

Clay Intercalation Catalysts Interlayered with Rhodium Phosphine Complexes. Surface Effects on the Hydrogenation and Isomerization of 1-Hexene

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Clay intercalation catalysts formed by interlayering of Na⁺-hectorite with rhodium phosphine complexes of the type Rh(NBD)(PPh₃)₂⁺ and Rh(NBD)(dppe)⁺, where NBD = norbornadiene and dppe = 1,2-bis(diphenylphosphino)ethane, were examined as catalyst precursors for the hydrogenation-isomerization of 1-hexene in methanol. Relative to reaction under homogeneous solution conditions, the intercalated catalysts exhibit a much lower tendency to isomerize the substrate to the less reactive internal olefin 2-hexene. In the case of Rh(NBD)(PPh₃)₂⁺-hectorite, the dramatic dependence of the hexene: 2-hexene product ratio on substrate concentration and water content indicates that the intrinsic Brønsted acidity of partially hydrated Na⁺ ions in the clay interlayers causes the protonic equilibrium between surface intermediates responsible for the isomerization and hydrogenation pathways to be shifted in favor of hydrogenation. Rh(NBD)(dppe)⁺-hectorite also favors hydrogenation over isomerization relative to homogeneous solution. In this case, however, a catalytically important protonic equilibrium is not involved in the reaction mechanism, and the reaction is insensitive to factors which influence surface acidity. The results demonstrate that surface chemical effects can dramatically alter the catalytic properties of metal complexes immobilized in clay interlayers.

INTRODUCTION

The swelling layered silicates known as smectite clays are of catalytic interest, in part, because they offer a unique crystalline matrix for the immobilization of cationic homogeneous metal complex catalysts. A variety of minerals, including montmorillonite, hectorite, saponite, and beidellite, among others, belong to this class of layered silicates (1). They all exhibit appreciable ion exchange capacities (50-130 meq/100 g), very large internal surface areas (~750 m²/g), and the ability to undergo uniaxial swelling through the adsorption of polar molecules on their interlamellar surfaces. Intercalation complexes can be formed with almost any desired metal cation catalyst by simply displacing some or

all of the alkali metal and alkaline earth ions that occupy the interlamellar regions of the native mineral.

Recent studies (2) of alkyne hydrogenation with layered silicate intercalation catalysts containing Rh(PPh₃)₂⁺ as the catalyst precursor have shown that substrate selectivity can be regulated by controlling the extent of interlayer swelling relative to the size of the substrate. Surface-oriented intermediates with critical dimensions equal to or smaller than the average interlayer swelling are favored over intermediates with larger critical dimensions. Also, enhanced selectivity has been observed (3) in the distribution of terminal and internal olefin products obtained from the hydrogenation of 1,3-butadienes over hectorite containing intercalated Rh(dppe)⁺ (diphos = 1,2-bis(diphenylphosphino)ethane). Under the appropriate conditions of swelling, the intercalation catalyst favors the synthetically more valuable terminal olefins,

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whereas the internal olefins predominate under homogeneous reaction conditions.

Equally significant selectivity effects have been observed for the hydrogenation of a terminal olefin, such as 1-hexene, over Na^+ -hectorite containing $\text{Rh}(\text{PPh}_3)_2^+$ as the catalyst precursor (2). Although extensive terminal to internal olefin isomerization occurs with this precursor under homogeneous conditions, hydrogenation is preferred over isomerization when the precursor is intercalated in the layered silicate. In this case, however, size- or shape-dependent factors do not appear to be important in influencing selectivity. Instead, the deviations from solution behavior seem to arise from surface chemical effects which influence the positions of catalytically important equilibria.

The purpose of the present study is to examine further the factors which influence the hydrogenation and isomerization of 1-hexene over rhodium phosphine complexes intercalated in hectorite. Two types of catalyst systems were selected for study. The system studied in greatest detail is derived from $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$, where NBD = norbornadiene. The second system is derived from $\text{Rh}(\text{NBD})(\text{dppe})^+$ as the catalyst precursor.

EXPERIMENTAL

Materials. Natural sodium hectorite with an idealized unit cell formula of $\text{Na}_{0.6}[\text{Mg}_{5.4}, \text{Li}_{0.6}](\text{Si}_{8.0})\text{O}_{20}(\text{OH})_4$ was obtained from the Baroid Division of NL Industries in spray-dried form and with a particle size $< 2 \mu\text{m}$. The cation exchange capacity was determined to be 70 meq/100 g by exchanging Na^+ ions in the air-dried mineral with 1.0 M $\text{Cu}(\text{NO}_3)_2$ and subsequently analyzing the mineral for Cu^{2+} . $[\text{Rh}(\text{NBD})\text{Cl}]_2$ was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Engelhard Industries) by the method of Abel *et al.* (19). $\text{Rh}(\text{NBD})\text{acac}$ was obtained by reaction of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ and acetylacetone according to the method of Cramer (20). Methanol was purchased from Matheson, Coleman and Bell having 0.1 or 0.2% water; a higher

percentage of water in methanol was achieved by addition of deionized water. The exact percentages of water in methanol were determined by the Karl-Fischer method. 1-Hexene was distilled from over activated Al_2O_3 under an argon atmosphere prior to use as a substrate. All samples were prepared in an inert atmosphere and all solvents and liquid reagents were degassed by repeated freeze-vacuum-thaw cycles.

$[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]\text{PF}_6$. This cationic rhodium complex salt was prepared by reaction of $[\text{Rh}(\text{NBD})(\text{Cl})_2]$ with triphenylphosphine in the presence of KPF_6 according to the method of Schrock and Osborn (21). The bright orange crystals decompose above 190°C . The proton and phosphorus NMR spectra of the product were in good agreement with the previously reported spectra. ^1H (CDCl_3) 4.56 (4, olefin), 4.02 (2, methine). ^{31}P NMR (CH_2Cl_2) -28.3 ppm (d, $J_{\text{Rh-P}} = 154$ Hz). Infrared (mull) 1439s, 1495s cm^{-1} ($\text{C}=\text{C}$). λ_{max} (CH_2Cl_2) = 446 nm.

$[\text{Rh}(\text{NBD})(\text{dppe})]\text{ClO}_4$. This compound was prepared by reaction of the acetylacetone complex, $\text{Rh}(\text{NBD})\text{acac}$, and dppe in THF in the presence of HClO_4 according to the method of Schrock and Osborn (21). The proton and phosphorus NMR of the orange complex are in good agreement with the previously reported spectra. ^1H NMR (CD_2Cl_2) 5.34 (4, olefin), 4.33 (2, methine), 1.84 (2, methylene), 2.37 (4, $\text{PCH}_2\text{CH}_2\text{P}$). ^{31}P NMR (CH_2Cl_2) -55.8 ppm (d, $J_{\text{Rh-P}} = 159$ Hz). Infrared (mull) 1439s, 1485s cm^{-1} ($\text{C}=\text{C}$). λ_{max} (CH_2Cl_2) = 473 nm.

$[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]^+$ -hectorite. Na^+ -hectorite (200 mg, 0.14 meq) was stirred for 30 min in 5 ml of methanol and then $[\text{Rh}(\text{NBD})(\text{PPh}_3)_2]\text{PF}_6$ (14.5 mg, 0.015 meq) in 5 ml of the same solvent was added. Stirring was continued for 10 min and the yellowish orange intercalate was filtered and washed several times with 5-ml portions of solvent to ensure complete removal of unexchanged rhodium complex. Elemental analysis indicated 0.72 ± 0.02 wt% Rh. In-

frared (mull) 1439, 1485 cm^{-1} ($\text{C}=\text{C}$). λ_{max} (mull) = 464 nm.

$[\text{Rh}(\text{NBD})(\text{dppe})]^+$ -hectorite. This catalyst precursor was prepared by the above method using 11.5 mg (0.015 meq) $[\text{Rh}(\text{NBD})(\text{dppe})]\text{ClO}_4$. Infrared (mull) 1439, 1485 cm^{-1} ($\text{C}=\text{C}$). λ_{max} = 465 nm.

Hydrogenation studies. The catalyst solutions or suspensions were placed in a specially designed flat-bottom flask to minimize creeping of the finely divided mineral-supported catalyst during the course of reaction (2). In a typical experiment, the flask was charged with 0.015 mmole of rhodium catalyst precursor in the required amount of solvent and then was attached to a manifold fitted with a mercury manometer and a gas buret with a mercury leveling bulb. The entire assembly was evacuated and purged with dry hydrogen. A 1-hr hydrogenation period preceded the injection of substrate into flask. The hydrogen uptake was monitored at 25°C and a total pressure of 740 Torr. After each run with the intercalation catalyst, the catalyst was filtered off and the clear filtrate was checked for hydrogenation activity to ensure that the observed rates were due to only immobilized catalyst. Product analysis was carried out by gas chromatography. The columns were 10 ft \times $\frac{1}{8}$ in. 10% UCW-98 (Hewlett-Packard) on 80 to 100-mesh Chromosorb-W and 6 ft \times $\frac{3}{16}$ in. 20% B,B'-Oxydipropionitrile on 80 to 100-mesh Chromosorb-W.

RESULTS

Homogeneous Catalysts

Figure 1A illustrates the results for the homogeneous hydrogenation of 1.0 M 1-hexene in methanol at 25°C with $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ as the catalyst precursor. As can be seen from these data, hydrogenation is accompanied by extensive isomerization of the substrate to 2-hexene. The initial rate of isomerization is almost twice that for hydrogenation. At 90% conversion the product distribution is 33% hexane and 67% 2-hexene. The rate of 2-hexene hydro-

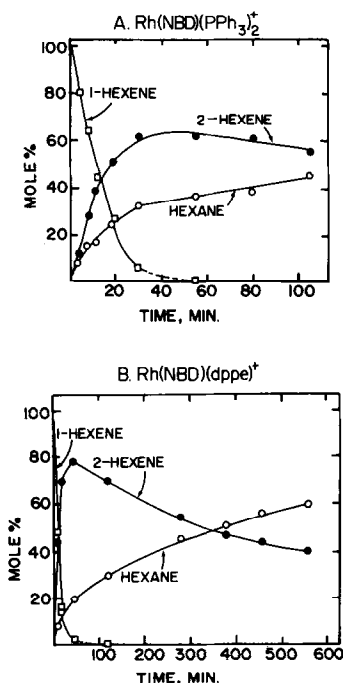


FIG. 1. Homogeneous hydrogenation at 25°C of 1-hexene in methanol (0.2 wt% H_2O) with (A) $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ and (B) $\text{Rh}(\text{NBD})(\text{dppe})^+$ as the catalyst precursor. The initial substrate concentrations were 1.0 M and 1.2 M, respectively. The amount of rhodium complex used was 0.015 mmole in 15 ml of solution.

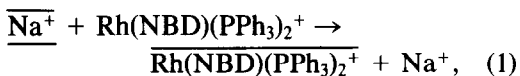
genation is approximately two orders of magnitude lower than the rate of 1-hexene hydrogenation. For 1-hexene, the initial hydrogen uptake rate over the first 5% reaction is 17 mole/min/mole Rh. The initial rate drops to 15 and 2.0 mole/min/mole Rh, respectively, when the concentration of 1-hexene is decreased to 0.60 M and 0.10 M, but isomerization still predominates under these conditions.

The properties of $\text{Rh}(\text{NBD})(\text{dppe})^+$ as a catalyst precursor for the homogeneous hydrogenation of a terminal olefin are even less desirable than those exhibited by $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$. Figure 1B illustrates the results for hydrogenation of 1.2 M 1-hexene in methanol. The initial rate of isomerization is at least five times larger than the initial rate of hydrogenation. At 80% conversion, the product distribution is 15% hexane and 85% 2-hexene. Since the rates

of 1-hexene and 2-hexene hydrogenation are comparable to those observed for $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$, we conclude that $\text{Rh}(\text{NBD})(\text{dppe})^+$ is a better isomerization catalyst precursor than is $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$.

Intercalated Catalysts

$\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ and $\text{Rh}(\text{NBD})(\text{dppe})^+$ are readily intercalated in hectorite by ion exchange reaction with the Na^+ form of the mineral in methanol suspension. The exchange reaction of $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ with Na^+ -hectorite is schematically illustrated by



wherein the parallel lines represent the silicate sheets. Under the exchange condition employed, approximately 11% of the interlayer Na^+ ions are replaced by rhodium complex. Based on the estimated sizes of the rhodium complexes from molecular

models ($160\text{--}200 \text{ \AA}^2$), approximately 25–30% of the interlayer surface is occupied by rhodium complex. The remaining surface is covered by solvent and unexchanged Na^+ ions. An increase in 001 X-ray spacings from 12.6 to 17.7 \AA is observed upon the replacement of Na^+ with $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$. $\text{Rh}(\text{NBD})(\text{dppe})^+$ exchanged into hectorite gives a 001 spacing of 18.4 \AA . The increase in 001 spacing confirms the presence of the rhodium complexes in the interlayer regions of the mineral.

The data in Table 1A for 1-hexene hydrogenation show the catalytic properties of $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ -hectorite to be very dependent on the initial substrate concentration and extent of conversion. Regardless of conversion, the degree of 1-hexene to 2-hexene isomerization is significantly lower for the intercalated catalyst than the homogeneous catalyst. At initial concentrations $\geq 0.6 M$, isomerization accompanies hydrogenation over the entire range of conversion, but at initial concentrations $\leq 0.7 M$

TABLE I

Hydrogenation of 1-Hexene in Methanol with Intercalated and Homogeneous $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ as the Catalyst Precursor^a

[1-Hexene] ^b	Initial rates (mole/min/mole Rh)		Hexane: 2-hexene product ratio	
	Hydrogenation	Isomerization	50% Conver.	90% Conver.
A. Intercalated catalyst				
0.10	4.4	1.1	84 : 16	80 : 20
0.40	11	13	60 : 40	72 : 28
0.60	16	21	44 : 56	58 : 42
0.70	29	c	>95 : 5	74 : 26
0.80	33	c	>95 : 5	79 : 21
1.0	26	c	76 : 24	73 : 27
1.2	33	c	69 : 31	72 : 28
B. Homogeneous catalyst				
0.10	2.0	4.3	30 : 70	32 : 68
1.0	17	33	32 : 68	33 : 67

^a All reactions were carried out at 25°C under a hydrogen atmosphere at a total pressure of 1 atm. The amount of rhodium complex used in each experiment was 0.015 mmole/15 ml of 1-hexene solution. The water content of the solvent was 0.2 wt%.

^b Initial concentration in moles/liter.

^c Isomerization was inhibited at the initial stages of reaction.

isomerization is inhibited until 40–60% of the substrate has been hydrogenated, and then isomerization is initiated.

The inhibition of isomerization for 0.8 *M* 1-hexene is illustrated in Fig. 2. Included in the figure for comparison are the hydrogenation–isomerization data for 0.1 *M* 1-hexene. The induction effect for isomerization cannot be attributed to slow kinetics for the formation of the surface species responsible for isomerization. If the reaction mixture shown in Fig. 2 for 0.8 *M* 1-hexene is filtered before the onset of isomerization (~50% conversion) the intercalated catalyst can be reused for the hydrogenation of a fresh 0.80 *M* solution without loss of hydrogenation selectivity up to 50% conversion. Therefore, the surface species responsible for isomerization most likely is in rapid equilibrium with the species responsible for hydrogenation, but the position of

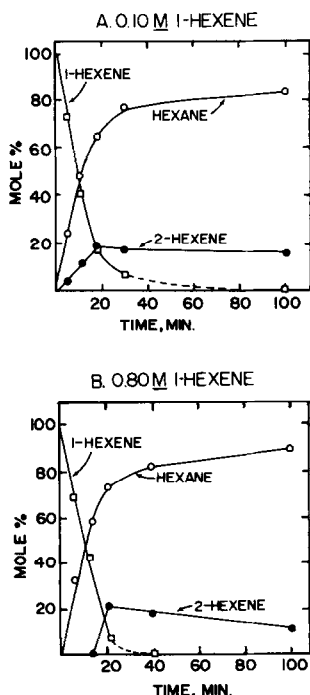


FIG. 2. Hydrogenation in methanol (0.20 wt% H₂O) of (A) 0.10 *M* 1-hexene and (B) 0.80 *M* 1-hexene at 25° with Rh(NBD)(PPh₃)₂⁺-hectorite. The amount of intercalated rhodium used was 0.015 mmole in 15 ml of solution.

TABLE 2

Effect of Water on the Hydrogenation of 0.80 *M* 1-Hexene in Methanol with Intercalated and Homogeneous Rh(NBD)(PPh₃)₂⁺ Catalyst Precursor^a

Wt% H ₂ O ^b	Initial rates (mole/min/mole Rh)		Hexane : 2-hexene at 50% Conv.
	Hydrogenation	Isomerization	
A. Intercalated catalyst			
0.10	33	^c	>95 : 5
0.20	33	^c	>95 : 5
0.50	4.0	5.3	56 : 44
1.0	4.0	5.3	50 : 50
B. Homogeneous catalyst			
0.20	11	21	40 : 60
0.50	10	20	32 : 68
1.0	11	26	34 : 66

^a Reaction conditions are the same as described in Table 1.

^b Water content of the methanol solvent.

^c Isomerization was inhibited at the initial stages of reaction.

the equilibrium is strongly dependent on the composition of the reaction mixture.

The hydrogenation of 1-hexene with intercalated Rh(NBD)(PPh₃)₂⁺ also exhibits a remarkable dependence on the water content of the reaction medium. Table 2A summarizes the change in initial reaction rates and product distribution for hydrogenation of 0.8 *M* 1-hexene containing between 0.10 and 1.0 wt% water. Almost complete inhibition of isomerization is observed up to ~50% conversion at water contents of 0.1 and 0.2 wt%. At 0.5 and 1.0 wt% H₂O, however, the isomerization reaction competes favorably with hydrogenation so that approximately equal yields of hexane and 2-hexene are obtained at 50% conversion. In sharp contrast to the intercalated catalyst, the homogeneous catalyst shows little or no dependence on water content (cf. Table 2B). These results strongly suggest that protonic equilibria influence the reaction pathways of the surface-immobilized catalyst.

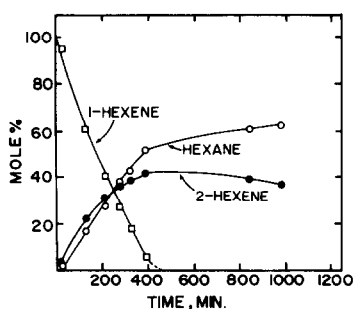


FIG. 3. Hydrogenation at 25°C of 1.2 *M* 1-hexene in methanol (0.20 wt% H₂O) with Rh(NBD)(dppe)⁺-hectorite. The reaction mixture contained 0.015 mmole Rh in 15 ml of solution.

The intercalation of Rh(NBD)(dppe)⁺ in hectorite also results in substantial deviations from solution behavior. Figure 3 provides the results for hydrogenation of 1.2 *M* 1-hexene in the presence of Rh(NBD)(dppe)⁺-hectorite. A comparison of the results in Fig. 3 with those reported in Fig. 1B for the homogeneous catalyst reveals two important differences. First, the reaction rate for the intercalated catalyst is an order of magnitude lower than that for the homogeneous catalyst. Second, the initial rates of hydrogenation and isomerization are nearly equal for the intercalated catalyst, but for the homogeneous catalyst the isomerization and hydrogenation rates differ by at least a factor of 5.

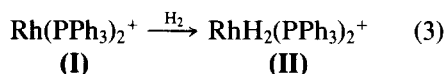
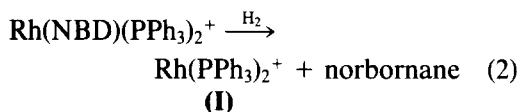
Although intercalation reduces the reactivity of the Rh(NBD)(dppe)⁺ catalyst precursor and alters the relative rates of hydrogenation and isomerization, the relative rates are essentially insensitive both to substrate concentration over the range 0.1–1.2 *M* and to water content over the range 0.1–1.0 wt%. This latter behavior is in marked contrast to the more sensitive Rh(NBD)(PPh₃)₂⁺ precursor which dramatically favors hydrogenation over isomerization at high initial substrate concentration and low water content.

DISCUSSION

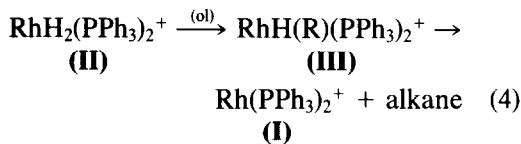
The above results illustrate that relative to homogeneous solution the properties of Rh(NBD)(PPh₃)₂⁺ and Rh(NBD)(dppe)⁺ as

catalyst precursors for 1-hexene hydrogenation are significantly altered by intercalation in hectorite. For both metal complexes, surface chemical effects decrease the extent of undesirable isomerization of the substrate. The product distribution with Rh(NBD)(PPh₃)₂⁺-hectorite depends strongly on the initial substrate concentration, the extent of conversion, and the water content of the reaction medium, but the catalytic properties of Rh(NBD)(dppe)⁺-hectorite are insensitive to these factors. To better elucidate the surface chemistry influencing catalytic properties, we consider first the mechanism of olefin hydrogenation and isomerization.

The homogeneous hydrogenation of olefins with Rh(diene)(PPh₃)₂⁺ involves formation of Rh(PPh₃)₂⁺ (**I**, Eq. (2)) as a reaction intermediate (**4**). This intermediate rapidly adds hydrogen to form an active dihydridorhodium complex (**II**, Eq. (3)).



The addition of olefin (**ol**) to **II** leads to the formation of a metal alkyl (**III**, Eq. (4)) and, finally, to reductive elimination of alkane.



Little or no isomerization of the olefin occurs by rearrangement of **III**, because hydrogen is rapidly transferred to the primary alkyl. However, **II** can coexist in dissociative equilibrium with a monohydride complex (**IV**, Eq. (5)), which is a potent isomerization catalyst as well as a good hydrogenation catalyst.



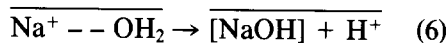
The monohydride (**IV**) adds olefin to form a metal alkyl of the type $\text{Rh}(\text{R})(\text{PPh}_3)_2^+$, which may either isomerize to yield an internal olefin or add H_2 to reductively eliminate alkane. Most of the isomerization which accompanies olefin hydrogenation under homogeneous reaction conditions involves the monohydride pathway. The addition of a protonic acid (HClO_4) or a weakly nucleophilic base ($\text{N}(\text{C}_2\text{H}_5)_3$) to the reaction medium will shift the equilibrium described by Eq. (5). Thus isomerization is minimized under acidic conditions, but under basic conditions isomerization is greatly favored (2, 4).

The above reaction mechanisms for $\text{Rh}(\text{NBD})(\text{PPh}_3)_2^+$ as a homogeneous catalyst precursor most likely apply also to the intercalated catalyst. Thus the enhancement of the hexane: 2-hexene product distribution upon intercalation of the complex in hectorite strongly suggests a shift in the protonic equilibrium between **II** and **IV** (Eq. (5)). Relative to homogeneous solution, the surface-bound dihydride (**II**) appears to be more strongly favored over the monohydride (**IV**), especially when the initial substrate concentration is $>0.6 \text{ M}$ and the water content of the reaction medium is low ($\leq 0.2 \text{ wt}\%$).

Two mechanisms may be postulated for the stabilization of the dihydride complex on the interlamellar silicate surfaces. The complex simply may be stabilized by electrostatic forces; that is, the charge on the silicate layers may be better neutralized by $\text{RhH}_2(\text{PPh}_3)_2^+$ than by solvated protons. In addition, the intrinsic Brønsted acidity of smectite clays may tend to shift the dihydride–monohydride equilibrium in favor of the dihydride complex. It is unlikely that electrostatic forces alone are responsible for stabilization of the active dihydride intermediate. Such forces should not be especially sensitive to relatively small variations in substrate concentration and water content of the solvent. However, the Brønsted acidity of the clay interlayers is known to be very sensitive to water content and other

factors, especially to the nature of the interlayer exchange cation (5–7). The dependence on water content and exchange cation is understood in terms of the hydrolysis of the exchange cation. Several examples of Brønsted-acid-catalyzed reactions on smectite clays have been reported which clearly demonstrate the acidity of clay interlayers (7–14).

In the intercalation catalysts used in the present work, approximately 90% of the exchange sites are occupied by Na^+ . Although Na^+ is not an acidic ion under ordinary hydration conditions in solution, the *partially* hydrated ion on clay interlayers is sufficiently acidic to protonate detectable amounts of tetraphenylporphyrin (15). Thus the hydrolysis of partially hydrated Na^+ ions (Eq. (6)) probably plays a role in determining the position of the equilibrium described by Eq. (5).



As the number of water molecules solvating the interlayer Na^+ ions is decreased, the charge on Na^+ should become progressively less shielded, and the extent of water dissociation should increase. Therefore, a low water content should increase the surface proton activity and favor $\text{RhH}_2(\text{PPh}_3)_2^+$ over $\text{RhH}(\text{PPh}_3)_2$. Similarly, the interlayer acidity is expected to increase with increasing substrate concentration. As the amount of adsorbed olefin is increased at the expense of the interlayer methanol, the interlayers should become less hydrophilic. A decrease in the hydrophilic character of the interlayers will lower the surface concentration of water and increase the extent of Na^+ hydrolysis. Thus the inhibition of olefin isomerization at low water content and high substrate concentration is qualitatively consistent with an increase in interlayer Brønsted acidity which tends to shift the equilibrium in Eq. (5) in favor of the dihydride complex.

An attempt was made to explore further the effect of interlayer acidity on the $\text{RhH}_2(\text{PPh}_3)_2^+ - \text{RhH}(\text{PPh}_3)_2$ equilibrium by

selectivity is a demonstrated (2) and potentially important property of clay intercalates, surface chemical effects on catalytic selectivity can be equally important.

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