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Synthesis and Characterization of Al-Pillared Interlayered Bentonites

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ABSTRACT

The effects of OH^-/Al^{3+} ratio within the range of 1.0-2.5, on physico-chemical properties of Al-pillared clays obtained from Hancili (Turkey) bentonites and the change of these properties with the calcination temperature were examined. Characterization studies were performed by use of XRF, XRD, FTIR, SEM and N_2-adsorption/desorption analysis. Basal spacing and multi point BET surface area values of Al-pillared clays obtained from Hancili White Bentonite (HWB) increased from 1.69 nm and 149 m^2g^{-1} to 1.83 nm and 198 m^2g^{-1} by the increase of OH^-/Al^{3+} ratio from 1.0 to 2.0 similar to the ones obtained from Hancili Green Bentonite (HGB). Decreases in these values were observed with temperature; however, even after calcination at 700ºC, they were higher than those of natural bentonite clays. HWB host resulted in samples with higher surface area values with the gained thermal stability. Calcium content of the products (determined by XRF) decreased to zero level with increasing OH^-/Al^{3+} ratio and a corresponding decrease of Si/Al ratio. Presence of peaks at 1550 cm^{-1} corresponding to Brønsted acid site and at 1450 cm^{-1} corresponding to Lewis acid sites confirmed the existence of both physical and chemical acid sites in the synthesized samples.

Key Words: Bentonite, Al-pillared interlayered bentonites, Synthesis, Characterization.

1. INTRODUCTION

Pillared interlayered clays (PILCs) are interesting micro-mesoporous materials with the gained molecular sieve properties in adsorption and catalytic applications. Pillaring is achieved by (i) a quasi-reversible intercalation by exchanging the interlayer inorganic cations with voluminous cationic pillars, causing up to a 5-fold increase in basal spacing (d_{001}) of the clay mineral determined by XRD; (ii) heating at high temperatures to obtain thermally stable porous solids. During the heating, basal spacing may decrease, but should not collapse. It is also recommended that the intercalation species must not fill the entire interlayer clay space in order to have accessible porosity with high surface area values. The pillared material must have chemical and thermal stability with the preserved crystal structure [1-4].

The layer of 2:1 phyllosilicates consists of an octahedral sheet sandwiched between two opposing tetrahedral sheets. In the smectite type phyllosilicates, the layer is negatively charged because of the joint oxygen found in the corner and they are equilibrated by taking the small exchangeable cations such as Na^+ and Ca^{2+} within the layers [1, 5]. Due to the swelling properties of these types of clays, they have an enlargeable cage structure obtained by the exchange of structural cations with voluminous cations. Having these kinds of properties gives an advantage to montmorillonite clay mineral to be the host in the pillaring. By the choice of correct pillar agents, solids with the desired pore dimensions are obtained. Many kinds of pillaring agents and various pillaring processes have been investigated in an effort to improve the porous and catalytic properties of the pillared clay. Most of the research on PILCs has been focused on Al_{13} polyoxocation (Keggin ion) as a pillaring precursor. The solutions containing this complex are prepared through the hydrolysis of several salts of aluminium solution up to OH^-/Al^{3+} ratio of 2.5. Al-PILCs possessing the basal spacing (d_{001}) of 1.6–2.8 nm and high thermal stability were synthesised by several workers [2-4, 6-16].

When compared with other porous materials, pillared clays have some advantages, such as use of natural material and simple synthesis conditions. Because of

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[♠] Corresponding author, e-mail: ftomul@mehmetakif.edu.tr this, it is important to examine the suitability of the Middle Anatolian clay resources in pillared clay synthesis. In this study, Al-pillared bentonites synthesis has been achieved by using natural bentonite samples. In Al-PILCs, the degree of hydrolysis or basicity (OH_{base}/Al_{salt} ratio) is an important factor controlling the pH of the solution. Natural and pillared clays were characterized using XRF, XRD, FTIR, SEM and textural analysis by using N_2-adsorption/desorption isotherms. The effects of OH^-/Al^{3+} ratio in the pillaring solution on physico-chemical properties of Al-pillared clays and the change in these properties with the change in calcination temperature were examined.

2. EXPERIMENTAL

As the host materials, natural bentonite samples from Hancili region (Middle Anatolia, Turkey), named as Hancili Green Bentonite (HGB) and Hancili White Bentonite (HWB) according to their appearance, were used. Before the synthesis, bentonite samples, in the ratio of “gram bentonite/mL solution=1/11”, were mixed with a $CaCl_2$ solution (1 mol dm^{-3}) for 24 hours. Saturated bentonites were washed with deionized water until excess chloride ions were removed (checking with silver nitrate test) and dried at the room temperature [17].

2.1. Al-PILCs Synthesis

Synthesis of Al-pillared bentonite clays were carried out using the method mentioned in the reference [18], with some modifications**.** The pillaring solutions were prepared by adding 0.4 mol dm^{-3} NaOH solutions into the quantity, providing the desired OH^-/Al^{3+} ratio (between 1.0-2.5) at the flow rate of 0.5 mL min^{-1} onto the solutions of 0.4 mol dm^{-3} $AlCl_3.6H_2O$ at room temperature, while stirring vigorously. These solutions were aged at 65ºC for 18 hours in a shaking water bath and kept at room temperature for cooling.

The solutions of pillaring agents with different OH^-/Al^{3+} ratios were added by a flow of 2 mL min^{-1} to previously prepared 2 mass % bentonite suspension which was swelled in water for two days with pH of 9.10 under stirring. The derived suspension was stirred for 4 hours at room temperature and then kept overnight at room temperature. Then intercalated bentonites were filtrated, washed with deionized water several times to remove Cl^- anions, dried at room temperature and calcined at various temperatures (300ºC, 500ºC and 700ºC) for three hours. The synthesis conditions are shown in Table 1 [17].

2.2. Characterization of Samples

Chemical compositions of the natural and Al-pillared bentonite clays were determined using Philips X’ Cem X-Ray Fluorescence (XRF). Scanning electron micrographs were obtained from JEOL JEM 1200. E.X. scanning electron microscope. X-ray diffraction (XRD) patterns were derived with a Philips PW 3710 diffractometer using CuKα radiation. Single point BET surface area values of oven dried samples were determined at 77 K under continuous flow of 30 % nitrogen and 70 % helium mixture by using Quantachrome Monosorb Direct Surface Area Analyzer. The nitrogen adsorption/desorption isotherms, at 77 K, were obtained by using Quantachrome Authosorb 1C. Before the analysis, the samples were outgassed at 300ºC for 3 hours. FTIR spectra of pillared bentonites calcined at 300ºC and the pyridine adsorbed/desorbed samples at room temperature were obtained in the region of 400- 4000 cm^{-1} with a Ati Unicam Matson 1000 FTIR spectrometer by using KBr pelet technique. All samples were oven dried at 105°C to remove any adsorbed water. Each sample (approximately 1 mg) was finely ground, combined with oven–dried spectroscopic grade KBr (approximately 100 mg) and pressed into a disc and placed into a quartz IR cell.

3. RESULTS AND DISCUSSION

3.1. Properties of the Bentonites Used

Physicochemical and mineralogical characteristics of Hancili White Bentonite (HWB) were previously discussed in Balcı and Gökçay’s [19] research and they are reported in Table 2 together with the measured properties of the Hancili Green Bentonite (HGB). The mild greenish color of HGB comes from its iron content. The Si/Al ratio of HWB with a value of 3.98 was higher than the one of HGB. The exchangeable cations of HWB were lower than the contents of HGB. In X-ray powder diffraction patterns, it was shown that reflections belonging to 001 plane, natural bentonite clays HGB (d-spacing =1.24 nm, 2θ=7.12º), HWB (d-spacing = 1.25 nm, 2θ=7.06º) were in Na^+ form (Table 2, Figure 1).

3.2. Effect of the Host on the Properties of Al-Pillared Bentonites

The XRD patterns of Al-pillared bentonite clays calcined at different temperatures are shown in Figure 1 and the basal spacing values are summarized with the surface area values in Table 1. Both properties depend on the chemical nature of the host and the synthesis conditions of the pillar agent. The pillared bentonites showed the properties usually described for Al-pillared clays, widely studied in the literature [2, 3, 9, 11, 20-23].

The number of intercalating species introduced between the layers have effects especially on the interpillar distance- and as a result large effects on surface area values and strength of crystal structure- while the size of them have more effects on basal spacing (d_{001}). Both interpillar distance and basal spacing could be modified by the synthesis conditions and the calcination step. The pillar density, within the samples synthesized from HWB, could be high due to the high cation exchange capacity, so HWB host resulted in samples with higher surface area values with the gained thermal stability than the ones obtained from HGB.

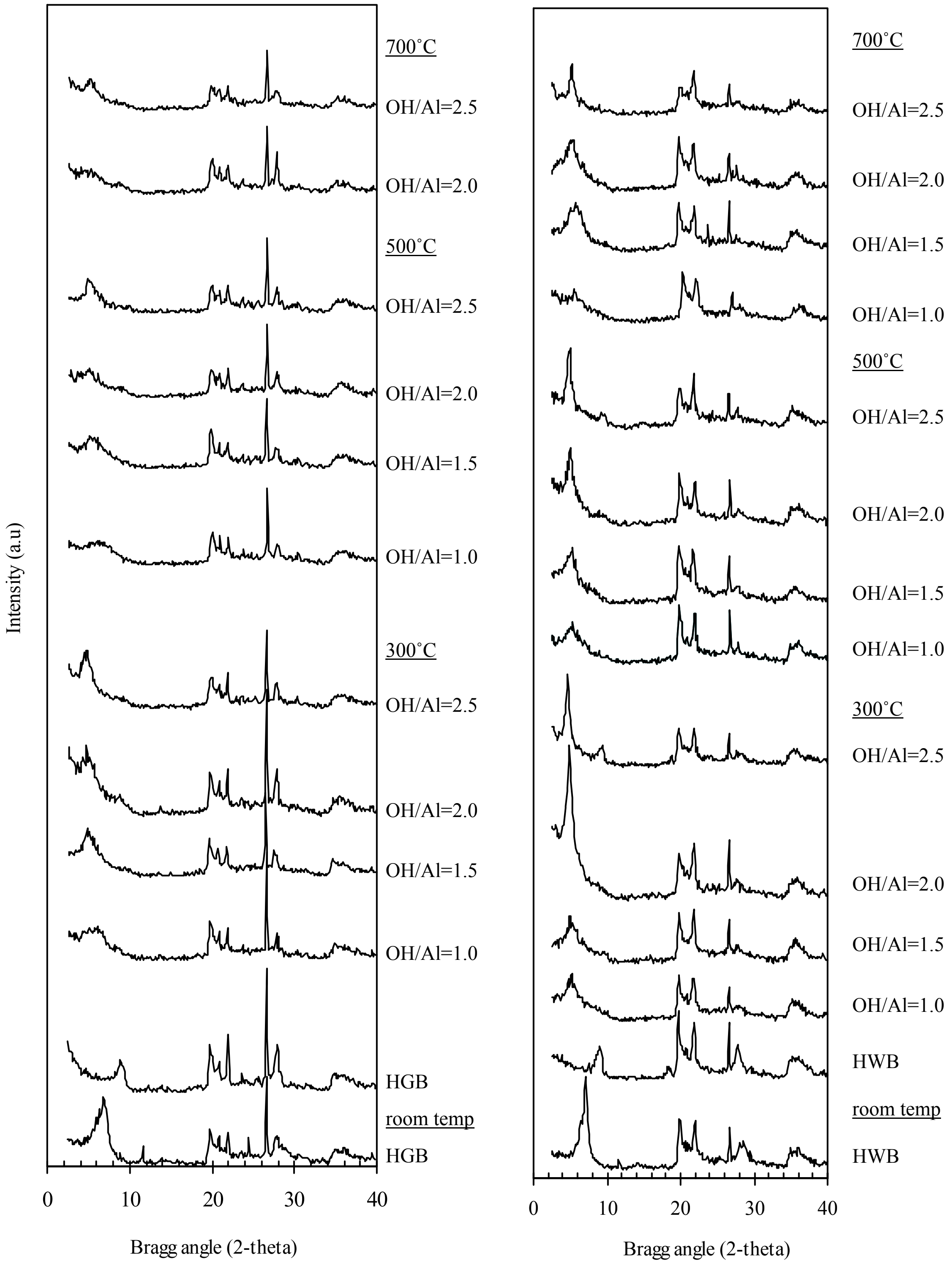
Table 1. Synthesis conditions of Al-pillared bentonite clays and basal spacing (d_{001}) and single point surface area ($S_{sp,\ BET}$) values at different calcination temperatures (aging temp.=65ºC, aging time=18 h, ion exchange time=4 h, ion exchange temp.=room temperature, 2 mass % bentonite suspension).

Host mineral	OH^-/Al^{3+}	Synthesis conditions				Al-PILC calcined at 300ºC		Al-PILC calcined at 500ºC		Al-PILC calcined at 700ºC	
		pH of the pillaring solution before aging	pH of the pillaring solution after aging	pH of the pillaring sol.-bentonite suspension before ion exchange	pH of the pillaring sol.-bentonite suspension after ion exchange	d_{001} (nm)	$S_{sp,\ BET}$ (m^2g^{-1})	d_{001} (nm)	$S_{sp,\ BET}$ (m^2g^{-1})	d_{001} (nm)	$S_{sp,\ BET}$ (m^2g^{-1})
HGB	1.0	3.63	3.93	4.02	3.71	1.62	126	pno	95	-	83
HGB	1.5	4.04	3.89	4.21	4.30	1.77	147	1.70	120	-	86
HGB	2.0	4.12	3.78	4.06	3.90	1.80	213	1.71	139	1.68	125
HGB	2.5	5.08	4.81	5.44	5.33	1.84	214	1.76	173	1.71	144
HWB	1.0	3.50	3.66	3.82	3.75	1.69	164	1.65	132	1.51	90
HWB	1.5	3.78	3.75	4.02	3.94	1.78	178	1.65	147	1.54	111
HWB	2.0	4.14	4.06	4.17	4.15	1.83	227	1.78	191	1.76	152
HWB	2.5	5.62	5.08	5.73	5.31	1.90	259	1.81	196	1.78	169

pno : peak was not observed

Table 2. Physicochemical compositions of the natural and Al-pillared HWB clays.

Metal oxides %	HGB	HWB[19]	Al-pillared Hancili White Bentonite clays			
			OH^-/Al^{3+}-1.0	OH^-/Al^{3+}-1.5	OH^-/Al^{3+}-2.0	OH^-/Al^{3+}-2.5
SiO_2	66.95	70.51	65.85	65.04	63.79	59.09
Al_2O_3	18.38	17.70	23.84	24.34	24.65	29.09
Fe_2O_3	6.11	4.11	4.11	4.33	4.59	4.55
MgO	2.75	3.26	2.83	2.89	3.10	3.24
CaO	1.80	1.59	0.01	0.04	0.00	0.00
Na_2O	2.81	2.10	2.62	2.62	3.03	3.20
K_2O	1.19	0.74	0.74	0.74	0.84	0.83
Single point BET, $S_{sp,\ BET}$ (m^2g^{-1})	76.8	56.8				
d_{001}, nm (at room temperature)	1.24	1.25				
d_{001}, nm (at 300^{0}C)	0.99	0.99				
CEC, meq $(100g)^{-1}$	50	66				



(A) Hancili Green Bentonite

(B) Hancili White Bentonite

Figure 1. XRD patterns of host bentonites (HGB and HWB) and of Al-pillared bentonite clays synthesized with different OH/Al ratios and calcined at different temperatures.

In Al-pillared bentonite clays calcined at 300°C, an increase of 001 diffraction peak intensities and basal spacing and surface area values were observed parallel to the increase of OH^-/Al^{3+} ratio in pillaring solutions. However, when OH^-/Al^{3+} ratios were increased, there was no difference at diffraction peaks between values 20º and 40º of 2-theta. For the samples obtained with OH^-/Al^{3+} ratio of 1.0, the basal spacing values were measured as 1.62 nm (2θ=5.45º) for HGB and 1.69 nm (2θ=5.22º) for HWB and small increases were obtained by increasing OH^-/Al^{3+} ratios till 2.0. The values were reached to 1.84 nm (2θ=4.79º) and 1.90 nm (2θ=4.65º) respectively for the ones obtained with OH^-/Al^{3+} ratio of 2.5. The single point BET surface area values of Al-pillared bentonites obtained from HGB and HWB with OH^-/Al^{3+} ratio of 1.0 were measured as 126 m^2g^{-1} and 164 m^2g^{-1} levels respectively at 300ºC and showed an increasing trend with increasing OH^-/Al^{3+} ratio. Use of pillaring solutions with high OH^-/Al^{3+} ratio (between 2.0-2.5) in the pillaring process, size/stability of pillaring agents and distribution within the matrix resulted in development of surface properties, hence thermal stability of pillared bentonite clays. As a result of this, for Al-pillared bentonite clays with a OH^-/Al^{3+} ratio of 2.0 and especially 2.5, narrow and high intensity 001 diffraction peaks were observed with higher surface area values. Observation of narrow peak width supported the formation of similar sized pores as the result of uniform distribution of pillars within the clay sheets (see Section 3.4). This distribution of pillars minimizes deformation of the pillared structure that could occur with temperature increase (Table 1, 3, Figure 1).

The increase of calcination temperature caused decreases in basal spacing and single point BET surface area values for both types of the Al-pillared bentonite clays synthesized, especially with OH^-/Al^{3+} ratio < 2.0, as seen in Table 1 and Figure 1. The structure on the 001 plane acquired a tendency to be ruined after the calcination at 500°C; so broadening of peak and, as a result, decrease in surface area values, were observed. The most obvious decrease in single point BET surface area by temperature was observed in HGB product whose OH^-/Al^{3+} ratio was 1.0 and on which peak hadn't been seen on the 001 plane with 95 m^2g^{-1} value. The increase of OH^-/Al^{3+} ratio caused increases in thermal stabilites of Al-PILCs resulting in a more sturdy structure parallel to the increase of basal spacing and surface area values. Single point BET surface area values of pillared bentonite clays obtained from HGB and HWB with OH^-/Al^{3+} ratio of 2.5, determined as 214 m^2g^{-1} and 259 m^2g^{-1} at 300ºC calcination temperature, showed around 33-35 % decrease by the increase of calcination temperature to 700ºC. The surface area of Al-pillared HWB was preserved even at 700ºC, resulting in 169 m^2g^{-1} value by use of pillaring solution with OH^-/Al^{3+} ratio as 2.5.

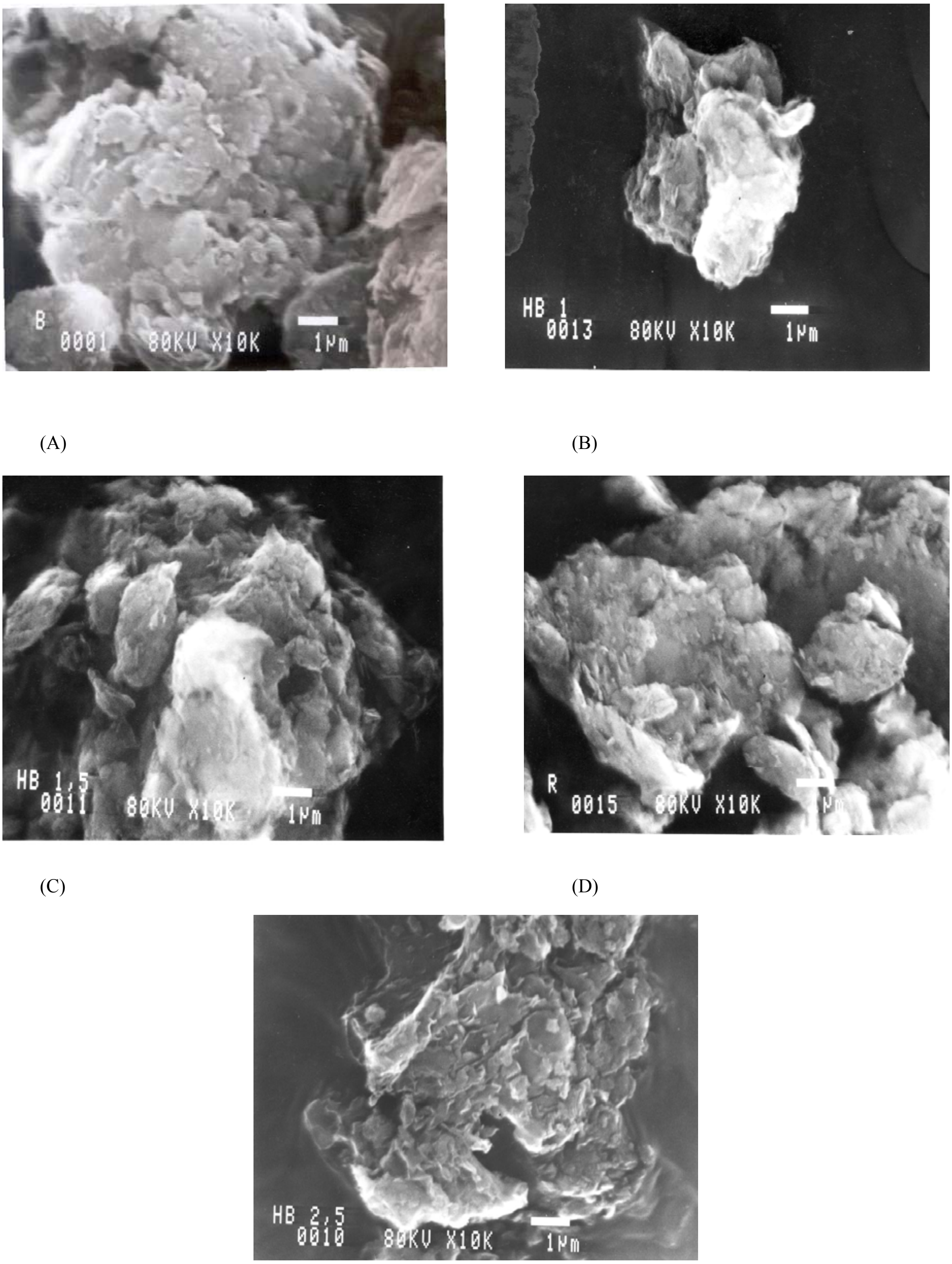
3.3. Chemical Compositions of Al-Pillared Bentonites Synthesized from HWB

Chemical compositions of pillared bentonite clays are given in Table 2. As expected, Al_2O_3 contents of the products were found to be higher than the host and increased by the increase of OH^-/Al^{3+} ratio. This observation supported that Al-pillaring agents were settled between clay layers and increasing of OH^-/Al^{3+} ratio resulted in the formation of larger sized pillaring agents with high aluminium content. Si/Al ratio, which was observed as 3.98 for HWB, decreased to 2.59 and 2.03 after pillaring by the use of pillaring solutions having OH^-/Al^{3+} ratio of 2.0 and 2.5 respectively. In addition, considerable decrease of Ca^{2+} content with pillaring showed that the mainly exchanged cation with the Al-pillaring agent was the calcium cation. The observed increase in Na_2O content by the increase in OH^-/Al^{3+} ratio could have resulted from the possible absorption of Na^+ ions that were liberated with ionic decomposition of NaOH by clay structure.

3.4. Textural Properties of Al- Pillared Bentonites Synthesized from HWB

It was established that there was an improvement in porous structure with increasing OH^-/Al^{3+} ratio and that tightly packaged structure of the original clay sample were opened in the products, especially for products synthesized with base/metal ratio is 2.0 and 2.5 (Figure 2).

The nitrogen adsorption/desorption isotherms of the natural and Al-pillared HWB clays are shown in Figure 3. All isotherms were type IV of the BDDT classification, and in all isotherms H4 type hysteresis (that shows formation of mesopores between interlayers) formed during desorption because of absorption in mesopores in high partial pressures [24]. Internal total surface area (S_t), external surface area (S_{ext}), and micropore volume (V_μ) values were obtained from t-plots using de Bore thickness and are summarized in Table 3 together with multi point BET surface area ($S_{mp,\ BET}$), BJH meso surface area (S_{BJH}), total pore volume (V_p), cumulative mesopore volume ($\sum V_{mp}$) and pore diameter (d_a and d_{mp}) values.

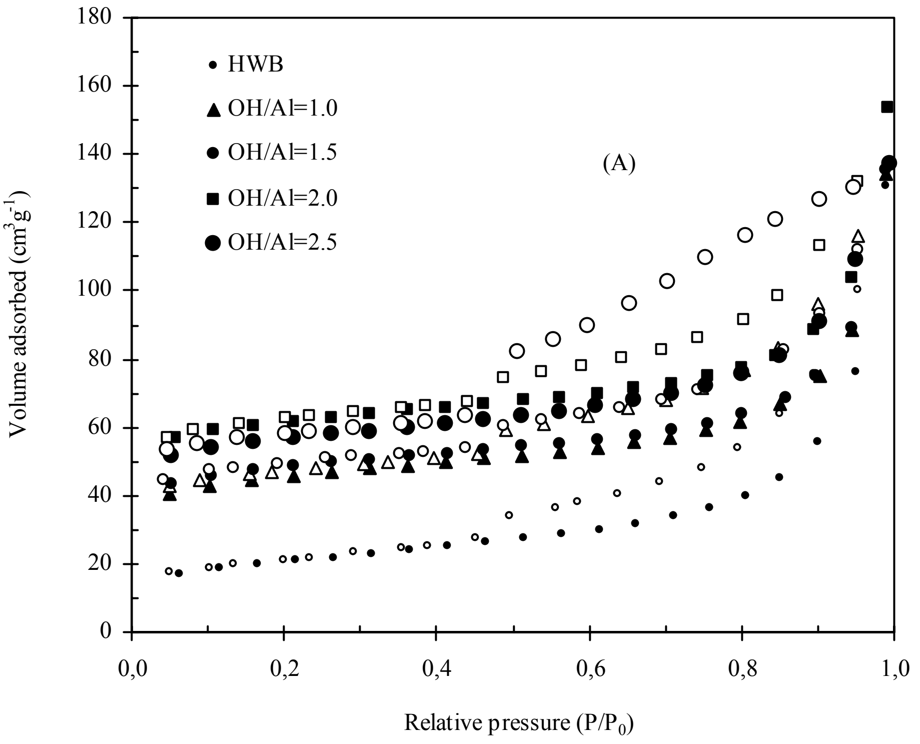


(A) (B)

(C) (D)

(E)

Figure 2. SEM micrographs of natural (HWB) and Al-pillared HWB clays synthesized with different OH/Al ratios (A) HWB; (B) OH/Al = 1.0 (C) OH/Al=1.5 (D) OH/Al = 2.0 (E) OH/Al = 2.5.



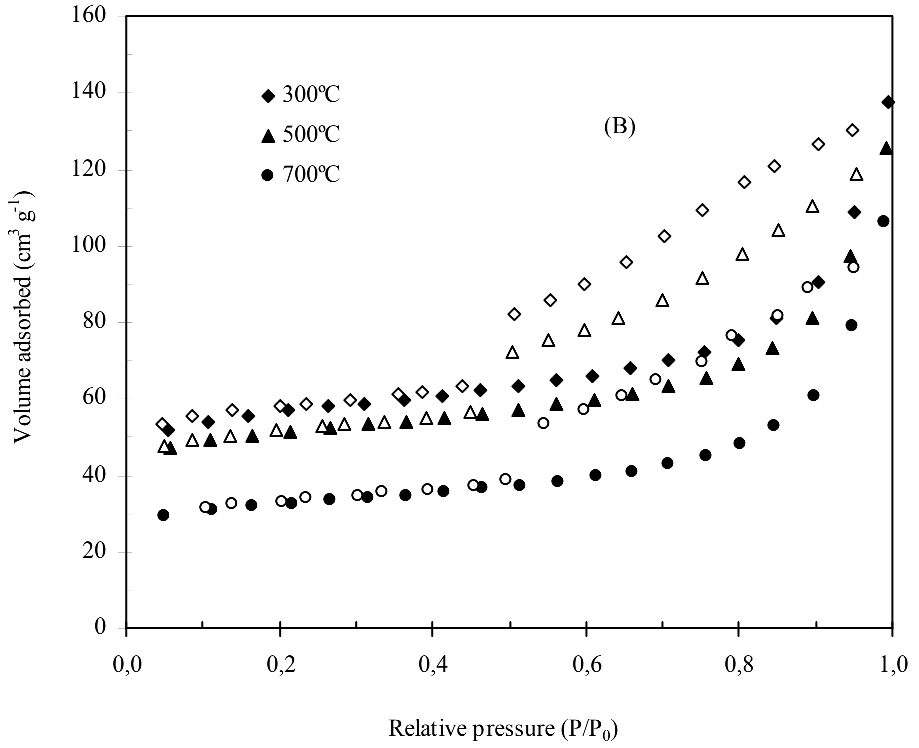


Figure 3. Nitrogen adsorption/desorption isotherms at 77 K (filled symbols for adsorption; open symbols for desorption) (A) natural HWB and Al-pillared HWB clays with different OH/Al ratios, calcined at 300ºC (B) Al-pillared HWB with OH/Al=2.5, calcined at different temperatures.

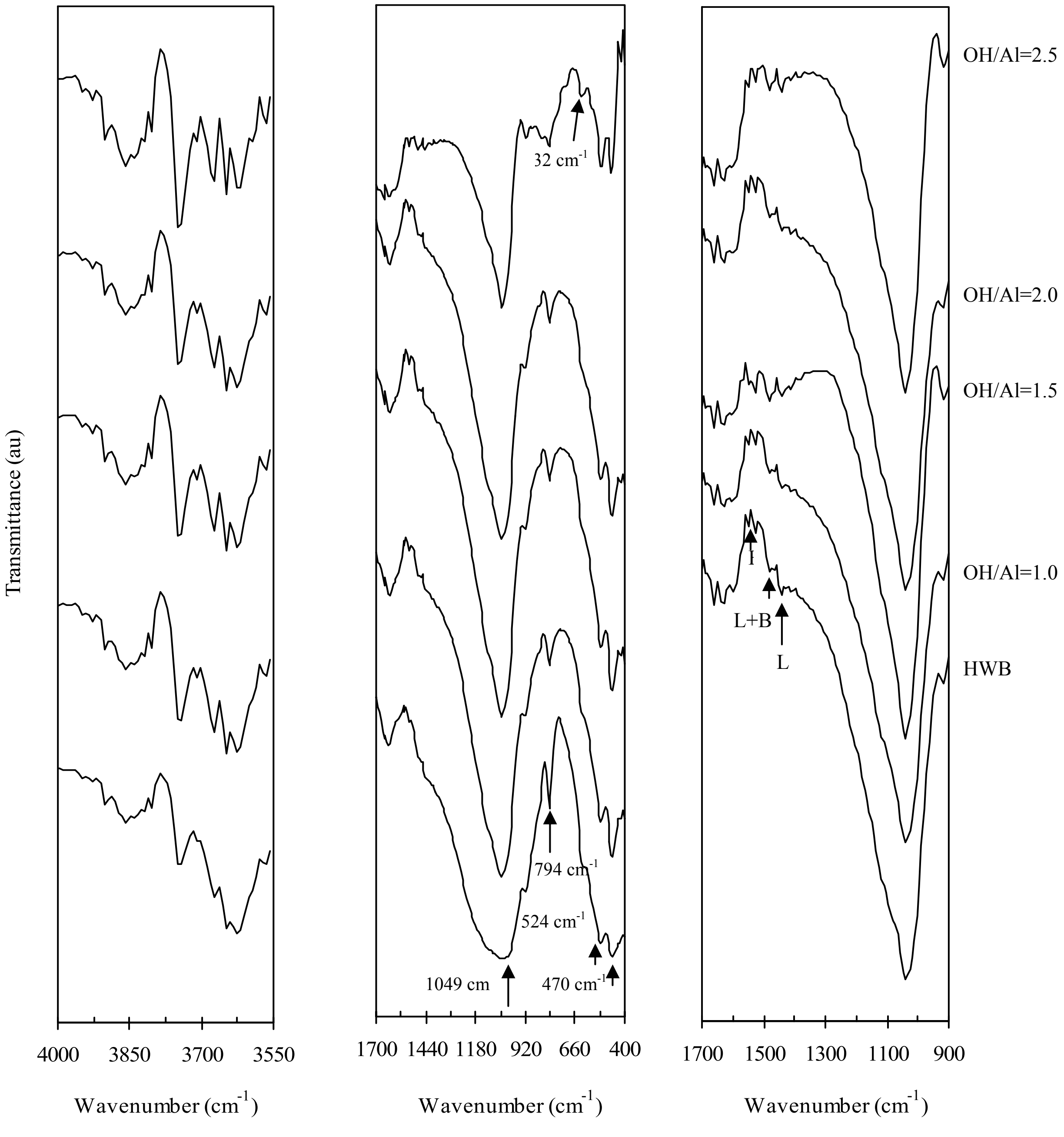
Table 3. Textural properties and basal spacing values of the natural HWB and of the Al-pillared HWB clays.

OH^-/Al^{3+}	Surface area (m^2g^{-1})				Pore Volume (cm^3g^{-1})			Pore Diameter (nm)		Basal spacing (nm)
	S_t	$S_{mp,BET}$	$S_{ext.}$	S_{BJH}	V_p	V_μ	$\sum V_{mp}$	d_a	d_{mp}	d_{001}
300ºC										
natural	77	70	64	64	0.180	0.001	0.148	11.48	3.81	0.99
1.0	168	149	53	59	0.193	0.045	0.131	5.57	3.80	1.69
1.5	192	157	50	52	0.194	0.051	0.117	5.34	3.72	1.78
2.0	248	198	52	57	0.218	0.071	0.131	4.81	3.73	1.83
2.5	227	182	62	119	0.198	0.058	0.164	4.43	3.81	1.90
500ºC										
2.5	209	164	57	95	0.186	0.052	0.146	4.74	3.84	1.81
700ºC										
2.5	124	105	54	98	0.154	0.023	0.148	6.24	3.83	1.78

S_t : Internal total surface area obtained from the slope of the first linear segment of t-plot
$S_{mp,BET}$: Multi point BET surface area obtained from nitrogen isotherm ($0.05 < P/P_0 \leq 0.26$)
$S_{ext.}$: External surface area (corresponding to larger pores) obtained from the slope of second linear segment of t-plot ($0.05 < P/P_0 \leq 0.96$)
S_{BJH} : Cumulative desorption surface area obtained from BJH method ($P/P_0>0.30$)
V_p : Total pore volume at $P/P_0=0.98$
V_μ : Specific micropore volumes (obtained from the intercept of second linear segment of t-plots)
$\sum V_{mp}$: Cumulative mesopore volume obtained from desorption data (for $P/P_0 < 0.96$)
d_a : Average pore diameter from single pore model
d_{mp} : Mesopore diameter determined from BJH desorption data ($P/P_0>0.30$)
d_{001} : basal spacing

It was observed that natural bentonite and Al-pillared clays' surface properties developed via pillaring and increase of OH^-/Al^{3+} ratio. Total internal surface area and multi point BET surface area values of natural bentonite clay (HWB) were determined as 77 $m^2\,g^{-1}$ and 70 $m^2\,g^{-1}$ and were increased to 168 m^2g^{-1} and 149 m^2g^{-1} respectively by pillaring with OH^-/Al^{3+} ratio of 1.0 (Figure 3A and Table 3). Despite no considerable increase being observed, in total pore volume of natural clay with pillaring process, micro pore volume determined as 0.001 $cm^3\,g^{-1}$ had reached to 0.045 $cm^3\,g^{-1}$ in pillared clay with OH^-/Al^{3+} ratio of 1.0. However, it was observed that the increase in total surface area and micropore volume values continued until OH^-/Al^{3+} ratio of 2.0. The surface area values (S_{ext} and S_{BJH}), which gave an idea about the mesopore distribution, were also decreased within the same range. So it could be said that the increase of OH^-/Al^{3+} caused increases in the number of micropores and value of micropore surface area [25]. Further increase in OH^-/Al^{3+} resulted in decreases in total surface area and pore volume. This result could be explained as a change in mesopore structure by the formation of larger sized pores. Around 12 % of cumulative mesopore volume values decreased due to pillaring with OH^-/Al^{3+} of 1.0. However, it was established that by the increase in OH^-/Al^{3+}, mesopore volume values were increased about 25%. The increase in OH^-/Al^{3+} ratio caused negligible changes in mesopore diameter values, while average pore diameter values, which were calculated by single pore model approach, were decreased. The surface area values (S_{ext} and S_{BJH}) which gave an idea about the mesopore distribution were also decreased with pillaring in pillared bentonites with OH^-/Al^{3+} ratio of 1.0-2.0.

As in the basal spacing values, it was observed that the surface area and pore volume values were decreased by the increase in calcination temperature. However, the fact that obtained values were higher than the values of the host clay, despite the decrease in surface properties in relation to increase in calcination temperature from 300ºC to 700ºC, showed that pillared structure was preserved and products were stable up to 700ºC. This result was also confirmed by small changes that occured in 001 diffraction peak intensities and widths, in the X-ray diffraction patterns at 700ºC calcination temperature (Tables 1-3, Figure 1).



(A) (B) (C)

Figure 4. FTIR spectra of HWB and Al-pillared HWB clays with different OH/Al ratio and calcined at 300ºC in the range of (A) 4000-3550 cm^{-1} (B) 1700-400 cm^{-1} and (C) after pyridine desorption at room temperature 1700-900 cm^{-1}.

3.5. Acidic Characteristics of Al-Pillared Bentonites Synthesized from HWB

FTIR spectra of natural HWB and Al-pillared bentonite clays are given in Figure 4. For natural HWB and Al-pillared bentonite clays having various OH^-/Al^{3+} ratios, bands corresponding to the water molecules present in the interlayers and the structural hydroxyl groups in the clay layers were observed in the region between 3550-4000 cm^{-1}; and there occurred an increase in peak intensities with pillaring and increase in OH^-/Al^{3+} ratio. Characteristic silicate bands were found between 1200-400 cm^{-1}. It was also observed that there was no change by pillaring in 1049 cm^{-1} broad peak, resulting from Si-O-Si stretching vibration, but there occurred a small decrease in peak width. The bands at 524-470 cm^{-1} originated from Si-O bending and Al-O stretching vibration, and there were no changes in Si-O bending, but a small increase in Al-O stretching in intensity by pillaring. This situation was supported by the increase in Al content of pillared samples by the increase in OH^-/Al^{3+} ratio (Table 2). Aluminum pillaring agent had caused a decrease in the free silica peak intensity which occurred at 794 cm^{-1}. A new band was observed in 632 cm^{-1} in the product whose OH^-/Al^{3+} ratio is 2.5. This band pointed to the Al-O connection that was in a tetrahedral coordination with aluminum cations, which is at the centre of Al_{13}-pillaring agent [11-13].

When spectra of Al-pillared bentonites obtained after pyridine adsorption/desorption were evaluated, it had been revealed that Al-pillared bentonites could have some small bands characterizing Lewis (1450 cm^{-1}), Lewis+Brønsted (1488 cm^{-1}) and Brønsted (1550 cm^{-1}) acid sites [2, 11]. The location and intensities of acidic bands didn't change with OH^-/Al^{3+} ratio values (Fig. 4c).

4. CONCLUSIONS

In Al-pillared bentonite clays' synthesis, solutions prepared in 1.0-2.5 OH^-/Al^{3+} ratios by base hydrolysis of aluminium chloride and natural bentonite clays were used. It was observed that physico-chemical properties of Al-pillared bentonite clays changed in relation to OH^-/Al^{3+} ratio in pillaring solution and calcination temperature, as mentioned in the literature. It was observed that basal spacing, surface area values and resistance against temperature effects of pillared bentonites improved by the increase of OH^-/Al^{3+} ratio. Higher surface area and basal spacing values were resulted by use of HWB with the gained thermal stability. Results obtained from FTIR spectra showed that there were changes in the clay structure with pillaring. FTIR spectra showed that Al-pillared Hancili White Bentonite possesses both Lewis and Brõnsted acid sites.

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