

Asymmetric hydrogenation of itaconates by hectorite-intercalated Rh-DIOP complex

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Received 9 December 1997; accepted 5 March 1998

Abstract

Rhodium complex with a chiral phosphine ligand was intercalated into sodium hectorite by cation exchange method. The intercalation compound was characterized by FT-IR, XRD and TEM measurements. The basal spacing of the compound was estimated to be 2.29 nm from XRD measurement. This novel heterogenized catalyst exhibited a characteristic chiral as well as size recognition of the substrates in the hydrogenation of itaconates. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Asymmetric hydrogenation; Intercalation; Layer compounds; Cation exchange; Rhodium complex; Chiral phosphine ligand; Host–guest catalyst; Molecular recognition

1. Introduction

Recently, layered compounds, such as clay minerals, zirconium phosphates, and transition metal oxides, have drawn much attention [1]. Among clay minerals, smectites (e.g., hectorite, montmorillonite, etc.) possess suitable properties for catalyst supports such as a large surface area, a high cation exchange capacity, swelling, and intercalation.

There have been extensive studies for shape and size selective catalyses in the interlayer space of inorganic layered compounds [2]. So far, shape and size selectivities were ascribed to molecular sieving effect by their layer structures. We have modified clay minerals toward chiral recognizing catalysis [3]. In the interlayer

space, the guest molecules were well ordered depending on the host structures and the various interactions between hosts and guests at their specific sites [4]. These observations suggest that sophisticated modification forms suitable interactions between substrates and active sites which enhance the selectivity [5]. The intercalated guest molecules contacted with chiral selectors are not only well ordered but also rigidly fixed, so that the interlayer space becomes more effective for chiral recognition [3,6]. Though Pinnavaia [7] and Mazzei et al. [8] reported asymmetric hydrogenation of organic acids by clay intercalated rhodium chiral phosphine complexes, the clay intercalated complex catalysts have been neither well characterized nor utilized to catalytic reactions. We previously reported the characterization of hectorite intercalated chiral rhodium complexes and asymmetric selectiv-

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ity on the clay intercalated catalysts [9]. The selectivity depended on the variable interlayer spacing of the clay swollen with solvents employed.

In addition, compared with homogeneous catalyst, the immobilization of complex catalysts in the layer makes it possible to conduct solution-like reactions in the suspension state [10].

In this paper, the influence of the size of substrates on the asymmetric selectivity was studied by the clay intercalated chiral rhodium complex which possesses a constant interlayer spacing in the suspension state. Multi-functional recognition, both of the chirality and the size, was observed for the intercalated rhodium complex in the hydrogenation of itaconates.

2. Experimental

2.1. Materials

Synthetic sodium hectorite, NaHT (Topy Industries) was used as a host material (cation exchange capacity: 86.6 mmol/100 g clay). (*S,S*)-DIOP ((*S,S*)-DIOP = (4*S,5S*)-4,5-bis (diphenylphosphinomethyl)-2,2-dimethyldioxolane) was employed as a chiral phosphine ligand obtained from Kanto Chemical. [Rh((*S,S*)-DIOP)(COD)]ClO₄ (Rh-DIOP⁺), COD = 1,5-cyclooctadiene, was prepared according to the method given in the literatures [11,12]. Dimethyl, diethyl, and di-1-butyl itaconates were obtained from Tokyo Kasei and di-1-propyl, di-1-pentyl, and di-1-hexyl itaconates were synthesized by a conventional method [13].

2.2. Instruments

IR spectra of the catalysts were measured by a JEOL JIR-7000 spectrometer. XRD data were obtained by a Mac SCIENCE MXP³V powder diffractometer using Ni filtered Cu K α radiation. Intercalation amounts of Rh-DIOP⁺ were estimated from CHN analyses by a Perkin-Elmer-2400. Transmission electron microscopy

(TEM) images of Rh-DIOP⁺/HT were observed by a JEOL JEM-4000 FX II with accelerating voltage at 400 kV.

2.3. Preparation of clay intercalated rhodium complex and catalytic reaction

The intercalation of Rh-DIOP⁺ into NaHT was carried out in the following manner. The acetonitrile solution (50 ml) of [Rh((*S,S*)-DIOP)(COD)]ClO₄ (0.42 g, 1.2 equivalent of cation exchange capacity) was added into NaHT (0.50 g) swollen with deionized water (50 ml), followed by stirring for 24 h at ambient atmosphere. After the reaction the suspension was filtered off, washed with a CH₃CN/H₂O = 1 solution, and dried in vacuo. This intercalated complex is denoted as Rh-DIOP⁺/HT. Catalytic hydrogenation was carried out in a Schlenk tube (10 ml) at 303 K under 1.01 \times 10⁵ Pa of hydrogen. The catalyst was dried in vacuo and dispersed in 1-PrOH. This suspension was degassed by five freeze–pump–thaw cycles, followed by stirring for 2 h under 1.01 \times 10⁵ Pa of hydrogen. The reaction started with the addition of the substrate. Hydrogenated products were analyzed by ¹H, ¹³C-NMR, and HPLC using CHIRALCEL-OD column (Daicel Chemical).

3. Results and discussion

3.1. Characterization of clay intercalated rhodium complex

Fig. 1 shows XRD patterns for NaHT and Rh-DIOP⁺/HT. The distinct *d*₀₀₁-peak of NaHT shifted to lower angle after the intercalation, indicating the expansion of the interlayer space. The clearance space (*d*₀₀₁-thickness of the silicate layer) of Rh-DIOP⁺/HT expanded to 1.33 nm (Table 1) and agreed well with the molecular size of Rh-DIOP⁺ whose *C*₂-axis was nearly parallel to the NaHT sheet. It is presumed that rhodium complexes are taken up in a monolayer and the square planer sheet of each complex is arrayed parallel to the silicate layer as shown in

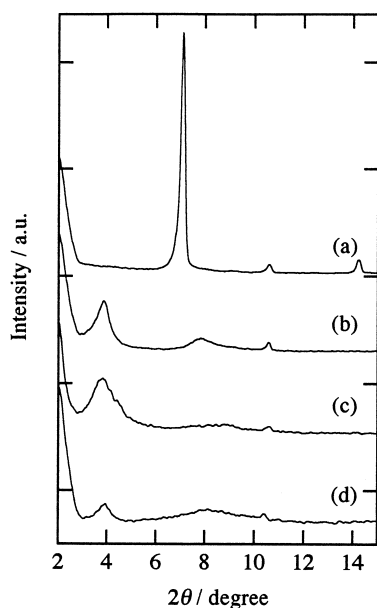


Fig. 1. XRD patterns for (a) NaHT, (b) Rh-DIOP⁺/NaHT (as prepared), (c) Rh-DIOP⁺/NaHT (after reaction), and (d) Rh-DIOP⁺/NaHT (swollen with 1-PrOH).

Fig. 2. Fig. 1d shows the XRD pattern of Rh-DIOP⁺/HT swollen with 1-PrOH. This result clearly indicates that the layer structure of the catalyst was retained in the hydrogenation. The clearance space of the catalyst was nearly the same even after the catalytic reactions.

The TEM photograph of Rh-DIOP⁺/HT is shown in Fig. 3. Here, the fringe was assumed to be the regular layer stacking of the individual hectorite silicate layers. The average interplanar spacing was 1.98 ± 0.25 nm which was ca. 0.3 nm smaller than that estimated from XRD. This

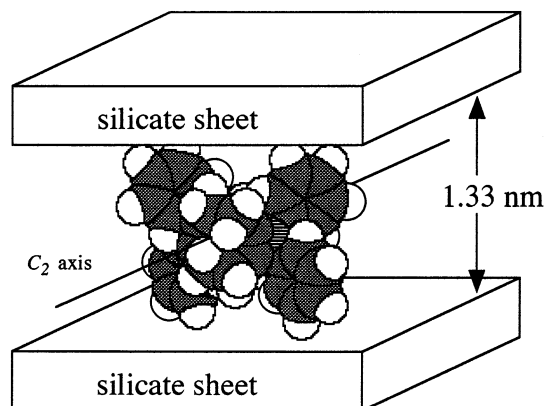


Fig. 2. Plausible configuration of Rh-DIOP⁺ in the silicate sheet of hectorite.

shrinkage of the basal spacing in the TEM measurement can be explained by the removal of additional adsorbed water molecules whose molecular size is ca. 0.3 nm. These results also evidenced the regular orientation of Rh-DIOP⁺ guests in the silicate layer.

The IR bands of Rh-DIOP⁺ and Rh-DIOP⁺/HT are summarized in Table 2. The peaks for ν P–C, ν C–H, and δ C–H due to (S,S)-DIOP and COD were observed in each sample. The peaks for ClO₄⁻ of Rh-DIOP⁺ disappeared in Rh-DIOP⁺/HT. The above measurements indicate that Rh-DIOP⁺ was intercalated into NaHT by cation exchange. The CHN

Table 1
XRD parameters for NaHT and Rh-DIOP⁺/HT^a

Sample	2θ (°)	d ₀₀₁ (nm)	c.s. ^b (nm)
NaHT	7.10	1.24	0.28
Rh-DIOP ⁺ /HT ^c	3.86	2.29	1.33
Rh-DIOP ⁺ /HT ^d	3.87	2.28	1.32
Rh-DIOP ⁺ /HT ^e	3.94	2.24	1.28

^aCu Kα.

^bClearance space = d₀₀₁-thickness of the silicate layer (0.96 nm).

^cAs prepared.

^dAfter reaction.

^eSwollen with 1-PrOH.

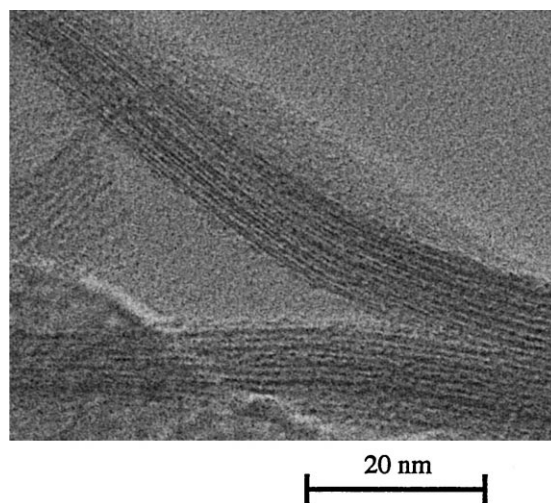


Fig. 3. TEM photograph of Rh-DIOP⁺/HT.

Table 2
IR spectra for Rh-DIOP⁺ and Rh-DIOP⁺/HT

Assignment (cm ⁻¹)	Sample		
	Rh-DIOP ⁺	Rh-DIOP ⁺ / HT ^a	Rh-DIOP ⁺ / HT ^b
$\nu\text{C-H}(\text{sp}^2)$	3058	3055	n.d. ^c
$\nu\text{C-H}(\text{sp}^3)$	2932	2935	2931
$\nu\text{P-C}$	1436	1438	1436
$\delta\text{C-H}(\text{Arom})$	744	746	738
	698	693	696
ClO_4^-	623	n.d. ^c	n.d. ^c

^aAs prepared.

^bAfter reaction.

^cNot detected.

analysis showed the intercalation amount of Rh-DIOP⁺/HT to be 27.6 mmol/100 g NaHT.

3.2. Catalytic reactions

In the catalytic system, itaconates were used as substrates to research multifunctional recognition such that chirality and size can be distinguished simultaneously (Scheme 1). The influence of the substrate size on the asymmetric selectivity by the intercalated complex can be examined by using the various itaconates with different sizes of ester groups. The clearance space of the clay intercalated catalysts were assumed to be constant in reaction solvents.

The asymmetric hydrogenations of itaconates with straight chains from dimethyl to di-1-hexyl ester were performed by Rh-DIOP⁺/HT and Rh-DIOP⁺ in 1-PrOH. The yields and enantiomeric excess (e.e.) in the catalytic reaction are summarized in Table 3. The most of the yields were 100% except for the runs where

Table 3
Asymmetric selectivity in the hydrogenation of itaconates by Rh-DIOP⁺ and Rh-DIOP⁺/HT in 1-PrOH^a

Catalyst	Substrate ^b	e.e. (<i>R</i>) (%) ^c	Reaction time (h)	Yield (%)
Rh-DIOP ⁺	methyl	24.8	1.3	100
Rh-DIOP ⁺	ethyl	29.6	2.0	100
Rh-DIOP ⁺	1-propyl	33.6	2.0	100
Rh-DIOP ⁺	1-butyl	28.8	1.0	100
Rh-DIOP ⁺	1-pentyl	23.4	1.5	100
Rh-DIOP ⁺	1-hexyl	9.6	8.2	100
Rh-DIOP ⁺ /HT	methyl	1.4	3.0	100
Rh-DIOP ⁺ /HT	ethyl	20.3	6.0	100
Rh-DIOP ⁺ /HT	1-propyl	3.6	6.0	100
Rh-DIOP ⁺ /HT	1-butyl	1.4	160.3	21
Rh-DIOP ⁺ /HT	1-pentyl	5.8	64.0	58
Rh-DIOP ⁺ /HT	1-hexyl	0.4	5.0	100

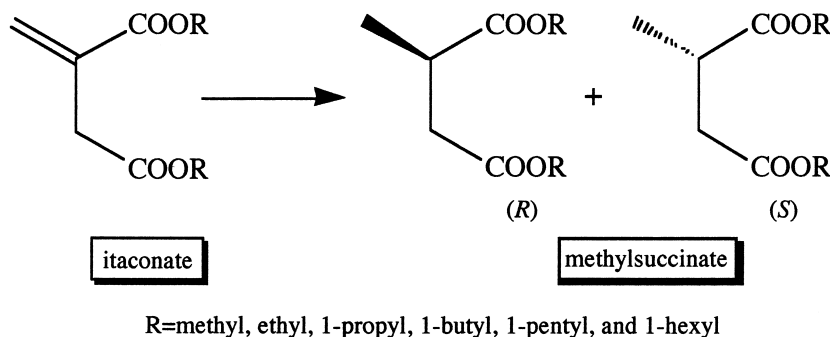
^aReaction conditions: solvent, 3 ml; $P_{\text{H}_2} = 1.01 \times 10^5$ Pa; $T = 303$ K; substrate, 6.25×10^{-4} mol; substrate/Rh = 100.

^bEster groups are indicated.

^cEnantiomeric excess (e.e.) is defined as $\text{e.e. } (R) = [(R) - (S)] / [(R) + (S)] \times 100\%$; Estimated error is within $\pm 3.0\%$.

di-1-butyl and di-1-pentyl esters were utilized for Rh-DIOP⁺/NaHT.

In the homogeneous catalyst the selectivity for Rh-DIOP⁺ varied from ca. 9 to 34% e.e. depending on the size of substrates, where the highest selectivity was obtained when di-1-propyl ester was employed. On the contrary for the host-guest catalyst, Rh-DIOP⁺/HT, only the diethyl ester gave the highest selectivity, i.e., 20.3% e.e., but the other substrates did lower selectivity. It was surprising that the less bulky methyl ester did show remarkably low selectivity for the hectorite catalyst compared with the homogeneous system. We speculate that the



Scheme 1. Asymmetric hydrogenation of itaconates.

chiral conformation of the Rh-complex in the hectorite layer might be more rigidly constrained than that of the complex in solution and the less flexible conformation be suitably fitted with the diethyl ester. These findings conclude that the host–guest catalyst strictly recognizes the enantio face of substrates as well as size compared to the homogeneous catalyst. The notable size recognition of Rh-DIOP⁺/HT in asymmetric selectivity can be ascribed that the coordinational conformation of substrates to rhodium complex in the interlayer space is varied by the bulkiness of the substrates.

Acknowledgements

This work has been supported by the Science Research Grant from the Ministry of Education, Japanese Government (No. 07651073).

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