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Catalytic Hydrogenation of 1-Hexene by Rhodium Complexes in the Intracrystal Space of a Swelling Layer Lattice Silicate

Sir:

There has been considerable recent interest[1-14] in converting homogeneous transition metal catalysts into heterogeneous catalysts by anchoring the complexes to insoluble support matrices such as organic polymers and metal oxides. We have been investigating, as an alternative means of achieving some of the combined advantages of homogeneous and heterogeneous catalysis, the feasibility of conducting metal ion-catalyzed reactions in the intracrystal space of naturally occurring swelling layer lattice silicates known as smectites. These relatively abundant minerals possess mica-like structures in which the crystallites are made up of alternating layers of cations and negatively charged silicate sheets[15] as illustrated in Figure 1. Unlike the micas, however, the interlayer cations (mainly Na^+ and Ca^{2+}) are readily exchangeable, and the intracrystal space occupied by the electrostatically bonded cations can be swelled by sorption of water, alcohols, and a variety of other substrates on the large internal surface area (~800 m^2/g). The degree of swelling depends on the nature of the interlayer cation, the substrate, and the negative charge density on the silicate sheets.

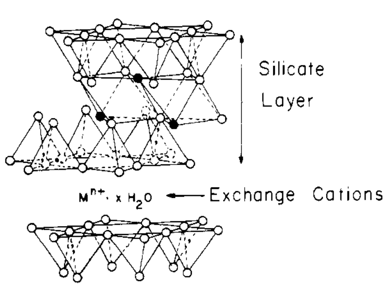

Figure 1. Schematic representation of a smectite structure (adapted from ref 15). Open circles are O^{2-}, dark circles are OH^- or F^-. In hectorite, which has an idealized anhydrous unit cell composition of $Na_{0.66}[Li_{0.66}, Mg_{5.34}](Si_8)O_{20}(OH, F)_4$, Si^{4+} fills the tetrahedral sites, Li^+ and Mg^{2+} fill the octahedral positions, and Na^+ is the interlayer exchange cation.

Electron spin resonance studies[16,17] have shown that fully hydrated Cu^{2+} and Mn^{2+} in smectite interlayers 10-12 Å thick possess local structures and mobilities similar to those found for the ions in bulk solution. The solution-like properties of the ions suggested to us that, with an appropriately designed exchange ion-substrate system, the interlayer ions should be accessible to attack by reagent molecules from solution and that one should be able to conduct cation-catalyzed reactions in the intracrystal environment. This concept is demonstrated by the preliminary results communicated herein for the catalyzed hydrogenation of 1-hexene by rhodium complexes derived from Rh_2^{4+} in the intracrystal space of the mineral hectorite.

Native $[Na_{0.66}^+]$-hectorite with the approximate unit cell composition given in the caption to Figure 1 was converted to its proton exchange form by passing a suspension of the microcrystalline, colorless mineral in methanol through a column of acid-exchanged Dowex 50 resin. An amount of Rh_2^{4+} equivalent to ca. 6% of the cation exchange capacity of the mineral was then introduced to the intracrystal surfaces[18] by exchange reaction with 8×10^{-3} *M* Rh_2^{4+} in methanol[2] under oxygen-free conditions. The uv-visible absorption spectrum of the light green $[(Rh_2^{4+})_{0.01}, H_{0.62}^+]$-hectorite as a Nujol mull exhibited the same intense charge transfer band found near 256 nm for Rh_2^{4+} in methanol (ϵ 3.1×10^3),[2] though the weak solution bands at 423 (ϵ 61.8) and 612 nm (ϵ 55.0) could not be detected in the mineral environment.

The addition of triphenylphosphine in methanol solution to $[(Rh_2^{4+})_{0.01}, H_{0.62}^+]$-hectorite causes the mineral-bound metal ion to be reduced at room temperature to a red rhodium(I)-triphenylphosphine complex of the type $Rh(PPh_3)_x^+$. An analogous reduction has been demonstrated by Wilkinson and his coworkers[2] for Rh_2^{4+} in methanol solution and at the exchange sites of a cation exchange

Table I. Hydrogenation Rates for 1.0 *M* Hexene in Methanol at 25°

Initial complex	Mol of Rh/mol of olefin	Mol of PPh_3/mol of Rh	H_2 uptake[a] (ml/min/mmol of Rh)
$[(Rh_2^{4+})_{0.01}, H_{0.62}^+]$-Hectorite	1.2×10^{-4}	0	4.9[b]
		6.0	14
		9.0	23
		11.0	22
		14.0	23
$[(Rh(PPh_3)_{2.3}^+)_{0.12}, Na_{0.54}^+]$-Hectorite	8×10^{-4}		20
$[Rh_2^{4+}, H^+]$-Dowex 50W resin	1.0×10^{-2}	2.0	7[c]
Rh_2^{4+}, homogeneous solution[d]	2.5×10^{-3}	2.0	140

[a] H_2 pressure = 640 Torr, unless otherwise noted. [b] The uncertainty in rates for $[(Rh_2^{4+})_{0.01}, H_{0.62}^+]$-Hectorite is ca. ±10% due to comparable uncertainty in the rhodium content of the catalyst. [c] This value is taken from data presented in ref 2; H_2 pressure = 450 Torr. [d] This solution was prepared by protonation of $Rh_2(OOCCH_3)_4 \cdot 2CH_3OH$ with HBF_4.[2]

resin. Their formulation of the red complex as a monomeric rhodium(I) complex was supported in part by the isolation of $Rh(PPh_3)_3BF_4$ crystals from the solution reaction. Triphenylphosphine most likely functions as the reducing agent in the reaction as $POPh_3$ more recently has been shown to be the oxidation product obtained in the related reduction of Rh_2^{4+} to $Rh(PPh_3)_3(OCOCH_3)$ in presence of PPh_3 and $Li[OCOCH_3]$.[19]

$Rh(PPh_3)_x^+$ ions also can be introduced to the interlamellar surfaces of the mineral by direct exchange reaction between its Na^+ exchange form and a freshly prepared 8×10^{-3} *M* solution of the complex in methanol. This method of preparation affords a red mineral with an elemental composition that corresponds to $[(Rh(PPh_3)_{2.3}{}^+)_{0.12}, Na_{0.54}{}^+]$-hectorite. The observed PPh_3 to Rh ratio suggests the possible presence of two or more solvated $Rh(PPh_3)_x^+$ species, perhaps in dissociative equilibrium, on the mineral surfaces.

The addition of oxygen-free hydrogen to a suspension of $[(Rh_2{}^{4+})_{0.01}, H_{0.62}{}^+]$-hectorite in methanol at 25° results in the formation of a light yellow to colorless rhodium hydride complex which functions in the mineral environment as a catalyst for olefin hydrogenation. Analogous hydride formation and catalytic activity is observed for $[(Rh(PPh_3)_{2.3}{}^+)_{0.12}, Na_{0.54}{}^+]$-hectorite and for the $Rh(PPh_3)_x^+$-containing mineral prepared by addition of PPh_3 to $[(Rh_2{}^{4+})_{0.01}, H_{0.62}{}^+]$-hectorite. Catalytically active hydrides derived from the red rhodium(I)-triphenylphosphine complexes are known also to form in homogeneous methanol solution,[2] but Rh_2^{4+} in absence of phosphine ligand is reported to be inactive and does not react with hydrogen in methanol except at elevated temperatures when it is reduced to the metal.[2] Apparently, when the ion is present on the charged, intracrystal silicate surfaces, its reactivity toward metal hydride formation is enhanced greatly.

The hydrogenation rates obtained for 1.0 *M* 1-hexene in methanol are given in Table I. Hydrogen was allowed to bubble through the mineral-methanol mixtures at least 2 hr to ensure complete hydride formation, and then the olefin was added. After a brief induction period of ca. 15-20 min, linear hydrogen uptake occurred in each case. Included in the table are the rates for Rh_2^{4+} in the presence of PPh_3 ligand and at the exchange sites of a resin and in homogeneous solution at a PPh_3 to Rh ratio (2:1) which is known to provide an optimum rate.[2]

The mixed Rh_2^{4+}, H^+ exchange form of hectorite requires a PPh_3/Rh value greater than 6 to achieve an optimum rate of 22 ± 2 ml of H_2/min/mmol of Rh. Because the same rate is obtained at a much lower PPh_3 to Rh ratio in $[(Rh(PPh_3)_{2.3}{}^+)_{0.12}, Na_{0.54}{}^+]$-hectorite, the presence of hydrogen ion on the silicate surface apparently inhibits the formation or reactivity of the active hydride. Nonetheless, the hydrides derived from Rh_2^{4+} in the presence of PPh_3 are substantially more efficient as catalysts in the mineral environment than at the exchange sites of the resin.

The mineral-bound hydrides showed no activity toward hydrogenation of benzene in methanol at room temperature. This verifies that the activity toward olefin hydrogenation is due to metal hydride formation and not to trace amounts of metallic rhodium, which is an excellent catalyst for reduction of aromatic hydrocarbons as well as for olefins.[20] Moreover, all catalytic activity was lost when hydrogenated $[(Rh_2{}^{4+})_{0.01}, H_{0.62}{}^+]$-hectorite was washed with NaCl in methanol. This latter treatment would be expected to displace a cationic hydride complex from the silicate surface but not the free metal. No evidence for metal formation in the mineral environment was observed in the presence or absence of PPh_3 except at temperatures above 50° when the catalysts became gray and, finally, black.

Finally, the same type of metal hydride formation and catalytic activity observed above for hectorite has been achieved with montmorillonite. In this latter smectite, the negative charge on the silicate sheets arises mainly from isomorphous substitution of Mg^{2+} for Al^{3+} in two-thirds of the octahedral positions.

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Biosynthesis of Sitosterol from (2*R*)- and (2*S*)-[2-^{3}H]Mevalonic Acid in the Pea. The Incorporation of a 15α-Tritium Atom Derived from (3*RS*, 2*R*)-[2-^{14}C,2-^{3}H]Mevalonic Acid

Sir:

The biosynthetic elaboration of sterols from lanosterol in rat livers[1] and yeast homogenates is thought to proceed via a $\Delta^{8,14}$-intermediate. The olefin is presumed to be formed in the course of the 14α-demethylation and involves the abstraction of a hydrogen derived from 2-pro *S* of mevalonic acid[2-4] (MVA) from C-15. Subsequently reduction of the Δ^{14} takes place through the acquisition of 14α-[5] and 15β-hydrogen[4,6] atoms. The overall sequence of reactions results in the inversion of the configuration[4,6] of the retained at C-15 hydrogen atom derived from 2-pro *R* of MVA from its 15β configuration, in protosterols[7] and lanosterol, to the