

Removal of Ag ions by selective wet etching from shape controlled Pt nanoparticles leads to highly active hydrogenation catalysts

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Introduction

There are numerous approaches to control size and shape of metal nanoparticles because of their interesting optical and catalytic properties. The introduction of foreign metal ions to colloidal metal nanoparticle synthetic procedures leads to control of particle shape [1]. The mechanism for this control is not well known, but it is proposed that the foreign metal ions prevent growth along one direction, or enhance the rate along another leading to particles with metastable shapes. The addition of increasing amounts of Ag to Pt particle synthesis led to exquisite shape control [2]. However, the rate of ethylene hydrogenation decreased with increasing retention of Ag in the nanoparticles [3]. In this work, selective etching of Ag with HNO₃ is employed in colloidal solution to remove Ag from the Pt nanoparticle. After etching, Ag is removed from the nanoparticle surface and catalytic activity increases five hundred fold.

Materials and Methods

Pt nanoparticles (~ 9 nm) were prepared by a modified polyol procedure in the presence of Ag ions. Millimolar solutions of chloroplatinic acid and poly(vinylpyrrolidone) (PVP) were added drop-wise to an ethylene glycol/Ag colloid solution at reflux. Increasing the concentration of Ag in solution led to changes in particle shape without change in size. Cubes were terminated by (100) surfaces, octahedra by (111) and cuboctahedra by both surfaces. Nanoparticles were characterized by high resolution electron microscopy and x-ray diffraction (XRD). Ag was not detected by XRD, but elemental analysis of particles of each shape confirmed that the nanoparticles retained most of the Ag [3]. Etching of PVP-protected Pt nanoparticles was conducted in 5 M HNO₃ aqueous solutions. After nanoparticle synthesis (and acid washing), they were encapsulated by in-situ hydrothermal growth of SBA-15 silica [4]. Particle size was determined by XRD and chemisorption. The extent of Ag removal was assessed with ethylene hydrogenation turnover frequencies for both as-synthesized and etched supported nanoparticles.

Results and Discussion

The rate of ethylene hydrogenation decreases monotonically as the residual Ag content increases. The exact location of the Ag is unknown, and energy dispersive X-ray (EDX) analysis of individual particles demonstrated that the Ag content was not uniform from particle to particle. Elemental analysis of the nanoparticles demonstrated 100% of the Ag quantity specified in the synthesis of the cube and cuboctahedra was retained in the particles while 40% was retained in the octahedra. It is proposed that Ag is present on the Pt nanoparticle surface as highly dispersed clusters [3].

Silver was removed by selective etching using nitric acid at 50°C, which reacts with Ag to form soluble AgNO₃, water and nitrogen oxides. The evolution of AgNO₃ is followed in

solution by UV-VIS during etching and the final Ag content is determined by elemental analysis. Etching octahedral particles supported on SBA-15 for 20 minutes decreased the Pt/Ag molar ratio from 0.14 to 0.013. Correspondingly, the rate of ethylene hydrogenation on Pt(octahedra)/SBA-15 catalysts increased by two orders of magnitude and the apparent activation energy decreased after washing (Table 1).

Table 1. Rate of ethylene hydrogenation on shape control Pt catalysts

Catalyst	Pt/Ag molar ratio	TOF at 298K (s ⁻¹)	E _a (kcal mol ⁻¹)
Pt(cube)/SBA-15	0.014	8.6	9.9
Pt(cuboctahedra)/SBA-15	0.102	0.4	10.8
Pt(octahedra)/SBA-15	0.123	0.02	13.4
Pt(octahedral- no etch)/SBA-15	0.14	0.015	10.6
Pt(octahedral- etched)/SBA-15	0.013	6.8	9.4

A control experiment in which 6.6 nm Pt nanoparticles were synthesized and ethylene hydrogenation rates for unetched and etched samples compared. Rates differed only by a factor of two, but the rate on the etched control is a factor of three higher than the etched octahedra sample. It appears that only a small amount of residual Ag is required to alter the activity of Pt for olefin hydrogenation. The cubes (without etching) contain a comparable amount of Ag as etched octahedra samples, and hydrogenation rates were similar. The same cubes in Langmuir-Blodgett monolayers were highly active for carbon monoxide oxidation [5].

Etching had no apparent effect on the size of the octahedra or particle shape. The kinetics of etching is studied by UV-VIS spectroscopy and the change in Ag content in the nanoparticles followed by EDX and x-ray absorption spectroscopy. The ability to remove Ag and maintain the size and shape of the original nanoparticle enables reaction rates and selectivity to be measured as a function of particle shape and compared with single crystal measurements. Kinetic studies of well-known structure sensitive reactions will be examined as function of particle shape for etched Pt nanoparticles.

Significance

Shape controlled nanoparticles have well-defined surface structure and are fundamentally important for the elucidation of structure-function relationships.

References

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