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BÉLa Török [a], Katalin Balázsik [a], Imre Dékány [b] & MihÁLy Bartók [a]

[a] Organic Catalysis Research Group of the Hungarian Academy of Sciences and Department of Organic Chemistry, József Attila University, Dóm tér 8, Szeged, H-6720, Hungary

[b] Department of Colloid Chemistry, József Attila University, Aradi Vt. l. Szeged, H-6720, Hungary

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Preparation and Characterization of New Chirally Modified Laponites

BÉLA TÖRÖK[a], KATALIN BALÁZSIK[a], IMRE DÉKÁNY[b] and MIHÁLY BARTÓK[a]

[a]*Organic Catalysis Research Group of the Hungarian Academy of Sciences and Department of Organic Chemistry, József Attila University, Dóm tér 8, Szeged, H-6720 Hungary and* [b]*Department of Colloid Chemistry, József Attila University, Aradi Vt. 1. Szeged, H-6720 Hungary*

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Chirally modified hectorites (laponite RD) were prepared by ion exchange with (*R*)- and (*S*)-*N*-alkyl-phenylethyl ammonium salts. The structure of the chiral clay-organocomplexes were studied by X-ray diffraction and FT-IR-spectroscopy. Due to the low charge density of the laponite the organic modifiers lay on the inner surface of lamellae, no pillaring effect was observed. Using the chiral nanoreactors obtained in a catalytic process enantiodifferentiation was observed.

Keywords: laponite; chiral modification; X-ray diffraction; catalysis

INTRODUCTION

According to the large number of important chiral molecules there still is a growing interest to explore new routes for their preparation. Over recent years due to the nature of large scale industrial processes and environmental considerations there is a strong driving force to find alternatives to hazardous homogeneous catalysts. One of the most promising candidates for this purpose

is the group of clay minerals. In H-form they have relatively high acid strength [1] and are effective catalysts for organic transformations[2]. Their special layered structure can be modified by ion-exchange or intercalation[3,4]. It is very surprising therefore, that their chirally modified organocomplexes are only rarely prepared and applied in catalytic processes[5,6]. In contrast, the modifications with nonchiral organics belongs to the most popular areas in clay chemistry[7-10]. Swelling layer silicates are especially good targets for hydrophobization with cationic organic compounds, usually ammonium salts [8, 9]. The structure of these clay-organocomplexes is determined primarily by the charge density of the clay and the chain length of the organic cation[4-8]. In our recent papers[11, 12] this idea was mainly applied in order to prepare chirally modified clay minerals which are potential catalytic nanoreactors for asymmetric synthesis. In present work we describe the chiral modification of the layered laponite by ion-exchange using various alkylammonium salts to provide suitable chiral nanoreactors.

EXPERIMENTAL

Materials The laponite RD (LP) was a Laporte product (CEC=65±8 mequiv./100 g). Chiral 1-phenylethyl amines (Fluka) were protonated (C0) and alkylated by decyl-(the product denoted as C10), dodecyl-(C12), cetyl-(C16) and octadecyl-(C18) bromides (Aldrich) to produce the secondary amine salts. The reactant used for catalytic test was phenyloxirane (Aldrich).

Methods The *ion-exchange process* was carried out at 25 °C under continuous stirring as described earlier[12]. *Catalytic reactions* were performed in a conventional batch reactor at 25 °C. The product mixtures were analyzed by a HP-5890 GC—HP-5970 MSD system, while the enantiomeric excesses were determined with a HP-5890-FID GC (30m Cyclodex-B column).

Characterization *FT-IR* studies were carried out with a Mattson Genesis 1 spectrometer in KBr pellets. *X-Ray Diffraction* measurements were taken on a Philips PW 1820 diffractometer (CuKα, λ=0.154 nm, PW 1830 Philips generator with options of 50 kV and 40 mA). The carbon content of the products was determined by a CHN-1 analyzer (L.R., Praha) with a reproducibility of ±0.2%.

RESULTS AND DISCUSSION

Synthesis and characterization The ion-exchange process was carried out at room temperature by the standard ion-exchange method[12]. After the removal of the physically adsorbed amine salts the organic content of the products was characterized by FT-IR spectroscopy. Fig. 1 shows the difference FT-IR spectra of the data for the laponite–(*R*)(+)-modifier organocomplexes. Since the nature of enantiomers only the (*R*)(+)-series are displayed, however, it is important to note that the data for (*S*)(-)-isomers, as expected, were within a margin of 0.5%. The selected wavenumber regions 1400-1700 and 2700-3100 cm^{-1}. The characteristic bands for the organic modifiers can be found around 1400-1500 cm^{-1} (benzene ring stretchings, ν_{19a}~1495 cm^{-1}, ν_{19b}~1460 cm^{-1}) and the 2600-3000 cm^{-1} (CH_2 skeletal stretchings, ν_{as}~2950 cm^{-1}, ν_s~2870 cm^{-1}) region. On the other parts of the spectra no significant changes were observed relative to the parent laponite. In order to get more insight into the position and orientation of the organic guest in the laponite structure X-ray diffractometry (XRD) was applied. In order to get more insight into the position and orientation of the organic guest in the laponite structure X-ray diffractometry (XRD) was applied. The X-ray diffractograms are shown in Fig. 2. As the XRD patterns indicate the basal distance of the parent laponite is approximately 15Å. After intercalation the peak maxima shifted to lower 2Θ values.

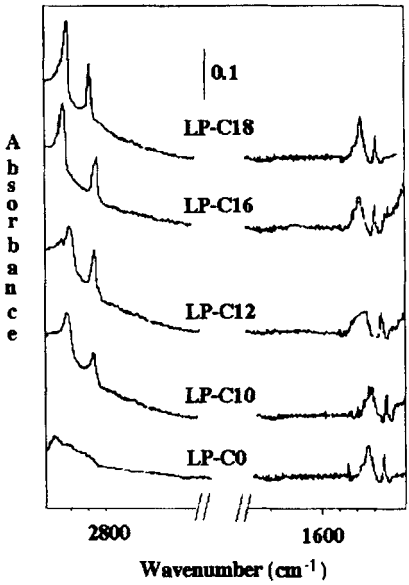

FIGURE 1 Difference FT-IR spectra of modified laponite-organocomplexes

This clearly shows that the organic molecules are positioned into the interlamellar space of the clay. However, the increased basal distances are not as high as expected on the basis of a previous study[12]. As a result, the possible d_L values were calculated and compared to the experimental data. Both series are tabulated in Table 1 (*wide infra*). As the data show, in the case of C0 and C10 intercalation only a slight change in the basal spacing was observed. A comparison with the calculations indicates that in these cases a monolayer forms inside the lamellae and the organic molecules lay down on the silicate surface. Figure 3(a) and 3(b) represent a schematic interpretation of this phenomenon. However, the basal spacing significantly increases using modifiers with longer alkyl-chains from LP-C12 to LP-C18. As the theoretical calculations show the basal distance obtained more or less corresponds to a bilayer orientation when the long alkyl-chains lay on the lamellae (Fig. 3(c)). In our opinion, it is due to the relatively low charge density of the synthetic laponite.

Catalytic applications The chiral laponite organocomplexes were studied in the isomerization of (±)-phenyloxirane. The effect of modifiers was characterized through the determination of the conversions and ee% (100([R]-[S])/[R]+[S]) during the consumption of the reactant.

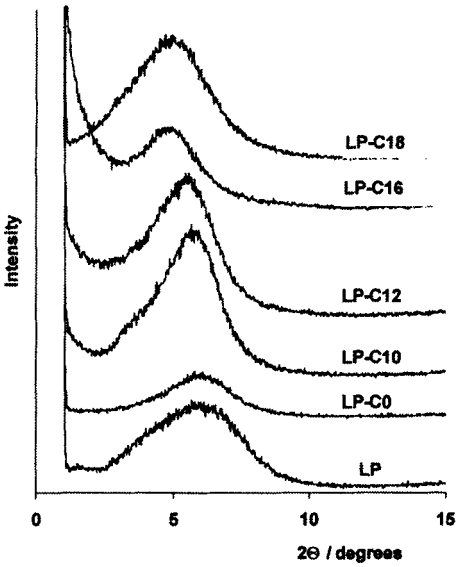

FIGURE 2 XRD patterns of laponite and its derivatives

The data are shown in Table I. As shown, the new organocomplexes provided a slight enantio-differentiation in the reaction indicating that the chiral nanoreactors prepared works. The moderate optical yields may increase using a larger charge density clay and better contact (eg. other type of reaction) between the modifier and reactant.

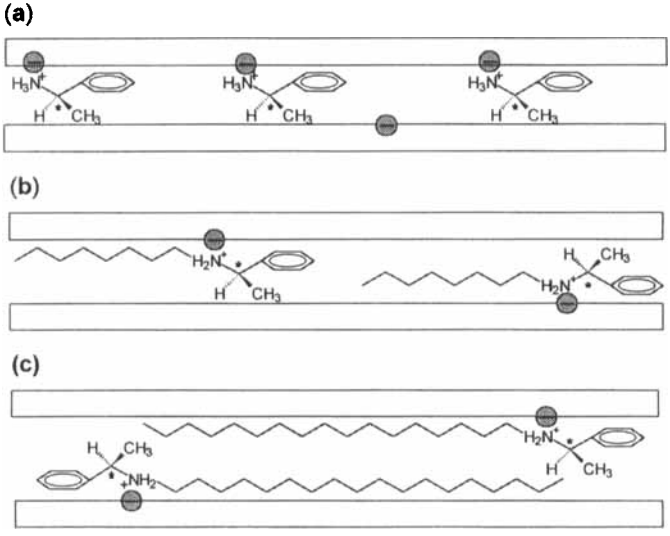

FIGURE 3 Representation of the structure of laponite-organocomplexes

TABLE I Characteristic data of the laponite-alkylammonium salt complexes

$PhCH(CH_3)N^+H_2$-R R	d(001) (calc.) Å	d(001) (exp.) Å	total C (mmol kg^{-1})	PhOx ee% (conv%)[a] (S)(-)	(R)(+)
original laponite	-	15.20	-	0(61)	
H	14.2 - monolayer	15.40	6.1	1.2(26)	-2.0(42)
$C_{10}H_{21}$	14.2- monolayer	15.60	5.2	2.5(22)	-3.0(50)
$C_{12}H_{15}$	18.8 - mono- /bilayer	16.26	5.2	2.9(47)	-3.2(45)
$C_{16}H_{33}$	18.8 - bilayer	18.45	3.8	3.1(37)	-2.8(36)
$C_{18}H_{37}$	18.8 - bilayer	18.02	4.0	2.9(27)	-3.1(24)

[a]PhOx-phenyloxirane, the actual conversions after 30 min are shown in parenthesis.

CONCLUSION

New chiral *N*-alkyl-phenylethylammonium–laponites were prepared and characterized. It was concluded that the organic modifiers lay on the silicate lamellae independently on its size due to the low charge density of the clay. The enantiodifferentiation observed is promising for the future progress.

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