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Asymmetric Recognition of Hectorite Modified with Chiral Arylethylammonium

Makoto IWAI, Hiroshi SHOJI, Shogo SHIMAZU,* and Takayoshi UEMATSU*
Department of Applied Chemistry, Faculty of Engineering,
Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263

Asymmetrically modified hectorites (HTs) were prepared by the cation exchange method with (R)- and (S)-1-arylethylammonium (aryl=phenyl, *p*-tolyl, and 1-naphthyl). Enantioselective entrapment of 1-phenylethylamine with the modified HTs was observed. ***In situ*** X-ray diffraction measurements confirmed that the asymmetric recognition occurred in the interlayer of the modified HT.

Layered compounds such as clay minerals and metal phosphonates are attractive materials on account of their size- and shape-selective intercalation ability connected with various guest compounds.[1,2] The stereoselective entrapment by a layered compound modified with chiral metal chelates was first reported by Yamagishi's group,[3] and there have been much attention about the chirally modified layered compounds in terms of resolution and catalysis. In contrast to chiral metal chelates, there are few studies about layered compounds modified with simple chiral "organic" guests in spite of many advantages, such as variety of structures, functionalities, and especially commercial availability. For example, Choudary et al.[4] reported on the Ti-pillared clay modified with chiral tartalates as a chiral heterogeneous catalyst. Cao et al.[5] prepared zirconium phosphate modified with a fancy chiral selector group already used in chromatography, that is a dinitro-benzoyl derivative of L-leucine, and they achieved an enantioselective recognition.

The authors have been studied on the role of the guest compounds as reagents for the modification of layered compounds in the stand point of catalysis and interlayer-modification,[6-8] and thus introduced the concept of "tuning guest" for the first time.[9] In this letter, the authors describe a layered clay compound which modified with optically-active arylethylammoniums as tuning guests. The clay modified with the simple chiral organics exhibited enantioselective entrapment of racemic amines, and the selectivities depended on the chiral structure of the ammoniums. The phenomenon of the asymmetric recognition was confirmed by means of ***in situ*** X-ray diffraction measurements.

Asymmetrically modified clay was synthesized by cation exchange of synthetic sodium hectorite ($Na_{1/3}Mg_{8/3}Li_{1/3}Si_4O_{10}F_2$, designated as HT, kindly donated from Topy Ind. Ltd.) with (R)- or (S)-1-arylethylammonium (aryl = phenyl, *p*-tolyl, and 1-naphthyl, designated as PEA, TEA, and NEA, respectively) halide salts[10] in an aqueous solution for 2 h. The sample was filtered and dried at room temperature for 12 h *in vacuo*. Samples of the modified hectorites incorporated with PEA, TEA, and NEA are designated as PEA/HT, TEA/HT, and NEA/HT, respectively. The basal spacings were measured by powder X-ray diffraction using Ni-filtered CuKα radiation. The cation exchange amount of the organic compounds was determined by CHN analyses. Introduction of the organic species to HT was confirmed by FT–IR spectra. Selective entrapment of (RS)–1–phenylethylamine ($PENH_2$) was carried out in cyclohexane solution at 23 °C with a closed system.[11] Supernatant solution was collected and used for GC analysis. A 50 m Chrompack CP–cyclodex–β–236M was used as a GC column. *In situ* XRD measurements were carried out to monitor the intercalation of the chiral amines. A modified HT sample mounted on a measurement cell was swollen by the addition of a neat (R)– or (S)–$PENH_2$ and sealed with polyethylene film. XRD data were taken at 2 °(2θ)(min)$^{-1}$ as a scanning speed and 2 °< 2θ <10 ° as a scanning range.

Table 1 shows the XRD parameters and the loading amounts of modifier for the modified HT. The basal spacings (d_{001}) were increased after the modification. The diffraction peak of the original sodium hectorite was completely absent for all of the patterns of the modified samples. These results indicated that the asymmetric arylethylammoniums were introduced to the interlayer, and formed monomolecular layer of the chiral molecules between the silicate sheets.

Selective incorporation of racemic $PENH_2$ with (R)–modified HT was observed as shown in Fig. 1. The values of enantiomeric excess (e.e.) reached a plateau within 3 min in all of the experiments. The selectivity depended on the structure of the modifiers (arylethylammoniums), that is, the e.e. of the amine at the plateau was increased in the following order, NEA/HT, TEA/HT, and PEA/HT. (S)–PEA/HT also exhibited enantioselective incorporation of the amine, however, the supernatant solution at 3 min was 60 % e.e. of S–isomer. These results indicated that (R)–modified HT entrapped (S)–amine, while (S)–modified HT entrapped (R)–amine selectively. There wasn't $PENH_2$ detected after stirring a virgin sample of (R)– or (S)–PEA/HT and the solvent in the same condition of the experiment. These results indicated that the deintercalation and neutralization of the tuning guests (ammoniums) didn't take place due to the utilization of nonpolar solvent.

The diffraction peak of (R)–PEA/HT was changed by the addition of (R)– and (S)–$PENH_2$ as shown in Fig. 2 and 3. Original diffraction peak gradually disappeared and a new peak appeared in both of the experiments. The basal spacing of the new peaks in Fig. 2–d) and 3–d) are 1.68 and 1.70 nm, respectively. The formation rate of the new peak in Fig. 2 was apparently

Table 1. XRD parameters and loading amounts of modifiers for the asymmetrically modified hectorite

Compound	d_{001}(nm)	Loading(mmol/100 g)[12]
(R)–PEA/HT	1.50	40.6
(S)–PEA/HT	1.50	39.0
(R)–TEA/HT	1.52	42.6
(R)–NEA/HT	1.62	42.6
HT	1.22	--

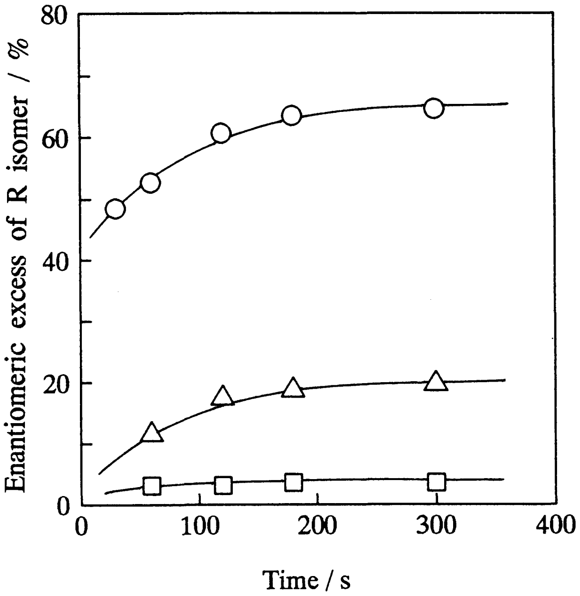

Fig. 1. Enantiomeric excess of $PENH_2$ in solution after the addition of the modified HTs : ○, (R)–PEA/HT; △,(R)–TEA/HT; □,(R)–NEA/HT.

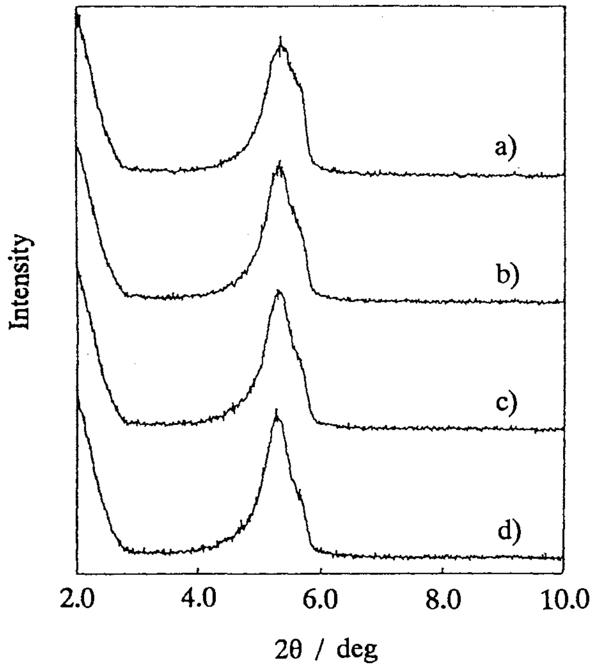

Fig. 2. *In situ* XRD patterns for (R)-PEA/HT intercalated with (S)-$PENH_2$: a) 1 min after addition of the amine, b) after 5 min, c) 10 min, and d) 20 min.

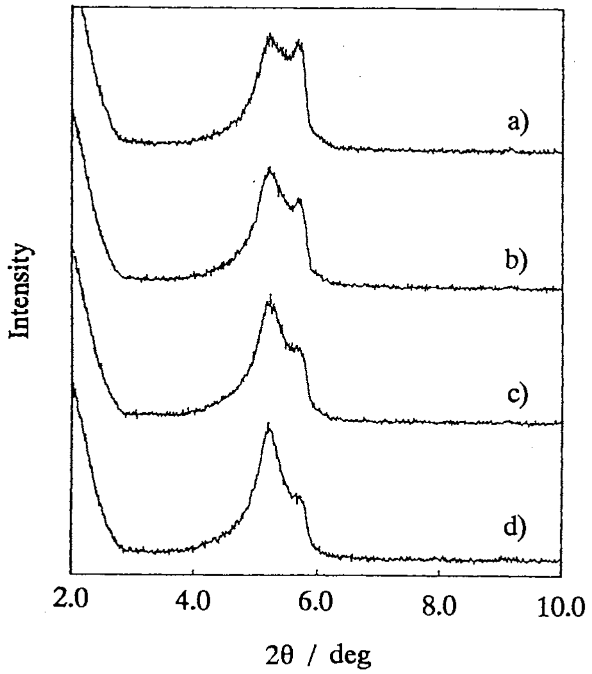

Fig. 3. *In situ* XRD patterns for (R)-PEA/HT intercalated with (R)-$PENH_2$: a) 1 min after addition of the amine, b) after 5 min, c) 10 min, and d) 20 min.

faster than that in Fig. 3. Quantitative analyses of the rate were carried out as follows. The peaks in Fig. 2 and 3 were deconvoluted into the original and the new peak, and the time dependence of the ratio of two peaks was calculated. The results of the calculation, combined with the results of (S)-PEA/HT, are shown in Fig. 4. The data indicated that the formation rate of the new peak in (R)-(S)[13] or (S)-(R) pair was faster than that of (R)-(R) or (S)-(S) pair. This result revealed that the asymmetric recognition occurred accompanied with a increasing of the interlayer distance, and suggested that the formation of the (R)-(S) or (S)-(R) pair was kinetically and thermodynamically more favorable than that of (R)-(R) or (S)-(S) pair.

The novel modified clay was synthesized by using asymmetric arylethylammoniums as tuning guests, and the modified clay showed chiral recognition for a asymmetric amine. It is suggest-

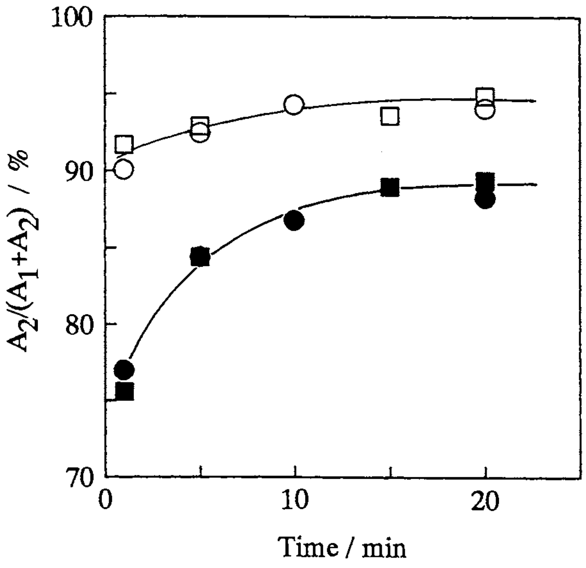

Fig. 4. Time dependence of the peak intensity ratio in the *in situ* XRD measurements : A_1, area intensity of the original peak; A_2, area intensity of the new peak : ○, (R)-(S)[13]; ●, (R)-(R); □, (S)-(R); ■, (S)-(S).

ed that the selective entrapment was performed by the interaction between R- and S-species in the interlayer. To clarify the mechanism of this system, the attempt to synthesize and to investigate the layered compounds modified with asymmetric tuning guests with various structures and functionalities is under way.

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10) The (R)- or (S)-1-arylethylammonium halides were synthesized from corresponding amines, which were purchased from Wako pure chemical Ind. Ltd. and Tokyo Chemical Ind. Co., Ltd. The ammonium samples were recrystallized from water/ethanol solution. The results of the elemental analyses were almost consistent with the calculated values from chemical formula.
11) Typical experimental condition : 0.5 g of the modified clay was mounted in a 10 ml glass vial fitted with rubber septa. Cyclohexane solution (3.0 ml) of (RS)-PENH$_2$ added to the vial. The solution of the amine was prepared in a molar ratio of the amine in solution to the ammonium ion in the HT 1.0 : 3.0.
12) The loading amounts were estimated from the content of C and N in the modified HTs. The results in Table 1 were the average value of the calculations from C and N.
13) (R)-(S) means (R)-PEA/HT incorporated with (S)-PENH$_2$. (S)-(R), (R)-(R), and (S)-(S) mean in a similar manner as noted above.

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