

## THE REDUCTION OF HEXACHLOROPLATINIC(IV) ACID ON THE SURFACE OF ALUMINA

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### Abstract

Platinum particles were deposited onto alumina by the chemical reduction of hexachloroplatinic(IV) acid using various carboxylic acids. The surface of the alumina was treated with reagents, hydrochloric acid and sodium hydroxide, to generate new active sites on the surface. All the samples were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Better control of the platinum particle size and distribution was achieved with a low-temperature preparation and surface pretreatment. Energy-dispersion X-ray (EDX) microanalysis was used for platinum detection on the surface of the alumina.

**Key words:** platinum, particles, alumina, support, carboxylic acids, reduction

### Introduction

Noble-metal nanoparticles are used in a wide variety of scientific and technical fields because they possess remarkable properties. The high reactivity of nanoparticles makes them good candidates for environmental catalysts for the treatment of automotive exhaust for the abatement of volatile organic compounds and in Fuel Cells.<sup>1,2</sup> Other major industrial applications of supported metal catalysts include naphta reforming, selective hydrogenation and hydroformylation reaction.<sup>3,4,5</sup> These catalysts contain a small concentration of a noble metal on an inert or active porous support.

To produce these catalysts, the noble metal precursor is deposited as a thin layer on a support material, such as alumina or silica, with a high specific surface area. Because of the nanometer-thick outer layer of active noble metal, only tiny amounts of the expensive noble metal are needed to provide highly active catalyst. The performance of catalytic converters depends on the characteristics of both the support and the active metal catalysts and their interactions.<sup>6</sup>

Many of the physical and chemical properties of solid materials depend on the size of the material. High reactivity of nanoparticles is a consequence of the high ratio of surface to core atoms in comparison with conventional particles.<sup>18</sup> This makes them ideal candidates for catalytic applications. The preparation of nanoparticles by the chemical reduction of metal species on various substrates at relatively low temperatures has already been reported for both aqueous and nonaqueous solutions.<sup>6,7,8,9</sup>

Controlling the particle size continues to be the most difficult challenge because individual nanoparticles tend to agglomerate during the preparation process.<sup>9,10,11</sup> It was discovered that a complex interaction exists between the porous support material, such as alumina or silica, and the thin outer-shell of precursor and deposit of the noble metal, such as platinum, palladium, rhodium and ruthenium, on the support surface.<sup>12, 13</sup> The catalytic activity depends on the size of the crystallites, and it was shown that it decreases with increasing crystallite size because of a very strong interaction on low coordination sites, whose proportion increase at high dispersion.<sup>8</sup> The temperature used for the preparation of the catalyst influences the mean crystallite size.<sup>7,12</sup>

### Experimental

Aluminium oxide (particle size: 0.2-0.063 mm) was used as a support material on which to deposit the platinum. The as-received substrate was thermally treated at 1500 °C for 12 hours, and then some of the substrate was placed in a glass tube. The carboxylic acid (formic, ascorbic or acetic) was then added dropwise to the Al<sub>2</sub>O<sub>3</sub>. The addition of the acid took about 30 min. The initial platinum content in the solution of hexachloroplatinic(IV) acid was 1 wt.%. This platinum solution was introduced through a layer of Al<sub>2</sub>O<sub>3</sub>, which was previously impregnated with carboxylic acid, and the excess platinum solution was left to flow away. The platinum solution was deposited at room temperature. The impregnated samples were dried in an oven at 105 °C in air for 8 h and further thermally treated for 8 hours at 500 °C.

The distribution of platinum on the alumina was observed with a JEOL-6400 scanning electron microscope. Energy-dispersion X-ray (EDX) microanalysis was used

to detect the platinum on the surface of the substrate. X-ray powder diffraction (Philips X'Pert diffractometer (CuK $\alpha$ , Si external standard)) was used for the measurement of the mean crystallite size.

### Reagents

Aluminium oxide anhydrous ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), 141 m<sup>2</sup>/g, Merck, Darmstadt

H<sub>2</sub>PtCl<sub>6</sub>×6H<sub>2</sub>O (~40% Pt), for synthesis, Merck, Darmstadt

Formic acid, 99%, p.a., Merck, Darmstadt

Acetic acid, 99%, p.a., Merck, Darmstadt

L(+)-Ascorbic acid, 99.7%, GR for analysis, Merck, Darmstadt

HCl, 37%, p.a., Merck, Darmstadt

NaOH, p.a., Merck, Darmstadt

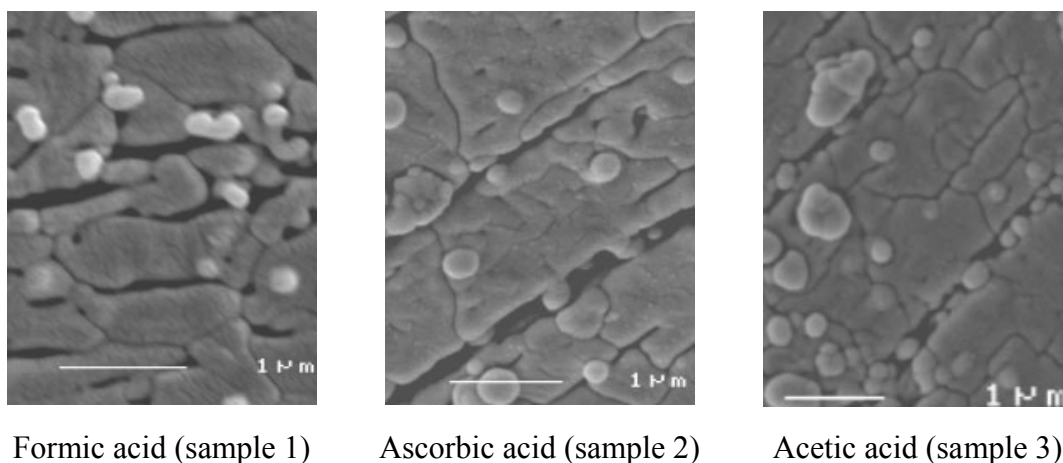
### Results and discussion

The techniques for preparing supported-noble-metal catalysts are chosen so that fine dispersions of the metal are achieved, which results in high activity for a given metal loading. Previous work on the preparation of such catalysts by the classical impregnation method revealed the limitations of such a method:<sup>14</sup> the possibilities to influence the dispersion of platinum on the substrate and the particle size were rather limited.

Better control of the process and the deposition of platinum on the appropriate substrate can be achieved by the reduction of platinum ions from its precursor solutions. Finer dispersions can be obtained by varying the process conditions and the support pretreatment. Nanosized metal particles are easily obtained by reduction with carboxylic acid, but there is a strong tendency for the primary particles to agglomerate, especially with a high concentration of metal ions and at higher temperatures. Surfactants are often used for the control of the morphology, but they should not be used when preparing catalysts because of the risk of contamination.<sup>8</sup>

### The chemical reduction of platinum ions

The platinum ions in a thin film of the solution adhering to the support surface can be reduced by an appropriate reducing agent. In this study, formic, ascorbic and acetic acids were used as the reducing agents. Approximately 10 min after the start of the reaction, at room temperature, the colour of the substrate changed from gray to black. The results of an EDX analysis showed that the formic acid reduced the platinum precursor to platinum metal without any further thermal treatment. The hexachloroplatinum complex was stable at room temperature, and was not reduced by ascorbic and acetic acids; it was necessary to heat the substrate to 100 and 200 °C to obtain platinum. Platinum metal can also be obtained from hexachloroplatinum acid without the addition of carboxylic acid, by thermal decomposition at higher temperatures, i.e. at 500 °C. The advantages of reducing with carboxylic acids are a better control of the conditions and a process that is completed at appreciably lower temperatures without calcinations. Reduction with carboxylic acid resulted in platinum nanoparticles that did not coalesce under the experimental conditions used in this study, although the reduced amount of agglomeration might also be due to reduced levels of particle diffusion on the surface of the substrate.



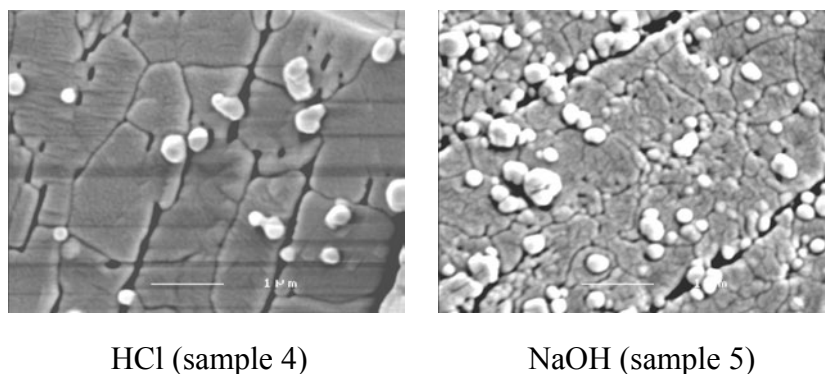
**Figure 1.** Microstructure of samples 1-3 after reduction with carboxylic acid.

The SEM pictures in Figure 1 show the presence of small particles and aggregates of particles. The aggregates are well distributed on the surface of the alumina with an average size of about 200 nm.

Carboxylic acids, especially acetic acid, are widely used both as solvents and reactants in heterogeneous catalytic reactions over alumina-containing catalysts. Alumina and acetic acid react to produce oxonium cation which can have an effect on a chemical reaction. By analogy, similar compounds may be formed with other carboxylic acids.<sup>15</sup>

### Surface pretreatment

Many applications of metal oxides depend on surface properties, which include Brønsted acidity or basicity, Lewis acidity, and the coordination unsaturation or redox properties of the surface-metal ions. In order to generate the desired surface, it is common to perform treatments, such as high-temperature calcinations to dehydroxylate the surface or functionalization by reacting the surface hydroxyl groups with various reagents.<sup>16</sup>

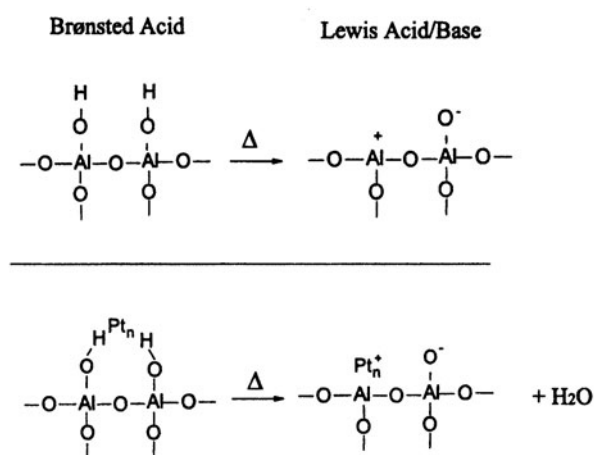


**Figure 2.** Microstructure of surface-pretreated samples (4, 5) after reduction with ascorbic acid.

Etching with HCl solution fixes some point defects on the surface to which the platinum is bound. HCl is a competitor whose role is to set the equilibrium between the platinum precursor in the solution and that fixed on the alumina support. These competing agents, which have a strong affinity for alumina, become irreversibly fixed on the external sites of the support and force the platinum precursor to migrate farther towards the centre of the grain to find free sites.<sup>17</sup> From the SEM results (Figure 2) it is clear that most of the platinum spheres are fixed near the edges of the grains. However, an increase in the pH (Brønsted or Lewis acid sites) results in a more uniform occupation of the surface by the metallic complex. Hydroxyl groups are formed on the

surface of the alumina by pretreating with NaOH and these OH<sup>-</sup> groups either bind or exchange with Cl<sup>-</sup> groups on the coordination site of H<sub>2</sub>PtCl<sub>6</sub>.

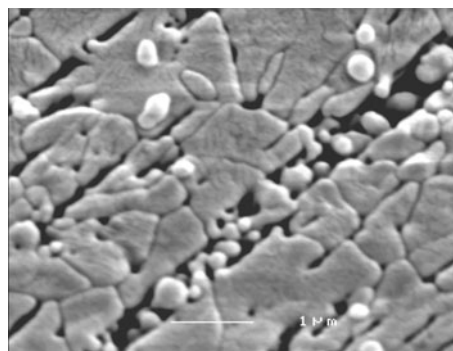
Figure 3 shows a plausible interaction of the primary platinum clusters at the anchoring site on the alumina. Brønsted acid sites are present on as-received alumina. After heating to 350 °C and above, Lewis acidity becomes predominant. Strong interaction with Lewis acid sites leads to the electronic polarization of platinum clusters, forming a stable Pt<sub>n</sub><sup>+</sup>Al(O)<sub>3</sub> local structure.<sup>10</sup>



**Figure 3.** Proposed Pt-cluster interaction with the surface-acid sites of Al<sub>2</sub>O<sub>3</sub>.<sup>10</sup>

### Ethanol medium

Using an alcohol solution (ethanol absolute) of platinum ions (1 wt.%) lower surface tension was achieved and most of the platinum particles were deposited in the pores of the alumina.



Pt/EtOH (sample 6)

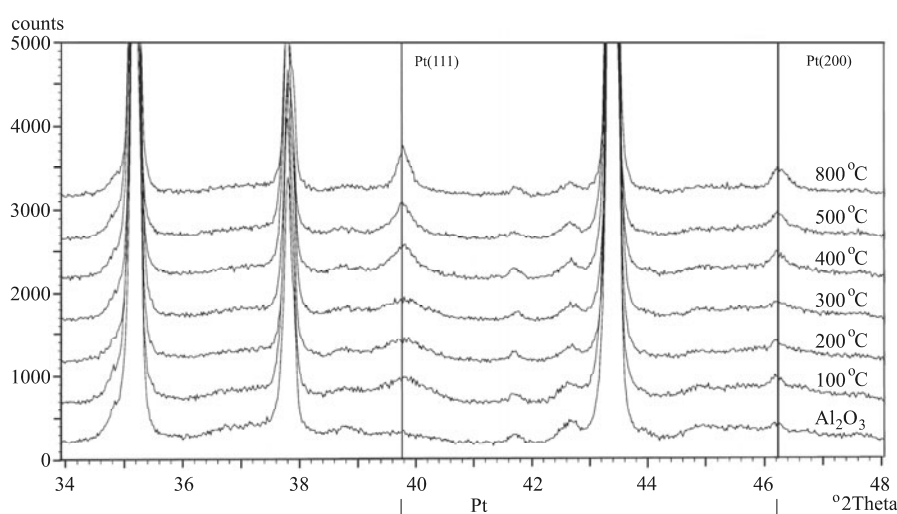
**Figure 4.** Microstructure of sample 6 after reduction.

## XRD results

The Bragg peaks were analyzed by using the Scherrer formula to calculate the crystallite size. The results are shown in Table 1.

**Table 1.** Crystallites size of samples 1-3.

Sample	Crystallites size (nm)
Sample 1 (Formic acid)	25
Sample 2 (Ascorbic acid)	15
Sample 3 (Acetic acid)	15



**Figure 5.** XRD diagram Pt/Al<sub>2</sub>O<sub>3</sub> catalysts prepared at different temperatures.

The XRD patterns show clearly that the mean crystallite size of the platinum increases with increasing temperature (Figure 5). The effects of the processing temperature and the reaction time on crystallite size were studied. Temperature has the influence on the mean crystallite size:<sup>17</sup> as expected, the crystallite sizes increased with temperature. The reactivity also depended on crystallite size and was found to decrease with increasing crystallite size.

## Conclusions

The described method produces metallic platinum on the surface of alumina and appears to be promising for the preparation of supported-metal catalysts. It involves very simple operations, low preparation temperature, and can produce well-dispersed

platinum metal particles (with a crystallite size between 15 and 25 nm) on the substrate surface. Control of the size, distribution and dispersion of particles was possible by using various reducing agents, surface pretreatments and modifications to the final step of the catalyst preparation, e.g. drying and calcinations. Formic, ascorbic and acetic acids were used as reducing agents. Formic acid reduced the platinum precursor without any additional thermal treatment, whereas for ascorbic and acetic acids it was necessary to heat the substrate with the platinum precursor up to 100 and 200 °C, respectively, to obtain metallic platinum. Nevertheless, this process significantly lowered the temperature of the reduction from 500 to 200 °C and platinum metal was obtained without the need for calcinations. Surface pretreatments using reagents (HCl, NaOH), generated new active sites on the surface of the alumina (Brønsted or Lewis acid sites), and strong interactions of the small platinum clusters with the Lewis acid sites resulted in strong anchoring of the platinum clusters onto the alumina. The platinum nanoparticles did not coalesce under the experimental conditions used in this study although a lesser degree of agglomeration was observed due to the reduced levels of particle diffusion on the surface of the substrate. Further improvements that would shorten the preparation time and better control the conditions would be advantageous.

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### Povzetek

Velika uporabnost platine v industriji in raziskavah je posledica njene reaktivnosti, ki je odvisna od velikosti delcev kovine. Posebej pomembna je uporaba nanodelcev platine pri katalitskih procesih. Z redukcijo platinskega prekursorja v adsorbiranem filmu raztopine na površini nosilca smo pripravili iz nanodelcev sestavljen nanos platine.

Pri pripravi nanosa platinskih delcev na površini aluminijevega oksida, smo uporabili redukcijo heksakloroplatinske kisline z različnimi karboksilnimi kislinami. Površino oksida smo predhodno aktivirali s HCl in NaOH. Karakteristike dobljenih nanosov smo merili z rentgensko difrakcijo in elektronsko mikroskopijo z mikroanalizo (SEM, EDX). Ugotovili smo, da uporabljena metoda priprave nanosa platine na površino aluminijevega oksida omogoča nižjo temperaturo priprave in dobro kontrolo velikosti nanodelcev platine v nanosu.