

Removal of surface templating polymers from colloidal nanoparticles for applications in heterogeneous catalysis

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Introduction

A number of methods are now available for the synthesis of catalytically relevant metal and metal oxide nanoparticles. These methods generally involve the use of molecular or polymeric phases to stabilize the particles in solution [1]. These templating agents prevent aggregation in solution and remain on the particle surface after adsorption onto high surface area or planar supports [2]. Colloidal Pt nanoparticles (1.7–7 nm) were synthesized by solution based reduction methods in the presence of poly(vinylpyrrolidone) (PVP) to create nearly monodisperse PVP-capped Pt nanoparticles. The nanoparticles are encapsulated by hydrothermal synthesis of mesoporous silica using triblock copolymers as templates for the inorganic mesostructure [3]. The particles are active after PVP removal by combustion and reduction, but the particle size determined by chemisorption is larger than x-ray diffraction and electron microscopy methods.

Materials and Methods

Monodisperse Pt nanoparticles with sizes between 1.7 and 7.1 nm were synthesized by reduction of chloroplatinic acid in alcohol solution in the presence of PVP. Pt nanoparticles were encapsulated by in-situ hydrothermal growth of SBA-15 silica [2, 3]. Thermogravimetric analysis (TGA) and temperature programmed oxidation (TPO) were used to follow the weight loss and product formation during PVP decomposition in oxidizing (O₂ or diluted NO₂) atmospheres. Diffuse reflectance infrared spectroscopy (DRIFTS) of as-synthesized catalysts and CO adsorption on catalysts before and after thermal treatment demonstrates CO adsorbs on PVP covered surfaces and surfaces where a majority of the PVP is removed, in agreement with Raman spectroscopy [4]. PVP was removed by either ex-situ or in-situ calcination treatments [5, 6]. A structure insensitive reaction, ethylene hydrogenation, was used to follow the extent of PVP removal after cyclic-oxidation reduction cycles.

Results and Discussion

Ex-situ calcination in oxygen was employed to remove PVP from the nanoparticle surface, followed by reduction in hydrogen. This method has proven effective but requires long calcination times and relatively high temperatures (723 K) for high catalytic activity. Oxidation in stronger oxidants such as NO₂ had no advantage over oxygen. Evolution of polymer oxidative decomposition products from as-synthesized Pt/SBA-15 catalysts is dependent on the Pt:PVP molar synthesis ratio and the as-synthesized Pt particle size. CO₂ and H₂O evolution due to polymer template and PVP combustion are released at low temperature over a very narrow temperature range from 7.1 nm particles, while the same combustion products begin to appear in the gas phase at a similar temperature but continue to evolve over a

larger range for 2.9 nm particles. In either case, no nitrogen containing products were observed in the gas phase. Short *in-situ* oxidation/reduction cycles are more effective for polymer template and PVP removal for 7.1 nm particles. The most effective treatment was 473 K (Figure 1), in agreement with TPO results. Diffuse reflectance infrared investigations of Pt/SBA-15 demonstrate that large C-H absorption bands attributable to copolymer and PVP, as well as the carbonyl stretch of PVP are observed before calcination. Both bands significantly decrease in intensity after calcination. *In-situ* oxidation-reduction treatments were shown by infrared spectroscopy to have a less pronounced effect on the intensity of the polymer bands for a 2.9 nm sample consistent with TPO results. Adsorption of carbon monoxide is unhindered on uncalcined samples suggesting that a significant fraction of copolymer is removed from the silica channel and some fraction of PVP-capped Pt nanoparticle surface is accessible to small molecules. Catalytic activity was assessed with ethylene hydrogenation and catalysts treated by *in-situ* short oxidation-reduction cycles were more active than catalysts calcined *ex-situ* in oxygen or NO₂ in the case of 7.1 nm particles. Different behavior was observed for 2.9 nm particles. The present work demonstrates polymer removal is a critical step requiring optimization to maximize the catalytic activity of supported nanoparticles.

Significance

These catalysts contain monodisperse particles and therefore [presumably] similar catalytic behavior, enabling formulation of very accurate structure-function relationships.

References

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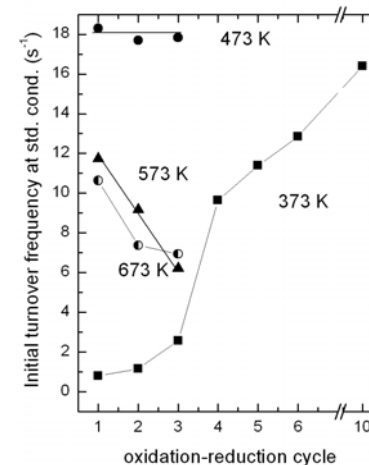


Figure 1. Rate of ethylene hydrogenation for Pt(7.1 nm)/SBA-15 with number of O₂-H₂ cycles.