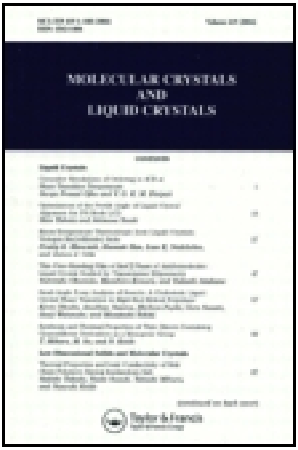

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Preparation, Characterization and Application of K-10 Montmorillonite Modified with Chiral Ammonium Halides

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Chiral modification of K-10 montmorillonite was carried out with chiral amine salts. The ion-exchanged K-10 samples were characterized by CHN analysis, XRD, FT-IR and ^{29}Si NMR spectroscopies and tested in catalytic reactions.

Keywords: K-10 montmorillonite, chiral modification, microwave irradiation, electrophilic catalysis

INTRODUCTION

Despite the large number of important chiral compounds there is still a growing interest to explore new synthetic routes for the preparation of these compounds. Over recent years, due to environmental considerations there is a strong driving force to find alternatives to very hazardous or sensitive catalysts. Extensive efforts involving asymmetric synthesis have been carried out to replace the sensitive soluble metal complexes and design chiral heterogeneous catalysts. Clays are one of the most promising candidates for this purpose, especially K-10 montmorillonite, which has relatively high acid strength[1] and an excellent catalyst for electrophilic organic reactions[2]. Due to the reactive character of clays their properties can be modified by ion-exchange or intercalation[3]. Both processes are excellent ways to immobilize chiral modifiers on the surface or in the interlamellar space of clays. As a result, the modification of clays by organic compounds[4] belongs to the most popular research areas in clay chemistry. It is surprising therefore, that this idea was rarely applied for the preparation of chirally modified clays[5]. The known examples are related to the intercalation of chiral metal complexes and their use in hydrogenation reactions[6]. However, we are not aware of any literature data with respect to the intercalation of chiral compounds into clays in order to prepare new chiral solid acid catalysts.

In the present paper we extend these studies with the modification of K-10 montmorillonite, using chiral amine salts applying various methods. The emphasis will be placed on the characterization of the products with parallel catalytic testing in electrophilic transformations.

EXPERIMENTAL

Materials The K-10 montmorillonite was an Aldrich product. (*R*)- and (*S*)-1-phenylethyl amines (Fluka) were alkylated by dodecyl-bromide or cetyl-bromide (both from Aldrich) to produce the secondary amine salts, which were characterized by ^{1}H and ^{13}C-NMR. The reactants used for catalytic tests were phenyloxirane (L. Light & Co), 2-octanol and 1-phenyl-ethanol (Aldrich).

Methods: The *ion-exchange processes* were carried out at 25 °C or in a conventional microwave oven (Samsung 4168, 400 W, 4 min). Solvents and solvent mixtures used are specified in Table I.

All *catalytic test reactions* were performed in a conventional glass batch reactor under continuous stirring at various reaction temperatures (25 °C for phenyloxirane, 125 °C for phenyl-ethanol and 180 °C for 2-octanol). The product mixtures were analyzed by a HP-5890 GC—HP-5970 MSD system (50 m HP-1 column), while the enantiomeric excesses were determined with a HP-5890-FID GC equipped with a 30-m-long Cyclodex-B capillary column.

Characterization The *carbon content* of the products was determined by a CHN-1 analyzer (L.R., Praha) with a reproducibility of ±0.2%.

^{29}Si MAS NMR spectra were recorded with a Bruker AM400 spectrometer using TMS as a reference sample. *FT-IR* studies were carried out with a Mattson Genesis 1 spectrometer in KBr pellets. *X-Ray Diffraction* measurements were taken on a Phillips PW 1820 diffractometer (CuKα, λ=0.154 nm, PW 1830 Phillips generator with options of 50 kV and 40 mA). The basal distances were calculated by the Bragg equation using the PW 1877 automated powder diffraction program with an accuracy of ±0.01 nm.

RESULTS AND DISCUSSION

Synthesis and characterization The ion-exchange process of K-10 montmorillonite was carried out at room temperature or by using microwave irradiation. As a medium, several organic solvents were applied. After the removal of the physically adsorbed amine salts the organic content of the products was determined by CHN-analysis. The exact experimental details and the carbon contents are collected in Table I (X-ray diffractograms not shown). Table I contains the data for (*R*)(+)-enantiomers, however, it is important to note that the data for (*S*)(-)-isomers, as expected, were within a margin of 0.5%. As shown, the amount of organic guest strongly depended on the experimental process applied. The microwave assisted ion-exchange was found to be the most effective synthetic way. As an additional advantage of the microwave irradiation in these ion-exchange processes is the very short reaction time. This is in accordance with earlier applications in the synthesis of intercalation compounds[7].

TABLE I Preparation and characteristic data for ion-exchanged K-10

$PhCH(CH_3)N^+H_2$-R R	Solvent	T (°C) /t (h)	Total C (g kg^{-1})	IE (mmol kg^{-1})	d(001) (Å)
original K-10	-	-	-	-	10.14
H	H_2O	25/144	36.5	3.5	14.29
H	1-butanol	μw/4 min	45.5	4.4	15.51
$C_{12}H_{15}$	70% aq. 1-propanol	25/72	35.1	1.3	15.06
$C_{16}H_{33}$	EtOH	25/36	25.5	0.8	14.98

IE - ion exchange, molar amount

The size of the second alkyl group is a determining factor for the ion-exchange concerning the molar amounts introduced. However, the highest basal distance was found for the sample prepared by microwave irradiation.

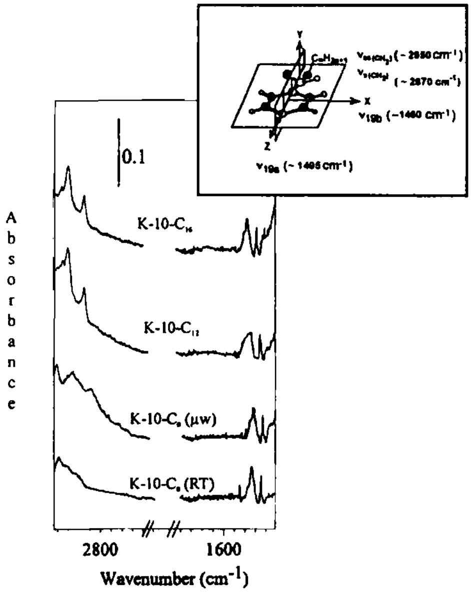

FIGURE 1 Difference FT-IR spectra of modified K-10 samples with schematic interpretation

Selected wavenumber regions of the difference FT-IR spectra are shown in Fig. 1. As shown on the schematic representation, the characteristic bands for the organic modifiers can be found in the 1400-1500 cm^{-1} (benzene ring stretching) and the 2600-3000 cm^{-1} (CH_2 skeletal stretching) region. On the other parts of the spectra no significant changes were observed relative to the parent K-10. A strong, broad OH signal can be detected at ~3300 cm^{-1} indicating that the ammonium exchange hardly decreases the acid strength. The ^{29}Si MAS NMR spectra shown in Fig. 2 prove this statement. As it can be seen the spectra contains three major peaks at -91, -100 and -110 ppm. These signals indicate the presence of the tetrahedral sheet of montmorillonite (-91), kaolinite (-100) and quartz or quartz like species. The peak distribution largely differs from the usual montmorillonite spectrum due to the acid treatment during the K-10 production. The spectra unambiguously indicate the partially destroyed structure of K-10. Organic guests induce a slight upfield shift (~2ppm) of the signal of the tetrahedral sheet.

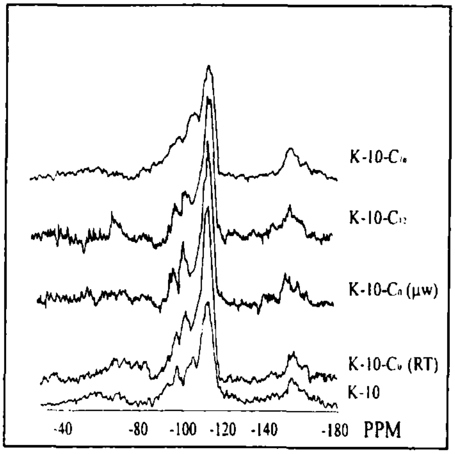

FIGURE 2 ^{29}Si MAS NMR spectra of K-10 and its modified derivatives

Catalytic applications The modified K-10 samples were studied in catalytic reactions such as the dehydration of (±)-2-octanol and (±)-1-phenylethyl alcohol, and 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 reactants. The data are shown in Table II. In accordance with the IE data (Table I) and the spectra, the ion-exchanged K-10 samples exhibit high activity. Moreover, the catalytic activity of C_{16} exchanged product is almost the same as the parent K-10. In the case of other modifiers the reaction rates decreased. The other, more important factor for the reactions is the ee% values. As Table II shows enantioselection was observed in all reactions during the consumption of the starting materials with ee% data varying between 0.2-4.8%. This indicates that the modifiers do affect the reactions, however, the enantioselection is only moderate. Since the molar amount of the modifiers are low relative to the number of acidic centers the ratio of reactive spots in chiral environment is low. In contrast, using asymmetric metal complexes the organic guest brings both the reactive center and the chiral environment. As a consequence, higher amount of the modifier is necessary to improve the enantioselectivity in these acid catalyzed reactions.

TABLE II Enantioselection in electrophilic reactions catalyzed by chiral K-10 montmorillonites (the actual conversions are shown in parenthesis)

$PhCH(CH_3)N^+H_2$-R	PhOx[a] (ee%)		$PhCH(OH)CH_3$ (ee%)		2-octanol (ee%)	
R	(*S*)(-)	(R)(+)	(*S*)(-)	(R)(+)	(*S*)(-)	(R)(+)
original K-10	0 (95)		0(99)		0(95)	
H (25 °C)	1.8(47)	1.6(55)	3.2(91)	3.5(88)	1.2(27)	-2.0(26)
H (μw)	4.0(48)	3.4(53)	0.2(12)	-0.5(12)	-	-
$C_{12}H_{15}$	4.8(40)	3.2(38)	-0.4(46)	-1.7(91)	1.0(8)	3.2(32)
$C_{16}H_{33}$	1.2(60)	1.3(67)	3.2(99)	2.6(99)	2.9(87)	1.1(94)

[a] phenyloxirane

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The financial supports (OTKA F023674 and T016109) and the traveling fellowship from ISIC9 Organizing Committee (B. T.) are highly appreciated.

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