

EFFECTS OF SYNTHESIS CONDITIONS ON THE THERMAL STABILITY OF A TEXAS MONTMORILLONITE EXPANDED WITH $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ CATIONS

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INTRODUCTION

Smectites, when expanded with metal clusters, can generate layered microporous solids with an appropriate acidity, pore size, and thermal stability required for catalysts used in conventional chemical (Pinnavaia, 1983) and petrochemical processes (Figueras, 1988; Occelli, 1989). The detailed description of the ion-exchange reactions that produce pillared interlayered clay (PILC) and the conditions necessary to generate thermally stable PILC are still a subject of some debate and controversy.

Investigations of the hydrolysis reactions of aqueous solutions of aluminum salts (Hsu and Bates, 1964; Baes and Mesmer, 1976; Bottero *et al.*, 1980, 1982; Brosset *et al.*, 1954; Bailar, 1956) showed a complicated, pH-sensitive equilibrium between $Al(H_2O)_6^{3+}$, $[Al_2(OH)_2(OH_2)_4]^{4+}$, $[Al_3(OH)_4(OH_2)_9]^{5+}$, and the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ($= Al_{13}$). Dilution and refluxing of the aluminum chlorhydrol (ACH) solution affects the concentration of the Keggin species in the pillaring solution (Bottero *et al.*, 1982). Nonetheless, in PILC, the Keggin ion may not be the sole ion in the phyllosilicate interlayer (Schoonheydt *et al.*, 1994). Upon heating, Keggin ions may undergo condensation reactions in the interlayer with the formation of higher polymers such as the Al_{24} -polycation (Fu *et al.*, 1991). Moreover, the $[Al_{41}O_{32}(OH)_{48}(H_2O)_{24}]^{11+}$ complex has been isolated from aged ACH solution (Fitzgerald, 1988), and its presence in certain PILC samples cannot be excluded.

The micropores of calcined Al_{13} -pillared montmorillonites and volumes computed by multiplying the number of pillars present by the density of bulk alumina have been studied previously (*e.g.*, Maes *et al.*, 1995). The calculated volume was ~47% larger than the experimental value determined using the t-plot method of Lippens and de Boer (De Boer *et al.*, 1966). The volume discrepancy was attributed to layer collapse owing to the presence of pillaring agents different from the Keggin ion (Maes *et al.*, 1995).

Schutz *et al.* (1987) have reported that although nuclear magnetic resonance (NMR) analysis of the pil-

laring solution gave an $^{VI}Al/^{IV}Al$ ratio of 12 consistent with Al_{13} (Plee *et al.*, 1985; Johansson, 1960), pillared beidellites did not appear to be expanded. Expansion of the interlayer by Keggin ions was obtained only after extensive washing of the reaction product with water. The purpose of this note is to report the effects of post synthesis washing on montmorillonite expanded with ACH solutions and to examine the dependence of PILC thermal stability on the concentration of the reactants.

EXPERIMENTAL METHODS

All PILC samples were prepared using bentolite-H (Na-bentonite) obtained from Southern Clay Products, Inc., Gonzales, Texas. The sample contains >90% montmorillonite. Quartz (~3.9%) is the main impurity; trace amounts of calcite, dolomite, and rutile are also present. It was assumed that the sample is free from colloidal silica impurities. Chemical analysis gave a unit-cell composition of $[(Si_{8.0})(Al_{3.02}Mg_{0.50}Ca_{0.06}Fe_{0.18}Ti_{0.02}Na_{0.22})O_{20}(OH)_4]Na_{0.97}K_{0.01}$ and a charge per cell of 0.98 for the 2:1 layer. If present, colloidal silica could affect the derived composition and the accuracy of the calculations presented in this paper.

ACH, an acidic solution which contains 24.0 wt. % Al_2O_3 , was diluted to 1.0 wt. % solution with deionized water and aged at 70°C for 12 h. A 5.0-g sample of Na-rich montmorillonite was dispersed in 0.5 L of deionized water and stirred at 60°C for 12 h. The ACH solution was added to the clay slurry, and deionized water was then added to the resulting suspension until the final volume was 1.0 L; the slurry pH was ~5.0. This mixture was stirred at 60°C for 8 h, then filtered and washed with deionized water until no chloride was detected in the filtrate. The samples were air-dried at room temperature for 24 h and then oven-dried at 100°C for an additional 24 h. This process produced a PILC sample that was further examined.

Effects of post synthesis washing with water were investigated by using the exchanged montmorillonite described above. The pillared product was filtered, and a small portion of the cake (sample A) removed for later analysis. The pH of the filtrate was determined

Table 1. Washing volumes for PILC samples prepared from ACH/clay = 1.0.

Sample	wt. % Al	Washing volume (mL)	Filtrate pH
1. ACH-S3-A	10.52	0.0	5.0
2. ACH-S3-B	10.61	400	5.4
3. ACH-S3-C	10.44	800	6.3
4. ACH-S3-D	10.36	1200	6.9
5. ACH-S3-E	10.42	1600	7.2

(Table 1). The remaining cake was resuspended in 400 mL of deionized water and stirred at room temperature for 2 h. After filtration, a second portion (sample B) was removed from the washed cake. This procedure was repeated until the original exchanged montmorillonite had been resuspended in a total of 1.6 L. All samples collected were first air-dried at room temperature for 24 h and then oven-dried at 100°C for another 24 h. See Table 1 for results.

Determination of Al and Si concentration was performed by Galbraith Laboratories, Knoxville, Tennessee, using atomic absorption; the accuracy is $\pm 2\%$. The atomic force microscope used to examine clay surfaces was described in detail elsewhere (Occelli and Gould, 1993).

Powder X-ray diffraction data were collected on a Scintag X1 diffractometer with unfiltered $\text{CuK}\alpha$ radiation, fixed divergence slits, and a Peltier-cooled solid-state detector. A convergent slit width of 1 mm and a scatter slit width of 2 mm were employed for the beam source; a receiving slit width of 0.3 mm and scatter slit width of 0.5 mm were used for the detector. Data were analyzed using version 1.12 DMSNT software. Clay samples were pre-dried at 100°C for 12–24 h under a 30-mm Hg vacuum immediately prior to data collection. Scans were made in continuous mode at a rate of 2°/min or less.

Nitrogen-sorption isotherms were collected using a Micromeritics ASAP 2010 adsorption instrument equipped with version 3.0 software. Prior to analysis, samples weighing from 0.1 to 0.3 g were outgassed in vacuum at 400°C for at least 16 h. The total pore volume was derived from the amount of nitrogen adsorbed at a relative pressure close to unity ($p/P_0 = 0.995$) by assuming that all the accessible pores were then filled with liquid nitrogen.

RESULTS AND DISCUSSION

Effects of washing

Elemental-analysis results for the Al-PILC are given in Table 1. These samples were prepared with an excess of ACH. Data in Table 1 indicate that, as the amount of water increases, the filtrate pH increases to 7.2 from 5.0. In addition, the various steps in washing did not significantly affect the Al content of the PILC. Thus, differences in d value observed in the powder

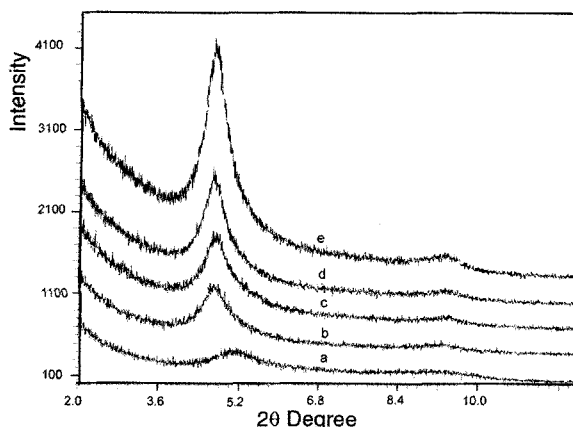


Figure 1. X-ray diffractograms for Al_{13} -PILC washed with: a) 0, b) 400, c) 800, d) 1200, and e) 1600 cc of water. Intensity is in counts per seconds (cps).

X-ray diffractograms (Figure 1) cannot be attributed to interlayer Al removal during washing. Figure 1a shows that initially, the $d(001)$ peak of the Al-PILC is broad and weak owing to the presence of different interlayer expansion, but then shifts to ~ 1.89 nm after the first washing (Figure 1b). The $d(001)$ reflection becomes sharper as the washing is repeated (Figure 1c–e). The expansion of the washed Al-PILC is consistent with the formation of the Al_{13} species. Similar observations were reported for pillared beidellite (Plee *et al.*, 1985).

The increase in d spacing with repeated washings (Figure 1) indicates that after the pillaring reaction, the primary intercalants are not Keggin ions and that the Al_{13} complex is forming *in situ* via base hydrolysis of the different oligomers present in the interlayer. In fact, washing with water having a pH of 5 did not generate an expansion of the clay, as indicated in Figure 1. Post-exchange washing is therefore an essential step in producing an expanded clay containing Keggin ions that is also free of Cl^- impurities.

Effects of ACH/clay ratios

The effects of the concentration of the reactants on PILC properties are shown in Table 2. These samples were washed with an excess (1.6 L) of water; powder X-ray diffraction (XRD) data for these samples are

Table 2. Elemental analysis of several PILC samples prepared from different ACH/clay ratios.

Sample	ACH/clay	wt. % Al	wt. % Si	mol Si/Al
Bentolite-H	—	6.70	32.2	4.27
ACH-S3-1	0.20	9.87	—	—
ACH-S3-2	0.40	10.06	30.0	2.86
ACH-S3-3	0.60	10.16	28.3	2.67
ACH-S3-4	0.80	10.30	—	—
ACH-S3-5	1.00	10.63	—	—

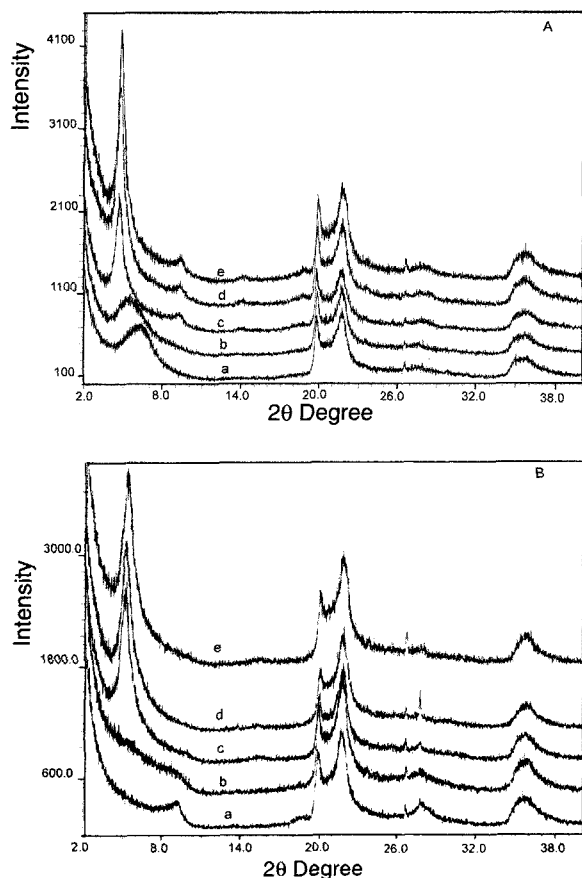


Figure 2. X-ray diffractograms for Al_{13} -PILC samples containing the following wt. % Al: a) 9.87, b) 10.06, c) 10.16, d) 10.30, and e) 10.63. A) Al_{13} -PILC samples dried at $100^\circ\text{C}/12$ h and, B) Al_{13} -PILC samples calcined at $500^\circ\text{C}/10$ h. Intensity is in counts per seconds (cps).

shown in Figure 2. Reaction mixtures containing an ACH/clay (wt./wt.) ratio of <0.6 yield a pillared product in which the d value involving the Keggin ion is noticeably absent (Figure 2A). In fact, the broad (001) peaks in the diffractogram of samples 1 and 2 are at $2\theta = 4\text{--}7^\circ$, that is, between the predicted expansion of the Keggin-containing PILC and the $d(001)$ value of the parent clay. The width of this peak indicates that variations in the interlayer spacing are present. After calcination at 500°C , an expanded structure disappears and the $d(001)$ peak for samples 1 and 2 (Table 2) is reduced to 0.99 nm, which is close to the 0.96-nm value observed in the parent clay (Figure 2B).

As the ACH/clay ratio in the reaction mixture increases to >0.6 , the $d(001)$ reflection of the pillared product shifts to lower diffraction angles, indicating that expansion of the clay by Keggin ions has occurred (Figure 2A). For ACH/clay ratios <0.6 , clay expansion is not present after heating at 500°C . In contrast, samples prepared from mixtures with ACH/clay ratios >0.6 undergo only a small decrease in d value (sam-

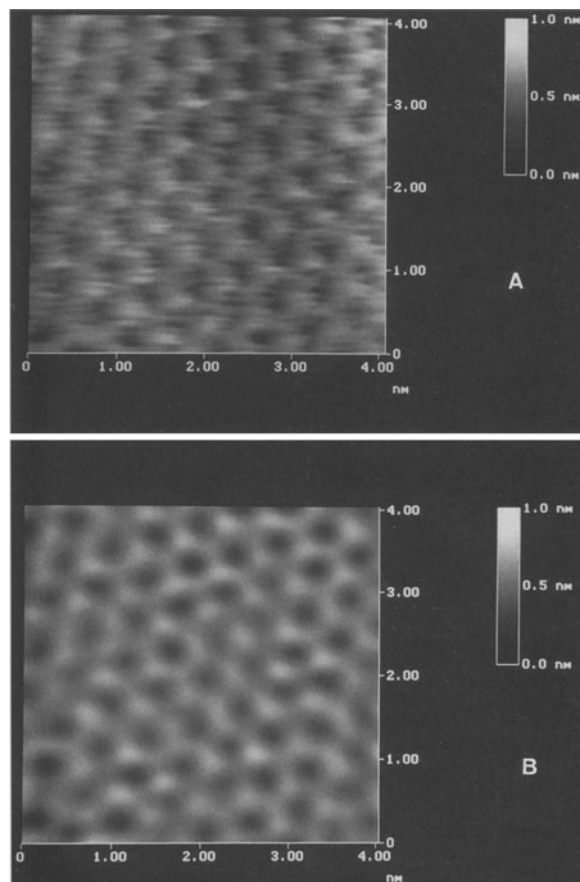


Figure 3. Molecular scale AFM images of a PILC prepared from a reaction mixture with ACH/clay = 1. A) Raw image and B) the raw image after two-dimensional fast Fourier transform filtering.

ples 3, 4, and 5) on calcination that is attributed to Keggin-ion dehydroxylation (Figure 2B). The BET surface area (SA) of these PILC samples after drying in air at 100°C and calcination at 500°C was in the $254\text{--}275$ m^2/g range and their pore volume was $0.18\text{--}0.20$ cc/g . Therefore, PILC prepared from reaction mixtures with ACH/clay <0.6 are not as thermally stable as those prepared from mixtures with ACH/clay >0.6 . With these XRD results and the data in Table 2, it is possible to estimate the minimal amount of interlayer Al species required for a microporous PILC structure to be stable at 500°C .

Pillar density and thermal stability

Atomic force microscopy (AFM) images of the basal (001) plane of the PILC are shown in Figure 3. Images of the surface of the PILC tetrahedral sheet are composed of hexagonal rings of white spots (Hartman *et al.*, 1990; Lindgreen *et al.*, 1991), where each white spot is believed to represent the three basal oxygens that form a SiO_4 unit (Occelli *et al.*, 1993). The repeat

distances between white spots are 0.54 and 0.93 nm, in agreement with the unit-cell dimensions. Thus, the images in Figure 3 suggest that, with the synthesis procedure used here, the surface does not contain sorbed Al-rich species. Thus all the Keggin ions are located within the montmorillonite interlayer.

To compute the PILC pillar density and possibly to relate pillar density to thermal stability, the amount of extraframework Al within the interlayer must be first determined. The parent clay contains 6.7 wt. % Al and 32.2 wt. % Si. However, XRD results indicated the presence of ~ 3.9 wt. % quartz. The contribution of this impurity must be subtracted from the sample total Si concentration to determine the framework Si content of the clay. The contribution of this impurity (Si_q) to the total silicon content is 0.018 g Si/g clay. After subtracting the quartz contribution, the clay framework contains 30.4 wt. % Si, implying a structural Al/Si molar ratio of 0.229. The wt./wt. ratio of extraframework silicon (Si_q) to the clay total Si concentration is $\text{Si}_q/\text{Si}_{\text{clay}} = (1.8)/(32.2) = 0.0559$. In subsequent calculations, it is assumed that this ratio remains constant after the pillaring process.

XRD results (Figure 2) show that a PILC containing 10.06 wt. % Al and 30.0 wt. % Si (sample 2, Table 1) is unstable at 500°C. If we let $\text{Si}_q/\text{Si}_{\text{clay}} = \text{Si}_{q,\text{PILC}}/\text{g PILC}$, then this PILC will contain $0.30 \times 0.0559 = 0.0168$ g $\text{Si}_{q,\text{PILC}}/\text{g PILC}$ and the PILC has a framework silicon content of $0.30 - 0.0168 = 0.2832$ g Si/g PILC implying an Al/Si molar ratio of 0.370. The number of moles of extraframework Al can now be calculated by subtracting from the Al/Si molar ratio of the Al-PILC the structural Al/Si molar ratio of the parent clay. Thus $\text{Al/Si} = 0.370 - 0.229 = 0.141$ are the moles of extraframework Al per mole of framework Si. By multiplying this ratio by the moles of framework Si in the PILC, the number of moles of extraframework Al are obtained. That is, $(0.141)(1.01 \times 10^{-2}) = 1.424 \times 10^{-3}$ mol Al/g PILC. Assuming that all the extraframework Al is in the form of Al_{13} ions, then the number of pillars in the clay interlayer will be $(1.424 \times 10^{-3})/13 = 1.1 \times 10^{-4}$ mol Keggin ion/g PILC.

The more thermally stable Al-PILC sample (sample 3, Table 1) contains 10.16 wt. % Al and 28.30 wt. % Si. Using the assumptions given above, elemental analysis data yield a structural Al/Si ratio of 0.396 and an extraframework Al content of 0.176 mol Al/Si. Since there are 9.5×10^{-3} Si/g PILC, it follows that the higher thermally stable expanded clay contains 1.672×10^{-3} mol Al/g PILC or 1.3×10^{-4} mol Keggin ion/g PILC equivalent to 0.91 meq Keggin ion/g PILC. Knowing that in the calcined PILC: g clay/g PILC = 1.0 - (g extraframework $\text{Al}_2\text{O}_3/\text{g PILC}$) - (g quartz/g PILC) = $1.0 - 0.08527 - 0.03384 = 0.88$ g clay/g PILC, the pillar density can be expressed as 1.02 meq Keggin ion/g clay, a result slightly higher

than the cation-exchange capacity (CEC) of the Texas montmorillonite. Thus to ensure higher relative thermal stability, sufficient Keggin ions must be present to compensate the negative charge that exists on the 2:1 layer.

SUMMARY AND CONCLUSIONS

After exchanging montmorillonite with an aluminum chlorhydroxide solution containing the dodecameric $[\text{Al}_{13}(\text{O})_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ion, XRD results indicate that the initial cations present in the interlayer are not Keggin ions. This ion is formed *in situ* by repeatedly washing the ion-exchanged montmorillonite with water. AFM images indicate that the external Al-PILC surface is free from Al complexes. Thus, the thermally stable PILC contains 0.13 mmoles Keggin ion/g PILC which causes an initial expansion of the lattice by ~ 0.93 nm, a dimension consistent with the Keggin ion size (Johansson, 1960).

Small differences in pillar density have significant effects on thermal stability. In fact, a PILC sample with a structural Si/Al molar ratio of 2.70 and containing $\sim 1.424 \times 10^{-3}$ moles extraframework Al/g PILC collapsed upon calcination at 500°C, whereas a sample with Si/Al = 2.520 and containing 1.672×10^{-3} moles of extraframework Al/g PILC did not. Therefore, the minimum number of Keggin ions required for increased relative thermal stability is between 0.11–0.13 mmol $[\text{Al}_{13}(\text{O})_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}/\text{g PILC}$. The preparation of thermally stable PILC requires reaction mixtures with ACH/clay > 0.6 as well as extensive washing of the reaction product.

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