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HYDROGENATION OF OLEFINS WITH CATIONIC RHODIUM COMPLEX INTERCALATED IN FLUORO TETRASILICIC MICA

Takayuki MIYAZAKI, Akio TSUBOI, Hisao URATA, Hiroharu SUZUKI,
Yutaka MORIKAWA,* Yoshihiko MORO-OKA, and Tsuneo IKAWA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta-cho, Midori-ku, Yokohama 227

The hydrogenation of olefins was studied with a Rh complex catalyst intercalated in a synthetic mica. Steric influence due to the interlayers on the hydrogenation rate is observed not with aliphatic olefins but with cycloolefins. The intercalated catalyst shows enhanced selectivity relative to the homogeneous catalyst in the hydrogenation of 4-vinylcyclohexene.

The swelling layer lattice silicates have metal ions between the silicate sheets, which are easily exchangeable with organic and inorganic cations by a simple ion exchange method. The metal ions can be replaced even with bulky cations including cationic metal chelate complexes because the interlayer spacing is expandable. Making use of the layer lattice silicate with these properties, homogeneous metal complex catalysts are expected to be immobilized in the interlayer region. Pinnavaia and co-workers have demonstrated that the catalytic activities of Wilkinson-type complexes are improved by the intercalation in hectorite because of the limited spacing and an acidic atmosphere of the interlayers.[1-4)]

Fluoro tetrasilicic mica (TSM) is a synthetic mica with the chemical formula $Na[Mg_{2.5}Si_4O_{10}F_2]$. Recently, we found that TSM has no acid site[5)] and a metal ion exchanged form of TSM shows the characteristic activity of the metal ion for the conversion of methanol[6)] and the isomerization of butenes.[7)] In this communication, we report the catalytic activity of cationic rhodium complex $[Rh(COD)(PPh_3)_2]^+$, abbreviated to Rh^+, immobilized in the structure of TSM for the hydrogenation of olefins.

Rh^+ was obtained in the form of tetrafluoroborate salt $Rh^+BF_4^-$ and intercalated in TSM by direct exchange with its interlayer Na^+ ions. TSM was dispersed into a mixed solvent of acetone and water in the volume ratio of 10 : 7 and stirred for 40 min to swell sufficiently. A prescribed amount of $Rh^+BF_4^-$ was added to the dispersion and stirred for 2 h in an oil bath at 50 °C. The orange intercalate was filtered, washed well to ensure complete removal of Rh^+ adsorbed on TSM, and dried at room temperature in vacuo. All procedures were conducted in an argon atmosphere with deoxygenated solvents. The intercalate showed typical absorption bands of Rh^+ in the infrared spectrum. The catalyst sample, abbreviated to Rh-TSM, used in this study contained 22 wt% Rh^+ corresponding to the chemical formula $Rh^+_{0.15}Na^+_{0.85}[Mg_{2.5}Si_4O_{10}F_2]$.

The hydrogenation of olefins was carried out at 40 °C under an atmospheric pressure of hydrogen with a solution of $Rh^{+}BF_4^{-}$ or a suspension of *Rh*-TSM. The catalyst (3.9×10^{-3} meqRh^{+}) and a substrate olefin (0.3 mmol) were stirred for 8 h in a solvent (15 ml) under an argon atmosphere. Subsequently, the hydrogenation was started by replacing the argon with hydrogen. Acetone, a mixture of benzene and acetone (5 : 1 in volume ratio) or THF was used as the solvent after careful degassing. TSM showed no activity for the hydrogenation.

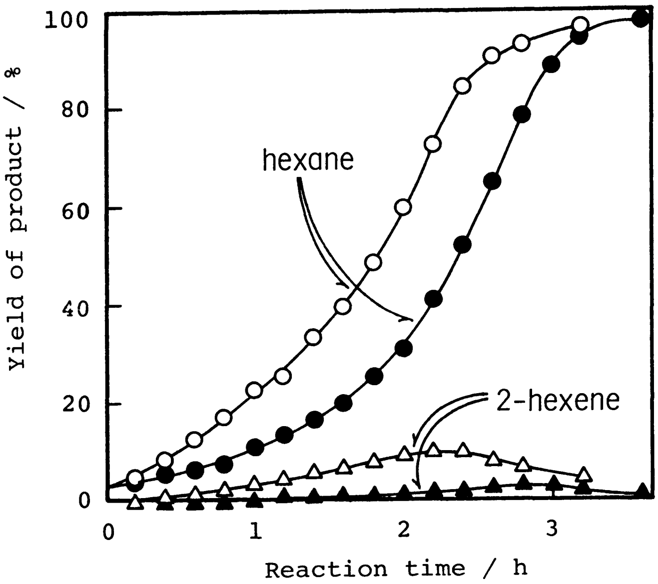


Fig. 1. Hydrogenation of 1-hexene in acetone with homogeneous (open) and intercalated (solid) catalyst.

The hydrogenation proceeded catalytically for all olefins employed here and neither demetalation nor deactivation of catalyst was observed in both homogeneous Rh^{+} and *Rh*-TSM system. After the hydrogenation with *Rh*-TSM, the catalyst was filtered off. The filtrate was clear and showed no activity for the hydrogenation. For a typical example, the results of 1-hexene hydrogenation in an acetone solvent are illustrated in Fig. 1. The results show that the hydrogenation reaction is accompanied by isomerization of 1-hexene to 2-hexene. The catalytic activity of Rh^{+} for the isomerization is much lower in the interlamellar region than in homogeneous solution. Similar tendency was observed in the hydrogenation of 1- and 2-octene. The results agree with the observations of Pinnavaia et al.[1)] They have inferred that the Brønsted acidity of the clay interlayers swollen by water causes the protonic equilibrium between catalytically active intermediates, $RhH_2(PPh_3)_2^{+} \rightleftharpoons RhH(PPh_3)_2 + H^{+}$, to be shifted in favor of hydrogenation. Our recent investigations have suggested that water molecules retained in TSM are dissociated by metal ions in the interlayer region to generate Brønsted acidity, although the silicate sheets of TSM are not acidic.

As can be seen in Fig. 1, the hydrogenation proceeds through an induction period. Rh^{+} seems to be transformed into dihydride form responsible for the hydrogenation during the induction period. When the catalyst was stirred in the solvent under a hydrogen atmosphere prior to the reaction, the hydrogenation took

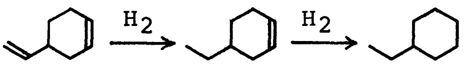
Table 1. Hydrogenation Rates (mol·molRh^{-1}·h^{-1}) for Various Olefins in Acetone with Homogeneous (R_h) and Intercalated (R_i) Catalysts

	R_h	R_i	R_i/R_h	(R_i/R_h)
1-hexene	49.2	61.4	1.25	0.35[a]
1-octene	90.1	82.1	0.91	0.18[a]
2-octene	29.1	25.5	0.88	0.36[a]
cyclohexene	40.7	46.7	1.15	0.17[b]
4-methyl-cyclohexene	27.4	13.9	0.51	0.087[b]

a) Used benzene/acetone as a solvent.

b) Used THF as a solvent for the convenience of gas chromatographic analysis.

place at a constant rate from the biginning. However, undesirable demetalation of Rh^+ was observed in the pretreatment with hydrogen. To minimize the effect of the induction period and the substrate concentration, the rates of hydrogenation were estimated at 50% conversion for homogeneous (R_h) and intercalated (R_i) system. Table 1 summarizes the results obtained with various olefins. When acetone was used as a solvent, the hydrogenation rate of olefin with *Rh*-TSM was comparable to that with homogeneous solution of Rh^+ ($R_i/R_h \approx 1$) regardless of the size of the olefin. The results suggest that the substrates are able to penetrate easily into the interlayers of TSM swollen by acetone and all the immobilized Rh^+ act as catalysts effectively. The value of R_i/R_h for the hydrogenation in acetone is close to unity with cyclohexene and one half with a little bigger substrate, 4-methylcyclohexene. In contrast to flexible shape of alkyl chains in aliphatic olefins, the rigid molecular shape of cycloolefins seems to cause the difference by the sizes in diffusibility for the limited spacing of the interlayers of *Rh*-TSM. The interlayers of TSM are expanded to less extents by less polar solvents. Correspondingly, the values of R_i/R_h are much lower than unity for the hydrogenation in benzene/acetone or THF solvent. Similar results have been obtained by Pinnavaia et al. for the hydrogenation of alkynes.[1]

The value of R_i/R_h was 0.3 for the hydrogenation of 4-vinylcyclohexene in an acetone solvent. The value is smaller than that for 4-methylcyclohexene, supporting that the reaction rates are influenced by a steric factor as inferred above. In addition, *Rh*-TSM showed excellent selectivity in the consecutive hydrogenation of 4-vinylcyclohexene, . Vinylcyclohexane was not detected in any cases. The results are summarized in Fig. 2 and Table 2. As seen in Fig. 2, the final hydrogenation product, ethylcyclohexane, is formed at a considerable rate during the reaction with homogeneous Rh^+ solution. The rate is negligible in the reaction with *Rh*-TSM until most of the substrate has been consumed to form ethylcyclohexene. The relative rate of ethylcyclohexene to ethylcyclohexane formation for *Rh*-TSM system is 3 times larger than that for homogeneous Rh^+ system at 50% conversion of the substrate. The factor increased

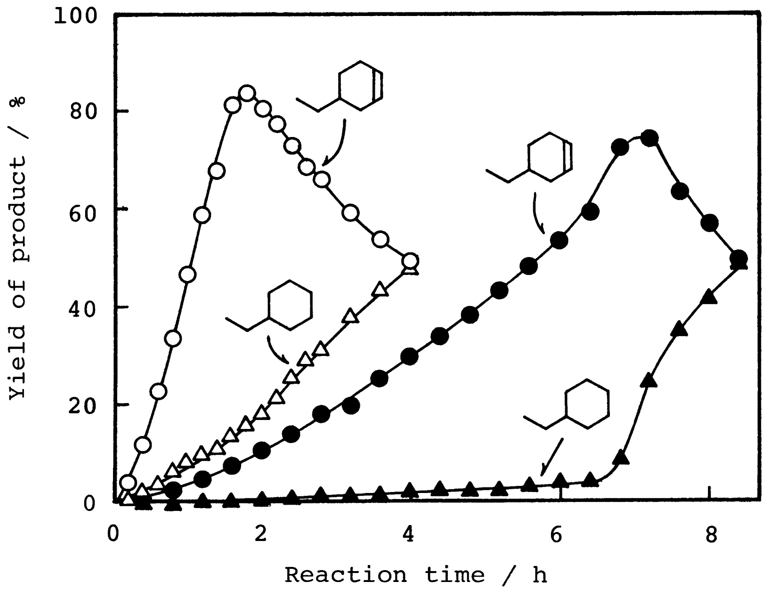
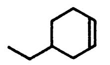
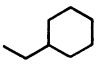
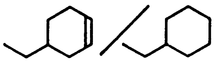


Fig. 2. Hydrogenation of 4-vinylcyclohexene in acetone with homogeneous (open) and intercalated (solid) catalyst.

Table 2. Rate of Formation ($mol \cdot molRh^{-1} \cdot h^{-1}$) for Hydrogenation of 4-Vinylcyclohexene in Acetone with Homogeneous and Intercalated Catalysts

	Rate of Formation		Relative Rate	
				
Homogeneous	29.6	5.0	5.9	(4.9)[a]
Intercalated	7.1	0.39	18.2	(20.0)[a]

[a] Results of the hydrogenation in benzene/acetone.

remarkably at the lower conversion. This enhanced selectivity of *Rh*-TSM is not explainable at this stage of investigation. It is, however, speculated that the coordination of a double bond on a rigid cyclohexene ring is restricted more extensively than that on a slender aliphatic chain in the interlayer spaces crowded with bulky ligands of Rh^+.

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