

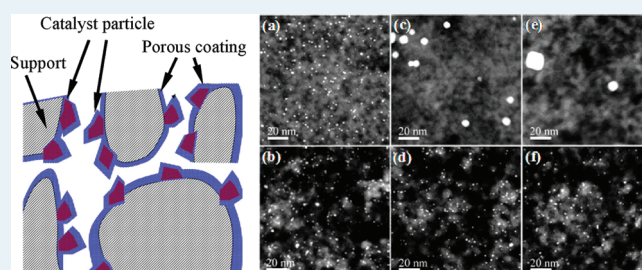
Stabilization of Supported Metal Nanoparticles Using an Ultrathin Porous Shell

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ABSTRACT: Supported Pt nanoparticles (<2 nm) were stabilized by a highly porous, alumina nanofilm that was deposited on the Pt and its high surface area silica support. The alumina film with subnanometer thickness control resulted from thermal decomposition of an aluminum alkoxide layer that was deposited by molecular layer deposition (MLD). A catalyst with a porous ultrathin alumina layer was much more stable to calcination in air, even at 800 °C. The alumina-coated Pt nanoparticles were less catalytically active, most likely because of the small size of the pores in the alumina layer.

KEYWORDS: ultrathin porous layer, Pt nanoparticles, catalysis, molecular layer deposition (MLD)



Noble metals are dispersed on high surface area supports so that the resulting metal nanoparticles have a high fraction of their atoms on the surface. However, supported metal catalysts deactivate at high temperatures when these metal particles sinter to form larger particles.^{1–5} Optimizing the interaction with a support material is one method to stabilize particles against sintering,⁶ but this is only effective at relatively low temperatures. Many catalytic processes, such as catalytic combustion, steam reforming, and automobile-exhaust control, have reaction temperatures typically in excess of 300 °C. Unsupported nanoparticles have been stabilized by hollow sphere encapsulation⁷ and core–shell particle configurations.⁸ Nanoparticles with core–shell structures, where the metal core is surrounded by a porous oxide, only sinter at much higher temperatures. The outer shells isolate the metal nanoparticle cores and inhibit sintering. Somorjai et al.⁸ encapsulated unsupported 14 nm Pt cores with a 17 nm thick mesoporous silica shell (Pt@mSiO₂) by silica polymerization. Zaera et al.⁹ demonstrated that 3 nm Pt nanoparticles dispersed on 120 nm silica beads were stabilized by a mesoporous silica layer having a thickness of 20 nm. Recently, Elam et al.¹⁰ demonstrated that less than 16 cycles of alumina overcoating on Pd nanoparticles by atomic layer deposition (ALD) did not affect the catalytic activity of nanosized Pd ALD catalysts and prevented the sintering of Pd nanoparticles during methanol decomposition in an inert atmosphere up to 270 °C. However, a thicker dense alumina ALD film (more than 16 cycles) completely encapsulated the Pd catalyst and thus significantly decreased the catalytic activity of the catalyst for methanol decomposition. The authors also demonstrated that Pd nanoparticles with 16 alumina ALD cycles were stable after heated at 500 °C for 6 h in a flow of argon. However, the catalytic performance of the 500 °C-treated catalysts was not evaluated, and the thermal stability of the ALD coated catalysts in air was not studied. In the current study, we use a thin film coating technique to prepare thermally stable, highly dispersed, supported

metal nanoparticle catalysts (<2 nm) having an ultrathin, porous ceramic shell, as shown schematically in Figure 1.

Recently, we fabricated highly porous alumina films having a bimodal pore size distribution (average pore sizes of 0.6 and 3.8 nm). These films were produced by oxidizing aluminum alkoxide (alucone) hybrid polymer films,¹¹ obtained from the alternating reactions of trimethylaluminum (TMA) and ethylene glycol (EG) via molecular layer deposition (MLD).¹² The size and size distribution of the pores in the oxide layers can be controlled by proper choice of MLD precursors and oxidation conditions (temperature and oxidant). MLD is a layer-by-layer, vapor phase deposition process utilizing two alternating surface reactions. It provides excellent control over the coating uniformity and composition. The alucone MLD films can be precisely controlled to subnanometer thicknesses. In this paper, we coat an ultrathin, highly porous film onto a catalyst surface. This approach has advantages over other methods of stabilizing supported metal catalysts because the porous oxide layers can completely encapsulate the catalyst particles, which can significantly improve the thermal stability of the catalyst. Also, the oxide layers are only 1–4 nm thick. Thus, the reactant molecules only need to diffuse a short distance through small pores, instead of significantly longer distances (~1 μm) for zeolite layers.¹³ Likewise, the product molecules can readily exit through these pores. The Pt catalysts on porous silica, which were prepared by ALD, are shown to be much more resistant to sintering when coated with a porous alumina layer than the uncoated catalysts.

The Pt nanoparticles were deposited on mesoporous silica particles by ALD using a fluidized bed reactor, as described in detail elsewhere.¹⁴ The silica particles are 30–75 μm in diameter, their average pore size is 15 nm, and their Brunauer–Emmett–Teller (BET) surface area is 240 m²/g. The Pt particles were deposited

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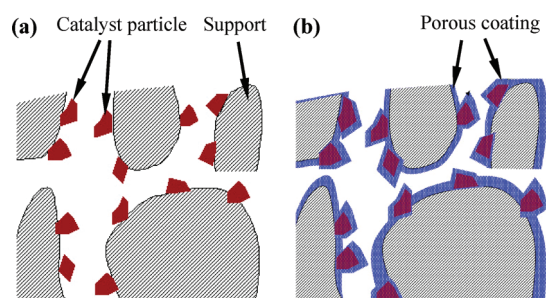


Figure 1. Schematic representation of supported metal catalysts (a) before and (b) after a porous coating on all surfaces of the catalyst particles.

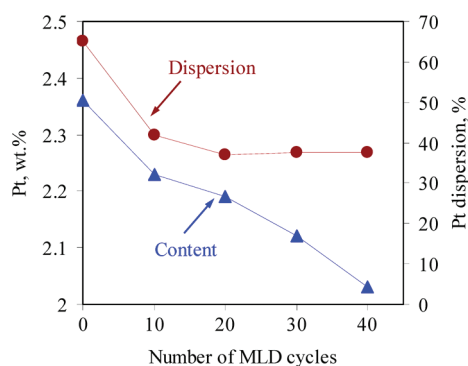


Figure 2. Pt content and Pt metal dispersion versus the number of MLD coating cycles.

using methylcyclopentadienyl-(trimethyl) platinum(IV) (MeCpPt-Me_3) and oxygen as precursors. Five cycles of Pt ALD were carried out at 320 °C to obtain a Pt loading of 2.4 wt %, as measured by inductively coupled plasma, atomic emission spectroscopy (ICP-AES). Hydrogen chemisorption analysis was carried out using a Quantachrome Autosorb⁻¹ on 0.5 g samples. The samples were evacuated at 200 °C for 60 min, reduced in H_2 at 350 °C for 4 h, evacuated at 350 °C for 90 min to remove residual H_2 , and then cooled to 40 °C for analysis. The Langmuir method was used to estimate a metal dispersion of 65%. The average Pt particle size was 1.7 nm, and the Pt surface area was 3.8 m^2/g . The catalyst particles were coated with four thicknesses of alucone MLD films, deposited with 10, 20, 30, and 40 cycles at 160 °C by alternating reactions of TMA and EG. Four corresponding thicknesses ($\sim 1, 2, 3,$ and 4 nm) of porous alumina films were then formed by oxidation at 400 °C in air, as described elsewhere.¹¹ The content of Pt in the catalyst decreased slightly as the number of MLD cycles increased, as shown in Figure 2, because the alumina layer increased the catalyst weight.

The Pt dispersion decreased to 38% (about 58% of its original value) following 20 MLD cycles, and did not change for additional cycles, as shown in Figure 2. An approximately 1 nm thick porous alumina film formed using 10 MLD cycles may not cover all the catalyst surface. However, since the dispersion reached a constant value by 20 MLD cycles, all the catalyst was covered after 20 cycles. The decrease in metal surface area implies that the alumina film directly contacts the Pt particles. Elam et al.¹⁰ studied an alumina ALD coating on Pd nanoparticles using diffuse reflectance IR spectroscopy (DRIFTS) and found that the TMA precursor reacts not only with the hydroxyl groups on the substrate, but also with the most energetic

Table 1. Dispersion of Pt/SiO₂ Catalysts with MLD Alumina Layers after Heat Treatment

	temperature, °C	number of MLD cycles				
		0	10	20	30	40
Pt dispersion, %		65	42	37	38	38
	400	59	42	48	43	42
	600	12	37	42	39	43
	800	3.9	10	27	25	34

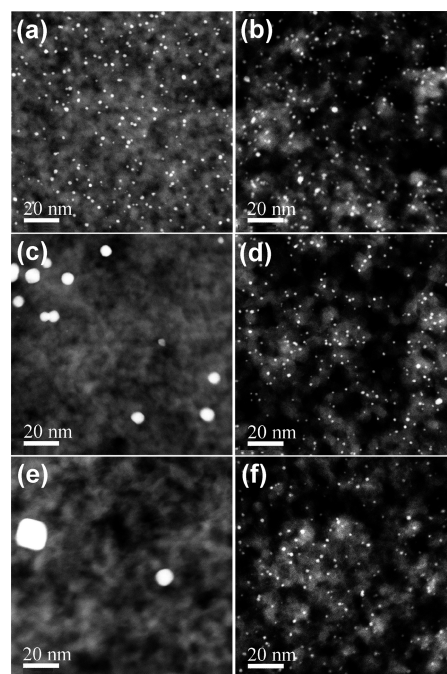


Figure 3. Cross-sectional STEM images of Pt/silica catalysts and porous alumina coated Pt/silica (40 MLD cycles) after calcination for 4 h at: (a, b) 400 °C, (c, d) 600 °C, (e, f) 800 °C.

(e.g., edge and corner) sites of Pd nanoparticles. Their Pd nanoparticles were completely covered by more than 16 alumina ALD cycles. Similarly, during the alucone MLD coating on supported Pt nanoparticles using TMA and EG, it is possible that the first few cycles preferentially deposited onto the silica substrate and the low coordination sites rather than uniformly blanketing the particles. After 20 MLD cycles, the Pt nanoparticles were completely covered. Consequently, porous alumina films covered the Pt particles after removal of the organic component by oxidation in air. Additional MLD coating did not further reduce the Pt dispersion; the loss of the dispersion was mainly caused by the alumina films covering the catalyst surface.

The thermal stability of the Pt particles was studied by holding the catalysts at 400 °C, 600 °C, or 800 °C for 4 h in air. As shown in Table 1, the dispersion of the original catalyst samples decreases dramatically as the treatment temperature increases. After 4 h at 400 °C, the Pt dispersion slightly decreases from 65% to 59%, but for 4 h at 600 °C, the Pt dispersion decreases to 12%. After 4 h at 800 °C, the Pt dispersion further decreases to 3.9%. The porous alumina layer significantly reduces the rate of Pt particle sintering, particularly for thicker alumina films. The catalyst with 10 MLD cycles only loses about 12% of its starting

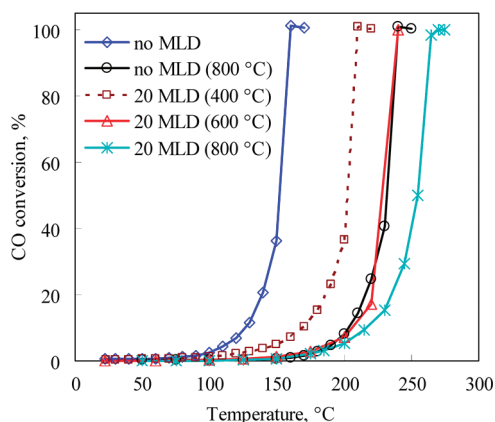


Figure 4. Effects of the sintering temperature and the alumina layer on the CO oxidation reaction.

dispersion after 4 h at 600 °C. The dispersion decreases from 42% to 37%. After 4 h at 800 °C, however, the Pt dispersion dramatically decreases to 10%. The catalyst with 10 MLD cycles, after heating at 800 °C, has approximately the same dispersion as the original catalyst that was heated at 600 °C. That is, a 1 nm thick alumina coating increases the stability of the Pt by 200 °C. A catalyst with a thicker alumina layer (40 MLD cycles) does not sinter during 4 h at 600 °C, and even after 800 °C for 4 h, the Pt dispersion is still 34%.

Scanning transmission electron microscopy (STEM) images of the original and alumina-coated catalysts after heat treatment (Figure 3) show that the original catalyst sinters much more than the alumina-coated catalyst at the higher temperatures. The particle sizes of the original catalyst do not appear to change at 400 °C, but they increase significantly after treatment at 600 °C (Figure 3c). After treatment at 800 °C, only two large Pt particles are seen over a large area (Figure 3e). In contrast, the Pt particle size does not appear to change significantly for catalysts with 40 MLD cycles, in agreement with the H₂ chemisorption measurements shown in Table 1.

The reactivity of the catalysts was evaluated by CO oxidation. Gas mixtures were fed to a fixed bed reactor consisting of a hollow quartz tube with a porous quartz disk on which the catalyst was supported. The catalyst was held in place using quartz wool on top of the catalyst. An electric heating coil wrapped around a quartz shell was used as a furnace. A thermocouple measured the temperature that was controlled by a temperature controller. Catalyst samples were pretreated by oxidation in 10% O₂/90% He for 30 min at 500 °C and then reduced in 50% H₂/50% He for 30 min at 500 °C. The reactor was then flushed with He and cooled to ambient conditions. Carbon monoxide oxidation was carried out with 2% CO, 2% O₂, and 96% He. The total gas flow rate was 50 sccm. The reactor effluent concentrations were measured with a Blazers quadrupole mass spectrometer. All samples had the identical Pt loading even though the total mass within the reactor increases as the number of cycles for MLD increases.

For 32 mg of the catalyst with 20 MLD cycles (without high temperature treatment), CO was completely oxidized at 210 °C. The Pt nanoparticles covered by an ultrathin porous alumina shell were still catalytically active and accessible to CO and O₂. However, the porous coating decreased the catalytic activity of the catalyst, as shown in Figure 4, and thus increased the temperature to obtain complete CO oxidation. The catalyst with 20 MLD cycles (without

high temperature treatment), requires a temperature 50 °C higher than the original catalyst without MLD coating for the same conversion, most likely because of the small size of the pores in the alumina layer. The catalyst with 20 MLD cycles after treatment at 800 °C was less catalytically active than the one after treatment at 600 °C. This is believed to be partly due to crystallization of the amorphous alumina film to form γ -alumina, and this would change the porous structure of the alumina film.¹⁵

Platinum nanoparticles covered by an ultrathin porous alumina shell have comparable or even higher thermal stability than catalysts with a relatively thick mesoporous silica shell.^{8,9} The morphology of most Pt@mSiO₂ nanoparticles was maintained at 750 °C in air, but some Pt cores in Pt@mSiO₂ nanoparticles diffused through the mesoporous silica shell into neighboring Pt@mSiO₂ particles around 750 °C. The Pt@SiO₂ exhibited high catalytic activity for ethylene hydrogenation and CO oxidation, since silica shells had mesopores of 2–3 nm, and no significant mass transfer resistance was observed.⁸ The synthetic strategy developed by Zaera et al.⁹ using mesoporous silica greatly increased the thermal stability of the catalysts, which were shown to resist sintering during calcination at temperatures as high as 800 °C. However, the mesoporous silica layer collapsed and fused after calcination above 630 °C, and this resulted in a significant loss of catalytic activity. Since the thickness of the mesoporous silica films could not be precisely controlled, these methods will be difficult to apply to catalysts supported on high surface area substrates. The self-limiting feature of MLD enables the deposition of the protective layer on highly porous substrates. In this study, the alumina-coated Pt nanoparticles were less catalytically active, most likely because of the 0.6 nm pores in the alumina layer. The mass transfer resistance was controlled by these 0.6 nm pores. On the other hand, the deposition of alumina films into the porous structure of silica gel can reduce the pore size of the silica gel and may increase the mass transfer resistance. Alumina films with larger pores should decrease the catalytic activity less. The size and size distribution of the pores in the oxide layers can be controlled by proper choice of MLD precursors (e.g., organic precursors with longer carbon chains) and oxidation temperature and oxidant. The design concept used in this study can be extended to other metal/metal oxide compositions. In addition, diffusion through the oxide layers would preferentially slow the access of larger molecules to the catalytic surface and thus increase reaction selectivity for certain reactions.

In summary, supported Pt catalysts (1.7 nm Pt average particle size), when coated with a porous ultrathin alumina layer are much more stable to calcination in air, even at 800 °C. The thickness of the alumina layer can be precisely controlled by the number of MLD coating cycles. The porous coating decreases the catalytic activity of the catalyst, most likely because of the small size of the pores in the alumina layer. Porous oxide films obtained from organic precursors with longer carbon chains should have larger pores and may decrease catalytic activity less than the films prepared in this study. Improvements to this thin film technique have the potential to stabilize commercial catalysts and thus, dramatically prolong catalyst lifetime.

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