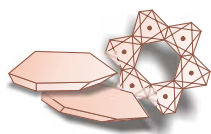


REDUCED CHARGE Al-PILLARED MONTMORILLONITES: ON THE POSSIBILITY OF CONTROLLING THE PILLAR DENSITY



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Abstract: The microporosity of Al-pillared Li-montmorillonites with different layer charges obtained by thermal treatment at different temperatures was studied by nitrogen adsorption/desorption at $-196\text{ }^{\circ}\text{C}$. A correlation was observed between the decreasing sorption capacity of samples derived from lithiated precursors heated at ever increasing temperature and the increasing contribution of the collapsed pyrophyllite-like areas inactive in pillaring. The dominant micropore radius remained below $3.5 \times 10^{-1}\text{ nm}$ for all pillared samples, showing that, contrary to the common belief, the layer charge reduction by Hofmann-Klemen effect fails to bring about substantial changes in the lateral interpillar distances.

Key words: porosity, nitrogen adsorption/desorption, pillar density, pillared clay, lithiation, reduced charge montmorillonite.

Introduction

It has long been known that upon heating at about $200\text{--}300\text{ }^{\circ}\text{C}$ Li-exchanged montmorillonites gradually lose the cation exchange capacity (CEC) (Hofmann & Klemen 1950; Greene-Kelly 1953; Calvet & Prost 1971; Alvero et al. 1994; Theng et al. 1997; Karakassides et al. 1997). This effect is due to migration of the interlamellar Li^+ ions into the layer, causing the neutralization of the layer charge. A similar phenomenon is observed with other cations of small radius ($<0.7 \times 10^{-1}\text{ nm}$) (Purnell et al. 1991). By applying different temperatures of the heat treatment, montmorillonites with their layer charge reduced to a different degree may be obtained (Calvet & Prost 1971; Madejová et al. 1996; Komadel et al. 1996). This approach has been used by several authors, who aimed at preparation of the pillared clays of different pillar density (Suzuki et al. 1988, 1991; Horio et al. 1991; Purnell 1992; Jones & Purnell 1993, 1994; Sychev et al. 1997, 2000). Since the number of pillars that may be incorporated between the clay layers depends on the layer charge density of clay, it follows that upon reduction of the layer charge fewer pillars with larger lateral interpillar distances will be formed, leading to the development of the sorption capacity of the micropore system as well as to the increase of the micropore radius. Interestingly, the data presented in the quoted works usually show an opposite effect, that is, the micropore specific surfaces and micropore volumes actually decrease with lowering of the layer charge. Such a phenomenon seems most puzzling and calls into question the generally accepted views on the suitability of the lithiating treatment as a means for generating the materials with controlled lateral spacing of pillars.

In the present study we decided to shed more light on this problem by investigating the structure and texture of a series of Al-pillared clays prepared from Li-montmorillonite, layer charge of which was reduced prior to pillaring to a different degree by applying thermal treatment at different temperatures.

Experimental

Materials

The material used in this study was the less than $2\text{ }\mu\text{m}$ particle-size fraction extracted by sedimentation from Milowice bentonite originating from the coal mine “Saturn” in Sosnowiec-Milowice, Poland. The structural formula of the montmorillonite is $\text{Na}_{0.38}\text{Ca}_{0.16}\text{K}_{0.19}(\text{Al}_{2.91}\text{Fe}_{0.39}\text{Mg}_{0.70})[(\text{Si}_{7.81}\text{Al}_{0.19})\text{O}_{20}](\text{OH})_4$ and its cation exchange capacity 84 meq per 100 g. The starting material for pillaring procedures was the lithium form of this montmorillonite, obtained by treatment with 1 M LiNO_3 solution, followed by multiple washing with distilled water. The product, air dried at ambient temperature is referred to as Li-mt. Li-mt was divided into six portions, and used for preparation of LiX-mt series, by 24 h heating at temperature X (50, 90, 120, 170, 200 and $250\text{ }^{\circ}\text{C}$). These materials were used as matrices for preparation of Al-pillared samples, following the procedure described by Vaughan & Lussier (1980). Chlorhydrol (commercial aluminium hydroxychloride manufactured by the Reheis Chemical Company) was added to the vigorously stirred water suspension of an appropriate lithiated sample, in the amount corresponding to 6 mmol Al^{3+} per gram

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of clay. After 30 min of stirring the pH of the suspension (4.9) was brought down to 2 with a diluted HCl solution and the mixture heated at 70 °C for 30 min. After washing till the removal of Cl⁻, and drying in air at 50 °C, a series of solids, denoted LiX/Al-mt, was obtained. After an additional 3 h of calcination in air at 500 °C the samples were referred to as LiX/Al-PILC.

Methods

XRD analyses were performed on oriented samples prepared by spreading of the sample suspension on a glass slide followed by drying at room temperature. The XRD patterns were obtained with a DRON-3 diffractometer using Ni-filtered Cu K α radiation. Nitrogen adsorption/desorption experiments were performed at -196 °C using a static volumetric method (Micromeritics ASAP 2000V2.03). Prior to adsorption the samples were degassed down to 1.0×10^{-3} Torr at 200 °C. Adsorption/desorption of nitrogen was carried out in the relative pressure range of $0.01 < p/p_0 < 1.00$ using 0.1 g of sample. Specific surface areas were determined from adsorption isotherms by applying BET and Langmuir equations (S^{BET} and S^{L} , respectively) in the relative pressure range of $0.05 < p/p_0 < 0.25$, and the t method (S^{t}), which consists in comparing the given isotherm with the reference one obtained for a non-porous solid (De Boer et al. 1966; Sing et al. 1985). In the present case the nitrogen adsorption isotherm obtained for the sodium-montmorillonite heated for 20 h at 800 °C was used as a reference absolute isotherm. Mesopore surface areas were determined from the adsorption branch using the BJH method ($S_{\text{mp}}^{\text{BJH}}$) and, independently, from V_a -t plots (S_{mp}^{t}) (Bahranowski et al. 2000). Micropore surface areas (S_{mp}^{t}) were calculated by subtracting the mesopore surface areas S_{mp}^{t} from the total specific surface areas S^{t} . Mesopore volumes (V_{mp}) were determined from the adsorption branch using the BJH method (Barrett et al. 1973), while micropore volumes (V_{mp}^{t}) and the micropore dominant radius (r_d) were calculated with the MP method (Mikhail et al. 1968; Mikhail & Brunauer 1975), using 0.25×10^{-1} nm intervals for computations. For the sake of comparison the micropore volumes (W_0) were also calculated using the Dubinin-Radushkevich method (Dubinin et al. 1975; Dubinin 1981).

Results and discussion

The XRD patterns of LiX/Al-mt and LiX/Al-PILC samples are presented in Figs. 1 and 2, respectively. The $d_{(001)}$ basal spacing of all uncalined samples is in the range 19.8 – 20.8×10^{-1} nm ($4.2^\circ < 2\theta < 4.5^\circ$), and as the lithiating temperature (X) increases the 001 peak becomes broader and less intense. Simultaneously, the intensity ratio $I_{\approx 10 \times 10^{-1} \text{ nm}} / I_{\approx 20 \times 10^{-1} \text{ nm}}$ grows in the order 0.2 (50 °C), 0.2 (90 °C), 0.4 (120 °C), 1.3 (170 °C), 1.5 (200 °C), 2.0 (250 °C). Such a phenomenon can be understood if one recalls that the reflection around 10×10^{-1} nm ($2\theta \approx 8.8^\circ$), which is characteristic for the second order 002 peak of the $\approx 20 \times 10^{-1}$ nm basal reflection of the pillared montmorillonite, may also be due to the montmorillonite with collapsed pyrophyllite-like layers. Thus, the observed increase in

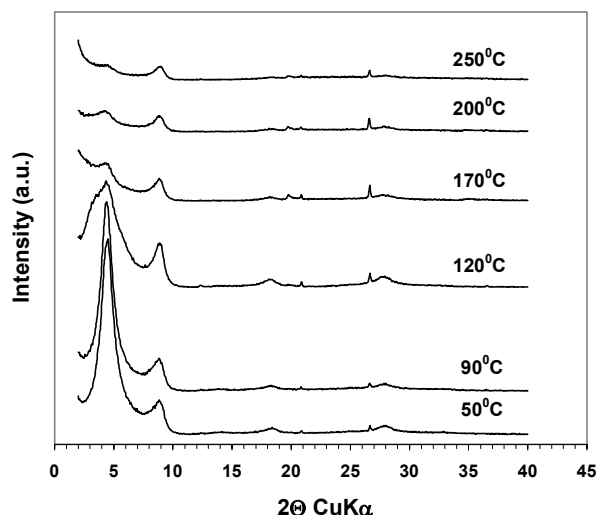


Fig. 1. XRD patterns of LiX/Al-mt samples (X — temperature of lithiation).

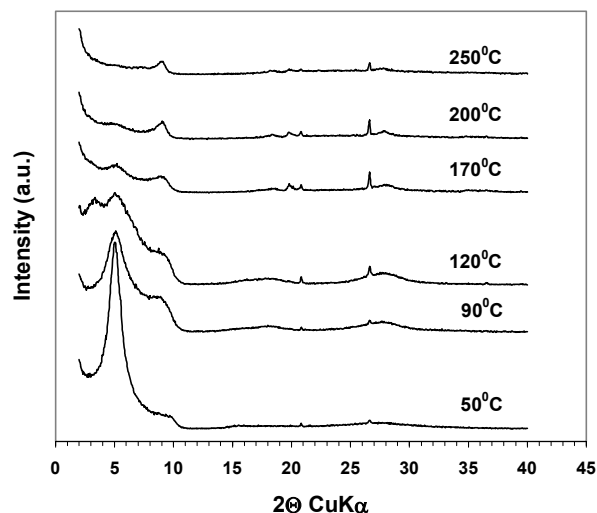


Fig. 2. XRD patterns of LiX/Al-PILC samples (X — temperature of lithiation).

the intensity ratio $I_{\approx 10 \times 10^{-1} \text{ nm}} / I_{\approx 20 \times 10^{-1} \text{ nm}}$ may be interpreted as due to the increasing contribution from the pyrophyllite-like areas generated in lithiated samples by thermal treatment. It is worthwhile to note that in the sample dried at 120 °C a weak shoulder around 30×10^{-1} nm ($2\theta \approx 3.0^\circ$) may be seen, suggesting a possible existence of interstratified areas with pyrophyllite-like/pillared smectite layer ordering. The XRD patterns of calcined LiX/Al-PILC samples show a qualitatively similar effect. The 001 reflections are broader and more diffuse, with $d_{(001)}$ values between 17.3 – 18.3×10^{-1} nm ($4.8^\circ < 2\theta < 5.1^\circ$). Their intensity rapidly decreases with the increasing temperature of preparation of the Li-mt precursor. In contrast, the peak at ca. 10×10^{-1} nm persists and its intensity relative to the 001 reflection increases, so that it dominates the patterns of Li200/Al-PILC and Li250/Al-PILC samples. Thus, it appears, that upon increasing the temperature of lithiation, increasing areas of montmorillonite become unable to reopen during

treatment with pillaring solution. This indicates that the layer charge reduction is by no means homogeneous, and even at relatively low temperatures collapsed areas exist in LiX-mt precursors. A similar effect has already been reported by other authors (Madejová et al. 1996; Komadel et al. 1996). Komadel et al. (1996), who investigated the Li-exchanged thermally treated Jelšovský Potok montmorillonite. They found that on increasing the temperature of heat treatment, ever larger non-swelling areas appeared. They were identified as pyrophyllite-like layers, whose contribution reached 20 % already at a temperature as low as 135 °C. In some cases the authors observed the formation of interstratified pyrophyllite-like/smectite phases. The latter phenomenon is also seen in the present study in the pillared sample derived from Li120-mt. The existence of the superstructure, indicated by the shoulder in the XRD diagram of the uncalcined Li120/Al-mt sample, becomes more obvious after calcination. Here, the XRD pattern of Li120/Al-PILC shows a resolved maximum at ca. 28×10^{-1} nm ($2\theta \approx 3.2^\circ$), confirming the occurrence at this temperature of pyrophyllite-like/pillared smectite interstratification.

Fig. 3 shows the nitrogen adsorption/desorption isotherms obtained for Li-mt and all investigated LiX/Al-PILC samples. The highest sorption capacities are observed for the Li50/Al-PILC and Li90/Al-PILC materials. Further increase of the pre-treatment temperature results in a steady downward shift of the corresponding isotherms. The data gathered in Table 1 show that all samples have predominantly microporous character, as the specific surface area associated with this group of pores corresponds to 70–90 % of the total value. The existence of significant microporosity affects the applicability of the BET formalism. In such cases the Langmuir equation may give a better fit. Indeed, when the specific surface areas are also calculated using the t method, the S^t values are very close to the Langmuir specific surface areas. The most important message conveyed by the data in Table 1 is that the main effect upon increasing temperature of lithiation consists in reduction of the total surface available for adsorption, which occurs on the account of decreasing microporosity. Starting from 120 °C pre-treatment, all parameters describing microporosity become steadily reduced. An important information is provided by the MP method, which shows that in all samples the dominant micropore radius is below 3.5×10^{-1} nm. Consequently, any possible change in the pillar density, in particular an increase of the interpillar distance leading to the increase of the micropore

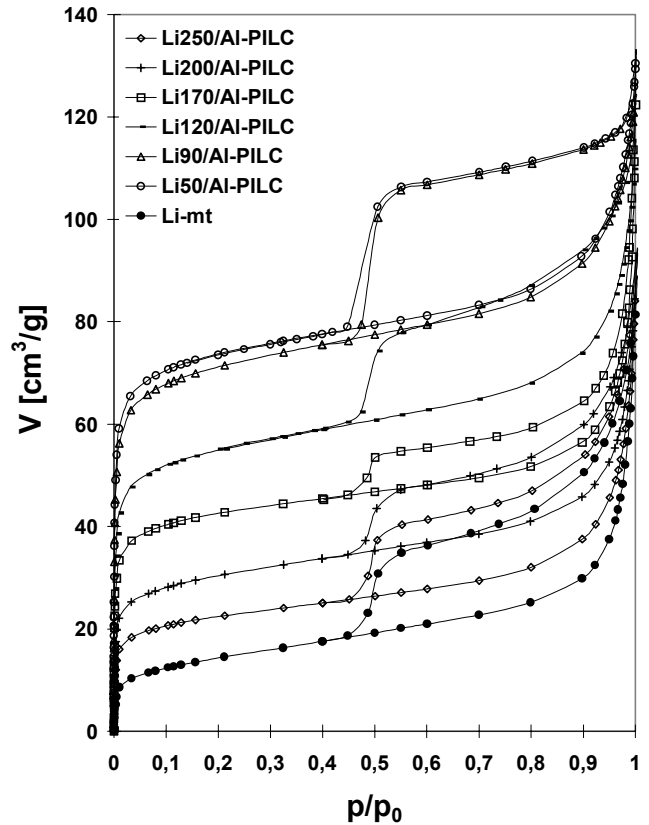


Fig. 3. N_2 adsorption/desorption isotherms at -196 °C for Li-mt and LiX/Al-PILC samples (X — temperature of lithiation).

size, must be rather small and remains in the range not probed by the MP method. Thus, the picture that emerges from the nitrogen sorption experiments confirms the conclusions drawn on the basis of XRD analysis. The main effect occurring upon increasing the temperature of thermal treatment of Li-mt precursor is the progressively increasing contribution of clay areas unable to open upon pillaring, rather than formation of material of increasing micropore sizes.

The above described mechanism of pillaring appears to be due to the inhomogeneous character of layer charge reduction and might be specific for a given montmorillonite. However, in view of a similar observation reported for Jelšovský Potok (Madejová et al. 1996; Komadel et al. 1996), and numerous

Table 1: Textural characteristics of LiX/Al-PILC (the meaning of abbreviations in the Methods).

Parameter	Li-mt	Li50/Al-PILC	Li90/Al-PILC	Li120/Al-PILC	Li170/Al-PILC	Li200/Al-PILC	Li250/Al-PILC
S^{BET} (m^2/g)	51	265	255	196	152	107	79
S^L (m^2/g)	70	332	322	249	193	140	104
S^t (m^2/g)	55	336	321	244	189	128	92
S_{up}^t (m^2/g)	32	306	288	214	171	104	70
S_{mp}^t (m^2/g)	23	30	33	30	19	23	22
S_{mp}^{BIH} (m^2/g)	32	38	41	39	27	32	27
V_{up}^t (cm^3/g)	0.016	0.103	0.098	0.074	0.060	0.039	0.026
V_0^{D-R} (cm^3/g)	0.019	0.122	0.120	0.090	0.068	0.046	0.034
V_{mp}^{BIH} (cm^3/g)	0.099	0.089	0.092	0.098	0.089	0.083	0.096
r_d ($nm \times 10$)	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5
Hysteresis loop	H-3	H-4	H-4	H-3	H-3	H-3	H-3

studies in which the main effect of lithiation at increasing temperatures on the properties of pillared materials was the reduction of the sorption capacity (Purnell 1992; Jones & Purnell 1993, 1994; Suzuki et al. 1988, 1991; Horio et al. 1991; Sychev et al. 1997, 2000), it seems that the phenomenon is of a general nature. Thus, the common belief that the layer charge reduction by Hofmann-Klemen effect allows an easy control of lateral interpillar distances and enhancement of the textural properties appears to be unsubstantiated.

Conclusions

Investigation of the reduced charge Li-montmorillonite thermally treated at increasing temperatures and pillared with Al oligomers shows that the layer charge reduction occurs in an unhomogeneous manner, resulting in ever increasing areas inactive in the pillaring process. In consequence, the sorption capacity of the samples, associated mainly with the microporosity, diminishes. No evidence of an increase of the dominant micropore radius can be detected by the MP calculations, indicating that, any effect, if present, remains below the 3.5×10^{-1} nm radius probed by this method. In view of the similar sorption characteristics of pillared reduced charge clays reported previously by other authors, the proposed explanation of the phenomena accompanying lithiation appear to be of general significance.

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