

Mesoporous Pt/Ru Alloy from the Hexagonal Lyotropic Liquid Crystalline Phase of a Nonionic Surfactant

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Recently, we reported that metals, such as platinum and tin, having a well-defined periodic mesoporous nanostructure can be obtained by the reduction of metal salts dissolved in the aqueous domains of the liquid crystalline phases of oligoethylene oxide surfactants.^{1–3} In these structured reaction systems, the metal is formed between the surfactant supramolecular assemblies that constitute the building blocks of the phases. Consequently, the porous nanostructure of the resulting metal is effectively a cast of the supramolecular architecture of the phase in which it was synthesized.⁴ The range of pore architectures that can be accessed using this synthetic methodology reflects the rich lyotropic liquid crystalline polymorphism of surfactant/water systems. As has been described extensively for nanostructured silicas, the pore diameters of the metals can be selected within the range 1.7–15 nm by using surfactants with different chain lengths, hydrophobic additives such as *n*-alkanes, or polymeric surfactants.⁵ The mesoporous metals that are obtained after removal of the surfactant are granular, typically with particle sizes >100 μm , and have extremely high volumetric surface areas (300–1500 m^2 per cm^3 of material). The combination of high surface areas, uniform pore diameters, and large particles makes these materials of considerable interest for applications as catalysts in fuel cells, automotive emission controls, hydrogenation reactions, and combustions of volatile organic compounds.

Although the liquid crystal templating strategy has been used successfully to produce mesoporous metals, it is desirable to extend the synthetic methodology to the production of alloys. The ability to produce binary intermetallic materials that have a uniform dispersion of the constituent metals is of considerable importance for the development of new catalysts, as in principle catalytic activity can be related to a well-defined and reproducible surface chemistry for such systems.^{6,7}

Furthermore, in many cases, alloying affords materials whose catalytic activity/performance is enhanced significantly in comparison with that of the constituent metals.^{8,9} Thus it is reasonable to expect that the production of binary alloys of platinum that combine high specific surface areas, controllable pore diameters, and a uniform distribution of metal species will impact a wide range of catalytic processes.

Our approach to the synthesis of a mesoporous bimetallic platinum/ruthenium alloy (denoted by $\text{H}_1\text{-Pt/Ru}$) involved adapting the method reported by Watanabe¹⁰ to the conditions we reported for the synthesis of $\text{H}_1\text{-Pt}$.¹ Brij 76, a commercially available nonionic surfactant that nominally corresponds to decaethyleneoxide mono-octadecyl ether ($\text{C}_{18}\text{EO}_{10}$) was employed. In previous studies, we and others showed that, despite the polydispersity of the ethyleneoxide headgroup, the H_1 liquid crystalline phase of Brij 76 can be used to produce high-quality hexagonally nanostructured silicas and metals.^{11,12} Hexachloroplatinic acid hydrate (3.0 g) and ruthenium trichloride (1.52 g) were dissolved in 2.84 mL of deionized water contained in a sealable glass vial. The amounts of metal salts were chosen so as to produce an alloy with a nominal 1:1 atomic ratio of platinum to ruthenium. Brij 76 (9.0 g) was added to the solution, and the mixture was mixed vigorously using a plastic spatula. The vial was sealed, and its contents were heated to ca. 80 °C using a hot air gun and, while hot, mixed using a vortex mixer. The heating/mixing process was repeated three times, and the mixture was allowed to stand for 4 h at room temperature. A sample was withdrawn from the clear dark gray-green mixture and viewed as a thin film under a polarized light microscope. The sample exhibited a uniform optical texture characteristic of the H_1 phase of Brij 76. A solution consisting of 0.5 g of KOH in 2.5 mL of deionized water mixed with 2.5 mL of formaldehyde (40% solution in water) was added dropwise to the mixture with vigorous stirring over a period of 20 min. The reaction mixture was sealed and allowed to stand at room temperature for 2 h. The contents of the vial were transferred to a conical flask and stirred with 200 mL of deionized water for 3 h. Solids were isolated by centrifugation (2500 rpm for 20 min). The washing/centrifugation procedure was repeated six times, and after the final wash, the solids were dried in an oven at 60 °C for 12 h to afford $\text{H}_1\text{-Pt/Ru}$ as a fine black powder.

Transmission electron microscopy studies of $\text{H}_1\text{-Pt/Ru}$ show that it has a mesoporous nanostructure analogous to that of $\text{H}_1\text{-Pt}$ (Figure 1). Measurements taken from the micrographs indicate that $\text{H}_1\text{-Pt/Ru}$ has

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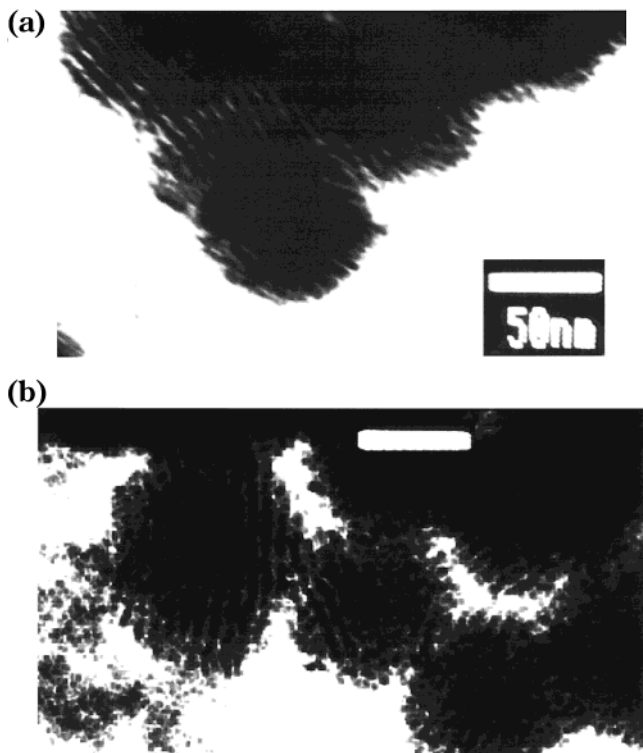


Figure 1. Transmission electron micrographs of H_I -Pt/Ru with a nominal Pt:Ru ratio of 1:1 prepared using sodium borohydride as the reducing agent: (a) side view of the pores, (b) top view of the pores. The scale bars correspond to 50 nm.

a pore diameter of $37 (\pm 1)$ Å and a wall thickness at the point of nearest contact between the pores of $34 (\pm 1)$ Å. These values are comparable with those observed for H_I -Pt obtained from the hexagonal phase of Brij 76.¹² The specific surface area of H_I -Pt/Ru was measured using nitrogen BET porosimetry. The adsorption/desorption isotherms are typical of mesoporous materials and show little hysteresis. The specific surface area was determined to be $86 \text{ m}^2 \text{ g}^{-1}$. Low-angle X-ray diffraction studies of the H_I -Pt/Ru alloy shows a reflection at 1.47° (2θ), which corresponds to a lattice parameter of 60.3 Å and a hole-to-hole distance of 69.6 Å.

The reduction of isotropic aqueous binary mixtures of metal salts has been widely reported as a route to intermetallic nanoparticles with diameters ranging from a few nanometers to >100 nm. The use of microemulsions to produce materials consisting of uniform-sized nanoparticles has also been reported.¹³ However, co-reduction of binary mixtures does not necessarily produce intermetallic materials with a homogeneous distribution of metal atoms. In particular, it is often the case that the reaction products consist of a physical mixture of nanoparticles of each of the two metals (i.e., no alloying). Even when alloying is achieved successfully, it is often observed that the metal distribution is not uniform within a particle.¹⁴ Wide-angle X-ray diffraction spectroscopy and EXAFS were therefore employed to investigate whether H_I -Pt/Ru was indeed an intermetallic material. The diffraction data are sum-

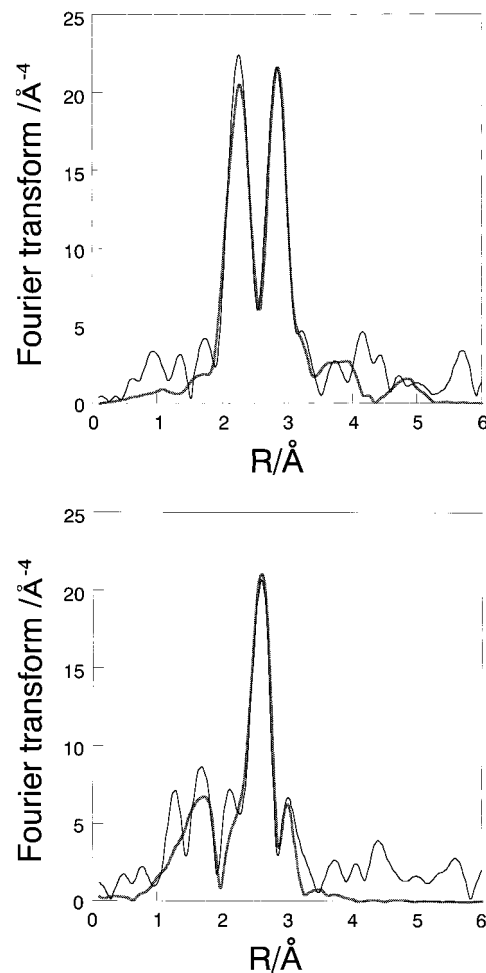


Figure 2. k^3 -weighted [$k^3\chi(k)$] Fourier transform of EXAFS data for H_I -Pt/Ru (dark curves) and theoretical fits to data (pale curves). (a) Data for Pt L_{III} edge, (b) data for Ru K edge.

Table 1. Summary of Wide Angle X-ray Diffraction Data^a Obtained Using Cu $K_{\alpha 1}$ Radiation^b for Bulk Platinum,¹⁵ Platinum Black, H_I -Pt, and H_I -Pt/Ru

hkl	bulk platinum ($Fm\bar{3}m$)		platinum black		H_I -Pt		H_I -Pt/Ru	
	d (Å)	I (au)	d (Å)	I (au)	d (Å)	I (au)	d (Å)	I (au)
111	2.2650	100	2.26	100	2.25	100	2.24	100
200	1.9616	53	1.96	54	1.96	54	1.95	48
220	1.3873	31	1.38	29	1.38	29	1.37	27
311	1.1826	33	1.18	31	1.19	31	1.18	30

^a I denotes the intensities of the diffraction peaks, and d their positions in real space. ^b $\lambda = 1.5405$ Å.

marized in Table 1. The diffractogram for H_I -Pt/Ru shows four reflections that are in excellent agreement with those reported for nanoparticulate Pt/Ru alloy with a nominal Pt:Ru ratio of 1:1, which was prepared by co-reduction in an isotropic reaction mixture,¹⁰ and that are consistent with H_I -Pt/Ru having an fcc structure ($Fm\bar{3}m$ space group). Confirmation of the intermetallic nature of the H_I -Pt/Ru material, as well as of the uniform distribution of the metallic components, was achieved using EXAFS. The k^3 -weighted Fourier transforms of the Pt L_{III} and Ru K edge EXAFS data are shown in Figure 2. Structural parameters obtained by fitting the data are summarized in Table 2. The fit to the Pt L_{III} edge data H_I -Pt/Ru indicates that the first-shell Pt-Pt coordination number is $5.4 (\pm 0.3)$, whereas the first-shell Pt-Ru coordination number is $2.9 (\pm 0.2)$.

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Table 2. Structural Parameters for H₁-Pt/Ru Obtained from Theoretical Fits of the EXAFS Data^a

sample (edge)	neighbor	<i>N</i>	<i>R</i> (Å)	2σ ² (Å ²)	<i>E_f</i> (eV)	<i>R</i> _{EXAFS} (%)
H ₁ -Pt/Ru (Pt L _{III})	Pt-Pt	5.4 (±0.3)	2.737 (±0.002)	0.013	-10.1	38
	Pt-Ru	2.9 (±0.2)	2.709 (±0.003)	0.014		
	Pt-Pt	1.4 (±0.7)	3.81 (±0.02)	0.015		
H ₁ -Pt/Ru (Ru K)	Ru-Ru	3.2 (±0.3)	2.668 (±0.006)	0.013	1.33	49
	Ru-Pt	2.7 (±0.4)	2.714 (±0.008)	0.014		
	Ru-O	1.2 (±0.3)	1.95 (±0.02)	0.011		

^a The absorption spectra were processed using EXBROOK.¹⁷

The Pt-Pt coordination distance obtained from the fit is 2.737 Å, compared with a distance of 2.742 Å for H₁-Pt prepared from Brij 76 (data not shown). This reduction in coordination distance on alloying is consistent with previous EXAFS investigations of Pt/Ru particles supported on carbon,¹⁶ and with the wide-angle X-ray diffraction data. The fit to the Ru K edge data indicates a Ru-Ru first-shell coordination number of 3.2 (±0.3) and a Ru-Pt first-shell coordination number of 2.7 (±0.4). The latter is in excellent agreement with the value obtained from the fit to the Pt L_{III} edge data, confirming that H₁-Pt/Ru consists of a well-mixed 1:1 alloy of the two metals. The presence of an oxygen neighbor in the first coordination shell of Ru indicates that H₁-Pt/Ru is slightly oxidized, with the oxide forming preferentially at the ruthenium sites. Because surface enrichment effects have been reported for alloys prepared by co-reduction, the possibility that H₁-Pt/Ru could have internal surfaces that are enriched in ruthenium compared with the bulk cannot be ignored. However, EXAFS data obtained from H₁-Pt are consistent with ca. 40% of the atoms in the sample being surface atoms. Because of the large proportion of surface atoms in H₁-Pt/Ru, the segregation of one metal to the internal surfaces would have significant effects on the EXAFS results. Our EXAFS data show no evidence of surface segregation, and so we are confident that the metals in H₁-Pt/Ru are distributed uniformly throughout the structure.

We have also conducted preliminary experiments aimed at assessing the electrocatalytic activity of H₁-Pt/Ru. In these experiments, a commercial platinum catalyst supported on carbon (40 wt % Pt, Johnson Matthey, XC72-R) and H₁-Pt or H₁-Pt/Ru (1:1 atomic ratio) were formed into electrodes using carbon and

Nafion such that the platinum loading was the same in each electrode. Cyclic voltammetry was employed to determine the peak potential for carbon monoxide oxidation. Each electrode was held at a potential of 0.05 V (all potentials are quoted relative to the reference hydrogen electrode) in 1 M sulfuric acid at 60 °C and exposed to CO for 15 min. The electrodes were then purged with nitrogen for 30 min, with the potential held at 0.05 V. Following purging, cyclic voltammograms were recorded at a scan rate of 10 mV s⁻¹. We observed that the peak for CO oxidation shifted from 0.725 V for the commercial catalyst, to 0.64 V for H₁-Pt, and down to 0.525 V for H₁-Pt/Ru. These results are significant in the context of fuel cell electrodes because they indicate that the oxidation of CO is more facile on the surfaces of the mesoporous alloy than on either the commercial catalyst or the mesoporous platinum.

By conducting the reduction of binary mixtures of metal salts within the aqueous domains of an hexagonal lyotropic liquid crystalline phase, we were able to produce a mesoporous bimetallic alloy. Preliminary data on the catalytic properties of these materials illustrate the viability of employing a liquid crystal templated route for the production of alloy catalysts that have enhanced performance over nanoparticle alloys.

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Supporting Information Available: Description of the processing of the EXAFS data and fitting of the EXAFS curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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