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THERMAL BEHAVIOR OF Al-, AlFe- AND AlCu-PILLARED INTERLAYERED CLAYS

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Abstract

The purified bentonite parent clay, fraction ≤ 2 μm of montmorillonite type, has been pillared by various polyhydroxy cations, Al, AlFe and AlCu, using conventional pillaring methods. The thermal behavior of PILCs was investigated by combination of X-ray diffraction (XRD), thermal analysis (DTA, TG) and low temperature N_2 adsorption/desorption (LTNA). Thermal stability of Al-, AlFe- and AlCu-PILC samples was estimated after isothermal pretreatment in static air on the temperatures 300, 500, 600 and 900°C. Crucial structural changes were not registered up to 600°C, but the fine changes in interlayer surrounding and porous/microporous structure being obvious at lower temperatures, depending on the nature of the second pillaring ion. AlFe-PILC showed higher thermal stability of the texture, the AlCu-PILC having lower values and lower thermal stability concerning both overall texture and micropore surface and volume. Poorer thermal stability of AlCu-PILC sample at higher temperatures was confirmed, the presence of Cu in the system contributing to complete destruction of aluminum silicate structure, by 'extracting' aluminum in stabile spinel form.

Keywords: AlCu-pillared clay, AlFe-pillared clay, Al-pillared clay, pillared montmorillonite, textural properties, thermal stability

Introduction

Clay materials are for long time applied in the fields of catalysis and adsorption, being promising due to their great abundance and low cost and especially because of the particular properties and structures with great potential for further tailoring [1]. By intercalating of layered clays, particularly montmorillonite with metal oxide clusters the microporous solids with an appropriate texture, surface properties and thermal stability for catalytic application could be obtained [2]. Diversification of sur-

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face nature and pore structure provides a great potential for these solids to be used for developing catalysts and adsorbents [1].

The intercalation process comprises exchanging the charge balancing interlayer cations of the parent clay with bulky, highly charged inorganic cationic polymeric species, which upon heating transform into robust oxide particles as pillars which prop the expended layers of the clay [3]. The expended clays may be used as a shape selective catalyst, catalyst support or as an adsorbent material, the resulting properties being more characteristic of crystalline zeolites than clays [4]. Complex characteristics of intercalated products, referred as pillared interlayer clays (PILC), depend on the nature of the host clay, nature and loading of pillaring agents and preparation methods [5]. Although pillaring has been primarily used in order to increase the surface area of clay minerals, the pillaring agent may create new heterogeneous catalytic sites in the resulting pillared structure, with subsequent effect on catalytic performance of PILC [6–8].

Most frequently, aluminum-containing polyhydroxy species of Keggin structure were used as intercalates, Al_{13} [3]. The composition of this ion can be given as $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, where 12 aluminum ions of octahedral coordination surround the 13th Al^{3+} of tetrahedral coordination. Upon heating, it is believed that dehydroxylation of Al_{13} results in γ-Al_2O_3 type material.

Thermal stability is one of the key characteristics qualifying PILCs for catalytic and adsorption application [9–11]. PILCs show a restricted thermal and hydrothermal stability, the collapse with a loss of interlaminar space and surface area observed even below 500°C [5]. Even if the Al-PILC thermal stability was found to lower than montmorillonite analogue, the heat treatment of the samples in the stability region could enhance the stability of interlayer spacing of Al-PILCs [12]. One of the strategies to avoid the sintering of the pillared clays is the introduction of mixed oxide pillars [5, 10, 13].

The difference in the thermal stability for the various Al-hydroxy intercalated clays is attributed to the presence of some cations intercalated with Al_{13} oligomers, which induces several interactions between oligomers and the clay surface layers [14]. It was reported that both the tetrahedrally and the octahedrally coordinated aluminum may be replaced by other ions such as Fe^{3+}, Cr^{3+}, Ga^{3+}, V^{3+}, Re^{3+}, La^{3+}, Ge^{4+} and Mg^{2+}, but the feasibility of these substitutions has been questioned [15]. Vaughan [4] reported that iron can be isomorphously substituted both in the tetrahedral and in the octahedral position of the Al_{13} Keggin ions in the formation of the mixed metal pillars. Kiricsi *et al*. [15] reported that there is no substitution in the tetrahedral position, but a small portion of Al^{3+} can be replaced by Fe^{3+} in octahedral position. Mössbauer parameters showed that Fe^{3+} octahedral in octahedral sheets are distorted in PILCs obtained from Cu-montmorillonite and undisturbed in that obtained from Fe-montmorillonite [14]. The curves for Al-PILCs obtained from natural, Fe- and Ce-montmorillonites displayed distinct steps at 225 and 650°C, attributed to the dehydration of Al_{13} oligomers, and the dehydroxylation of the surface layer, respectively. By contrast, the curves of Al-PILCs obtained from Cu-montmorillonite displayed one step between 250 and 700°C for both dehydration and dehydroxylation [14]. Special behavior for Cu-based samples was observed also on pure alumina and kaolinite [16–18]. Accelerated polymorphous transformations of metastable aluminas to α-Al_2O_3 in presence of Cu^{2+} is explained as catalytic, considering the Cu^{2+} electron configuration in terms of the Jahn–Teller effect. In Cu promoted kaolinite sample treated at 900°C formation of mullite, $3Al_2O_4{\cdot}2SiO_2$ proceeds, whereas pure and Fe^{3+} kaolinite do not undergo detectable changes in sense of chemical reactions.

Synthesis of PILCs with mixed oxide pillars could be carried out by three different methods: *i*) incorporation of second cation into calcined Al-PILC sample by impregnation; *ii*) incorporation of second cation into Al-PILCs sample by adding its oligomeric solution to the former slurry; *iii*) preparation of pillaring solutions of both Al and the other following cations. Method *iii*) results mixed oxide PILCs with the best thermal properties [5].

In the present study, the thermal stability of mixed AlFe- and AlCu-PILC in comparison to Al-PILC was examined. The selection of second pillaring ion was based on already mentioned controversial behavior of Cu in PILC and other clay/based systems [14, 16, 17].

The purified parent bentonite clay with enhanced montmorillonite content was used for PILC sample preparation. Al-PILC was synthesized by intercalation with hydroxyoligomeric solution of aluminum as described elsewhere [5]. Mixed oxide pillars were obtained by using oligomeric solutions of both Al and second metal ion. The PILCs samples were thermally pretreated in the temperature range 300–900°C.

In approaching the problem of thermal stability, the following experimental strategy was applied. Thermal behavior in thermal analysis experiments was considered as the initial, even being aware of difficulties in interpreting DTA/TG results for montmorillonite material type [19]. The textural investigations were selected as the other experimental approach, since these properties are target properties of pillaring procedure, and therefore the thermal stability of the texture could be considered as meritorious in estimating the applicability of PILC. XRD analysis was used in structural investigations.

Experimental

Materials

Clay

The purified parent bentonite clay (Sipovo, Republic Srpska, Ca-type as confirmed by chemical analysis) was used for PILC sample preparation. Raw bentonite clay was dried (105°C), milled and sieved (63 μm). The hydro separation procedure [20] was used in order to separate the grain size <2 μm, expected to increase the montmorillonite mineral ratio as confirmed by XRD analysis. The term raw clay used for the separated fraction (dried at 105°C), which was applied as a raw material for PILC preparation.

Table 1 Experimental conditions used for PILC synthesis

Characteristic	Al-PILC	AlFe-PILC	AlCu-PILC
OH/metal molar ratio	2	2	2
Metal/clay (mmol g^{-1})	5	5	5
Metal salt solution	0.05 M $Al(NO_3)_3 \cdot 9H_2O$ 1000 mL	0.05 M $Al(NO_3)_3 \cdot 9H_2O$ 500 mL 0.05 M $Fe(NO_3)_3 \cdot 9H_2O$ 500 mL	0.09 M $Al(NO_3)_3 \cdot 9H_2O$ 500 mL 0.01 M $Al(NO_3)_3 \cdot 3H_2O$ 500 mL

Pillared clay (PILC) synthesis

Pillaring solution was prepared by slow adding of basis (0.2 M NaOH) to the salt solution (Table 1) under constant stirring, aging afterwards overnight at room temperature. The 1 mass% clay water suspension was doped by pillaring agent dropwise under constant stirring and aged overnight at room temperature. Filtered and washed samples were air-dried, first at ambient and afterwards at 105°C for 4 h, refer to as fresh PILC.

The isothermal pretreatment at 300, 500, 600 and 900°C was performed in static air for 2 h.

Methods

The thermal analysis was performed by simultaneous thermal analytical method in Derivatograf MOM, Hungary, from ambient temperature to 1000°C, at heating rate 5°C min^{-1} in static air atmosphere. The sensitivity for DTA was 1/10, TG – 100 mg and DTG – 1/20 in all of the measurements. In TG results, the mass loss is referred to initial mass of sample.

Textural properties were examined by low temperature N_2 adsorption/desorption (LTNA), Micromeritics ASAP 2000. BET adsorption isotherm and *t*-plot were applied in data processing.

XRD analysis, Philips APD 1700 CuK_{α} in the range $2\theta=3–65$, was applied in structural investigations.

Results and discussion

Thermal analysis

Fresh montmorillonite

Simultaneous thermal analysis of raw clay (Fig. 1) fits very well to the pattern of montmorillonite clay type, concerning endothermal effects at 165 and 475°C which result from interlayer and constitutional water removal respectively. Endo/exo inversion

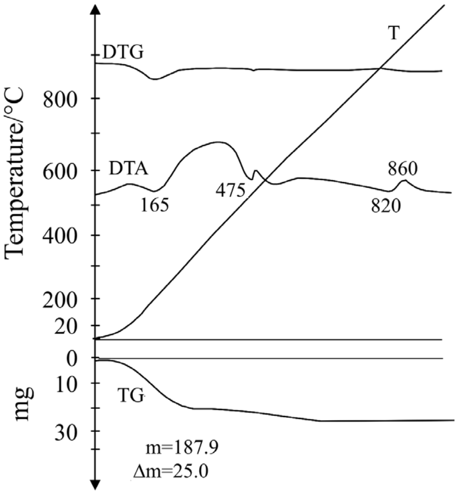

Fig. 1 TA curves of raw clay

at 820/860°C corresponds to crystal structure destruction with possible consecutive formation of variable products (mullite, crystobalite, cordierite, spinel, periclase), as mentioned in [19].

PILCs samples

The results of simultaneous thermal analysis for different PILCs samples are presented in Figs 2–4. The data are summarized in Table 2, presenting thermal effect position/nature and mass loss in three arbitrary selected stages in the defined temperature intervals. The first stage (I) corresponds to the temperature interval up to ca. 220°C, in which no thermal effects were registered in the analyzed samples, but the mass loss is still present due to deliberation of physically adsorbed water. The next interval (II), up to 420°C, corresponds to the temperature range of endothermal constitutional water removal, and third (III), up to the final analysis temperature (1000°C). The distinct mass loss stage registered on TG curve is marked with (peak), no mark corresponding to gradual loss in mentioned interval.

Al-PILC

Three thermal effects were registered on DTA curve of fresh sample (Fig. 2a). Endothermal effect at 265°C associated with mass loss stage (4.6 mass %) is due to interlayer water deliberation. When compared to initial clay behavior (Fig. 1), the process is switched to higher temperature even for 100°C, which we explain as the result of ‘resistance’ of formed pillar architecture. The following endo effect interconnected with constitutional water removal is registered at somewhat lower temperature (470°C) than in initial clay structure (475°C). The high temperature endo/exo inversion at 820/865°C is the consequence of pillar structure destruction, with consecutive re-

Table 2 Thermal effects of raw clay and PILC samples

Sample	I stage		II stage		III stage			Total
	TG mass%	DTA/ °C	TG mass%	DTA/ °C endo	TG mass%	DTA/°C		TG mass%
						endo	endo/ exo	
Raw clay	6.4	165	1.6	–	1.6(peak) 3.7 5.3 total	475	820/860	13.3
Al-fresh	4.1	–	4.6(peak) 3.1 7.7 total	265	3.1(peak) 2.5 5.6 total	470	820/865	17.4
Al-300	5.3	–	1.5	–	2.4(peak) 3.4 5.8 total	465	820/865	12.6
Al-500	1.6	–	0.5	–	1.1(peak) 2.7 3.8 total	460	820/865	5.9
Al-600	1.0	–	–	–	1.0(peak) 2.0 3.0 total	460	825/865	4.0
AlFe-fresh	4.7	–	1.6(peak) 2.2 3.8 total	240	3.2(peak) 2.7 5.9 total	455	820/860	14.4
AlFe-300	4.6	–	1.0	–	3.6(peak) 2.6 6.2 total	460	820/885	11.8
AlFe-500	2.5	–	0.5	–	1.5(peak) 2.0 3.5 total	460	830/870	6.5
AlFe-600	2.2	–	–	–	1.1(peak) 1.6 2.7 total	465	840/880	4.9
AlCu-fresh	4.1	–	4.1(peak) 3.1 7.2 total	235	3.6(peak) 4.1 7.7 total	470	800/830 865 endo	19.0
AlCu-300	3.9	–	1.5	–	3.4(peak) 3.4 6.8 total	462	785/820	12.2
AlCu-500	1.5	–	–	–	2.1(peak) 3.1 5.2 total	460	785/820	6.7
AlCu-600	4.7	–	1.0	–	1.0(peak) 2.6 3.6 total	460	785/820	9.3

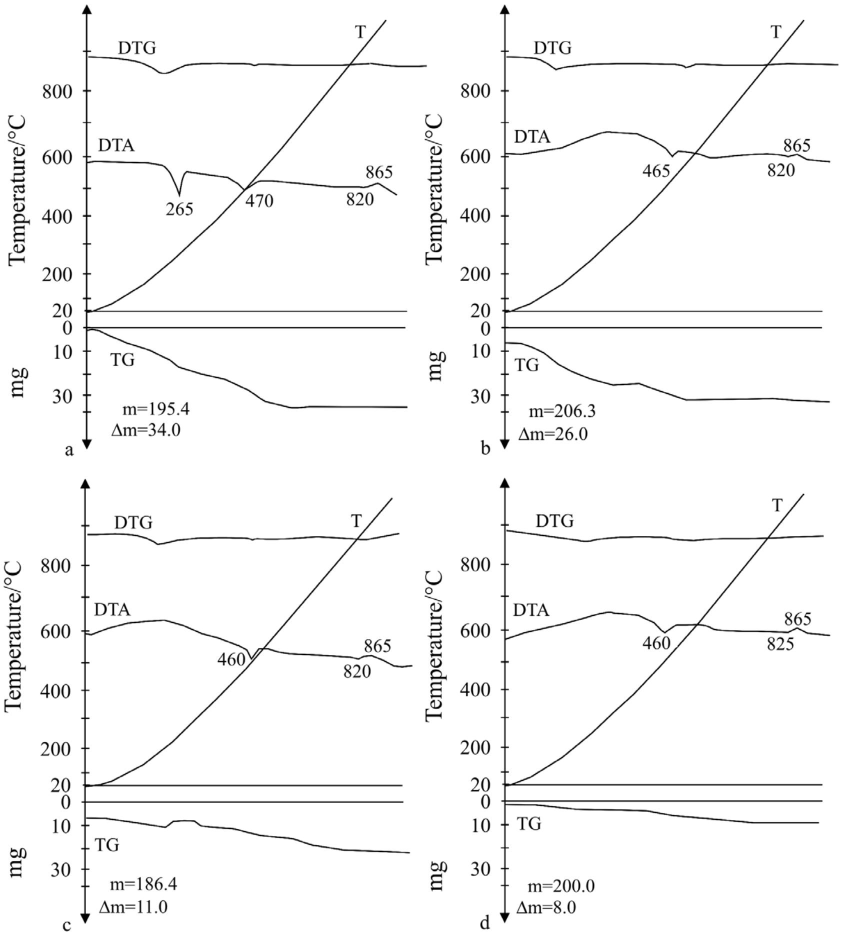

Fig. 2 TA curves of fresh and thermally pretreated Al-PILC samples: a – fresh, b – 300°C, c – 500°C, d – 600°C

crystallization/solid state reactions similar to montmorillonite [19]. The position of this peak is very important in estimating thermal stability of pillar/clay structure.

The general characteristic for all previously thermally treated samples (Figs 2b–d) is the absence of thermal effect corresponding to interlayer water deliberation. It could be concluded that interlayer water is almost completely removed by isothermal treatment even at 300°C (slight mass loss indicating some residues) and definitely after 500°C thermal treatment. The process being practically irreversible as confirmed by repeated thermal analysis of the sample after two-hour exposure to water environment.

There are no pronounced differences in high-temperature pattern of the thermally treated samples as well as in comparison to the fresh Al-PILC samples.

AlFe-PILC

The general thermal pattern of fresh AlFe-PILC (Fig. 3a) sample is similar to the corresponding Al-PILC, but with the TG results indicate multiple stages of low temperature water loss, the DTA peak corresponding to interlayer water being less pronounced and shifted to somewhat lower temperature. The DTA peak assigned to constitutional water deliberation is shifted to lower temperature (Δ15°C).

The isothermally pretreated samples show similar trend to corresponding Al-samples (Figs 3b–d). The interlayer water is also almost removed by thermal pretreatment even at 300°C and completely at higher pretreatment temperatures. The constitutional water is removed at similar temperatures as in corresponding Al-samples, the quantity decreasing with increasing pretreatment temperature. The effects correlated to structure destruction are present (endo/exo inflections), but shifted

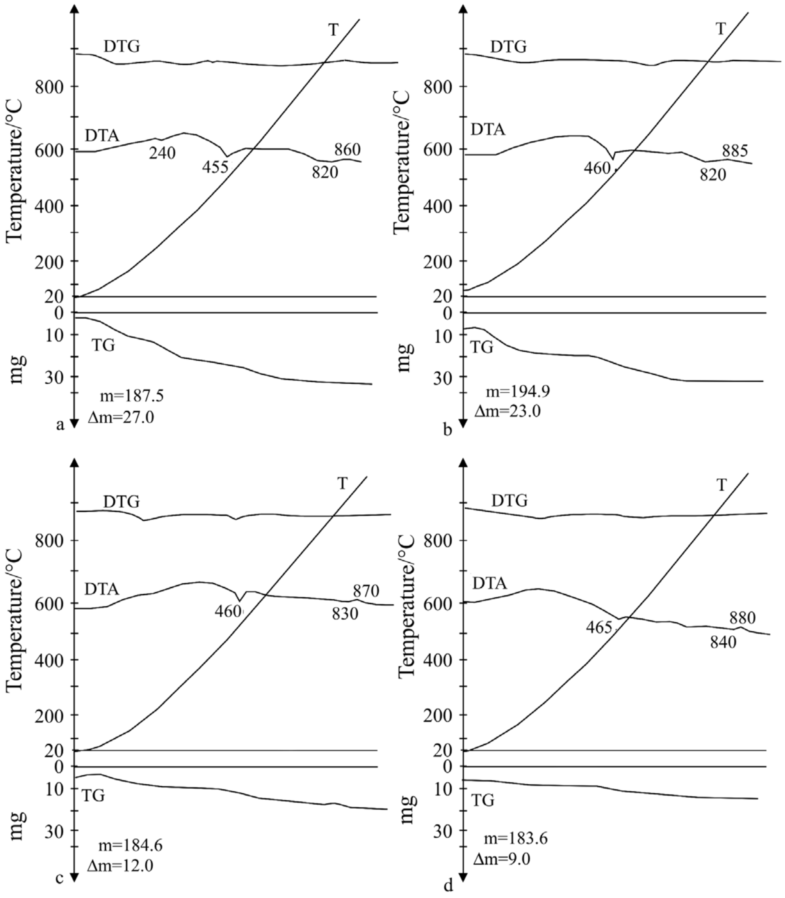

Fig. 3 TA curves of fresh and thermally pretreated AlFe-PILC samples: a – fresh, b – 300°C, c – 500°C, d – 600°C

to higher temperatures than in corresponding Al-samples (Table 2). Also, with the increase of pretreatment temperature, the shift is more pronounced, indicating that thermal pretreatment of the samples stabilized to certain extent pillar structure. It could be concluded that the incorporation of Fe in pillar structure favored to certain extent thermal stability.

AlCu-PILC

The thermal pattern of fresh and thermally pretreated AlCu-PILC samples fits very well to the previously observed general trend of thermal changes (Fig. 4), but with some differences both in temperature interval and quantitative data. The interlayer water present in fresh sample (Fig. 4a) is removed over a broader temperature interval up to 420°C. Thermal pretreatment irreversibly removes this type of water. There

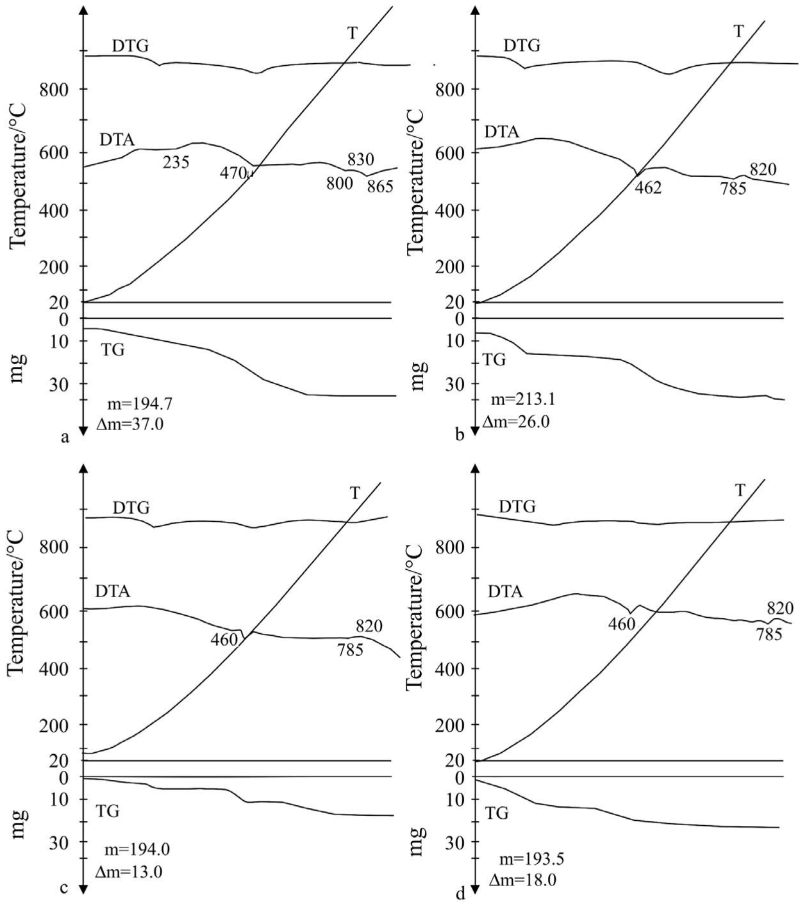

Fig. 4 TA curves of fresh and thermally pretreated AlCu-PILC samples: a – fresh, b – 300°C, c – 500°C, d – 600°C

is no pronounced difference concerning position of constitutional water effects in both fresh and pretreated samples (Figs 4a–d). The quantity of constitutional water is increased in comparison to corresponding Al- and AlFe-samples (Table 2), with broader temperature interval of monotonically mass decrease following the distinct TG stage. The endo/exo inflection associated with structure collapse appears at lower temperatures than in both Al- and AlFe-samples, with different type of behavior also at temperatures approaching 1000°C, indicating lower thermal stability of the structure of both fresh and thermally pretreated samples, being even more pronounced in pretreated samples.

Textural properties

Surface area and pore volume of all the prepared PILC samples (Table 3, Fig. 5) are in interval 70–160 $m^2 g^{-1}$ and 0.114–0.191 $cm^3 g^{-1}$ respectively, being lower or at the lower range limit of these textural characteristics for pillar clay materials [4, 11]. The adsorption isotherms of the PILC samples are intermediate between Type I and IV of BET classification [21], indicating microporous/mesoporous type of material [1]. The isotherm shapes indicate the presence slit pore type as expected.

The surface areas of fresh Al- and AlCu-PILC are less developed than in compared to initial clay analogue (Table 3), which might be explained by considerable quantity of interlayer water present as confirmed by thermal analysis of PILC samples (Table 2, stage II). Thermal pretreatment of these samples contribute to stability or increase of surface area of these samples up to 500°C, with consecutive decrease at 600°C pretreatment (Fig. 5a). In contrary, Fresh AlFe-PILC sample has relatively de-

Table 3 Textural properties of raw clay and PILC samples

Sample PILC	Surface area/ $m^2 g^{-1}$	Pore volume/ $cm^3 g^{-1}$	Micropore surf. area/$m^2 g^{-1}$	Micropore volume/$cm^3 g^{-1}$
Raw clay	111.8	0.112	30.30	0.0136
Al-fresh	87.2	0.1145	17.56	0.0077
Al-300	159.8	0.1777	33.56	0.0148
Al-500	158.5	0.1808	5.21	0.0006
Al-600	119.0	0.1701	0.00	0.0000
AlFe-fresh	162.7	0.1808	21.14	0.0085
AlFe-300	152.7	0.1828	25.75	0.0110
AlFe-500	127.1	0.1816	14.77	0.0058
AlFe-600	111.0	0.1805	10.71	0.0040
AlCu-fresh	91.1	0.1252	12.27	0.0050
AlCu-300	110.6	0.1556	21.35	0.0093
AlCu-500	129.1	0.1915	15.36	0.0061
AlCu-600	72.6	0.1447	0.56	0.0000

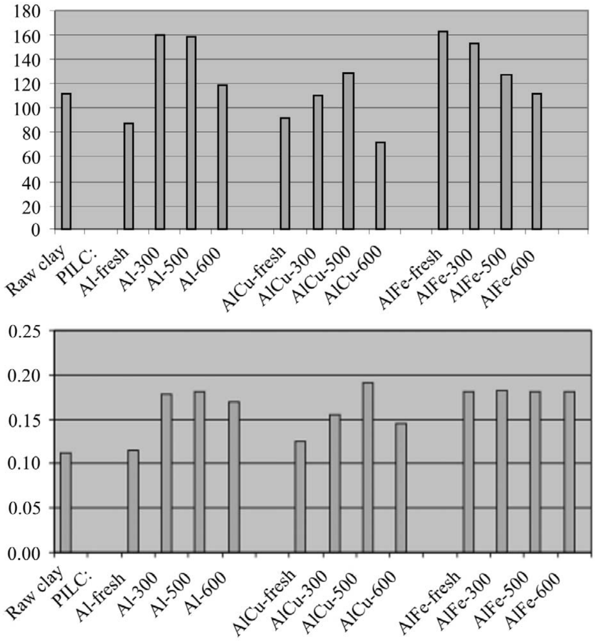

Fig. 5 BET surface area and pore volume of raw clay and PILC samples: a – surface area, b – pore volume

veloped area, probably caused by lower interlayer water content, with continuous decrease in function of pretreatment temperature (Fig. 5a).

The pore volume of Al-PILC samples is increased by 300°C pretreatment, relatively stabile up to 500 with further decrease at 600°C pretreatment (Fig. 5b). AlCu-PILC samples have the maximum of pore volume at 500°C pretreatment. AlFe-samples have relatively stabile pore volume even at 600°C pretreatment, which could be explained by the contribution of micropore volume (Table 3, Fig. 6b).

It could be concluded that the textural properties, both BET surface area and pore volume, and thermal stability of texture depend considerably on chemical composition of pillars.

Microporous texture (Table 3, Fig. 6) speaks in favor of this conclusion. In all PILC samples the increase of both surface and volume of micropores is observed at 300°C pretreatment (Al>AlFe>AlCu), with consecutive decrease at higher pretreatment temperatures, the intensity being dependent on the chemical nature of the samples. The highest micropore area within the series is registered for Al-300°C sample, with intensive decrease at 500°C, making Al-series most thermally sensitive concerning microporous texture. The AlCu-series have relatively lowest values of micropore area and volume within all series, being almost completely lost at 600°C pretreatment, which is in accordance with the thermal analysis results indicating lowest stability of this PILC type. The AlFe-PILC samples have the highest stability of

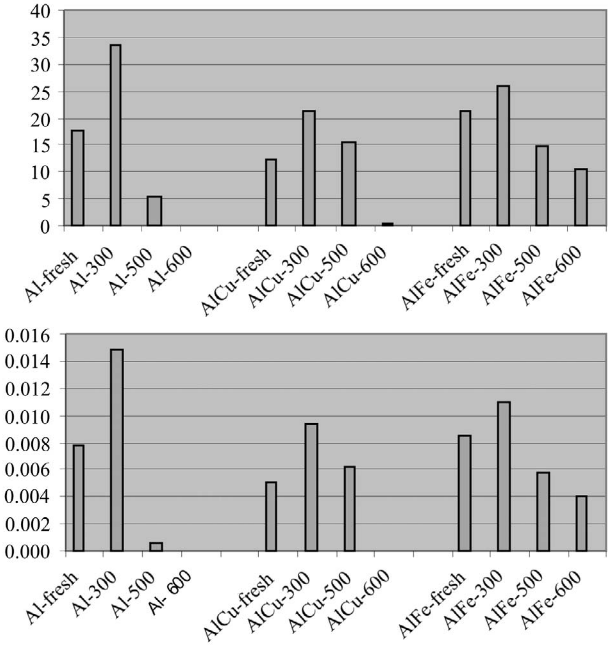

Fig. 6 Surface area and volume of micropores: a – surface area, b – pore volume

microporous texture, which is also in accordance with previously mentioned textural properties and thermal analysis results.

Structure

XRD analysis of the separated fraction confirmed montmorillonite structure of the purified clay (Fig.7a). In XRD pattern of raw clay sample well defined characteristic diffraction lines of montmorillonite mineral [ASTM 13-135] were registered, no other diffraction lines being present. As previously mentioned, the purification procedure applied was successful in separating montmorillonite from raw bentonite clay.

XRD analysis (Figs 7b–d) confirmed formation of pillared structure for all fresh PILC samples [5, 14]. We refer specially to the presence of characteristic diffraction line for basal spacing *d*(001)/nm: Al-PILC 1.773, AlFe-PILC 1.804, AlCu-PILC 2.005, being expended in comparison to montmorillonite 1.533 (Table 4).

Table 4 Basal *d*(001) spacing, nm

Sample	105	300	500	600	900
Raw clay	1.53	–	–	–	–
Al-PILC	1.77	1.77	1.73	1.67	–
AlFe-PILC	1.80	1.78	1.65	1.60	–
AlCu-PILC	2.00	1.40	1.38	1.36	–

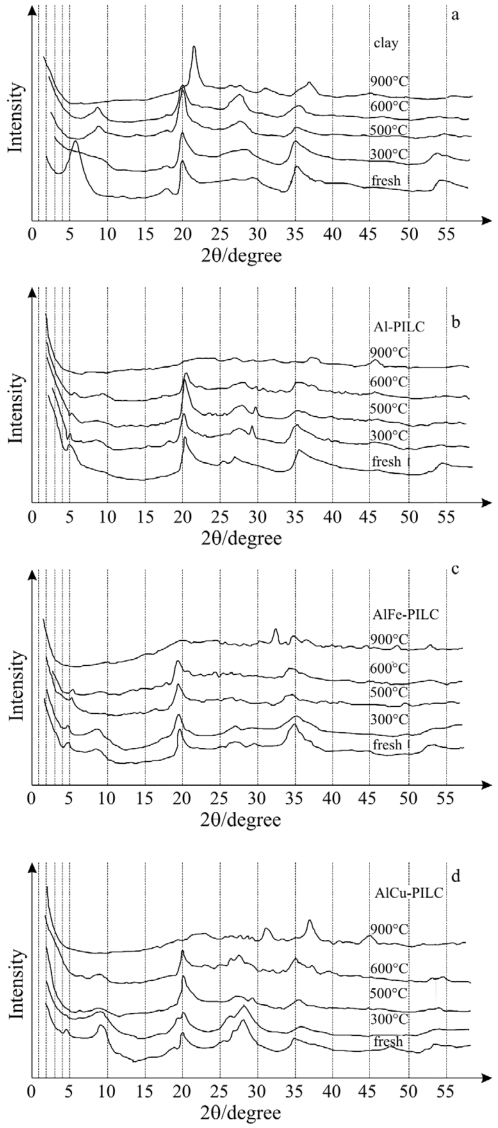

Fig. 7 XRD patterns of the samples: a – clay, b – Al-PILC, c – AlFe-PILC, d – AlCu-PILC

Thermal pretreated PILC samples retained pillar structure up to 600°C, with no pronounced differences in both the position and intensity of characteristic diffraction lines. The pretreatment of raw clay and all the PILC samples at 900°C brought about considerable structural changes, the nature of changes being dependent on the chemical nature of the system. Montmorillonite structure of raw clay was destructed at mentioned temperature, the pattern being similar to formation of cristobalite [ASTM 11-695] with possible minor quantity of other silicates as well. The Al-PILC sample (Fig. 7b) is characterized by practically quasi-amorphous structure, with diffuse lines at 2θ 37.5 and 46.5°. Similar behavior was observed also by other authors [3]. The AlFe-PILC pattern (Fig. 7c) is similar to formation of aluminum silicate (Ca,Mg,Fe,Al)(SiAl)O [ASTM 25-1217]. The diffuse character of diffraction lines in both systems indicate that the formation of new phases is not completed and therefore could not be explicitly identified. In the case of AlCu-PILC (Fig. 7d), the formation of spinel $CuAl_2O_4$ [ASTM 2-1414] is clearly identified.

Based on overall results of thermal, textural and structural analysis it could be concluded that crucial structural changes in PILCs do not occur in the temperature interval up to 600°C. But, the fine differences both in thermal behavior and the texture are present at lower temperatures, being dependent on the nature of the second ion and heat pretreatment. The layered structure is retained, the interlayer distances being slightly changed, but with considerable changes in both BET surface and micropore network. AlFe-PILC showed highest thermal stability of the texture, the AlCu-PILC being most sensitive to thermal treatment, particularly concerning micropores.

Destruction of crystal structure occurs at higher temperatures, but the nature depending on the type of pillaring metal. It is obvious that the presence of Cu in the system contributes to complete destruction of aluminum silicate structure, by ‘extracting’ aluminum in stabile spinel structure. Even if XRD analysis of this system did not show considerable structural changes at lower pretreatment temperatures, it is possible that fine structural changes take place already at lower temperature regime, as showed by decreased thermal and textural stability of the system by other methods. It could be anticipated that the Cu ions diffuse from pillar structure to octahedral sites of alumina structures specially at higher temperatures, causing the distortion of the local ligand symmetry [22, 23]. This mechanism was previously confirmed in alumina systems, with pronounced contribution of Cu ion to both rapid sintering and polymorphous transformations of metastable alumina forms [16, 17], and could be anticipated also for destruction of pillars being supposed as γ-Al_2O_3 material type [3]. But, the more pronounced influence of Cu ion on the BET surface area than on micropore volume and surface (Table 3) speaks in favor of considerable bulk structural changes taking place in the sample.

Conclusions

Pillaring of montmorillonite clay with Al- and mixed AlFe and AlCu polyhydroxy cations, gave materials of pillared structure. Characteristic diffraction line for basal spacing *d*(001)/nm: Al-PILC 1.773, AlFe-PILC 1.804, AlCu-PILC 2.005 is being expended in comparison to montmorillonite analogue, 1.533. Microporous/mesoporous type of material with slit-like pores were obtained, the surface area and pore volume being lower or at the lower range limit for pillar clay materials. During isothermal treatment of PILCs in static air, crucial structural changes do not occur in the temperature interval up to 600°C, but fine changes in interlayer surrounding and porous/microporous structure being observed, depending on the nature of the second pillaring ion. By introduction of mixed oxide pillars the pore structure, particularly in micropores and its thermal stability, can be tailored and even fine-tuned. The higher thermal stability of the texture is observed in AlFe- in comparison to AlCu-PILC, the AlCu-sample having the lowest values and lowest thermal stability concerning both overall texture and micropore surface and volume. Poorer thermal stability of AlCu-PILC sample at higher temperatures was confirmed, the presence of Cu in the system contributing to complete destruction of aluminum silicate structure, by ‘extracting’ aluminum in stabile spinel form.

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