

Synthesis of Dendrimer Encapsulated One Nanometer Rh and Pt Particles and Their Catalytic Activity for Ethylene and Pyrrole Hydrogenation

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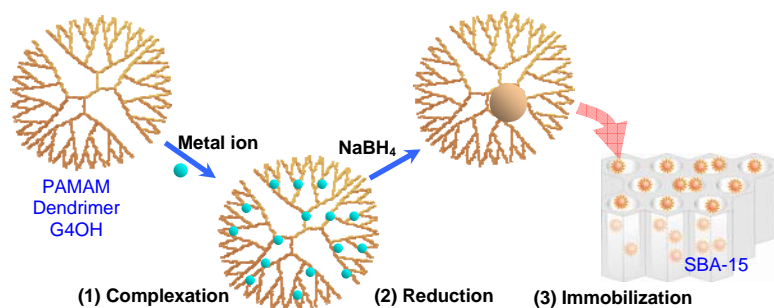
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Introduction

Monodisperse metal nanoparticles smaller than 1 nm (tens of atoms) are of great importance in catalysis. These particles may help understand the transition between homogeneous and heterogeneous catalysis. Dendrimer templating and capping is an effective method for synthesizing ~ 1 nm nanoparticles [1]. In the current study, we synthesized monodisperse Rh and Pt nanoparticles within a 4th generation PAMAM dendrimer and then immobilized them onto a high-surface-area SBA-15 mesoporous support. Catalytic activity of the SBA-15 supported Rh and Pt nanoparticles was studied for ethylene and pyrrole hydrogenation reactions after different pretreatment conditions.

Materials and Methods

Scheme 1 demonstrates the preparation and immobilization of dendrimer encapsulated nanoparticles to mesoporous SBA-15 support. Generation 4 dendrimers (G4OH) were purchased from Dendritech Inc. (Midland, MI) as 10.20 wt. % methanol solution. A 250 μ M dendrimer stock solution was prepared by adding the dendrimer methanol solution to water. The dendrimer stock solution was mixed with 15–40 mole equivalent of an aqueous solution of 0.01 M RhCl_3 (Rh, 38–40%) or K_2PtCl_4 (99.9+ %) (Sigma-Aldrich, Inc., St. Louis, MO). After 18 h, 20 fold of freshly prepared 0.5 M NaBH_4 was injected into the vial drop wise during vigorous stirring. The reaction solution was stirred for several hours and purified by dialysis. The Rh and Pt nanoparticles are immobilized onto SBA-15 for catalytic studies.



Scheme 1. Synthesis of dendrimer encapsulated metal nanoparticles and the subsequent immobilization of the nanoparticle on mesoporous SBA-15 support.

Results and Discussion

The SBA-15 supported nanoparticles were imaged by TEM (FEI Tecnai G2 S-Twin electron microscope at an accelerating voltage of 200 kV). As shown by Figure 1a, the $\text{G4OH}(\text{Rh}_{30})$ (30 Rh atoms) nanoparticles were evenly distributed over the support. Figure 1b showed the initial ethylene hydrogenation activity over the $\text{Rh}_{30}/\text{SBA-15}$ catalyst after reduction at different temperature. The catalyst was active without removing the dendrimer capping, but reached its highest activity after reduction at a moderate temperature (423 K). X-ray photoelectron spectroscopy indicated that the as-synthesized Rh and Pt nanoparticles were mostly oxidized. When treated at a higher temperature (473, 573, and 673 K) in hydrogen, catalytic activity decreased. Using the treatment that led to maximum ethylene hydrogenation activity, catalytic activity was also demonstrated for pyrrole hydrogenation.

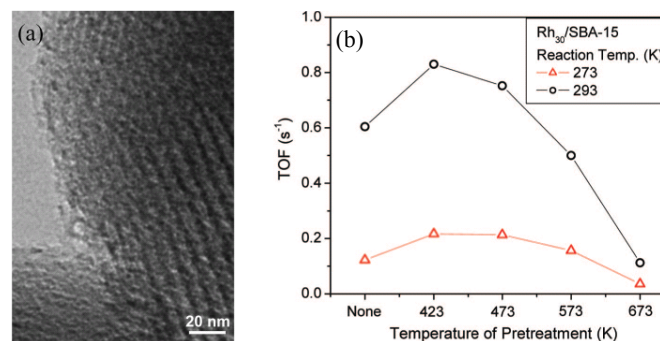


Figure 1. (a) TEM image of $\text{Rh}_{30}/\text{SBA-15}$ catalyst. (b) Initial ethylene hydrogenation activity over $\text{Rh}_{30}/\text{SBA-15}$ after reducing in 76 torr of H_2 balanced with He at different temperature. Reaction mixture was 10 Torr C_2H_4 and 100 Torr H_2 .

Significance

For nanoparticles of 1 nm, more than 90 % of atoms are located on the surface and their atomic coordination number is smaller than that in larger nanoparticles (12 for an f.c.c. lattice) which has a substantial fraction of the atoms in the bulk. At sizes smaller than ~ 1 nm, nanoparticles have shorter metal-metal bonds [2], lower melting points [3], and are easier to be oxidized than larger particles [4]. All of these remarkable properties for ~ 1 nm particles could lead to their distinctly different performance in catalytic reactions [5].

References

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