column was used with 0.05 M phosphate buffer, pH 2.3, as solvent. The amount detected was 3.8×10^{-8} mol. A very approximate electrical yield based on the integrated current was 30%. The solution could also be directly analyzed electrochemically, taking advantage of the hydroquinone group on dopamine. This was accomplished by using a clean carbon disk. Cyclic voltammetry or differential pulse voltammetry showed the expected response due to dissolved dopamine. A control experiment consisted of soaking 40 coated electrodes in electrolyte for a equivalent time with no electrolysis. No dopamine could be detected in the solution.

Similar experiments have shown that only very small amounts of dopamine are released under any circumstances yet investigated. For example, an electrode with $\Gamma_i = 3 \times 10^{-9}$ mol cm^{-2} released only a 10% coulometric yield of dopamine. Studies in progress are aimed at developing electrodes that are capable of promptly releasing larger amounts of neurotransmitter and demonstrating that such released neurotransmitters have an effect on neurons.

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Registry No. 3, 82741-47-7; dopamine, 51-61-6; isonicotinic acid, 55-22-1; thionyl chloride, 7719-09-7; isonicotinoyl chloride, 14254-57-0; 3,4-bis(benzyloxy)-β-phenethylamine HCl, 1699-56-5; poly((chloromethyl)styrene), 9080-67-5.

Selective Preparation of Catalytically Active Zeolite-Encapsulated Rhodium Complexes

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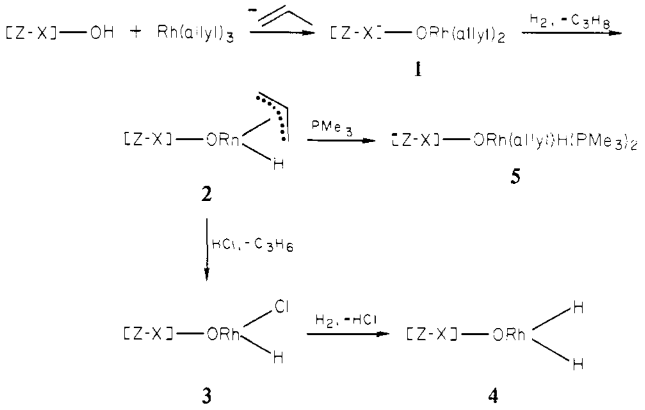
Metal-containing zeolite materials have long been of significance as catalyst systems; however, little is known concerning specific deposition of metal complexes *inside* preformed zeolite cavities: due to size restrictions of the zeolite channels and to the distribution of potentially ligating sites on the particle surface or in the channels as well as in the cavity, it is difficult to introduce metals selectively into zeolite cavities via their "inorganic" compounds by conventional ion-exchange methods. Indeed, it has been found to be advantageous in a practical sense to cocrystallize an "inorganic" metal complex and the zeolite to obtain a desired species.[1] Procedures for activation of such materials as catalysts can often lead to migration of metallic centers to the external surface of the zeolite and, since activation is usually performed under strongly reducing conditions, to their aggregation to metal particles. Specific preparation of catalytically active, zeolite-encapsulated metal species, therefore, can be difficult; this in turn hampers rational development of this class of species as selective catalysts. We have recently reported the synthesis and several reactions of families of oxide-bound rhodium hydride complexes, for example, [Si]–ORh(allyl)H,[2] formed by protolytic deposition of a soluble organorhodium species onto an hydroxylated metal oxide. These complexes can be studied on the "molecular level" and have been proven useful as catalysts for hydrogenation of olefins and arenes. We have now demonstrated that this deposition technique using a soluble organometallic complex can be implemented with use of partially proton-exchanged zeolites (for example, those with "super cages" >10 Å in diameter) and have demonstrated the *selective entrapment* of the transition metal inside the "supercage". A zeolite-encapsulated catalyst species can thus exhibit properties different from those of simple oxide-bound ones: such modification can derive from the "molecular sieve" property of the zeolite microcrystals and from the possibility that "three-dimensional" environmental aspects of the supercage can influence substrate–catalyst interactions.

Scheme I. Formation and Reactions of Zeolite-Supported Rhodium Hydrides[a]



[a] [Z-X] = zeolite; [Z-X]-OH = hydroxyl group inside the supercage.

Triallylrhodium reacts with surface hydroxyl groups (Brønsted acid sites), particularly those located within the zeolite cavities of partially proton-exchanged X-type zeolites ([Z-X]–OH), under mild conditions to form the supported diallylrhodium complex [Z-X]–ORh(allyl)$_2$, **1** (see Scheme I). In a typical experiment a solution of 85 mg (0.38 mmol) of Rh(allyl)$_3$ in 5 mL of octane was added to a slurry (in 20 mL of octane) of 1.6 g of partially (15%) proton-exchanged Linde 13X molecular sieve at room temperature. Propylene evolved during deposition (50 h) was identified by GC/MS and was determined quantitatively by using a calibrated PV manometer; on average, 2 equiv of rhodium were deposited per unit cell of the zeolite. Subsequent treatment of **1** with H_2 (1 atm, room temperature, 48 h) led to the formation of dark gray zeolite-bound rhodium hydride **2** ($\nu_{Rh-H} = 2010$ cm^{-1}) with concomitant evolution of 1 equiv of propane. In contrast to its silica-supported analogue,[2] no bridging hydride ligands could be detected by IR analysis; this suggests a distribution of mononuclear complexes in the zeolite cage. The remaining allylic group of **2** could be removed either via slow hydrogenolysis (>10 days, 1 atm, room temperature) or by reaction with gaseous HCl (24 h, 1 atm, room temperature); this latter process gave propene (0.34 equiv), propane (0.46 equiv), and hexane (0.06 equiv).[2] Zeolite-supported rhodium hydridochloride species (**3**) is likely formed.[2] Treating **3** with H_2 gave **4**; two Rh–H bands of equal intensity were observed by IR analysis ($\nu_{Rh-H} = 2098, 2029$ cm^{-1}). No bridging hydride ligands could be detected.[3,4]

Silica-supported rhodium hydride complexes catalyze hydrogenation of variously substituted olefins with relative rates depending solely on local steric congestion about the double bond.[2] In contrast, whereas **2** did exhibit high catalytic activity for olefin hydrogenation, size/shape selectivity for the substrate (attributed to the "molecular sieve" nature of the zeolite support) was also noted. With **2**, linear uptake of H_2 was observed in catalyzed hydrogenation experiments for all olefins studied (Figure 1). However, *rates* (at 1 atm) *for hydrogenation of olefinic substrates larger than cyclohexene were negligible*, demonstrating that the catalytically reactive center is located *within* the intracrystalline volume of the zeolite: transport restrictions preclude hydrogenation of molecules of sizes unable to pass through the crystalline channels. Thus, with [Si]–ORh(allyl)H, rates for catalyzed hydrogenation of 1-butene, 1-hexene, and 1-octene are comparable

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(1) Weisz, P. B.; Firilette, V. J.; Maatman, R. W.; Mower, E. B. *J. Catal.* **1962**, 1, 307.

(2) Ward, M. D.; Schwartz, J. *J. Mol. Catal.* **1981**, **11**, 397. Ward, M. D.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 5253.

(3) According to this stoichiometry, [Z-X]–ORhCl$_2$ is likely formed too. It would not be possible to detect this species directly by using spectroscopic techniques available to us. The dichloride should, however, be converted to **3**, and thence to **4**, under the hydrogenation reaction conditions.[2,4]

(4) Ward, M. D.; Schwartz, J. *Organometallics* **1982**, **1**, 1030.

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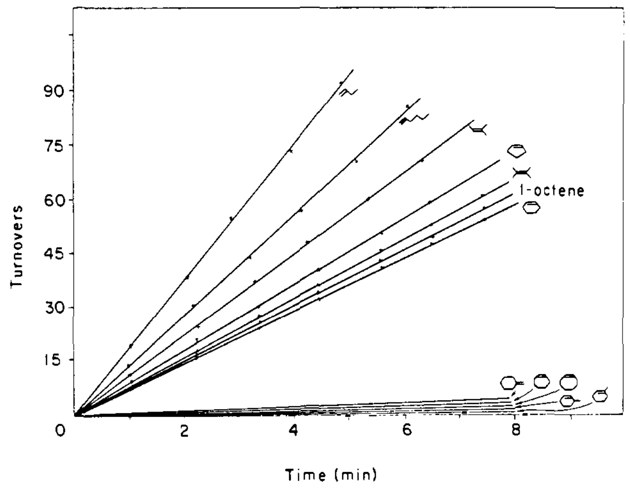

Figure 1. Rate of hydrogenation of olefins catalyzed by (Z-X)-ORh(allyl)H. Conditions: catalyst (50 mg, 0.01 mmol of Rh); (olefin) = 0.2 M in hexane; H_2 (1 atm); 20 °C.

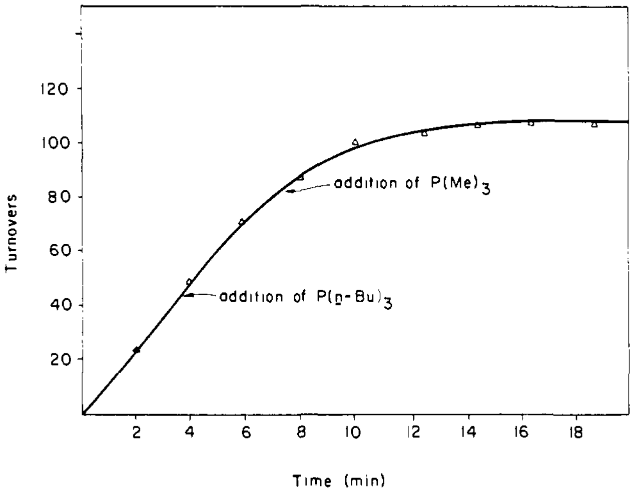

Figure 2. Hydrogenation of 1-butene by (Z-X)-ORh(allyl)H followed by sequential additions of $P(n\text{-}Bu)_3$ and PMe_3.

and are greater than that for 2,3-dimethyl-2-butene; for **2**, however, these rates decrease in the order 1-butene > 1-hexene > 1-octene, and transport limitations are such that locally highly substituted, but "small", 2,3-dimethyl-2-butene is hydrogenated *more readily* than is the "larger" long-chain primary olefin, 1-octene.[5] Consistent, too, with the notion of size/shape selectivity is the observation that **2** efficiently catalyzes benzene hydrogenation to cyclohexane at an appreciable rate (500 psig H_2, 120 °C, 203 (mol of product) (mol of Rh)$^{-1}$ h^{-1}), but under the same conditions toluene was hydrogenated only slowly (<20 (mol of product) (mol of Rh)$^{-1}$ h^{-1}).

Complex **2** coordinates 2 equiv of PMe_3 to give **5**, but n-Bu_3P (of larger cone angle:[6] $\theta_{PMe_3} = 118°$; $\theta_{PBu_3} = 132°$) is not coordinated by **2**. Therefore, a selective poisoning experiment could be used to substantiate the contention that the catalytically active rhodium complex is located *inside* the zeolite cavity. When excess n-Bu_3P and Me_3P were added sequentially to a reaction mixture during hydrogenation of 1-butene catalyzed by **2**, it was found that adding n-Bu_3P did not detectably alter the rate of hydrogenation of the olefin. However, introducing PMe_3 caused the hydrogenation rate to drop, almost immediately, to ca. zero (see Figure 2).

The work described herein presents a new approach to specific deposition and activation of metal complexes inside zeolite cavities. Deposition occurs protolytically most rapidly (and, therefore, can occur specifically) at hydroxylic sites (of the bulk zeolite material) of greatest acidity (which, apparently, are those inside the supercage). This approach, therefore, should be of general utility for deposition of protolytically labile complexes of any metallic entity into proton-exchanged zeolite species. Activation of the bound species as a catalyst can be accomplished under mild conditions which minimize degradation of the active site. Of particular interest to us is the possibility that the cage environment of the zeolite might impart an environmental effect to the reactivity of substrate molecules through specific substrate/environment interactions.

Acknowledgment. We acknowledge support for this research provided by the National Science Foundation.

Registry No. $Rh(allyl)_3$, 12082-48-3; 1-butene, 106-98-9; 2-methyl-2-butene, 513-35-9; 1-hexene, 592-41-6; 1-octene, 111-66-0; 2,3-dimethyl-2-butene, 563-79-1; 1-octene, 111-66-0; benzene, 71-43-2; toluene, 108-88-3; cyclohexene, 110-83-8; cyclopentene, 142-29-0.

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(5) Rates for olefin hydrogenation relative to that for 1-methylcyclohexene catalyzed by [Si]-ORh(allyl)H were as follows: cyclohexene, 1.18; 2,3-dimethyl-2-butene, 0.02. For the catalyst [Z-X]-ORh(allyl)H, these rates were as follows: cyclohexene, 57; 2,3-dimethyl-2-butene, 57. Relative rates for hydrogenation of the small olefin 1-butene with use of [Z-X]-ORh(allyl)H vs. [Si]-ORh(allyl)H were 0.54:1. For actual hydrogenation rates for a series of olefins catalyzed by [Si]-ORh(allyl)H, see ref 2; for those catalyzed by [Z-X]-ORh(allyl)H, see Figure 1.

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Discotic Mesophases Obtained from Substituted Metallophthalocyanines. Toward Liquid Crystalline One-Dimensional Conductors[1]

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A new type of liquid crystals, the discotic mesophases,[2] has recently been described.[3-8] They are observed with organic compounds whose structure is characterized by a flat aromatic core surrounded by several flexible hydrocarbon chains. The molecules are stacked in columns, the different columns forming a hexagonal array (see Figure 1). The spines formed by the superposition of the aromatic cores are isolated by the molten aliphatic tails. This led us to envisage a new class of one-dimensional conductor in which the conducting chains would be composed of the spine of the discotic mesophase. The columns are separated from each other by 10–20 Å of a nonpolar medium. This ensures a very good "insulation" of the various conducting chains. Metallophthalocyanines (PcM) seemed to us particularly suitable for that purpose, since their conducting properties are now well established[9-13] (see Figure 2). Columnar phases formed

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(1) Part 7 of Annelides. For the part 6 see: Markovitsi, D.; Knoesel, R.; Simon, J. *Nouv. J. Chim.*, in press.

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