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Preparation and Characterization of Hydroxysilicoaluminum Pillared Clays

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Solutions containing hydroxy–SiAl(HSA) oligocations were prepared by two procedures: (1) treatment of a mixture of silicic acid, which was prepared by dispersing silica sol in an ultrasonic generator, and AlCl$_3$ with aqueous NaOH, followed by aging of the product and (2) preliminary preparation and aging of hydroxy–Al$_{13}$ oligocations followed by reaction of the latter with silicic acid. Exchange of Na–montmorillonite with HSA oligocations yielded pillared clays (designated as SiAl–PILC obtained using method 1, and GSiAl–PILC obtained using method 2) showing mixed maximum *d*(001) values of 2.65 and 1.90 nm for air-dried samples and maximum surface areas of $\sim$267 m^2/g after outgassing at 200 °C/101 kPa. Elemental analysis showed a gradual increase in the Si/Al ratio in the intercalated HSA oligocations with increasing Si/Al ratio in the pillaring solution. The pillaring structure, thermal stability, and surface acidity of the pillared clay products have been determined using ^{27}Al-NMR, X-ray diffraction (XRD), XPS, DTA, IR, and temperature-programmed desorption (TPD) measurements. The results suggest that the thermal stability of the pillared clays was improved by incorporating silica. Hydroxy–SiAl pillared clays show sharply higher concentrations of strong acid sites, especially Bronsted acid sites, compared with reference Al–PILC obtained by pillaring with hydroxy–Al$_{13}$ oligocations. This increased acidity is probably due to the presence of acidic, surface silanol groups in the HSA oligocations. The cracking of cumene and the disproportionation and alkylation of 1,2,4-trimethylbenzene were carried out in a pulse reaction system at 400 °C over the pillared clay catalysts. Incorporating silica into an alumina pillar increased the cracking activity of cumene and the activity and selectivity for the disproportionation of 1,2,4-trimethylbenzene compared to those observed for Al–PILC.

Introduction

Earlier work on the synthesis, structure, and properties of cross-linked smectites (CLS), described also as pillared clays (PILCs), has been reviewed by Pinnavaia,[1] Shabtai et al.,[2] and Tokarz and Shabtai.[3] Major additional progress in this field has recently been reported by several authors; in particular, the range of pillaring agents and preparative conditions have been considerably enlarged, and efforts to elucidate the structure of CLS materials and improve their properties have been intensified.[4] Pinnavaia et al.[5] reported the preparation of a large-size hydroxy–Cr oligocation by hydrolysis at 95 °C of a Cr(NO$_3$)$_3$ solution with aqueous Na$_2$CO$_3$ using a base:Cr molar ratio of 1.5–2.5 and a hydrolysis time of 6–36 h. Pillaring of Na$^+$–montmorillonite with such oligocations yielded a hydroxy–Cr–montmorillonite product [*d*(001) = 2.68 nm (25 °C); surface area = 433 m^2/g] which showed significant catalytic dehydrogenation activity.

Sterte[6] prepared a TiO$_2$-pillared montmorillonite which had an unusually high basal spacing of $\sim$2.8 nm and which was thermally hydrothermally stable to 700 °C. The TiO$_2$–PILC material was prepared in two steps, i.e., pillaring with oligomeric Ti-containing cations obtained by partial hydrolysis of TiCl$_4$ in aqueous HCl, followed by further in situ hydrolysis of the oligocations and heating to 700 °C to produce stable TiO$_2$ cross-links between the smectite layers. Yamanaka et al.[7] prepared a Fe$_2$O$_3$-pillared montmorillonite by ion-exchange of the smectite with a solution containing trinuclear (acetato)hydroxoiron(III), i.e., [Fe$_3$(OCOCH$_3$)$_7$OH]$^+$, cations. The product, after being calcined at 500 °C, showed a *d*(001) value of 1.67 nm and a surface area of 280 m^2/g. A relevant study has disclosed a class of mixed-metal complexes of pillared clays reported to be comprised of, for example, hydroxy–CrAl, NiAl, CoAl, and FeAl pillared clays.[8–11] These materials increased the kinetic stability and activity of cracking compared to hydroxy–Al pillared clay.

Another direction of recent research has been the preparation of SiO$_2$-intercalated smectites. Endo et al.[12] and Pinnavaia et al.[1] reported the introduction of silica in montmorillonite and other clays by (1) ion exchange of the swollen smectite with tris(acetylacetonato)silicon cations (Si(acac)$^{3+}$), followed by hydrolysis of the latter, or (2) in situ reaction of acetylacetone-solvated smectites with SiCl$_4$. Calcination of the resulting Si(acac)$^{3+}$-exchanged smectites resulted in carbon-free, SiO$_2$-intercalated smectites showing relatively low surface areas (40–190 m^2/g) and a maximum *d*(001) value of 1.26 nm, indicating the presence of monolayer siloxane chains between the layers. In an important subsequent development, Lewis et al.[13] pillared the smectite with polyhedral oligosilsesquioxane compounds, which upon calcination gave rise to two-layer silica structures between the layers. The pillaring agent consisted of one or more compounds having the general formula (ZSiO$_{1.5}$)$_n$(OSiZ$_2$)$_m$, in which Z is an organic moiety serving as an ion-exchange or coordinating group. Typically, 4-(2-(trichlorosilyl)ethyl)pyridine or 2-(2-silyethyl)-pyridine were subjected to hydrolysis, and the resulting oligosilsesquioxane pillaring agent was intercalated in the smectite at a pH < 6. Calcination at 350–700 °C yielded pillared products with interlayer spacing, Δd(001), of 0.66–1.02 nm and surface areas of 140–400 m^2/g. A Pt-loaded SiO$_2$-pillared montmorillonite showed moderate catalytic activity for hydroisomerization. In a different approach to silicon incorporation in the pillaring component of PILCs systems, Atkins and Ashton[14] silanized the Al$_2$O$_3$ pillars of calcined hydroxy–Al smectites by reacting the

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latter with tetraethoxysilane. On the other hand, Occelli[15] reported the use of submicrometer-size Al_2O_3-coated silica to produce Al_2O_3/SiO_2-pillared montmorillonite.

In view of the above studies it was of interest to synthesize well-defined hydroxy–SiAl (HSA) oligocations for use as pillaring agents. Calcination of PILC materials intercalated with such mixed oligocations should result in the formation of products having stable SiO_2–Al_2O_3 pillars. Of particular interset as a model were HSA oligocations based on a core of $Al_{13}O_4(OH)_{24}{}^{7+}$ oligocations, which have been structurally well characterized. Such hydroxy-Al_{13} oligocations,[16] designated as HA, form when a strong base, e.g., NaOH, is added to an aqueous solution of an aluminum salt, e.g., aluminum chloride. The maximal concentration of HA oligocations is obtained at pH ~ 4.3.[17] The percentage of Al present in this form is also dependent on the total Al concentration, the equilibration time and temperature, and the rate of neutralization.[18,19] These authors found that the relative amount of Al present as HA oligocations is lower in dilute solution and that the total amount present in this form decreases with time. These same authors demonstrated that the concentration and stability of HA oligocations increases if the rate of neutralization is low.

Wada and Wada[20] showed that Si can be incorporated in the structure of oligomeric hydroxy–Al ions by reacting a mixture of orthosilicic acid, aluminum chloride, and sodium hydroxide. Several possible mechanisms for this reaction were discussed by Luciuk and Huang;[21] for formation of a HSA oligocation, structurally based on a hydroxy–Al_{13} oligocationic intermediate, the predominant pathway indicated by Wada and Wada[20] was

$$[Al_{13}O_4(OH)_{23}(H_2O)_{12}]^{7+}\text{–}OH + Si(OH)_4 \rightarrow [Al_{13}O_4(OH)_{23}(H_2O)_{12}]^{7+}\text{–}O\text{–}Si(OH)_3 + H_2O \quad (1)$$

They suggested, however some contribution of a second reaction, (2), as indicated by a slight increase in the acidity of the product mixture during the equilibration period.

$$[Al_{13}O_4(OH)_{24}(H_2O)_{11}]^{7+}\text{–}OH_2 + Si(OH)_4 \rightarrow [Al_{13}O_4(OH)_{24}(H_2O)_{11}]^{7+}\text{–}O\text{–}Si(OH)_3 + H_3O^+ \quad (2)$$

Inasmuch as the main reaction, (1), proceeded with retention of the oligocationic charge, even if the silanization process affected several OH groups, the HSA oligocation produced could be considered as a suitable species for smectite cross-linking. Thus, intercalation of mixed HSA oligocations in the interlamellar space of the smectite, followed by calcination to yield stabilized SiO_2–Al_2O_3 pillars, could result in a PILC product of augmented thermal stability and acidity. On the other hand, Holy[22] showed that surface silanol groups react smoothly with various catalytically active compounds, thereby allowing for introduction of new active functional groups in pillared smectite catalysts, including those needed for shape-selective organic and biochemical reactions at low (<300 °C) temperature.[23]

The present paper reports the synthesis and characterization of PILC materials prepared by controlled pillaring of montmorillonite with hydroxy–SiAl oligocations prepared by two different methods. The effects of the Si/Al ratio in the pillaring solution upon the properties of derived PILC products are also reported. The pillaring structure, thermal stability, and surface acidity of the pillared clay products were determined using ^{27}Al-NMR, X-ray diffraction (XRD), XPS, DTA, IR, and temperature-programmed desorption (TPD) measurements.

Experimental Section

Starting Materials. Original clay was used as received in its Ca^{2+}-exchanged form from Heishan, Liaoning, China. This clay is reported to be composed of 62.90% SiO_2, 15.62% Al_2O_3, 2.49% Na_2O, 2.66% MgO, 1.96% CaO, 0.02% K_2O, and 3.76% Fe_2O_3. The cation-exchange capacity was quoted by the supplier as 73 mequiv/100 g and the particle size as less than 2.0 μm. This material was exchanged to the Na^+ form with a Na^+-exchange resin.[24]

Hydroxy–SiAl Oligomeric Solution (HSA). The preparation of the oligomeric HSA solution, used as pillaring agents, was carried out by two methods. **Method A** was essentially the same as that described by Wada.[20] Silicic acid solution was prepared by diluting a solution of silica sol with 2 L of deionized water, with a pH value adjusted from 4 to 5 with a aqueous NaOH solution (0.02 M), in ultrasonic generator for 2 h. An equal amount of aqueous 0.1 M $AlCl_3$ was then gradually added to the silicic acid solution, resulting in product solutions having various Si/Al ratio. An aqueous NaOH solution (0.1 M) was then added with constant stirring at a rate of about 4 cm^3/min until a final OH/Al ratio of 2.0 was reached. The resulting solutions were aged for two weeks and then aged at 120 °C for 4 h before use.

Method B. A solution containing hydroxy–Al oligocations having an OH/Al ratio of 2.4 was prepared by the method of Lahav et al.[25] and Shabtai[26] and aged for 14 days. After aging, calculated amounts of silicic acid prepared according to method A were added with constant stirring over a period of 24 h and dispered by ultrasonic generator for 2 h to produce HSA-containing solutions with Si/Al mol ratios of 0.0, 0.2, 0.5, 1.0, and 2.0. These solutions were left to stand for 7 days and aged at 120 °C for 4 h before use.

Cross-Linking Procedure. The clay sample (3.0 g) was dispersed in 1000 mL of deionized water by magnetic stirring. Equal amounts of solutions containing hydroxy–SiAl oligocations (HSA) prepared by method A or method B were used as pillaring reactants to obtain ratios of 5 mmol of Al/g of smectite. After completion of the reaction (usually 1–2 h), the product was allowed to stand in contact with the solution for 16 h. The precipitated product was then separated from the solution by centrifugation, washed with deionized water until chloride-free, and air-dried at 120 °C.

Analysis of Products. The basal spacings [d(001) values] were measured on a Rigaku D/max-b X-ray diffractometer with Ni-filtered Cu Kα (λ = 1.5418 Å) radiation. A China National Instrument Digital 2500 instrument was used to obtain N_2 BET surface area data. The thermal stability of the pillared clays was examined by determining the basal spacings of samples heat-treated at 300–500 °C for 2 h under air. Elemental analyses were obtained by inductively coupled plasma spectrometry (ICPS). The SiO_2 content was determined by the gravimetric analysis. Differential thermal analysis (DTA) was obtained with a Perkin-Elmer PE-1700 analyzer using a heating rate of 10 °C/min; N_2 (30 cm^3/min) was used as a purge gas, and the sample weight was about 15 mg.

^{27}Al-NMR spectra of pillaring agents were acquired on a Varian FT-80A spectrometer at 80.0 MHz. The chemical shifts are referred to 1 M $NaAlO_2$. The properties of silica in the sample were determined from X-ray photoelectron spectra (XPS) obtained with a VG Labmk II ESCA spectrometer. Monochromatic Al Kα radiation (1486.6 eV) was used as the excitation source in all experiments. The carbon peak at 284.5 eV, due to adventitious carbon, was used as an internal reference standard. Infrared spectra (IR) were obtained with a Perkin-Elmer PE-580 spectrometer; self-supporting wafers were prepared by pressing 8-mg samples on a 15-mm-diameter die. Prior to pyridine sorption, the wafers were mounted in an optical cell and degassed by heating at 400 °C for 2 h at 1.3 × 10^{-3} Pa. The pyridine-loaded wafers were then heated (in vacuo) in the 100–400 °C temperature range (at 100 °C intervals) for periods of 1 h and the spectra recorded for each temperature. In each temperature-programmed desorption (TPD) experiment, 0.1 g was placed in the cell and pretreated in vacuo at 400 °C for 2 h and then cooled to 100 °C. An excess amount of n-butylamine was adsorbed at 100 °C and

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Table I. Basal Spacing on ($d(001)$) of Hydroxyaluminsilicate Pillared Clay Products with Various Si/Al Ratios and Calcining Temperatures

sample	Si/Al ratio in pillaring solution	d(001) (nm)			
		120 °C	300 °C	400 °C	500 °C
Al-PILC	0	1.82	1.88	1.84	1.78
GSiAl-PILC-0.2	0.2	2.35, 1.90	2.38, 1.85	2.36, 1.89	1.83
GSiAl-PILC-0.5	0.5	2.60, 1.84	2.48, 1.81	2.47, 1.80	1.79
GSiAl-PILC-1	1	2.61, 1.90	2.57, 1.89	2.51, 1.85	1.77
GSiAl-PILC-2	2	2.65, 1.81	2.65, 1.81	2.57, 1.80	1.75
SiAl-PILC-0.2	0.2	2.48, 1.86	2.42, 1.84	2.44, 1.82	1.81
SiAl-PILC-0.25	0.25	2.51, 1.88	2.54, 1.81	2.49, 1.81	1.79
SiAl-PILC-0.5	0.5	2.59, 1.90	2.54, 1.84	2.49, 1.80	1.82
SiAl-PILC-1	1	2.64, 1.88	2.60, 1.86	2.54, 1.86	1.83

Table II. Elemental Composition (wt %) and Surface Areas (m^2/g) of Hydroxyaluminosilicate Pillared Clay Products

sample	composition			S (m^2/g)
	SiO_2	Al_2O_3	Fe_2O_3	
SiAl-PILC-1	64.93	20.00	2.02	242
SiAl-PILC-0.5	63.59	20.07	2.39	235
GSiAl-PILC-1	66.00	20.15	1.27	247
GSiAl-PILC-2	72.49	20.74	1.33	267
Al-PILC	59.72	19.89	3.57	232
Na-clay	62.90	15.62	3.76	64

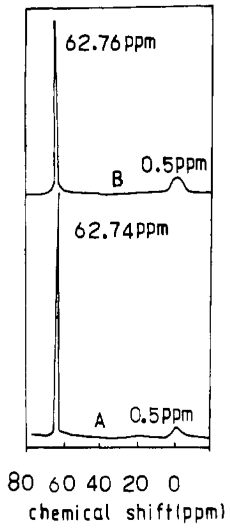

Figure 1. ^{27}Al-NMR spectra of the hydroxy-SiAl (HSA) oligocations: (A) hydroxy-Al oligocation; (B) hydroxy-SiAl oligocation.

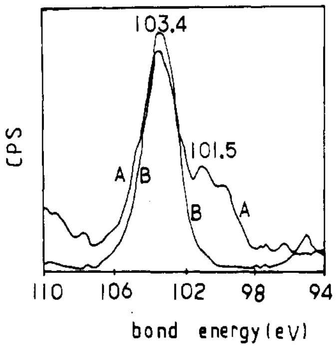

Figure 2. Si_{2p} XPS spectra of hydroxy-SiAl pillared clay products. (A) fresh SiAl-PILC-1; (B) SiAl-PILC after calcination at 500 °C for 2 h.

evacuated for 30 min. This sample was kept in a stream of helium (60 mL/min, 1.33 kPa) for 1 h to attain a steady flow, followed by heating at a rate of 16 °C/min. A mass spectrograph (HP-5980) was used to monitor desorbed n-butylamine and other species since water was desorbed simultaneously with ammonia in a temperature range higher than the pretreatment temperature.

Catalytic Activity. The cracking of cumene and conversion of 1,2,4-trimethylbenzene were carried out in a pulse reaction system at 400 °C over the pillared clays. Catalysts (0.1 g as a powder or pellets) were pretreated with helium (35 mL/min) for 60 min. The amount of cumene, 1,2,4-trimethylbenzene (1,2,4-TrMB), or mixtures of 1,2,4-TrMB with methanol (mole ratio, 1:3) was 0.5 μL. The products were analyzed by means of gas chromatography using a flame ionization detector and a quartz capillary separation column with temperature-programmed heating from 70 to 180 °C. Helium was used as a carrier gas (35 mL/min).

Results and Discussion

Hydroxy-SiAl Pillared Clays (SiAl-PILC). Hydroxy-SiAl pillared clay products denoted as SiAl-PILC were prepared using the method A pillaring solution obtained by dispersing Na-montmorillonite with HSA oligomeric solutions of Si/Al ratios of 0.2, 0.25, 0.5, and 1.0. The OH/Al ratio of each HSA solution was adjusted to 2.0, and the aging period was kept at 14 days. The total amount of HSA solution applied in each preparation was such as to contain 5 mmol of Al/g of montmorillonite.

A second series of hydroxy-SiAl pillared clay products, denoted as GSiAl-PILC products, were prepared using the method B pillaring solution obtained by dispersing the above montmorillonite with HSA oligomeric solutions of Si/Al ratios 0.2, 0.5, 1.0, and 2.0. In these preparations, the OH/Al ratio of the HSA solution was adjusted to 2.0 and the amount of HSA solution used in each case was such as to contain 5 mmol of Al/g of montmorillonite. A reference sample pillared with hydroxy-Al oligocations only (Si/Al ratio = 0) was prepared also by this method.

The $d(001)$ values of the above products are summarized in Table I. Two first-order peaks between 2.6 and 1.86 nm were generally observed in XRD diagrams of hydroxy-SiAl pillared clay products prepared by methods A and B. The $d(001)$ values of air-dried samples increased with increasing Si/Al ratios in the pillaring solution. Samples had slightly higher surface areas (267 m^2/g) compared with that of Al-PILC (232 m^2/g). Samples prepared by method B showed $d(001)$ values similar to those prepared by method A. The surface areas of th samples were also similar to those prepared by method A. This indicates that the structure of the pillared clays prepared by method A are similar to those prepared by method B. The basal spacings near 1.90 nm are similar to that of Al-PILC and indicate that the dimension of the HSA cross-linking species (before calcination) in a direction vertical to the smectite layers is similar to that of hydroxy-Al_{13} oligocations.[3,16]

The elemental compositions of the pillared clays are summarized in Table II. The SiO_2 content of hydroxy-SiAl pillared clays is more than that of reference hydroxy-Al pillared clay, and gradually increases with the Si/Al ratio of the pillaring solution. The SiO_2 content of products derived by method B is more than that of products prepared by method A. The results indicate that Si is probably incorporated into oligomeric hydroxy-Al pillars, and is related to the Si/Al ratios of the pillaring solution. More SiO_2 is incorporated into the alumina pillars prepared by method B compared to those derived by method A.

Evidence for the structure of hydroxy-SiAl oligocation in the pillaring solution is provided by ^{27}Al-NMR in Figure 1. HSA with various of Si/Al ratio prepared by two different synthetic routes displays two bands at 62.76 and 0.45 ppm similar to that of the hydroxy-Al oligocation (see Figure 1A). J. Akitt et al.[16] have shown that the former band may arise from tetrahedral alumina in hydroxy-Al oligocation, Al_{13}, $\{Al_{13}O_4(OH)_{24}(H_2O)_{12}\}^{7+}$, and the latter band arises from free Al^{3+} ion. This suggests that the structures of HSA with various Si/Al ratios prepared by two different synthetic routes are similar to that of the hydroxy-Al oligocation, which has the Keggin structure. XPS spectra were used to determine the properties of Si in the products. Figure 2 presents XPS spectra in the Si 2p region for each of the uncalcined and calcined at 500 °C for 2 h hydroxy-SiAl pillared clay products. Two peaks for Si $2p_{3/2}$ at ca. 103.4 and ca. 101.5 eV were generally observed in the XPS spectral diagrams of fresh

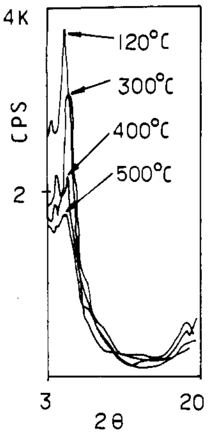

Figure 3. XRD pattern of hydroxy–SiAl pillared montmorillonites after calcination at different temperatures.

hydroxy–SiAl pillared clay products. The peak at ca. 103.4 eV is similar to that of the calcined sample and is assigned to the Si 2p band in the clay lattice, but the peak at 101.5 eV only appears in XPS spectra of fresh hydroxy–SiAl pillared clay products and is assigned to the Si (2p) band of colloidal silica.[27] The *d*(001) peak is observed at about 2.60 nm by the reaction with hydroxy–Al oligocation similar to (2):

$$[Al_{13}O_4(OH)_{23}(H_2O)_{12}]^{7+}\text{–OH} + HO\text{–}[Si(OH)_2]_n\text{–OH} \rightarrow [Al_{13}O_4(OH)_{23}(H_2O)_{12}]^{7+}\text{–O–}[Si(OH)_2]_n\text{–OH} + H_2O \quad (3)$$

$$13AlCl_3 + 28OH^- + 9H_2O + HO\text{–}[Si(OH)_2]_n\text{–OH} \rightarrow [Al_{13}O_4(OH)_{23}(H_2O)_{12}]^{7+}\text{–O–}[Si(OH)_2]_n\text{–OH} \quad (4)$$

Thermal Stabilities. The observation of the effect of treatment temperature on the (001) line width and *d*(001) values is a convenient way to investigate the thermal stability of pillared clays. As shown in Figure 3, treatment of SiAl–PILC in the temperature range 300–500 °C hardly affects the (001) line. This result means that the regularity of the two-dimensional lattice generated upon intercalation is fairly well retained after treatment in this temperature range. However, the *d*(001) reflection at about 1.90 nm shifted to a higher angle after treatment at high temperature; the layer distance shrank by 0.05 or 0.12 nm when the treatment temperature increased from 300 to 500 °C. The layer distance shrinkage was independent of the Si/Al ratio in the pillaring agent. This indicates that incorporating Si into the alumina pillar does not affect the thermal stability of the pillared clays. This shrinkage may arise from dehydration of SiAl–PILC into complex silicate aluminum oxide and destruction of the pillars. On the other hand, the *d*(001) reflection near 2.6 nm shifted to a higher angle after calcination at 120–400 °C and disappeared after treatment at 500 °C. This suggests that larger colloidal silica in the pillars can transfer to silicon oxide similar to the observation in the clay lattice. The suggestion is also supported by the XPS result.

DTA was used to investigate the thermal stability of the pillared clays. As shown in Figure 4, SiAl–PILC shows one extotherm peak at about 650 °C assigned to dehydroxylation of any remaining hydroxide pillars besides one extotherm near 120 °C induced by dehydration.[24] This also indicates that the thermal stability of SiAl–PILC is fairly good.[24] It should be noted that the temperature of the peak is higher than that of hydroxy–Al pillared clays and indicates that the thermal stability of the pillared clays is improved by incorporating Si into the oligocationic pillars.[24] This interpretation is supported by the higher *d*(001) values and better constancy of the surface areas of SiAl–PILC products, compared with those of hydroxy–Al pillared clay. This result is consistent with the previously observed higher thermal stability of hydroxy–SiAl pillaring clays compared with that of corresponding hydroxy–Al pillared clays.[2,28]

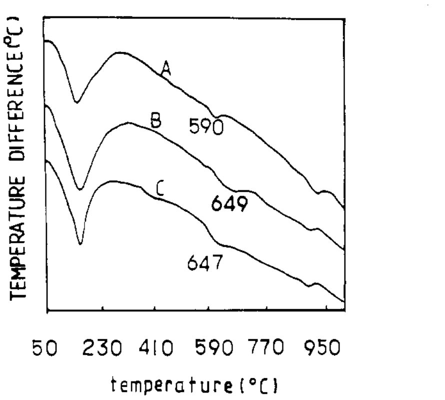

Figure 4. DTA profiles of pillared clay products: (A) Al–PILC; (B) SiAl–PILC-1; (C) GSiAl–PILC-1.

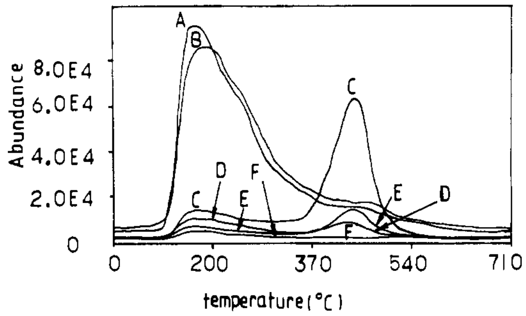

Figure 5. *n*-Butylamine TPD spectra of hydroxy–SiAl pillared montmorillonites: (A) amine ($m/e = 30$); (B) *n*-butylamine ($m/e = 73$); (C) butene ($m/e = 56$); (D) propylene ($m/e = 40$); (E) propane ($m/e = 43$); (F) ethylamine ($m/e = 45$). All spectra were recorded on a mass spectrograph.

Acidic Properties. Acidic properties were measured by means of *n*-butylamine TPD and IR spectroscopy using pyridine as a probe molecule. In an *n*-butylamine TPD spectrum of SiAl–PILC (Figure 5), it was observed that butene ($m/e = 56$), propane ($m/e = 43$), propylene ($m/e = 40$), and ethylamine ($m/e = 45$) may be adsorbed in addition to *n*-butylamine ($m/e = 73$). The cracking reaction takes place in the course of adsorbing of *n*-butylamine, so that we can estimate the acidic intensity of pillared clays by the desorbed amount of butene, propane, propylene, and ethylamine. The *n*-butylamine TPD data for the pillared clays are summarized in Table III. The desorbed amount of *n*-butylamine and other species from SiAl–PILC was larger than that from the original clay, Na^+–montmorillonite. This indicates that the acidity of pillared clays comes from their pillars and that the acid strength is enhanced by pillaring. As seen in Table III, hydroxy–SiAl pillared clay products give considerably larger amounts of desorbed *n*-butylamine and other species compared with Al–PILC. It is obvious from these results that SiAl–PILC products have a higher concentration of strong acid sites as compared with the reference Al–PILC sample which was obtained by pillaring with the Si-free, hydroxy–Al oligocation.

Spectra for the pillared clays in the OH stretching region show a prominent free OH band centered about 3653 cm^{-1} (see Figure 6) similar to that of Al–PILC. After evacuation at 500 °C a weaker shoulder at 3737 cm^{-1} caused by those surface OH which are easy to react with pyridine[24] is seen in all the samples studied (Figure 6). IR spectra for the pillared clays in the OH stretching region were independent of the Si/Al ratio, and the strength of

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[27] Baker, A. D.; Betteridge, D. *Photoelectron Spectroscopy*; Pergamon Press Ltd.: Oxford, Great Britain, 1972; p 266.

[28] Sterte, J.; Shabtai, J. *Clays Clay Miner.* **1987**, *35*, 429.

Table III. Peak Temperature and Relative Areas of *n*-Butylamine TPD of Hydroxyaluminosilicate Pillared Clay Products

	$m/e = 73$		$m/e = 56$		$m/e = 43$		$m/e = 45$		$m/e = 40$	
catalyst	*T* (°C)	area	*T* (°C)	area	*T* (°C)	area	*T* (°C)	area	*T* (°C)	area
Na–clay	150	47	147, 366	145.4	146, 323	54	147	52	146, 592	54.2
Al–PILC	224	100	238, 421	28.6	178, 404	179.4	197	101.8	177, 421	336.5
GSiAl–PILC-1	168	117	162, 432	645.9	161, 415	191.7	162	115.2	161, 434	336.8
SiAl–PILC-1	209	225	166, 419	1030	162, 419	265.3	165	171.1	161, 436	465.6

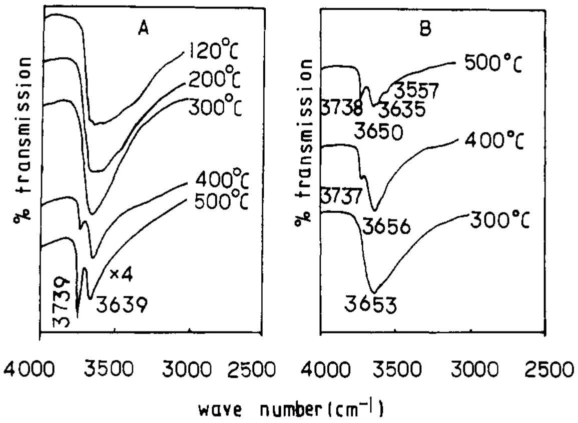


Figure 6. Hydroxy absorption bands for hydroxy–SiAl pillared montmorillonites prepared by two synthetic routes degassing at different temperature. (a) Al–PILC; (b) GSiAl–PILC-1 prepared by method A; (c) SiAl–PILC-1 prepared by method B.

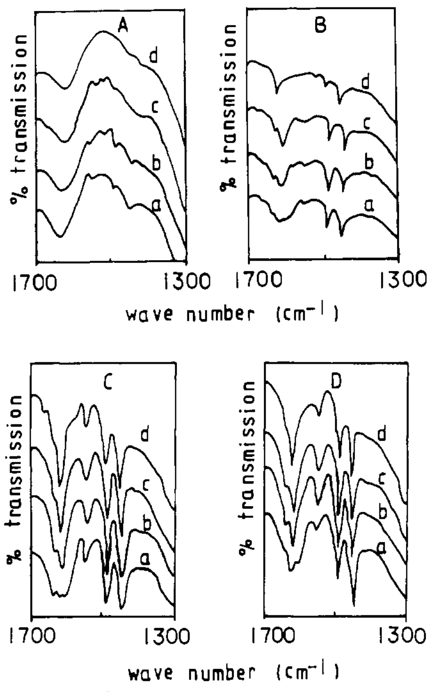
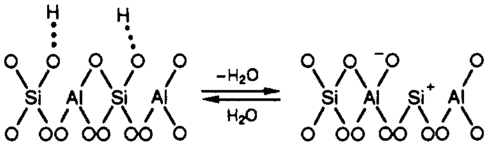


Figure 7. IR spectra of pyridine sorbed on the pillared clay: (A) Na–clay; (B) Al–PILC; (C) GSiAl–PILC; D, SiAl–PILC. Spectra were obtained after degassing at (a) 100, (b) 200, (c) 300, and (d) 400 °C.

the OH stretching of the samples was decreased with calcination temperature. This change of surface acidity with temperature implies that surface acidity is relative to the surface OH of the pillared clays. On the other hand, several bands near 3650, 3635, and 3557 cm^{-1} were observed in the IR spectra for SiAl–PILC after calcination at 500 °C and assigned to OH stretching of silanol groups in hydroxy–SiAl pillared clay products.[28]

Infrared spectra in the region 1300–1700 cm^{-1} obtained by evacuating the pyridine-containing pillared clays at different temperatures are shown in Figure 7. As reported previously,[29] these pillared clays contained both Bronsted and Lewis acid sites as characterized by the absorption bands of pyridine appearing at 1540 and 1450 cm^{-1}, respectively, when evacuated at 200 °C. Data of the IR spectra of adsorbed pyridine on the pillared clays are summaried in Table IV. Intensities of bands assigned to pyridine coordinated onto Lewis and Bronsted acid sites are reduced with calcination temperature. With regard to SiAl–PILC above 300 °C, in vacuo, the intensities of its bands at 1544 cm^{-1} assigned to pyridine coordinated onto Bronsted acid sites are reduced slightly compared to that of hydroxy–Al pillared clay. As shown in Table IV, pillared clays have both larger Bronsted and Lewis sites compared to the original clay (Na–clay). Compared to hydroxy–Al pillared clay, SiAl–PILC products have more both Bronsted and Lewis acid sites and a lower L/B ratio; therefore, we could conclude that incorporating Si into an alumina pillar increased the Bronsted acid site and decreased the L/B ratio. The increase in the acidity of SiAl–PILC products indicated the presence of acidic silanol groups in the hydroxy–SiAl cross-links. By analogy with the surface chemistry of H^+-form of zeolites,[30] silanol groups possessing protonic acidity were probably present at the surface of the hydroxy–SiAl pillars. Dehydroxylation of the pillars at high temperature should have converted a major part of such groups into Lewis acid groups, in accordance with previously proposed schemes,[30] as follows:



Both Bronsted acidity and Lewis acidity in pillared clays were previously reported by Shabtai[31] and Occelli.[15]

Catalytic Activity. Table V summarizes the cracking activities of catalysts for cumene. Cracking activities for Zeolites such as ZSM-5, HY, and H–Mordenite, are markedly higher than those for the pillard clays. This indicates that pillared clays have lower acidities than those of zeolites. Comparing cracking data for cumene using the nonpillared clays (Na–clay) and the pillared clays reveals that the effect of pillaring increases the activity of the catalyst. The result corresponds to the increase of acidities after pillaring. Incorporating Si into pillars of the clay results in an increase of the cracking activity with respect to Al–PILC. The increase of the cracking activity is consistent with the increase of strong acid sites and indicates that the cracking activity of cumene is depended on Bronsted acid sites of pillared clays.

Table VI summarizes the catalytic activities of pillared clay compounds for disproportionation and alkylation of 1,2,4-trimethylbenzene with methanol (1:3 mole ratio). As shown in Table VI pillared clays show shape selective properties for the formation of 1,2,4,5-tetramethylbenzene (1,2,4,5-TeMB) through disproportionation and alkylation of 1,2,4-TrMB. Therefore, pillared clays have pores of a larger size range that allow catalytic conversion of a high molecular weight aromatic hydrocarbon. The catalytic activities and selectivities for disproportionation of hydroxy–SiAl pillared clay products are higher compared with

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(29) Occelli, M. L.; Finseth, D. H. *J. Catal.* **1986**, *99*, 316.

(30) Ward, J. H. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed., American Chemical Society: Washington, DC, 1976; pp 118–284.

(31) Shabtai, J.; Massoth, F. E.; Tokarz, M.; Tsai, G. M.; McCauley, J. In *Proceedings of the 8th International Congress on Catalysis, Berlin*; Verlag Chemie: Weinhein, Germany, 1984; Vol. IV, pp 735–745.

Table IV. IR Spectral Data for Adsorbed Pyridine on the Pillared Clays

	100 °C			200 °C			300 °C			400 °C		
catalyst	AL	AB	L/B	AL	AB	L/B	AL	AB	L/B	AL	AB	L/B
Na–clay	20	2.5	8	4.5	0.56	8						
Al–PILC	72	10	7.2	64	20	3.2	38	9	4.2	24	3.6	6.7
GSiAl–PILC-1	77	65	1.2	64	35.7	1.8	65	45	1.4	60	24	2.5
SiAl–PILC-1	103	30	3.5	90	55	1.6	72	45	1.6	65	36	1.8

Table V. Cracking Activities of the Pillared Clay Compounds for Cumene[a]

catalyst	% conversion	selectivities for benzene
H–ZSM-5	94.9	75.9
Na–ZSM-5	96.2	67.8
HY	97.9	53.3
H–Mordenite	98.1	55.6
Na–clay	18.7	34.0
Al–PILC	60.6	39.5
SiAl–PILC-1	76.8	55.1
SiAl–PILC-0.5	69.8	49.8
SiAl–PILC-0.2	66.8	48.2
GSiAl–PILC-2	69.3	54.0
GSiAl–PILC-1	65.7	48.1
GSiAl–PILC-0.2	61.6	45.9

[a] Reaction conditions: pulse amount of 0.5 μL; catalyst weight, 0.1 g; reaction temperature, 400 °C.

Table VI. Catalytic Activities of the Pillared Clay Compounds for the Conversion of 1,2,4-TrMB

	disproportionation			alkylation		
catalyst	Al–PILC	GSiAl–PILC-1	SiAl–PILC-1	Al–PILC	GSiAl–PILC-1	SiAl–PILC-1
product distribn (wt %)						
toluene	2.86	2.92	3.60	0.36	0.84	1.00
p,*m*-xylene	16.92	14.37	19.97	5.11	6.69	7.22
o-xylene	10.62	7.46	9.06	2.94	2.68	9.06
1,3,5-TrMB	4.45	12.70	12.16	6.45	7.43	17.96
1,2,4-TrMB	23.54	22.19	19.90	24.87	22.12	20.46
1,2,3-TrMB	8.92	10.30	6.93	5.97	4.29	5.76
1,2,4,5-TeMB	17.75	18.42	20.67	29.50	36.23	32.36
1,2,3,5-TeMB	3.28	5.86	3.43	6.70	7.46	6.92
1,2,3,4-TeMB	0.66	0.48	1.73	2.02	0.27	4.68
selectivity for disproportionation	50.82	57.71	61.74	24.24	27.24	29.82
isomerization	30.56	29.94	22.80	16.54	15.05	13.80
dealkylation	17.31	6.89	13.56			
TeMB	28.37	32.22	34.47	50.89	56.45	55.28
fraction of 1,2,4,5-TeMB in TeMB (F)	81.84	74.40	80.02	77.15	82.41	73.61
conversion (x)	76.46	77.82	80.10	75.13	77.88	79.54

[a] Reaction conditions: pulse amount of 0.5 μL; catalyst weight, 0.1 g; reaction temperature, 400 °C.

those of Al–PILC. The results are consistent with the increase of acid sites and indicate that conversion of 1,2,4-trimethylbenzene is taking place on strong acid sites. Since Kikuchi and co-workers[32] have shown that the selectivities for disproportionation depend on the pore structure of the catalysts, it would seem that incorporating Si into pillars changes the pore structure of the pillared clays.

Summary and Conclusions

The results of this study indicate that hydroxy–SiAl pillared clays with mixed basal spacing of about 2.6 and 1.90 nm could be prepared by two different synthetic routes. The basal spacings of the pillared clay products increase with the Si/Al ratio in the pillaring solution. Hydroxy–SiAl pillared clays have higher surface areas compared to hydroxy–Al pillared clay obtained by pillaring with Si-free, hydroxy–Al oligocations. The thermal stability of the pillared clay products are improved by incorporating Si into an alumina pillar. Hydroxy–SiAl pillared clays show sharply higher concentration of both Bronsted and Lewis acid sites and higher cracking activity of cumene and conversion and selectivity for disproportionation of 1,2,4-trimethylbenzene compared to hydroxy–Al pillared clay. This increased acidity is probably due to the presence of acidic, surface silanol groups in the pillars of hydroxy–SiAl pillared clays. The pore structure of the pillared clays could be changed by incorporating Si into the pillars.

Acknowledgment. This work was supported by the Foundation of National Catalysis Laboratory of China.

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[32] Kikuchi, E.; Matsuda, T.; Fujiki, H.; Morita, Y. *Appl. Catal.* **1984**, *11*, 331.