

Propylene Hydrogenation over Cubic Pt Nanoparticles Deposited on Alumina

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Pt nanoparticles loaded on alumina through an impregnation at room temperature was prepared using K_2PtCl_4 and acrylic acid as capping material. Transmission electron microscopy showed that the deposited Pt particles indicate *ca.* 80% cubic shapes with a narrow distribution of 8-10 nm in size. Propylene hydrogenation over the catalyst has been carried out to evaluate their catalytic performance by the values of activation energy. It is determined from the initial rate, reaction order, and rate constant and is found to be 9.7 ± 0.5 kcal/mol. This value has been discussed by comparing to those of encapsulated- and truncated octahedral Pt nanoparticles deposited on alumina, respectively, to study influence of the particle size and shape, and capping material used on the activation energy.

Key Words : Platinum, Cube, Nanoparticle, Propylene, Hydrogenation

Introduction

Metallic nanoparticles have been studied in various fields such as semiconductors,^{1,2} synthesis and catalysis,³⁻⁵ photochemistry of semiconductor nanoparticles and non-linear optical properties of metal cluster-doped glasses.⁶ The specific properties of nano-sized metal particles in catalysis are usually associated with a change in their electronic properties relative to the bulk samples. This change is a result of size effects giving rise to an increase in the surface energy and a characteristic high surface-to-volume ratio. These lead to an enhancement of their catalytic properties⁷ as large fractions of the active metal atoms are on the surface and thus are accessible to reactant molecules and available for catalysis.⁸

Catalytic property depends on the size and the shape of the nanoparticles because reactant molecules have different sorption structures on the various surface planes and on highly exposed atomic structures such as those in steps and kinks.⁹ For example, selectivity of crotonaldehyde hydrogenation to the primary products butyraldehyde and crotyl alcohol depends critically on the Pt particle size and shape (facet).¹⁰ In detail, Pt(111) surfaces favor the adsorption of crotonaldehyde via the carbonyl bond leading to selective hydrogenation of the carbonyl group. On the other hand, both double bonds (C=C and C=O) are allowed to be an unrestricted sorption on Pt(100) and on edges and corners (steps and kinks).¹⁰ Therefore the synthesis of well-controlled shapes and sizes of nanoparticles could be critical for our understanding of the whole phenomena of catalysis and the design of more ideal catalysts for different chemical transformations.

In this study, cubic Pt nanoparticles are synthesized using

K_2PtCl_4 solution and acrylic acid as the capping material and impregnated on alumina support. The particle size/shape are characterized by transmission electron microscopy (TEM). The catalytic activities as are measured by the values of the activation energy as studied for the heterogeneous hydrogenation of propylene.

Experimental Section

K_2PtCl_4 (99.99%), acrylic acid (97%), and alumina (neutral, surface area 155 m²/g, pore size 5.8 nm) were obtained from Aldrich. All solutions were prepared using doubly deionized water. Propylene (99.9995%) and hydrogen (99.995%) were purchased from Matheson and were used without further purification. The purity of the propylene was checked by mass spectrometry.

The deposited-Pt on alumina (Pt/Al₂O₃) catalyst was prepared as follows. First we prepared the Pt nanoparticles in aqueous solution by using the methods reported by Rampino and Nord¹¹ and Henglein *et al.*¹² 8 mL of 0.1 M acrylic acid was added to 250 mL containing 8.0×10^{-5} M K_2PtCl_4 solution. The initial concentration ratio of K_2PtCl_4 to acrylic acid was 1 : 40. The pH of the solution was adjusted to 7 with diluted HCl solution and purged with Ar for 20 min. The Pt complexes were reduced by bubbling H₂ for 5 min. The solution was left for 12 h in the dark. To this solution, 5 g alumina was added and impregnated using rotary evaporation at room temperature under reduced pressure. Finally, it was dried at 110 °C for 12 h.

TEM was used to determine the particle size and shape of the Pt nanoparticles studied. TEM images were taken by using a JEM 100C operated at an acceleration voltage of 100 kV. The particle size and shape were determined from an enlarged TEM images.

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Results and Discussion

TEM images of Pt/Al₂O₃. We present two TEM images in Figure 1 before and after deposition of the Pt nanoparticles on alumina. Figure 1a indicates clear TEM pictures of Pt nanoparticles consisted of over 70 nanoparticles in which the particles were synthesized with 1 : 40 concentration ratio of K₂PtCl₄ to acrylic acid. The particles are aligned with monolayers, which attached each other through capping material. The average size of the particles is about 10 nm with narrow distribution and the shapes are consisted of more than 80% cube and few truncated tetrahedral and octahedral. The TEM pictures of Pt/Al₂O₃ prepared by impregnating with the cubic Pt nanoparticles solution at room temperature under reduced pressure are seen in Figure 1b. As can be observed in the TEM pictures, the Pt particles on alumina show images even in the presence of alumina. The nanoparticles are randomly distributed on the support without agglomeration and keep the constant size and shape after impregnation comparing to colloidal Pt particles. The particle size of the cubic Pt is larger than the alumina pore aperture (5.8 nm) from which these nanoparticles might be located on the external surfaces of the alumina support.

Catalysis of propylene hydrogenation. The propylene hydrogenation has been carried out in a batch reactor. The catalyst was first preheated to 210 °C for 2 h under an Ar flow and then evacuated under high vacuum at this temperature to remove water and volatile impurities adsorbed. The hydrogenation experiments were run in the presence of 0.12 g of cubic Pt(0.078 wt.)/Al₂O₃, propylene (24 torr), and hydrogen (165 torr) in the 30–70 °C range. An aliquot of the reaction mixture was taken out at different reaction times and were analyzed by mass spectrometry (VG Analytical, 70-SE). The relative intensities of propane to propylene mass peaks in the hydrogenation reaction were calibrated from known standard propylene/propane gas mixtures.

Under our mild reaction conditions, propane is the only

reaction product detected and no deactivation processes are observed during the reaction. Less than 1% of propane is found to dehydrogenate to produce propylene in the high temperature region of our reaction.

The reaction is assumed to follow the reaction rate law:

$$\text{Initial Reaction Rate} = k [\text{C}_3\text{H}_6]^\alpha [\text{H}_2]^\beta$$

Where α and β are the order of the reaction with respect to C₃H₆ and H₂, respectively. By determining the initial rates at different reactant concentrations, the α and β are found to be 0.21 and 0.87 respectively.

The specific rate constant k at different temperatures is calculated from these initial reaction rates, the reaction order, and the corrected initial H₂ and propylene concentrations at the different temperatures. Figure 2 gives the Arrhenius plot of the natural logarithm of the rate constant vs 1/T for the reaction catalyzed by cubic Pt/Al₂O₃. As shown,

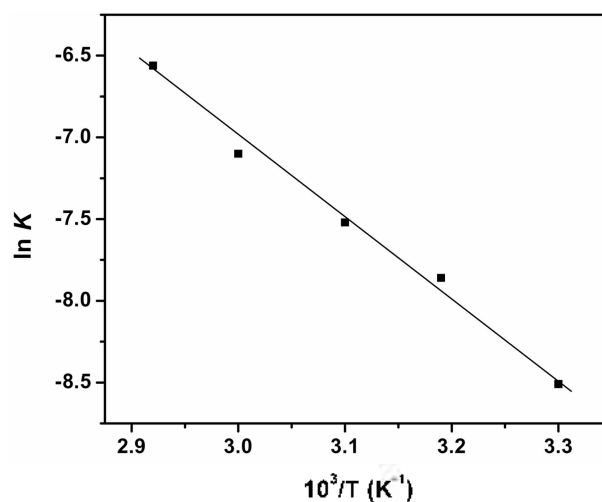


Figure 2. Arrhenius plots of the natural logarithm of rate constant vs 1/T for the propylene hydrogenation over cubic Pt/Al₂O₃ catalyst.

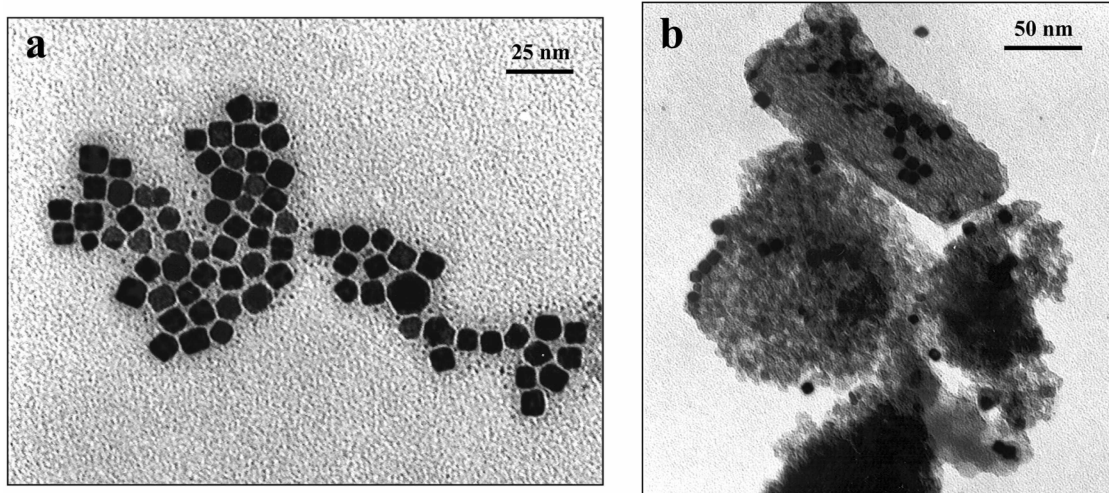


Figure 1. TEM images of (a) Pt nanoparticles prepared with a concentration ratio of 1 : 40 platinum complex to acrylic acid. (b) impregnation (a) on alumina at room temperature.

normal Arrhenius behavior is observed in the temperature range of 30-70 °C. The activation energy of the reaction is calculated to be 9.7 ± 0.5 kcal/mol from the observed slope of the linear part of the Arrhenius plot.

A few workers^{13,14} have reported the activation energy in the propylene hydrogenation using propylene and hydrogen catalyzed by Pt supported on silica and titania. The supported Pt particles have been prepared by impregnation/ion-exchange methods by immersing the calcined supports in an aqueous or organic solution of Pt precursors without the addition of capping material. The Pt catalysts are reduced in flowing of hydrogen at about 450 °C. These methods typically give amorphous nanoclusters although there is no detailed description about the particle shapes. From reviewing the work on the propylene hydrogenation reported, it is found that the activation energy ranges from 10 to 14 kcal/mol.^{13,14} The activation energies were found to be dependent upon the type of support (silica, titania) and the structure (anatase, rutile) due to the different interactions between the Pt and the support giving different electronic effects.^{13,14} However, there are no explanations of effects of the Pt size and shape on the activation energy. Recently, our group synthesized Pt nanoparticles-encapsulated in nanoporous alumina prepared by reduction K_2PtCl_4 solution using hydrogen in the presence of alumina and capping material.¹⁵ After extraction of the Pt nanoparticles from the alumina channels, various shapes such as truncated octahedra, cube, tetrahedra, and sphere with a size around 5 nm are observed. The encapsulated particles have various shapes but are about half in size than those prepared in K_2PtCl_4 solution with polyacrylate in the absence of alumina. Using FT-IR studies, the capping material initially used in Pt/ Al_2O_3 is not found in the alumina channels, meaning pure Pt nanoparticles could be prepared inside alumina. This might be due to the fact that the polymer (average MW 2,100) is too large to be accommodated within the alumina pores. Using these Pt nanoparticles, the activation energy for propylene hydrogenation is found to be 5.7 kcal/mol. This value is 40% low comparing to that (9.7 ± 0.5 kcal/mol) of cubic Pt/ Al_2O_3 . Differences between two catalytic systems are the deposited particles size, shapes, and capping materials. The cubic Pt/ Al_2O_3 has more than 80% cube with 8-10 nm in size and the catalyst surfaces are covered by the capping material used. On the other hand, encapsulated-Pt in alumina shows mainly truncated octahedral and few cubic, tetrahedral, and spherical having 4-5 nm size. The encapsulated Pt/ Al_2O_3 have pure Pt particles to be located inside alumina channel without attachment of the capping material. The smaller activation energy of the encapsulated Pt/ Al_2O_3 rather than cubic Pt/ Al_2O_3 could be attributed to small particles size (large surface area) and clean Pt surface. As a second example for comparison, truncated octahedral Pt nanoparticles supported on alumina (TO Pt/ Al_2O_3) was prepared by similar method of cubic Pt/ Al_2O_3 except capping material type used.¹⁶ Both catalysts exhibit almost same in terms of particles size (8-10 nm), cover with the capping material, and deposition on external surface of

alumina. Difference is only the particles shape. The activation energy of TO Pt/ Al_2O_3 in the propylene hydrogenation is calculated to be 8.4 ± 0.2 kcal/mol, which is slightly lower than results of cubic Pt/ Al_2O_3 . The TO platinum nanoparticles are mainly defined by the {100}, {111}, and {110} facets, on which numerous atom-high surface steps, ledges and kinks have been observed.¹⁷ These atomic-scale fine structures of the surfaces of our TO platinum nanoparticles are expected to have lower activation energy than those of cubic Pt/ Al_2O_3 . From the above results, it can be concluded that the activation energy of propylene hydrogenation over Pt/ Al_2O_3 catalysts is affected by the Pt particles size, capping material adsorbed on metal surfaces, and atomic structures of the surfaces of the Pt nanoparticles.

Conclusions

The cubic Pt/ Al_2O_3 was synthesized by using K_2PtCl_4 in the presence of acrylic acid following by deposited on alumina by impregnation method. From TEM observation, the nanoparticles are mainly cubic shape with 8-10 nm in range of size, which are randomly dispersed on the external surface of alumina since the particle size is larger than the alumina pore aperture (5.8 nm).

The cubic Pt/ Al_2O_3 catalyst has been used for the propylene hydrogenation to evaluate its catalytic activity as measured by the value of its activation energy. The activation energy is found to be 9.7 ± 0.5 kcal/mol, which is about 70% larger value than that (5.7 kcal/mol) of the encapsulated Pt/ Al_2O_3 catalyst. It might be due to the encapsulated catalyst having the small particle size (4-5 nm) and the capping material-free clean surface comparing to those of the cubic Pt/ Al_2O_3 . The TO Pt/ Al_2O_3 catalyst is revealed to have 8.4 ± 0.2 kcal/mol, which is slightly small in respect to that of the cubic Pt/ Al_2O_3 . The TO nanoparticles have mainly the {100}, {111}, and {110} facets, on which numerous steps, ledges and kinks have been observed. These atomic-scale fine structures of the surfaces of our TO platinum nanoparticles are expected to have lower activation energy than that of the cubic Pt/ Al_2O_3 . The activation energy of propylene hydrogenation over Pt/ Al_2O_3 catalysts is affected by the Pt particles size, capping material adsorbed on metal surfaces, and atomic structures of the surfaces of the Pt nanoparticles.

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