Chem. Mater. **1992**, *4*, 1433-1437

Improved Synthesis of Alumina-Pillared Montmorillonite by Surfactant Modification

Laurent J. Michot[†] and Thomas J. Pinnavaia[*]

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

Received July 28, 1992. Revised Manuscript Received September 27, 1992

An improved synthesis of alumina-pillared montmorillonite has been achieved by incorporating a nonionic surfactant of general formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_5$ (abbreviated $C_{12-14}E_5$) into the $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ pillaring reagent. The co-intercalation of Al_{13} oligomer (0.086 mol) and $C_{12-14}E_5$ (0.42 mol) per $O_{20}(OH)_4$ unit cell formula resulted in an X-ray scattering domain size of 256 Å along the layer stacking direction, as compared to 81 Å in the absence of surfactant. The enhanced crystallographic ordering was manifested in a substantially narrower micropore distribution for the alumina pillared montmorillonite formed by calcination of the Al_{13} intercalate at 500 °C. Also, the presence of the surfactant greatly improved the hydrolytic stability of the intercalated Al_{13} oligomer. Normally, uncalcined Al_{13}–montmorillonite hydrolyzes to a chlorite-like phase within a few weeks of aging under ambient conditions. However, no hydrolysis was noted for the surfactant-modified product after 8 months of aging. The calcined alumina-pillared product obtained by surfactant-modified synthesis exhibits a more uniform micropore distribution than the material produced without surfactant modification. Thus, the use of surfactant provides an effective means of mediating the pore structure and, potentially, the shape-selective catalytic and adsorption properties of pillared clays. Finally, the use of $C_{12-14}E_5$ surfactant during synthesis facilitates clay platelet flocculation and reduces greatly the amount of water needed for product processing. This latter property can be important for the large-scale production of pillared clay materials.

Introduction

Metal oxide pillared clays are a relatively new class of microporous solid acids discovered in the late 1970s.[1-4] 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 galleries. 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 base hydrolysis of an aluminum chloride solution.[5,6] Thermal dehydration and dehydroxylation converts the intercalated polycations to aluminum oxide pillars which act to separate the clay layers and provide for a two-dimensional microporous network. The interlayer surfaces of the clay thus become accessible for absorption and acid-catalyzed reactions such as petroleum cracking.[7]

The synthesis method can greatly affect the catalytic properties of alumina-pillared clays. We have observed variations in the porosity or acidity of pillared clays depending, in part, on the hydrolysis method used to form the polycation, the method used to dry the products, and other processing variables.[8] Furthermore, it is usually necessary to calcine the Al_{13} intercalate soon after preparation to form the alumina-pillared product. Otherwise, hydrolysis of the Al_{13} polycation occurs upon aging at room temperature and the pillared structure collapses. Even after calcination, however, the final alumina-pillared product exhibits rather mediocre ordering along the 001 stacking direction, and the micropore-size distribution is rather broad. Also, it is noteworthy that the synthesis and processing of pillared clays generally require large amounts of water for dispersion of reagents and washing the products free of excess salts. Water consumption can be a limiting economic factor in the industrial production of pillared clays.

The incorporation of nonionic polyether surfactants of the type $RO(CH_2CH_2O)_nH$ into the Al_{13}-exchanged form of montmorillonite has been recently shown to greatly improve the adsorption capacity of the clay toward organic molecules in solution.[9] Pillared clays prepared in the presence of such nonionic surfactants also have been reported in the patent literature[10] to exhibit an improved methane storage capacity and enhanced methane/ethane and ethane/propane molecular sieving. These improvements in adsorption properties suggest that the surfactant can favorably influence the pillar distribution in the clay galleries. In the present work we report many additional benefits derived from the use of polyether surfactants in the synthesis of pillared clays. Most importantly, the surfactant greatly increases the hydrolytic stability of the Al_{13} ion on the gallery surfaces, improves layer stacking order along the *c* axis, and enhances the uniformity of the micropores. The specific polyether surfactant used in this work was the secondary alcohol derivative $C_{12-14}H_{25-29}O(CH_2CH_2O)_5H$ (abbreviated $C_{12-14}E_5$).

Experimental Section

Materials. The clay used for this study was natural Wyoming sodium montmorillonite SWy-1, purchased form the Source Clay Minerals Repository at the University of Missouri, Columbia, MO. Prior to use, the clay was purified by sedimentation and converted to the Na^+-exchanged form by three ion-exchange reactions with 1.0 M NaCl. The unit cell formula is reported as $Na_{0.65}(Al_{3.04}Fe_{0.46}Mg_{0.50})$ $(Si_{7.85}Al_{0.15})O_{20}(OH)_4$.[11] The cationic

---

[†] Present address: URA 235 BP40 54501, Vandoeuvre Cedex, France.

[*] To whom correspondence should be addressed.

(1) Brindley, G. W.; Sempels, R. E. *Clay Miner.* **1977**, *12*, 229.

(2) Lahav, N.; Shani, U.; Shabati, J. *Clays Clay Miner.* **1978**, *26*, 107.

(3) Vaughan, D. E. W.; Lussier, R. J. *Preprints 5th Int. Conf. Zeolites, Naples, Italy, June 2–6*, 1980.

(4) Pinnavaia, T. J. *Science 220*, 365–371.

(5) Johansson, G. *Acta Chem. Scand.* **1960**, *14*, 771.

(6) Bottero, J. Y.; Cases, J. M.; Fiessinger, F.; Poirier, J. E. *J. Phys. Chem.* **1980**, *84*, 2933.

(7) Sterte, J.; Otterstedt, J.-E. *Appl. Catal.* **1988**, *38*, 131. Tichit, D.; Fajula, F.; Figueras, F.; Ducourant, B.; Mascherpa, G.; Gueguen, G.; Bousquet, J. *Clay Clay Miner.* **1988**, *36*, 369. Occelli, M. *Stud. Surf. Sci. Catal.* **1988**, *35*, 101.

(8) Butruille, J.-R.; Pinnavaia, T. J. In *Characterization of Catalytic Materials*; Wachs, I., Ed.; Butterworth-Heinemann: Boston, 1992; Chapter 8, pp 149–165.

(9) Michot, L.; Pinnavaia, T. J. *Clays Clay Miner.* **1991**, *31*, 634.

(10) Fahey, D. R.; Williams, K. A.; Harris, R. J.; Stapp, P. R. U.S. Patent 4,845,066, 1989.

0897-4756/92/2804-1433$03.00/0

exchange capacity is 80 mequiv/100 g.

The $C_{12-14}E_5$ nonionic surfactant, Tergitol 15S-5, was provided by Union Carbide Corp. This surfactant, which is a derivative of a secondary alcohol containing five ethylene oxide units with the general chemical formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_5H$, has an average molecular weight of 420 and a specific gravity of 0.961.

Pillared Clay Synthesis. A pristine $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ solution[12] was prepared by slowly adding 0.4 M NaOH to 0.4 M $AlCl_3$ to obtain a final hydrolysis ratio $OH^-/Al^{3+} = 2.4$. To a 200-mL portion of the pillaring solution (23.5 mmol Al^{3+}) was added 600 mg (1.43 mmol) of $C_{12-14}E_5$ surfactant in 500 mL of deionized water. The pH of the pillaring solution (4.47) was virtually unaltered by the addition of the surfactant. The surfactant-modified Al_{13} clay was then prepared by adding dropwise to the pillaring solution 330 mL of a 0.60 wt % suspension of sodium montmorillonite (1.58 mequiv) under vigorous stirring. The overall stoichiometry for reaction was Al^{3+}/mequiv of clay. The suspension was allowed to age overnight, and the product was collected by centrifugation or filtration, washed, and dried in air.

For comparison purposes, a "conventional" Al_{13}–montmorillonite pillared clay was prepared in the same way with no surfactant added to the Al_{13} solution. To avoid possible dilution effects,[13] 500 mL of deionized water was added to the pristine Al_{13} solution. The final alumina-pillared products were calcined in a programmable oven at 500 °C for 12 h. A heating rate of 1 °C/min was used to reach the calcination temperature.

Characterization Methods. Samples for chemical analyses by ICP emission spectroscopy were prepared using the lithium metaborate technique. A 50-mg quantity of sample was mixed with 300 mg of lithium metaborate and heated for 10 min at 1000 °C. The fused product was then dissolved in 3% HNO_3. Carbon analyses were performed by Galbraith Laboratories, Knoxville, TN. X-ray diffraction patterns were obtained for oriented film samples using a Rigaku diffractometer equipped with rotating anode and Cu Kα radiation.

Adsorption/desorption experiments using N_2 or argon were carried out at −196 °C on an Coulter Omnisorb 360 CX Sorptometer. The samples were outgassed at 150 °C under a vacuum of 10^{-5} Torr. Two different types of experiments were performed. Nitrogen isotherms, obtained by the quasi-equilibrium volumetric method,[14-16] were utilized for determining the surface area, total micropore volume, and mesopore size distribution of the samples. Surface areas were obtained using the BET equation. The *t*-plot method[17] was applied to determine the total micropore volume, as well as the nonmicroporous surface area. The desorption branch was treated according to a parallel mesopore model developed for phyllosilicates.[18] To study micropore size distribution, adsorption isotherms of argon at −196 °C were obtained by a conventional static method over the partial pressure range 10^{-6}–0.6. It has been shown that the static method ensures equilibrium within narrow micropores.[19] The micropore size distribution was determined using the model developed by Horvath and Kawazoe.[20]

Results and Discussion

Na$^+$–montmorillonite (1.0 mequiv) in aqueous suspension was found to react at room temperature with excess Al_{13} polycations (1.14 mmol) in the presence of a nonionic $C_{12-14}E_5$ surfactant (0.91 mmol) to form a surfactant-modified intercalation complex. The product, which was well flocculated and easily recovered by filtration, was readily washed free of excess electrolyte with 2 volumes of water. In contrast, an equivalent product formed by the reaction of Na$^+$–montmorillonite with Al_{13} oligomer in the absence of surfactant was difficult to filter and required approximately 6 volumes of water to remove excess electrolyte and to achieve flocculation. Thus, the presence of surfactant greatly reduced the amount of water needed for product processing. This latter feature of the surfactant-modified synthesis can be an important consideration in the large-scale industrial production of alumina pillared clays. In addition to the processing benefit of surfactant-modified synthesis, certain physical and chemical properties of the pillared product are greatly improved through the use of a nonionic surfactant, as revealed by the results presented below.

Table I. Compositions of Al_{13}–Montmorillonites Prepared in the Presence and Absence of $C_{12-14}E_5$ Surfactant

	mol per $O_{20}(OH)_4$ unit cell		
product[a]	Al_{13}	$C_{12-14}E_5$	$C_{12-14}E_5/Al_{13}$
surfactant-modified	0.086	0.42	4.9
no surfactant	0.091		

[a] Each air-dried product was prepared at 25 °C from a reaction mixture containing 1.14 mmol of Al_{13} oligomer/mequiv of Na$^+$–montmorillonite. The reaction mixture used to form the surfactant-modified product contained 0.91 mmol of $C_{12-14}E_5$/mequiv of clay.

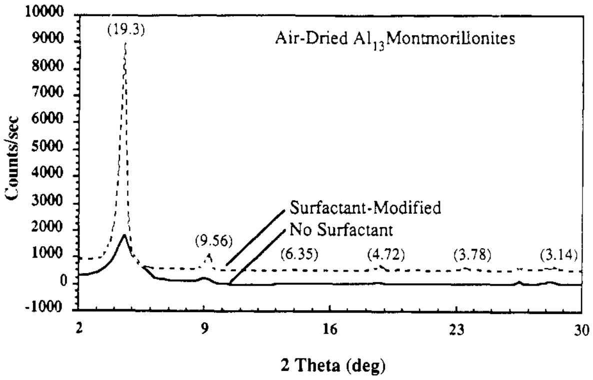

Figure 1. X-ray diffraction patterns for oriented film samples of air-dried Al_{13} montmorillonite prepared in the presence (dashed lines) and absence (solid lines) of $C_{12-14}E_5$ surfactant.

Table I compares the unit cell composition of the Al_{13} intercalate prepared in the presence of $C_{12-14}E_5$ surfactant with the composition of the conventional product prepared under equivalent conditions using the pristine Al_{13} oligomer. Interestingly, the two products contain almost the same amount of Al_{13} oligomer (0.089 ± 0.03 mol/$O_{20}(OH)_4$ unit cell). Apparently, the presence of surfactant does not appreciably limit the extent of Al_{13} exchange. Another interesting feature of the data in Table I is that the surfactant:Al_{13} ratio in the final product (4.9:1.0) is substantially larger than the ratio used in the initial reaction mixture (0.80:1.0). Thus, more surfactant is incorporated into the surfactant-modified product than might be expected solely on the basis of a simple complexation of Al_{13} by surfactant. However, the overall loading of surfactant (0.42 mol/$O_{20}(OH)_4$ unit cell) is relatively low, corresponding to only 0.88 molecules/100 Å^2 of lateral gallery space. Thus, most of the surfactant probably is bound to the clay basal surfaces. Our earlier studies of $C_{12-14}E_5$ binding to Al_{13}–montmorillonite[9] have indicated that much

---

(11) Whitney, G. *Clays Clay Miner.* **1990**, *38*, 343-350.

(12) Bottero, J. Y.; Axelos, M. A. V.; Tchoubar, D.; Cases, J. M.; Fripiat, J. J.; Fiessinger, F. *J. Colloid Interface Sci.* **1987**, *117*, 47-57.

(13) Harris, J. R. In *Perspectives in Molecular Sieves Science*; Flank, W. H., Whyte, E., Eds.; American Chemical Society: Washington, DC, 1988; p 253.

(14) Grillet, Y.; Rouquerol, F.; Rouquerol, J. *J. Chim. Phys.* **1977**, *74*, 179.

(15) Northrop, P. S.; Flagan, R. C.; Gavalas, G. R. *Langmuir* **1987**, *3*, 300.

(16) Michot, L.; Francois, M.; Cases, J. M. *Langmuir* **1990**, *6*, 677.

(17) De Boer, J. H.; Lippens, B. C.; Linsen, B. G.; Broekhoff, J. C. P.; Van den Heuvel, A.; Osinga, Th. J. *J. Colloid Interface Sci.* **1966**, *21*, 405-414.

(18) Delon, J. F.; Dellyes, R. *C. R. Acad. Sci. Paris Ser.* **1967**, *265*, 116.

(19) Rodriguez-Reinoso, F.; Torregrosa, R.; Venero, A. F. *Langmuir* **1991**, *7*, 350.

(20) Horvath, G.; Kawazoe, K. *J. Chem. Eng. Jpn.* **1983**, *16*, 470.

higher levels of surfactant loadings can be achieved, but the surfactant at high loadings is contained mainly in mesopores and on external surfaces.

The X-ray diffraction pattern for an oriented film sample of surfactant-modified Al_{13}-montmorillonite is compared in Figure 1 with the pattern for the analogous conventional product formed from the pristine Al_{13} oligomer. Both materials exhibit a 001 reflection near 19 Å as expected for intercalates consisting of 9.6-Å layers and 10-Å Al_{13} polycations. However, the line width at half-height is much sharper for the surfactant-modified product ($\beta \simeq 0.007$ rad) than for the intercalate prepared by conventional means ($\beta \simeq 0.017$ rad). Also, the surfactant-modified material exhibits at least six well-resolved higher order harmonics. These differences in 001 diffraction properties indicate that the layer stacking along the *c* axis is substantially improved by the co-intercalation of surfactant. On the basis of the Scherrer equation, $L = \lambda K(\beta \cos \theta)^{-1}$, where λ is the radiation wavelength (1.54 Å) and $K = 1.0$, the scattering domain size (L) is estimated to be 256 and 81 Å, respectively, for the surfactant-modified and conventional Al_{13} intercalates.

Under ambient conditions of aging over a period of several weeks, air-dried Al_{13}-montmorillonite will undergo hydrolytic alterations that lead to a decrease in basal spacing and the concomitant loss of intracrystal microporosity. The potential role of $C_{12-14}E_5$ as a stabilizing complexant for Al_{13} ions provided our initial rationale for selecting the alkyl polyether as a nonionic surfactant for the improved synthesis of alumina-pillared montmorillonite. Under the condition of the pillaring reaction, the concentration of surfactant (1.5×10^{-3} M) is substantially larger than the cmc ($<10^{-5}$ M). Thus most of the surfactant is aggregated (micellular) in solution. Light-scattering studies currently in progress[21] suggest that the surfactant does indeed bind to the aluminum oligomers in solution, most likely through the ethylene oxide chains. However, as noted earlier, the $C_{12-14}E_5$:Al_{13} ratio for the air-dried product (4.9:1.0) is larger than expected based on a 1:1 surfactant:Al_{13} complexation mechanism. Surface area measurements, which will be presented below, indicate that much of the surfactant is physically bound between Al_{13} units within the gallery environment. Consequently, the hydrolysis chemistry of the Al_{13} oligomer should be strongly mediated by the presence of the surfactant. Indeed, we find that co-intercalation of surfactant dramatically inhibits the hydrolytic degradation process.

The effect of $C_{12-14}E_5$ surfactant on the hydrolytic stability of Al_{13}-montmorillonite is illustrated by the comparison of X-ray diffraction patterns shown in Figure 2. After only 2 weeks of aging at room temperature under ambient conditions, the Al_{13}-montmorillonite formed by conventional synthesis in the absence of surfactant has undergone substantial hydrolysis as evidenced by the broadened diffraction peaks. A new chlorite-like phase, wherein sheets of $M(OH)_6$ octahedra are incorporated between the 2:1 smectite layers to give a basal spacing of 15.9 Å, becomes clearly evident after 6 weeks of aging. After aging 8 months, the original 19-Å phase is completely replaced by the chlorite-like hydrolysis product. In the case of the surfactant-modified product, the X-ray pattern is not appreciably affected by aging in air. The initial 19-Å structure is retained with no evidence for the formation of a hydrolysis product even after 8 months of aging.

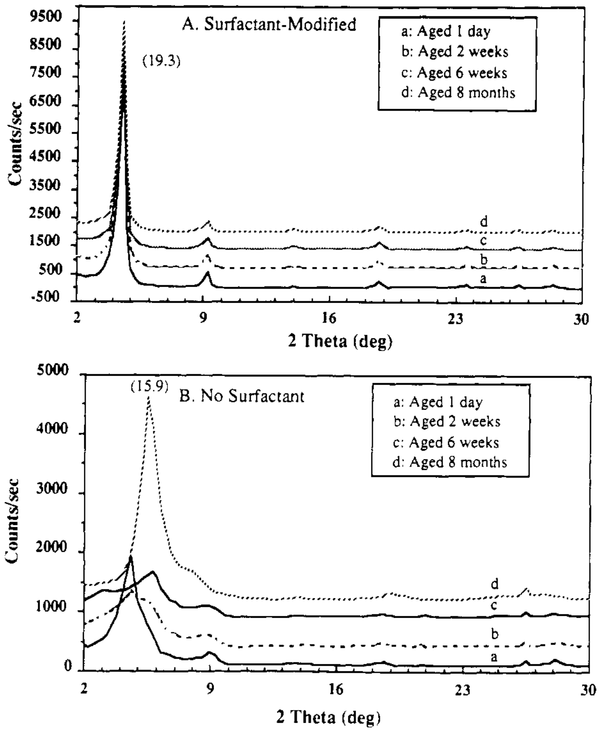

Figure 2. X-ray diffraction patterns of aged samples of air-dried Al_{13}-montmorillonites prepared by (A) $C_{12-14}E_5$ surfactant modification and (B) conventional synthesis in absence of surfactant. Aging was carried out in air under ambient conditions for the following periods: (a) 1 day, (b) 2 weeks, (c) 6 weeks, (d) 8 months.

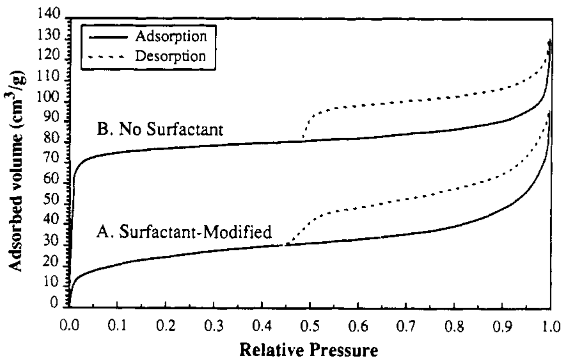

Figure 3. Nitrogen adsorption–desorption isotherms obtained at −196 °C for air-dried Al_{13}-montmorillonites: (A) product prepared by surfactant-modification; (B) product prepared by conventional methods. Outgassing of both samples was carried out under dynamic vacuum at 150 °C for 15 h.

Nitrogen adsorption-desorption isotherms for the air-dried Al_{13} intercalates before calcination are presented in Figure 3. The isotherm obtained for the conventional Al_{13} clay (curve A) is very similar to a type I isotherm identified in the classification scheme of Brunauer et al.[22] This type of isotherm is characteristic of a microporous material with a pore diameter < 20 Å. In contrast, the surfactant-modified product (curve B) exhibits a much lower capacity for nitrogen adsorption, indicating that the surfactant has been adsorbed into the interlayer space of the clay and has blocked most of the micropores. The desorption branches for both samples exhibit hysteresis, indicating the presence of some mesopores.

The equivalent BET surface areas, micropore, and mesopore surface areas are presented in Table II, part A, for the two air-dried Al_{13}-montmorillonites. The mesoporous surface areas were obtained form the desorption branch of the isotherms, whereas *t* plots of the adsorption data

---

(21) Michot, L. J.; Barres, O.; Hegg, E. L.; Pinnavaia, T. J., unpublished results.

(22) Bruanauer, L. S.; Deming, L. S.; Deming, W. S.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.

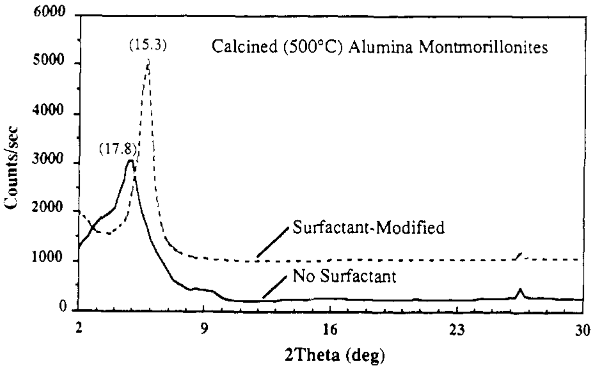

Figure 4. X-ray diffraction patterns for oriented film samples of calcined alumina pillared montmorillonites (500 °C, 12 h) prepared by $C_{12-14}E_5$ surfactant modification (dashed line) and by conventional methods in the absence of surfactant.

were used to obtain the micropore volumes and nonmicroporous surface areas. The mesoporous surface areas are close to the nonmicroporous surface areas, which supports the choice of the parallel plate model used for treating the desorption data. The equivalent BET surface areas are 305 and 93 $m^2\ g^{-1}$ for the conventional and surfactant-modified Al_{13} montmorillonites, respectively. The difference in microporosity also is reflected in the respective liquid microporous volumes of 0.104 and 0.0077 cm^3/g. These large differences in surface areas and microporosity are attributed to the nearly total blocking of the micropores in the surfactant-loaded material. It is noteworthy that the mesoporous surface areas are very close to the surface area of the starting Na^+-montmorillonite,[23] suggesting that the mesopores in both samples are interparticle mesopores.

The Al_{13}-montmorillonite reaction products prepared by surfactant modification and conventional methods were converted to alumina-pillared derivatives by dehydration and dehydroxylation in air at 500 °C for 12 h. Carbon analysis of the surfactant-modified product after calcination indicated that all of the surfactant had been removed by oxidation. Figure 4 provides the X-ray diffraction patterns for oriented film samples of the calcined materials. The 001 reflection for the product obtained by surfactant modification (d = 15.3 Å) is much sharper and symmetrical than the corresponding reflection for the product prepared in absence of surfactant ($d \simeq$ 17.8 Å). Thus, the improved stacking order achieved for the air-dried product in the presence of surfactant is maintained upon calcination at 500 °C. The slightly larger basal spacing observed for the conventional alumina-pillared clay may arise from a greater degree of condensation polymerization of Al_{13} units within the gallery. Condensation of Al_{13} units in solution has recently been demonstrated by Nazar and her co-workers.[24] The presence of surfactant between pillaring oligomers may limit the condensation of Al_{13} units within the gallery and this may lead to the smaller basal spacing of 15.3 Å for the calcined product.

Figure 5 presents the nitrogen adsorption–desorption isotherms for the alumina-pillared clay analogues after calcination at 500 °C. Both isotherms are now typical of microporous materials. It is clear that calcination at 500 °C removes surfactant from the gallery micropores of the $C_{12-14}E_5$-modified product. The absence of surfactant was confirmed by elemental analysis of the calcined product, which revealed no carbon. Surface areas and microporous volumes for the calcined alumina pillared montmorillonites are present in Table II, part B. The equivalent BET surface area of the clay prepared by surfactant modification is slightly higher than that for the pillared clay prepared by conventional methods (305 vs 279 m^2/g). Also, the surfactant-modified route may afford a slightly larger microporous liquid volume V_{mic} (0.0955 vs 0.0924 cm^3/g). As in the case of the air-dried Al_{13}-montmorillonites before calcination (cf. Table II, part A) the mesoporous surface areas obtained from the desorption hysteresis are very close to the nonmicroporous surface areas determined by the t-plot method. However, the pillared clay obtained by surfactant modification seems to have slightly more mesopores. This feature of the chemistry, which will require further investigation to fully illucidate, could be very interesting for catalytic applications. The presence of mesopores might circumvent diffusion problems by facilitating access of reactant and product molecules into and out of the active microporous sites of the clay.[25]

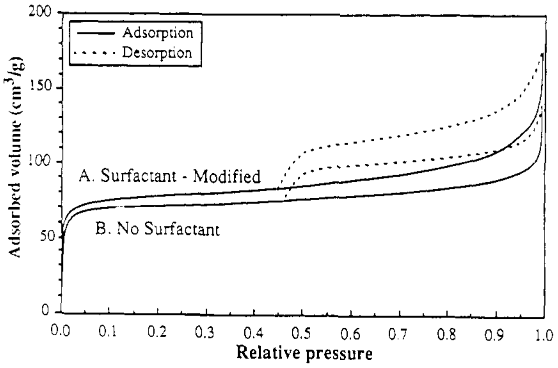

Figure 5. Nitrogen adsorption–desorption isotherms obtained −196 °C for alumina-pillared montmorillonites after calcination at 500 °C for 19 h: (A) $C_{12-14}E_5$ surfactant modification; (B) product prepared by conventional methods.

Table II. Surface Area and Pore Volume Analysis Based on Nitrogen Adsorption/Desorption Isotherms at −196 °C[a]

synthesis	S_{BET}, m^2/g	V_{mic}, cm^3/g	S, m^2/g	S_{meso}, m^2/g
(A) Air-Dried Al_{13}-Montmorillonites				
surfactant-modified	93	0.0077	59	54
no surfactant	305	0.104	31	45
(B) Calcined (500 °C) Alumina-Pillared Montmorillonites				
surfactant-modified	305	0.0955	58	72
no surfactant	279	0.0924	39	48

[a] The liquid microporous volumes (V_{mic}) and the nonmicroporous surface areas (S) were obtained from t plots; mesoporous surface areas (S_{meso}) were obtained from desorption isotherms using a parallel plate model.

Argon adsorption isotherms were carried out on the two calcined alumina pillared clays in order to obtain their micropore size distributions by the Horvath–Kawazoe method.[20] We chose a cross-sectional area of 0.138 nm^2 for argon, at this value has been recommended in the case of hydroxylated surfaces.[26] The results are presented in Figure 6. Significantly, the pore distributions are substantially different for the products prepared with and without surfactant modification. In the case of the surfactant-modified synthesis, the pore diameter distribution of the alumina pillared clay is bimodal over the range 0.6–0.9 nm. Most of the pores occur over a very narrow range centered near 0.65 nm. A secondary pore maximum occurs near 0.72 nm. The presence of the secondary

---

(23) Fripiat, J. J.; Van Olphen, H. *Data Handbook for Clay Minerals and Other Non-metallic Materials*; Pergamon: London, 1979.

(24) Fu, G.; Nazar, L. F.; Bain, A. D. *Chem. Mater.* **1991**, *3*, 602.

(25) Butruille, J. R.; Pinnavaia, T. J. *Catal. Today* **1992**, *14*, 141.

(26) Rouquerol, F. Thèse de Doctorat d'Etat, Paris, 1965.

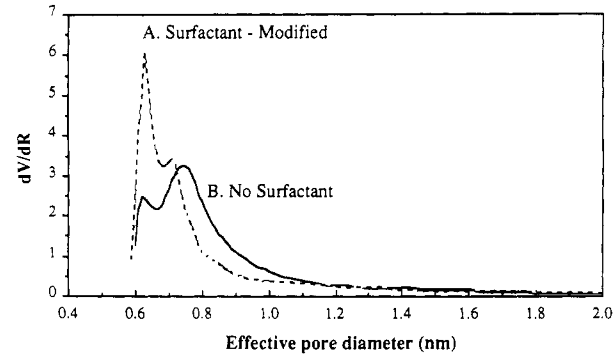

Figure 6. Micropore size distribution for calcined (500 °C, 19 h) alumina-pillared montmorillonites as determined by fitting the argon adsorption isotherm at −196 °C to the Horvath and Kawazoe model: (A) product obtained by $C_{12-14}E_5$ surfactant modification; (B) product prepared by conventional synthesis.

Table III. Comparison of Surface Areas and Pore Volumes Obtained from the Nitrogen and Argon Adsorption Isotherms for Calcined (500 °C) Alumina Pillared Clays[a]

	N_2 adsorption		Ar adsorption		
synthesis method	S_{BET}, m^2/g	V_m, cm^3 STP/g	S_{BET}, m^2/g	V_m, cm^3 STP/g	$[V_{liqN_2}/V_{liqAr}]$[b]
surfactant-modified	305	63.8	302	81.3	1.06
no surfactant	279	69.8	270	72.8	1.08

[a] Total surface areas (S_{BET}) and monolayer volumes (V_m) were obtained from a fit of the adsorption data to the BET equation. [b] Ratio of liquid monolayer pore volumes obtained by nitrogen and argon adsorption.

maximum is not understood at this time, but it may reflect the variation in layer charge distribution of the host clay.

A bimodal pore distribution also is observed for the pillared montmorillonite product prepared by conventional synthesis in the absence of surfactant. However, in this case the pore distribution occurs over a much broader range, from 0.6 to 1.1 nm. Also, much of the micropore structure found near 0.65 nm for the surfactant-modified clay has been replaced by a much broader pore distribution centered near 0.8 nm and extending beyond 1.1 nm in diameter. Thus, the surfactant-modified synthesis affords a pillared product with greatly improved pore size fidelity. The enhanced pore regularity might be facilitated in part by surfactant inhibition of Al_{13} hydrolyses prior to calcination to the final alumina-pillared product. Further studies are needed to test this hypothesis.

We also note from the results in Table III that the surface areas and microporous volumes obtained by argon and nitrogen adsorption are similar for the two adsorbates. In the case of a regularly microporous material, the ratio V_{mN_2}/V_{mAr} should be equal to 1, according to Gurvitsh's rule.[27] The ratio is somewhat closer to one for the clay prepared by surfactant modification, which is consistent with the more regularly microporous character of this material.

In a recent study related to our results for surfactant-modified pillared clay synthesis, Suzuki et al.[28] found that the addition of poly(vinyl alcohol) (PVA) to Al_{13} pillaring solutions increases the gallery height of alumina pillared fluorohectorite. In contrast to our $C_{12-14}E_5$ polyether surfactant, which causes immediate layer flocculation during Al_{13} exchange and does not alter the loading of Al_{13} oligomers in the galleries, PVA leaves the gallery space expanded and provides conditions for condensation of smaller Al oligomers into larger species. By controlling the gallery loading of aluminum, they were able to vary the gallery height of the alumina pillared clay over the range 9–19 Å. Whether the expanded galleries of PVA-modified pillared clay remained pillared or “stuffed” cannot be decided in the absence of surface area and pore volume data. The important point, however, is that $C_{12-14}E_5$ and PVA affect the gallery arrangement of Al_{13} oligomers in complementary ways and this adds diversity to strategies for manipulating the pore structure of pillared clays.

Acknowledgment. The support of this research under NIEHS Grant ESO-4911B is gratefully acknowledged.

---

(27) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: London, 1982; p 113.

(28) Suzuki, K.; Masakazee, H.; Masuda, H.; Mori, T. *J. Chem. Soc., Chem. Commun.* 1991, 873.

Structural Features of Sol-Gel-Derived Hybrid Inorganic-Organic Network Ceramer Materials by Small-Angle X-ray Scattering

D. E. Rodrigues, A. B. Brennan, C. Betrabet, B. Wang, and G. L. Wilkes*

Department of Chemical Engineering, Virginia Polytechnic Institute & State University,
Blacksburg, Virginia 24061

Received May 5, 1992. Revised Manuscript Received September 21, 1992

Hybrid inorganic–organic materials called ceramers have been prepared in our laboratories utilizing the sol–gel approach. These materials have been previously characterized, and a general morphological mode has been proposed based primarily on the small-angle X-ray scattering (SAXS) data. This paper focuses on the morphological model and tests its validity (using SAXS) under a variety of variables such as temperature, metal alkoxide content, oligomer spacer length, effect of different solvents, etc. The last part of this paper further addresses the nature of the inorganic particles formed in these systems and discusses their physical features based on fractal concepts.

Introduction

In recent years the sol–gel process has been utilized in our laboratories to react metal alkoxides such as titanium(IV) isopropoxide, zirconium *n*-propoxide, aluminum *sec*-butoxide, and tetraethylorthosilicate with oligomers such as poly(tetramethylene oxide), polyimide, poly(ether ketone), and polysulfone end-capped with silicon alkoxide functionalities to yield hybrid inorganic–organic network

---

* To whom correspondence should be addressed.