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THERMAL BEHAVIOUR OF MONTMORILLONITE PILLARED WITH DIFFERENT METAL OXIDES

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Natural montmorillonite was pillared by various polyhydroxy cations. The resulting pillared layer clays (PILCs) were characterized by X-ray fluorescence, X-ray diffraction (XRD) and infrared (IR) spectroscopies. The thermal behaviour of Al-PILC was investigated in detail by a combonation of XRD, derivatography IR spectroscopy and a comparison to natural montmorillonite is given. It was found that thermal stability of Al-PILC is lower than that of natural montmorillonite. However, heat treatment in the stability region results in significant sintering of natural montmorillonite, while the interlayer spacing of Al-PILC is hardly affected.

Keywords: derivatograph, IR spectroscopy, montmorillonite, pillared layer clays, X-ray diffraction, X-ray fluorescence

Introduction

Montmorillonite is a type of acidic solid with layered structure [1]. Principally, it can be used for shape-selective catalysis due to its swelling property. However, it swells only in certain solvents and the 'pillared' structure collapses when the solvent is removed. It is also known that cations which stabilize its basic structure can be ion-exchanged. These two properties provide a way to prepare a porous structure even in the absence of organic solvents. Polyhydroxy cations can be exchanged in-between the layers and heat treatment converts these polymeric

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species into oxides with different structures [2, 3]. These oxides keep the layers apart and create a substance with two dimensional channels. The opening of these channels are larger than those of zeolites, thus these pillared layer clays (PILCs) may serve as alternative to zeolites in shape-selective catalysis of large molecules. However, the thermal and hydrothermal stability of these materials are much worse than those of zeolites, therefore they could not be commercialized in cracking of heavy oil fractions.

It is true that these substances mostly do not survive high temperature (the accurate temperature of collapsing varies depending on the pillaring agent and method of preparation), nevertheless they are promising catalysts for selectively transforming molecules of varying size under milder conditions.

In this study, we report on the preparation and characterization of montmorillonites pillared with different metal oxides, and on the effect of thermal treatment on the basal spacings of natural and Al-pillared montmorillonite.

Experimental

Na-montmorillonite was prepared from bentonite originated from Kuzmice (Czechoslovakia) by fractionation of Na_2CO_3 (2.5%) treated suspension followed by dialysation (*pH* = 7.6). The air-dried material was stored in a desiccator.

Al-PILC was prepared basically after the method described by Lahav *et al.* [4]. $AlCl_3 \cdot 6H_2O$ (Reanal) was dissolved in double-distilled water (0.25 mol/dm^3) and 1 mol/dm^3 of NaOH solution was added to it until OH/Al=2. 100 cm^3 of this solution was aged for 24 hours. These solutions were added to the well-stirred suspension of Na-montmorillonite and stirring was prolonged for an additional hour. Then, the suspension was filtered and washed with double-distilled water until it became free of chloride. The resulting solid substance was dried at room temperature.

Ti-PILC was prepared from $TiCl_4$ (Aldrich Chemical Co.) dissolving it in 6.0 mol/dm^3 HCl (15.19 g of $TiCl_4$ in 16.8 cm^3 of HCl solution) [5]. The resulting solution was diluted to 100 cm^3. 25 cm^3 of this solution was aged for 24 hours and was added dropwise to the well-stirred suspension of Na-montmorillonite (2 g/500 cm^3 double-distilled water) and stirring was prolonged for sixteen hours. Then, the suspension was handled as for Al-PILC.

Cr-PILC was prepared following the method of Pinnavaia *et al.* [6]. 20 g of $Cr(NO_3)_3 \cdot 9H_2O$ (Merck) was dissolved in double-distilled water and diluted to 500 cm^3. 2.4 g solid Na_2CO_3 was added to 450 cm^3 of this solution with continuous stirring. This basic solution was kept under reflux at 368 K for 36 hours. After cooling to room temperature, it was added dropwise to a well-stirred suspension of 3 g Na-montmorillonite in 300 cm^3 double-distilled water. After one and a half hour stirring the solid was filtered and air-dried.

Fe-PILC was prepared by the method described by Tatarchuk *et al.* [7]. 4.92 g of $FeCl_3 \cdot 6H_2O$ (Reanal) was dissolved in 300 cm^3 of double-distilled water. 2.43 g of Na_2CO_3 was dissolved in 100 cm^3 of double-distilled water and was added dropwise to a suspension of Na-montmorillonite (8 g clay in 800 cm^3 double-distilled water). This suspension was stirred for two hours at 338 K. Then, the solid material was filtered, washed free of chloride and dried at ambient temperature.

Zr-PILC was prepared following methods described in the literature [8, 9]. 21.47 g of $ZrOCl_2 \cdot 6H_2O$ (Reanal) was dissolved in 250 cm^3 of double-distilled water and the solution was aged for 24 hours at 373 K. The aged solution was added to the $FeCl_3$ solution. After refluxing for 36 hours at 368 K the cool solution was added dropwise to a suspension containing 8 g of Na-montmorillonite in 80 cm^3 of double-distilled water under vigorous stirring. Then, the suspension was further refluxed for 24 hours at 383 K. When the suspension was cooled to room temperature, the solid material was separated and washed free of chloride. Finally, it was dried at ambient temperature.

For preparation of Sn-PILC, $(NH_4)_2SnCl_6$ was made from $SnCl_4$ and NH_4Cl. 3.67 g of salt was dissolved in 100 cm^3 of double-distilled water and was added dropwise to montmorillonite suspension (8 g montmorillonite in 100 cm^3 water) under vigorous stirring. After one hour, 200 cm^3 of double-distilled water was added and stirring was prolonged for two hours at ambient temperature followed by refluxing the suspension for two hours at 373 K. The solid was separated by filtering and washed chloride free with double-distilled water.

Composition of the samples prepared was determined using X-ray fluorescence analysis. Spectra taken in the range of 1–8 keV can be seen in Fig. 1. Quantitative evaluation was possible for some components using analytical standards for calibration (Fe-PILC, Fe: 12.8 atom%; Ti-PILC, Ti: 5.3 atom%, Cr-PILC, Cr: 3.45 atom%).

For characterization of PILC samples, various techniques such as XRD, derivatography, IR spectroscopy were used.

The XRD patterns of pretreated and powdered samples were taken on a DRON 3 diffractometer using CuK_α radiation.

For investigation of thermal behaviour of pillared clay samples, a Hungarian made derivatograph (Derivatograph-Q) was utilized. The powdered material was placed on a platinum plate sample holder and investigated under the following conditions: mass of sample 100 mg, heating rate 10 $deg \cdot min^{-1}$, temperature range 300 to 1270 K.

KBr pellet technique was applied for monitoring the change in the IR spectra of samples. IR spectra of Na-montmorillonite and the pillared clays pretreated at various temperatures were taken in the range of 400–4000 cm^{-1}.

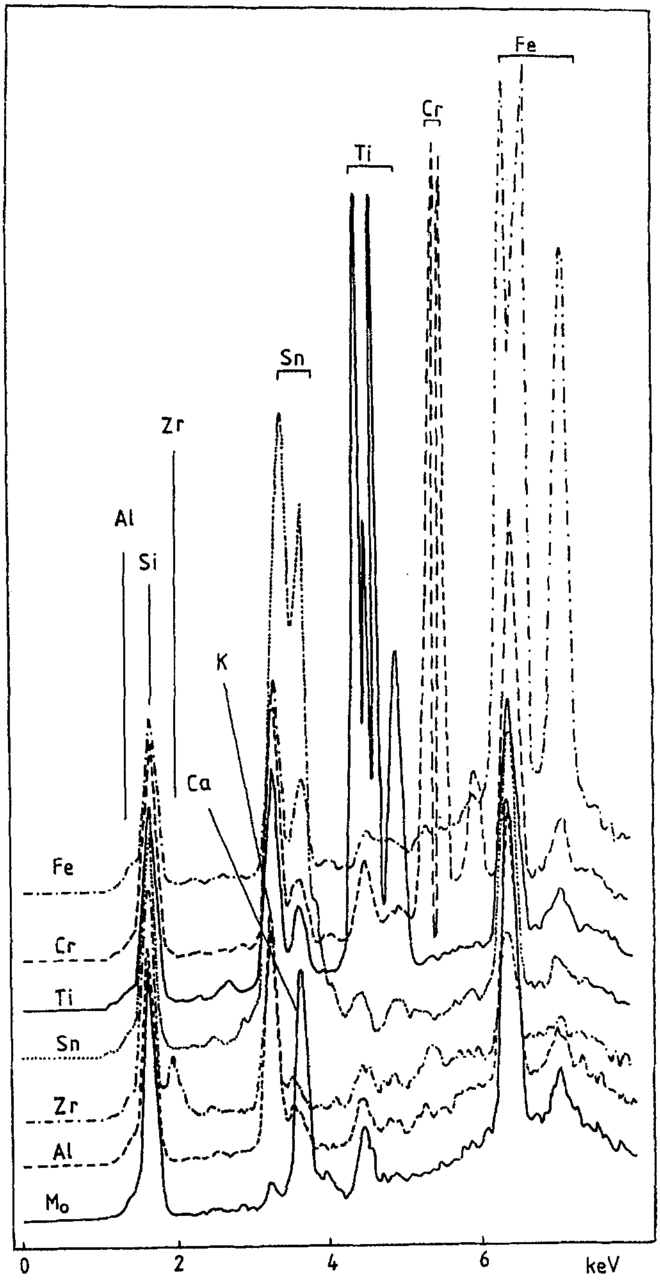

Fig. 1 X-ray fluorescence spectra of natural montmorillonite and its derivatives pillared by various polyhydroxy cations

Table 1 The position of the first reflection and related $d_{(001)}$) distances

Sample	2Θ	$d_{(001)}$/nm
Na-montmorillonite	6.9	1.20
Al-PILC	4.9	1.80
Ti-PILC	5.4	1.64
Cr-PILC	5.8	1.52
Fe-PILC	6.1	1.45
Sn-PILC	6.1	1.45
Zr-PILC	6.2	1.42

Results and discussion

Table 1 lists the position of the first reflection related to the (001) surface and the relevant interlayer distances.

Data listed clearly show that interlayer distances ($d_{(001)}$) vary with different pillaring agents. The spacing between the neighbouring sheets is much higher in the PILCs than in the parent montmorillonite. However, it seems to be risky to draw further conclusions about the role of pillaring agent on the interlayer distances since numerous experimental parameters may affect the characteristics of the pillared product.

The IR spectra of the various PILC preparations (Fig. 2) supplement X-ray data. They prove excellent crystallinity of the samples as they contain well-developed bands in the range of framework vibrations.

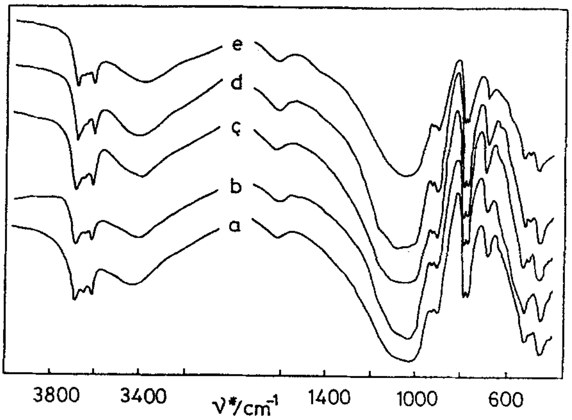

Fig. 2 Infrared spectra of montmorillonite pillared by various polyhydroxy cations in air-dried condition, a: Al-PILC, b: Fe-PILC, c: Cr-PILC, d: Zr-PILC, e: Ti-PILC

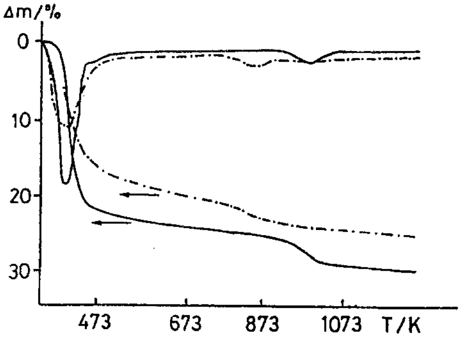

Fig. 3 TG and DTG curves of montmorillonite (—) and Al-PILC (-·-)

As far as thermal behaviour is concerned, Al-PILC was selected for further investigations and a comparison to the thermal properties of natural montmorillonite is given below.

As TG curve show (Fig. 3) two characteristic weight-loss steps were found for both the starting montmorillonite and its Al-pillared alternative:

i) Na-montmorillonite (383 K, 963 K);

ii) Al-PILC (378 K, 853 K)

The first step is due to the dehydration of the specimens. This procedure involves the removal of adsorbed water from both type of clays and the probably complete dehydration of the pillaring Al-polyhydroxy cation as well, since the interlayer spacing decreases from 1.80 nm of the freshly prepared and non-treated Al-PILC to 1.55 nm for the heat-treated (373 K, 1 hour) sample. However, this distance is practically not affected by heat treatment at higher temperatures. Derivatographic pattern of the parent montmorillonite shows the second weight-loss at 963 K, which means that the basic sheet-silicate structure is preserved up to this temperature. The TG curve of this substance contains a rather flat plateau between 500 and 800 K. As the DTG curve shows (it does not run on the zero line) some slow processes accompanied by weight-loss are continuously taking place in this range. A comparison of the TG curves of Na-montmorillonite and Al-PILC reveals that (i) the second weight-loss for Al-PILC is at much lower temperature than that of the parent sample (ii) the slope of the plateau is much higher for Al-PILC. The second weight-loss step is due to the dehydroxylation of samples accompanied by structural collapse, and data obtained mean that the pillared derivative has lower thermal stability than the starting clay.

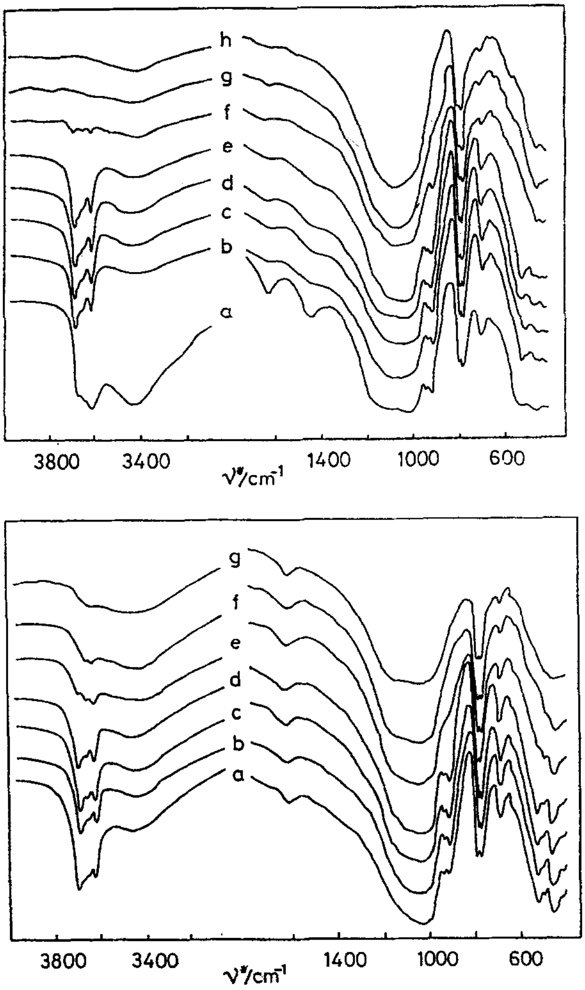

Fig. 4 *a*) Infrared spectra of natural montmorillonite pretreated at various temperatures (a: room temperature, b: 373 K, c: 473 K, d: 573 K, e: 673 K, f: 773 K, g: 873 K, h: 973 K) *b*) Infrared spectra of Al-PILC pretreated at various temperatures (a: room temperature, b: 473 K, c: 573 K, d: 673 K, e: 773 K, f: 873 K, g: 973 K

As far as structural collapse is concerned, IR investigations were performed to find the pretreatment temperature which results in characteristic change in the IR spectrum.

Spectra taken from Na-montmorillonite and Al-PILC are to be seen in Figs 4a-b, respectively. The spectra reveal that after treatment at 773 K the crystallinity for both sample decreased. This can be detected by the disappearance of the bands at around 900 cm^{-1}. The changes in the OH stretching region (3800– 3400 cm^{-1})

support this conclusion since the intensities of OH bands decrease and the structure of the spectrum is damaged in this temperature region.

Table 2 The effect of heat treatment characterized by X-ray diffraction data

Temperature	Na-montmorillonite			Al-PILC		
/K	2Θ	*d*/nm	I/I_o*	2Θ	*d*/nm	I/I_o*
298	6.9	1.28	100	4.9	1.80	100
373	7.6	1.16	14	5.7	1.55	32
473	7.8	1.13	14	5.6	1.57	34
573	8.0	1.10	14	5.7	1.55	34
673	8.4	1.05	12	5.7	1.55	25
773	8.7	1.02	12	6.0	1.47	24
873	8.8	1.00	9	5.8	1.52	20
973	9.1	0.97	9	5.9	1.50	9

* The respective intensities in percentage of the first reflections

Aiming at shape-selective catalytic utilization, it is important to study the effect of pretreatment temperature on the basal spacings of Al-PILC and compare to those of Na-montmorillonite. The samples were heat-treated for an hour in an oven at 373, 473, 573, 673, 773, 873 or 973 K, respectively, then they were cooled to ambient temperature and stored in closed vials (basically in air) until the measurements were performed i.e. specimens could rehydrate partially. The values of interlayer spacings are summarized in Table 2. It is clear that the interlayer distance is much higher for the pillared sample than for natural montmorillonite. Furthermore, for Al-PILC, heat treatment just slightly affects the

Table 3 Characteristic thermogravimetric data

Sample	Temperature of weight loss	
	T_1/K	T_2/K
Ti-PILC	378	813
Cr-PILC	373	800
Fe-PILC	373	843
Sn-PILC	378	863
Zr-PILC	373	833
Al-PILC	378	853
Na-montmorillonite	383	963

interlayer spacings, while for Na-montmorillonite its effect is a lot more detrimental.

The above results clearly show that despite its lower thermal stability, Al-PILC is a better candidate as catalyst for transforming larger molecules than natural montmorillonite, due to its larger interlayer distance which is hardly affected by heat treatment until the structure collapses and crystallinity ceases.

Clays pillared with other polyhydroxy cations display similar thermal behaviour. Thermogravimetric measurements also show two weight losses at similar temperatures (Table 3) indicating that development of the structure proceeds basically in the same way as for Al-PILC.

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Zusammenfassung — Natürliche Montmorillonite wurden durch verschiedene Polyhydroxy-Kationen gestützt. Die resultierenden gestützten Schichttonmaterialien (PILC) wurden mittels Röntgenfluoreszenz, Röntgendiffraktion und IR-Spektroskopie charakterisiert. Mittels einer Kombination von Röntgendiffraktion, Derivatographie und IR-Spektroskopie wurde das thermische Verhalten von Al-PILC im Detail beschrieben und ein Vergleich zu natürlichem Montmorillonit angestellt. Man fand, daß die Thermostabilität von Al-PILC geringer ist, als die von natürlichem Montmorillonit. Unabhängig davon hat eine Hitzebehandlung in der Stabilitätsregion ein signifikantes Sintern von natürlichem Montmorillonit zur Folge, während der Zwischenschichtabstand von Al-PILC stark beeinflußt wird.