carried out in a magnetically stirred 100 ml glass reactor. In the standard procedure 20 mg catalyst in 10 ml 2-propanol (Fluka, 99.8%) was pretreated in-situ under flowing hydrogen
for 5 min at 1 bar and room temperature. 1 mg cinchonine (CN, Fluka, 98\%) was added and after 5 min stirring the reaction was started by addition of 50 mg 4-methoxy-6-methyl-2-pyrone 1 (Aldrich, purified by sublimation in vacuum, followed by re-crystallization from n-hexane) [20]. As shown earlier by Künzle et al. [27] external mass transfer is not an issue for this relatively slow reaction.

Conversion, chemoselectivity (Figure 2.2, amount of 2 related to the total amount of 2 and 3 and enantiomeric excess ($ee(\%) = |R(\%) - S(\%)|$) were determined by chromatographic analysis using a Chrompack Chirasil-DEX CB column. Using cinchonine as chiral modifier afforded excess of the ($R$)-enantiomer. If not otherwise stated, enantioselectivity and chemoselectivity were determined at 50 \% conversion.

2.3 Results

2.3.1 Catalyst properties

Flame spray pyrolysis (FSP) of the palladium/alumina precursor solutions resulted in spherical alumina particles in the size range of 10-30 nm with well dispersed palladium particles attached to the surface (Fig. 2.3). Different Pd/Al$_2$O$_3$ powders containing 0-7.5 wt\% Pd were produced using the same flame conditions (liquid feed rate: 3 ml/min, O$_2$ dispersion gas flow rate: 3 L/min) and for selected 5 wt\% Pd under different flame conditions (sheath gas: 20 L/min O$_2$, air or N$_2$, dispersion gas: 3 ml/min O$_2$, air or N$_2$). XRD-measurements revealed small $\gamma$-alumina crystals for all flame made powders giving rise to some line broadening.
Figure 2.3: Scanning transmission electron microscopy (STEM) picture of flame-made Pd/Al₂O₃ prepared at standard conditions. Small Pd particles (1-5 nm) are well dispersed and confined to the alumina surface. The inset shows the corresponding Pd particle size distribution of 500 counted particles with a Sauter mean diameter $d_S = 2.7$ nm and the mass-based geometric standard deviation $\sigma_{g,3} = 1.3$. 
## 2.3 Results

### Table 2.1: Numbers of different materials as described in Table 1.2

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>pretreat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5% Pd/Al$_2$O$_3$ N$_2$ disp.</td>
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</tr>
<tr>
<td>2</td>
<td>5% Pd/Al$_2$O$_3$ air disp.</td>
<td>none</td>
</tr>
<tr>
<td>3</td>
<td>5% Pd/Al$_2$O$_3$ N$_2$ sheath</td>
<td>none</td>
</tr>
<tr>
<td>4</td>
<td>5% Pd/Al$_2$O$_3$ air sheath</td>
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</tr>
<tr>
<td>5</td>
<td>5% Pd/Al$_2$O$_3$ 1 ml liquid feed</td>
<td>none</td>
</tr>
<tr>
<td>6</td>
<td>5% Pd/Al$_2$O$_3$ 6 ml liquid feed</td>
<td>none</td>
</tr>
<tr>
<td>7</td>
<td>5% Pd/Al$_2$O$_3$ standard conditions</td>
<td>none</td>
</tr>
<tr>
<td>8</td>
<td>5% Pd/Al$_2$O$_3$ standard conditions 1h 500°C H$_2$</td>
<td>none</td>
</tr>
<tr>
<td>9</td>
<td>5% Pd/Al$_2$O$_3$ (E40692)</td>
<td>none</td>
</tr>
<tr>
<td>10</td>
<td>5% Pd/Al$_2$O$_3$ (E40692) 1h 400°C H$_2$</td>
<td>none</td>
</tr>
<tr>
<td>11</td>
<td>5% Pd/TiO$_2$ a</td>
<td>none</td>
</tr>
<tr>
<td>12</td>
<td>5% Pd/TiO$_2$ a 1h 400°C H$_2$</td>
<td></td>
</tr>
</tbody>
</table>

*a* Prepared according to recipe given in [20].

Adding Pd had no influence on BET-SSA and alumina crystal structure as determined by XRD.

Tables 1.1 and 1.2 give an overview of structural and catalytic properties of different FSP-derived materials and two standard reference catalysts. Using standard conditions the specific surface area of FSP-derived Pd/Al$_2$O$_3$ was about 120 m$^2$/g. Changing the dispersion or sheath gas from O$_2$ to air or N$_2$ had no significant influence on specific surface area and Pd dispersion. However, varying the liquid flow rate from 6 to 1 ml/min resulted in specific surface areas ranging from 70 to about 200 m$^2$g$^{-1}$. 
Table 2.2: Catalytic behavior and structural properties of flame-made 5 wt% Pd/Al₂O₃ and reference catalysts

<table>
<thead>
<tr>
<th>No.</th>
<th>SSA</th>
<th>Disp.(^a)</th>
<th>(d_{Pd})</th>
<th>TOF(^b)</th>
<th>(r_0/\text{kg}_{Pd})</th>
<th>Sel.(^c)</th>
<th>ee</th>
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<tr>
<td></td>
<td>m² g(^{-1})</td>
<td>%</td>
<td>nm</td>
<td>min(^{-1})</td>
<td>mol(^{-1}) min(^{-1})</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
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<td>26</td>
<td>4.3</td>
<td>0.59</td>
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<td>60</td>
</tr>
<tr>
<td>2</td>
<td>108</td>
<td>24</td>
<td>4.7</td>
<td>0.55</td>
<td>1.24</td>
<td>81</td>
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</tr>
<tr>
<td>3</td>
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<td>39</td>
<td>2.8</td>
<td>0.12</td>
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</tr>
<tr>
<td>6</td>
<td>73</td>
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<td>0.65</td>
<td>1.17</td>
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<td>60</td>
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<tr>
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<td>120</td>
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<td>0.42</td>
<td>1.06</td>
<td>81</td>
<td>57</td>
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<tr>
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<td>26</td>
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<td>80</td>
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<tr>
<td>9</td>
<td>205</td>
<td>29</td>
<td>3.9</td>
<td>0.69</td>
<td>1.88</td>
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<td>66</td>
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<td>5.3</td>
<td>0.66</td>
<td></td>
<td>1.31</td>
<td>84</td>
<td>74</td>
</tr>
</tbody>
</table>

\(^a\) Determined by CO-pulse chemisorption.

\(^b\) TOF is given per Pd surface atoms, as determined by CO-pulse chemisorption.

\(^c\) Chemoselectivity: Amount of 2 related to the total amount of 2 and 3 (Scheme 1).

\(^d\) Determined at 20 % conversion.
Figure 2.4: HRTEM pictures of 5 wt% Pd/Al$_2$O$_3$ made by flame spray pyrolysis. A: as prepared; and after pretreatment in flowing hydrogen at B: 500 °C and C: 700 °C. Pictures with higher magnification on the right hand side depict the corresponding crystalline Pd particles with lattice planes.
Figure 2.3 shows an STEM image of the flame-made Pd/Al$_2$O$_3$ catalyst. The palladium particles, with a diameter of 1 to 5 nm are confined to the alumina surface, and ”uniformly” dispersed. The mass-based palladium particle size distribution derived from STEM images is rather narrow with geometric standard deviation $\sigma_g = 1.3$ and Sauter mean diameter $d_S = 2.7$ nm.

Figure 2.4 shows high-resolution-transmission-electron-microscopy (HR-TEM) images. As-prepared (A) and hydrogen treated (B: 500 °C, C: 700 °C) 5 wt% Pd/Al$_2$O$_3$ powders depict crystalline palladium for all samples. The Pd particle size seemed to increase after pretreatment at 700 °C in flowing hydrogen. For the sample pretreated at 500 °C, the Pd particle size did not changed compared to the unpretreated, as-prepared material.

The influence of pretreatment temperature (1 h under flowing hydrogen) on the dispersion is shown in Figure 2.5. The Pd dispersion stays virtually constant up to 600 °C and decreases at higher pretreatment temperatures (from 28% at 600 °C down to 8% at 800 °C) as the Pd particle size increases.

Pore size distributions of a typical flame-made powder and the references catalysts are shown in Figure 2.6. The FSP-derived material and the Pd/TiO$_2$ reference are nonporous, whereas the commercial standard catalyst (E40692) is a mesoporous material.
2.3 Results

Figure 2.5: Palladium dispersion and calculated Pd-particle diameter \( d_{P,PD} \) as a function of pretreatment temperature under flowing hydrogen for 1 h.

### 2.3.2 Enantioselective Hydrogenation

As-prepared materials were tested for the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone using cinchonine as chiral modifier (Scheme 1). This modifier affords the \((R)-4\)-methoxy-6-methyl-5,6-dihydro-2-pyrone (2) as major enantiomer (Scheme 1). Figure 2.7 shows the typical dependence of enantioselectivity and chemoselectivity on conversion. Chemoselectivity decreased with higher conversion while ee was virtually unaffected. This behavior was observed for all flame-made materials as well as for the reference catalysts. Figure 2.8 depicts enant-
Figure 2.6: Pore size distribution as determined from the nitrogen desorption isotherm of a typical flame-made Pd/Al$_2$O$_3$ powder, a precipitated Pd/TiO$_2$ [20] and a commercial Pd/Al$_2$O$_3$ catalyst (E40692).

tioselectivity and turnover frequency (TOF) as a function of palladium dispersion of flame-made catalysts with 1 - 7.5 wt% Pd prepared at standard conditions and 5 wt% Pd produced with different liquid flow rate (1 - 6 ml/min). Enantiomeric excess (ee) as well as activity decreased with higher metal dispersion. Figure 2.9 shows the catalytic performance as a function of the hydrogen pretreatment temperature of the catalyst. The performance in terms of activity, enantioselectivity and chemoselectivity increased up to a pretreatment temperature of 500 - 600 °C and
2.3 Results

Tables 1.1 and 1.2 give an overview of catalytic data of different FSP-derived materials and the reference catalysts. Catalysts were tested either as-prepared or after a heat pretreatment under flowing hydrogen. Using different sheath or dispersion gases (O₂, air or N₂) for the flame-synthesis of Pd/Al₂O₃ had only slight influence on the catalytic performance. Note that the flame-made catalysts with similar dispersion as the two reference catalysts showed lower enantioselectivity and decreased for higher temperatures.
rate. However, the hydrogen pretreatment increased turnover frequency, chemoselectivity and enantioselectivity to ($R$)-4-methoxy-6-methyl-5,6-dihydro-2-pyrone formation for the flame-made powder (from 60 up to 80 % ee), whereas the corresponding properties of the reference catalysts were much less improved. Turnover frequency increased for alumina supported catalysts (flame-made and E40692), whereas it decreased for the pretreated Pd/TiO$_2$ reference.

**Figure 2.8:** Enantiomeric excess (ee) and turnover frequency (TOF) as a function of Pd dispersion of flame-made catalysts containing 1 - 7.5 wt% and 5 wt% Pd produced under standard conditions and varying liquid flow rate (1 - 6 ml/min), respectively.
Figure 2.9: Catalytic performance of an FSP-derived 5 wt% Pd/Al$_2$O$_3$ catalyst as a function of pretreatment temperature for 1 h under flowing hydrogen.
2.4 Discussion

2.4.1 Catalyst properties

The alumina support of Pd/Al₂O₃ made by flame spray pyrolysis mainly consists of spherical, poorly crystalline γ-alumina particles, as previously observed for flame-made alumina [10]. Adding palladium did not affect the morphology or crystallinity of the alumina support consistent with an earlier study on Pt/alumina [7]. Changing the flame conditions by applying different dispersion or sheath gases (O₂, air, N₂) did not have a major effect on the morphology of the alumina support or the Pd-particles. These flame conditions with different sheath and dispersion gases resulted in similar flame heights, indicating similar particle residence times at high temperature, where particle grow by coagulation and sintering. However, changing the precursor flow rate alters the enthalpy content of the flame that results in different residence times at high temperature and, consequently, particles with different size and specific surface area ranging from 70 to 200 m²g⁻¹ (Tables 1.1 and 1.2). This is consistent with flame spray synthesis of alumina and other oxides [7, 28].

Palladium forms small particles on the alumina surface ranging from 1 to 5 nm in diameter with a narrow size distribution (Fig. 2.3), similar to supported platinum catalysts made in vapor- or liquid-fed flames [5, 7]. In general, higher palladium loadings, achieved by increasing the Pd content or decreasing the alumina surface area, lead to larger metal particles and thus lower dispersion.

The particle formation process of alumina supported palladium is illus-
trated in Figure 2.1. Alumina has a much lower vapor pressure than Pd/PdO in the hot flame environment, and consequently alumina particle formation starts earlier. Further downstream the flame, at lower temperatures, Pd/PdO starts to form small particles and/or deposits directly on the alumina support. This particle formation mechanism was also suggested for Pt/TiO$_2$ [5] and Pt/Al$_2$O$_3$ [7].

Hydrogen treatment up to 600 °C of FSP-derived Pd/Al$_2$O$_3$ has no significant influence on metal dispersion, indicating high thermal stability of these catalysts. However, at higher temperatures palladium starts sintering as indicated by a drop in dispersion, i.e. from 28% at 600 °C down to 8% at 800 °C (Fig. 2.5). This sintering behavior above 600 °C was also observed in a model study [29]. Closer inspection of the HRTEM-images (Fig. 2.4) indicates an enhanced formation of facetted palladium as a result of the hydrogen treatment at 500 °C.

### 2.4.2 Enantioselective Hydrogenation

Flame-made Pd/Al$_2$O$_3$ chirally modified by cinchonine is a suitable catalyst for the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone to (R)-4-methoxy-6-methyl-5,6-dihydro-2-pyrone (2), in terms of activity, chemo- and enantioselectivity. Considerable improvement of the properties is achieved after pretreatment of the flame-made material in flowing hydrogen at elevated temperatures. After this pretreatment the flame-made materials show similar enantioselectivity and turnover frequency as the best known catalyst (5 wt% Pd/TiO$_2$) for this reaction [20] and better performance than an often used commercial Pd/Al$_2$O$_3$
catalyst (Tables 1.1 and 1.2). Interestingly the hydrogen pretreatment has a much stronger positive effect on the catalytic properties for the flame-made Pd/Al$_2$O$_3$ catalyst, whereas its effect on the Pd/TiO$_2$ reference catalyst is even negative, corroborating earlier studies [21].

The degree of Pd dispersion affects the catalytic performance remarkably (Fig. 2.8). TOF decreases nearly linearly with increasing metal dispersion and a significant drop in enantioslectivity is observed for catalysts with Pd dispersion higher than about 30 %. Nitta et al. [30] observed a similar dependence of metal dispersion of Pd/TiO$_2$ catalysts for the enantioselective hydrogenation of phenylcinnamic acid. This indicates, that the reaction is structure sensitive and small palladium particles result in lower enantioselectivity and turnover frequencies. An earlier study on flame-made Pt/Al$_2$O$_3$ revealed a similar dependence on metal loading for the enantioselective hydrogenation of ethyl pyruvate [7].

For the flame-made catalysts activity, chemoselectivity and enantioselectivity increased continuously up to a pretreatment temperature of about 500 °C and decreased rapidly for temperatures above 600 °C (Fig. 2.9). Nitta et al. [30] reported a similar behavior for Pd/TiO$_2$ concerning the enantioselectivity, however the catalytic activity behaved differently and decreased already after pretreatment in hydrogen at low temperatures. The steep decrease in activity can by explained by the sintering of palladium above 600 °C (Fig. 2.5), resulting in much smaller palladium surface area that is accessible for catalysis. Possible reasons for the increase of the catalytic performance after hydrogen pretreatment are cleaning (decontamination) and/or restructuring of the alumina-support and the Pd surface, resulting in a smooth surface exposing mainly thermody-
namically more stable low index planes. Some evidence for palladium surface restructuring emerges from the HRTEM images (Fig. 2.4) indicating more facetted palladium particles after heat pretreatment in hydrogen. It should be noted that an increase of the catalytic performance after heat pretreatment in hydrogen is commonly observed for enantioselective hydrogenation with cinchona-modified Pt/alumina catalysts [31]. The effect of the hydrogen pretreatment at higher temperature is however not understood yet on the atomic level and requires further studies on well-defined single crystal palladium surfaces.

2.5 Conclusions

The flame spray pyrolysis method has been successfully applied for the synthesis of Pd/Al$_2$O$_3$ hydrogenation catalysts. Materials with good catalytic performance in the enantioselective hydrogenation of 4-methoxy-6-methyl-2-pyrone could be produced in a single-step flame synthesis process. The catalysts are made up of small palladium particles (1 - 5 nm) attached to the surface of agglomerated, nonporous alumina particles (10 - 30 nm) and exhibit high thermal stability. Hydrogen pretreatment at elevated temperatures improved drastically the catalytic properties (TOF, ee, chemoselectivity) of flame-made catalysts in the hydrogenation of 4-methoxy-6-methyl-2-pyrone. After pretreatment flame-made catalysts showed higher rate and enantioselectivity than reference catalysts prepared by conventional methods. The flame-made catalysts with different Pd particle size revealed a significant structure sensitivity of the reaction.
References


[25] I. Kun, B. Török, K. Felföldi and M. Bartòk. “Heterogeneous asym-


Flame-made Pd/La$_2$O$_3$/Al$_2$O$_3$ nanoparticles: Thermal stability and catalytic behavior in methane combustion \(^1\)

Abstract

Palladium nanoparticles supported on lanthanum stabilized alumina were prepared by flame spray pyrolysis. The as-prepared materials were characterized by high-resolution transmission electron microscopy, CO chemisorption, nitrogen adsorption, X-ray diffraction and temperature programmed reduction. These materials were tested for the catalytic combustion of methane with a focus on the thermal stability of the support and the palladium particles. Flame spray pyrolysis afforded small palladium particles (<5 nm) attached to the surface of the supporting La$_2$O$_3$/Al$_2$O$_3$ ceramic nanoparticles with specific surface areas in the range of 50-180 m$^2$/g. Compared to commercial reference materials

\(^1\)Part of this chapter is published in *J. Mater. Chem.*, **15** (2005) 605.
the flame-made catalysts showed excellent thermal stability in terms of specific surface area up to 1200 °C and retarded gamma-alpha-alumina transformation. Catalysts were tested as-prepared (small Pd particles, <5 nm) and after sintering at 1000 °C (large Pd particles, 50-150 nm). By cycling the temperature several times from 200 to 1000 °C during catalytic combustion, it could be shown, that all catalytic materials, regardless of specific surface area, lanthanum content, and preparation method (flame-synthesis or impregnated), exhibited similar catalytic performance after an initial conditioning cycle.
3.1 Introduction

The catalytic combustion of methane, the main component in natural gas, has been studied extensively and was covered in several recent review articles [1–3]. Natural gas is a relatively clean source of energy, since the combustion of CH$_4$ produces the highest amount of energy per CO$_2$ molecule. The use of a catalyst reduces the emission of CO, soot and unburned hydrocarbons and, due to lower process temperatures compared to traditional homogeneous combustion, prevents the formation of thermal NO$_x$. It further improves process stability and makes it possible to obtain complete fuel oxidation at low temperatures with low fuel-to-air ratios. Supported noble metal catalysts, especially Pd/Al$_2$O$_3$, have turned out to be the most active catalysts for low temperature combustion [4]. However, these catalysts gradually deactivate during methane combustion due to sintering of alumina and palladium and the transformation of PdO to Pd [5]. The addition of structural stabilizers like lanthanum or neodymium to the Pd/Al$_2$O$_3$ system is one possibility to lower catalyst deactivation and sintering of the support [6–8]. Changing the catalyst’s structure and morphology by altering the preparation methods could be another way to improve the longterm stability of the catalyst. Persson et al. [9] observed a strong influence of different wet-phase preparation techniques of Pd/Al$_2$O$_3$ on the catalytic activity and the palladium oxidation behavior. Flame synthesis is a novel preparation method for supported noble metal and metal-oxide catalysts [10]. Johannessen and Koutsopoulos [11] prepared Pt/TiO$_2$ catalysts for SO$_2$ oxidation using a vapor-fed aerosol flame reactor. Flame spray pyrol-
ysis offers the possibility to use nonvolatile precursors and was applied for the synthesis of Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ hydrogenation catalysts [12, 13] as well as for Au supported on TiO$_2$ and SiO$_2$ [14]. Mdler et al. showed very good thermal stability for flame-made ceria nanoparticles [15]. Flame synthesis is used on large scale today to produce carbon black, fumed silica and titania pigments. In general, flame synthesis and especially flame spray pyrolysis are continuous, well controllable and versatile processes for the production of a wide variety of different nanoparticles [16]. Here we have extended the scope of catalytic materials prepared by flame spray pyrolysis to a three component system made up of palladium nanoparticles dispersed on a mixed oxide La$_2$O$_3$/Al$_2$O$_3$ support. In the focus are the thermal stability, and structural and catalytic properties of these materials. Their behavior in the catalytic combustion of methane is compared to that of catalysts prepared by conventional incipient wetness impregnation.

### 3.2 Experimental

#### 3.2.1 Catalyst Preparation

The experimental setup for the synthesis of Pd/La$_2$O$_3$/Al$_2$O$_3$ by flame spray pyrolysis has been described earlier15. The precursor solution consisted of aluminium(III) sec-butoxide (Aldrich, 97%), lanthanum isopropoxide (Alfa Aesar, 98%) and palladium acetylacetonate (Fluka, 98%) dissolved in xylene (Riedel deHaen, 96%). The aluminium concentration was kept constant at 0.47 M for all experiments. The liquid pre-
cursor mixture was fed at 3-8 ml/min in the center of a methane/oxygen flame by a syringe pump (Inotech) and dispersed by oxygen (3-6 L/min), forming a fine spray. The pressure drop at the capillary tip was kept constant at 1.5 bar by adjusting the orifice gap area at the nozzle. The spray flame was surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing, at a radius of 6 mm). The total gas flow rate through this premixed methane/oxygen supporting flame ring was 3.5 L/min with a fuel/oxygen ratio of 0.94. Product particles were collected on a glass fibre filter (Whatmann GF/D, 25.7 cm in diameter) with the aid of a vacuum pump (Busch, Seco SV 1040C). The gas liquid mass ratio (GLMR) was calculated according to:

$$GLMR = \frac{\dot{m}_g}{\dot{m}_l}.$$  

where denotes the dispersion gas and the liquid precursor mass flow rate. The resulting material was designated as wPdxLaAl y/z, where w and x denote the weight fraction of Pd and La$_2$O$_3$, respectively, y the liquid feed rate in ml/min and z the dispersion gas flow rate in L/min.

Reference catalysts were prepared by incipient wetness impregnation according to Thevenin et al. [17]. The following supports have been employed: Al$_2$O$_3$ (Sasol, Puralox HP 14-150) and 3% La$_2$O$_3$/Al$_2$O$_3$ (Sasol, Puralox, SCFa-140 L3). A Pd(NO$_3$)$_2$ solution (Alfa Aesar, 8.4 wt%) was used for impregnation resulting in a final Pd content of 2.5 wt%. The catalysts were dried for 12 h at 120 °C and calcined for 4 h in air at 500 °C. For some experiments the as-prepared catalysts were annealed at different temperatures for 4 h in air.
3.2.2 Catalyst characterization

The specific surface area (SSA) of the as-prepared powders was determined by nitrogen adsorption at 77 K using the BET method (Micromeritics Tristar). All samples were outgassed at 150 °C for 1 h prior to analysis. The powder X-ray diffraction pattern were recorded with a Bruker D8 advance diffractometer from 20° to 65°, step size 0.06° at a scan speed of 0.72 °/min. 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 Tecanai 30F microscope (Philips; field emission cathode, operated at 300 kV). The high-resolution TEM (HRTEM) images were recorded on a slow-scan CCD camera. Scanning transmission electron microscopy (STEM) images, obtained with a high-angle annular dark field (HAADF) detector, showed the metal particles with bright contrast (Z contrast).

Palladium dispersion was determined by CO-pulse chemisorption at 40 °C using a He flow of 50 ml/min and pulses of 0.5 ml (10% CO in He) on a Micromeritics Autochem II 2920 unit. Prior to dispersion analysis all samples were freshly reduced for 1 h at 250 °C under flowing hydrogen (20 ml/min) and then flushed by He (50 ml/min) at 260 °C for 90 min. In order to calculate the metal dispersion, an adsorption stoichiometry of Pd/CO = 2 was assumed [18]. Temperature programmed reduction of PdO by hydrogen was measured on a Micromeritics Autochem II 2920, equipped with a TCD-detector, by flowing a mixture of 5% H2 in argon (20 ml/min). The temperature was ramped from -100
3.2 Experimental

to 900 °C with the aid of a liquid nitrogen fed sub-ambient cooler at a heating rate of 10 °C/min. Prior to this analysis palladium was oxidized in flowing oxygen at 500 °C.

Methane oxidation was measured in a conventional fixed-bed flow microreactor at atmospheric pressure. The reactor, consisting of a quartz tube of 5 mm ID, was placed in an electric furnace. The catalytic material (5 mg, 100-250 µm) was diluted with 200 mg quartz sand and fixed with quartz wool in the reactor. A thermocouple was inserted in the center of the catalyst bed. A mixture containing 1.0 vol% methane and 4.0 vol% oxygen in helium was flown through the reactor at 100 ml/min. Mass spectrometry (Thermostar, Pfeiffer Vacuum) was used to determine all gas concentrations in the effluent gas stream. The carbon mass balance was always closed within an error of ±5%. Pertinent tests concerning possible external and internal mass transfer influences were performed according to the procedures described by Baldwin and Burch [19]. These tests indicated that in the relevant temperature range (350-600 °C) no mass transfer limitation occurred. However, possible external and internal mass transfer limitation at the highest temperatures can not be ruled out. The transient behavior and conditioning/deactivation of the catalysts was measured by cycling the temperature several times from 200 °C up to 1000 °C at a heating or cooling rate of ± 10 °C/min.


3.3 Results and Discussion

Flame spray pyrolysis of the liquid precursor mixture resulted in palladium nanoparticles well-dispersed on agglomerated La$_2$O$_3$/Al$_2$O$_3$ particles, similar the Pd/Al$_2$O$_3$ system [13]. The STEM-image of as-prepared material shown in Fig. 3.1A corroborates this structural feature. The palladium particles are discernible as bright dots.

3.3.1 Thermal stability

The influence of the initial surface area on the sintering behavior of 5% La$_2$O$_3$/Al$_2$O$_3$ was studied by using powders produced under different flame conditions. By changing the GLMR the specific surface area (SSA) of the as-prepared materials could be varied from ca. 55 to 175 m$^2$/g (Fig. 3.2). Powders with higher initial surface area sintered faster resulting in a higher loss of surface area. This behavior is consistent with findings for flame-made ceria and molecular dynamics studies for alumina [15, 20].

A comparison of the sintering behavior of flame-made powders with commercial reference materials revealed higher thermal stability for the pure and the lanthanum doped flame-made alumina (Fig. 3.3). Samples with slightly lower initial surface area as the reference exhibited a lower reduction in surface area with calcination up to 1100 °C. At even higher temperatures (1200 °C) lanthanum addition stabilized the alumina, resulting in higher specific surface areas for these doped materials. This stabilizing effect was much more prominent for the flame-made powders,
3.3 Results and Discussion

Figure 3.1: STEM images of 2.5Pd5LaAl 5/5. A: as-prepared; B: annealed at 800 °C; C: after reaction (5 cycles from 200-1000 °C); D: after annealing at 1000 °C.

yielding specific surface areas up to 80 m²/g after annealing at 1200 °C.

Consistent with the lower reduction in specific surface area, the γ- to α-Al₂O₃ transformation was retarded for the flame-made powders. Additionally to sintering, the crystal phase transformation can contribute to the loss of surface area [7]. Figure 3.4 shows XRD-patterns of the flame-made and reference materials calcined at different temperatures. Alumina is known to transform from γ- to α-Al₂O₃ over the interme-
Figure 3.2: Specific surface area (SSA) after annealing at 1000 and 1200 °C of 5LaAl prepared with different GLMRs.

For the undoped commercial alumina (Al ref.) phase transformation occurred at 1100 °C and after calcination at 1200 °C only very sharp peaks of α-Al₂O₃ were found, whereas the flame-made γ-Al₂O₃ (Al 5/5) was stable up to 1100 °C. The addition of lanthanum retarded the phase transformation for both materials. However, for the reference material (3LaAl ref.) significant formation of the intermediate δ- and θ-phases occurred after calcination at 1100 °C, while γ-Al₂O₃ was the predominant phase for the flame-made powder (5LaAl 5/5) up to 1200 °C. After 1300 °C the reference was completely transformed into α-alumina and La-β-aluminate. The flame-made ma-
Figure 3.3: Specific surface area of flame-made and commercial supports after annealing at different temperatures in air for 4 hours.

The sintering behavior of palladium was investigated by CO-pulse chemisorption measurements. Table 3.1 gives an overview of metal dispersions for as-prepared and annealed catalysts. All catalysts showed only a slight decrease of palladium dispersion after heating at 800 °C in air for 4 hours. At higher temperatures (1000 °C) palladium sintered strongly resulting in a high decrease of metal dispersion. Additional STEM investigations corroborated these results (Fig. 3.1 B and D). No visible change of Pd particle size was observed after annealing at 800 °C,
Figure 3.4: X-ray diffraction patterns of flame-made and commercial Al₂O₃ and La₂O₃/Al₂O₃ calcined at different temperatures in air for 4 h (γ-Al₂O₃, γ; θ-Al₂O₃, θ; α-Al₂O₃, α; La-β-Al₂O₃, o).
### Table 3.1: Overview of flame-made and reference catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing$^a$</th>
<th>SSA (m$^2$/g)</th>
<th>Pd disp. (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flame-made</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5PdAl 5/5</td>
<td>none</td>
<td>125</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>800 °C</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>106</td>
<td>11</td>
</tr>
<tr>
<td>2.5Pd5LaAl 5/5</td>
<td>none</td>
<td>120</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>800 °C</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>109</td>
<td>11</td>
</tr>
<tr>
<td><strong>References</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5PdAl ref.</td>
<td>none</td>
<td>145</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>800 °C</td>
<td>118</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>90</td>
<td>6</td>
</tr>
<tr>
<td>2.5Pd3LaAl ref.</td>
<td>none</td>
<td>135</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>800 °C</td>
<td>128</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>99</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$ Annealed for 4 h in air at the given temperature.

$^b$ Derived from CO-pulse chemisorption.
whereas large PdO particles (50-150 nm) were formed beyond 1000 °C (Fig. 3.9). The large difference in sintering of Pd at 800 and 1000 °C can be explained by the low mobility on the alumina surface of PdO, which is stable at 800 °C in air.

Figure 3.5: Palladium dispersion as determined by CO chemisorption of as-prepared and annealed flame-made 2.5Pd5LaAl synthesized with different GLMR.

Reduced, metallic Pd, formed at 1000 °C, is highly mobile at this temperature leading to strong sintering of the Pd particles [22]. Figure 3.5 depicts the palladium dispersion before and after annealing of flame-made materials prepared at different flame conditions resulting in sur-
face areas from 50 up to 175 m²/g (compare Fig. 3.2). Higher specific surface areas (high GLMR) lead to increased metal dispersions, that is smaller Pd particles. After annealing at 800 °C the differences in dispersion equalized, due to the redispersion and sintering of palladium in the powders with low and high surface area, respectively. Except for the sample with the lowest SSA, the Pd dispersion was around 5 % for all catalysts after annealing at 1000 °C, independent on the surface area.

Figure 3.6 depicts TPR profiles of the as-prepared and calcined materials with the corresponding amounts of consumed and released hydrogen given in Table 3.2. The H₂:Pd ratio of the total amount of consumed hydrogen was similar for all samples (0.96-1.11) and close to the theoretical value of 1. In all samples palladium was reduced between 0 and 50 °C with only slight differences in the position of the peak maximum. The release of hydrogen from bulk Pd-H species was observed at around 70 °C, resulting in an increase of the hydrogen concentration [23]. However, the release of hydrogen was not observed for the as-prepared flame-made catalysts. This may be attributed to very small palladium particles not capable to form bulk palladium hydride species [24]. Compared to the reference, the flame-made materials showed also a broader signal during hydrogen uptake.
Figure 3.6: $H_2$-TPR profiles of flame-made and reference catalysts. (Straight lines: as-prepared powders; dotted lines: after annealing at 1000 °C)
Table 3.2: Temperatures of maximum hydrogen consumption (peak position) and amount of $H_2$ consumed and released during TPR of flame-made and reference materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing$^a$</th>
<th>1$^{st}$ peak position (°C)</th>
<th>2$^{nd}$ peak position (°C)</th>
<th>$H_2$/Pd ads.$^b$</th>
<th>$H_2$/Pd rel.$^c$</th>
<th>$H_2$/Pd total$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5PdAl 5/5</td>
<td>none</td>
<td>20</td>
<td>-</td>
<td>0.96</td>
<td>0</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>21(40)</td>
<td>67</td>
<td>1.26</td>
<td>0.15</td>
<td>1.11</td>
</tr>
<tr>
<td>2.5Pd5LaAl 5/5</td>
<td>none</td>
<td>30</td>
<td>-</td>
<td>0.98</td>
<td>0</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>21</td>
<td>65</td>
<td>1.19</td>
<td>0.15</td>
<td>1.04</td>
</tr>
<tr>
<td>2.5PdAl ref</td>
<td>none</td>
<td>10</td>
<td>67</td>
<td>1.10</td>
<td>0.06</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>17</td>
<td>70</td>
<td>1.21</td>
<td>0.18</td>
<td>1.03</td>
</tr>
<tr>
<td>2.5PdAl 5/5</td>
<td>none</td>
<td>25</td>
<td>67</td>
<td>0.10</td>
<td>0.09</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>13(43)</td>
<td>67</td>
<td>1.15</td>
<td>0.16</td>
<td>0.99</td>
</tr>
</tbody>
</table>

$^a$ Calcination temperature before experiment for 4 hours in air.

$^b$ $H_2$/Pd ratio of consumed hydrogen during reduction (first peak).

$^c$ $H_2$/Pd ratio of released hydrogen from Pd-H (second peak).

$^d$ $H_2$/Pd ratio of the total amount of $H_2$ consumed (consumed - released hydrogen).
3.3.2 Catalytic combustion

The as-prepared and annealed materials were tested for the catalytic combustion of methane. To study the effects of conditioning and deactivation during the reaction the temperature was cycled several times between 200 and 1000 °C. Figure 3.7 shows typical activity profiles during the first, second and fifth cycle for a typical flame-made catalyst. After light-off at around 300 °C the activity increased reaching a maximum around 700 °C. The loss of activity at higher temperature is attributed to the complete reduction of palladium oxide into less active palladium [17]. The strong hysteresis effect upon cooling with a reactivation of the catalyst around 600 °C is commonly related to the kinetically inhibited Pd re-oxidation [25]. A comparison of the first and second cycle revealed a significant change in the behavior towards methane oxidation. While the catalyst was activated in the low temperature regime, it lost in activity at higher temperatures, corresponding to high methane conversion. Further cycles showed a gradual deactivation of the catalyst without significant changes in the temperature dependence. During cycles 2-5 PdO decomposition during heating was slightly shifted towards lower temperatures and temperatures for re-oxidation during cooling increased subsequently for all catalysts. The formation of larger Pd particles by gradual sintering at high temperatures during the cycles, as shown in Fig. 3.1C, may be the reason for these shifts. Weaker metal-support interaction of larger particles with lower interfacial contact results in easier reduced PdO and re-oxidized Pd species.

Figure 3.8 depicts the temperature of 20% methane conversion ($T_{20}$) for
3.3 Results and Discussion

Figure 3.7: Methane conversion as a function of temperature for a typical flame-made catalyst (2.5Pd5LaAl 5/5). Arrows indicate the corresponding activity during heating and cooling.

flame-made and reference catalysts as a function of cycle number. The impregnated reference catalyst (2.5PdAl ref.) possessed the highest initial activity with 20% conversion at 324 °C in the first cycle. The T$_{20}$ for a flame-made catalyst with the same composition and similar surface area (2.5PdAl 5/5) was more than 30 °C higher. The addition of lanthanum significantly increased T$_{20}$ for both preparation methods. However, after a first cycle (200-1000 °C) the performance changed, leading to similar T$_{20}$ values for all catalysts (360-370 °C). During the next cycles (2-5) the activity decreased slowly. The deactivation (2.5PdAl ref.)
or even activation (2.5Pd5LaAl 5/5) in the first cycle can be attributed to the restructuring and sintering of palladium under reacting conditions [25]. At high temperatures, when PdO was completely reduced or decomposed, the small Pd particles (<5 nm) of the as-prepared powders sintered strongly and upon re-oxidation formed PdO particles in the range of 50-150 nm as observed by STEM (Fig. 3.1C and D) and TEM (Fig. 3.9) investigations.

The influence of specific surface area on the catalytic activity and the de-activation was studied with flame-made catalysts containing 5% La (Fig.
3.3 Results and Discussion

Table 3.3: Catalytic activity of flame-made and reference samples after annealing at 1000 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{20}$ 1$^{st}$ cycle / °C$^a$</th>
<th>$T_{20}$ 2$^{nd}$ cycle / °C$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5PdAl 5/5</td>
<td>436</td>
<td>407</td>
</tr>
<tr>
<td>2.5Pd5LaAl 5/5</td>
<td>417</td>
<td>408</td>
</tr>
<tr>
<td>2.5PdAl ref.</td>
<td>470</td>
<td>406</td>
</tr>
<tr>
<td>2.5Pd3LaAl ref.</td>
<td>425</td>
<td>408</td>
</tr>
</tbody>
</table>

$^a$ Temperature of 20% methane conversion during the first heating cycle

$^b$ Temperature of 20% conversion during the second heating cycle

The activity increased after a first cycle and decreased steadily further on. The specific surface area had only little effect on the catalytic performance and the activation/deactivation processes during catalysis. Only the powder with the highest SSA (175 m$^2$/g) needed slightly higher temperatures for 20% conversion. It seems that the surface area of the support did not affect the restructuring and sintering of the palladium particles.

The initial activity of big Pd particles was studied with pre-sintered catalysts (1000 °C, 4 h, air). After this annealing, Pd particles were formed in the size range of 20-150 nm (Fig. 3.1 and Fig. 3.9B) with dispersions between 2.8 and 6% for different catalysts (Table 3.1). Table 3.3 gives $T_{20}$ values for pre-sintered catalysts during the first and second cycle. In the first cycle the flame-made catalysts exhibited a higher activity than similar reference materials. However, after a first cycle all catalysts showed exactly the same catalytic performance in the second cycle.
In contrast to the as-prepared catalysts the addition of lanthanum decreased the temperature of 20% conversion ($T_{20}$). The differences in the first cycle may be explained by the different Pd dispersions of the catalysts (Table 3.1) as the catalyst with the lowest metal dispersion needed higher temperatures for 20% conversion. In the first cycle PdO undergoes reduction and re-oxidation, probably accompanied by restructuring and re-dispersion of the Pd particles. We assume that this re-dispersion of Pd leads to comparable metal dispersions and this could be a reason for the similar activities in the second cycle.

![Figure 3.9: TEM-images of 2.5Pd5LaAl 5/5 after 5 reaction cycles (A) and after annealing at 1000 °C (B). PdO (001, $D = 3.4\text{Å}$) lattice planes are visible in both samples.](image)

Surprisingly the catalytic activity for methane combustion seems independent on the addition of lanthanum, specific surface area and preparation method (flame-synthesis or impregnation) after exposure to high temperatures (1000 °C) during reaction. After reduction and re-oxidation of palladium the metal-support interactions seem to be min-
3.4 Conclusions

Flame-spray pyrolysis was applied for the one-step synthesis of Pd catalysts supported on La-stabilized Al₂O₃. The addition of lanthanum resulted in materials with excellent thermal stability as judged from the

Figure 3.10: Temperature of 20% methane conversion as a function of the initial surface area of flame made 2.5Pd5LaAl x/y. The numbers indicate the activity during the corresponding cycle.

3.4 Conclusions

Flame-spray pyrolysis was applied for the one-step synthesis of Pd catalysts supported on La-stabilized Al₂O₃. The addition of lanthanum resulted in materials with excellent thermal stability as judged from the
loss in specific surface area and the transformation of $\gamma$- into $\alpha$-alumina. The catalysts were tested for their performance in the combustion of methane and compared to corresponding impregnated reference catalysts. After restructuring and sintering of palladium during an initial temperature cycle under reacting conditions (200-1000 °C) all catalysts showed similar activities that slowly decayed during the following cycles. It seemed that after this conditioning the catalytic performance is independent of preparation method, lanthanum content and specific surface area of the catalyst, indicating a very low metal-support interaction after palladium sintering and restructuring.

**References**


Chapter 4

Flame-made alumina supported Pd-Pt nanoparticles: Structural properties and catalytic behavior in methane combustion

Abstract

Bimetallic palladium-platinum nanoparticles supported on alumina were prepared by flame spray pyrolysis. The as-prepared materials were characterized by scanning transmission electron microscopy (STEM), CO chemisorption, nitrogen adsorption (BET), X-ray diffraction (XRD), temperature programmed reduction (TPR), thermogravimetric analysis (TGA) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The materials were tested for the catalytic combustion of methane with a focus on the thermal stability of the noble metal particles. After flame synthesis the noble metal components of the materials were predominantly in oxidized state and finely dispersed on the alu-

\(^1\)Part of this chapter is published in *Catal. Lett.*, **104** (2005) 9.
mina matrix. Reduction afforded small bimetallic Pd-Pt alloy particles (<5 nm) supported on Al₂O₃ ceramic nanoparticles. The addition of small amounts of platinum made the palladium particles more resistant against sintering at high temperatures and further lowered the deactivation observed during methane combustion.
4.1 Introduction

Catalytic combustion of methane, the main component in natural gas, has been extensively studied during the past years and progress has been covered in several recent review articles [1–3]. Natural gas is a relatively clean source of energy, since the combustion of methane produces the highest amount of energy per CO$_2$ molecule. The use of a catalyst reduces the emission of carbon monoxide, soot and unburned hydrocarbons and, due to lower process temperatures compared to traditional homogeneous combustion, prevents the formation of thermal NO$_x$. The catalytic process further improves the process stability and makes it possible to obtain complete oxidation of the fuel at low temperatures with low fuel-to-air ratios.

Palladium is an often used catalyst with high activity in methane combustion. However, the use of palladium has some drawbacks, including large hysteresis effects due to the transformation of palladium oxide into metallic palladium and deactivation at higher temperatures due to sintering. In order to stabilize the catalyst, the addition of another noble metal such as Pt, Rh, Ru, etc. has been proposed by several authors. Ersson et al. [4] studied the influence of Pt and Rh on the behavior of Pd/Al$_2$O$_3$ catalysts and found an increased stability when Pt was used as a co-metal. Narui et al. [5] observed decreased sintering of the metal particles when platinum was added to palladium. The preparation method can have significant influence on the activity and stability of bimetallic Pd-Pt catalysts [6, 7]. In general, bimetallic catalysts are prepared either by non selective or selective deposition of the metals.
on the supporting material [8]. Only the selective deposition by redox methods [9], surface organometallic chemistry [10] or the deposition of heterobinuclear complexes [11] assures the close vicinity of the two components leading to supported alloy particles. Alloy formation has been investigated in several studies and often evidenced using EXAFS [12–16].

Flame synthesis is a one-step preparation method for mixed oxides and supported noble metal catalysts [17]. Compared to conventional vapor-fed flame aerosol synthesis, as used for synthesis of Pt/TiO$_2$ [18], flame spray pyrolysis offers the possibility to use nonvolatile precursors and was applied for synthesis of Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ hydrogenation catalysts [19, 20] as well as for Au supported on TiO$_2$ and SiO$_2$ [21]. Flame synthesis is used on large scale today to produce carbon black, fumed silica and titania pigments. In general, flame synthesis and especially flame spray pyrolysis are continuous, well controllable and versatile processes for the production of a wide variety of nanoparticles [22].

As shown earlier, flame made Pd/La$_2$O$_3$/Al$_2$O$_3$ catalysts show good performance in the combustion of methane and exhibit excellent thermal stability concerning the loss of specific surface area [23]. In this study flame spray pyrolysis was used as a single-step process for the synthesis of bimetallic Pt-Pd catalysts supported on alumina.
4.2 Experimental

4.2.1 Catalyst Preparation

The experimental setup for the synthesis of Pd-Pt/Al₂O₃ catalysts by flame spray pyrolysis has been described earlier [24]. The precursor solution consisted of aluminium(III) sec-butoxide, palladium(II) acetylacetone and platinum(II) acetylacetonate dissolved in a mixture of xylene and acetonitrile (2:1 vol%). The aluminium concentration was kept constant at 0.67 M for all experiments. The liquid precursor mixture was fed at 5 ml/min in the center of a methane/oxygen flame by a syringe pump (Inotech) and dispersed by oxygen (5 L/min), forming a fine spray. The pressure drop at the capillary tip was kept constant at 1.5 bar by adjusting the orifice gap area at the nozzle. The spray flame was surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing, at a radius of 6 mm). The total gas flow rate through this premixed methane/oxygen supporting flame ring was 3.5 L/min with a CH₄/2 O₂ ratio of 0.92. Product particles were collected on a glass fiber filter (Whatmann GF/D, 25.7 cm in diameter) with the aid of a vacuum pump (Busch, Seco SV 1040C). The resulting material was designated as wPdxPt, where w and x denote the weight fraction in percent of Pd and Pt, respectively, and the balance was Al₂O₃. For all samples the total noble metal content was kept constant at 2.5 wt%. The mass fraction of platinum (W) in relation to the total mass of noble metals was defined as .
4.2.2 Catalyst characterization

The specific surface area (SSA) of the as-prepared powders was determined by nitrogen adsorption at 77 K using the BET method (Micromeritics Tristar). The powder X-ray diffraction patterns were recorded with a Bruker D8 advance diffractometer.

For scanning transmission electron microscopy (STEM), 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 (FEI (Eindhoven); field emission cathode, operated at 300 kV). Scanning transmission electron microscopy (STEM) images, obtained with a high-angle annular dark field (HAADF) detector, reveal the metal particles with bright contrast (Z contrast). The focused electron beam was then set on some of the bright points to analyze the ratio Pd:Pt of these particles qualitatively by energy dispersive X-ray spectroscopy (EDXS; detector (EDAX) attached to the Tecnai F30 microscope).

Extended X-ray absorption fine structure (EXAFS) spectroscopy measurements were carried out at beamline X1 at the Hamburger Synchrotronlabor (HASYLAB at DESY, Germany). A Si (311) double crystal was used for monochromatization of the beam. By detuning the crystals to 70 % of the maximum intensity, higher harmonics were effectively eliminated. The measurements were carried out in a continuous-flow reactor cell, which allowed simultaneous gas analysis and structural studies [25, 26]. The as-prepared powders were mounted in a capillary as described earlier [25] and reduced in situ by flowing 5% H$_2$/He at 250 °C.
prior to the measurements. Three ionization chambers were used to measure the incident and outcoming X-ray intensities, located before and after the in situ cell as well as after a Pd foil for energy calibration. The ionization chamber gases (Ar, Kr) and their pressure were adjusted in a way that about 10 % were adsorbed in the first ionization chamber and 40 % in the second and third ionization chamber. EXAFS spectra were taken around the Pd K-edge in the step-scanning mode between 24,000 and 25,800 eV. During dynamic changes (temperature, gas change) faster spectra in the region 24,300 - 24,600 eV were taken in the continuous scanning mode (QEXAFS). The EXAFS function was extracted using the WINXAS 3.0 software [27]. The EXAFS data were fitted in R-space. Scattering amplitudes and phase shifts of the Pd-Pd and the Pd-Pt shell (only first shell) were calculated using the FEFF6.0 code [28].

Noble metal dispersion was determined by CO-pulse chemisorption at 40 ºC using a He flow of 50 ml/min and pulses of 0.5 ml (10 % CO in He) on a Micromeritics Autochem II 2920 unit. Prior to the measurement, all samples were freshly reduced for 1 h at 250 ºC under flowing hydrogen (20 ml/min) and then flushed by He (20 ml/min) at 260 ºC for 90 min. The oxidation behavior of palladium was measured by thermogravimetric analysis (TGA/SDTA851e, LF/1100 ºC, Mettler Toledo AG). The powders were heated in nitrogen to 250 ºC at 10 ºC/min and held at this temperature for 30 min. Then the atmosphere was changed to air and two heating-cooling cycles from 250 ºC to 1050 ºC were recorded with a heating or cooling rate of ±20 ºC/min.

Temperature programmed reduction of PdO by hydrogen was measured
on a Micromeritics Autochem II 2920, equipped with a TCD-detector, by flowing a mixture of 5 % H$_2$ in argon (20 ml/min). The temperature was ramped from -80 to 900 °C with the aid of a liquid nitrogen fed sub-ambient cooler at a heating rate of 10 °C/min. Prior to analysis, palladium was oxidized in flowing oxygen at 500 °C.

Methane oxidation was measured in a conventional fixed-bed flow microreactor at atmospheric pressure. The reactor, consisting of a quartz tube of 5 mm ID, was placed in an electric furnace. A mixture of 5 mg catalyst (100-250 m) and 200 mg quartz sand (100-300 µm) was placed in the reactor and fixed with quartz wool. A thermocouple was inserted in the center of the catalyst bed. A mixture containing 1.0 vol% methane and 4.0 vol% oxygen in helium was flown through the reactor at 100 ml/min. Mass spectrometry (Thermostar, Pfeiffer Vacuum) was used to determine all gas concentrations in the effluent gas stream. The transient behavior and conditioning/deactivation of the catalysts was measured by cycling the temperature several times from 200 °C up to 1000 °C at a heating or cooling rate of ±10 °C/min.
4.3 Results and Discussion

4.3.1 Catalyst Characterization

Bimetallic Pd-Pt catalysts supported on Al$_2$O$_3$ were prepared by single-step flame spray pyrolysis. The specific surface area of all as-prepared powders was around 120 m$^2$/g and not influenced by the noble metal composition. Figure 4.1A shows an STEM image of an as-prepared material, containing 1.5 wt% palladium and 1 wt% platinum. The noble metals form small particles in the range of 1-5 nm on top of agglomerated alumina nanoparticles. EDXS analysis ($d = 2$ nm) of single noble metal particles revealed the coexistence of palladium and platinum in the same particle. After artificial sintering at 1000 °C, the noble metals formed large particles (Figure 4.1B) in the range of the noble metal particle size observed after catalytic combustion [23]. The inset depicts a corresponding EDXS analysis of a single metal particle, showing the presence of Pt and Pd in the same particle after sintering at 1000 °C.

Further evidence for alloy formation of the Pd-Pt particles emerged from EXAFS investigations. The radial distribution functions of the Fourier transformed EXAFS data (Figure 4.2) show that the palladium is in oxidized state after preparation. No contribution at 2.8-3.5 Å is found, which would be characteristic for larger PdO particles (for reference spectra of PdO see for example [29]) or the possible formation of larger, oxidized Pt-Pd particles. Hence, palladium is finely dispersed in the oxide matrix. The EXAFS spectra also did not indicate any metallic palladium in the as-prepared samples. After reduction of the 1.5Pd1Pt
Figure 4.1: STEM images of as-prepared 1.5Pd1Pt (A) and after annealing at 1000 °C (B) with corresponding EDX analysis of an individual Pd-Pt particle.
4.3 Results and Discussion

Figure 4.2: Comparison of Fourier transformed EXAFS data of the 1.5Pd1Pt catalyst before and after reduction in 5%H$_2$/He at 250 °C with the 2.5Pd catalyst and Pd foil.

catalyst with hydrogen, the backscattering of the nearest neighbors of the 1.5Pd1Pt sample differs from the pure 2.5Pd sample, indicating alloying of the Pt-Pd particles. This is supported also by fitting of the EXAFS data of the different samples (Table 4.1, Figure 4.3). Obviously, the Pd-Pt-based particles are alloyed after the reduction procedure. The number of Pt neighbors around the Pd absorber atoms decreases if the concentration of Pt decreases. In addition, both the low coordination number and the absence of higher shells in the EXAFS spectra indicate
a small particle size. The number of nearest neighbors in the first coordination shell is significantly below 12 for both Pd and Pt-Pd samples. The absence of distinct reflections due to Pd or Pt in the XRD pattern of the as-prepared catalysts (not shown) and the STEM investigations (Figure 4.1) give further evidence for the formation of small metal particles. In conclusion, the alloyed Pt-Pd-particles are not formed upon preparation but rather during the reduction in hydrogen. The good dispersion of both Pt and Pd in the matrix probably favors the formation of mixed Pt-Pd particles and not monometallic particles, as also observed when using other preparation methods [15, 30, 31].
Figure 4.3: Experimental and fitted Fourier transformed $k^3$-weighted $(k)$-functions of selected flame-made Pd- and Pd-Pt-based catalysts.
Table 4.1: Structural parameters determined by fitting of EXAFS spectra at the Pd K-edge of selected Pd-Pt/Al$_2$O$_3$ catalysts after their in situ reduction in 5%H$_2$/He

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A$^a$ - Bs$^b$</th>
<th>r$^c$ / Å</th>
<th>N$^d$</th>
<th>$\sigma^{2e}$ / Å</th>
<th>$\Delta E_0^f$ / eV</th>
<th>Residual $^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5Pd1Pt</td>
<td>Pd-Pd</td>
<td>2.75</td>
<td>4.2</td>
<td>0.008</td>
<td>-3.5</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Pd-Pt</td>
<td>2.75</td>
<td>6.0</td>
<td>0.015$^h$</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>2Pd0.5Pt</td>
<td>Pd-Pd</td>
<td>2.75</td>
<td>7.0</td>
<td>0.007</td>
<td>-1.8</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Pd-Pt</td>
<td>2.75</td>
<td>4.0</td>
<td>0.017$^h$</td>
<td>-2.07</td>
<td></td>
</tr>
<tr>
<td>2.5Pd</td>
<td>Pd-Pd</td>
<td>2.75</td>
<td>8.6</td>
<td>0.007</td>
<td>-2.5</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>Pd-Pt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1.5Pd1Pt</td>
<td>Pd-Pd</td>
<td>2.75</td>
<td>5.0</td>
<td>0.0075$^i$</td>
<td>-4.13</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Pd-Pt</td>
<td>2.75</td>
<td>3.6</td>
<td>0.0075$^i$</td>
<td>-0.37</td>
<td></td>
</tr>
<tr>
<td>2Pd0.5Pt</td>
<td>Pd-Pd</td>
<td>2.75</td>
<td>7.0</td>
<td>0.007$^i$</td>
<td>-1.27</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Pd-Pt</td>
<td>2.75</td>
<td>1.5</td>
<td>0.007$^i$</td>
<td>-0.45</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Absorber, $^b$ Backscatterer, $^c$ Distance, $^d$ Coordination number, $^e$ Debye-Waller factor, $^f$ Shift of the energy threshold, $^g$ Quality of fit [27], $^h$ Note the high Debye-Waller factor if that of the Pd-Pt and Pd-Pd shell are not corrected., $^i$ fixing the Debye-Waller factor of the Pd-Pt and the Pd-Pd shell to the same value.
The influence of platinum on the thermal stability of palladium, and vice versa, was investigated by sintering the as-prepared materials at 800 and 1000 °C for 4 hours in air. Figure 4.4 depicts the relative amount of CO chemisorbed on the noble metals after this annealing as a function of the Pt mass fraction (W). After annealing at 800 °C pure platinum sintered strongly, whereas for the only palladium containing sample a lower sintering effect was observed. The addition of very small amounts of Pt to Pd (W = 4%) stabilized the Pd particles and prevented any sintering at 800 °C. Furthermore, Pd stabilized the Pt particles compared
to pure Pt/Al₂O₃. At 1000 °C the noble metals sintered strongly, as shown by a drop in the amount of CO chemisorbed. Corresponding to the results at 800 °C even very small amounts of platinum stabilized the palladium particles, resulting in the smallest metal particles for Pt metal mass fractions between 2 and 14%.

Figure 4.5: XRD pattern of Pd-Pt/Al₂O₃ after annealing at 1000 °C for 4 hours. Peak positions of M₀ (Pd or Pt cubic) and MO (PdO or PtO tetragonal) are given at the bottom.

X-ray diffraction patterns (Figure 4.5) measured after annealing of the materials at 1000 °C showed the formation of crystalline M₀ and MO domains (M = Pd or Pt). A higher Pt mass fraction (W) increased the
amount of crystalline M° and lowered the amount of MO.

Figure 4.6: Temperature programmed reduction (TPR) profiles of bimetallic Pd-Pt/Al₂O₃ after sintering at 1000 °C.

Figure 4.6 depicts TPR profiles of the calcined materials (1000 °C) with the corresponding amounts of consumed and released hydrogen given in Table 4.2. The H₂:Pd ratio of the total amount of consumed hydrogen was similar for all samples (1-1.05) and close to the theoretical value of 1. In all samples palladium was reduced between 0 and 50 °C. The addition of platinum broadened the peaks and shifted the peak maximum to slightly lower temperatures. The release of hydrogen from bulk Pd-H species was observed at around 70 °C, resulting in an increase of
the hydrogen concentration. However, no hydrogen release occurred for Pt mass fractions higher than 4% (2.4Pd0.1Pt). The distortion by the added platinum atoms may lead to smaller palladium domains that are not capable to form bulk palladium hydride species [32]. The broadening of the hydrogen uptake peaks is an additional indication for this behavior as smaller Pd particles tend to show broader signals [23].

Figure 4.7 shows TGA profiles measured in air during the second heating/cooling cycle of as-prepared flame-made Pd-Pt catalysts. Upon heat-
Table 4.2: Temperatures of maximum hydrogen consumption (peak position) and amount of $H_2$ consumed and released during TPR of flame made Pd-Pt/Al$_2$O$_3$ after annealing at 1000 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$1^{st}$ peak pos. (°C)</th>
<th>$2^{nd}$ peak pos. (°C)</th>
<th>$H_2$/Pd ads.$^a$</th>
<th>$H_2$/Pd rel.$^b$</th>
<th>$H_2$/Pd total$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5Pd</td>
<td>22</td>
<td>69</td>
<td>1.22</td>
<td>0.21</td>
<td>1.01</td>
</tr>
<tr>
<td>2Pd0.5Pt</td>
<td>13</td>
<td>65</td>
<td>1.18</td>
<td>0.18</td>
<td>1.00</td>
</tr>
<tr>
<td>1.5Pd1Pt</td>
<td>11</td>
<td>-</td>
<td>1.03</td>
<td>-</td>
<td>1.03</td>
</tr>
<tr>
<td>1Pd1.5Pt</td>
<td>18</td>
<td>-</td>
<td>1.05</td>
<td>-</td>
<td>1.05</td>
</tr>
</tbody>
</table>

$^a$ $H_2$/Pd ratio of consumed hydrogen during reduction (first peak).

$^b$ $H_2$/Pd ratio of released hydrogen from Pd-H (second peak).

$^c$ $H_2$/Pd ratio of the total amount of $H_2$ consumed (consumed - released hydrogen).

ing of pure palladium supported on alumina (2.5Pd), PdO decomposed into Pd$^0$ between 850 - 950 °C and re-oxidized between 540 and 610 °C during cooling, as indicated by a decrease and increase in weight, respectively. The addition of small amounts of platinum resulted in two distinct steps for the reduction of PdO, one in the temperature range of the pure palladium and an additional one at lower temperatures (770 - 810 °C), which increased when more Pt was added. For Pt mass fractions higher than 20% only one reduction step was observed at lower temperatures. This behavior was also reported by others [4] and can be attributed to the promotion of PdO reduction by platinum addition. Concerning re-oxidation of Pd, Pt addition shifted the re-oxidation point towards lower temperatures, and resulted in flattened re-oxidation profiles. This indicates that platinum kinetically inhibits the re-oxidation
of palladium, since the large hysteresis in Pd reduction/re-oxidation is usually attributed to a kinetically inhibited re-oxidation process of palladium [33]. From these results, it can be concluded that platinum addition stabilizes palladium in its reduced form.

4.3.2 Catalytic combustion

The as-prepared bimetallic catalysts were tested towards their deactivation during methane combustion by cycling the temperature 4 times between 200 and 1000 °C. Figure 4.8 depicts the transient behavior in methane combustion of flame-made materials with different Pt mass fractions during cycles 1 and 2. The conditioning attributed to sintering and restructuring of the catalysts during the first cycle, led to significantly different activity profiles for the later cycles. Catalysts with low Pt mass fractions were activated, whereas a high Pt content resulted in a deactivation during the first cycle. In the first cycle, materials with a low Pt mass fraction (W = 20%) showed ”Pd-like” activity profiles with a distinct decrease in methane conversion between 600 and 800 °C, generally attributed to the reduction of PdO into less active Pd [34]. In contrast, catalysts with a higher Pt mass fraction (W = 40%) exhibited ”Pt-like” activity profiles without deactivation due to PdO decomposition. Ersson et al. [4] found a similar transient behavior for bimetallic Pd-Pt catalysts. The conditioning during the first cycle resulted in a change from a ”Pt-like” to a ”Pd-like” profile for the catalyst with a Pt weight fraction of 40% (1.5Pd1Pt). Corroborating the results of thermogravimetric analysis in air (Figure 4.7), platinum stabilized palladium in
Figure 4.8: Transient behavior in methane combustion of bimetallic Pd-Pt catalysts during cycles 1 and 2.
its reduced form and shifted the onset of deactivation (by the PdO→Pd transformation) towards lower temperatures.

Figure 4.9: Deactivation of catalysts with different Pd-Pt ratios as expressed by the temperature of 20% methane conversion ($T_{20}$) during cycles 2-4 (200-1000 °C).

Figure 4.9 depicts the deactivation of bimetallic Pd-Pt catalysts in terms of the temperature needed for 20 % methane conversion ($T_{20}$). After an initial conditioning in a first temperature cycle all catalysts deactivated during the following cycles, indicated by higher temperatures needed for 20 % conversion. This deactivation can be attributed to the sintering of the active palladium particles at the high temperatures of up to 1000 °C.
The addition of platinum slowed down this deactivation process resulting in lower temperatures needed to achieve the same conversion. Different authors observed similar stabilization effects for Pd combustion catalysts made by impregnation techniques and reported a maximum in activity and stability for Pt mass fractions in the range of 20-40% [4, 5, 7, 35]. Here however, a lower platinum mass fraction of 4% turned out to be an optimal compromise between slower deactivation and lower intrinsic activity, due to the lower activity of Pt compared to Pd, and resulted in the highest activity after several cycles. This stabilization is mainly caused by the beneficial effect of platinum on the sintering behavior of the palladium particles containing small amounts of platinum. This is further confirmed by the CO-chemisorption measurements of annealed catalysts (Figure 4.4).

4.4 Conclusions

Flame-spray pyrolysis has been applied for the one-step synthesis of alumina-supported bimetallic Pd-Pt catalysts. These catalysts were tested in the combustion of methane in the temperature range up to 1000 °C. The as-prepared materials consisted of agglomerated alumina nanoparticles on which the metal components are well-dispersed. After reduction the metal constituents formed small bimetallic particles supported on alumina. EDX and EXAFS measurements indicated that the metal particles are alloyed. Platinum influenced the PdO ↔ Pd transformation, favoring palladium in its reduced form. Furthermore, added in small amounts (Pt mass fraction <10%), platinum increased the re-
sistance of the metal particles towards sintering at high temperatures. This stabilization by Pt improved the behavior of the catalysts in the combustion of methane.

References


References


[29] J. D. Grunwaldt, M. Maciejewski and A. Baiker. “In situ X-ray absorption study during methane combustion over Pd/ZrO$_2$ cata-


Unprecedented formation of metastable monoclinic BaCO$_3$ nanoparticles

Abstract

Barium carbonate nanoparticles (50-100 nm) were prepared by flame spray pyrolysis. The rapid quenching during the preparation process resulted in the unprecedented formation of pure monoclinic BaCO$_3$. The as-prepared materials were characterized by electron microscopy, X-ray diffraction as well as by thermogravimetric and differential scanning calorimetric analyses. At ambient conditions the metastable monoclinic phase transformed easily into the thermodynamically stable orthorhombic BaCO$_3$ (witherite) within a few days.

---

5.1 Introduction

Witherite (orthorhombic BaCO$_3$) occurring in nature and formed during conventional precipitation synthesis is the only stable phase of BaCO$_3$ at room temperature. Before complete decomposition into BaO the orthorhombic form undergoes transitions into a hexagonal phase at ca. 810 °C and into a cubic form around 980 °C [1–4]. Additionally, monoclinic BaCO$_3$ stabilized by a partial anion substitution of CO$_3^{2-}$ in the host lattice by SO$_4^{2-}$ is accessible by rapid quenching a mixture of BaCO$_3$ and BaSO$_4$ from 800 °C into liquid nitrogen [5]. The metastable monoclinic phase was also observed for BaCO$_3$ particles supported on Al$_2$O$_3$ as applied in nitrogen oxides storage-reduction (NSR) catalysts [6]. Here, flame spray pyrolysis (FSP) was used for the synthesis of pure BaCO$_3$ nanoparticles. FSP is usually applied for the preparation of metal and metal-oxide nanoparticles [7, 8]. Recently it has been shown, that also nanosized salts such as carbonates, phosphates and halogenides can readily be made by flame synthesis [9–11].

5.2 Experimental

Barium carbonate was prepared by flame spray pyrolysis, using barium (II) 2-ethylhexanoate (75% in 2-ethylhexanoic acid, Alfa Aesar, 99.8%) dissolved in ethanol (Alcosuisse, 98%) as precursor (Ba concentration 0.2 M). The liquid mixture was fed at 5 ml/min into a spray nozzle, dispersed by oxygen (5 L/min, pressure drop 1.5 bar at capillary tip) and ignited by a surrounding premixed methane/oxygen flame [12]. The
as-prepared particles were collected on a glass fibre filter by the aid of a vacuum pump. The specific surface area was determined according to the BET method on a Micromeritics Tristar. The BET particle diameter ($d_{BET}$) was calculated according to $d_{BET} = 6/(SSA \times \rho)$ where SSA and $\rho$ stand for the specific surface area and density, respectively. XRD analysis was carried out on a Siemens D5000 powder X-ray diffractometer between 16 and 65° 2Θ with a step of 0.01° and 2 s/step. 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 CM30 ST (Philips, LaB6 cathode, operated at 300 kV). Thermal analysis (TA) combined with mass spectrometry (MS) was carried out on a Netzsch STA 409 thermoanalyzer. The thermogravimetric (TG) and differential scanning calorimetric signals (DSC) were recorded during heating with a rate of 10 °C/min in the atmosphere of pure Ar (flowing rate 50 ml/min). The composition of the gas phase was monitored by the OmniStar (Pfeiffer Vacuum) quadrupole mass spectrometer connected to the thermoanalyzer. The amount of evolved CO$_2$ resulting from the evolution of adsorbed species was determined by PulseTA technique [13] by the comparison of the integral intensity of the CO$_2$ (m/z = 44) with the integral intensities of 1 ml pulses of CO$_2$ injected after total decomposition of the sample. Three as-prepared samples were calcined with a rate of 10 K/min to 600, 261 and 102 °C, respectively and analyzed after fast cooling by XRD.
Figure 5.1: Transmission electron micrograph of flame-made BaCO$_3$ nanoparticles. The inset depicts the corresponding electron diffraction pattern.
5.3 Results and Discussion

Table 5.1: Crystal data for monoclinic BaCO$_3$

<table>
<thead>
<tr>
<th>Material</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCO$_3$ (flame-made)</td>
<td>6.863</td>
<td>5.276</td>
<td>4.520</td>
<td>154.89</td>
</tr>
<tr>
<td></td>
<td>$\beta$ = 108.89°</td>
<td>$V = 154.89 \text{ Å}^3$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$Z = 2, P2_1/m$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$ stabilized BaCO$_3$ a:</td>
<td>6.913</td>
<td>5.295</td>
<td>4.545</td>
<td>158.32</td>
</tr>
<tr>
<td></td>
<td>$\beta = 107.89°, V = 158.32 \text{ Å}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Z = 2, P2_1/m$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a from Nishino et al. [5].

5.3 Results and Discussion

The as-prepared material consisted of non-agglomerated crystalline BaCO$_3$ nanoparticles (Fig. 5.1). TEM analysis further revealed the formation of “bean-like” shaped particles with length of about 100 nm and width of approximately 50 nm. The corresponding BET-particle diameter for a spherical particle was 70 nm (specific surface area (SSA): 20.5 m$^2$/g) in good agreement with the TEM observations. Figure 5.2A depicts the XRD pattern of as-prepared BaCO$_3$ 1 hour after its preparation. Crystalline, monoclinic BaCO$_3$ was observed with only traces of the stable orthorhombic form. The electron diffraction pattern (inset Fig. 5.1) revealed, however, the presence of orthorhombic BaCO$_3$ indicating that the monoclinic phase is not preserved during TEM analysis and rapidly transforms into orthorhombic BaCO$_3$.

As BaCO$_3$ would not be stable and decompose into BaO and CO$_2$ at the high temperatures in the flame, it can be assumed that in a first step BaO particles are formed. Later downstream at lower temperatures and exposed to a significant amount of CO$_2$ from the combustion process
Figure 5.2: A: XRD pattern of as-prepared (a.p.) BaCO₃. The unlabeled reflections belong to the monoclinic BaCO₃. Only traces of the orthorhombic phase ("O") were detected. B: XRD patterns of BaCO₃ as a function of time (marked in hours on the curves). Within 95 hours complete transformation of monoclinic (M) to orthorhombic (O) BaCO₃ takes place.
BaO transforms into BaCO$_3$. At 1300 °C the equilibrium CO$_2$ partial pressure for the reaction BaO + CO$_2$ ↔ BaCO$_3$ would be 0.1 bar, a reasonable value for CO$_2$ in the flame [14]. A temperature of 1300 °C is reached at about 15 cm above the nozzle [12]. The formation of BaCO$_3$ instead of BaO in the flame process is not surprising as flame synthesis resulted also in the formation of CaCO$_3$ [10], which would decompose into CaO at even lower temperatures than BaCO$_3$ [14].

![Figure 5.3: Degree of the transformation of monoclinic into orthorhombic barium carbonate. The degree $\alpha$ was calculated using the integral intensities of two monoclinic (M1, $d = 4.2534$ Å, and M2, $d = 4.1166$ Å) and two orthorhombic (O1, $d = 3.7236$ Å, and O2, $d = 3.6604$ Å) reflections.](image-url)
Table 7.1 depicts the unit cell parameters for flame-made, monoclinic BaCO$_3$ in comparison with the data reported for SO$_4^{2-}$ stabilized monoclinic BaCO$_3$ [5]. Despite the smaller cell volume of 154.89 Å$^3$ instead of 158.32 Å$^3$, the crystal structure was the same. The absence of larger SO$_4^{2-}$ groups in the crystal structure leads to smaller unit cell volume. At ambient conditions the monoclinic phase transformed into the orthorhombic BaCO$_3$ (Fig. 5.2B). Figure. 5.3 shows the detailed evolution of this transformation by monitoring the intensity of monoclinic and orthorhombic reflections of BaCO$_3$. Exposed to air at room temperature the monoclinic BaCO$_3$ completely transformed into the orthorhombic form within 4 days.

Thermogravimetric (TG) and differential scanning calorimetric (DSC) results of as-prepared BaCO$_3$ are shown in Figure. 5.4. The amount of CO$_2$ evolved during decomposition of BaCO$_3$ into BaO in the range 800-1350 °C was determined by quantification of the m/z=44 signal. The amount of CO$_2$ was equivalent to 99.3% of the stoichiometric amount of CO$_2$ in the sample. Three endothermal events were observed on the DSC curve. The first and the second originate from the polymorphic transformation of the orthorhombic into hexagonal phase (818 °C) followed by the transformation of hexagonal into cubic phase (981 °C) [1, 2]. The peak at 1123 °C indicates the maximal rate of the endothermic barium carbonate decomposition. No distinct DSC signal was observed for the transformation of monoclinic into the orthorhombic phase. The XRD analysis of monoclinic BaCO$_3$ after heating up to 600, 261 and 102 °C, respectively, has shown that already upon heating to 102 °C only orthorhombic and no monoclinic BaCO$_3$ could be ob-
Figure 5.4: Thermal analysis and XRD investigations of monoclinic BaCO₃. A: Change of the mass (TG) and thermal effects (DSC) recorded during heating of BaCO₃ in Ar with a rate of 10 K/min. The samples analyzed later by XRD were collected after separate runs stopped at 600 (2), 261 (3) and 102 °C (4). B: XRD patterns of BaCO₃ heated up to the temperatures marked on TG curve.
served by XRD (Fig. 5.4B). This shows clearly the very unstable nature of the monoclinic phase. The unique formation of this phase is traced to the rapid quenching of the flame-made particles undergoing a steep temperature profile from ca. 2000 °C down to 300 °C within a few milliseconds [7, 12]. In contrast in the conventional preparation process via precipitation the stable orthorhombic BaCO$_3$ is formed.

5.4 Conclusions

Monoclinic BaCO$_3$ nanoparticles (50-100 nm) were prepared by flame spray pyrolysis. As a result of the rapid quenching during the flame synthesis process, monoclinic BaCO$_3$ was formed without the addition of any stabilizing sulphate anions. At ambient conditions the monoclinic phase transformed into orthorhombic BaCO$_3$ within 4 days. Although no distinct DSC signal could be observed for this transformation, only orthorhombic BaCO$_3$ was found after heating the powder up to 100 °C.

References


Two-nozzle flame synthesis of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} for NO\textsubscript{x}-storage-reduction \textsuperscript{1}

Abstract

A novel two-nozzle flame spray pyrolysis (FSP) process has been developed for one-step preparation of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} particles as used for NO\textsubscript{x} storage-reduction (NSR) catalysts. The materials were characterized by transmission electron microscopy, CO chemisorption, nitrogen adsorption, X-ray diffraction, and temperature programmed decomposition and tested for their NO\textsubscript{x} storage behavior. The use of two separate nozzles, one as aluminium and the other as 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. In contrast, using a single nozzle process resulted in Al\textsubscript{2}O\textsubscript{3} particles with amorphous Ba species with negligible NO\textsubscript{x} storage capacity. Increasing the internozzle distance resulted in late mix-

ing of the two flame-products and increased the amount of crystalline BaCO₃. At ambient conditions, as-prepared monoclinic BaCO₃ transformed into orthorhombic BaCO₃. In contrast to impregnated catalysts, no "bulk-like" BaCO₃ (decomposition above 900 °C, HT-BaCO₃) and even at high Ba loadings, only BaCO₃ showing a low thermal stability (decomposition below 900 °C, LT-BaCO₃) was formed. These structural differences of flame-made and conventionally prepared catalysts affected strongly their NOₓ storage efficiency. The absence of the HT-BaCO₃ phase in flame-made catalysts results in improved NOₓ storage potential at high Ba-loadings. Studies with repeated NSR cycles however, indicated a possible conversion of the more active LT-BaCO₃ phase into the less active HT-BaCO₃ with flame-made catalysts leading to some decrease in storage efficiency upon repetitive use.
6.1 Introduction

A novel, two-nozzle flame process was developed for synthesis of Pt/Ba/Al$_2$O$_3$ in one step allowing controlled mixing of two particle streams. Flame aerosol and in particular flame spray technologies are versatile and continuous processes for production of a variety of ceramic nanoparticles [1–3]. In contrast to spray pyrolysis, flame spray pyrolysis (FSP) is based on combustible precursor solutions, which provide the energy for the process [3–5]. A metal containing precursor solution is dispersed, ignited and combusted. After evaporation and conversion of the metal precursor, particles are formed in the gas phase [3, 6].

Supported noble metal catalysts (i.e. Pt/Al$_2$O$_3$) consisting of Pt particles (<5 nm) finely dispersed on Al$_2$O$_3$ particles (10-40 nm) have been made by FSP [7]. Recently, FSP has been also successfully applied for the preparation of platinum supported on ceria/zirconia [8] or titania resulting in Pt clusters down to less than 2 nm for Pt loadings of 5 wt% by additional rapid quenching of the flame [9]. In general, flame-made materials are nonporous and only the external surface of the nanoparticles contributes to the high surface area [7] resulting in materials with good thermal stability [10, 11]. In the case of mixed metal oxides it is rather difficult to control the distribution of two or more components in the material. As temperatures during synthesis are very high (>2000 °C) usually the thermodynamically most favored product is formed, i.e. homogeneous nanoparticles (i.e. YAlO$_3$ [12], Y$_2$O$_3$/ZrO$_2$ [13], mullite [14] and perovskite structures [15]) or segregated phases of different species (i.e. ZnO in SiO$_2$ [16] and Al$_2$O$_3$/TiO$_2$ [17]).
The Pt/Ba/Al\textsubscript{2}O\textsubscript{3} material is of particular interest as NO\textsubscript{x} storage-reduction catalyst (NSR) for engines operating under lean conditions [18, 19]. A decade ago, Toyota proposed the NO\textsubscript{x} storage-reduction concept (NSR) for the NO\textsubscript{x} abatement of lean-fuel engines [20]. According to the NSR concept, NO\textsubscript{x} is stored under lean conditions in the form of alkali or alkaline-earth nitrates (in particular Ba(NO\textsubscript{3})\textsubscript{3}) and reduced over a noble metal into N\textsubscript{2} during fuel rich periods [21]. Generally these catalysts are prepared by wet impregnation of an alumina support from aqueous solutions of barium and platinum precursors [21]. Recently it has been shown, that different Ba phases of impregnated materials strongly affect the NO\textsubscript{x} storage capacity of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} and BaCO\textsubscript{3} decomposing at low temperatures, the so-called LT-BaCO\textsubscript{3} has been identified as the most active Ba species in the NO\textsubscript{x} storage process [22, 23].

Compared to the conventional single nozzle setup during FSP [3], the present stereoscopic two-nozzle setup adds further flexibility for the control of important flame parameters, such as temperature and concentration fields, that affect particle formation, and affords excellent control of particle mixing at the nano level in multicomponent systems. Here we show how a two-nozzle system can be beneficially used to control the structure of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalysts leading to enhanced NO\textsubscript{x} storage behavior.
6.2 Experimental

6.2.1 Preparation Procedure

The setup for synthesis of Pt/Ba/Al$_2$O$_3$ consisted of two separate FSP nozzles, each able to disperse and ignite a liquid precursor solution (Figure 6.1). The angle between the two nozzles (\(\varphi\)) was fixed at 120° and the internozzle distance between the angle tip and each nozzle center (d) was varied symmetrically between 3 and 7 cm. The individual spray nozzle has been described earlier in detail [24].

The Al precursor solution was fed at 5 ml/min through the first nozzle and the Pt/Ba precursor solution at 3 ml/min through the second by syringe pumps (Inotech). Each sprayed solution was dispersed by 5 L/min oxygen (PanGas, 99.95%) forming two fine sprays. Both sprays were surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing, at a radius of 6 mm). The gas flow rates of these two individually premixed methane/oxygen supporting flames were 3.5 L/min each with a CH$_4$/O$_2$ ratio of 0.46. Product particles were collected on a glass fiber filter (Whatman GF/D, 25.7 cm in diameter) with the aid of a vacuum pump (Busch, Seco SV 1040C).

For the two nozzle FSP two separate precursor mixtures were prepared, one containing the Al precursor and the other containing the Pt and Ba precursors. The aluminum precursor solution consisted of aluminum (III) tri-secbutoxide (Alfa Aesar, 95%) dissolved in a 2:1 vol% mixture of diethylene glycol monobutyl ether (Fluka, 98%) and acetic anhydride (Riedel de-Han, 99%). The Al concentration was kept con-
stant at 0.5 mol/L. For the Pt/Ba precursor solution, barium (II) 2-ethylhexanoate (75% in 2-ethylhexanoic acid, Alfa Aesar, 99.8%) and platinum (II) acetylacetonate (Strem, 98%) were dissolved in ethanol (Alcosuisse, 98%). The barium and platinum concentrations were adjusted for the desired Ba and Pt content in the final product, respectively.

For comparison Pt/Ba/Al$_2$O$_3$ powder was produced also by standard, one-nozzle FSP with precursor feed rate 5 ml/min and oxygen dispersion gas flow rate 5 L/min. In that precursor solution aluminum (III) tri-sec-butoxide, barium (II) 2-ethylhexanoate (Aldrich, 98%) and platinum (II) acetylacetonate were dissolved in toluene (Al = 0.5 mol/L).

Unless otherwise stated, the nominal Pt:Ba:Al$_2$O$_3$ weight ratio in the feed was 1:20:100.

For comparison Pt/Ba/Al$_2$O$_3$ was prepared by incipient wetness impregnation using Pt(NH$_3$)$_2$(NO$_2$)$_2$ and Ba(CH$_3$COO)$_2$ as precursors, and commercial γ-Al$_2$O$_3$ (OMG, B.E.T. surface area 210 m$^2$/g) as support. The detailed preparation procedure has been described in a preceding study [22]. As prepared samples with a Pt content of 1 wt% were dried for 12 hrs at 80 °C and then calcined at 500 °C for 2 hrs, all in air. After calcination the samples were impregnated with Ba(CH$_3$COO)$_2$ solutions affording nominal Ba loadings of 4.5, 9, 16.7, 22 and 28 wt. %, respectively, and then dried for 12 hrs in air at 80 °C.
Figure 6.1: Schematic of the flame spray pyrolysis setup using two separate nozzles. The image shows two flames producing Pt/Ba/Al$_2$O$_3$ (blue flame (left): Al, yellow-greenish flame (right): Pt and Ba).
Figure 6.2: TEM-images of flame-derived Pt/Ba/Al$_2$O$_3$ made with one nozzle (A) and 2 nozzles at $d = 6$ cm and low enthalpy solvent (B). The corresponding ESI mappings of Ba are shown as a red overlay.
6.2.2 Materials characterization

The specific surface area (SSA) of the as-prepared powders was determined by nitrogen adsorption at 77 K using the BET method (Micromeritics Tristar). The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 advance diffractometer in step mode ($2\Theta = 15$-$75^\circ$ with a step size of 0.04$^\circ$ and a scan speed of 0.48 $^\circ$/min. The mass fraction of monoclinic BaCO$_3$ (ICSD collection code: 63257) and witherite (ICSD: 15196) was derived from the corresponding XRD-patterns based on the fundamental parameter approach and the Rietveld method using the software TOPAS [25].

Platinum dispersion was determined by CO-pulse chemisorption at 40 $^\circ$C with 50 ml/min He and pulses of 0.5 ml (10% CO in He) on a Micromeritics Autochem II 2920 unit. Prior to dispersion analysis all samples were freshly reduced for 1 h at 250 $^\circ$C under flowing hydrogen (20 ml/min) and then flushed by He (50 ml/min) at 260 $^\circ$C for 90 min. To calculate the metal dispersion, an adsorption stoichiometry of Pt/CO = 1 was assumed [26].

Temperature programmed decomposition (TPD) of BaCO$_3$ was measured with 35 mg powder on a Micromeritics Autochem II 2920 in a helium flow (20 ml/min) from 50 to 1000 $^\circ$C at 10 $^\circ$C/min. The gas phase composition was monitored by a mass spectrometer (Thermostar, Pfeiffer Vacuum). After each experiment the CO$_2$ signal (M/Z = 44) was calibrated by injecting a well defined pulse of CO$_2$ (0.35 ml).

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 (FEI (Eindhoven); field emission cathode, operated at 300 kV). TEM images were recorded with a slow-scan CCD camera. An energy filter (Gatan imaging filter, GIF), which is installed below the Tecnai 30 FEG, allows recording element specific images (elemental maps) of barium (Ba-L edge at an energy loss = 781 eV) by means of the electron spectroscopic imaging (ESI) technique [27].

NO\textsubscript{x} storage measurements were carried out on a Netzsch STA 409 thermoanalyzer which was connected to valve device enabling pulse thermal analysis (Pulse TA) [28]. The composition of the gas phase was monitored by a ThermoStar Pfeiffer Vacuum GSD 301 O1 mass spectrometer, which was connected to the thermoanalyzer by a heated (ca. 200 °C) stainless steel capillary. Prior to each experiment the samples were calcined in 20 % O\textsubscript{2}/He at 500 °C (temperature ramp of 10 °C/min) for 2 hrs. Cooling was conducted in a controlled atmosphere as well.

NO\textsubscript{x} storage tests were performed at 300 °C in a 5 % O\textsubscript{2}/He atmosphere, with repeated 1 cm\textsuperscript{3} NO pulses injected into a carrier gas stream till saturation (maximal mass uptake) was reached. After saturation the amount of stored NO was quantified by monitoring the amount of evolved NO (M/Z = 30) from thermal decomposition of Ba(NO\textsubscript{3})\textsubscript{2} during heating the in He up to 1000 °C at 10 °C/min. The M/Z = 30 signal was calibrated by injecting a pulse of NO (1 ml) after each experiment.

NO\textsubscript{x} storage-reduction (NSR) in an inert atmosphere was performed at 300 °C in He with 1 cm\textsuperscript{3} C\textsubscript{3}H\textsubscript{6} pulses injected alternatively with a certain number of NO/O\textsubscript{2} pulses. NSR in the presence of oxygen was tested at 300 °C in a 8000 ppm O\textsubscript{2}/He atmosphere.
6.3 Results and Discussion

Figure 6.1 shows a stereoscopic two-nozzle FSP unit producing Al₂O₃ particles on the left burner (blue flame) and Pt/Ba in the right one (yellow-green flame). The yellow-green color is characteristic for barium. The use of two nozzles strongly altered the structural properties of the Ba containing phase. Figure 6.2 shows TEM images of flame-made Pt/Ba/Al₂O₃ using one (A) and two nozzles (B), respectively. The Ba-mapping as measured by ESI of the corresponding TEM pictures is shown as a red overlay. The conventional single nozzle FSP process resulted in the distribution of Ba over all the Al₂O₃ nanoparticles (Figure 6.2A), whereas the material prepared with two nozzles consisted of distinct BaCO₃ particles (10-30 nm) that were dispersed within the Al₂O₃ particles (Figure 6.2B).

When the internozzle distance is increased, the mixing of the Al- and Ba-laden flames occurs further downstream at lower temperatures and later particle formation stages reducing the high temperature residence time of particles and the product particles size [29]. One can see that the two flame tips come in contact where the respective flame-products start to mix (Figure 6.1). Considering that during FSP ceramic particle formation starts typically below the middle of the visible part of the flame [29], both alumina and barium species formation has been well advanced by the time the two flames meet. In contrast, noble metal particles form further downstream [9] and it is quite likely that Pt formation may take place near the point of flame mixing. This means that the Al and Ba precursors have evaporated separately in the two flames. So, Al- and Ba-
containing particles have formed individually. At the point of mixing the two sorts of particles only agglomerate and do not sinter into a single particle as lower temperatures prevail late in the flame[9]. In contrast to this, the one nozzle FSP process, where Al and Ba evaporate and form in the same flame, leads to particles consisting of both Al and Ba (Figure 6.2A) by subsequent sintering and recombination of Al and Ba particles at the high temperatures.

Figure 6.3: X-ray diffraction patterns of as-prepared Pt/Ba/Al$_2$O$_3$ made with either one nozzle or two nozzles at $d = 3$ or $7$ cm.
6.3 Results and Discussion

Figure 6.4: XRD patterns showing the transformation of monoclinic BaCO$_3$ into the thermodynamically more stable witherite as a function of time (Pt:Ba:Al$_2$O$_3$ = 1:50:100, d = 6 cm). The inset shows the corresponding amounts of monoclinic and orthorhombic BaCO$_3$ over time.

Powder prepared with a single FSP-nozzle consisted of crystalline γ-Al$_2$O$_3$ and no crystalline Pt- or Ba-species could be detected (Figure 6.3). Considering the low Pt content (< 1 wt%) this was expected for platinum [7]. Only amorphous Ba species were present. In contrast to this, crystalline BaCO$_3$ was formed with two nozzles (Figure 6.3): monoclinic and orthorhombic BaCO$_3$ (witherite) along with γ-Al$_2$O$_3$. The
fraction of crystalline BaCO$_3$ increased with increasing internozzle distance (d). As BaCO$_3$ would not be stable and decompose into BaO and CO$_2$ at the high temperatures in the flame (>1500 °C), it can be assumed that in a first step BaO particles are formed. Later downstream at lower temperatures and exposed to a significant amount of CO$_2$ from the combustion process BaO transforms into BaCO$_3$. At 1300 °C the equilibrium CO$_2$ partial pressure for the reaction BaO + CO$_2$ $\leftrightarrow$ BaCO$_3$ would be 0.1 bar, a reasonable value for CO$_2$ in the flame [30]. A temperature of 1300 °C is reached at about 15 cm above the nozzle [9, 31]. The formation of BaCO$_3$ instead of BaO in the flame process is not surprising as flame synthesis resulted also in the formation of CaCO$_3$ [32], which would decompose into CaO at even lower temperatures than BaCO$_3$ [30].

At ambient conditions the metastable monoclinic BaCO$_3$ of the as-prepared material was transformed into the thermodynamically stable orthorhombic form (witherite) [33, 34]. Figure 6.4 depicts this transformation for a flame-made powder (Pt:Ba:Al$_2$O$_3$ = 1:50:100, d = 6 cm). Monoclinic BaCO$_3$ was transformed completely into pure orthorhombic BaCO$_3$ (witherite) over a time period of approximately 1 month. The formation of this metastable monoclinic phase was also observed for unsupported flame-made BaCO$_3$ and can be attributed to the rapid quenching during flame synthesis [35]. In general, the steep cooling during flame synthesis often results in metastable phases or high temperature modifications as reported e.g. for ZrO$_2$ [36] or Y$_2$O$_3$ [37].

Figure 6.5 shows the BaCO$_3$ decomposition as measured by CO$_2$-TPD (M/Z = 44) for powders made with one nozzle and two nozzles placed
Figure 6.5: TPD CO$_2$ evolution profiles during decomposition of BaCO$_3$ for as-prepared Pt/Ba/Al$_2$O$_3$ from one or two nozzles at internozzle distance (d) of 3 and 6 cm.
Figure 6.6: Relative amount of Ba in the form of BaCO$_3$ as a function of internozzle distance (d) for Pt/Ba/Al$_2$O$_3$. Increasing d resulted in later mixing of Ba with Al at lower temperatures favoring less interaction of Ba with Al that limits the formation of BaCO$_3$. For this reason Pt/Ba/Al$_2$O$_3$ prepared with one nozzle contained virtually no BaCO$_3$. 
at different distances. The CO₂ evolution below 300 °C corresponds to CO₂ desorption from the particle surface. The peaks between 200 and 400 °C can be attributed to combustion of carbon-containing impurities with some residual oxygen as the CO₂ evolution was accompanied by water evolution (M/Z = 18). The main peak occurring at about 600 °C arises from BaCO₃ decomposition into BaO and CO₂. This temperature is much lower than that of bulk BaCO₃ decomposing between 900 and 1200 °C [22]. For all two-nozzle FSP-made Ba-containing powders only the so-called LT-BaCO₃ (T_d < 900 °C) and no HT-BaCO₃ (T_d > 900 °C) was observed [22]. Particles made with one nozzle showed CO₂ evolution only from desorption of surface-CO₂-species and virtually nothing from BaCO₃ decomposition. At increased internozzle distances more CO₂ evolved consistent with XRD observations (Figure 6.3).

Figure 6.6 depicts the relative amount of Ba in the form of BaCO₃ for Pt/Ba/Al₂O₃ prepared with one and two nozzles. The amount of BaCO₃ was derived from TPD profiles (Figure 6.5) by integrating the amount of CO₂ evolved above 400 °C to distinguish from CO₂ desorption. Figure 6.6 clearly shows that more BaCO₃ is formed when using the two-nozzle system. The amount of BaCO₃ increased with the internozzle distance up to 5 cm and levelled off close to the theoretical maximum.

Figure 6.7 shows the Pt dispersion and the specific surface area for Pt/Ba/Al₂O₃ prepared with either one nozzle or two nozzles as a function of the internozzle distance (d). The specific surface area of the product particles was hardly affected by the different nozzle geometries and the surface area increased only slightly with larger internozzle distances, indicating a little effect of the second flame on the Al₂O₃ particle
formation process. In contrast, increasing the internozzle distance \((d)\) the Pt dispersion increased from 56% \((d = 3\) cm\) up to 75% \((d = 7\) cm\). This is attributed to shorter Pt residence times at high temperatures as the later mixing of the two flames reduces the temperature encountered by Pt. As Pt particles form later at lower process temperatures compared to the \(\text{Al}_2\text{O}_3\) particles [9], the Pt dispersion is more affected by the additional heat contribution of the second flame at lower internozzle distance.

The influence of the previously discussed structural differences of one- or

**Figure 6.7:** Platinum dispersion and specific surface area of \(\text{Pt/Ba/Al}_2\text{O}_3\) made by FSP with either one or two nozzles as a function of internozzle distance \((d)\).
Figure 6.8: NO<sub>x</sub> storage behavior of flame-derived Pt/Ba/Al<sub>2</sub>O<sub>3</sub> made with one and two nozzles (d = 6 cm) as measured gravimetrically by injecting pulses of NO into 5vol% O<sub>2</sub>/He. MS trace (m/z = 30) indicating NO pulses in the outlet gas is shown at the bottom.

two-nozzle-made Pt/Ba/Al<sub>2</sub>O<sub>3</sub> on the NO<sub>x</sub> storage behavior is shown in figure 6.8. The NO<sub>x</sub> uptake was monitored gravimetrically and results in a mass increase of the catalysts by the formation of Ba(NO<sub>3</sub>)<sub>2</sub> according to BaCO<sub>3</sub> + 2 NO<sub>2</sub> ↔ Ba(NO<sub>3</sub>)<sub>2</sub> + CO<sub>2</sub>. A high mass increase and thus a significant storage of NO<sub>x</sub> in the form of Ba(NO<sub>3</sub>)<sub>2</sub> was observed for Pt/Ba/Al<sub>2</sub>O<sub>3</sub> made with two nozzles (3.6 wt%). In contrast, the powder made with one nozzle exhibited a very low mass uptake coming mainly
from the adsorption of NO$_x$ on the alumina surface. Therefore, it is evident that the formation of individual BaCO$_3$ particles as achieved by the two-nozzle process is crucial for the ability of the catalyst to store NO$_x$ in the form of Ba(NO$_3$)$_2$. This is in agreement with the observations for conventionally prepared catalyst, where the formation of BaAl$_2$O$_4$ at high temperatures leads to the loss of NO$_x$ storage capacity [38, 39]. A thorough investigation of the NO$_x$ storage and reduction behavior of flame-made Pt/Ba/Al$_2$O$_3$ concerning the influence of Ba content and nozzle setup in comparison with impregnated catalysts will be presented in a forthcoming study.

![Figure 6.9: BET specific surface area and platinum dispersion as a function of the Ba content of Pt/Ba/Al$_2$O$_3$ made with two-nozzle FSP (d = 6 cm).](image-url)
The influence of Ba content on the structural properties was investigated with powders consisting of Pt:Ba:Al$_2$O$_3$ = 1:x:100 with x ranging from 0 up to 50. Figure 6.9 shows the specific surface area and the Pt dispersion as a function of the Ba content (two nozzles at d = 6 cm). Compared to pure Pt/Al$_2$O$_3$, the addition of a small amount of Ba (4.6 wt% Ba) reduced the specific surface area from 155 to 133 m$^2$/g. However, adding more Ba had hardly any influence on the specific surface area. This is in contrast to impregnated Ba/Al$_2$O$_3$ catalysts, where the addition of Ba results in a high loss in specific surface area by clogging the pores of the support [40]. Flame-made materials are usually non-porous and the high surface area comes only from the external surface of the nanoparticles [7]. For Pt/Ba/Al$_2$O$_3$ made with two spray nozzles, mainly Al$_2$O$_3$ contributes to the surface area. As the Al$_2$O$_3$ and BaCO$_3$ particles are formed separately no clogging occurs and the high surface area is retained.

The Pt dispersion increased with higher Ba contents (Figure 6.9). A large difference in Pt particle size was observed when changing the Ba content from 0 to 4.6 wt%. The Pt dispersion of no Ba containing Pt/Al$_2$O$_3$ made with two nozzles was much lower than of Pt/Al$_2$O$_3$ made with one nozzle and similar Pt content as reported earlier [7]. For the Pt/Al$_2$O$_3$ powder made with two nozzles, Pt particles were formed separately in one flame without any Ba particles present. Noble metals tend to form larger particles (>20 nm) in the absence of a support [41]. If no Ba particles are present in the Pt containing flame, the Pt particle growth is not stopped until coagulation with Al$_2$O$_3$ particles from the other flame and so larger Pt particles are observed. In contrast, in
Ba containing powders the Pt particle growth is arrested on the BaCO$_3$ particles. For comparison a Pt/BaCO$_3$ powder was prepared containing no Al$_2$O$_3$ (Pt:Ba = 1:20). The Pt dispersion of this material was slightly lower (57%) than of a comparable Pt/Ba/Al$_2$O$_3$ made with two nozzles (i.e. 70% for d = 6 cm). This indicates that a small fraction of Pt is formed on the Al$_2$O$_3$ particles. It can be expected, that co-formation of BaCO$_3$ and Pt in one flame assures a close proximity of the Pt and BaCO$_3$ particles in the final product. This close contact between the two active species may be beneficial for NO$_x$ storage reduction [38].

Figure 6.10 depicts CO$_2$ evolution profiles from Pt/Ba/Al$_2$O$_3$ made at d = 6 cm containing different amounts of Ba. The experiments were carried out after complete transformation of monoclinic BaCO$_3$ into witherite, approximately 1 month after preparation. With higher Ba loadings the amount of CO$_2$, which evolved from BaCO$_3$ decomposition, increased. The relative amount of Ba in the form of BaCO$_3$ was always around 80% independent of Ba loading. Interestingly, not even for powders containing up to 28.9 wt% Ba the formation of so-called bulk or HT-BaCO$_3$ was observed. All materials made with the two-nozzle FSP process showed mainly formation of LT-BaCO$_3$. This behavior differs from that of Pt/Ba/Al$_2$O$_3$ catalysts prepared by impregnation, where no BaCO$_3$ was observed for low Ba contents and HT-BaCO$_3$ was the main form of Ba for high Ba loadings [22].

The investigation of the influence of the different distribution of BaO, LT- and HT-BaCO$_3$ in flame-made (FM) and impregnated (WI) catalysts on the efficiency of NO$_x$ storage was the next stage of our studies. For this comparison flame-made catalysts with different Ba content pre-
Figure 6.10: TPD CO$_2$ evolution profiles from BaCO$_3$ of flame-made Pt/Ba/Al$_2$O$_3$ with different Ba loadings (d = 6 cm). TPD was measured 1 month after sample preparation (Ba content (%) is shown on the curves). The inset depicts the amount of Ba in the form of BaCO$_3$ as derived from integrating the TPD profiles above 400 °C.
pared with two nozzles at 6 cm were used. As HT-BaCO\textsubscript{3} was proven to be responsible for the limited NO\textsubscript{x} storage efficiency in impregnated catalysts [23], the absence of this phase in flame-made catalysts should result in a better performance at higher Ba-loadings. To test this hypothesis catalysts calcined up to 500 °C were exposed at 300 °C to NO pulses in 5% O\textsubscript{2}/He atmosphere till saturation of the active storage sites was achieved.

NO\textsubscript{x} storage over BaCO\textsubscript{3}-containing catalysts occurs according to the following global reaction:

$$BaCO_3 + 2NO + \frac{3}{2}O_2 = Ba(NO_3)_2 + CO_2$$ (6.1)

therefore the mass changes observed during this process result from two counteracting processes: (i) a mass loss due to CO\textsubscript{2} evolution and (ii) a mass gain due to barium nitrate formation. A direct comparison of the TG curves recorded during NO\textsubscript{x} storage is presented in Fig. 6.11. Note that saturation of the active sites by NO\textsubscript{x} was approached in flame-made catalysts after the third NO pulse, while much more NO pulses were required for impregnated catalysts. The monitored MS signal m/z = 44 (not shown) revealed that the end of evolution of CO\textsubscript{2} corresponds to the end of the mass change for FM catalysts. This indicated a correlation between the saturation of active sites and the consumption of the LT-BaCO\textsubscript{3} phase. The same relationship between TG and CO\textsubscript{2} signals was previously observed for impregnated samples [23]. Catalysts made by two-nozzle FSP showed a similar behavior even at higher Ba-loadings (Fig 5.11, bottom).
Figure 6.11: $NO_x$ storage over differently Ba-loaded WI and FM catalysts: TG mass-gain signals registered during NO/O$_2$ pulses at 300 °C in He atmosphere (nominal Ba content (wt.% is indicated in brackets).
Figure 6.12: NO evolution profiles of flame-made catalysts after NO$_x$ storage on different Ba-loaded samples.
Quantification of the NO stored on differently Ba-loaded samples was achieved by TPRD (Fig. 6.12). Similar m/z = 30 traces were observed for FM and WI samples. The amount of NO (in mg) stored per mg of catalyst is shown in Fig. 6.13, top part. The bottom part of this figure shows the NO$_x$ storage efficiency of the flame-made and impregnated catalysts with different Ba-loading expressed as a percentage of Ba species active in NO$_x$ storage versus Ba-loading.

The different distribution of BaO, LT- and HT-BaCO$_3$ significantly affects the NO$_x$ storage capacity at high Ba-loadings, as illustrated in Fig. 6.13. The absence of HT-BaCO$_3$ in flame-made catalysts improves the NO$_x$ storage capacity and efficiency in high Ba-loaded sample compared to corresponding impregnated catalysts (Figs. 5.11 and 5.13), where the bulk-like HT-BaCO$_3$ was shown to be less active and to cause diffusional limitation for Ba-loadings higher than 17 wt%.

At low Ba-loadings in WI catalysts two phases contribute to the storage of NO$_x$ species: very active BaO formed by decomposition of LT-BaCO$_3$ and not decomposed LT-BaCO$_3$. In FM catalysts the main phase contributing to NO$_x$ storage at all Ba-loadings is LT-BaCO$_3$. Its thermal properties are very similar to properties of this phase in WI samples but its activity in NO$_x$ storage is lower due to the significantly lower interaction with the alumina support compared to that in conventionally prepared WI samples. This explains why despite the larger LT-BaCO$_3$ content, especially at low Ba-loadings, the storage activity of FM catalysts is comparable to that of corresponding WI catalysts.

The reduction of stored NO$_x$ species was carried out by pulsing of C$_3$H$_6$ at 400 °C over NO$_x$ saturated samples. C$_3$H$_6$ pulses were injected in the
Figure 6.13: $NO_x$ storage efficiency of FM and WI Pt-Ba/Al$_2$O$_3$ catalysts: mg of NO stored per mg of catalysts (top); Ratio of Ba-containing species involved in $NO_x$ storage to total amount of Ba species as a function of Ba-loading (bottom).
Figure 6.14: \( NO_x \) storage (\( NO/O_2 \) pulses) and reduction (\( C_3H_6 \) pulses) at 300 °C. TG curve indicates the mass change (wt. %) due to contribution of both simultaneous reactions: the uptake of \( NO_x \) and evolution of \( CO_2 \), arrows indicate the first pulse of \( C_3H_6 \) after each storage step.
system under He atmosphere after a certain number of NO/O₂ pulses (i.e. 1, 3 and up to active NOₓ storage sites saturation (Fig 5.14). Reduction of stored NOₓ species was monitored by the TG signals indicating a significant rapid mass loss upon injection of C₃H₆ pulses. Repeated C₃H₆ pulsing allowed an almost complete reduction of previously formed barium nitrate revealing similar storage-reduction activity for FM and WI catalysts even after repeated NSR cycles.

For very high Ba-loadings, i.e. when approaching the maximal NOₓ storage capacity, a clear limitation in the reduction activity of the catalysts was observed (Fig. 6.15). This limitation was more prominent in FM materials. At high Ba-loading TG traces indicated that WI Pt-Ba(28) was still active (Fig. 6.15, A), whereas the FM catalyst with the highest loading showed a substantially decreased in reduction activity (Fig. 6.15, B). Subsequent TPRD experiments confirmed that a major amount of NOₓ containing species was still present in the FM sample after the reduction (Fig. 6.15, C). These results seem to be due to a lower activity of the highly dispersed Pt sites in highly Ba-loaded FM catalysts (Fig. 6.9). Note that differences in the reduction activity with standard Pt-Ba(16.7) samples were more evident when maximal NOₓ storage was reached (i.e. during the last cycle of NO/O₂), indicating a direct influence of the concentration of NOₓ containing species on the catalyst’s reduction behavior. This lowering of the reduction activity at higher Ba-loading can be caused by: (i) covering of Pt sites by a compact layer of barium nitrate, and (ii) the influence of high Ba content on the Pt dispersion.

The injection of a single pulse of C₃H₆ after a chosen number of NO/O₂
Figure 6.15: TG traces obtained during NSR over highly Ba-loaded WI Pt-Ba(28) (A) and FM Pt-Ba(33) (B) catalysts (arrows indicate the first pulse of C_{3}H_{6} after each storage step): corresponding TPRD NO evolution profiles after complete saturation are shown at the bottom (C).
pulses allowed correlating the Pt activity with the amount of trapped NO\textsubscript{x} species. The increase of the concentration of stored NO\textsubscript{x} species results in a decrease of its reduction by C\textsubscript{3}H\textsubscript{6} pulses, indicating, in turn, a lower Pt activity. A feasible explanation is that the formation of a larger amount of Ba(NO\textsubscript{3})\textsubscript{2} leads to surface reconstruction due to the higher molar volume of that compound compared to BaCO\textsubscript{3} [42]. This process may lead to blocking of active Pt sites and consequently limit the reduction activity of the catalyst. Interestingly, the FM Pt-Ba(33) sample shows a lower reduction activity already at low concentrations of stored NO\textsubscript{x} species (i.e. after 3 NO/O\textsubscript{2} pulses), suggesting the existence of an additional limiting factor. In FM catalysts Pt dispersion increases with the Ba-loading limiting the growth of Pt particles (Fig. 6.9), accordingly, FM Pt-Ba(33) possesses very dispersed Pt sites. The correlations between Pt dispersion and activity in NSR catalysts has been debated and it seems well accepted that a high dispersion does not favor NSR efficiency [21, 43]. Highly dispersed Pt sites tend to be more easily oxidized, thereby limiting their catalytic activity [43] as in the case of the FM Pt-Ba(33) sample.

A lowering of the NSR efficiency with increasing Ba-loading was also previously reported by Castoldi et al. [40] who found a decrease of selectivity in highly Ba-loaded WI Pt-Ba/Al\textsubscript{2}O\textsubscript{3} catalyst during the reduction with H\textsubscript{2} of previously stored NO\textsubscript{x} species. Thus to benefit from the better NO\textsubscript{x} storage performances of FM catalysts at higher Ba-loadings an improved control of the Pt dispersion is needed to preserve the reduction activity.

An important aspect of the NSR concept is the possibility of cycling
perpetually the storage and reduction steps. It seemed to be important to verify if the distribution of the \( \text{BaCO}_3 \) phases is regenerated after repeated NSR cycles. Figure 6.16 depicts TPD performed after reduction of differently Ba-loaded flame-made catalysts indicating a change of the distribution of the \( \text{BaCO}_3 \) phases compared to that in corresponding fresh in situ calcined samples (Fig. 6.10). The only exception in similarity in both profiles is observed for FM Pt-Ba (33), showing only a partial regeneration of \( \text{BaCO}_3 \) phases during reduction process (due to a diminished reduction activity) and the formation of traces of previously absent HT-BaCO\(_3\) (peak centered at ca. 900 °C, bottom right). This finding suggests the partial conversion of LT-BaCO\(_3\) into less efficient HT-BaCO\(_3\) and is in line with the interconversion between the two dif-
ferent alumina-supported Ba-NO\textsubscript{x} species recently described by Chen et al. [44]. This process has to be taken into account as a possible origin of aging phenomena of Pt-Ba/Al\textsubscript{2}O\textsubscript{3} and as a reason for NSR catalyst deactivation. A rewarding goal is therefore to improve the efficiency and stability of NSR catalysts by maximizing and stabilizing the LT-BaCO\textsubscript{3} phase and minimizing the formation of the HT-BaCO\textsubscript{3} phase.

6.4 Conclusions

A novel two-nozzle flame spray pyrolysis (FSP) process was developed for one-step synthesis of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} consisting of individually crystalline BaCO\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} nanoparticles well-mixed at the nano level. In contrast, amorphous Ba species dispersed over the Al\textsubscript{2}O\textsubscript{3} particles were formed by the conventional single nozzle FSP process. The formation of individual BaCO\textsubscript{3} particles as achieved by the two-nozzle process was beneficial for the NO\textsubscript{x} storage behavior, whereas no NO\textsubscript{x} was stored on the single nozzle-made material. The amount of crystalline BaCO\textsubscript{3} could be controlled by varying the internozzle distance or in other words the point of mixing of the two flames. Increasing the Ba content did not clog the pores of the support as observed during wet impregnation and resulted only in a slight loss in specific surface area. Different distribution of BaO, LT-BaCO\textsubscript{3} and HT-BaCO\textsubscript{3} was found dependent on the preparation process (flame synthesis or impregnation). For flame-made catalysts, independent of the Ba loading the BaCO\textsubscript{3} were only in the form of LT-BaCO\textsubscript{3}). Even high Ba-loaded flame-made catalysts are virtually free of HT-BaCO\textsubscript{3} and exhibit an improved NO\textsubscript{x} storage ca-
pacity compared to corresponding impregnated catalysts. On the other hand, impregnated catalysts show a better NO\textsubscript{x} storage efficiency for low Ba loadings due to the larger Ba/Al\textsubscript{2}O\textsubscript{3} interface favoring NO\textsubscript{x} storage over active Ba sites. Reduction tests revealed some limitation of the activity of high Ba-loaded flame-made catalysts possibly related to the high Pt dispersion and to blocking of active Pt sites by Ba(NO\textsubscript{3})\textsubscript{2}. Prolonged NSR cycling indicated the conversion of active LT-BaCO\textsubscript{3} into HT-BaCO\textsubscript{3} during the aging of the catalyst and revealed a so far unknown deactivation process of NSR catalysts. Further improvement of flame-derived Pt-Ba/Al\textsubscript{2}O\textsubscript{3} NSR catalysts should be achievable by more rigorous control of the platinum dispersion and increasing the stability of the LT-BaCO\textsubscript{3} phase at high Ba-loadings

References


stabilized zirconia nanoparticles.” *Nanotechnology*, 16(6), (2005) 609.


Flame-derived Pt/Ba/CexZr1−xO2: Influence of support on thermal deterioration and behavior as NOx storage-reduction catalysts

Abstract

Pt/Ba catalysts for NOx storage-reduction (NSR) supported on ceria/zirconia were prepared by two-nozzle flame spray pyrolysis. Emphasis was placed on the influence of the support composition on the thermal deterioration and the related behavior during NOx storage and reduction. The materials were characterized by X-ray diffraction (XRD), nitrogen adsorption (BET), electron microscopy (TEM) and temperature programmed decomposition (TPD). The as-prepared material consisted of intimately mixed agglomerates of BaCO3 and CexZr1−xO2 particles.

Low thermal stability of BaCO$_3$ resulted in a high NO$_x$ storage capacity. The support composition (Ce$_x$Zr$_{1-x}$O$_2$) strongly affected the NO$_x$ reduction activity of Pt. Higher Ce contents favored the formation of stable Pt oxides exhibiting lower reduction activity. Thermal deterioration was investigated in different atmospheres. At 800 °C BaCO$_3$ transformed into inactive Ba zirconate and Ba cerate. At high Ce contents BaCO$_3$ was re-formed when exposed to CO$_2$ at high temperatures recovering its high NO$_x$ storage capacity. During the high temperature treatment, however, Pt strongly deactivated resulting in a loss of the catalyst’s NO$_x$ reduction activity.
7.1 Introduction

Lean burn engines operating at high air to fuel ratios are a promising concept to comply with stricter regulations regarding fuel consumption of automotive engines. However, neither conventional three-way catalysts nor diesel exhaust catalysts are capable to reduce NO\textsubscript{x}-emissions to acceptable levels under lean conditions. Among others, NO\textsubscript{x} storage reduction (NSR) catalysts are the most promising concept to reduce NO\textsubscript{x} under lean conditions [1–3]. In general, NSR catalysts consist of a noble metal (Pt, Pd, Rh) for oxidation and reduction of NO\textsubscript{x} and of a storage compound (typically containing Ba or K) to store NO\textsubscript{x} species in the form of nitrates under lean conditions. During short rich periods NO\textsubscript{2} is released and reduced in N\textsubscript{2} over the noble metal [2–5]. The two components are supported on a thermally stable carrier material which is typically Al\textsubscript{2}O\textsubscript{3}.

The major drawback of NSR-catalysts is the high sensitivity to sulfur poisoning and the related deterioration during regeneration resulting in a steady deactivation of the catalyst [3, 6–10]. This is mainly attributed to the formation of sulfates with the support and especially with the storage compound (i.e. BaSO\textsubscript{4}) [10–12]. These sulfates are much more stable than the corresponding nitrates and high temperatures (800 °C) are required to decompose the sulfates and regenerate an active storage material [11, 12]. At these temperatures thermal deterioration occurs by particle growth, loss in surface area and especially the formation of mixed oxides between the storage compound and materials from the support or washcoat (i.e. BaAl\textsubscript{2}O\textsubscript{4}). In general, the formation of such mixed
oxides reduces the NO$_x$-storage capacity of the catalyst. Two strategies have been proposed to solve these problems: (i) The development of catalysts that can be regenerated at lower temperatures preventing the formation of BaAl$_2$O$_4$ [6, 13, 14]; and (ii) using supporting materials that either do not form any mixed oxides with the storage material or form mixed oxides that easily decompose with CO$_2$ or NO$_x$ being present [15]. Recently it has been shown, that after formation of barium cerate (BaCeO$_3$) BaCO$_3$ and CeO$_2$ can easily be regenerated in a CO$_2$ containing atmosphere [15].

Here, the second strategy is explored, namely, the influence of support of Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ ($x = 0$-1) catalysts on thermal behavior and NOx storage reduction activity. The ceria/zirconia supported Pt-Ba NSR catalysts were prepared by two-nozzle flame spray synthesis as already applied for synthesis of Pt/Ba/Al$_2$O$_3$ NSR-catalysts exhibiting good NSR activity [16, 17]. The use of two nozzles prevents the formation of Ba containing mixed oxides and results in individual but well mixed BaCO$_3$ and support particles. Flame spray pyrolysis (FSP) has already been applied for synthesis of Pt/Al$_2$O$_3$ and Pt/Ce$_x$Zr$_{1-x}$O$_2$ catalysts [18, 19]. Flame-made ceria/zirconia nanoparticles stand out by an almost ideal atomic mixing of Ce and Zr (solid solution) and very high thermal stability [19–21]. The unique ability of ceria to store and release O$_2$ makes automotive three-way catalysts (TWC) the most important application of ceria and especially zirconia-stabilized ceria [22]. However, only few studies investigated the applicability of CeO$_2$ and Ce$_x$Zr$_{1-x}$O$_2$ as a support material for NSR-catalysts [23–25].
7.2 Experimental

7.2.1 Apparatus and preparation

The Pt/Ba/Ce\textsubscript{x}Zr\textsubscript{1–x}O\textsubscript{2} catalysts were prepared by two-nozzle flame spray pyrolysis [16]. The Ce-Zr precursor solution consisted of cerium 2-ethylhexanoate (Alfa Aesar, 49% in 2-ethylhexanoic acid) and zirconium 2-ethylhexanoate (Alfa Aesar, >96%) dissolved in a 1:1 mixture of 2-ethylhexanoic acid (Fluka, >98%) and toluene (Riedel-de Haën, >99.5%) [21]. The total metal concentration (Ce+Zr) in this solution was always 0.2 mol/L. For the Pt/Ba containing solution, corresponding amounts of barium 2-ethylhexanoate (Alfa Aesar, 75% in 2-ethylhexanoic acid) and platinum acetylacetonate (Strem, 98%) were dissolved in toluene. The setup consisted of two separate FSP nozzles. The angle between the two nozzles was 120° and the distance between the angle tip and each nozzle center was 6 cm [16]. The individual spray nozzle has been described earlier in detail [26]. The Ce-Zr precursor solution was fed at 5 ml/min through the first nozzle and the Pt/Ba precursor solution at 3 ml/min through the second nozzle. Each solution was dispersed by 5 L/min oxygen (PanGas, 99.95%) forming two fine sprays. Both sprays were surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing, at a radius of 6 mm). The gas flow rates of these two individually premixed methane/oxygen supporting flames were 3.5 L/min each with a CH\textsubscript{4}/O\textsubscript{2} ratio of 0.46. Product particles were collected on a glass fiber filter (Whatman GF/D, 25.7 cm in diameter) with the aid of a vacuum pump (Busch, Seco SV 1040C). The nominal Pt:Ba:Ce\textsubscript{x}Zr\textsubscript{1–x}O\textsubscript{2} weight ratio was always 1:20:100. Assuming all Ba
present in the form of BaCO$_3$ the nominal Ba content was 15.4 wt%.

7.2.2 Characterization

The specific surface area (SSA) was determined by nitrogen adsorption at 77 K using the BET method (Micromeritics Tristar). Prior to analysis, samples were outgased for 1 h in N$_2$ at 150 °C. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 advance diffractometer in step mode ($2\theta = 15$-75°) with a step size of 0.04° and a scan speed of 0.48 °/min. Temperature programmed decomposition (TPD) of BaCO$_3$ was measured using a Micromeritics Autochem II 2920 by heating (10 °C/min) 35 mg powder in a helium flow (20 ml/min) from 50 to 1000 °C. Gas phase composition was monitored by a mass spectrometer (Thermostar, Pfeiffer Vacuum). After each experiment the CO$_2$ signal (M/Z = 44) was calibrated by injecting a well-defined pulse of CO$_2$ (0.35 ml).

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 (FEI (Eindhoven); field emission cathode, operated at 300 kV). TEM images were recorded with a slow-scan CCD camera. An energy filter (Gatan imaging filter, GIF), which is installed below the Tecnai F30, allows recording element specific images (elemental maps) of of Zr (180 eV), Ba (790 eV) and Ce (890 eV) by means of the electron spectroscopic imaging (ESI) technique [27].

Thermal stability was studied by annealing the catalysts at 800 °C for
2 h in air or for 1 h in 10% O\textsubscript{2}/He followed by 1 h in 20% CO\textsubscript{2}/He. The heating and cooling rates were ±10 °C/min.

The NO\textsubscript{x} storage reduction (NSR) measurements were performed with 20 mg catalyst in a fixed-bed reactor (d = 4 mm) allowing fast switches between lean and rich conditions. The reactor was connected to a valve device allowing fast switches between oxidizing and reducing atmospheres. The NO and NO\textsubscript{2} concentration in the effluent gas was monitored by a chemiluminescence detector (ECO Physics, CLD 822 S) whereas other gases were analyzed by a mass spectrometer (Thermostar, Pfeiffer Vacuum). The NO\textsubscript{x} conversion was derived from the corresponding NO\textsubscript{x} outlet concentration according to:

\[
\text{NO}_{x}\text{conversion} = \frac{\text{NO}_{\text{in}} - \text{NO}_{x,\text{out}}}{\text{NO}_{\text{in}}} \cdot 100\%
\]

The NSR was measured at 300, 350 and 400 °C by switching 5 times between oxidizing (3 min in 667 ppm NO and 6.67 % O\textsubscript{2} in He) and reducing atmospheres (1 min in 667 ppm NO, 1333 ppm C\textsubscript{3}H\textsubscript{6} in He). The total gas flow rate was always 60 ml/min. At the end of each experiment the catalyst was kept under reducing conditions for 10 min followed by oxidizing conditions until its saturation. For some experiments, catalysts were pretreated in 5% H\textsubscript{2}/Ar at 500 °C for 30 minutes. Additionally some catalysts were directly exposed to lean conditions until saturation (90 min) and followed by a rich phase for 45 min without any previous cycles.
7.3 Results and Discussion

7.3.1 Structural properties

Two-nozzle flame spray pyrolysis of Pt/Ba/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> resulted in well-mixed but individual BaCO<sub>3</sub> and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> nanoparticles. Figure 7.1 shows TEM images with the corresponding Ba, Ce and Zr elemental mappings for the as-prepared materials with different Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> composition. It clearly shows that BaCO<sub>3</sub> particles are intimately mixed with the Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> particles. The ratio of Ce:Zr in the supporting material had hardly any influence on the morphology of the Ba component which was similar to Pt/Ba/Al<sub>2</sub>O<sub>3</sub> prepared by two nozzles FSP [16]. So it can be expected, that BaCO<sub>3</sub> and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> form separately before mixing of the two flames [16].

Figure 7.2 depicts XRD-patterns of the as-prepared materials. Without Zr being present ceria crystallized in its cubic crystal structure [20, 26] while tetragonal zirconia was formed without Ce [28]. Fast cooling rates during preparation prevent the transformation into monoclinic ZrO<sub>2</sub> and favor the formation of tetragonal ZrO<sub>2</sub>, the high temperature form of zirconia. Crystalline (tetragonal) solid solutions of Ce and Zr where formed for Ce-Zr mixed oxides [20, 21]. The addition of Ba and Pt did not influence the phase composition of the support. Barium was in the form of crystalline BaCO<sub>3</sub> and no crystalline BaO was observed [29]. For Ce:Zr ratios higher than 1, only orthorhombic BaCO<sub>3</sub> was found (Fig. 7.2A and B). However, with more Zr being present Ba was mainly in the form of monoclinic BaCO<sub>3</sub> (Fig. 2C), which was formed
Figure 7.1: TEM images of as-prepared Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ with the corresponding elemental mappings of Ba and Ce or Zr on the right.
Figure 7.2: X-ray diffraction patterns of Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ with different support composition: (a.p.) as-prepared; (air) after 2 h, 800 °C, air; (CO$_2$) after 1h, 800 °C, 10% O$_2$/He followed by 1h, 800 °C, 20% CO$_2$/He. JSPDS numbers of the corresponding crystal structures are shown in parenthesis.
during rapid quenching and gradually transformed into orthorhombic BaCO$_3$ when stored at ambient conditions [29, 30]. For Ce$_{0.1}$Zr$_{0.9}$O$_2$ this transformation took place within 5 days whereas on ZrO$_2$ about 1 month was needed. This suggests, that ZrO$_2$ stabilizes the metastable monoclinic form of BaCO$_3$ similar to Al$_2$O$_3$ [16].

![Figure 7.3: TPD CO$_2$ evolution profiles during decomposition of BaCO$_3$ for as-prepared Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ with different support composition. Temperatures of maximum decomposition rate are indicated.](image)

Temperature programmed decomposition of BaCO$_3$ in inert atmosphere was monitored by the evolution of CO$_2$ (M/Z = 44) and is shown in
Figure 7.3 for as-prepared materials. The evolution of CO$_2$ below 500 °C can mainly be attributed to desorption of surface-bound CO$_2$ species. The main peak occurring between 600 and 900 °C originates from the decomposition of BaCO$_3$ into BaO and CO$_2$. Note that decomposition of BaCO$_3$ is most probably accompanied by formation of BaZrO$_3$ and BaCeO$_3$ (see Figure 7.2). These decomposition temperatures are much lower than that of bulk-BaCO$_3$ (>900 °C) [31].

This low stability can be attributed to the close interaction of BaCO$_3$ with the supporting material, and has also been observed for flame-made [16] and impregnated Ba on Al$_2$O$_3$ [31]. However, the decomposition temperatures of BaCO$_3$ in flame-made Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ are much lower than those reported for impregnated Pt-Ba on CeO$_2$ [15] and ZrO$_2$ [32]. On CeO$_2$ two kinds of BaCO$_3$ have been reported with maximum decomposition rate at 874 and 1100 °C [15, 23]. In contrast, the corresponding flame-made material contained only BaCO$_3$ decomposing at low temperature (840 °C). Similar for Pt/Ba/ZrO$_2$: Two kinds of BaCO$_3$ were reported for impregnated catalysts (T$_d$ = ca. 750 and mainly 1000 °C [32]) whereas BaCO$_3$ decomposed completely at 738 °C on flame-made ZrO$_2$. These observations are in line with earlier results of flame-made and impregnated Pt/Ba/Al$_2$O$_3$ catalysts [17]. In any case the flame-made BaCO$_3$ decomposes at lower temperatures than the corresponding impregnated catalyst. The lower thermal stability of flame-derived BaCO$_3$ could be caused by several factors of which: (i) Different structural properties of BaCO$_3$ and smaller particle size in flame-made catalysts; and (ii) strong interfacial contact between support and BaCO$_3$ promoting BaCO$_3$ decomposition and/or formation of Ba mixed oxides,
are probably the most crucial.

**Figure 7.4:** Specific surface area of flame made Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ as a function of the support composition before and after annealing at 800 °C in air (air, 2h) or in CO$_2$ containing atmosphere (10% O$_2$/He, 1h followed by 20% CO$_2$/He, 1h).

The specific surface area of as-prepared and annealed (air, 800 °C, 2 h or with additional CO$_2$ treatment) catalysts is shown in figure 7.4. For as-prepared materials it was around 90 m$^2$/g that slightly increased with higher ceria content. Strongest sintering at 800 °C was observed for CeO$_2$ (26 m$^2$/g), which is not surprising as Zr is commonly used as stabilizer for ceria. ZrO$_2$ and Ce-Zr mixed oxides retained between 50
and 60 m\(^2\)/g after annealing [33]. For all materials BaCO\(_3\) decomposed during the high temperature treatment in air and the corresponding Ba-cerate (BaCeO\(_3\)) or zirconate (BaZrO\(_3\)) was formed as shown in Figure 7.2. With both Zr and Ce being present in the support, only BaZrO\(_3\) and no BaCeO\(_3\) could be observed. This results also in a Ce enrichment in the ceria/zirconia solid solution as confirmed by a shift of the Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) peaks towards lower diffraction angles [20, 33].

The re-formation of BaCO\(_3\) in CO\(_2\) containing atmosphere after decomposition and BaCeO\(_3\) formation [15] was investigated by annealing the powders for 1 hour at 800 °C in 10% O\(_2\)/He followed by 20% CO\(_2\)/He for another hour at 800 °C and cooling to room temperature at 10 °C/min. XRD-patterns recorded after this annealing procedure are shown in Figure 7.2 and the corresponding SSA in Figure 7.4. The BaCO\(_3\) (orthorhombic and monoclinic) was easily re-formed from BaCeO\(_3\) (Fig. 7.2A, CO\(_2\), air). Note that larger BaCO\(_3\) crystallites were formed after this treatment compared to the as-prepared powder, as indicated by sharper reflections in the BaCO\(_3\) crystal pattern (Fig. 7.2A, CO\(_2\)). Similar behavior was observed for Pt/Ba/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\). However less BaCO\(_3\) was re-formed and crystalline BaZrO\(_3\) was, although less prominent, still present (Fig. 7.2B, CO\(_2\)). This indicates that BaZrO\(_3\) partly decomposes during the CO\(_2\) treatment when Ce is present in the support. In contrast, for Pt/Ba/ZrO\(_2\) the additional CO\(_2\) treatment hardly affected the crystal structures compared to annealing in air and Ba was still present as BaZrO\(_3\) (Fig. 7.2C, CO\(_2\)).

TEM-analysis of the CO\(_2\)-annealed catalysts with corresponding elemental mapping as shown in Figure 7.5 confirmed these observations. For
**Figure 7.5**: TEM pictures of Pt/Ba on CeO$_2$ and ZrO$_2$ after annealing in CO$_2$ containing atmosphere. The corresponding elemental mappings of Ba, Ce and Zr are shown on the right. BaCO$_3$ and BaZrO$_3$ domains are indicated by arrows.
Pt/Ba/CeO₂, the BaCO₃ particles contained no discernible Ce from elemental mapping. Similar to the as-prepared material (Fig. 7.1), after CO₂ annealing the BaCO₃ domains are still well-mixed with the CeO₂ particles which are larger due to sintering. In agreement with the XRD results for Pt/Ba/ZrO₂ (Fig. 7.2C), elemental mapping revealed the presence of Zr in the Ba containing domains indicating the formation of BaZrO₃ at 800 °C. Interestingly no distinct Pt particles or domains were observed by TEM (Fig. 7.5) or STEM analysis (not shown) indicating that no significant sintering occurred during annealing at 800 °C.

![Graph showing TPD CO₂ evolution profiles during decomposition of BaCO₃ for Pt/Ba/CeₓZr₁₋ₓO₂ after annealing at 800 °C in 10% O₂/He (1h) and 20% CO₂/He (1h). Temperatures of maximum BaCO₃ decomposition rate are indicated.](image-url)

**Figure 7.6:** TPD CO₂ evolution profiles during decomposition of BaCO₃ for Pt/Ba/CeₓZr₁₋ₓO₂ after annealing at 800 °C in 10% O₂/He (1h) and 20% CO₂/He (1h). Temperatures of maximum BaCO₃ decomposition rate are indicated.
The TPD profiles recorded after CO$_2$ annealing further corroborate these results (Fig. 7.6). Recalling the CO$_2$ evolution from as-prepared materials (Fig. 7.3) it clearly shows the re-formation of BaCO$_3$ on CeO$_2$. The amount of evolved CO$_2$ is even slightly higher than for the as-prepared Pt/Ba/CeO$_2$. This may be attributed to small amounts of BaO, Ba(OH)$_2$ or BaCeO$_3$ in the as-prepared material, which are not detectable by XRD. These species then transform into BaCO$_3$ upon treatment in CO$_2$. Additionally, maximum decomposition rate was shifted towards higher temperatures (880 instead of 840 °C) indicating the formation of larger BaCO$_3$ particles. On the other hand, with Ce$_{0.5}$Zr$_{0.5}$O$_2$ the BaCO$_3$ was only partly recovered in CO$_2$ and consequently less CO$_2$ evolved during TPD compared to the as-prepared material. Also in accordance with XRD, no CO$_2$ stemming from BaCO$_3$ decomposition was observed for Pt/Ba/ZrO$_2$ after CO$_2$ annealing and only CO$_2$ desorbing from the surface at low temperatures was detected, indicating complete BaZrO$_3$ formation.

7.3.2 NO$_x$ storage reduction

Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$ catalysts were tested for their behavior in NO$_x$ storage and reduction. Figure 7.7 depicts the NO, NO$_2$, NO$_x$ and CO$_2$ outlet concentrations during the 5$^{th}$ lean-rich cycle at 350 and 400 °C. After 3 min under lean conditions (667 ppm NO, 6.67 % O$_2$, He) the feed gas was abruptly switched to rich for 1 min (667 ppm NO, 1333 ppm C$_3$H$_6$, He), which was accompanied by a sharp increase in NO$_x$. This breakthrough is commonly observed when switching from lean to rich conditions and
Figure 7.7: $NO_x$ storage reduction on as-prepared $Pt/Ba/Ce_xZr_{1-x}O_2$ with different support composition at 350 and 400 °C. Effluent gases ($NO$, $NO_2$, $NO_x$ and $CO_2$) are shown during the 5th lean-rich cycle. After 3 min under lean atmosphere the gas composition was switch to rich conditions for 1 min.
can be attributed to partly mixing of O\textsubscript{2} and C\textsubscript{3}H\textsubscript{6} resulting in combustion and formation of a high amount of CO\textsubscript{2} (Fig. 7.7). With this CO\textsubscript{2} being present Ba(NO\textsubscript{3})\textsubscript{2} transforms into BaCO\textsubscript{3} releasing NO\textsubscript{x} which is not reduced as long as C\textsubscript{3}H\textsubscript{6} has been burnt off by O\textsubscript{2}. For all these experiments the amount of NO\textsubscript{2} in the off-gas was negligible. Distinct differences in storage and reduction behavior were found depending on the reactor temperature and the support composition.

![Graph](image)

**Figure 7.8:** NO\textsubscript{x} conversion as a function of temperature and support composition during the 5\textsuperscript{th} lean-rich cycle (compare Fig. 7.7). High conversions were observed for catalyst with Pt\textsuperscript{0} (gray colored material) instead of PtO\textsubscript{x} (orange colored material).

At 350 °C complete reduction of NO\textsubscript{x} by C\textsubscript{3}H\textsubscript{6} was only achieved for
for Zr-rich supports, whereas NO$_x$ was not reduced on CeO$_2$ and Ce$_{0.5}$Zr$_{0.5}$O$_2$ resulting in high NO$_x$ concentrations. Increasing the temperature to 400 °C facilitated NO$_x$ reduction also on these supports. Low reduction activity went along with a low NO$_x$ storage capacity. This can be attributed to the presence of occupied storage sites, which were formed during the previous cycles. As no or only little CO$_2$ is formed through oxidation of C$_3$H$_6$, Ba(NO$_3$)$_2$ is not transformed back into BaCO$_3$ and the previously formed Ba(NO$_3$)$_2$ survives the rich phase blocking active storage sites during the following lean phases. The CO$_2$ traces confirm these assumptions. It further shows that NO$_x$ storage is always accompanied by CO$_2$ evolution from BaCO$_3$, the active form of Ba in the storage process.
Figure 7.9: \(NO_x\) conversion during the 5\(^{th}\) lean-rich cycle for as-prepared Pt/Ba/CeO\(_2\) and after H\(_2\) pretreatment (5\% H\(_2\)/Ar, 500 \(^\circ\)C, 30 min) as a function of temperature.

Figure 7.8 shows the \(NO_x\) conversion on Pt/Ba/Ce\(_x\)Zr\(_{1-x}\)O\(_2\) during the 5\(^{th}\) lean-rich cycle at different temperatures. Independent of support composition, the \(NO_x\) conversion was very low at 300 \(^\circ\)C. As discussed before, this is mainly due to the low reduction activity of platinum at this low temperature. At 350 \(^\circ\)C, however, the higher reduction activity increased strongly the \(NO_x\) conversion, but only for catalysts containing little or none Ce in the support. For Ce:Zr ratios larger than 1 the conversion was still very low. At even higher temperatures (400 \(^\circ\)C), all catalysts reduced \(NO_x\) during rich phases (Fig. 7.7) resulting in high
NO\textsubscript{x} conversions.

Figure 7.7 and 7.8 clearly show the negative influence of ceria on the reduction activity of Pt and consequently on the NO\textsubscript{x} conversion. Similar observations have been made for NO reduction by CH\textsubscript{4} or C\textsubscript{3}H\textsubscript{6} on Pt/C\textsubscript{e\textsubscript{x}}Zr\textsubscript{1-x}O\textsubscript{2} [34, 35]. We assume that the low activity with CeO\textsubscript{2}-rich supports is caused by formation of platinum-oxides, which are less active. The formation of very stable PtO\textsubscript{x} on flame-made Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} has been reported earlier [19]. In that study a temperature of 300 °C was needed for complete reduction of PtO\textsubscript{x} (1wt% Pt) in 5% H\textsubscript{2}. The small size of Pt particles together with a PtO\textsubscript{x} stabilization by ceria results in the high stability of Pt in its oxidized form [19, 34]. Here, the presence of predominately PtO\textsubscript{x} or Pt\textsuperscript{0} was indicated by an orange/ brown or grey color of the powder, respectively. The observed color changes during reaction were in good agreement with the corresponding NSR-activity. That is for Ce:Zr > 1 the orange color was retained at 350 °C even for long rich periods but at 400 °C along with a strongly increased activity these materials turned gray indicating the formation of active Pt\textsuperscript{0}. The higher activity of Zr-rich catalysts can thus be attributed to easier reducible PtO\textsubscript{x} species. NSR experiments with pre-reduced catalysts further corroborate these findings.
Figure 7.10: $NO_x$ outlet concentration during saturation experiments at 400 °C after 5 lean-rich cycles for Pt/Ba/Ce$_x$Zr$_{1-x}$O$_2$. The inset depicts the corresponding $NO_x$ storage capacity as derived from the stored $NO_x$.

Figure 7.9 shows the $NO_x$ conversion of as-prepared and pre-reduced Pt/Ba/CeO$_2$. Reduction of Pt at 500 °C in 5% H$_2$/Ar prior to experiment strongly enhanced the $NO_x$ reduction activity of Pt at lower temperatures and thus increased the corresponding $NO_x$ conversions. Even at 300 °C, the pre-reduced Pt was active for $NO_x$ reduction resulting in a $NO_x$ conversion of 33.6%. The hydrogen pretreatment increased also the $NO_x$ reduction activity for Pt on ZrO$_2$ resulting in a $NO_x$ conversion of 52.8% at 300 °C instead of 10.6% for the as-prepared material (Table 7.1, Fig 7.8).
Figure 7.10 depicts the NO$_x$ outlet concentrations from Pt/Ba on four supports during complete storage until saturation at 400 °C measured after 5 lean-rich cycles. No breakthrough of NO$_x$ was observed for about 5 minutes. After 5 min the NO$_x$ concentration increased rapidly but not reaching the inlet concentration, indicating that NO$_x$ is still partly stored during another 50 minutes. These results show two different NO$_x$ storage activities of the catalysts: A fast NO$_x$ uptake during a first period with all NO$_x$ being stored followed by a slower process only partly storing NO$_x$. The first, fast process contributes approximately 15-20 % to the total amount of stored NO$_x$. The reason for these different rates can not be attributed to different storage activities of BaO or BaCO$_3$, as CO$_2$ evolved corresponding to the amount of NO$_x$ stored (compare Fig. 7.11). This demonstrates that only BaCO$_3$ is the active storage component. Another explanation for the different storage rates is much more plausible.

During the first period, NO$_x$ rapidly reacts on the surface of the BaCO$_3$ particles forming a Ba(NO$_3$)$_2$ surface layer. Once the surface is saturated, the slower storage process starts. Now the nitrates or NO$_2$ have to diffuse into the particles and carbonates or CO$_2$ to the surface where they can be releases. Compared to the fast surface reaction, this diffusion process is slower limiting the NO$_x$ uptake rate during the second period. This mechanism has been proposed earlier for Pt/Ba/Al$_2$O$_3$ and was evaluated by modelling approaches [36]. This behavior was observed for all support compositions. However, on supports with a high Ce content the second diffusion process occurred faster. The inset in figure 7.10 shows the corresponding NO$_x$ storage capacities as a function of support
### Table 7.1: NSR activity for as-prepared, CO\textsubscript{2} annealed and H\textsubscript{2} pretreated Pt/Ba/CeO\textsubscript{2} and Pt/Ba/ZrO\textsubscript{2} catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing</th>
<th>T (^{\circ}\text{C} )</th>
<th>NO\textsubscript{x} conv. (^{\circ}% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Ba/CeO\textsubscript{2}</td>
<td>none</td>
<td>400</td>
<td>58.1</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>400</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>300</td>
<td>33.6</td>
</tr>
<tr>
<td>Pt/Ba/ZrO\textsubscript{2}</td>
<td>none</td>
<td>400</td>
<td>87.1</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>400</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>300</td>
<td>52.8</td>
</tr>
</tbody>
</table>

\(^{a}\) A: 1 h at 800 \(^{\circ}\text{C} \) in 10\% O\textsubscript{2}/He followed by 1 h in 20\% CO\textsubscript{2}/He; B: 5\% H\textsubscript{2}/Ar, 500 \(^{\circ}\text{C} \), 30 min.
\(^{b}\) temperature during NO\textsubscript{x} storage reduction measurement.
\(^{c}\) NO\textsubscript{x} conversion during 5\(^{th}\) lean-rich cycle.

The NSR activity of Pt/Ba/Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} was also tested after thermal decomposition and recovery of BaCO\textsubscript{3} in CO\textsubscript{2} containing atmosphere. Table 7.1 depicts NO\textsubscript{x} conversion at 400 \(^{\circ}\text{C} \) during the 5\(^{th}\) lean-rich cycle for as-prepared and annealed catalysts. On both supports (CeO\textsubscript{2} and ZrO\textsubscript{2}) the NSR activity decreased dramatically after annealing. This is not surprising for Pt/Ba/ZrO\textsubscript{2} as no active BaCO\textsubscript{3} is recovered during the CO\textsubscript{2} treatment and only inactive BaZrO\textsubscript{3} is present (see Fig. 7.2). However, although BaCO\textsubscript{3} is reformed on CeO\textsubscript{2} still rather low NO\textsubscript{x} con-
versions were observed. Additional experiments investigating the NO\textsubscript{x} storage capacity without any previous NSR-cycles give more insight into the behavior of aa-prepared and CO\textsubscript{2} annealed catalysts.

Figure 7.11 depicts the NO\textsubscript{x} and CO\textsubscript{2} outlet concentrations during saturation experiments at 400 °C without any previous lean-rich cycles for as-prepared and annealed catalysts. Corresponding NO\textsubscript{x} storage capacities are shown in Table 7.2. On as-prepared materials NO\textsubscript{x} uptake and storage capacities are similar to those after lean-rich cycles (Fig. 7.8). However, only on ZrO\textsubscript{2} the reduction activity was retained after saturation and complete transformation of BaCO\textsubscript{3} into Ba(NO\textsubscript{3})\textsubscript{2}. Much lower reduction activity was observed for as-prepared Pt/Ba/CeO\textsubscript{2} after switching to rich conditions resulting in a large breakthrough of NO\textsubscript{x}. Note that the NO\textsubscript{x} outlet concentration is even higher than its inlet concentration. It took a long time (30 min) until the reduction activity was recovered and NO\textsubscript{x} was reduced completely. CO\textsubscript{2} evolution corroborates the low reduction activity of Pt/Ba/CeO\textsubscript{2} as no CO\textsubscript{2} was formed from C\textsubscript{3}H\textsubscript{6} oxidation. Compared to the reduction behavior after short storage periods (Fig. 7.7) much lower reduction activity was observed after complete storage. This may be attributed to blocking of active Pt sites by newly formed Ba(NO\textsubscript{3})\textsubscript{2} dispersing over the support [37].

Regarding the corresponding storage behavior of annealed catalysts (Fig. 7.11) it is obvious that hardly any NO\textsubscript{x} is stored on Pt/Ba/ZrO\textsubscript{2} exhibiting very low NO\textsubscript{x} storage capacity after the high temperature treatment (Table 7.2). This is a consequence of the absence of active Ba-containing species, Ba is predominately present as inactive BaZrO\textsubscript{3} (compare Fig. 7.2C and 6.6). In contrast, the re-formation of BaCO\textsubscript{3} from BaCeO\textsubscript{3}
Figure 7.11: NO$_x$ and CO$_2$ in the effluent gas during NSR on Pt/Ba/CeO$_2$ and Pt/Ba/ZrO$_2$, as-prepared and after annealing in CO$_2$ containing atmosphere. The catalysts were exposed to lean conditions until saturation (90 min) followed by reducing conditions for 45 min. The gray area indicates the amount of stored NO$_x$ (compare table 7.2).
Table 7.2: Amount of stored $NO_x$ and relative amount of Ba involved in the storage process during saturation experiments at 400 °C (compare Fig. 7.11).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing</th>
<th>$NO_x$ stored (mg $NO_x$ / g cat)</th>
<th>$NO_x$ storage capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Ba/CeO$_2$</td>
<td>no</td>
<td>51.8</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>62.2</td>
<td>92</td>
</tr>
<tr>
<td>Pt/Ba/Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>yes</td>
<td>32.5</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>no</td>
<td>40.9</td>
<td>61</td>
</tr>
<tr>
<td>Pt/Ba/ZrO$_2$</td>
<td>yes</td>
<td>6.6</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$ 1 h at 800 °C in 10% O$_2$/He followed by 1 h in 20% CO$_2$/He.

$^b$ Relative amount of Ba involved in storage process, assuming complete Ba(NO$_3$)$_2$ formation.

in CO$_2$ containing atmosphere recovers the $NO_x$ storage activity. The $NO_x$ storage capacity was even higher (92%) than for the as prepared Pt/Ba/CeO$_2$ (77%) which is in line with larger amounts of BaCO$_3$ on the annealed material (compare Figs. 7.2 and 7.6). The diffusion limited storage of $NO_x$ is more pronounced than for the as-prepared catalyst. This is in good agreement with the formation of larger BaCO$_3$ particles during the annealing procedure (see Figs. 7.2 and 7.5) exhibiting less accessible surface BaCO$_3$ for fast $NO_x$ uptake. BaCO$_3$ was partly reformed on Ce$_{0.5}$Zr$_{0.5}$O$_2$ and consequently this material recovered some of its $NO_x$ storage capacity after annealing (Table 7.2). However, independently of the support composition, the reduction activity of the annealed materials was completely lost. Neither stored $NO_x$ nor NO from the feed gas was reduced and hardly any formation of CO$_2$ was
visible during the rich period. This inactivity is also the reason for the low NO\textsubscript{x} conversions during short lean-rich cycles (Table 7.1). The reason for this deactivation is not clear yet. Strong sintering of Pt can be excluded as no large Pt particles were found by TEM analysis (Fig. 7.5) and no crystalline Pt, which would be characteristic for large Pt particles, could be detected by XRD after annealing. The reaction of Pt with the support and/or Ba seems to be a more feasible explanation for this deactivation. The formation of Ba\textsubscript{2}CePtO\textsubscript{6} perovskite structures at high temperatures has been reported [38]. Although no reflections of such phases were found in the diffraction patterns (Fig. 7.2) it is still possible that Pt deactivates by incorporation into the Ba and/or support matrix. However, further investigations are necessary to elucidate this deactivation of Pt at high temperatures.

### 7.4 Conclusions

Two-nozzle flame spray pyrolysis has been applied for synthesis of Pt/Ba/Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} consisting of individual BaCO\textsubscript{3} and ceria/zirconia particles. The as-prepared catalysts exhibited a high NO\textsubscript{x} storage capacity but high amounts of ceria in the support lowered the NO\textsubscript{x} reduction activity of Pt due to the formation of less active, stable Pt oxides. The catalysts could be activated by a reductive pre-treatment resulting in the formation of more active Pt\textsuperscript{0}. When exposed to CO\textsubscript{2}, active BaCO\textsubscript{3} could be recovered after BaCO\textsubscript{3} decomposition and BaZrO\textsubscript{3}/BaCeO\textsubscript{3} formation at high temperatures. Complete BaCO\textsubscript{3} recovery could be achieved on CeO\textsubscript{2}, whereas BaCO\textsubscript{3} was not or only partly reformed on
ZrO$_2$ or Ce-Zr mixed oxides, respectively. Pt was strongly deactivated during the annealing procedure resulting in a loss of the catalyst’s NO$_x$ reduction activity. It could be shown that flame-made Pt/Ba/ceria-zirconia NSR catalysts are efficient for NO$_x$ storage. However, further investigations on the reduction/oxidation compound (i.e. Pt, Pd, Ru) and its deactivation are necessary for improving the catalysts NSR activity.

References


References


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Chapter 7 Pt/Ba/Ce<sub>x</sub>Zr<sub>1−x</sub>O<sub>2</sub> NSR catalysts


Outlook and Research Recommendations

Over the last years flame synthesis methods have turned out to be very suitable for one-step synthesis of various catalysts including supported metals and mixed oxides. Most research concerning flame synthesis of catalysts however, focussed on the preparation of known catalytic systems which have already been prepared by conventional wet phase methods. Flame synthesis can result in the formation of novel and unique materials/structures, which are not available through conventional methods. This includes mainly mixed oxides, where novel crystal structures were observed. Rapid quenching from very high temperatures during synthesis can result in metastable high temperature phases. Regarding these novel materials it seems very promising to start evaluating their catalytic performances not relying on existing conventional catalytic systems and their field of application. Of course this is often a tedious trial and error process. However, combinatorial approaches combined with the fast preparation of different materials by flame processes can lead to the discovery of unknown catalytic properties.
Regarding more flexibility in preparation of complex crystalline materials through flame spray pyrolysis it is highly recommended to design flame reactors with longer residence times and especially lower cooling rates. The very short residence times of less than 10 ms in the high temperature zone as it is currently used at ETH often does not allow the synthesis of complex mixed oxide crystal structures and results in amorphous materials. However, for many applications - not only catalysis - highly crystalline materials are required. Slower cooling during flame synthesis will give atoms enough time for rearrangement and crystallization in complex crystal structures. Different approaches can and have already been used for lower velocities during flame spray pyrolysis including ultrasonic nebulizers for droplet generation or the design of other spray nozzles operating with lower gas velocities. Of course, longer residence times have also a drawback as larger particles will be formed by sintering at the high temperatures. Nevertheless it will extend the potential of flame spray pyrolysis for synthesis of nanoparticles with more complex crystal structures.

More specific recommendations concern NO\textsubscript{x} storage reduction (NSR) catalysts. Based on the results of chapter 4 and 5 it seems to be promising combining the advantages of the two different support systems (Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}). Pt on ceria is much less active than on alumina but Ba on Al\textsubscript{2}O\textsubscript{3} deactivates at high temperatures through formation of inactive BaAl\textsubscript{2}O\textsubscript{4}. This problem can probably be circumvented by depositing Ba on CeO\textsubscript{2} and Pt on Al\textsubscript{2}O\textsubscript{3}. By using multiple nozzles for flame synthesis this kind of material with the right mixing of the 4 components can be achieved. This NSR-catalyst would then combine temperature
resistance of Ba together with highly active Pt. Another possibility is the evaluation of other metals such as Pd, Ru, Co or even Au as oxidation/reduction catalyst during NSR. In contrast to Pt which exhibits a low activity on CeO$_2$ (chapter 5) these metals may show increased performance for oxidation and reduction during NSR. Concerning catalyst deactivation further investigations are necessary to elucidate the sulfur tolerance of flame-made NSR catalysts, their regeneration after sulfur poisoning as well as their long-term stability during cycling operation. Additionally the influence of CO$_2$ and water in the feed gas on the storage and reduction behavior should be investigated.
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Zurich, 2006
List of Publications

Refereed Publications


• R. Strobel, M. Piacentini, L. Mädler, M. Maciejewski, A. Baiker, S.E. Pratsinis, ”Two-nozzle flame synthesis of Pt/Ba/Al$_2$O$_3$” for NO$_x$ storage, Chem. Mater., 18 (2006) 2532.


Patents


Presentations


• R. Strobel, W. J. Stark, L. Mädler, S. E. Pratsinis, A. Baiker ”Hydrogenation catalysts made by flame spray pyrolysis” (poster, 373t) AIChE Annual Meeting, Indianapolis, IN, USA, November (2002).


- R. Strobel, M. Maciejewski, L. Mädler, S. E. Pratsinis, A. Baiker, “One-step flame-synthesis of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} nanoparticles and their behavior as NO\textsubscript{x} storage catalysts”, Symposia 9, Europacat-VII, Sofia, Bulgaria, August (2005).


- R. Strobel, M. Piacentini, M. Maciejewski, L. Mädler, A. Baiker, S. E. Pratsinis, ”One-step flame synthesis of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} NO\textsubscript{x} storage reduction catalysts”, Poster O3.5, MRS-Fall Meeting 2005, Boston, USA, November (2005).