Novel two-step synthesis of controlled size and shape platinum nanoparticles encapsulated in mesoporous silica

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Uniform shape and size platinum nanoparticles encapsulated in mesoporous silica (SBA-15) were prepared in the same solution by a novel two-step method. Platinum nanoparticles were prepared in aqueous solution of K_2PtCl_4, the reduction was carried out by bubbling hydrogen, the capping material was tri-block poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer. The mesoporous silica was synthesized using the same copolymer as template from tetraethyl orthosilicate by hydrolysis in acidic conditions. The "Pt-nanoparticles-in-mesoporous-silica" system was characterized by a combination of low-angle powder X-ray diffraction, transmission electron microscopy and N_2 porosimetry. The platinum nanoparticles are encapsulated in the mesopores and retained their size and morphology. It appears that this hybrid material should be a superior three-dimensional high-surface-area catalyst for selective platinum-catalyzed reactions.

KEY WORDS: metal nanoparticles; SBA-15; mesoporous silica.

1. Introduction

For multipath reactions that are carried out on supported platinum catalysts, selectivity to the desired product is the most important goal. For example, during reforming reactions that may be studied using *n*-hexane or *n*-heptane as the feedstock, conversion to branched isomers (isomerization) or to benzene (dehydrocyclization) yield high octane number fuels and valuable chemicals while the formation of methylcyclopentane (cyclization) or propane and methane (hydrogenolysis) are much less desirable. One of the experimental parameters that controls selectivity is the size of the platinum catalyst particles, which influences their surface structure [1]. The micro- or mesoporous support can also make an important contribution to the activity and selectivity of such catalysts [2,3]. In addition to its acid–base and redox properties, the pore size can be an important factor that may impose shape selectivity [4,5].

Recent progress in nanoscience led to discovery of preparation techniques of metal clusters with uniform size and morphology, often in aqueous solution. The application of a suitable surface-protecting agent is a prerequisite of the preparation of stable nanoclusters. Recently it was found that linear polymers (sodium polyacrylate, poly(*N*-vinyl-2-pyrrolidone), polyvinyl alcohol) have the potential to control not only the size but also the shape of the metal nanoparticles [6–8]. The size of the particles is controlled by changes in the fabrication techniques employed. We have been able to synthesize platinum nanoparticles in the 5–15 nm size range with narrow size distribution using linear triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$) as the capping agent in an aqueous solution. By adding TEOS to this solution, using the same linear triblock copolymer capping ligands followed by hydrolysis in HCl, we could grow a mesoporous silicate SBA-15 framework around the platinum nanoparticles. Combining the advantage of the uniform size and shape of the nanoparticles with the high surface area and uniform pore size of mesoporous silica a new and very interesting material could be obtained.

In this paper we report on a novel preparation method of uniform platinum nanoparticles in the mesoporous silicates SBA-15. The two-step procedure consists of growing platinum nanoparticles with polymer ligands and then the growth of porous silicate around them by hydrolysis of TEOS using the same polymer ligands as the structure-directing agent.

2. Experimental

2.1. Synthesis

Cubic Pt nanoparticles were prepared by the method of Rampino and Nord [9] but instead of using sodium polyacrylate as capping material a new compound, a tri-block poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$) copolymer was

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successfully applied. $EO_{20}PO_{70}EO_{20}$ was dissolved in 1×10^{-4} M freshly prepared K_2PtCl_4 solution to obtain Pt : polymer = 1 : 1 molar ratio, the pH was set to 7.5, and Ar gas was bubbled in this solution for 30 min to remove dissolved oxygen. Afterward, the reduction of platinum ions to form metal atoms as the precursor of platinum nanoparticles was carried out by bubbling hydrogen gas through the solution for 5 min. The reaction vessel was closed and left under H_2 atmosphere overnight. After 12 h a golden yellow color appeared, indicating the formation of Pt nanoparticles.

Mesoporous silica SBA-15 was synthesized in accordance with the procedure reported in ref. [10]. Briefly, a solution of $EO_{20}PO_{70}EO_{20}$: cc.HCl : TEOS : H_2O = 2 : 15 : 3.6 : 60 (mass ratio) was prepared, stirred for 24 h at 30 °C and then heated at 80 °C for 24 h. The solid white product was filtered and calcined at different temperatures.

Platinum-containing mesoporous silica SBA-15 was synthesized in the solution containing the platinum nanoparticles. Briefly, a solution of $EO_{20}PO_{70}EO_{20}$: cc.HCl : TEOS : Pt-sol = 2 : 15 : 3.6 : 60 (mass ratio) was prepared, stirred for 24 h at 30 °C and then heated at 80 °C for 24 h. The solid gray product was filtered and calcined at different temperatures.

Low-angle X-ray diffraction and transmission electron microscopy studies showed that the samples prepared have well-ordered hexagonal mesoporous structure with diameter around 10 nm.

2.2. Characterization

The "Pt-nanoparticles-in-mesoporous-silica" system was characterized by a combination of physical techniques. Low-angle X-ray diffraction (XRD) spectra were recorded on a Bruker general area diffraction detector system (GADS) D-8 working with Co K_α radiation ($\lambda = 1.79$ Å). Transmission electron microscopy (TEM) images were obtained using a JEOL 200 kV microscope. BET specific surface areas and the porosities were calculated from the nitrogen adsorption experiments measured at 77 K. Nitrogen porosimetry data were collected using a Quantachrome Autosorb 1 surface area analyzer with 60-point analyses at 77 K. Template-free samples were pretreated at 393 K for 8 h in vacuum immediately prior to data collection. The surface area was calculated using the BET adsorption–desorption method [11] and pore-size distribution was analyzed by the Barrett–Joyner–Halenda (BJH) method [12].

3. Results and discussion

In figure 1 the TEM images of platinum nanoparticles prepared using $EO_{20}PO_{70}EO_{20}$ as protecting agents are depicted. The high-resolution TEM of a Pt particle showed a lattice fringe of Pt(100) and the cubic nanoparticles were bounded by six (100) faces. These particles range in size from 3 to 20 nm with an average size around 12 nm. It is seen that the particle-size distribution is relatively broad. However, the shape of the majority of nanoparticles is cubic. It is worth noting that if the size of a particle is larger than 5–6 nm the shape is cubic in 90%, while the smaller particles are rather "shapeless". The $EO_{20}PO_{70}EO_{20}$ molecules can influence the shape of the metal particle when it reaches the size of 5–6 nm.

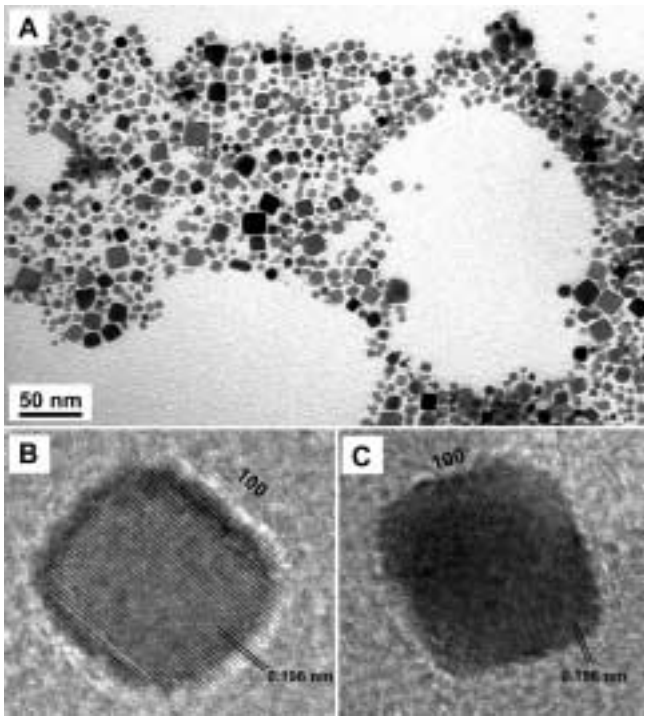

Figure 1. TEM images of platinum nanoparticles.

Figure 2 shows the XRD patterns of mesoporous structures both in the low- and high-angle regions. The XRD analysis showed Bragg reflections in the 2θ range 0.1–2.5. The reflections could be indexed to a hexagonal unit cell, $d_{100} = 9.2$ Å for SBA-15 and $d_{100} = 9.9$ Å for Pt/SBA-15 and indicates a lattice contraction of 7.5%. The retention of the SBA-15 unit cell after Pt incorporation indicates the high stability of the mesoporous structure. These spectra prove that (i) the silicate prepared in the presence of platinum nanoparticles preserves the structural characteristics since no changes can be observed in the reflections due to the mesoporous structure and (ii) the metal reflections appeared at their correct place, which is characteristic of the cubic platinum (45.9° and 53.7°).

TEM images taken on both the pure SBA-15 and the cubic platinum nanoparticles containing SBA-15 samples can be seen in figure 3. These pictures clearly show the platinum particles are inside the pores of SBA-15 silicate.

The calculated BET surface areas are 822 and 753 cm^2/g (SBA-15 and Pt/SBA-15, respectively), which are in the expected range for these mesoporous structures

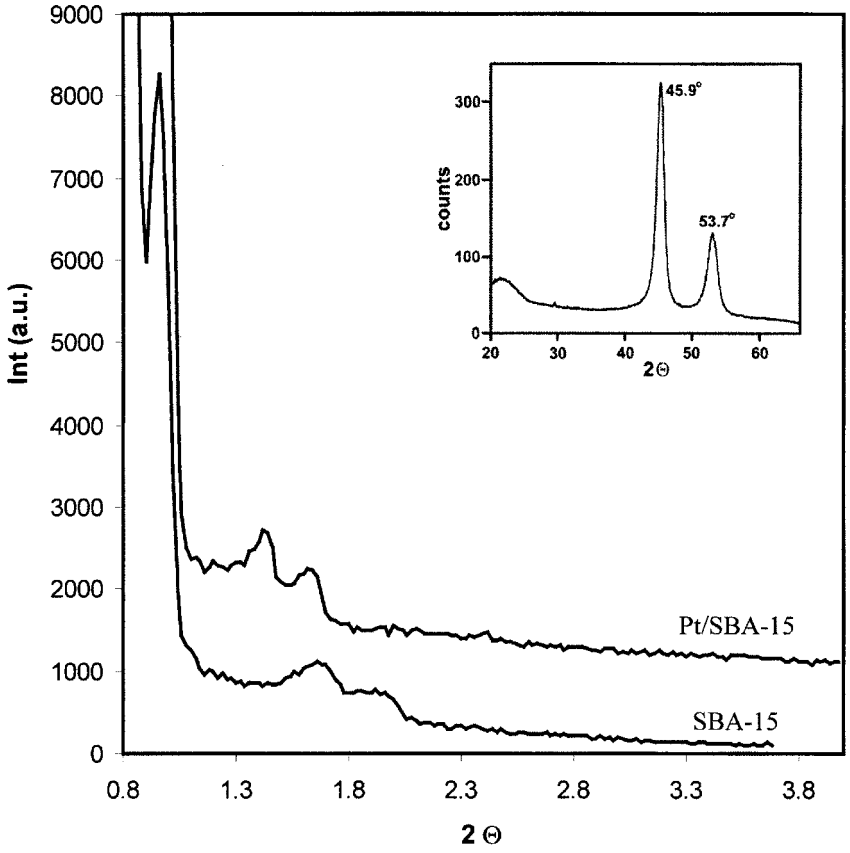

Figure 2. Powder XRD patterns of SBA-15 and Pt/SBA-15 samples. The inset shows the characteristic reflections of fcc platinum.

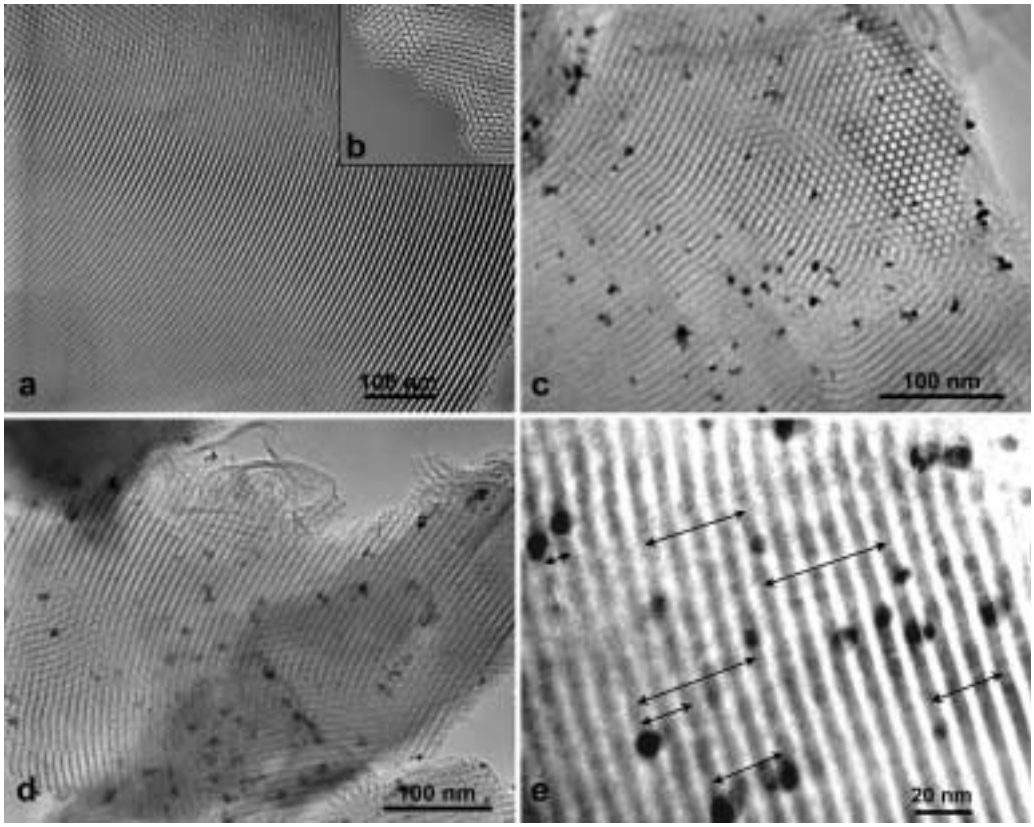

Figure 3. TEM pictures of pure SBA-15 host (a, b) and the encapsulated Pt nanoparticle-mesoporous silica system (c)–(e).

[13]. The isotherms are of type IV and exhibit a hysteresis loop of H1 type according to the IUPAC classification, typical of materials with pores of constant cross section. The pore-filling step in adsorption and desorption curves is sharp, corresponding to relatively sharp pore-size distribution. Hence, N_2 porosimetry in agreement with the XRD and TEM studies reveals that the sample possesses well-ordered structure. Since nearly identical isotherms were measured for platinum-containing and platinum-free samples, there is no change in the pore structure of the mesoporous materials upon platinum particle incorporation. In support of the XRD data, a narrow pore-size distribution was evident for the sample, indicating that the highly ordered structure is maintained after incorporation of the nanoparticles.

As no systematic change either in the surface area or in the shape of the adsorption–desorption isotherm was found, platinum nanoparticle incorporation into the silicate material does not appear to alter the adsorption–desorption properties of small molecules such as nitrogen. The key experimental parameter to this novel two-step preparation method is the use of the same polymer for preparation of platinum nanoparticles and for the synthesis of a mesoporous silicate structure from TEOS.

4. Conclusions

The two-step synthesis of encapsulated platinum nanoparticles in mesoporous SBA-15 silica structure does not alter either the size and morphology of the metal clusters or the pore structure of the mesoporous silica. Thus we believe that SBA-15 containing uniform, controlled platinum nanoparticles should be a promising three-dimensional high-surface-area catalyst in selective platinum-catalyzed reactions. Catalytic reaction studies and further studies of characterization to probe the chemical and thermal stability of our uniform "Pt-nanoparticles-in-mesoporous-silica (SBA-15)" system are in progress.

Acknowledgments

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