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Fabrication of two- and three-dimensional model catalyst systems with monodispersed platinum nanoparticles as active metal building blocks

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Dedicated to Professor Brian James.

Abstract

Well-defined Pt monodispersed nanoparticles within the catalytically relevant 1–10 nm size regime were synthesized in solution phase by several synthetic methods which differed in the choice of reducing agent, surface stabilizer, reaction temperature and solvent. Three-dimensional model catalysts were fabricated by incorporating the metal nanoparticles into ordered channels of high surface area mesoporous oxides such as SiO_2, Al_2O_3 and Ta_2O_5 through either sonication or direct synthesis of the oxide support around the particles. Deposition of the same nanocrystals onto silica supports by means of the Langmuir–Schaeffer technique produced two-dimensional model catalysts.

Keywords: Platinum nanoparticles; Oxide supports; Langmuir–Schaeffer technique

1. Introduction

In modern industrial heterogeneous catalysis, one can observe a shift of focus from high turnover rates towards high selectivity for a desired target molecule, resulting in fewer pollutants and side products, thus minimizing cost and maximizing process efficiency. The synthesis of supported metal catalysts with tunable properties, having great potential to produce more selective catalysts, has attracted attention. For the fabrication of such model catalyst systems, a combination of knowledge from two distinct fields in materials chemistry, metal nanoparticle and mesoporous oxide support material synthesis, is required. Catalysts synthesized by standard techniques such as impregnation or incipient wetness typically contain a wide distribution of particle sizes. The synthesis of monodispersed noble metal nanoparticles in the catalytically relevant size range (1–10 nm) under well-defined conditions (i.e., solution phase) provides superior control of metal particle size and surface morphology. Over the past decade, many such synthetic methods have become available through advances of nanotechnology [1–12] delivering nanomaterials of tunable size, shape and very sharp particle size distributions ($\sigma \pm 5\%$).

Here, we report on solution phase synthesis of monodispersed Pt-nanoparticles within the catalytically important size range (1–10 nm) and their use in making novel model catalysts. The different techniques employed in this work can be differentiated in terms of the methods of growth (direct reduction versus seeded growth), the reducing agents (linear alcohols, ethylene glycol, L(+)-ascorbic acid, trisodium citrate, H_2 or $NaBH_4$) or the capping agent (poly-*N*-vinylpyrrolidone (PVP) versus Pluronic L64 ($EO_{13}PO_{30}EO_{13}$) triblock copolymer). Purified nanoparticles obtained in this way were used to fabricate novel three- (3D) and two-dimensional (2D) model catalyst systems.

The synthesis of mesoporous oxide materials and their potential applications also represent major focus of numer-

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ous research groups. One application of mesoporous materials is as a catalyst support [13]. The surface chemistry of SBA-15 (mesoporous SiO_2) is analogous to amorphous SiO_2 which is used for supporting small metal nanocrystals but the former has properties (i.e., pore size) which are easy to control by varying the synthesis conditions. Ultimately, we are interested in controlling the pore size of SBA-15-like oxide support materials based on SiO_2, Al_2O_3 and Ta_2O_5 while maintaining long range order of the mesopores. Here, we report that a variety of mesoporous oxides were synthesized in our laboratory and used as supports for platinum nanoparticles for our 3D model catalyst systems. The techniques that have been used to characterize the platinum nanoparticle/mesoporous oxide systems include X-ray diffractometry (XRD), small angle X-ray scattering (SAXS), UV-Raman and infrared spectroscopies, transmission electron microscopy (TEM), physisorption and chemisorption measurements.

2D model catalysts are promising tools to study catalytic reactions on surfaces: the planar geometry of the system allows direct in situ probing of surface species and intermediates which occur during chemical reactions by means of optical (sum frequency generation spectroscopy) and scanning probe (STM and AFM) techniques. Such studies have great potential to provide insight into catalytic reactions and further our understanding of underlying reaction mechanisms. The Langmuir–Schaeffer technique [14] is an excellent tool to produce high density metal nanoparticle arrays [15].

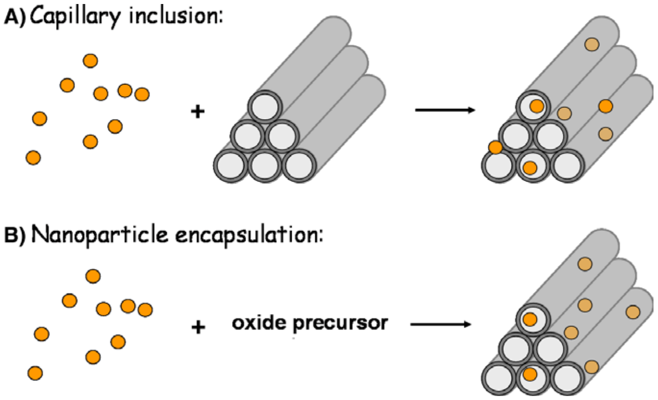
2. Experimental

2.1. Fabrication of three-dimensional Pt/mesoporous oxide catalyst systems

First monodisperse platinum nanoparticles in the size range of 1–10 nm were synthesized using a variety of wet chemical synthetic recipes. For each particle size, the reaction conditions (direct reduction or seeded growth method, capping agents, reducing agents, solvents, and reaction temperatures) were optimized to produce highly monodisperse samples. The Pt-nanoparticles produced this way were then incorporated into mesoporous silica (SBA-15) using low power sonication. Alternatively, the silica support was synthesized around the Pt nanoparticles (Scheme 1) in a process which is referred to as the nanoparticle encapsulation method. The synthesis of mesoporous Al_2O_3 and Ta_2O_5 with ordered, SBA-15-like structure was developed and provides additional materials which can be used as catalyst supports.

2.1.1. Synthesis of platinum nanoparticles with PVP capping agent by alcohol reduction

Pt nanoparticles in the size range of 1.7–7.1 nm were synthesized by an alcohol reduction method as described earlier [16–18]. Briefly, aqueous solution of hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was used as inorganic precursor and reduced by various types of alcohols (methanol, ethanol and ethylene glycol) at reflux temperatures. PVP (poly(vinylpyrrolidone)) of different molecular weights was used to stabilize the particles by capping them in aqueous media. After the synthesis, the nanoparticles were purified from the excess amount of PVP by alternating precipitation with hexane/2-propanol mixture and redispersion in water.



Scheme 1. Schematic representation of the three-dimensional catalyst preparations.

2.1.2. Synthesis of platinum nanoparticles with PVP capping agent by ascorbic acid reduction

PVP stabilized Pt nanoparticles with sizes between 2.0 and 5.3 nm were synthesized using direct reduction of $H_2PtCl_6 \cdot 6H_2O$ with ascorbic acid in a water/methanol solvent mixture. The H_2PtCl_6 precursor was added to a refluxing solution of PVP and ascorbic acid under vigorous stirring. After a few minutes, a color change from yellow to dark brown was observed indicating the formation of nanoparticles. After a 15 min reaction time, the solution was cooled to room temperature and nanoparticles were isolated by precipitation with acetone. Residual PVP was removed by repeated suspension of the crude product in ethanol and precipitation with hexanes. The particle size was controlled by the methanol content in the solvent mixture (boiling temperature), the concentration of the Pt-precursor and the reducing agent.

2.1.3. Synthesis of platinum nanoparticles with PVP capping agent by citrate reduction

PVP stabilized Pt-nanoparticles of 1.5 nm were obtained by direct reduction of $H_2PtCl_6 \cdot 6H_2O$ by trisodium citrate in boiling water in the presence of PVP. After a reaction time of 45 min, the mixture was cooled to room temperature and the nanoparticles precipitated with acetone. Purification of nanoparticles was affected by threefold suspension in ethanol and precipitation with hexanes.

2.1.4. Synthesis of platinum nanoparticles with Pluronic L64 capping agents

Platinum nanoparticles within a size range of 3.5–6.6 nm were synthesized according to a recently reported scheme [19] which uses the seeded growth method. First, homogeneous Pt seeds (3.5 nm) were produced by reducing $H_2PtCl_6 \cdot 6H_2O$ with $NaBH_4$ in the presence of Pluronic L64 ($EO_{13}PO_{30}EO_{13}$, EO = ethylene oxide, PO = propylene oxide) triblock copolymer dissolved in H_2O (Pluronic L64/$Pt^{+4} = 10$). A subsequent slow addition of the precursor hexachloroplatinic acid water solution to the Pt seed sol while H_2 was flowing through the reaction vessel led to larger nanoparticles (5–6.6 nm). After the second addition of the platinum precursor was completed, H_2 was bubbled for an additional 5 min and the reaction mixture was stirred overnight. The particles were isolated by precipitation with a 2-propanol/hexane mixture and redispersed in water.

2.1.5. Synthesis of SBA-15 mesoporous silica support

Mesoporous silica SBA-15 was prepared according to the method reported in the literature [20]. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) triblock copolymer (4.0 g) was dissolved in 30 g of water followed by the addition of 120 ml of a 2 M HCl (aq.) solution while stirring at 313 K for 30 min. Subsequently, 9.0 g of tetraethoxysilane (TEOS) was added to the solution with stirring at 313 K for 20 h. The mixture was aged at 373 K for 24 h. The white powder was recovered through filtration, washed with water and ethanol, and dried in air. The product was calcined at 823 K overnight to produce SBA-15.

2.1.6. Synthesis of mesoporous alumina and tantalum oxide supports

Highly ordered mesoporous alumina with SBA-15-like structure was prepared by a sol–gel based self-assembly method which was reported earlier [21]. To summarize, 1 g of Pluronic P123 was dissolved in 12 ml of absolute ethyl alcohol and stirred for 15 min at 313 K. At the same time a second solution was prepared containing various amounts of concentrated hydrochloric acid and 6 ml of absolute ethyl alcohol. In this method, no water was used in addition to the water present in the concentrated HCl solution. Aluminum tri-*tert*-butoxide (2.46 g) was added slowly to this solution under vigorous stirring. The two solutions were mixed and stirred further at 313 K. In the final reaction mixture, the ratio of Al^{3+}/Pluronic P123/EtOH/H_2O/HCl was 1/0.017/30/6/1. The resulting homogeneous sol was poured into a teflon container and aged for three days at 313 K under N_2 flow. Eventually the white sticky material that was produced was calcined at 673 K in a flow of oxygen, overnight to remove the polymers from the pores. Mesoporous Ta_2O_5 material with well-ordered structure was prepared according to the method in the literature [22,23]. One gram of Pluronic P123 was dissolved in 20 g of ethanol before the addition of 1.97 g of $TaCl_5$ and 0.32 g H_2O. After stirring, the solution was poured into a Petri dish and aged for 5 days at 313 K in an incubator and calcined at 673 K overnight.

2.1.7. Capillary inclusion (CI) method

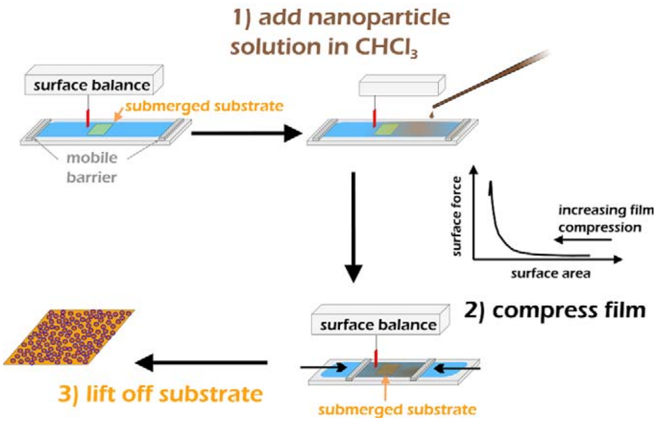
Previously prepared platinum nanoparticles in the size range of 1–10 nm were embedded into highly-ordered mesoporous silica (SBA-15) and other oxides by using low power sonication for 3 h [18]. The as-synthesized materials were calcined at 723 K under air to remove the template polymer (PVP) from the nanoparticle surface and reduced by H_2. The reduced catalysts were characterized by XRD, TEM, nitrogen physisorption and selective gas chemisorption.

2.1.8. Nanoparticle encapsulation (NE) method

An alternative technique to produce high surface area Pt/SBA-15 catalysts is the nanoparticle encapsulation method [24,25]. Monodisperse PVP-capped platinum nanoparticles (size range of 1.7–7.1 nm) obtained by alcohol reduction were used as templates and the silica support was synthesized around them. Briefly, 2.5 g of Pluronic P123 was completely dissolved in 50.5 mL of deionized water. The Pt colloidal aqueous solution (27.0 mL, 3×10^{-3} M) was mixed together with the polymer solution at 313 K, and stirred for 1 h to ensure complete dispersion of the particles. Then 0.375 mL of 0.5 M aqueous NaF solution and 3.91 mL of tetramethylorthosilicate (TMOS) were quickly added to the colloidal solution. The mixture was stirred for 20 h at 313 K. The resulting slurry was aged for an additional day at 373 K. The brown precipitates were separated by centrifugation, thoroughly washed with water and acetone, and dried in an oven at 373 K. Finally, the catalysts were cured by a recently developed, low temperature (373 K) oxidation–reduction treatment which effectively removes the PVP from the surface of the particles and residual polymer from the pores of the silica support [26].

2.2. Fabrication of two-dimensional Pt/SiO_2 model catalysts by means of the Langmuir–Schaeffer technique

2D model catalysts were fabricated by depositing PVP stabilized 7.1 nm Pt nanoparticles, synthesized by the ethylene glycol reduction, onto a silicon substrate exhibiting a native oxide layer by using the Langmuir–Schaeffer technique [14,27]. A schematic of the process is shown in Scheme 2. A Langmuir-trough was thoroughly cleaned and filled with ultrapure water. The silicon substrate was then placed onto an L-shaped aluminum holder which was attached to a motorized stage (dipper) and submerged in the water phase. A dilute suspension of freshly synthesized and purified 7.1 nm Pt-nanoparticles (ethylene glycol reduction) in chloroform was added dropwise to the water phase of the trough until the surface force reached a value of ≈3–5 mN/m. Following a 1 h equilibration period, the film was compressed at low compression rates (0.3 mN/m/min) until the desired surface force value was obtained.



Scheme 2. Schematic representation of the two-dimensional catalyst fabrication by the Langmuir–Schaeffer technique.

The substrate was then lifted off by means of the motorized dipper stage at a rate of 0.1 mm/min. 2D-nanoparticle films obtained in this way were left to dry in air and characterized by SEM.

3. Results and discussion

3.1. Synthesis of Pt nanoparticles

The size of the platinum nanocrystals was tuned uniformly in the range of 1–10 nm using different reaction conditions such as reaction temperature, solvent, reducing agent and surface stabilizing agent. The characteristics of the samples are shown in Table 1. Using alcohol reduction technique and PVP as the protective agent, Pt nanoparticles of five different sizes (1.7, 2.6, 2.9, 3.6 and 7.1 nm) were produced with narrow size distribution ($\sigma \sim 0.3$ nm).

When Pluronic L64 triblock copolymer was used as capping agent and the reduction of the platinum precursor molecules was carried out by $NaBH_4$ at room temperature, the formation of small nanoparticles of 3.5 nm was observed. These seeds were used as nuclei for producing larger particles (5.4, 6.0 and 6.6 nm); this is achieved by adding additional H_2PtCl_6 precursor to the reaction mixture under H_2 flow. Pluronic triblock copolymer was used as surface protective agent instead of the commonly used poly-*N*-vinylpyrrolidone (PVP). Because the former polymer does not have a pure carbon backbone it may decompose under milder oxidative conditions. This is a crucial step because it helps to eliminate the buildup of amorphous carbon/graphite on the nanoparticle surface during the stabilizer removal process.

An alternative synthetic route to fabricate Pt-nanoparticles in the 1–10 nm size range was explored. Sodium citrate and ascorbic acid reducing agents are often used for synthesizing Au and Ag nanoparticles [28–31]. They are both mild reducing agents and are typically used in aqueous solution, a very convenient fact, since most commonly used polymeric capping agents such as PVP, Pluronic L64, polyacrylic acid, poly-acrylate and poly-acrylamide materials are water soluble. Both sodium citrate and ascorbic acid were used to produce small (1.5–2.0 nm) and medium-sized (3.5–5.3 nm) Pt-nanoparticles. Fig. 1 shows TEM images of selected Pt nanoparticle samples synthesized by different methods.

3.2. Synthesis of mesoporous oxide supports

Well-ordered mesoporous oxide materials were prepared by sol–gel techniques for further use as catalyst supports. SBA-15 with a pore diameter of 9 nm, a surface area of $800\ m^2\ g^{-1}$ and a pore volume of $1.2\ cm^3\ g^{-1}$ was used as a model because of its well defined and easily tuneable properties.

Al_2O_3 and Ta_2O_5 with hexagonally ordered channel system, similar to that of SBA-15, were successfully synthe-

Table 1
The synthesis conditions and the characteristic sizes of the different Pt nanoparticle samples

Surface stabilizing agent	Reducing agent[a]	Temperature (K)	TEM size (nm)[b]	XRD size (nm)[c]
PVP	Ethylene glycol	469	1.7 ± 0.26	1.9
PVP	Ethanol	351	2.6 ± 0.22	2.5
PVP	Methanol	338	2.9 ± 0.21	3.0
PVP	Methanol	338	3.6 ± 0.26	3.8
PVP	Ethylene glycol	469	7.1 ± 0.37	7.8
Ascorbic acid (no PVP)	Ascorbic acid	338	2.0 ± 0.35	2.1
PVP	Ascorbic acid	353	3.4 ± 0.71	3.6
PVP	Ascorbic acid	353	5.3 ± 1.20	5.5
PVP	Sodium citrate	373	1.5 ± 0.25	
Pluronic L64	$NaBH_4$	293	3.5 ± 0.38	3.5
Pluronic L64	$NaBH_4 + H_2$	293	5.4 ± 0.77	5.0
Pluronic L64	$NaBH_4 + H_2$	293	6.0 ± 0.98	5.5
Pluronic L64	$NaBH_4 + H_2$	293	6.6 ± 0.67	6.2

[a] With Pluronic L64 stabilizing agent first Pt seeds were synthesized by reducing the precursor with $NaBH_4$. During the nanoparticle growth H_2 was used as reducing agent.

[b] The size of the particles determined by TEM measurements by counting 300 particles.

[c] The size of the nanoparticles determined by XRD using the Debye–Scherrer equation: $d = A\lambda/\Delta\theta\cos\theta$, where d is the particle diameter, A is a constant (generally = 1), λ is the X-ray wavelength (Co Kα = 1.79 Å), $\Delta\theta$ is the full width at half-max of the (1 1 1) peak in radians and θ is half the Bragg angle of the peak.

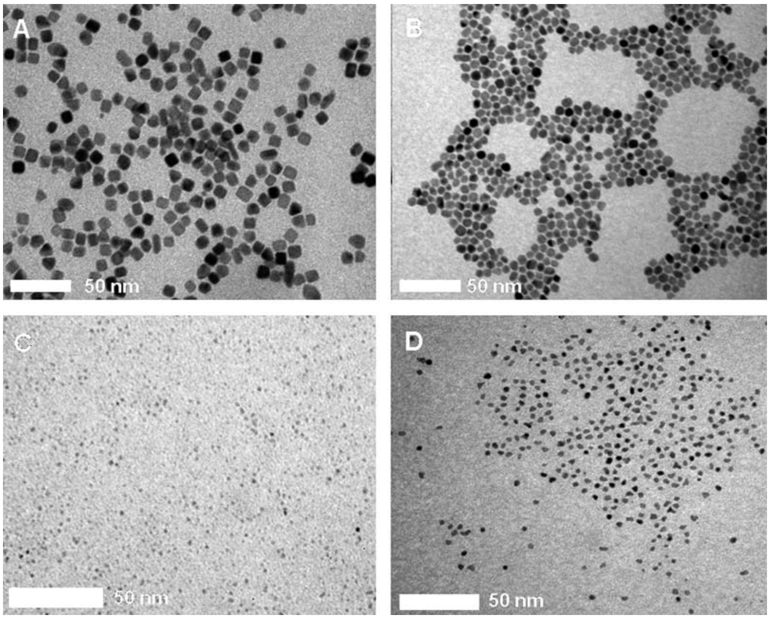


Fig. 1. TEM images of Pt nanoparticles synthesized by different techniques: (A) PVP coated Pt (7.1 nm) nanoparticles made by ethylene glycol reduction; (B) Pluronic L64 coated Pt (6.0 nm); (C) PVP coated Pt (3.5 nm) made by ascorbic acid reduction; (D) PVP coated Pt (1.5 nm) made by citrate reduction.

sized in powder form. The high long-range order of the organized mesoporous structures after the removal of the polymer (calcinations at 673–823 K under air) were revealed by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) measurements (not shown here). Physisorption measurements on the mesoporous alumina and tantalum oxide samples revealed a BET surface area of 400 and 120 $m^2 g^{-1}$ with a pore size of 7 and 4.0 nm, respectively. Although mesoporous alumina and tantalum oxide show lower thermal stability at higher temperatures than SBA-15, these oxides were stable during the template removal at 673 K and kept their hexagonally ordered structure intact.

3.3. Fabrication of three-dimensional catalysts

When using the capillary inclusion method (Scheme 1) to prepare catalysts, it was found that the size of the nanoparticles and the structure of the support (SiO_2, Al_2O_3 and Ta_2O_5) are unaffected by the sonication. However, TEM measurements also show that the nanoparticles mostly located on the outer surface of the oxide supports and only a smaller portion of them are incorporated into the channel system (Fig. 2).

Nanoparticle encapsulation is a "one-pot" synthetic method (Scheme 1). Template assisted nanoparticles are reduced in aqueous solution, upon which a triblock copolymer Pluronic P123, a silica source (TMOS) and NaF are added. The entire synthesis is conducted at pH 7 with the fluoride anion acting as a catalyst for the hydrolysis of silicate species. In the final material, all of the Pt particles are encapsulated within the SBA-15 framework. TEM investigations (Fig. 3A) and nitrogen physisorption measurements (not shown here) indicate that the nanoparticles are homogeneously dispersed inside the channels of the SBA-15, and neither aggregation nor blocking of the pore openings are key points in the design of high surface area model catalysts. From SAXS measurements, it has been determined that the lattice spacing (d_{100}) of the SBA-15 increases from 10.1–13.4 nm as Pt particles of 7.1 nm diameter are incorporated (Fig. 3B). The presence of the Pt-nanoparticles during the self-assembly of the Pluronic

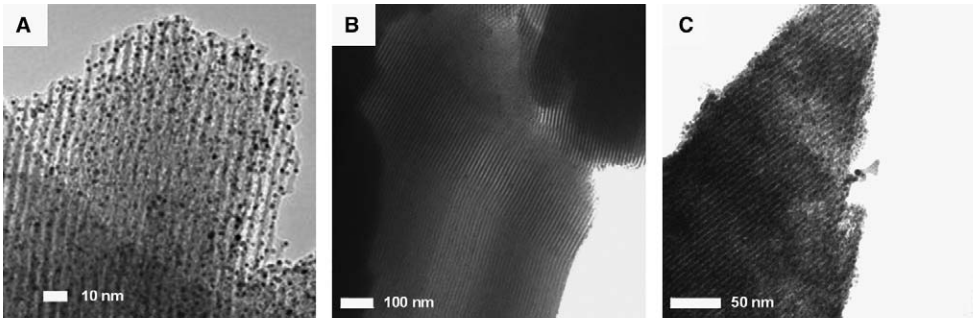


Fig. 2. Pt (2.9 nm)/SBA-15 (A), Pt (2.9 nm)/Al_2O_3 (B), Pt (2.9 nm)/Ta_2O_5 (C) catalysts prepared by capillary inclusion (CI) method.

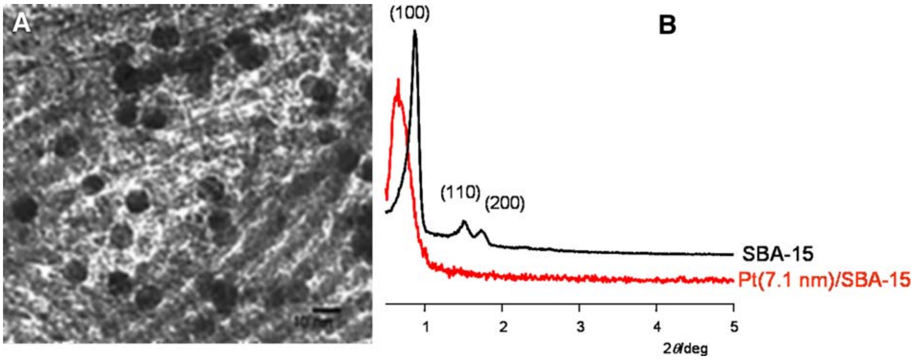


Fig. 3. TEM image (A) and SAXS spectra (B) of Pt(7.1 nm)/SBA-15 synthesized by nanoparticle encapsulation (NE).

P123 into its hexagonal micellar arrangement causes a swelling of individual micelles. This is a strong evidence that Pt is incorporated into the channel of the SBA-15 during growth. The nanoparticle encapsulation represents a more convenient procedure for the synthesis of metal nanoparticles/SBA-15 materials. The maximum Pt particle size that may be embedded in the SBA-15 channels by the inclusion method is ~7 nm, while the upper limit on nanoparticle inclusion for the encapsulated synthetic method is determined by the maximum expansion that the micelles can undergo without destruction (~15–20 nm). All Pt-nanoparticles are synthesized using a polymeric capping agent which controls the growth and stabilizes them in solution. Upon sonication in the mesoporous oxide channels or after the direct condensation of silica around the Pt nanoparticles, the nanoparticles are coated with ~1 monolayer of this capping agent. The stabilizing polymers are tightly bound to the Pt surface for entropic reasons. Removing these species from the Pt surface is difficult and constitutes a major effort of still ongoing research. Typically, heterogeneous catalysts are calcined in flowing oxygen or air prior to reduction in hydrogen which removes adsorbed oxygen in the form of water. The calcination step is used to remove carbonaceous deposits and other impurities from the Pt surface but the particle shape can be altered if the calcination temperature exceeds 600 K. We have recently developed a procedure (a series of oxidation–reduction cycles at relatively low temperatures, 373 K) which enables us to remove the PVP from the particle surface and the Pluronic P123 from the mesopores of the SBA-15 support at the same time. The observed catalytic activity of an untreated catalyst during ethylene hydrogenation increased by an order of magnitude increases (17–202 μmol g^{-1} s^{-1}) after undergoing five oxidation–reduction cycles at 373 K.

3.4. Fabrication of two-dimensional catalysts

7.1 nm cubic PVP stabilized Pt-nanoparticles synthesized by the ethylene glycol reduction method were deposited onto native oxide covered silicon wafers by means of the Langmuir–Schaeffer technique (Fig. 4). By varying the film compression, the surface coverage of the substrate with Pt nanoparticles can be adjusted. Using this methodology, a surface coverage up to 75% of a monolayer with Pt-nanoparticles was achieved. Removal of the PVP capping agent on 2D Pt-nanoparticle arrays however is more difficult than in the case of the 3D-analogues. When freshly prepared densely packed nanoparticle-films are exposed to mild (O_2-plasma or Ozone treatment at room temperature) or harsher oxidative conditions (O_2-annealing at 723 K), the particles aggregate. This behavior is highly undesirable for catalytic model studies since under normal reaction conditions such clusters would most probably fuse to form larger metal conglomerates. In order to keep individual particles finely dispersed on the substrate, they must be immobilized/chemically bound to the substrate surface prior to the capping agent removal. This can be accomplished by burying them with a thin film oxide (e.g., silica or alumina) deposited by either chemical vapor deposition (CVD), electron beam evaporation or atomic layer deposition (ALD).

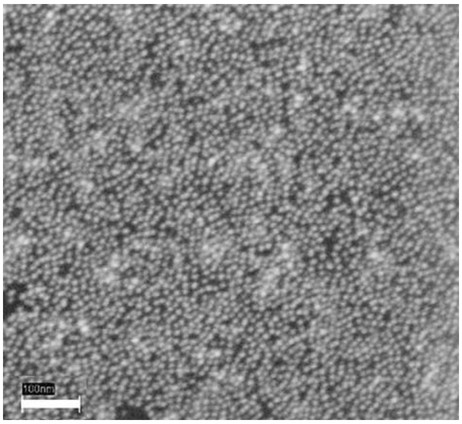


Fig. 4. SEM image of 2D Pt nanoparticle array deposited on silica wafer.

4. Conclusion

Several different fabrication methods used to produce model catalysts are reported. Such catalysts will be used in a systematic study of the variables that influence reaction selectivity: (1) the synthesis of Pt nanoparticles with tunable size and narrow size distribution was developed using a variety of synthetic conditions; (2) the synthesis of a high surface area mesoporous support materials with well-ordered structure made of different metal oxides (SiO_2, Al_2O_3 and Ta_2O_5) is described; (3) the fabrication of 3D catalysts combining the catalytically active metal particles with the support oxide materials was accomplished; (4) the fabrication of 2D catalysts using the Langmuir–Schaeffer method was developed; (5) the characterization of the model catalysts in both 3D and 2D forms was carried out using a combination of chemical and physical techniques.

Acknowledgments

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