Shape-Controlled Synthesis and Catalytic Behavior of Supported Platinum Nanoparticles

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ABSTRACT

A 5 wt% Pt/C catalyst with around 20 nm cubic platinum particles was prepared through a conventional preparation method (i.e. precursor impregnation, reduction, and calcination) by choosing of hydrophobic solvent in the impregnation procedure. These 20 nm cubic Pt particles showed high selectivity (ca. 99.4%) for the hydrogenation of *o*-chloronitrobenzene.

Keywords: nano-particle, shape control, supported catalyst, hydrogenation

1 INTRODUCTION

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. Since the researches show that shape control technologies may contribute the improvements to the final catalyst performance, the chemical industries are eager to apply this technology into commercial production [1-4]. However, in the last 5-10 years the efforts to use prevailing colloid shape control methods in industry were frustrated by many problems.

The most efficient method to precisely metal shape control was the colloid method by using functional polymer as capping agent or protective agent during the metal was reduced [5-9]. The stable metal colloidal solution was normally prepared in very low concentration. Impregnation of this well-defined metal nanopaticles colloid with supports is the convenient way to prepare supported catalyst with well metal shape-controlled. However in large-scale production or in order to prepare high loading supported catalyst, there is large amount of water needs to be very carefully evaporated off after the impregnation step. This process is not only energy and time consumed but also in the risk of nano-particles aggregation and lost of the morphological control. This inherent problem form colloid method itself restricts this method to be applied in large-scale catalyst production.

Traditionally, supported metal catalysts are typically made by impregnation of a porous supports with an aqueous solution of a metal salt, followed by reduction and calcination. This preparation method now is predominant in industry large-scale catalyst production but is always thought to lose ability for metal shape control.

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 acetylacetonate as precursor and methanol/ toluene as solvent in the supports pretreatment and precursor impregnation, evenly dispersed 20nm cubic Pt nanoparticles with 5 wt% loading on carbon was available. This method may be reproduced in most of supported metal catalyst preparation, if metal acetylacetonate analogues are available, without changing extant industrial device and procedure.

2 EXPERIMENTS

Preparation of 20 nm cubic 5% Pt/C catalyst (Cubic-Pt)

6.0 g activated carbon was soaked with 30 ml methanol for 12 hours. After removal of excess methanol, 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 kept rotated on rotary evaporator. Toluene was slowly evaporated out in 20mmHg vacuum and at 85 $^{\circ}$C. The activated carbon with platinum complex was dried in vacuum oven at 80 $^{\circ}$C for 6 hours and then reduced in 5% H_2 in N_2 flow at 100°C for 4 hours. After that gas flow was switched to nitrogen and let the system cool to room temperature.

General procedure of 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 sample collection 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 DISSCUSION

The HRTEM characterization of this carbon supported catalyst is shown in Figure 1. Figure 1 shows that very uniform Pt microcrystals are imbedded in the support. The size of the supported Pt crystallites was estimated to be 14.5nm from the broadening of the Pt (111) peak in X-ray diffraction (at $2\theta \approx 40^\circ$). The d_{TEM} of 20nm is in fairly good agreement with d_{XRD} of 14.5nm.
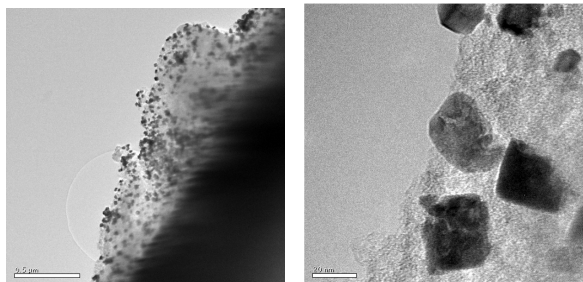

Figure 1. Left: Low-magnification TEM image of 5% wt. Pt /C, showing a uniform size distribution of the supported particles. Right: High-magnification image highlighting the cubic shape of the Pt nano–crystallites.

These cubic Pt nanocrystals supported on carbon, marked as **Cubic-Pt**, exhibit extra performance in catalytic hydrogenation of halo-nitrobenzene when compared to commercial available catalyst **DG-Pt**. **DG-Pt** is a commercial product from Degussa AG which composition is 5% Pt on carbon with bismuth doped as promoter.

Hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline is a tedious process and often yields many de-chloride byproducts during the reaction [10]. The results as shown in Table 1 indicated that catalyst **Cubic-Pt** took 10 h to almost complete the reaction, meanwhile catalysts **DG-Pt** only needed about 6 h. The product analysis showed that **Cubic-Pt** yielded the lowest concentration of de-chloride byproduct aniline (0.28% in 10 h) as compared to catalyst **DG-Pt** (0.48% in 6 h).

Catalysts [a]	Reaction Time (h)	Selectivity [b]			Conversion (%)
		o-CAN	AN	*o*-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
DG-Pt	4.5	90.73	0.39	8.88	100
	6	98.94	0.48	0.59	100

Table 1: Hydrogenation of *o*-CNB with Pt/C catalysts
Reaction conditions: T = 25 $^\circ$C; P_{H2} =10 bar; 4.04 g o-chloronitrobenzene in 60ml ethanol; 0.02g 5%Pt/C (substrate/catalyst = 5,050:1); [a] Catalyst, **Cubic-Pt**: 20 nm cubic 5% Pt/C; **DG-Pt**: 5% Pt/C with Bi doping bought from Degussa AG. [b] *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.

Efforts to prepare smaller size cubic Pt crystals on carbon as well as to optimize reaction parameters are ongoing. We believe that not only smaller size cubic Pt will increase hydrogenation rates but also more lateral boundary Pt atoms will result in a higher selectivity.

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