Flame Synthesis of Supported Platinum Group Metals for Catalysis and Sensors

NOVEL FLAME PROCESSES ALLOW SYNTHESIS OF SUPPORTED PGMs IN A SINGLE STEP

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Platinum group metals (pgms) supported on a carrier material are widely applied as catalysts. These catalysts are conventionally prepared by wet-phase processes in several steps, while recently developed flame processes allow synthesis of supported pgms in a single step including the support material. Here, we describe flame processes and how finely dispersed supported pgms are made in these flames. So Pt/Al2O3, Pd/ZnO, Rh/Al2O3, Pt/Ba/Al2O3 and others are highlighted regarding their materials properties and performance as catalysts as well as in gas sensors.

Introduction

Today, catalysts are mostly manufactured using wet-chemical techniques. Incipient wetness impregnation, sol-gel, precipitation, grafting and solid-state reactions, just to name a few, are batch processes requiring several aftertreatment steps, such as filtration, drying and calcination (1–3).

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, silica waveguide preforms, fumed SiO2 and alumina (4–6). Since the 1970s, flame-made materials have been used as catalyst supports (i.e. Al2O3, SiO2, TiO2) (1, 2, 7) and as photocatalysts (mainly TiO2) (8). Progress in flame technology during the last decade, especially the development of the so-called flame-spray pyrolysis (FSP), contributed decisively to the creation of new and sophisticated materials for catalysis (9) as well as for sensors, biomaterials, microelectronics and other applications (10). In fact, today it is possible to make up to 1 kg h⁻¹ of nanostructured materials by flame aerosol technology even in an academic laboratory. Figure 1 shows such a pilot FSP unit in operation along with a baghouse particle collection unit (10).

Among other materials, pgms supported on various ceramic carriers have been prepared by flame technology during the last decade. Figure 2 shows a schematic of wet and flame processes for synthesis of supported pgm catalysts. In contrast to conventional multi-step wet chemistry techniques, such as precipitation of the support with its washing, filtration, drying and calcination steps...
followed by impregnation with the pgm and the washing to calcination sequence, flame synthesis allows preparation of the support and the pgm in a single step. As-prepared particles can be separated easily from the gas phase by filtration. In general, flame-made supported pgms consist of finely dispersed pgms on top of a nonporous support (Figure 3) exhibiting high external surface area and thus good thermal stability and mass transfer properties (11–13).

Here, recent progress in flame synthesis of supported pgm as well as gold and silver catalysts and sensors is presented along with the unique structural and catalytic properties of these materials. Some examples which will be discussed here include supported platinum and palladium catalysts for enantioselective hydrogenation, bimetallic Pd-Pt catalysts for catalytic combustion of methane, Pt/Ba/Al2O3 for NOx-storage reduction, supported Au catalysts for selective oxidation of carbon monoxide, TiO2 and zinc oxide photocatalysts containing Pt and Ag as well as Pt/tin oxide gas sensors.

**Flame Synthesis of Supported PGMs**

Among other flame processes, FSP plays a dominant role in the manufacture of supported metals due to its versatility in terms of applicable precursors. Traditional flame synthesis as applied for the manufacture of fumed Al2O3, SiO2 or TiO2 relies on volatile precursors, which are evaporated...
prior to feeding them into the flame reactor (9). As volatile precursors at reasonable prices are rare and only available for a limited selection of metals, the development of the FSP technique, which relies on precursors dissolved in a combustible liquid (14–17), opened a new range of materials available through flame processes, including supported pgms. Possible precursors for the pgm and the support include metal salts (nitrates, carbonates, chlorides) or organometallic compounds, typically alkoxides, carboxylates or acetylacetonates. These metal precursors are dissolved in an appropriate solvent (such as alcohols, hydrocarbons or carboxylic acids), fed through a spray nozzle and dispersed by a gas, resulting in fine droplets. This spray is ignited, forming a spray flame, where the solvents and usually also the metal precursors are evaporated and combusted. Product particle formation then takes place by nucleation from the gas phase. Maximum flame temperatures typically lie between 2000 and 2500ºC and are quenched within a few milliseconds down to 400ºC (18, 19).

Flame synthesis of supported pgms generally results in well dispersed pgm particles on top of a ceramic carrier, which is the desired structure for catalysts. This suggests that supported metals are formed by a sequential pathway in the flame (13, 20). Figure 4 depicts the basic mechanism for formation of supported pgm particles. As the volatility of the ceramic supports is generally lower than that of the pgm, the support forms first by nucleation at higher temperatures than the pgm. Then the support particles grow by coagulation and sintering in the hot flame environment. Later, as the temperature drops further away from the flame, the pgm also nucleates (21). One can imagine two possible pathways: homogeneous nucleation of the pgm and subsequent deposition on the support, or direct heterogeneous nucleation on the support. The latter is the more
probable pathway (9). Compared to flame synthesis of pgms in the absence of a support, their deposition and immobilisation on the support slows down their sintering, resulting in particles typically smaller than 5 nm. Table I gives an overview of supported noble metals made in flames included in this review.

The FSP technique allows precise and reproducible control of the support surface area and the size of the pgm particles. The most important factor determining support and metal particle size is the high-temperature particle residence time, which can be controlled by precursor and dispersion gas flow rates during FSP (16, 22). Increasing precursor flow rates and/or lowering the dispersion gas flow rate results in longer flames and higher temperatures, and thus larger support particles as sintering after coagulation is enhanced. The size of the pgm particles is mostly determined by the metal loading in terms of weight per surface area of the support. Figure 5 shows the Pd particle size on Al₂O₃ for different Pd contents (1–7.5 wt.%, controlled by the Pd concentration in the precursor solution) and Al₂O₃ supports with different specific surface areas (23). The Pd particle size shows a nearly linear dependence on the Pd loading, increasing with higher Pd loadings. This shows that the control of Pd particle size is not independent of the support formation. In contrast, only for Au the particle size was independent of the support surface area or composition, suggesting homogeneous nucleation of Au particles and later deposition (24).

Support and metal formation can be decoupled by rapidly quenching the flame at a certain height either by expansion through a critical flow nozzle (9, 25) or by introduction of a cold gas stream (21). Depending on the point of quenching, particle growth can be stopped at any position in the particle formation sequence outlined in Figure 4. Early quenching resulted in smaller support particles (TiO₂) and polydisperse Pt particles (very large and very fine) by incomplete evaporation of the Pt precursor, while late quenching had no further effect on the support but froze the growth of the Pt particles. This gave a minimum in Pt particle size by quenching exactly at the point of complete Pt precursor evaporation (9, 21).

Table I
Overview of Flame-Made Supported Noble Metals with the Corresponding Support Material and Their Applications

<table>
<thead>
<tr>
<th>Metal</th>
<th>Support</th>
<th>Application</th>
<th>References*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>Al₂O₃</td>
<td>Enantioselective hydrogenation</td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>BaCO₃/Al₂O₃</td>
<td>NOx storage-reduction</td>
<td>(28)</td>
</tr>
<tr>
<td></td>
<td>Ce₃Zr₁₋ₓO₄</td>
<td>Three-way catalyst</td>
<td>(11)</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>Oxidation catalyst, photocatalysis</td>
<td>(20, 26, 31)</td>
</tr>
<tr>
<td></td>
<td>SnO₂</td>
<td>Sensor</td>
<td>(27)</td>
</tr>
<tr>
<td>Palladium</td>
<td>Al₂O₃</td>
<td>Enantioselective hydrogenation</td>
<td>(23)</td>
</tr>
<tr>
<td></td>
<td>La-Al₂O₃</td>
<td>Catalytic combustion</td>
<td>(12)</td>
</tr>
<tr>
<td></td>
<td>La₂O₃</td>
<td>Catalytic combustion</td>
<td>(36)</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>Hydrogenation</td>
<td>(37)</td>
</tr>
<tr>
<td></td>
<td>ZnO</td>
<td>Sensor</td>
<td>(38)</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Al₂O₃</td>
<td>Selective hydrogenation</td>
<td>(40)</td>
</tr>
<tr>
<td></td>
<td>Ce₃Zr₁₋ₓO₄</td>
<td>Syngas production</td>
<td>(41)</td>
</tr>
<tr>
<td>Gold</td>
<td>Fe₂O₃</td>
<td>Selective CO oxidation</td>
<td>(42)</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>Selective CO oxidation</td>
<td>(24)</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>Selective CO oxidation</td>
<td>(42, 43)</td>
</tr>
<tr>
<td>Silver</td>
<td>TiO₂</td>
<td>Photocatalysis, antimicrobial</td>
<td>(44)</td>
</tr>
<tr>
<td></td>
<td>ZnO</td>
<td>Photocatalysis</td>
<td>(45)</td>
</tr>
</tbody>
</table>

*See main text for Reference numbering
Platinum

Platinum supported on TiO₂ was the first supported PGM made in a flame by a vapour-fed aerosol flame process (20). It consisted of well dispersed Pt clusters on top of the TiO₂ support. However, the low volatility of the applied platinum(II) acetylacetonate (Pt(acac)₂) precursor limited the production rate to a few mg per hour. FSP quickly superseded that process, as it works with liquid precursor solutions and easily allows synthesis of large sample quantities within a few minutes. All of the following examples involve catalysts that have been prepared by this method.

FSP of solutions containing Pt(acac)₂ and aluminium sec-butoxide resulted in the formation of small Pt clusters (< 5 nm) well dispersed on top of Al₂O₃ nanoparticles in the range 10 to 30 nm (13). Similar structural properties have been observed for Pt on TiO₂ (26), CeₓZr₁₋ₓO₂ (11) or SnO₂ (27). Flame-made Pt/Al₂O₃ catalysts were tested for their behaviour in enantioselective hydrogenation, where the open structure of the support strongly increased the catalytic activity due to improved mass transfer properties, without losing selectivity compared to commercial catalysts (13).

Pt on solid solutions of ceria-zirconia is a standard automotive three-way catalyst, and when prepared by FSP the catalyst did not lose its low-temperature oxygen exchange capacity after exposure to high temperatures (1100°C) (11). The Pt clusters were oxidised in the as-prepared material and rather high temperatures were necessary for reduction into metallic Pt under a H₂ atmosphere.

More recently developed automotive catalysts are the so-called NOx storage-reduction (NSR) catalysts that are used for abatement of NOx under lean conditions. Fully functional Pt/Ba/Al₂O₃ NSR catalysts could be prepared by two-nozzle FSP as shown in Figure 6 (28). Spraying and combusting the precursors of all
three components together resulted in amorphous barium species which were not active for NOx storage. However, using two spray nozzles, one as an Al and the other as a Pt/Ba source, allowed synthesis of individual Al2O3 and BaCO3 particles with the Pt clusters on top of them. These materials exhibited similar behaviour to impregnated catalysts during NSR. At higher Ba loadings, however, the flame-made NSR catalysts showed faster and higher NOx uptake (29). This is attributed to the unique formation of relatively unstable BaCO3 in flame-made materials, even at high Ba content. Similar observations could be made for flame-made Pt/Ba/ CeO2–ZrO2. Replacing Al2O3 with Ce0.75Zr0.25O2 allowed regeneration of these NSR catalysts after thermal deterioration (30). Well-dispersed Pt clusters were also obtained on TiO2 and increased the activity of TiO2 for photocatalytic degradation of sucrose (26) and methyl orange (31).

Beyond the widespread application of Pt and Pd in catalytic processes, they can also be applied to enhance the gas sensing properties of semiconducting metal oxide sensors (27). Flame synthesis of sensor materials is attractive as it allows synthesis of the active sensing material and deposition on a sensor substrate in one step (32). This way, very porous (up to 98% porosity) Pt/SnO2 sensors have been prepared, exhibiting a very low detection limit for CO (down to 1 ppm) with high sensor response. Direct FSP deposition of a Pd/Al2O3 layer acting as a water filter on top of a sensing SnO2 layer decreased the influence of humidity on the sensor signal (33). Moreover, micropatterning of these directly deposited layers followed by flame annealing has made possible the synthesis of well adherent Pt/SnO2 sensing layers (34).

**Palladium**

Similar structural properties as for Pt were observed for Pd on Al2O3 (23). Figure 7 shows a scanning transmission electron microscope (STEM) image of flame-made Pd/Al2O3 containing 5 wt.% Pd and the corresponding Pd particle size distribution. In the as-prepared materials, Pd was in the form of PdO which was very stable and hardly reduced into metallic Pd compared to Pd/Al2O3 prepared by other methods (35). This can be traced to the generally strong metal–support interactions of flame-made materials. These Pd/Al2O3 catalysts exhibited good selectivity and activity in enantioselective hydrogenation (23). The easy control of pgm particle size, as shown in Figure 5, was used to elucidate the structure sensitivity of the reaction.

Flame-made Pd supported on very stable lanthanum-doped Al2O3 was used for catalytic combustion of methane and investigated for its high-temperature stability (12). After annealing at
1100°C, flame-made Al₂O₃ retained a surface area of 90 m² g⁻¹ compared to 57 m² g⁻¹ for a commercial Al₂O₃. Adding a few weight per cent of La increased the thermal stability of flame-made Al₂O₃ even further. The generally high thermal stability of flame-made supports is traced to the absence of small pores, which makes them promising catalysts for high-temperature processes. However, the deactivation of the catalyst in catalytic combustion up to 1000°C was mainly caused by sintering of Pd, with only marginal effects from the stability of the support, preparation method (impregnation, flame synthesis) or La content (12). Similar observations have been made for Pd on La₂O₃ particles which were made by spraying aqueous precursor solutions in a hydrogen flame. These particles were then directly collected in a water suspension that was directly applied to coat metallic honeycombs (36).

In a similar way Pd/SiO₂ containing 0.5–10 wt.% Pd has been prepared by FSP (37). These catalysts have been tested for selective hydrogenation of 1-heptyne. Pd has also been added to ZnO particles to improve their ethanol sensing behaviour (38). Further, flame-made Pd/CeO₂ particles have been applied successfully in solid oxide fuel cells (39).

**Rhodium**

A study comparing flame-made Rh/Al₂O₃ catalysts with two commercial ones has been published recently (40). The as-prepared flame-made material consisted of well dispersed Rh₂O₃ particles (< 5 nm) that needed relatively high temperatures (> 400°C) to be reduced into metallic Rh. In contrast to commercial catalysts, a large amount of cationic Rh species were formed during reduction, indicating a strong interaction between Rh and the Al₂O₃ support. Similarly to the previously described Pt/Al₂O₃ and Pd/Al₂O₃, the flame-made Rh/Al₂O₃ also showed much higher activity in the chemoselective hydrogenation of 3,5-di-(trifluoromethyl)-acetophenone than commercial catalysts, together with comparable selectivity. FSP was also applied for synthesis of Rh/CeZrO₄ catalysts that were used for syngas production from butane (41).

**Iridium, Osmium and Ruthenium**

These pgms are not as widely applied in catalysis as Pt or Pd and thus no reports on flame synthesis of them are available. So far they have only been prepared by FSP in combination with other metals as described later in the section on bimetallic systems.

**Gold and Silver**

Although not belonging to the pgms, supported Au will be discussed here as it has attracted a lot of interest since the discovery of its catalytic “non-inertness”. Therefore it is not surprising that flames have also been employed for the manufacture of supported Au catalysts. Au supported on TiO₂ and SiO₂ has been made by FSP (24). On both supports, the Au particle size was larger than the previously described pgms, and varied between 3 and 15 nm depending on the Au content (1–4 wt.%). The catalytic behaviour of FSP-made Au catalysts supported on SiO₂, TiO₂ and Fe₂O₃ in the selective oxidation of carbon monoxide was investigated, revealing similar relationships between Au particle size or support material and catalytic performance to those seen in conventionally prepared catalysts (42). Au/TiO₂ was also directly deposited from the gas phase onto surfaces in microsystems (43). Shadow masking allowed deposition of these catalysts in small microchannels, which were directly used for testing catalytic reactions in microreactors, here for instance the oxidation of CO.

Silver is also not a pgm but exhibits similar structural properties when made in flames. The formation of small Ag clusters has already been observed on TiO₂ (44), SiO₂ (42) and ZnO (45). Besides having some interesting applications due to its strong antimicrobial properties (44), Ag also enhances the photocatalytic activity of the support. The addition of Ag increased the photocatalytic activity of TiO₂ for decomposition of stearic acid (44) and the activity of ZnO for decomposition of methylene blue (45).

**Bimetallic Systems**

Alloying pgms is often used as a method for fine-tuning and optimising their properties. The
formation of bimetallic clusters can be difficult when working with conventional techniques. Flame synthesis facilitates formation of bimetallic clusters as both constituents are formed practically simultaneously in the flame. This has already been exploited for synthesis of bimetallic Pd-Pt/Al2O3, where Pd and Pt were present in the same clusters and form a Pd-Pt alloy upon reduction (46). Figure 8 shows an STEM image of this material with the corresponding energy dispersive X-ray (EDX) analysis of a single metal particle, revealing the presence of Pd and Pt in the same cluster. Here, the addition of 5% Pt to Pd increased its reducibility and especially the noble metal cluster stability against sintering at high temperatures (up to 800ºC), resulting in an improved resistance against deactivation during catalytic combustion of methane (46).

Similar observations were made for Au-Ag, used as a catalyst for selective CO oxidation. The catalyst was proved to consist of small alloyed Au-Ag bimetallic clusters (< 10 nm) dispersed on TiO2, Fe2O3 or SiO2 (42). Small alloyed Pt-Rh clusters were also deposited on Al2O3 and evaluated for their behaviour in the partial oxidation of methane (47). Alloy formation was also observed for unsupported Ag-Pd particles (48), whereas Pt-Ru was only partly alloyed either unsupported (49) or supported on Al2O3 (47). It can be assumed that simultaneous nucleation of noble metals in the gas phase or on the support, combined with similar oxidation states, leads to the formation of bimetallic clusters. This makes flame technology a promising alternative to wet-phase processes for preparation of various bimetallic or even “multi-metallic” catalysts, as already shown for a combination of four pgms (Pt, Pd, Rh and Ru) on Al2O3 for partial oxidation of methane (47).

**Conclusions**

Flame aerosol technology is well suited for one-step synthesis of supported pgms that can be applied in catalysis and as gas sensors. In general the pgms form finely dispersed clusters on top of nanostructured ceramic supports, which can consist of most metal oxides or their mixtures. A
characteristic property of flame-made support materials is their open structure, which gives high thermal stability and good mass transfer properties that can result in catalysts with improved activity and longevity. Strong metal–support interactions that can result in catalysts with improved activity thermal stability and good mass transfer properties materials is their open structure, which gives high characteristic property of flame-made support compositions.

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