New Clay-Supported Chiral Rhodium Complexes: Interlayer Modification with Structural Tuning Guests and Asymmetric Hydrogenation

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The novel host-guest catalysts, in which a chiral rhodium complex was intercalated into structural tuning guests modified smectites, were synthesized, and drastic change in catalysis was observed depending on the orientation of guest molecules.

Molecular recognition by inorganic layered hosts has been considered as a kind of shape selectivity by their molecular sieving effect.[1] So far, however, more sophisticated recognition such as chiral by the hosts has been scarcely known. Among the inorganic layered hosts, clay minerals, especially for smectites, exhibit swellability, ion exchange, and intercalation property[2] which make it possible to accommodate a wide variety of guest species.[3] Intercalated guest molecules formed highly ordered assemblies depending on the crystalline structure and the charge density of hosts.[4] We can therefore design the supramolecular architecture by modifying the interlayer space of hosts with various functional species : metal complexes as active species;[5] chiral ligands as chiral recognizing selectors.[6, 7] In the previous paper, we showed asymmetric hydrogenation of unsaturated organic esters by smectite-intercalated chiral rhodium complexes, where the selectivity was remarkably enhanced depending on the interlayer spacing of swollen clay.[8] Multi-functional recognition, both chirality and size, was also observed by the smectite-intercalated catalyst.[9] It can be presumed that in the interlayer space the orientation of the complex and the coordinational conformation of substrates to the complex gave rise to the characteristic recognition compared to the homogeneous system, that is, controlled layer structure by employed solvents gave notable dependence on the selectivity.

In order to control layer structure more precisely not by solvents but by structural tuning guests, we have synthesized the novel host-guest catalyst (MMS, multiple-modified smectite) in which smectites were modified with both chiral rhodium complex and bulky quaternary alkylammonium as a structural tuning guest. The influence of interlayer spacing and the guest orientation on catalytic activity as well as asymmetric selectivity was studied.

Synthetic sodium hectorite (NaHT[10]) and lithium taeniorite (LiTN[10]) were employed as host materials (Topy Industries Ltd.) whose cation exchange capacities (C.E.C.) were 86.6 and 268.2 mmol/100g-clay, respectively. [Rh((*S,S*)-DIOP)(COD)]ClO_4, (Rh-DIOP$^+$), was synthesized according to the method given in the literature;[11] ((*S,S*)-DIOP=(4*S*,5*S*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyldioxolane, COD=1,5-cyclooctadiene). Smectite-intercalated Rh-DIOP$^+$ complexes were synthesized by a cation exchange method described in the previous paper.[9] Dioctadecyldimethylammonium bromide (q-C_{18}), was used as a structural tuning guest. MMS was synthesized by the intercalation of Rh-DIOP$^+$ into q-C_{18}-modified smectite (q-C_{18}MS). The smectites-intercalated Rh-DIOP$^+$, q-C_{18}MS, and MMS are designated as 15.4/31.4/host, where the first and the second values indicate intercalated amounts (mmol·100g) of Rh-DIOP$^+$ and q-C_{18}, respectively, obtained from CHN analyses.

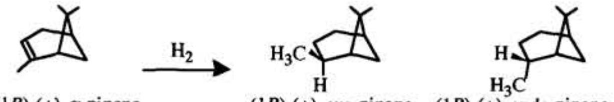
MMS was prepared in the following manner. Methanol solution (60 ml) of q-C_{18} (0.75 or 0.5 equivalent of C.E.C. of NaHT and 0.25 equivalent of C.E.C. of LiTN) were added into smectites (300 mg) swollen with deionized water (60 ml), followed by stirring for 48 h at an ambient atmosphere. After the reaction the mixture suspension was filtered off, washed with CH_3OH/H_2O=1, and dried *in vacuo* to give 0/49.4/NaHT, 0/36.4/NaHT, and 0/46.6/LiTN, respectively. (The intercalated amounts of q-C_{18}MS can be also expressed in % of C.E.C., *i.e.*, 0/57.1/NaHT, 0/42.0/NaHT, 0/17.4/LiTN, respectively.) Then, methanol solution (30 ml) of Rh-DIOP$^+$ (25 mg for 0/49.4/NaHT and 0/36.4/NaHT and 80 mg for 0/46.6/LiTN) were added into q-C_{18}MS (200 mg) swollen with deionized water (30 ml). The mixture suspension was treated in the above mentioned manner to give 7.4/41.8/NaHT, 15.4/31.4/NaHT, and 18.3/42.8/LiTN, respectively. With respect to MMS, the intercalated amounts expressed in % of C.E.C. were also 8.5/48.0/NaHT, 17.8/36.3/NaHT, 6.8/16.8/LiTN, respectively, indicating part of q-C_{18} was exchanged with Rh-DIOP$^+$.

Table 1. Structural data for MMS

Sample	c.s.[a] / nm	Tilting angle of q-C_{18}[b]/ °
NaHT	0.28	-[c]
27.6/0/NaHT	1.33	-[c]
0/49.4/NaHT	2.17	45
0/36.4/NaHT	2.49	60
7.4/41.8/NaHT	2.57	65
15.4/31.4/NaHT	2.46	58
LiTN	0.26	-[c]
10.2/0/LiTN	1.03	-[c]
0/46.6/LiTN	2.88	90
18.3/42.8/LiTN	2.88	90

[a] Clearance space = d_{001}-the thickness of silicate layer (0.96 nm). [b] Elevation angle of q-C_{18} longitudinal straight chain to the layer plane, based on c.s. [c] q-C_{18} is not present.

From the XRD measurements, the clearance space (c.s.) of each q-C_{18}MS was expanded from those of the original smectites. Their c.s. ranged from 2.17 to 2.88 nm as summarized in Table 1. The c.s. of each MMS ranged from 2.46 to 2.88 nm. Difference in the orientation of q-C_{18} between NaHT and LiTN was clearly observed. The tilting angle[12] of q-C_{18} was calculated from the c.s. and the molecular size of q-C_{18}.[13] The tilting angles for 0/49.4/NaHT and 0/36.4/NaHT were 45 and 60°, respectively. After the intercalation of Rh-DIOP$^+$ into q-C_{18}-modified NaHT, the tilting angles for 7.4/41.8/NaHT and 15.4/31.4/NaHT became 65 and 58°, respecctively, indicating that the orientation of q-C_{18} was changed in the NaHT host. In contrast, the tilting angle for 18.3/42.8/LiTN remained to be 90° despite of the intercalation of Rh-DIOP$^+$ into 0/46.6/LiTN. XRD patterns showed a sharp d_{001} peak with the second reflection for all of the MMS, indicating that both Rh-DIOP$^+$ and q-C_{18} were accommodated in the same gallery without segregation. In the IR spectra the bands at νP-C = 1437 and ν_{as}C-H = 2918 cm^{-1} due to Rh-DIOP$^+$ and q-C$_{18}$, respectively, were clearly observed and the band due to ClO_4^- was disappeared in each MMS. The above measurements evidenced that the intercalation proceeded by a cation exchange.



(1*R*)-(+)-α-pinene (1*R*)-(+)-*exo*-pinane (1*R*)-(+)-*endo*-pinane

Scheme. Asymmetric hydrogenation of (1*R*)-(+)-α-pinene.

A catalyst, (1*R*)-(+)-α-pinene as a substrate, and 3 ml of methanol were placed in an autoclave under argon atmosphere, followed by charging to 202 to 3030 kPa of H_2 at 303 K. After the reaction for 24 h, hydrogenated products were analyzed by GC-MS using Restek Rt-βDEXsa column.

Table 2. Asymmetric hydrogenation[a] of (1*R*)-(+)-α-pinene by Rh-DIOP$^+$, Rh-DIOP$^+$/smectites, and MMS

Entry	Catalyst[b]	Selectivity[c] / %	Conversion / %	$P\text{H}_2$ / kPa
1	Rh-DIOP$^+$	89.6	96.7	606
2		87.5	22.2	3030
3	27.6/0/NaHT	84.5	28.0	606
4	7.4/41.8/NaHT	52.0	1.6	606
5		50.5	1.7	1010
6		56.4	2.9	2323
7	15.4/31.4/NaHT	56.1	3.2	1010
8		69.5	7.3	3030
9	10.2/0/LiTN	86.2	48.5	1010
10	18.3/42.8/LiTN	80.2	25.7	202
11		88.4	80.1	606
12		89.6	97.4	1010
13		92.0	99.8	3030

[a]Reaction conditions: reaction time, 24 h; solvent, 3 ml of MeOH; T = 303 K; substrate, 6.25×10^{-4} mol; substrate/catalyst = 100. [b]The first and the second values indicate intercalated amounts of Rh-DIOP$^+$ and q-C$_{18}$ (mmol-100g), respectively. [c]Selectivity is defined as 100×(*exo-endo*)/(*exo+endo*).

(1*R*)-(+)-α-pinene was hydrogenated to yield (1*R*)-(+)-*endo* and *exo*-pinane as shown in scheme. Catalytic performance for homogeneous catalyst, Rh-DIOP$^+$ intercalated into NaHT (27.6/0/NaHT) and LiTN(10.2/0/LiTN), and MMS was summarized in Table 2. Although Rh-DIOP$^+$ and 27.6/0/NaHT gave high selectivity, the latter catalyst showed lower conversion (Entries 1 and 3). On the other hand, 7.4/41.8/NaHT showed much lower conversion and moderate selectivity at 606 kPa (Entry 4). No distinct enhancement in the activity and selectivity was observed despite of increasing $P\text{H}_2$ (Entries 5 and 6). Similar behavior was observed in 15.4/31.4/NaHT (Entries 7 and 8). Their low activities may arise from insufficient space around Rh-DIOP$^+$ for the reaction in the interlayer space. However, 18.3/42.8/LiTN exhibited high conversion drastically (Entries 11 and 12). The conversion and selectivity by 18.3/42.8/LiTN at 202 kPa were comparable to those by 27.6/0/NaHT at 606 kPa (Entry 10). Since alkyl tuning guests in LiTN were arrayed vertically to the silicate layer due to higher layer charge density (about three times to NaHT), the orientation of Rh-DIOP$^+$ in LiTN layer was assumed to be more regulated than in NaHT layer, that is, LiTN may provide sufficient space for the reaction to give high catalytic performance. In contrast, without the structural tuning guests, no noticeable enhancement both in the activity and selectivity was observed (Entries 3 and 9).

The dependence of catalysis on $P\text{H}_2$ was also observed in 18.3/42.8/LiTN, where the conversion and selectivity were superior to Rh-DIOP$^+$ at 3030 kPa (Entries 2 and 13). These $P\text{H}_2$ dependence on the selectivity may arise from the difference in the stability of Rh-DIOP$^+$-substrate adduct. We assumed that the hydrogenation *via* β-pinene (terminal olefin), which is isomerized from α-pinene, proceeded to yield lower selectivity under lower $P\text{H}_2$ because of less stable Rh-DIOP$^+$-β-pinene adduct. In contrast, the direct hydrogenation from α-pinene proceeded more to give higher selectivity under higher $P\text{H}_2$, since the corresponding adduct of α-pinene (internal olefin) was more sterically favorable. With respect to Rh-DIOP$^+$ the selectivity and conversion decreased with increasing $P\text{H}_2$ (Entries 1 and 2).

Table 3. Hydrogenation[a] of 4-*tert*-butylcyclohexanone by Rh-DIOP$^+$ and MMS

Catalyst	Selectivity[b] / %	Conversion / %
Rh-DIOP$^+$	98.9	94.2
7.4/41.8/NaHT	82.7	9.4
18.3/42.8/LiTN	99.6	95.1

[a]Reaction conditions are identical with the case of α-pinene except for $P\text{H}_2$ = 101 kPa. [b]Selectivity is defined as 100×(*cis-trans*)/(*cis+trans*).

MMS also exhibited similar recognition in the hydrogenation of 4-*tert*-butylcyclohexanone to yield *cis*-4-*tert*-butylcyclohexanol predominantly (Table 3.). 18.3/42.8/LiTN gave higher conversion and selectivity compared to 7.4/41.8/NaHT and Rh-DIOP$^+$, suggesting the recognition by MMS was applicable not only for α-pinene but also for other unsaturated substrates.

In summary, the novel host-guest catalyst was synthesized by a simple cation exchange under moderate atmosphere. The structural tuning guests play important roles in the orientation control of rhodium complexes as well as the expansion of interlayer space. Enhancement of catalytic activity and selectivity was accomplished by the suitable structural modification of host-guest catalysts. This work has been supported by the Grant-in-Aid from the Ministry of Education of Japan (No. 09650972).

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