A new method for depositing platinum exclusively on the internal surface of zeolite L

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that have been widely studied. Among these are the metal ion exchange reactions of the Cu(I) and Cu(II) states. Cu(I) states have been found to be particularly

useful for various catalytic reactions. For example, oxidation of propylene by cupric ion exchanged zeolite Y,1,2 cyclodimerization of butadiene,1 and the catalytic oxidation of ethylene by Pd/Cu metal ions on zeolite Y have been described. Platinitized zeolite L has been used in nonacidic catalytic deforming and dehydrocyclization reactions.3 Much of this chemistry has focused on creating encapsulated transition-metal catalysts. The principal role of the zeolite framework is to provide a compartmentalized environment, the metal being immobilized within the microporous structure. Molecules that poison the catalyst, if they are sufficiently large, may be size-excluded from the zeolite pore structure. With smaller pore zeolites such as ZSM-5 and ZSM-11, reactant or product selectivity in a metal-catalyzed reaction is achieved by forcing the reactant molecule to pass through the intracrystalline volume in order to contact the metal. Good selectivity is usually obtained by poisoning the metal sites on the external surface with bulky ligands that are too large to enter the structural metal sites.4-11 Intrazeolite reaction rates of course highly desirable in shape-selective catalysis since such selectivity may exceed that possible with liquid-phase catalysts.12

Some of the charge-balancing counterions of the anionic zeolite framework are readily exchangeable, and the usual route is to introduce metals by equilibration of cationic metal complexes or metal ions with a suspension of the zeolite. Thus Pt and Pd are easily loaded into the large-pore zeolites Y and L by exchanging Na⁺ or NH₄⁺ ions with Pt(NH₃)₄Cl₂ or Pd(NH₃)₄Cl₂.13 Different loadings of noble metal are readily obtained by this ion-exchange method. Transmission electron microscopy and gas adsorption measurements have shown that the bulk of the metal deposited is highly dispersed and that the zeolite walls are free of detectable metal. We have now prepared, using a neutral platinum complex, zeolite L powders that contain platinum metal exclusively on their inner surfaces. We describe two sensitive chemical tests that can differentiate between zeolites platinitized both inside and outside and those platinitized only on the inside. To our knowledge, this is the first time that chemical tests have established the absence of metal clusters or particles on the outer surfaces of a metalated zeolite. These platinitized zeolite L powders are part of an integrated system for light-driven vectorial electron transport and hydrogen evolution that is described elsewhere.14

Experimental Section

Materials. Zeolite L (ideal formula K₆Na₆Al₃Si₁₂O₃₀·2H₂O) and zeolite Y (Na₆Al₄Si₆O₁₆·25H₂O) powders were obtained from Union Carbide, Linde Division, and the remaining chemicals were obtained from Strem Chemicals. Methylviologen iodide was prepared from methylviologen hydroxide and iodine (both ACS reagent grade). 

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Natural and synthetic aluminosilicates are of practical importance as molecular sieves and catalysts. Synthetic zeolites modified with nonframework metals are among those materials that have been intensively studied with regard to cation-exchange properties, metal ion localization, and catalysis.1-3 Transition metal ion exchanged zeolites have been found to be particularly

efficient for various catalytic reactions. For example, oxidation of propylene by cupric ion exchanged zeolite Y,1 cyclodimerization of butadiene,2 and the catalytic oxidation of ethylene by Pd/Cu metal ions on zeolite Y have been described. Platinitized zeolite L has been used in nonacidic catalytic deforming and dehydrocyclization reactions.3 Much of this chemistry has focused on creating encapsulated transition-metal catalysts. The principal role of the zeolite framework is to provide a compartmentalized environment, the metal being immobilized within the microporous structure. Molecules that poison the catalyst, if they are sufficiently large, may be size-excluded from the zeolite pore structure. With smaller pore zeolites such as ZSM-5 and ZSM-11, reactant or product selectivity in a metal-catalyzed reaction is achieved by forcing the reactant molecule to pass through the intracrystalline volume in order to contact the metal. Good selectivity is usually obtained by poisoning the metal sites on the external surface with bulky ligands that are too large to enter the structural metal sites.4-11 Intrazeolite reaction rates of course highly desirable in shape-selective catalysis since such selectivity may exceed that possible with liquid-phase catalysts.12

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by allowing 4,4′-bipyridine to react with excess methyl iodide in acetonitrile, and this compound was converted to the chloride salt hydrate by ion exchange on a Dowex column. This salt was recrystallized from ethyl alcohol. Other chemicals were reagent grade and were used as received unless otherwise noted.

Platinization of Zeolites L and Y. Similar procedures were followed for both zeolite types. For platinization using Pt(NH3)2+, the zeolite (7 g) was washed with 800 mL of deionized water (from a Barnstead Nanopure II system, resistivity 18.3 MΩ cm) and dried at 100 °C in air for 4 days. The zeolite powder was then dispersed by sonication in 1 L of water, and 0.00010–0.24 g of Pt(NH3)2Cl2·H2O dissolved in 100 mL of water was added dropwise. Stirring of the suspension was continued for 6 h, and the powder was filtered. The sample was repeatedly suspended in water, centrifuged, and separated from the supernatant until the liquid was free of the Pt(NH3)2+ UV absorbance at 290 nm. Two methods of reduction of Pt(NH3)2+ to Pt0 were then used. In the first, the zeolite was carefully dehydrated and reduced with hydrogen, by using conditions specified in ref 8; the hydrogen reduction step was carried out at 300 °C. In the second, the Pt(NH3)2+-exchanged zeolite powder (7 g) was dried under flowing nitrogen at 40 °C for 16 h, suspended in 700 mL of H2O, and reduced by dropwise addition of 500 mL of 0.1 M aqueous NaBH4. After 8 h, the platinized zeolite was filtered, washed with copious amounts of water, and dried under flowing nitrogen at 40 °C. Samples prepared with higher levels of Pt loading (0.10 mmol/g of zeolite) were light gray; those prepared by smaller amounts of Pt–(NH3)2+ (0.02 mmol/g of zeolite or less) remained completely white.

Replatinization of zeolites Y and L with Pt(acac)3 was carried out in a similar fashion; because this complex is insoluble in water, dichloromethane (Fisher, Spectrograde) was used in the loading and subsequent resuspension/centrifugation steps. The zeolite powder (10 g, dried in air at 100 °C for 2 days) was stirred for 4 days with 0.5 g of Pt(acac)3 dissolved in 200 mL of dichloromethane. The powder was separated from the supernatant solution by centrifugation and was resuspended in 75 mL of dichloromethane. The last steps were then repeated (10–15 washings were typically required) until the complex was not detectable (λ290 nm < 0.02) in the supernatant by UV–visible spectroscopy. The zeolite powder was dried overnight at 40 °C under flowing nitrogen and then heated in air at 225–250 °C for 4 h. After it was cooled to room temperature, the platinized zeolite was reduced with aqueous NaBH4 solution and washed as described above for Pt(NH3)2+-exchanged zeolites.

Results and Discussion
The amount of Pt0 deposited inside the zeolite framework, with Pt(acac)3 as the source of platinum, is very small. Elemental analyses (Galbraith Laboratories) on hydrated samples establish that the loading level in zeolites Y and L is typically in the range (1.0–3.0) × 10–4 mmol of Pt/g; with Pt(acac)3 as the platinum source, the loading is continuously variable from 5.0 × 10–3 to 1.0 × 10–1 mmol of Pt/g. For the highest loading level, the Pt(111) line is discernible in X-ray powder diffraction patterns, but for samples with less than 2 × 10–4 mmol of Pt/g, the platinum is not detectable by X-ray diffraction. Auger spectroscopy, or X-ray photoelectron spectroscopy. Chemical methods were therefore used to verify the presence of Pt0 and to determine its distribution in/on the zeolite particles.

In the presence of H2 and Pt0, methylvioleign (MV2+) is reduced to the cation radical at pH > 7:

$$\text{MV}^{2+} + \frac{1}{2} \text{H}_2 \rightarrow \text{MV}^{++} + \text{H}^+$$

The dicaticionic MV2+ exchanges into zeolites L or Y to a maximum loading of ca. 1 MV2+ per large cavity (1 per unit cell in L, 8 per unit cell in Y). The excess remains in the solution phase. Because the rate of exchange between zeolite-bound and solution-phase methylviologen molecules is relatively slow, and because the formal potential of the MV2+/MV+ couple is slightly more positive inside the zeolite than in the solution,14,22 zeolites that are platinized only on the inside do not catalyze the rapid reduction of solution-phase MV2+. When Pt0/Zelite L prepared from Pt(acac)3 was treated with MV2+ and hydrogen was then bubbled though the suspension, only the zeolite particles turned blue. The color change typically took 30–60 s in 10 mM MV2+/1 mM NaHCO3 aqueous solution. The solution phase remained colorless. The blue coloration is characteristic of reduced viologen radicals, MV++. When zeolite L in which platinum was deposited both internally and externally (prepared from Pt(NH3)2+) was treated in the same manner, both particles and solution rapidly turned blue. In the latter case, the viologen in the aqueous phase readily contacts the platinum on the outer surface and is reduced. Zeolite Y platinized with either reagent gives blue solutions, even at the lowest level of loading (5.0 × 10–3 mmol of Pt/g), indicating Pt0 both inside and outside. This redox test not only establishes the presence of Pt0 but also differentiates between zeolites with platinum inside the cavities and those with platinum both inside the zeolite and on the external surface.

The absence of Pt0 on the external surface of zeolite L was verified by an additional chemical test. Ferricyanide, Fe(CN)63–, a triatomic species, does not enter the anionic framework of zeolites L and Y. This was established from UV–visible difference spectra of ferricyanide solutions equilibrated with the two zeolites. The ferricyanide ion undergoes a rapid reduction to Fe(CN)64– in the presence of platinum and H2 in aqueous solution. Platinum deposited exclusively within the zeolite L framework cannot make contact with ferricyanide when the particles are suspended in a 1 × 10–3 M Fe(CN)64– solution. UV–visible spectra of these solutions are identical before and after purging for 6 h with hydrogen (Figure 1). For zeolite L containing platinum on both the inner and external surfaces (Pt0/L prepared from Pt(NH3)2+), the identical treatment results in complete disappearance of the absorbance maxima at 302 and 418 nm attributable to the ferricyanide ion (Figure 1). Again, zeolite Y platinized by either method and reduced with either hydrogen or aqueous NaBH4 shows evidence for Pt0 on the outer surfaces, as it catalyzes the Fe(CN)64– reduction. The ferricyanide test is preferred for zeolite Y, since diffusion of MV2+ out of zeolite Y is known to be fast, and false positive tests for external Pt might be obtained by using the MV2+ test.

In order to determine the sensitivity of the ferricyanide test, we prepared nonporous SiO2 powder (made by grinding quartz glass to an average particle size of 5 µm) impregnated with Pt(acac)3, dried, and reduced as above for zeolites Y and L. With SiO2 as the support, Fe(CN)63– reduction was observable in 12 h with platinum loadings of (3–5) × 10–7 mmol of Pt/g but not with loadings 1 order of magnitude lower. This result suggests (assuming similar degrees of Pt dispersion on the external surfaces of zeolite L and SiO2) that zeolite L platinized with Pt(acac)3 has less than 0.1% of its platinum on the external surface.

We have described a new method for depositing platinum exclusively on the inner surfaces of zeolite L particles. The same selectivity is not observed for zeolite Y, even though the crystallographic channel diameters in Y and L (7.4 and 7.1 Å, respectively) are quite similar.16 The difference between zeolites


Figure 1. UV–visible spectra: (a) 1 × 10–4 M aqueous K3Fe(CN)6 solution; (B) the same solution after suspension of 10 mg/mL of zeolite L/Pt0 prepared from Pt(acac)3, 6-h hydrogen purge, and centrifugation; (C) same as (B), but zeolite L/Pt0 prepared from Pt(NH3)2+. The loading of Pt0 in (B) and (C) is 1 × 10–4 mmol/g.
Y and L, with regard to platinumization on the external surface, can probably be attributed to the connectivity of the large cages in the two structures. In the zeolite Y structure, each supercage has four nearest neighbors and molecular diffusion can occur freely in three dimensions. In zeolite L, however, the large cavities are linearly interconnected to form one-dimensional tunnels; diffusion of large molecules such as Pt(acac)3 is likely to be severely restricted. Hence it is possible with the L structure to wash the complex completely off the external surface and to dry the zeolite before substantial diffusion out of the bulk and onto the external surface can occur. The chemical tests outlined above are insensitive and sensitive and may be of general utility in locating noble-metal catalysts in/on zeolites.

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Registry No. Pt, 7440-06-4; Pt(acac)3, 15170-57-7; MV2+, 7440-06-4; Pt(aacac)3, 15170-57-7; Fe(CN)63−, 13408-62-3.


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Experimental Section

All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line, using freshly distilled solvents. Reagent grade benzene, toluene, and hexane were purified by distillation under nitrogen from sodium benzenophenone ketyl. Me3P was purchased from Strem Chemicals, Inc. (Newburyport, MA 01950). (Ph3P)2Rh-Ph, (Ph3P)2Rh-PhMe, 3 (Me3P)2Rh-Me6, (Ph3P)2Rh(CO)2Rh-Me6, and (Ph3P)2Rh(O)Ir-Me10 were prepared by the methods previously described. Proton NMR spectra were recorded on a Varian EM-390 spectrometer, whereas 13C and 19F NMR spectra were obtained on a Varian XL-200 spectrometer. Infrared spectra were determined on Perkin-Elmer 238B and IBM FTIR/85 or FTIR/32 spectrometers. GC experiments were performed with a Perkin-Elmer Sigma 2 gas chromatograph. The high-pressure infrared measurements were carried out on the IBM FTIR/85 spectrometer using a high-pressure IR cell (CIR cell, ZnSe) provided by Barnes Analytical. The reaction was carried out in a 300-mL Parr reactor connected to the CIR cell by '/16-in. stainless steel tubing. The sample was delivered directly from the reactor to the ccr with both maintained at the pressure of the reactor. Background spectra were determined in a completely analogous manner. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.


