

Platinum Nanoparticles on Silica: Control of the Particle Size by Method of Pt Addition and Calcination Temperature

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Introduction

Supported noble metal catalysts are used in a large number of commercially important processes, including hydrogenation, naphtha reforming, oxidation, automotive exhaust catalysts and fuel cells. In order to maximize the activity, it is necessary to make small particles. Typically, supported catalysts contain particles of less than about 10 Å. It is well known that for some reactions, the particle size affects the rate (per surface atom) and the selectivity. Thus, precise control of the particle size is essential for optimum performance.

Several steps in the preparation including the support composition, metal salt, method of metals addition, pH, calcination, etc., affect the ultimate particle size in the reduced catalyst. Incipient wetness impregnation (IWI) is commonly used to prepare catalysts. The metal salt is dissolved in sufficient water to just fill the pore volume of the support. The catalyst is dried, calcined (typically at 500°C) and reduced. For silica supports, this method generally leads to large particles with dispersions often less than 10%. An alternative method is to adsorb the metal complex (Ads) onto the support from a slurry in excess water. The amount of adsorbed metal is dependent on the charge on the metal complex and support surface at the pH of the solution.

The effect of the method of preparation and the calcination temperature from 100 to 700°C on the Pt particle size on silica has been determined. In addition, the changes that occur in the Pt oxidation state upon calcination have been determined from the XANES and EXAFS spectra.

Methods and Materials

IWI Catalyst preparation: To 45 g of silica (290 m²/g and 1.0 cc/g) was added 0.90 g of Pt(NH₃)₄(NO₃)₂ (PTA) in 45 mL H₂O. The catalyst was dried at 100°C.

Ads Catalyst preparation: 45 g of silica was slurried in 400 mL H₂O. The pH was increased to 9.5 by addition of NH₄OH; 0.90 g of PTA dissolved in 50 mL H₂O was added. After 1 hr, the solid was filtered and washed 2 × 250 mL H₂O and dried at 100°C.

Both catalysts were calcined at temperatures up to 700°C followed by reduction in H₂ at 250°C. The hydrogen chemisorption was determined by the double isotherm method.

The XANES spectra were obtained in transmission at room temperature in air. The fits were made by linear combination of experimental standards, Pt(NH₃)₄(NO₃)₂, Na₂Pt(OH)₆, and Pt foil.

Results and Discussion

In aqueous solution, surface hydroxyl groups of oxide supports interact with water and generate a surface charge [1, 2]. The support will be positively charged at a pH less than that of the point of zero charge or negatively charged at a pH greater than the point of zero charge [1-5]. In order for a support to adsorb a metal ion, the charge of the complex must be opposite that of the surface charge [1, 5]. For silica, the point of zero charge occurs at a pH of about 4 [5]. Thus, at basic pH, the support surface is negatively charged and will adsorb cationic Pt complexes [1]. Figure 1 shows the uptake of PTA as a function of pH.

At the pH of the IWI solution, ca. 5.5, there is little surface charge, and PTA would not be expected to strongly interact with the silica surface. Figure 2 shows the effect of the method of catalyst preparation and calcination temperature on the Pt dispersion. The particle sizes range from about 10-200 Å and can be systematically increased by increasing the calcination temperature. At a given calcination temperature, Pt

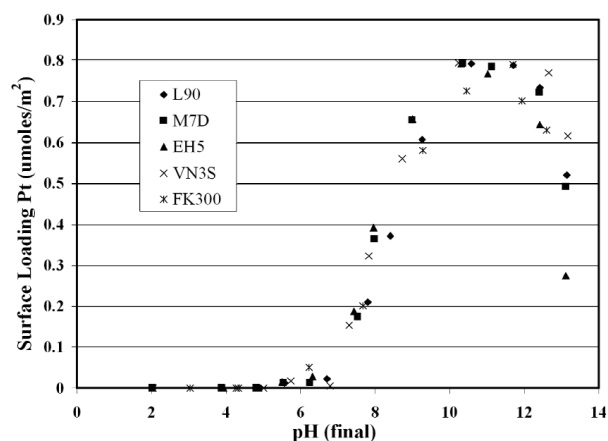


FIG. 1. Uptake of PTA on 5 different silicas as a function of pH; the surface loading was 2000 m²/g at 312 ppm Pt.

TABLE: XANES fit of 1.0% Pt/silica

Calcination Temp, °C	IWI			Ads		
	Pt ⁺²	Pt ⁺⁴	Pt(0)	Pt ⁺²	Pt ⁺⁴	Pt(0)
100	1.0	-	-	1.0	-	-
150	1.0	-	-	0.92	0.08	-
200	0.54	0.46	-	0.80	0.20	-
250	0.21	0.79	-	0.55	0.45	-
300	-	1.0	-	0.29	0.71	-
400	-	1.0	-	0.28	0.72	-
525	-	1.0	-	-	0.37	0.63
600	-	0.21	0.79	-	0.17	0.83
675	-	0.09	0.91	-	0.10	0.90

added by adsorption has higher dispersion than Pt prepared by IWI. In addition, as the calcination temperature increases, the dispersion decreases.

Independent of the method of preparation, calcination has a dramatic effect on the reduced particle size. The changes in the Pt species at different calcination temperatures were determined from the XANES and EXAFS spectra. The fits of the XANES spectra are given in the table. At low temperature, PTA is present in the Pt⁺² oxidation state. As the calcination temperature increases, the PTA is oxidized to Pt⁺⁴. The fraction oxidized is higher in the catalyst prepared by IWI. As the fraction of Pt⁺⁴ on the silica increases, the dispersion (after H₂ reduction) decreases. Above about

500°C, the Pt⁺⁴ species decompose (in air) to large metallic Pt particles. Not only is there autoreduction to metallic Pt, but also there appears to be significant sintering at high temperature. The results from fitting the EXAFS (not given) are consistent with the XANES results.

These results demonstrate that the Coulombic attraction of the metal complex with the charged oxide support not only influences the uptake of Pt but also influences the dispersion of the reduced catalyst. In addition, the strong metal complex-support interaction lowers the rate of Pt⁺² oxidation and growth of larger particles. By combination of the adsorption method of preparation and calcination temperature, very small to large metallic nanoparticles can be prepared.

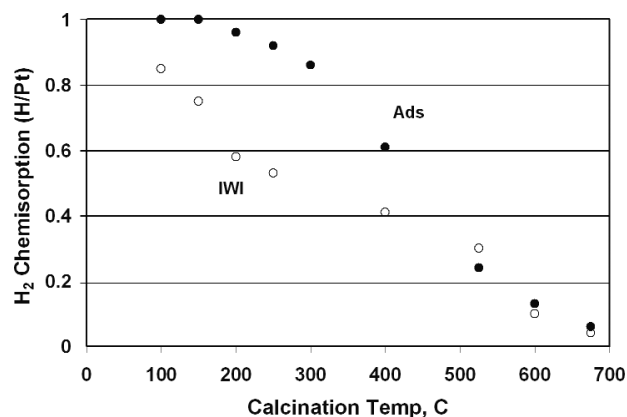


FIG. 2. Hydrogen chemisorption capacities of 1.0% Pt/silica prepared by Ads and IWI and calcination at different temperatures.

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