

PREPARATION AND CHARACTERIZATION OF HYDROXY-FeAl PILLARED CLAYS

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Abstract—Solutions containing hydroxy-FeAl oligocations (HFA) were prepared by two procedures: (1) treatment of a mixture of FeCl₃ and AlCl₃ with aqueous Na₂CO₃, followed by aging of the product and (2) preliminary preparation and aging of hydroxy-Al₁₃ oligocations followed by reaction of the latter with aqueous FeCl₃. Ion-exchange of Na-montmorillonite with HFA yield pillared clay (designated as FeAl-PILC) with d(001) values of 1.98–1.56 nm and a surface area of 230 m²/g. The pillar structure, thermal stability, surface acidity, and reduction behavior of the pillared clays were determined by ²⁷Al-NMR, XRD, DTA, Mössbauer spectroscopy, Py-IR, TPD, TPR. Fe/Al ratios greatly affect the pillar structure, surface area and thermal stability of FeAl-PILC. The pillar in FeAl-PILC with Fe/Al ratio <0.5 has a Keggin structure, similar to that of Al-PILC, but the pillar structures of FeAl-PILC with Fe/Al ≥0.5 are the ferric tripolymer species similar to those of Fe-PILC. The basal spacings, surface area, and thermal stability are decreased with increasing Fe/Al ratio. There is relatively strong interaction between Fe and Al in the pillars. The interaction is enhanced with decreasing Fe/Al ratio. Reduction of the Fe phase in FeAl-PILC was reduced by the interaction of Fe with Al.

Key Words—Acidity, Hydroxy-FeAl pillars, Pillared clay, Preparation, Stability.

INTRODUCTION

Naturally occurring montmorillonite clays are layered aluminosilicates which, in their natural state, are held together by weak electrostatic forces. New classes of materials have recently been developed by exchanging the small Na⁺ ions that are normally found between these layers with inorganic metal ions of larger size and charge (Brindley and Semples, 1977; Lahav *et al.*, 1978; Vaughan, 1979). The N₂ BET surface areas of these “pillared clays” increase typically from ca. 20 m²/g before pillaring to greater than 230 m²/g. Inorganic polymeric metal ions derived from watersoluble salts of Al, Fe, Cr, Bi, Mg, Zr, Co, and Ni appear to be the most widely explored pillaring agents (Leoppert *et al.*, 1979) although it has been reported that Mo, Nb, Si, and other metal ions have been successful (Endo *et al.*, 1980, 1981; Shabtai, 1980).

A related study recently disclosed a class of hydroprocessing catalysts reported (Shabtai and Fijal, 1986) to be comprised of, for example, a Ni⁺² or Co⁺² ion-exchanged smectite that is then cross-linked with hydroxy-Al oligomers. This material is calcinated at 400–500°C and treated with an ammonium molybdate solution to yield the hydroprocessing catalyst.

In view of the above studies it was of interest to

synthesize well-defined hydroxy-FeAl oligocations for use as pillaring agents. In this paper, a series of hydroxy-FeAl pillared clays (FeAl-PILC) with various Fe/Al ratios were prepared by two methods. The thermal stability, reduction behavior, structural properties, and surface acidity of the mixed pillared clays were determined by XRD, DTA, IR, TPR, TPD, and Mössbauer spectroscopy.

EXPERIMENTAL MATERIALS AND METHODS

Starting materials

The original clay was received in its Ca⁺²-exchanged form from Heishan, Liaoning, China. This clay is reported to be composed of: 62.90 wt. % SiO₂, 15.62 wt. % Al₂O₃, 2.49 wt. % Na₂O, 2.66 wt. % MgO, 1.96 wt. % CaO, 0.02 wt. % K₂O, and 3.76 wt. % Fe₂O₃ and the structural formula is Ca_{0.03}Na_{0.62}(Al_{2.16}Fe_{0.35}Mg_{0.5})(Si_{7.86}Al_{0.14})O₂₀(OH)₄·nH₂O. The cation-exchange capacity was quoted by the supplier as 73 meq/100 g and the particle size was less than 2.0 μm. This material was exchanged to Na⁺ form with Na⁺-exchange resin (Zhao, 1990).

Hydroxy-FeAl oligomeric solution (HFA)

The pillaring agents were prepared by two methods: (A) A solution containing hydroxy-Al oligocations with an OH/Al ratio of 2.4, was prepared by the method of Lahav *et al.* (1978) and aged for 14 days. After aging, calculated amounts of 0.1 M FeCl₃, whose pH values were regulated between 4 and 4.5 by 0.1 M Na₂CO₃,

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were added to the solution with constant stirring over a period of 2 hr, to produce hydroxy-FeAl oligocation (HFA) solutions having Fe/Al molar ratios of 0.0, 0.1, 0.2, 1.0. These solutions were allowed to stand for 7 days and aged at 120°C for 4 hr before use.

(B) A measured amount of aqueous 0.1 M AlCl₃ was gradually added to an aqueous 0.1 M FeCl₃ solution, the resulting product solutions having various Fe/Al ratios. An aqueous Na₂CO₃ solution (0.1 M) was then added to these solutions at a rate of about 4 cm³/min with constant stirring until a final OH/Al+Fe ratio of 2.0 was reached. The resulting solutions were aged for two weeks and then aged at 120°C for 4 hr before use.

Cross-linking procedure

The clay sample (Na-clay, 3.0 g) was dispersed in 1000 ml of deionized water with magnetic stirring. Equal amounts of solutions containing hydroxy-FeAl oligocations (HFA) prepared by method A or method B were used as pillaring reactants to obtain ratio of 10 m mol Al+Fe/g of smectite. After completion of the reaction (usually 1–2 hr), the product was allowed to stand in contact with the solution for 16 hr. The precipitated product was then separated from the solution by centrifugation, washed with deionized water until chloride-free, then air-dried at 120°C.

Analysis of the products

The basal spacings [d(001) values] were measured on a Rigaku D/max-b X-ray diffractometer with Ni filtered Cu-K α ($\lambda = 1.5418\text{\AA}$) radiation. A China National Instrument Digital 2500 was used to obtain BET surface areas by N₂ sorption. The thermal stability of the pillared clays was examined by determining the basal spacings of samples heat-treated at 300–500°C for 2 hr in air. Elemental analyses were obtained by inductively coupled plasma spectrometry (ICPS). The SiO₂ 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. N₂ (30 cm²/min) was used as a purging gas, and the sample weight was about 15 mg.

²⁷Al-NMR spectra of the pillaring agents were acquired on a Varian FT-80A spectrometer at 80.0 mHz. Infrared spectra (IR) were obtained with a Perkin-Elmer PE-580 spectrometer with self-supporting films 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, 1.3 $\times 10^{-3}$ Pa for 2 hr. The pyridine-loaded wafers were then heated (in vacuo) at 200–400°C temperature range (at 100 intervals) for periods of 1 hr. The spectra were recorded for each temperature. Transmission Mössbauer spectra were obtained on an AME-50 Mössbauer spectrometer at room temperature. Zero velocity was defined with respect to the centroid of the metallic Fe spectrum and positive velocity

was defined as the source approaching the absorber. Using an *in situ* Mössbauer cell, samples were reduced in 101 kPa of flowing hydrogen at a desired temperature and cooled to room temperature in the flowing hydrogen.

In each temperature-programmed desorption (TPD) experiment, 0.1 g sample was placed in the cell and pretreated in vacuo at 400°C for 2 hr and then cooled to 100°C. An excess amount of n-butylamine was adsorbed at 100°C and evacuated for 30 min. This sample was kept in a stream of helium (60 ml/min, 13.3 KPa) for 1 hr to attain a steady flow, followed by heating at a rate of 16°C/min. A mass spectrograph (HP-5980) was used to monitor the desorbed n-butylamine and other species such as butene ($m/e = 56$). Water was desorbed simultaneously with ammonia in a temperature range higher than the pretreatment temperature. In the temperature programmed reduction (TPR) measurement, the sample weighing 0.1 g was placed in the cell. A mixture of 10% H₂ in Ar was fed to the cell at 65 cm³/min and the temperature was ramped linearly at 10°C/min while the H₂ consumption was monitored by a thermal conductivity detector.

RESULTS AND DISCUSSION

Hydroxy-FeAl pillared clays (FeAl-PILC)

Hydroxy-FeAl pillared clay products denoted as FeAl-PILC-A were prepared using the method A pillaring solution obtained by dispersing Na-montmorillonite with HFA oligomeric solutions of Fe/Al ratios of 0.0, 0.1, 0.2, 1.0. The total amount of HFA solution applied in each preparation was such as to contain 10 m mol of Fe+Al/g of montmorillonite. A second series of hydroxy-FeAl pillared clay products, denoted as FeAl-PILC-B, was prepared using the method B pillaring solution obtained by dispersing the above montmorillonite with HFA oligomeric solutions of Fe/Al ratios of 0.1, 0.2, 0.5, 1.0, and 2.0. In these preparations, the OH/Fe+Al ratio of the HFA solution was adjusted to 2.0 and the amount of HFA solution used in each case was such as to contain 10 m mol of Fe+Al/g of montmorillonite. A reference sample pillared with hydroxy-Fe oligocations only (Fe/Al ratio = ∞) was also prepared by this method.

The d(001) values and surface areas of the above products are summarized in Table 1 and Table 2, respectively. The d(001) values of the samples prepared by method A and method B were in the range 1.98–1.50 nm at 120°C and decreased with increasing Fe/Al ratio in the pillaring solution. The d(001) values and XRD patterns of FeAl-PILC products prepared by method B were similar to those with the same of Fe/Al ratios prepared by method A. The surface areas of the samples also decreased considerably with increasing Fe/Al ratio. The basal spacings of the pillared clays with Fe/Al <0.5 were in the range 1.82–1.98 nm and

Table 1. Basal spacing, $d(001)$, of hydroxy-FeAl pillared clays with various Fe/Al ratios and calcining temperature.

Sample	Fe/Al ratio in pillaring solution	Method	$d(001)$ (nm)			
			120 °C	300 °C	400 °C	500 °C
Al-PILC	0	A	1.82	1.88	1.84	1.78
FeAl-PILC-A0.1	0.1	A	1.92	1.85	1.84	1.82
FeAl-PILC-A0.2	0.2	A	1.90	1.87	1.81	1.72
FeAl-PILC-A1	1	A	1.58	1.43	1.38	1.24
FeAl-PILC-B0.1	0.1	B	1.98	1.95	1.94	1.86
FeAl-PILC-B0.2	0.2	B	1.96	1.94	1.84	1.85
FeAl-PILC-B0.5	0.5	B	1.76	1.69	1.59	1.11
FeAl-PILC-B1	1	B	1.56	1.57	1.52	1.08
FeAl-PILC-B2	2	B	1.53	1.52	1.33	1.02
Fe-PILC	∞	B	1.50	1.50	1.23	1.03
Na-clay	—	—	1.23	1.08	0.98	0.96

Table 2. Surface area (m^2/g) of hydroxy-FeAl pillared clays as function of Fe/Al ratio in the hydroxy-FeAl (HFA) pillaring solution.

Sample	Fe/Al ratio	Method	Area (m^2/g)
Na-clay	—	—	64
FeAl-PILC-B0.1	0.1	B	237
FeAl-PILC-B0.2	0.2	B	201
FeAl-PILC-B1	1	B	170
Fe-PILC	∞	B	119
FeAl-PILC-A0.1	0.1	A	226
Al-PILC	0	A	232

slightly larger than the hydroxy-Al pillared clay (Al-PILC), but the basal spacings of the pillared clays with $\text{Fe/Al} \geq 0.5$ were in the range 1.56–1.50 nm and similar to that of hydroxy-Fe pillared clay (Fe-PILC). These results indicate that the dimension of the HFA cross-linking species with Fe/Al in a direction vertical to the smectite layers is similar to that of hydroxy- Al_{13} oligocation when Fe/Al is < 0.5 . Incorporation of the Fe^{3+} ion with a larger ionic radius (0.64 nm) than the Al^{3+} ion (0.51 nm) led to increasing $d(001)$ values, but the structure of the HFA pillaring species with $\text{Fe/Al} \geq 0.5$ is similar to that of hydroxy- Fe^{3+} oligomer (Yamanaka and Hattori, 1988).

Evidence for the structure of the hydroxy-FeAl oligocation in the pillaring solution is provided by the ^{27}Al -NMR spectra in Figure 1. HFA with Fe/Al ratio < 0.5 prepared by two different synthetic routes displays two bands at 62.68 ppm and 0.45 ppm similar to that of the hydroxy-Al oligocation. Akitt and Farthing (1981) have shown that the former band may arise from tetrahedral alumina in hydroxy-Al oligocation, Al_{13} , $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ and the latter is from free Al^{3+} ion. As shown in Figure 1, HFA with Fe/Al ratio ≥ 0.5 exhibits two bands attributed to AlO_2^- ion and Al^{3+} at 80.11 ppm and -0.68 ppm, respectively. These suggest that the structures of HFA with $\text{Fe/Al} < 0.5$ prepared by two different synthetic routes are similar to that of hydroxy-Al oligocation, or the Keggin structure. Vaughan (1987) has indicated that one or more of Fe^{3+} ions may substitute for either, or both, of the tetrahedral or octahedral Al in Al_{13} . This suggests that Fe^{3+} ions in the pillaring solution with $\text{Fe/Al} < 0.5$ prepared by method A, can react and replace the Al^{3+} in the Al_{13} . However, AlO_2^- and Al^{3+} ions may occur in the pillaring solution with $\text{Fe/Al} \geq 0.5$. This suggests that the structure of HFA with $\text{Fe/Al} \geq 0.5$ is similar to that of hydroxy-Fe oligomers and not the Keggin structure. ^{27}Al NMR spectra of FeAl-PILC products prepared by method B were similar to those with the same Fe/Al ratios prepared by method A. As shown by ^{27}Al NMR spectra and XRD, it is obvious that with the same Fe/Al ratio, the structure of FeAl-PILC products prepared by method B is the same as that prepared by method A and Fe^{3+} in the

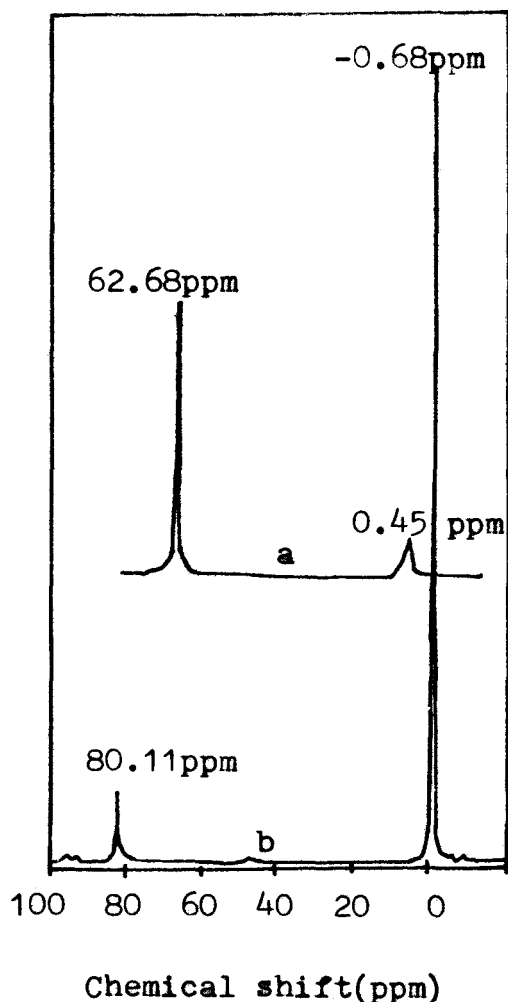


Figure 1. ^{27}Al -NMR spectra of hydroxy-FeAl (HFA) oligocations: a) with Fe/Al ratio of 0.2; b) with Fe/Al ratio of 1.0.

Table 3. Elemental composition (wt.%) and structural formula of hydroxy-FeAl pillared clay products.

Sample	Fe/Al ratio	Method	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Structural formula
FeAl-PILC-B0.1	0.1	B	55.13	24.61	3.65	Fe _{0.04} Al _{0.83} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-B0.2	0.2	B	59.83	18.76	5.91	Fe _{0.23} Al _{0.6} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-B0.5	0.5	B	58.59	18.31	10.55	Fe _{0.71} Al _{0.59} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-B1	1	B	58.83	14.74	12.10	Fe _{0.86} Al _{0.02} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-B2	2	B	40.07	9.39	34.21	Fe _{5.04} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
Fe-PILC	∞	B	33.99	3.76	43.18	Fe _{7.5} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-A0.1	0.1	A	61.61	20.01	4.26	Fe _{0.06} Al _{0.7} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-A0.2	0.2	A	60.37	16.83	7.62	Fe _{0.39} Al _{0.28} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
FeAl-PILC-A1	1	A	46.50	9.40	28.67	Fe _{3.29} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
Al-PILC	0	A	59.72	19.89	3.57	Al _{0.78} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄
Na-clay	—	—	62.90	15.62	3.76	Ca _{0.03} Na _{0.62} (Al _{2.16} Fe _{0.35} Mg _{0.5})(Si _{7.86} Al _{0.14})O ₂₀ (OH) ₄ ·nH ₂ O

pillaring solution prepared by method B can also react and copolymerize with the Al³⁺ and produce the species above.

The elemental compositions of the pillared clays are summarized in Table 3. The Fe₂O₃ content of products increased greatly relative to that of the reference Al-PILC with an increasing Fe/Al ratio in the pillaring solution. This result suggests that hydroxy-FeAl pillared clay products with different Fe₂O₃ contents can be prepared by adjusting the Fe/Al ratio in the pillaring solution. The structural formulas of the pillared clays are also summarized in Table 3. The sum of Fe and Al atoms in the pillars of hydroxy-FeAl pillared clay products with Fe/Al < 0.5 are similar to the numbers of Al in the pillars of Al-PILC by exchange of hydroxy-Al, the Al₁₃⁷⁺ oligocation, into interlayer of the clay. This suggests that the pillar structure of FeAl-PILC with Fe/Al < 0.5 is the Keggin structure and is produced by the substitution of Fe³⁺ ions with the Keggin ions in the hydroxy-Al oligocation solution. On the other hand, the sum of Fe and Al atoms in the pillars of FeAl-PILC with Fe/Al ≥ 0.5 are much larger than the number of Al atoms in the pillars of Al-PILC. This result suggests the possible presence of extra-layer Fe in hydroxy-FeAl pillared clay products in addition to intra-layer pillars. The pillar structure of FeAl-PILC with Fe/Al ≥ 0.5 is not the Keggin structure and may be similar to that of Fe-PILC.

Fe/Al ratio in the pillaring solution greatly affects XRD patterns and d(001) values of FeAl-PILC products (Table 1). As shown in Figure 2, XRD patterns of FeAl-PILC with Fe/Al < 0.5 are similar to that of Al-PILC and do not show (002), (003) lines (Figures 2A and 2B). On the other hand, XRD patterns of FeAl-PILC with Fe/Al ≥ 0.5 (Figures 2C, 2D and 2E) show (002), (003) lines, and a d(001) value about 1.56 nm similar to that of Fe-PILC. The FeAl-PILC products with different Fe/Al ratio have different pillar structures. Those with Fe/Al < 0.5 have the pillaring structure similar to that of Al-PILC and the others with Fe/Al ≥ 0.5 have the pillaring structure similar to that of Fe-PILC.

Thermal stabilities

The effect of treatment temperatures on the intensity of the (001) peak and the d(001) value is a convenient way to investigate the thermal stability of a pillared clay (Tichit *et al.*, 1985). As shown in Figure 3, after the original clay (Na-clay, Heishan, Liaoning) was cal-

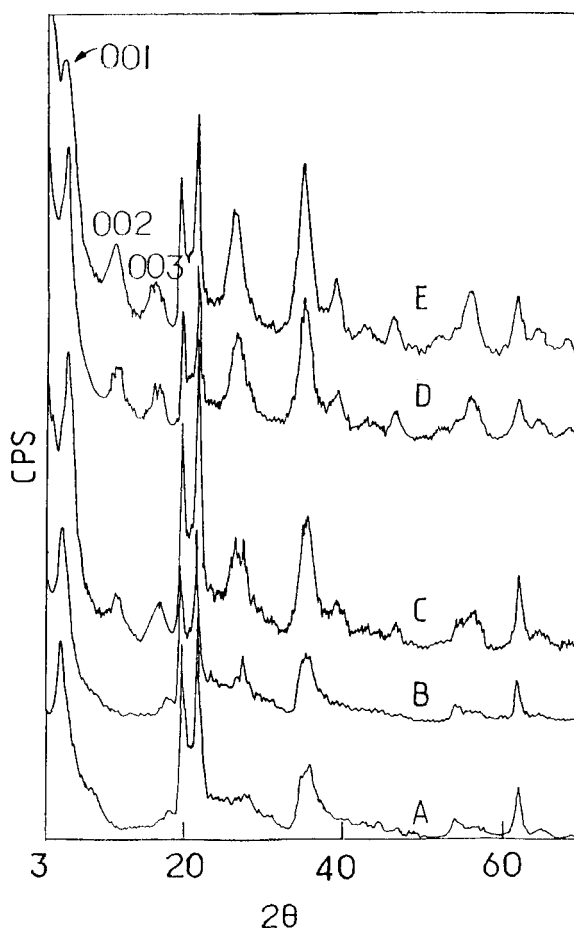


Figure 2. XRD pattern of hydroxy-FeAl pillared clay with Fe/Al ratio of: A) 0.1; B) 0.2; C) 0.5; D) 1; E) 2.

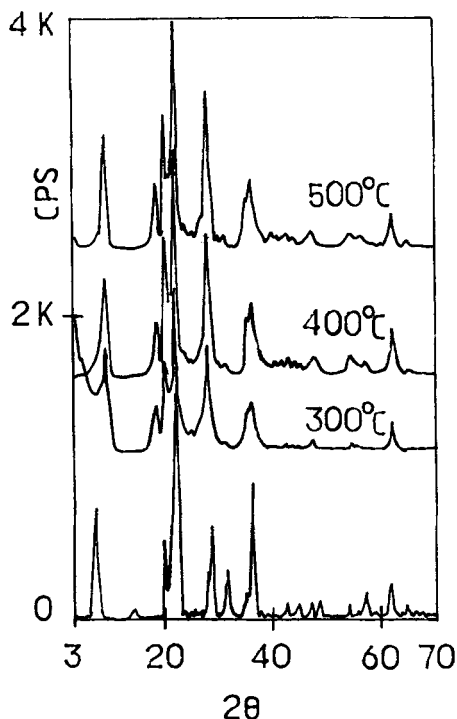


Figure 3. XRD pattern of original clay (Na-clay) calcined at different temperatures.

inated at the temperature range 300–500°C, the intensity of (001) line of this clay was hardly changed, although the $d(001)$ values changed to 0.96 nm from 1.23 nm (Table 1). The layer shrinkage arises from dehydration of the hydrous interlayer cations. As shown

in Figure 4, treatment of FeAl-PILC in the temperature range 300–500°C hardly affected the intensity of the (001) line. The regular intercalation of the two-dimensional lattice is fairly well retained after temperature treatments. However, the (001) line reflection shifted to a larger angle. The layer distance decreased by 0.1 to 0.51 nm when the temperature increased from 300 to 500°C. The shrinkage increases with the Fe/Al ratio in the pillaring agents. This indicates that the thermal stability of FeAl-PILC decreases with increasing Fe/Al ratio. This shrinkage may arise from dehydroxylation of hydroxy-FeAl oligomer pillars into a complex Fe-Al oxide and destruction of the pillars (Matsuda *et al.*, 1988).

DTA was also used to investigate the thermal stability of the pillared clays. As shown in Figure 5, FeAl-PILC products show one small endothermic peak at about 600°C assigned to dehydroxylation of any remaining hydroxide pillars besides one endotherm near 123°C induced by dehydration (Zhao, 1990). The thermal stability of FeAl-PILC is fairly good (Zhao, 1990). The temperature of the small peak rises with decreasing Fe/Al ratio suggesting that the thermal stability of FeAl-PILC products is increased with decreasing Fe/Al ratio. FeAl-PILC products with Fe/Al ratio ≥ 0.5 also show an endothermic peak at about 300°C, which is assigned to dehydroxylation of Fe-hydroxide pillars to Fe-oxide. This result is consistent with the possible presence of pillars in FeAl-PILC with Fe/Al ≥ 0.5 similar to the hydroxy-Fe oligomer in Fe-PILC. The temperature of the peak rises with decreasing Fe/Al ratios. The thermal stability of FeAl-PILC products decreases with increasing Fe/Al ratio.

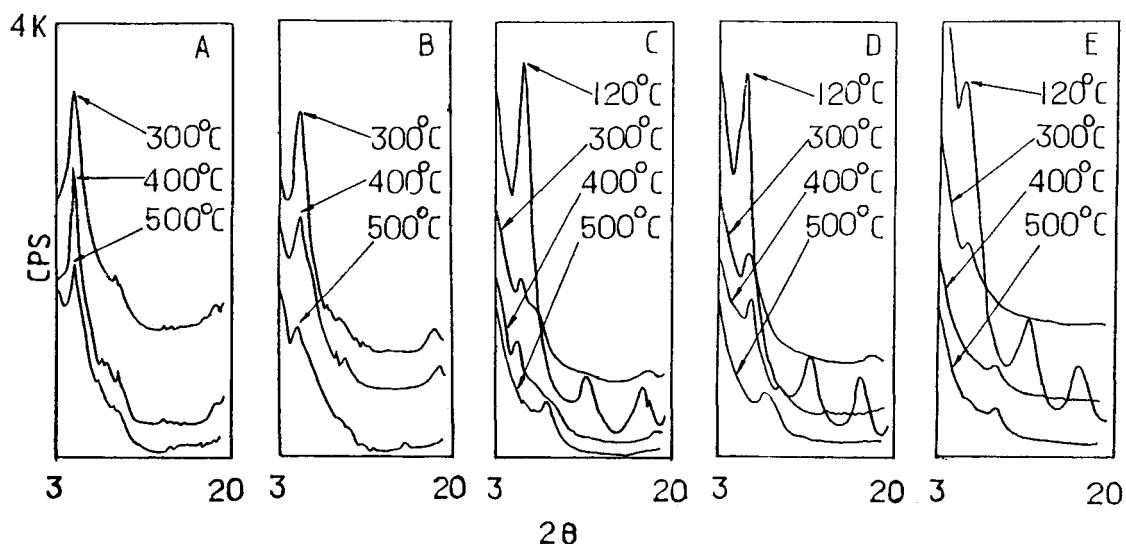


Figure 4. XRD patterns of pillared clay products calcined at different temperatures: A) FeAl-PILC-B0.1; B) FeAl-PILC-B0.2; C) FeAl-PILC-B0.5; D) FeAl-PILC-B1; E) FeAl-PILC-B2. B0.1, B0.2, etc. define the preparation procedure and the Fe/Al ratio.

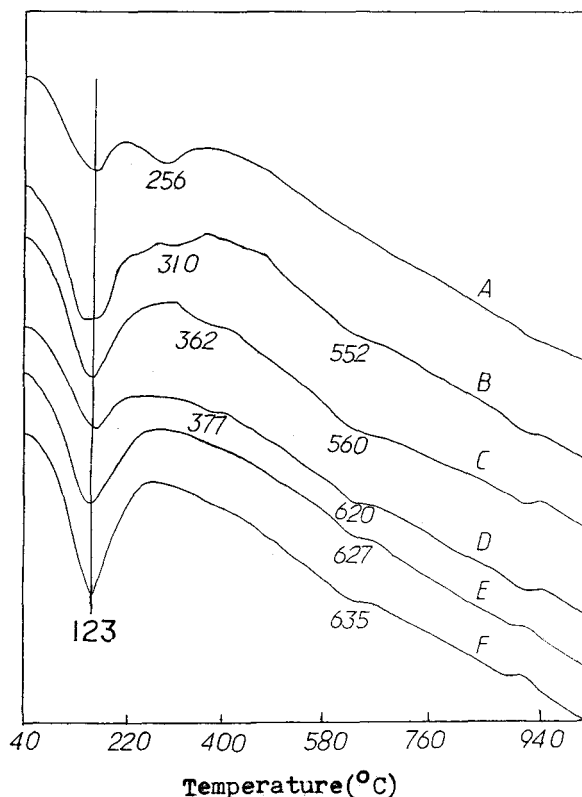


Figure 5. DTA profiles of pillared clay products: A) Fe-PILC; B) FeAl-PILC-B0.2; C) FeAl-PILC-B1; D) FeAl-PILC-B0.5; E) FeAl-PILC-B0.2; F) FeAl-PILC-B0.1. B0.1, B0.2, etc., same as Figure 4.

Acidic properties

The acidic properties of the clay compounds used in this study were measured by means of *n*-butylamine TPD and IR spectroscopy using pyridine as a probe molecule. In a *n*-butylamine TPD spectrum of FeAl-PILC products, it was observed that butene ($m/e = 56$), propane ($m/e = 43$), propylene ($m/e = 40$), and ethylamine ($m/e = 45$) may be desorbed besides *n*-butylamine ($m/e = 73$). In the course of desorption of *n*-butylamine from the pillared clays, a cracking reaction is taking place. The acidic intensity of pillared clay can then be estimated by the amount of the desorbed species such as butene ($m/e = 56$). The *n*-butylamine TPD data for the pillared clays are summarized in Table 4. The desorption of *n*-butylamine and other species from FeAl-PILC was much greater than from the original Na-montmorillonite. This indicates that the acidity of pillared clays comes from their pillars and the acid strength is enhanced by pillaring. As seen in Table 4, hydroxy-FeAl pillared clay products produced less desorbed *n*-butylamine and other species compared to Al-PILC. The amount of desorbed *n*-butylamine and other species also decreased with increasing Fe/Al ratio and indicates that the surface acidity of pillared clays

Table 4. Peak temperature and relative areas of *n*-butylamine TPD of hydroxy-FeAl pillared clay products.

Catalyst	$m/e = 73$		$m/e = 56$	
	T (°C)	Area	T (°C)	Area
Na-clay	150	47	147, 366	145
Al-PILC	224	100	238, 421	629
FeAl-PILC-B0.1	187	96	168, 430	581
FeAl-PILC-B0.2	170	95	162, 411	579
FeAl-PILC-B1	162	82	212, 402	445
FeAl-PILC-Al	162	62	166, 367	287
Fe-PILC	156	52	156, 358	202
FeAl-PILC-B0.1 ^a	220	84	239, 415	683
FeAl-PILC-B1 ^a	184	83	172, 367	293
FeAl-PILC-B1 ^a	200	56	227, 417	452
Fe-PILC ^a	236	52	236, 438	256

^a After H₂ reduction treatments at 400°C for 2 hr.

varies with pillaring composition when Fe is incorporated into the pillars.

Spectra for the pillared clays in the OH stretching region show a prominent free-OH band centered between 3629 and 3635 cm⁻¹ (Figure 6). After degassing at 400°C, a weaker shoulder near 3737 cm⁻¹ is seen in all the samples. The 3737 cm⁻¹ band is possibly due to silanol groups formed in the tetrahedral layer upon acidification. On the other hand, after adsorption of pyridine, the band at 3737 cm⁻¹ disappeared (seen in Figures 6B and D). It represents a bond that reacts readily with pyridine. After treatment at 500°C, IR spectra for the pillared clays in the OH stretching region differed with the Fe/Al ratio. Their intensity decreased greatly with an increasing Fe/Al ratio. The changes seem to correspond to the surface acidity changes with the Fe/Al ratio and are related to the surface OH of the pillared clays. Several bands near 3635, 3650 and 3709 cm⁻¹ were observed in the IR spectra for hydroxy-FeAl pillared clay products with Fe/Al ≥ 0.5, but were barely observed for hydroxy-Fe pillared clay after calcination above 400°C (see in Figure 6D, E, F). Na-montmorillonite, hydroxy-Al pillared clay and FeAl-PILC products with Fe/Al < 0.5 were not expected to lose all of their structural OH groups at such a low temperature. We think that there are extra-layer hydroxy-Fe in FeAl-PILC products with Fe/Al ≥ 0.5 in addition to intra-layer pillars. After calcination the extra-layer hydroxy-Fe can lose its hydroxy group, deposit on the clay layer surface, and occupy the surface OH group sites of the pillared clays, thus causing the loss of their surface OH groups.

Infrared spectra in the region 1400–1600 cm⁻¹ obtained by evacuating the pyridine-adsorbing pillared clays at different temperatures are shown in Figure 7. As reported previously (Ocelli and Finseth, 1986), these pillared clays contain both Bronsted and Lewis acid sites as characterized by the absorption bands of pyridine appearing at 1540 cm⁻¹ and 1450 cm⁻¹, respectively, when treated at 200°C. IR spectral data for

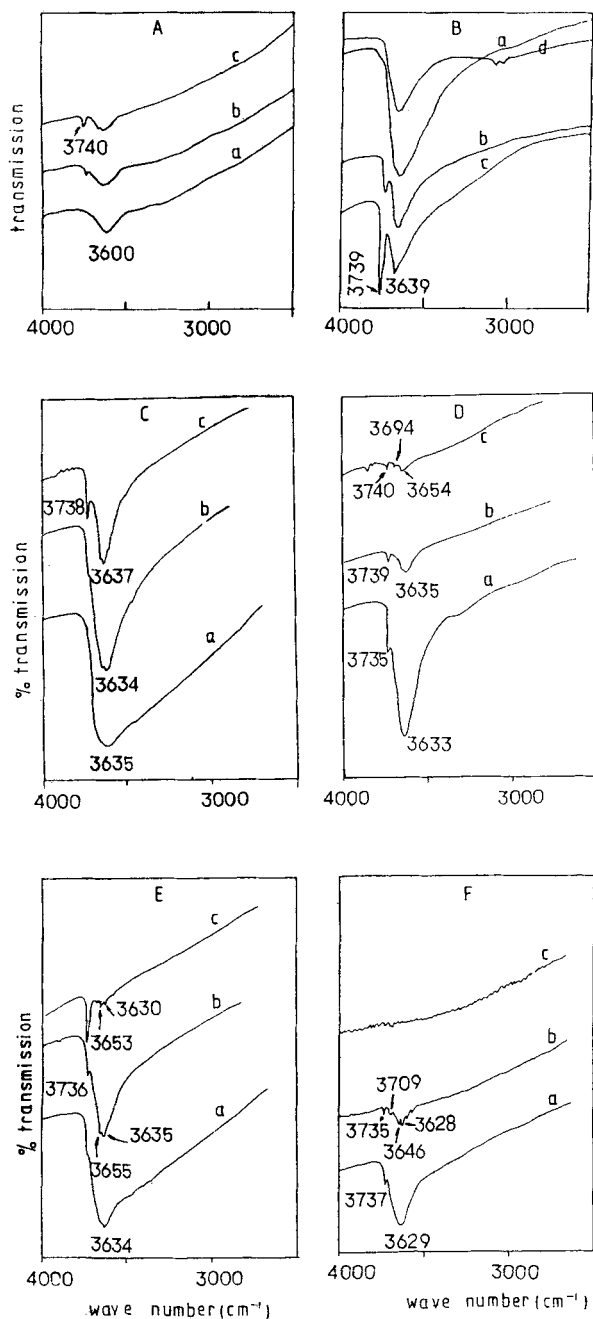


Figure 6. Hydroxy absorption bands for A) Na-clay; B) Al-PILC; C) FeAl-PILC-B0.2; D) FeAl-PILC-B1; E) FeAl-PILC-B2; F) Fe-PILC after degassing at different temperatures such that a = 300°C, b = 400°C and c = 500°C. Or, d = after pyridine adsorption and degassing at 400°C for 1 hr.

adsorbed pyridine are summarized in Table 5. Pillared clays have more Bronsted and Lewis sites compared to the original Na-clay. Compared to hydroxy-Al pillared clay, FeAl-PILC products have fewer Bronsted and Lewis acid sites and a higher L/B ratio. Intensities of bands assigned to pyridine coordinated with Lewis

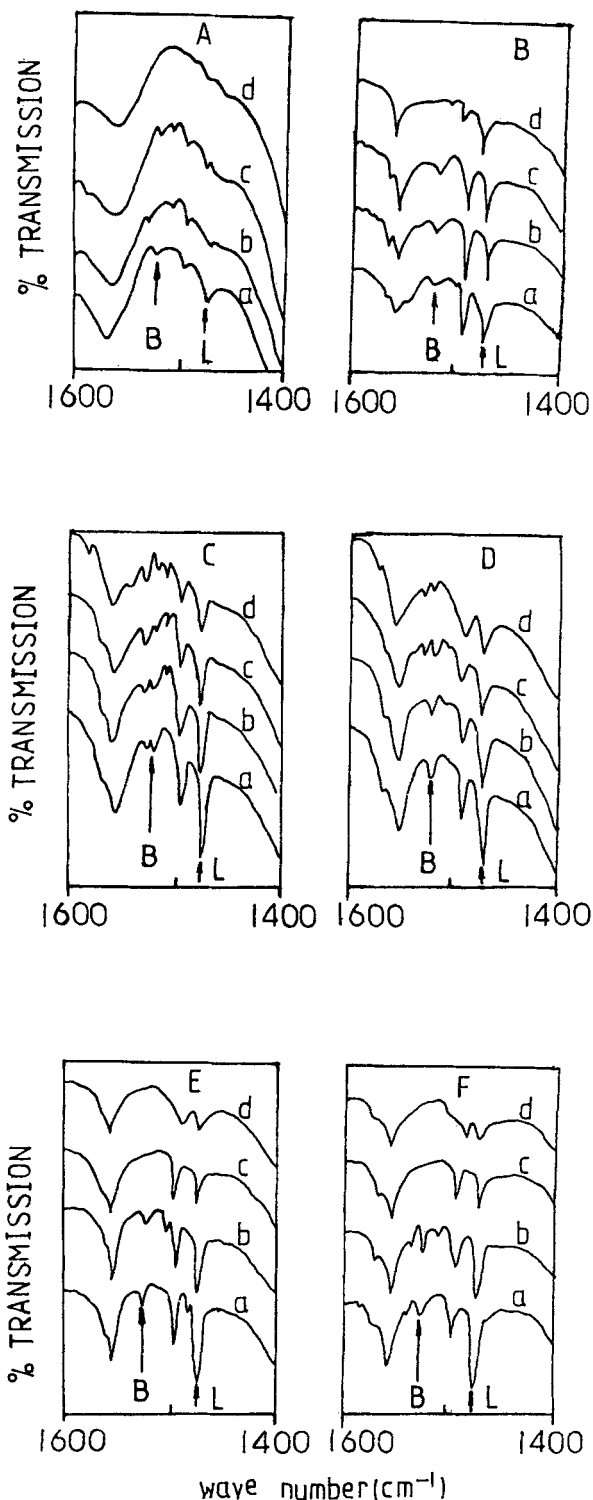


Figure 7. IR spectra of pyridine sorbed on pillared clay products: A) Na-clay; B) Al-PILC; C) FeAl-PILC-B0.2; D) FeAl-PILC-B1; E) FeAl-PILC-B2; F) Fe-PILC, after degassing at different temperatures such that a = 100°C, b = 200°C, c = 300°C, and d = 400°C.

Table 5. IR data for pyridine adsorbed on the pillared clays.

Catalyst	100°C			200°C			300°C			400°C		
	A _L	A _B	L/B	A _L	A _B	L/B	A _L	A _B	L/B	A _L	A _B	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
FeAl-PILC-B0.2	70	9	7.8	52.5	10	5.3	32	4.5	7.1	29.6	2.5	11.8
FeAl-PILC-B1	64	8	8	46.5	9.1	5.1	26.2	3.2	11.9	21	1	21
FeAl-PILC-B2	63	6	10.5	42	6	7	18	—	—	16	—	—
Fe-PILC	63	5	12.6	36	4.5	8	11.5	—	—	10.5	—	—

L = Intensity of band due to interaction with Lewis site.

B = Intensity of band due to interaction with Bronsted site.

and Bronsted acid sites are reduced with calcination temperature. With regard to FeAl-PILC with Fe/Al ≥ 0.5 above 300°C, in vacuo, pyridine is desorbed first from Bronsted sites and the intensities of its bands at 1544 or 1540 cm^{-1} are reduced significantly. However the bands assigned to pyridine on Lewis acid sites are retained even after degassing at 400°C. In contrast, FeAl-PILC with Fe/Al < 0.5 retained pyridine on Bronsted and Lewis acid sites even after evacuation at 400°C. The change in the Bronsted acidic sites in FeAl-PILC products with temperature is consistent with changes in the IR intensity of surface OH groups with calcining temperature and suggests that Bronsted acid

sites of the pillared clays come from their surface OH group. The stability of Bronsted and Lewis acidities in the pillared clay products seems to be relative to the Fe/Al ratio and incorporating Fe into an alumina pillar decreases the Bronsted acid sites, but increases the L/B ratio.

Reduction behavior of FeAl-PILC

The Mössbauer spectra obtained from FeAl-PILC with various Fe/Al ratios at 25°C are shown in Figures 8 to 10. The spectra consist of a broadened Fe^{3+} doublet with a peak width (FWHM) of 0.12–0.42 mm/s at an isomer shift of 0.42–0.48 mm/s. The fitted Mössbauer parameters including isomer shift (δ), quadrupole splitting (Δ), hyperfine splitting (H), and peak width (Γ) as listed in Table 6 are in agreement with those obtained from pillared clays by Lee *et al.* (1989). The Mössbauer features observed in Figure 8 are caused by Fe-complexed hydroxy ligands in pillars of FeAl-PILC and appear to be independent of Fe/Al ratio. However, after calcination at 300–500°C the Mössbauer features differ with Fe/Al ratio of the FeAl-PILC; the Mössbauer spectra (Figure 8E, F) obtained from Fe-PILC after calcining in air above 300°C contain six lines assigned to $\alpha\text{-Fe}_2\text{O}_3$. This indicates that the pillars in Fe-PILC are transformed to $\alpha\text{-Fe}_2\text{O}_3$. The transformation temperature of the pillars of FeAl-PILC with Fe/Al ratio of 1.0 to $\alpha\text{-Fe}_2\text{O}_3$ must be above 500°C.

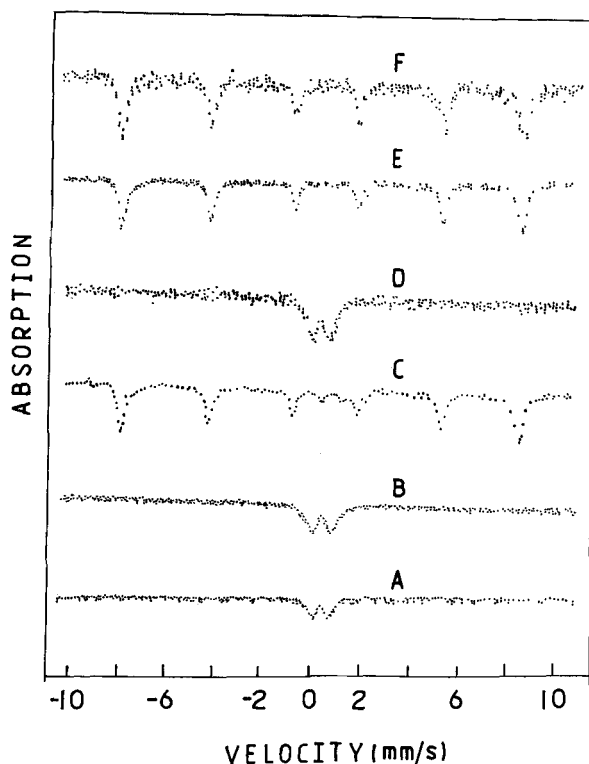


Figure 8. Room temperature Mössbauer spectra of hydroxy-FeAl pillared clay with Fe/Al ratio=1 (A, B, and C) and hydroxy-Fe pillared clay (D, E, and F) after calcining at 120°C (A and D), 300°C (B and E), and 500°C (C and F).

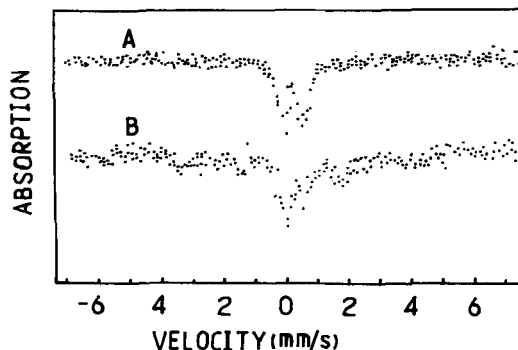


Figure 9. Room temperature Mössbauer spectra of A) original Na-clay and B) after treatment in H_2 at 500°C for 2 hr.

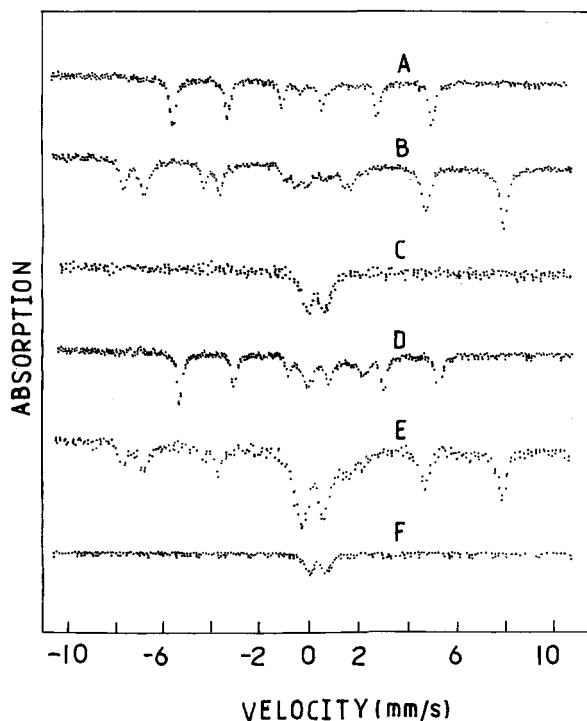


Figure 10. Room temperature Mössbauer spectra of hydroxy-Fe pillared clay (A, B, and C) and hydroxy-FeAl pillared clay with Fe/Al ratio=1 (D, E, and F) before (F and C) and after H_2 reduction treatments at 300°C (B and E) or 500°C (A and D) for 2 hr.

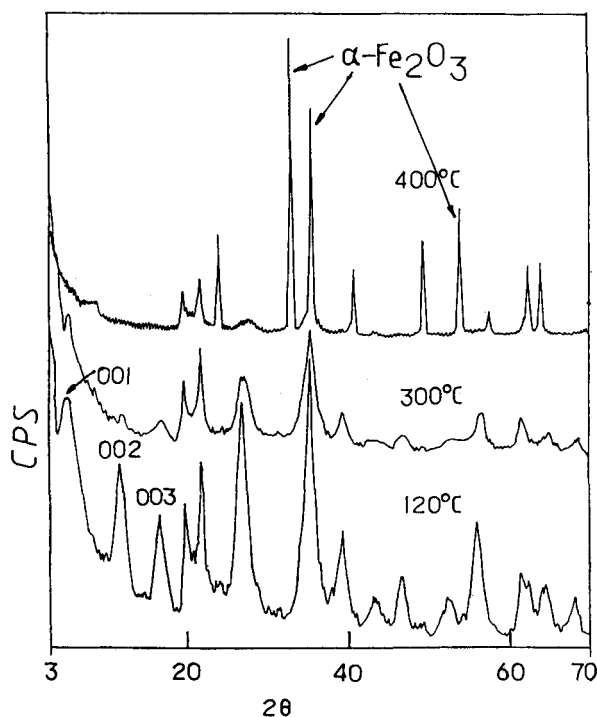


Figure 11. XRD pattern of hydroxy-Fe pillared clay calcinated at different temperatures.

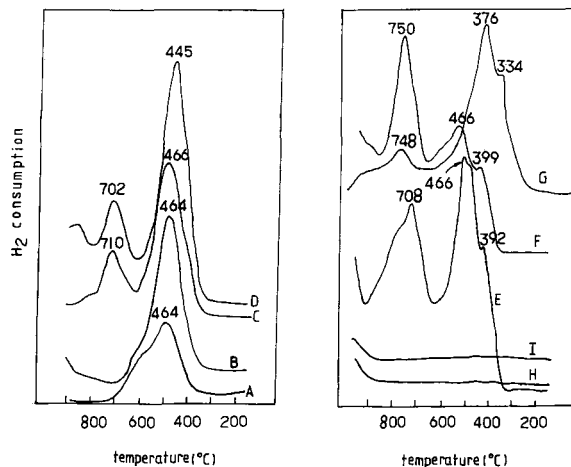


Figure 12. Temperature-programmed reduction (TPR) spectra for pillared clay products: A) Fe-PILC; B) FeAl-PILC-B2; C) FeAl-PILC-B1; D) FeAl-PILC-B0.5; E) FeAl-PILC-B0.2; F) FeAl-PILC-B0.1; G) Fe/Na-clay (5% Fe_2O_3 wt.); H) Al-PILC; I) Na-clay.

XRD patterns of the pillared clays (Figure 11) show that above 300°C, the Fe-PILC product contains several new lines at d-values of 0.272, 0.252, and 0.169 nm caused by α - Fe_2O_3 , but for FeAl-PILC with Fe/Al ratio of 1.0 these lines α - Fe_2O_3 only appear after calcination above 500°C. For FeAl-PILC products with ratio <0.5 these lines never appear after calcination in the above temperature range. The results indicate that the interaction of Fe with alumina in the pillars of FeAl-PILC products can occur.

The spectrum of the original clay (Na-clay) in Figure 9B obtained following treatment at 500°C in H_2 does not show any reduction and indicates that Fe oxides in the clay layer are difficult to reduce. However, the spectrum of Fe-PILC in Figure 10 B obtained following treatment at 300°C shows some reduction (ca. 70% and 10.6% spectral area) to Fe_3O_4 and Fe^{2+} , respectively. Following reduction at 500°C, 98.9% of the total spectral area belongs to metallic Fe as indicated by the six-line bands of metallic Fe (see Figure 10A and Table 6) and 1.1% belongs to Fe^{3+} retained. Below 300°C, the spectrum of FeAl-PILC with Fe/Al ratio of 1.0 provided Mössbauer trends of Fe_3O_4 and Fe^{3+} different from that observed for Fe-PILC. However, FeAl-PILC with Fe/Al ratio of 1.0 could be partly reduced (ca. 28.2% spectral area) to metallic Fe at temperature of 500°C as shown in Figure 10 F. Comparison of Fe-PILC specimens shown in Table 6 indicates that FeAl-PILC products are more difficult to reduce to the metallic Fe. Moreover after reduction at 300°C, FeAl-PILC with Fe/Al ratio of 1.0 could produce 32.6% Fe_3O_4 and 0.9% Fe^{2+} , whereas Fe-PILC specimens under the same conditions showed significant reduction (ca. 70.5% and 10.6% spectral area) to Fe_3O_4 and Fe^{2+} , respectively. The reduction behavior of FeAl-PILC is

Table 6. Fitted parameters for Mossbauer spectra of pillared clays.

Sample	Treatment condition	Mossbauer parameter				Iron species	Relative areas (%)
		δ (mms ⁻¹)	Δ (mms ⁻¹)	H (KOe)	Γ (mms ⁻¹)		
Na-clay	Fresh	0.29	0.84	0	0.40	Fe ³⁺	100
	Reduced in H ₂ at 500°C for 2 hr	0.29	0.84	0	0.35	Fe ³⁺	100
FeAl-PILC-B0.2	Fresh	0.42	0.68	0	0.42	Fe ³⁺	100
FeAl-PILC-B1	Fresh	0.44	0.71	0	0.24	Fe ³⁺	100
	Calcinated in air at 300°C for 2 hr	0.42	0.86	0	0.25	Fe ³⁺	100
	Calcinated in air at 500°C for 2 hr	0.42	0.86	615	0.16	Fe ₂ O ₃	100
	Reduced in H ₂ at 300°C for 2 hr	0.36	0.93	0	0.55	Fe ³⁺	66.5
		0.59	0	587	0.41	Fe ₃ O ₄	32.6
		0.93	0	553	0.62	Fe ₃ O ₄	
		1.32	1.01	0	0.72	FeO	0.9
	Reduced in H ₂ at 500°C for 2 hr	0	0	397	0.11	Fe ⁰	28.2
		1.18	2.33	0	0.28	Fe ₃ O ₄	42.7
		0.47	0.91	0	0.23	Fe ³⁺	23.4
	0.92	1.81	0	0.28	FeO	5.8	
FeAl-PILC-A1	Fresh	0.42	0.68	0	0.40	Fe ³⁺	100
FeAl-PILC-B2	Fresh	0.42	0.65	0	0.20	Fe ³⁺	100
Fe-PILC	Fresh	0.46	0.75	0	0.12	Fe ³⁺	100
	Calcined in air at 300°C for 2 hr	0.49	0.87	617	0.15	α -Fe ₂ O ₃	100
	Calcined in air at 500°C for 2 hr	0.68	0.24	618	0.29	α -Fe ₂ O ₃	100
	Reduced in H ₂ at 300°C for 2 hr	0.48	0.63	0	0.50	α -Fe ₂ O ₃	17.7
		0.67	0	557	0.31	Fe ₃ O ₄	70.5
		0.92	0	596	0.35	Fe ₃ O ₄	
		0.86	1.18	0	0.47	FeO	10.6
		0	0	428	0.18	Fe ⁿ	1.9
	Reduced in H ₂ at 500°C for 2 hr	0.45	0	0	0.15	Fe ³⁺	1.1
		0	0	398	0.14	Fe ⁰	98.9

similar to the behavior of supported Fe catalysts of low loading on alumina where reduction of Fe³⁺ to lower states than Fe²⁺ is difficult (Garten and Ollis, 1974) and spinel-like structures of Fe oxides are probably obtained. It is generally recognized that the interaction between Fe and alumina in the pillars of FeAl-PILC products is too strong to allow formation of metallic iron.

TPR spectra obtained for FeAl-PILC with various Fe/Al ratios are presented in Figure 12. H₂ consumption is not observed in the TPR spectra for the Na-clay (Figure 12I) and the hydroxy-Al pillared clay (Figure 12H) in the temperature range of 100–800°C. Fe oxides in the clay layer are difficult to reduce. The TPR spectra for FeAl-PILC with Fe/Al \geq 0.5 are composed of two peaks of H₂ consumption. As shown in previous reports (Hurst, 1982) and our Mössbauer spectra, it is obvious that the first peak corresponds to the reduction of Fe(III) in pillars of the pillared clays to Fe₃O₄ while the second peak corresponds to the reduction of Fe₃O₄ to large metallic Fe particles. The temperatures of both peaks of H₂ consumption decrease with increasing Fe/

Al ratio. Fe/Al ratio also affects the relative areas of these peaks. Only one H₂ consumption peak assigned to reduction of Fe³⁺ to Fe₃O₄ was observed in the TPR spectra for FeAl-PILC with Fe/Al < 0.5. These results suggest that the interaction of Fe with alumina in pillars of FeAl-PILC products can occur and is enhanced with decreasing Fe/Al ratio, but is too strong to allow formation of metallic iron in FeAl-PILC with Fe/Al < 0.5.

To illustrate the interaction between Fe and alumina in the pillars of the pillared clay products, the TPR spectra of Fe-PILC and FeAl-PILC products obtained after calcination in Argon at 400°C for 2 hr are shown in Figure 13. The temperature of both H₂ consumption peaks of FeAl-PILC products was higher and the areas of the these peaks decreased compared to those of the untreated samples. On the other hand, the TPR spectra of Fe-PILC after calcining hardly changed when compared to that of the untreated samples. It is possible that spinel-like structures of Fe oxides in pillars of FeAl-PILC products are formed during calcination and the interaction of Fe with alumina is stronger than in the untreated samples.

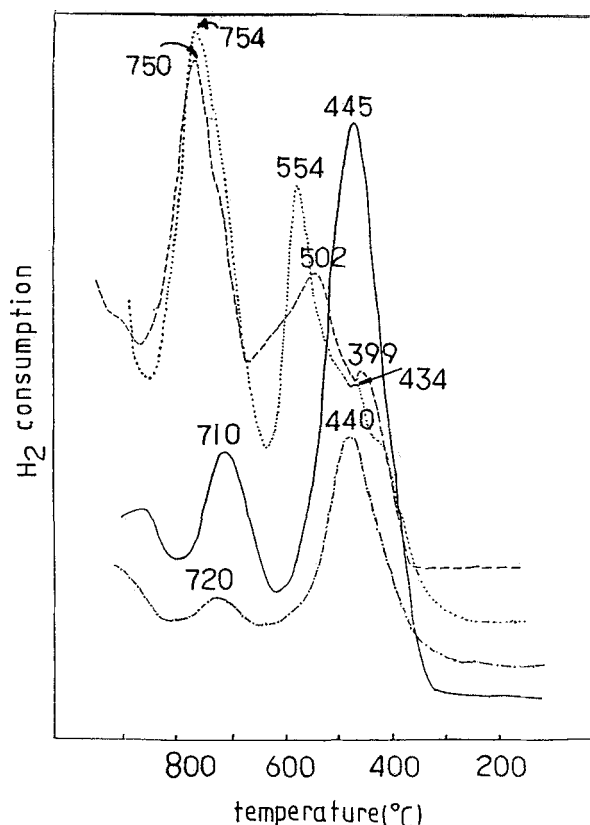


Figure 13. Changes in temperature-programmed reduction (TPR) spectra for pillared clay products after calcining at 400°C for 2 hr. FeAl-PILC-B1 untreated (—); calcined (·····); Fe-PILC untreated (---); calcined (-·-·-).

SUMMARY AND CONCLUSIONS

The results of this study confirm that hydroxy-FeAl pillared clays with various amounts of Fe oxides could be prepared by two different synthetic routes. The basal spacings, surface area, pillar structures, thermal stabilities, and surface acidity of the pillared clays are affected by the Fe/Al ratio. The pillar structure of FeAl-PILC products with Fe/Al < 0.5 is a Keggin structure similar to that of Al-PILC, and those with Fe/Al ≥ 0.5 are the ferric oligomers similar to those of Fe-PILC. Incorporating Fe into an alumina pillar decreases the Bronsted acid sites and surface acid strength of the pillared clay products. The interaction of Fe with alumina can occur in the pillars and is enhanced with increasing Fe/Al ratio of FeAl-PILC. Reduction of the Fe phase in FeAl-PILC was decreased by the interaction of Fe with alumina.

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