

Shape-controlled synthesis and catalytic behavior of supported platinum nanoparticles

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ABSTRACT

Supported metal catalysts are among the most important catalysts, being used on a large scale for refining of petroleum, conversion of automobile exhaust, hydrogenation of carbon monoxide, hydrogenation of fats, and many other processes. It is clear that significant improvements in the catalytic behavior can be achieved through an adequate morphological control of the supported metal particles. Colloidal method can provide precise shape control of nanoparticles but seems not suitable for large scale production. In this study we disclose that precise shape control of metal particle also can be achieved by traditional metal preparation method. By choosing of Pt acetoacetate as precursor and methanol/ toluene as solvent in the supports pretreatment and precursor impregnation, evenly dispersed 20nm cubic Pt nanoparticles with 5% loading on carbon was available. This Pt/C catalyst shows high selectivity in hydrogenation of halonitro-aromatics

Keywords: nanoparticle, shap-control, supported catalysts, hydrogenation

1. BACKGROUND

The physical and chemical properties of nanosized particles are greatly affected not only by their sizes but also by their shapes. It is clear that significant improvements in the catalytic behavior can be achieved through an adequate morphological control of the supported metal particles. Morphological control is still difficult especially for supported metal particles because the preparation process include the metal microcrystal formation, growth and the complex interaction between metal particles and supports. The final characteristics of the material are extremely sensitive to the history of preparation. One convenient method to minimize the preparation and supports effects on the metal morphology is to prepare well-defined metal nanoparticles at first, then deposit metal nano-particles on supports, but seems not to be suitable in large-scale supported catalysts production. In this work we have showed that very well shape-controlled and supported nanoparticles with high metal loading are also can be achieved through those classic methods (impregnation, calcinations, reduction) by carefully adjusting the reaction parameters.

2. EXPERIMENT

2.1 Preparation of 20 nm cubic 5% Pt/C catalyst

6.0 g activated carbon was soaked with 30 ml methanol for 12 h. After filtration the carbon solid was dispersed in 60 ml toluene and 0.605 g platinum (II) acetylacetonate in 20 ml toluene was added. The total suspension was keeping rotated on rotary evaporator for 12 h. Then toluene was slowly evaporated out in 20mmHg and 85 °C water bath. The activated carbon with platinum complex was dried in vacuum oven at 80 °C for 6 h and then reduced in 5% H₂ in N₂ flow at 100°C for 4 h. After that gas flow was switched to nitrogen and let the system cool to room temperature. The Pt/C was ready for use in hydrogenation reaction. The resulting catalyst had a weight composition of 5% Pt.

2.2 General selective hydrogenation of 2-chloro-nitrobenzene:

A typical hydrogenation procedure was conducted as follows: 4.04 g 2-chloro-nitrobenzene catalyst and proper amount of catalyst was dispersed in 60 ml ethanol. The suspension was added into a 300 ml stainless steel autoclave with glass liner equipped with a mechanically stir blade, a pressure gauge, a gas inlet tube attached to a hydrogen source and a cooling circler connected to the temperature controller. The autoclave was purged by nitrogen for three times. When the temperature stabilized at 25°C, the vessel was pressurized to 150 psi with hydrogen. During the reaction mixture was vigorously stirred and was temporarily stopped for collect sample or analysis when no pressure decrease was observed. The product was analyzed on gas chromatography Agilent 6890 equipped with a FID detector and Rtx-5 Amine column.

3. DISCUSSION

Hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline is a tedious process and often yields many de-chloride byproducts during the reaction. In this study, hydrogenation catalyzed by these three catalysts yielded aniline as the detectable de-chloride byproduct and *o*-hydroxylamine-chlorobenzene as the main intermediate of an incomplete reaction. The results as shown in Table 1 indicate that catalyst **Cubic-Pt** took 10 h to almost

complete the reaction, meanwhile catalysts **Amorp-Pt** and **DG-Pt** only needed about 6 h. The product analysis showed that **Cubic-Pt** yielded the lowest concentration of dichloride byproduct aniline (0.28% in 10 h) as compared to catalyst **Amorp-Pt** (4.83% in 6 h) and **DG-Pt** (0.48% in 6 h).

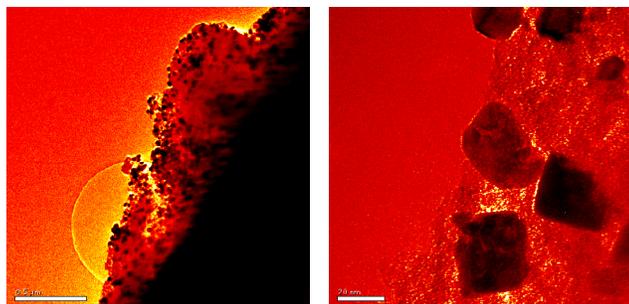


Figure 1. (A): Low-magnification TEM image of 5% wt. Pt /C, showing a uniform size distribution of the supported particles. (B): High-magnification image highlighting the cubic shape of the Pt nano-crystallites.

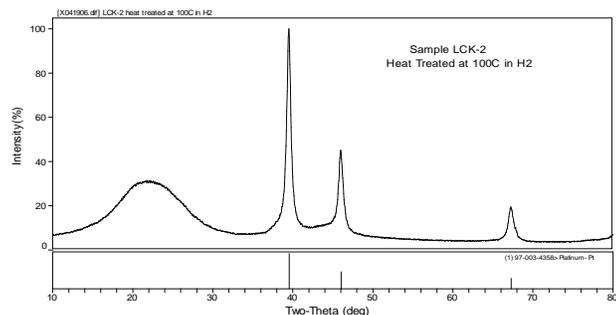


Figure 2. The XRD characterization of cubic 5%Pt/C

Table 1: Hydrogenation of *o*-CNB with Pt/C catalysts ^a

Cat ^b	Time (h)	Selectivity ^c			Conv. (%)
		<i>o</i> -CAN	AN	<i>o</i> -HOCAN	
Cubic-Pt	4.5	66.53	0.13	33.33	100
	6	86.16	0.19	13.65	100
	8.5	97.10	0.23	2.67	100
	10	99.41	0.28	0.31	100
Amorp-Pt	4.5	92.98	4.33	2.69	100
	6	94.23	4.83	0.94	100
DG-Pt	4.5	90.73	0.39	8.88	100
	6	98.94	0.48	0.59	100

^a Reaction conditions: T = 25 °C; P_{H₂} = 10 bar; 4.04 g *o*-chloronitrobenzene in 60ml ethanol; 0.02g 5%Pt/C (substrate/catalyst = 5,050:1); ^b Catalyst, **Cubic-Pt**: 20 nm cubic 5% Pt/C; **Amorp-Pt**: amorphous 5% Pt/C; **DG-Pt**: 5% Pt/C with Bi doping bought from Degussa AG. ^c *o*-CAN = *o*-chloroaniline, AN = aniline, *o*-HOCAN = *o*-hydroxylamine-chlorobenzene. Other byproducts or intermediates with concentration lower than 0.10% are exclusive from calculation.

For the mechanism in the hydrodehalogenation reaction of aromatic halides, most researches agree that there is an electrophilic attack of cleaved hydrogen on the adsorbed aromatic halides. It was believed that the electron-deficient state of the Pt particles would weaken the extent of electron feedback from the Pt particles to the aromatic ring in *o*-CAN, which would further suppress the hydrodechlorination of *o*-CAN. Based on this principle, many works have been done to synthesis Pt catalysts with different metals doping such as Cr, Mn, Fe, Bi, etc, or to support the Pt catalyst on magnetic support (for instance iron oxide etc.). The metals doping or magnetic supports changed the electronic circumstance surrounding of the Pt particle so the resulted Pt catalyst shows increased selectivity or decreased concentration of hydroxylamine-chlorobenzene intermediates during the hydrogenation of *o*-chloronitrobenzene. In our supported cubic Pt catalyst we believed that Pt particle located at lateral boundary has less adjacent atoms so that it was more electron-deficient than the atoms in the cubic faces and prone to absorb hydrogen atom by priority. So most hydrogenation was happened on lateral boundary area, wherein and electron-deficient Pt provides the high reaction selectivity is under expectation.

4. REFERENCE

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