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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

SYNTHESIS AND CHARACTERIZATIONS OF HYDROXY-ALUMINUM CROSS-LINKED MONTMORILLONITE

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Abstract

Cross-linked montmorillonite was prepared by reacting homoionic sodium form of bentonite (Na–M) from Istenmezeje (Hungary) with high molecular weight polyhydroxy-aluminum complex. The complex was prepared by controlled hydrolysis of alumina macrocation. The intercalated clay (Na–Al–M) was thermally treated to convert the hydroxy cations to oxide pillars. The pillared products were characterized by X-ray powder diffraction (XRD), Fourie transform infrared spectroscopy (FTIR), thermogravimetry (TG), differential thermal analysis (DTA) and thermal analysis-mass spectrometry (TA-MS) methods. The specific surface area as well as pore size and pore structure distribution of samples were measured by nitrogen, water and carbon tetrachloride adsorption, and the heat of immersion was also determined. The pillared products were characterized by $d(001)$ reflections of 19 Å, which is stable even at 500°C. The interaction of polymer alumina caused several changes in the obtained FTIR spectra due to the formation of different new bonds. The rate of dehydroxylation of the pillared product is very moderate, the water release occurred in different temperature ranges according to TA-MS results. Dehydration starts at interfaces and at the wall of pores, occurring nearly with uniform rate at 250–500°C. DTA curve indicates the formation of a new phase at 950°C. The obtained surface area of the pillared product by nitrogen adsorption becomes larger (208 $m^2 g^{-1}$) with respect to the non pillared clay, which decreases less than 10% upto 700°C. The pillared sample has a definite pore structure, the quantity of micropores (0–40 Å) decreased with increasing of macropores (>1000 Å). The obtained domestic pillared montmorillonite possesses a high degree of thermal stability and may be used as adsorbent.

Keywords: DTA, FTIR, Keggin ion, pillared montmorillonite, pore stucture, TA-MS, XRD

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Introduction

The concept of pillaring clay extends back to the early work of Barrer and MacLead [1], when they demonstrated that permanent microporosity could be introduced in montmorillonite by intercalation of tetraalkyl ammonium ions. Several other robust cations have been utilized as pillars in smectite clay chemistry [2, 3]. Metal oxide pillared clays are a relatively new class of microporous, high surface area solids discovered in the late 1970's years [4–5]. These materials are typically prepared by replacement of the interlayer cations of smectite clay by oligomeric polycations and subsequent calcination to form nanoscopic oxide aggregates in the clay. The most commonly used pillaring agent is the Keggin-like Al_{13} oligomer: $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ formed by hydrolysis of an aluminum chloride solution [7, 8]. Thermal dehydration and dehydroxylation convert the intercalated polycations to aluminum oxide pillars, which permanently drop open the clay layers and provide for a microporous network. The interlayer surfaces of the clay thus become accessible for adsorption of gases and vapors, as well as acid-catalyzed reactions such as petroleum cracking [9, 10]. In contrast organic pillaring agents generally decompose due to rupture of the carbon-carbon bond at temperature below 350°C. An advantage that pillared clays have with respect to zeolites is that the diameter of their micropores is greater, which allows larger molecules and therefore heavier oil fractions to be cracked. Moreover by varying the size of the pillar one may adjust the pore size to suit a particular application. Due to their unique polarity, pore-size distribution and surface area, pillared clays are potentially useful materials for the adsorption of environmental toxicants such chlorinated phenols [11]. These thermally stable microporous solids seem a promising new advanced material, which are of great interest because of their potential applications in various fields [12]. The incorporation of a nonionic surfactant greatly improved the hydrolytic stability of the intercalated Al_{13} oligomer exhibits a more uniform micropore distribution than the material produced without surfactant modification. The use of surfactant provides and effective means of the shape-selective adsorption and catalytic properties of pillared clays [13]. Another area of interest is that the relatively new microporous material has several advantages as a competitive water adsorbent. The capacities of water in the pillared clays are comparable to those zeolites and silica gel [14]. Recently the dehydration and rehydration behaviour of pillared smectites were also studied [15].

The objective of the present paper was to synthesize a thermally stable, porous aluminum-oxide-pillared material using a domestic bentonite and to investigate systematically its properties. The product was characterized using elemental analysis, X-ray powder diffraction, thermal analysis, Fourier transform infrared spectroscopy, nitrogen-, water- and carbon tetrachloride vapor adsorption, as well as immersion microcalorimetry. The reactivity of Hungarian montmorillo-

nite to polyoxycations of alumina was compared with those of reference sample from a Wyoming montmorillonite. Aluminum-27 and silicon-29 solid state NMR were also used [16] to investigate the structure present in sodium montmorillonite and in cross-linked montmorillonite.

Experimental

Materials

The clays used as the raw materials are from Istenmezeje (Hungary) and a commercial Volclay SPV-200 bentonite (Wyoming) as a reference material. The Hungarian bentonite contains mainly montmorillonite and some mineral contaminants (quartz, cristoballite and plagioclase) according to our identification by X-ray powder diffraction. Impurity of SiO_2 was removed by fractionation using conventional sedimentation techniques. The less than 2 μm fractions were practically free from impurities as determined by XRD method. These fractions were converted to sodium form by four ionexchange reaction with aqueous 1.0 M NaCl at 25°C. The exchanged clays were washed with double distilled water until chloride free and dried at 60°C. These prepared samples were used as starting material (Na–M).

Preparation of the pillaring agent

The aqueous alumina solution was prepared by starting with 0.2 M solution of $AlCl_3 \cdot 6H_2O$ and adding 0.2 M NaOH solution with constant rate (1 cm^3 min^{-1}) in the course of vigorous stirring to obtain an Al/OH ratio of 2.4. The hydroxy-alumina solution was aged in polyethylene flask at 80°C for two hours and cooled to room temperature.

Pillared clay synthesis

One gram of sodium montmorillonite was dispersed in 200 cm^3 double distilled water at 25°C by vigorous and prolonged stirring (5 h). The amount of pillaring solution required obtaining an Al/montmorillonite ratio of 20 mmol Al/g clay for the total suspension was then added with constant rate to the stirred dispersion. The resulting product was left in contact with the solution for 15 h and then separated by centrifugation. The product was washed by redispersing it in double distilled water and separated. This procedure was repeated until the supernatant was free from chloride ions and dried above 70% sulfuric acid solution. The dried samples (Na–Al–M) were investigated by different method.

Methods

Chemical analysis of Hungarian montmorillonite and of the pillared sample was carried out by atomic absorption spectroscopy (AAS) with a Perkin Elmer AAS 5000 instrument.

X-ray powder diffraction (XRD) measurements were performed with a Philips XRD PW-1050/25 diffractometer at 45 kV and 35 mA using CuK_α radiation.

Fourier transform infrared spectra (FTIR) of samples in KBr pellets were taken by a Philips FTS-7 BIO-RAD type spectrometer in the 4000–400 cm^{-1} range.

The thermal behavior of the samples was investigated by Mettler TA-1 Thermoanalyzer in flowing air at a heating rate 6°C min^{-1}. The mass loss was recorded in the range 25–1400°C. DTA curves were obtained using Al_2O_3 as a reference material. The gaseous decomposition products formed during heating were also investigated by Balzers QMG-420 mass spectrometer coupled to the thermoanalyzer in the range 25–1000°C.

Nitrogen adsorption-desorption isotherms were measured by Micromeritics Accusorb 2100 analyzer. The samples were previously degassed at 240°C for 5 h and the isotherms were recorded at liquid nitrogen temperature. Surface areas were calculated using BET equation. The water adsorption isotherms of sample were measured at room temperature (22±1°C) by gravimetric method.

The pore volume and pore size distributions were obtained by a conventional static method over the partial pressure range 0.1–0.99. Pore volume distributions were calculated from desorption isotherms.

The heat of immersion was measured by a Calvet-Setaram 70 isotherm microcalorimeter at 27°C.

Results and discussion

Elemental analysis

The investigated Hungarian clay contains different exchangeable cations. These affect the swelling properties and may also affect the pillared product. Therefore the particle size fraction less then 2 μm was converted to homoionic sodium montmorillonite (Na–M). Chemical composition of Na–M and of its intercalated product (Na–Al–M) is given in the Table 1. The increase of the aluminum content and the decrease of the sodium and calcium content of the clay clearly prove the incorporation of the polyhydroxy aluminum cation. Decrease of magnesium and silicon dioxide content is moderate.

X-ray powder diffraction

The homoionic Hungarian and the Wyoming montmorillonite were investigated. The $d(001)$ basal reflection of Hungarian clay is 10.8 Å and of Wyoming

Table 1 Chemical composition of Na–montmorillonite /Na–M/ and Al–pillared montmorillonite /Na–Al–M/

Metal oxide wt%	Na–M	Na–M
SiO_2	59.14±0.20	53.66±0.21
Al_2O_3	14.87±0.28	21.28±0.20
Fe_2O_3	2.52±0.02	2.65±0.02
MgO	3.51±0.03	2.22±0.01
CaO	0.48±0.005	0.08±0.001
K_2O	0.26±0.002	0.26±0.002
Na_2O	4.10±0.02	0.25±0.004
H_2O	13.50±0.13	18.50±0.19
Total	98.38	98.90

is 11.9 Å respectively. These reflections changed significantly to 18.9 and 19.2 Å due to intercalation of alumina polymer cation, which size – about 8 Å in height – corresponds well with the interlayer spacing obtained in the pillared products. Pillaring resulted in a considerable increase in the *d*-values of basal reflection as evidenced by the shift of the (001) peaks to lower angles. The *d*(001) peaks are quite sharp in the case if the pillar height is relatively homogeneous. The samples were stable for month. No separated alumina phases were observed. Rewetting of dried pillared samples with double distilled water resulted in a negligible (0.3 Å) increase in basal spacing.

Figure 1 compares the XRD patterns of the Hungarian montmorillonite and their thermal treated products. The samples were heated in flowing air to 300, 500 and 700°C, than cooled to ambient temperature and their XRD spectra were taken. The results proved, that the pillared products is stable even at 500°C, but at 700°C the original *d*(001) reflection reappears indicating the collapse of the pillared structure. However the structure of montmorillonite still exists.

FTIR spectroscopy

The infrared spectrum of montmorillonite has been extensively studied by Farmer and Russel [17]. The observed FTIR bands of Hungarian Na–M in this study were assigned according to Farmer [18].

Figure 2 shows the spectrum of Na–M and Na–Al–M in the frequency range at 4000–400 cm^{-1} at room temperature. Both stretching and bending vibrations of Al–OH–Al were observed at 3620 and 920 cm^{-1} at Na–M sample (see A curve). The bands at 3449 and 1650 cm^{-1} indicate the stretching and bending fre-

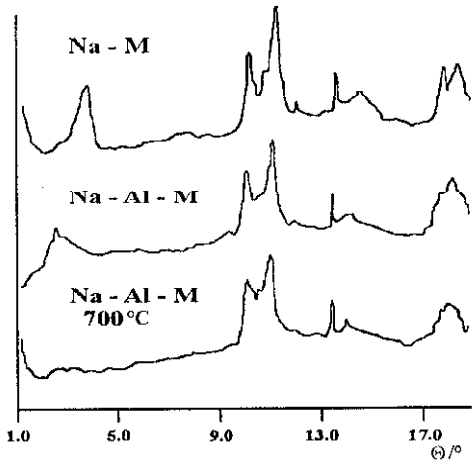

Fig. 1 XRD patterns of Na–M, Na–Al–M and preheated Na–Al–M samples

quencies of water. The absorbance band at 841 cm^{-1} has been assigned to Mg–OH–Al bending mode. The stretching vibration of Si–O groups is accompanied by three absorption bands at 1121, 1070 and 1020 cm^{-1}. A defined band at 790 cm^{-1} was observed and has been assigned to a silica phase impurity in the clay. No band appears at 890 cm^{-1} that assigns the Fe–OH–Al bending mode.

In the case of Na–Al–M sample several changes were observed in the spectrum. It appears from Fig. 2B that H–OH stretching bands show a considerable broadening and decreasing of intensity. The absorbance at 3449 cm^{-1} shifts to 3432 cm^{-1}. Decreasing of the band intensity and the change of wavenumber indicate the formation of different new Al–OH bands due to the interaction of montmorillonite with polymer alumina. The structure change is also indicated by the disappearance of the original three Si–O–Si bands at the range of 1121–1020 cm^{-1}.

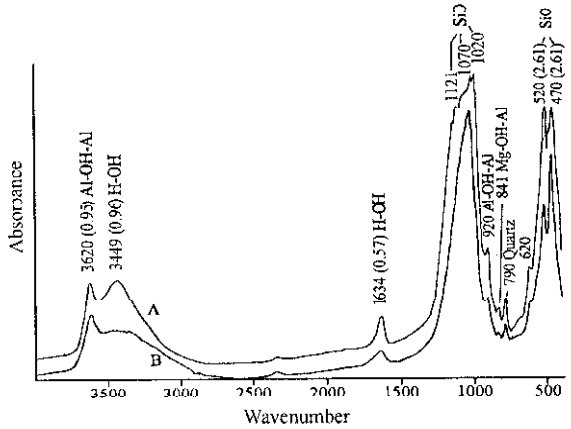

Fig. 2 FTIR spectra of Na–M (A) and Na–Al–M (B)

Only one very sharp band appears at 1046 cm^{-1} indicating the more ordered silicate layers. In accordance with our XRD results no distinctive vibrations of alumina compound were indicated, e.g. the whole amount of polymer alumina has been built into the silicate layers. The most important parameter in the preparation step is probably the ratio between the amount of crosslinking agent and the amount of smectite.

The results of thermally treated samples are summarized in Table 2.

300°C: sample Na–M

The intensity of Al–OH–Al and H–OH bands at 3620, 1634 and 920 cm^{-1} is considerably reduced after thermal treatment. The band at 3449 cm^{-1} shifts to lower frequency (3436 cm^{-1}). The three Si–O stretching vibrations vanish, only an intensive one exists at 1045 cm^{-1}. Similar changes at the Si–O frequency range were observed at the pillared sample without heat treatment (Fig. 3B). The effect of intercalation of polymer alumina into the silicate layer at ambient temperature is the same as the heat treatment of Na–M to 300°C. The obtained spectrum indicated that the band of Si–O at 520 and 473 cm^{-1} reduces in intensity. The vibrations of quartz at 790 and 620 cm^{-1} disappeared.

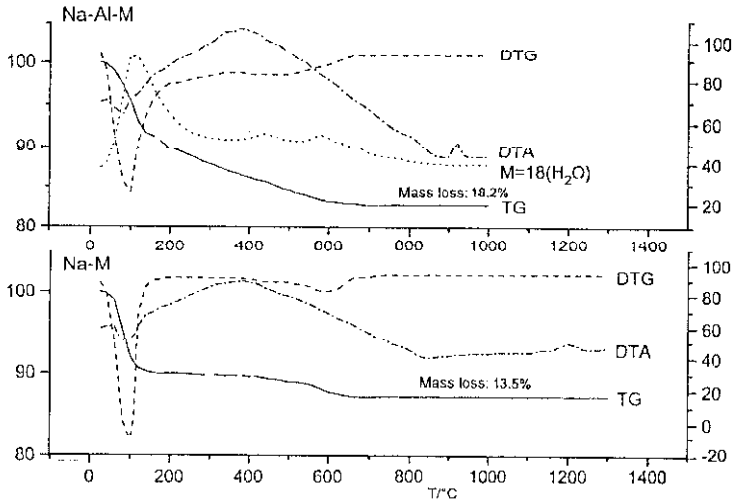

Fig. 3 TA-MS curves of Na–M and Na–Al–M samples

300°C: sample Na Al M

In contrary to Na–M sample the intensity of all band of Al–OH–Al and H–OH significantly increased due to thermal treatment. The wavenumber of those groups did not change practically.

Table 2 FTIR spectra of preheated Na–M and Na–Al–M samples

T/°C	Na–M		Na–Al–M		Assignment of bands
	cm^{-1}	absorbance	cm^{-1}	absorbance	
25	see Fig. 2				
300	3620	0.33	3623	0.48	Al–OH–Al
	3436	0.36	3436	0.41	H–OH
	1635	0.28	1634	0.32	H–OH
	1045	1.69	1046	1.79	Si–O
	920	0.54	921	0.58	Al–OH–Al
	845	0.32	841	0.36	Mg–OH–Al
	520	1.05	520	1.07	Si–O
	473	1.37	473	1.39	Si–O
500	3620	0.36	3632	0.38	
	3436	0.35	3436	0.35	
	1643	0.30	1646	0.30	
			1120	sh	
	1045	1.89	1052	1.25	
	520	1.12	520	sh	
	480	1.42	477	0.94	
700	3620		3626	0.22	
	3426	0.24			
			3325	0.20	
	1640	0.28	1670	0.19	
			1133	0.51	
	1046	0.95	1049	0.60	
			870	0.17	
	728	0.18	740	0.16	
			645	0.21	
	570	0.37	566	0.28	
	480	0.73	480	0.47	

500°C: sample Na–M

The band at 1634 cm^{-1} shifts to higher frequency (1643 cm^{-1}). The Al–OH–Al bending mode at 920 cm^{-1} and the Mg–OH–Al at 845 cm^{-1} completely disappear.

The absence of these bands clearly shows that the OH groups attached to magnesium and to aluminum in the octahedral layer are lost. The Al–OH–Al bending mode loses its intensity much more rapidly than its stretching counterpart. The onset of dehydroxylation effects the silicate sheets as evidenced by the shift of 470 cm^{-1} band to higher frequency at 480 cm^{-1} and by the disappearance of 620 cm^{-1} band.

500°C: sample Na–Al–M

In contrary to Na–M sample the stretching vibration of Al–OH–Al at 3620 cm^{-1} shifts to higher frequency (3632 cm^{-1}) with about 21% decreasing of intensity. Structural changes of silicate layer indicating by appearance of a shoulder at 1120 cm^{-1} and the shift of bands from 1046 cm^{-1} to 1052 cm^{-1}. The absorbance at 520 cm^{-1} is reduced, only a shoulder indicates the Si–O band. The intensity of the other Si–O band at 473 cm^{-1} decreases with further 32%.

700°C: sample Na–M

Increasing the temperature of heat treatment only a rest of the stretching vibration of Al–OH groups is present at 3620 cm^{-1}. The frequency of H–OH bend shift again to lower wavenumber, that is to 3426 cm^{-1} from 3436 cm^{-1} at 500°C. The band at 520 cm^{-1} disappeared and new bands exist at 570 and 728 cm^{-1}. The intensity of all other bands decreased significantly indicating structural transformation in Na–M sample.

700°C: sample Na–Al–M

The stretching vibrations of Al–OH band still exist although their intensity decreases with further 42% between the temperature range of 500–700°C. A new strong band appears at 3325 cm^{-1}, which indicates the formation of separated Al_2O_3 phase. Between 1670 and 480 cm^{-1} other new and intensive bands appeared but for their identification further investigations are required.

The FTIR results strongly suggest irreversible structural transformation in the Al–pillared and unpillared montmorillonite subjected to thermal treatment at 700°C.

Thermal analysis

Figure 3 shows the results of thermogravimetric (TG), differential thermogravimetric (DTG), differential thermoanalytical (DTA) and mass spectrometric curves of Na–M and Na–Al–M samples.

Two distinct mass losses occur when Na–M is heated according to TG and DTG curves. The first one (6.3%) belongs to the dehydration, when the physically adsorbed and the interlayered water release. This process is indicated by

endothermic peak at 100°C in DTA curve. The second mass loss (4.2%) primarily in the range 400–800°C with a peak in the DTG at about 650°C represents the dehydroxylation of the montmorillonite with endothermic reaction. The total mass loss to 1400°C is 13.5%. An endothermic DTA peak at 1200°C indicates the formation of a new high temperature phase.

The pillared montmorillonite showed a more gradual loss of both physically adsorbed water and water formed by dehydroxylation of pillars. Only one DTG peak indicates the first water release in accordance with the MS curve too. The mass loss to 200°C is much higher (12.3%) as in the case of Na–M. The rate of dehydroxylation of the pillared product presumably is very moderate. The curve of mass number 18 (H_2O) indicates further two temperature range of water release in 400–500°C and 500–700°C, in contrary to Na–M. Water release at 400 500°C can be associated with the dehydroxylation of the pillars, whereas the peak at about 600°C was connected with the dehydroxylation of the montmorillonite layers. The exothermal peak at 950°C indicated by the DTA curve seems to be proved that the formed Al_2O_3 at 700°C (see FTIR results) promotes the development of the new crystalline phase.

Nitrogen-, water adsorption-desorption and heat of immersion

The specific surface area as well as the pore size and pore structure of layer silicates is usually characterized by nitrogen and water vapor adsorption. Although there is a great deal of research on the pillared clays, the pore-size distribution and the pore structure are not well understood [19]. The obtained N_2 adsorption data proved that the surface area of the pillared product becomes larger (208 $m^2 g^{-1}$) with respect to the original sample of Na–M (150 $m^2 g^{-1}$). The surface area of Na–Al–M sample decreases less than 10% upto 700°C. This value corresponds to the literary data (175–350 $m^2 g^{-1}$).

In contrary the obtained surface area by water isotherm is different from the corresponding nitrogen isotherm. The area of Na–M sample is significantly larger (390 $m^2 g^{-1}$) at the case of water adsorption. Otherwise no similar tendency was observed in the case of the pillared sample, that is the measured surface area are similar by nitrogen- and water adsorption. It is worth to mention that the surface area of Na–Al–M obtained by water is smaller (214 $m^2 g^{-1}$) compare to the Na–M sample. It means that the number of adsorption centers for water molecules is less in the case of Al–pillared clay. Namely the quantity of the gel-structure water is greater at the latter sample. This type of water is the non-evaporable part at room temperature, which indicates the strongly bounded OH^-, H_3O^+ or H_2O species to the silicate layers. The difference may cause by the require of place of nitrogen molecule which size is greater as the size of very small pores. The smaller water molecules can enter into the small pores.

The investigated pore size distribution of Na–M and Na–Al–M samples are given in Table 3. Micro- and macropores are present in the same pore volume at

Table 3 Pore size distribution of Na–M and Na–Al–M samples

	Pore size/Å	Pore volume/%
Na–M	0–40	43.4
	>1000	44.1
Na–Al–M	0–40	36.6
	>1000	49.0

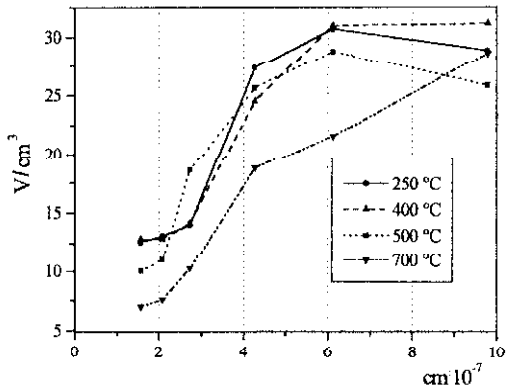

Fig. 4 Desorption pore volume distribution of preheated Na–Al–M samples

the case of Na–M but by intercalation of polycation the quantity of micropores decreased with increasing of macropores. The change of pore structure of pillared montmorillonite is accordance with our XRD results indicating by increasing basal spacing.

The obtained desorption pore volume distribution of preheated Na–Al–M samples at different temperature is given on Fig. 4. It is obvious that the pillared sample has a definite pore structure. It seems from the measurement that dehydration starts at interfaces and at the wall of pores. This process occurs nearly with uniform rate at 250–500°C temperature range. Upon 600°C the alumina polymer transformed into oxides which pillars allow the structure remain 'open'.

The heat of the wetting of pillared material was determined by water, carbon tetrachloride and methyl alcohol also to better understand the pore structure. The obtained $q_{w,water}$ is 11.47 J g_a^{-1}, $q_{w,carbon\ tetrachloride}$ is 11.55 J g_a^{-1} and $q_{w,ethanol}$ is 51.48 J g_a^{-1}. The latter value is surprising great because the $q_{w,water}$ is equal to the $q_{w,carbon\ tetrachloride}$ although the difference of their polarity is significant and their size differs too from each other: $a_{m,water}$=60.0 m^2 $mmol^{-1}$, $a_{m,carbon\ tetrachloride}$= 176.0 m^2 $mmol^{-1}$ and $a_{m,ethanol}$=94.0 m^2 $mmol^{-1}$. It can be suppose that water takes place on the surface of silicate layers with an ordered structure in contrary

to CCl_4 organizing randomly by the influence of geometric factors. According to the high q_w,ethanol value either chemical interaction (chemisorption) is possible or the methyl alcohol can enter to a place where the water molecule could not penetrate, because strong interaction exists (hydrogen bond) and therefore the further places of pores are closed. The same effect can occur in consequence of the rather great size of carbon tetrachloride molecule and therefore the accessibility of pores is smaller. Further investigation of pillared montmorillonite is required to establish the exact structure of pores.

Conclusions

All the obtained data reveal the building in of the cross-linked solution into Hungarian montmorillonite producing the thermally stable pillared structure with its characteristic properties. One of the possible application of the obtained product is the selective sorption properties which might be useful for the adsorption of environmental toxicants. The adsorption properties of this pillared material are now under investigation.

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