

## STUDY OF THE NATURE OF ACID SITES OF MONTMORILLONITES PILLARED WITH ALUMINIUM AND OLIGOSILSESQUOXANE COMPLEX CATIONS. 1. BRÖNSTED ACIDITY

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**Abstract**—Two samples, obtained by pillaring a Wyoming montmorillonite with hydroxy aluminium and oligosilsesquioxane cations, were studied by stepwise thermal desorption of ammonia and by highly sensitive diffuse reflectance IR-spectroscopy. For both clays, the adsorption of ammonia shows a total number of acid sites equal to 0.35 meq/g, with acid strengths comparable to that of HY zeolites. By IR reflectance spectroscopy, Brönsted acid sites with an acid strength comparable to that of bridging hydroxyls in zeolites were found in Al samples but not on Si-montmorillonites. These sites were characterized by an overtone band at 7100 cm<sup>-1</sup> and an activity for ethylene oligomerization at 300 K.

**Key Words**—Brönsted acidity, Diffuse reflectance IR-spectroscopy, Montmorillonites, Pillared clays.

### INTRODUCTION

Pillared interlayered clays (PILC) have now become an important family of shape-selective catalysts (Kikuchi and Matsuda, 1988). These solids combine a tunable acidity, regular porosity and relatively high thermal stability that makes them similar to zeolite-like materials. The synthesis of different PILCs and their catalytic properties in a variety of chemical reactions have been investigated in detail and reviewed by several authors (Kikuchi and Matsuda, 1988; Thomas, 1988; Figueras, 1988; He Ming-Yuan *et al.*, 1988; Schoonheydt, 1991); however, much less information is available concerning the nature of their acid sites.

The family of montmorillonite, hectorite, and beidellite pillared by Al<sub>13</sub> hydroxy cations has been most studied. The adsorption of such gaseous bases as pyridine or ammonia revealed the presence of strong Brönsted and Lewis acid sites (Tichit *et al.*, 1988a; Figueras, 1988), but their nature, localization, and particular properties are not yet well understood, except for the case of pillared beidellite for which high-resolution solid state NMR has provided a reasonable description of the formation of acid sites (Plee *et al.*, 1985).

Tennakoon *et al.* (1987) proposed that the protons of pillared montmorillonite are locked within the clay sheet and are, thus, unavailable for catalysis in the interlamellar region, hence explaining the poor activity at low temperature. If the clay sheet is involved in acidity, montmorillonites pillared by silicon cationic

species, which show good thermal stability (Lewis *et al.*, 1985), could exhibit properties similar to those of Al-PILC.

In connection to this, it should be noted that the study of Brönsted sites in PILCs encounters many problems because water interacts strongly with the clay and a considerable part of hydroxyl groups are hydrogen-bonded. Therefore, isolated OH-groups that are considered as active sites in catalysis are hardly visualized in the fundamental region of the IR-spectra due to the background of H-bonded hydroxyls.

The use of the very sensitive diffuse reflectance IR-spectroscopy technique and the expansion of the spectral range to the near IR-region (4000–10,000 cm<sup>-1</sup>) where the overtones and combination stretching plus bending bands of hydroxyl groups are placed enable one to obtain more profound information on the nature and properties of Brönsted sites in different catalysts and adsorbents (Kustov *et al.*, 1981; Kazansky *et al.*, 1984).

It can be pointed out that the catalytic properties of pillared clays for the cracking of gas oils can be appreciably affected by the method of preparation. The Al-PILCs used in this present work show high activities (80% conversion at 530°C), comparable to those of rare earth exchanged zeolites, for the cracking of a heavy fuel that is difficult to convert (Tichit *et al.*, 1988). The main difference between pillared clays and zeolites lies in a higher coke selectivity for clays, which can be accounted for partly by their Fe content (Lussier *et al.*, 1980) and partly by the presence of strong Lewis sites (Occelli and Finseth, 1986). By contrast, clays pillared by oligosilsesquioxane cations exhibited lower activities for the cracking of a light gas oil, much easier to

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Table 1. Chemical compositions in moles of oxides (dry basis) of the parent clay and of the two samples pillared with aluminium or silicon cationic species.

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	TiO <sub>2</sub>	K <sub>2</sub> O	CaO
Parent								
Clay	58.6	20.5	3.35	1.9	3.1	0.3	0.2	0.02
Al-PILC	58.6	43.4						
Si-PILC	68.4	20.5	3.37	3.01	0.2			

convert (Lewis *et al.*, 1985). These differences in catalytic properties should be related to differences in acidity, and it appeared then of interest to apply diffuse reflectance spectrometry to the investigation of the acidic properties of the montmorillonites pillared by aluminium or silicon containing complex cations.

### EXPERIMENTAL METHODS

A Wyoming montmorillonite was pillared by Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub><sup>7+</sup> polyoxocations in an aqueous suspension (Al/clay = 5 mmol/g, 20 g clay/liter) in the presence of NH<sub>4</sub><sup>+</sup> ions (NH<sub>4</sub><sup>+</sup>/Al = 10) using procedures described previously as effective for obtaining a homogeneous solid showing good thermal stability and high acidity (Figueras *et al.*, 1990). The preparation of Si-pillared clays has been described by Lewis *et al.* (1985) and extended to synthetic magadiite by Sprung *et al.* (1990). The sample characterized here was prepared by intercalation of the starting Wyoming montmorillonite by a solution of 2,2-trichlorosilyl-ethylpyridine aged three days at room temperature, following the procedure described by Fetter *et al.* (1990).

The chemical compositions of the samples studied are presented in Table 1. The values of their basal spacings (obtained from the X-Ray powder diffraction patterns) and of the specific surface areas at various pretreatment temperatures are given in Table 2. Si-PILCs develop a high surface area and micropore volume only after calcination above 800 K, which is required to burn the organic moiety of the pillars. The samples were heated from 300 K to 800 K in a flow of air. The temperature was increased at a rate of 0.6 K/min and maintained for 5 h at the final value.

The total acidity of these PILCs was determined by stepwise thermal desorption of ammonia. The solid was first saturated with ammonia at 373 K, weakly adsorbed NH<sub>3</sub> was eliminated by evacuation under dry nitrogen at the same temperature, and the temperature subsequently raised to 800 K in steps of 50 K while the cell was swept by a stream of dry nitrogen. The N<sub>2</sub> carrier gas was bubbled through a titrated acid solution and the amount of NH<sub>3</sub> evolved from the solid determined by conductimetry.

The diffuse reflectance Infrared spectra in the region of the fundamental stretching vibrations of OH-groups (2000–4000 cm<sup>-1</sup>) or in the region of the overtones (6000–8000 cm<sup>-1</sup>) were measured using a Perkin-Elmer 580 B or Acta M-VII Beckman spectrophotom-

Table 2. Evolution of basal spacings, surface area, and micropore volumes in function of the temperature of calcination, for the two pillared clays.

Sample	Pretreatment temp (K)	Basal spacing (nm)	Specific surface area (m <sup>2</sup> /g)	Micropore volume (ml/g)
Al-PILC	300	1.91	—	
	773	1.72	175	0.08
	973	1.68	184	0.08
	1073	1.59	50	
Si-PILC	300	2.24	19	0.01
	973	1.80	222	0.10
	1073	1.60		

eter, supplied with DR-attachments (Kustov *et al.*, 1981). The adsorption of benzene, acetonitrile, or ethylene was carried out at 300 K and pressures of 1–20 Torr. Before the spectroscopic measurements, the samples were pretreated by heating under vacuum for 5 h at 800, 900 or 1000 K.

### RESULTS AND DISCUSSION

The total acidity values, as determined by the amount of ammonia desorbed from the Si- and Al-PILCs pretreated at 773 K are represented in Figures 1b and 1c, together with a reference Linde LZ62 Y zeolite (Figure 1a). The Al-pillared sample retains NH<sub>3</sub> up to 773 K. The total number of acid sites (0.35 meq/g) is lower than that determined for HY zeolites (about 1.2 meq/g), and the acid strength, evaluated from the position of the temperatures at which maximal amounts of ammonia are desorbed, increases from the Si-PILC (T<sub>max</sub>: 473 K) to Al-PILC (T<sub>max</sub>: 523 K) and Y zeolite (T<sub>max</sub>: 573 K). However, the differences concerning relatively strong acid sites (desorbing ammonia between 623 and 773 K), which are responsible for cracking of paraffins, are not very large.

For the Si-pillared clay, the distribution of acid sites was determined after calcination at different temperatures. Strong acid sites are created after calcination at 873 and 973 K. The total number of acid sites goes through a maximum at 873 K, the temperature at which the surface area is also greatest. The number of acid sites is then 0.33 meq/g, close to the number of sites measured on the Al-PILC. Thus, the overall properties of the two pillared clays are rather similar, and desorption of ammonia cannot clearly discriminate between these two samples.

The IR spectra of these two PILCs in the fundamental OH stretching region are presented in Figures 2 and 3. For both samples, the similar broad unresolved bands with the maxima near 3650 cm<sup>-1</sup> are evident. In agreement with He Ming-Yuan *et al.* (1988), these bands should be assigned to the hydrogen bonded hydroxyl groups predominantly localized inside the triple T-O-T sheets of the parent clay structure. The residual OH- groups bonded to the pillars should also contribute to the absorbance.

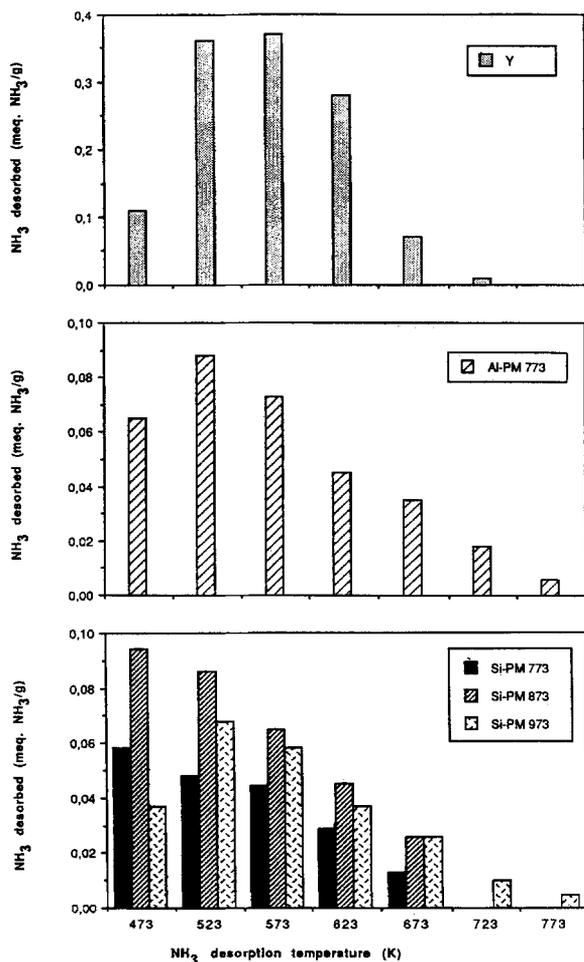


Figure 1. Stepwise thermal desorption spectra of a) HY zeolite, b) Al-montmorillonite pretreated at 773 K, and c) Si-montmorillonite pretreated at several temperatures.

The most obvious difference between the spectra of Al- and Si-pillared samples is the appearance in the latter case of a narrow band at  $3745\text{ cm}^{-1}$ , which should be attributed to silanol groups because the position of its maximum is close to that earlier reported for silica gel or zeolites (Ward, 1976). This assignment is also in line with the higher intensity of this band for Si-PILC as compared with Al-PILC. However, it is impossible to discriminate from these results whether these silanol groups are mainly connected with silicon-containing pillars or with impurities of amorphous silica gel.

The acidity of OH-groups can be estimated by the strength of their interaction with weak bases, such as benzene and acetonitrile, which induces a shift of the OH vibration frequency. For a given adsorbate, this shift is a measure of the acid strength, which has been related to the rate of cracking of cumene on a series of zeolites (Hedge *et al.*, 1988).

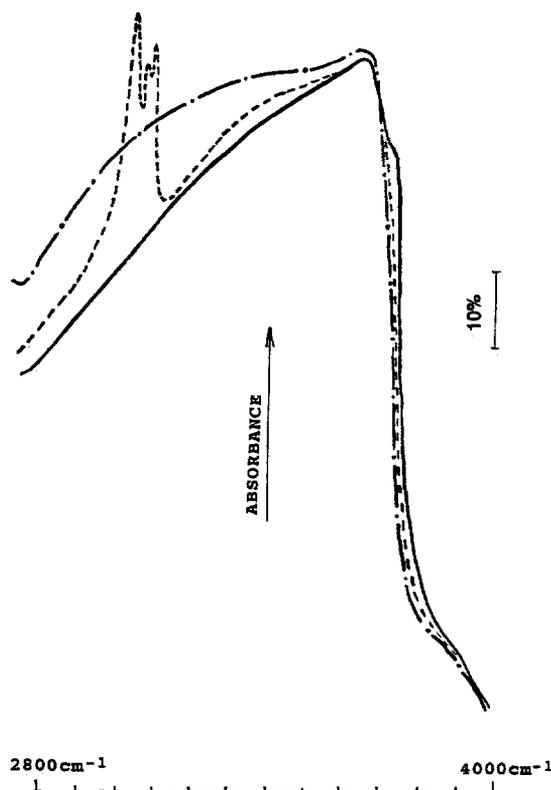


Figure 2. IR-spectra of Al-pillared montmorillonite pretreated at 770 K (—) and after adsorption of benzene (---) and  $\text{CD}_3\text{CN}$  (-·-·-).

After adsorption of benzene on the Si-PILC (Figure 3), this silanol band disappears and the band at  $3600\text{ cm}^{-1}$  is reinforced. Since the vibration of silanols is shifted by about  $150\text{ cm}^{-1}$  upon benzene adsorption (Kazansky *et al.*, 1983), this shifted band coincides then with the Al-OH vibrations, and the intensity is, therefore, increased in this region. By adsorption of acetonitrile, more basic than benzene, the shift is higher and the band is displaced to  $3400\text{ cm}^{-1}$  and broadened as expected for a stronger interaction.

In the case of the Al-PILC (Figure 4), the general situation after benzene adsorption is the same, with an increased absorbance in the region of Al-OH vibrations, but a broad band, which was not observed on the Si-PILC, appears at  $3400\text{ cm}^{-1}$ . The shift from  $3745$  to  $3400\text{ cm}^{-1}$  is too high to be ascribed to silanol groups. Such a large shift, confirmed by the appearance of a broad band at  $3200\text{ cm}^{-1}$  upon acetonitrile adsorption, thus corresponds to acid hydroxyls, invisible in the initial spectrum since their IR band is hidden under the background of the hydrogen bonded OH groups and is, therefore, unresolved in the initial spectrum.

On the basis of the position of these bands shifted upon adsorption of benzene and acetonitrile, it is possible to deduce that these hydroxyls, invisible in the

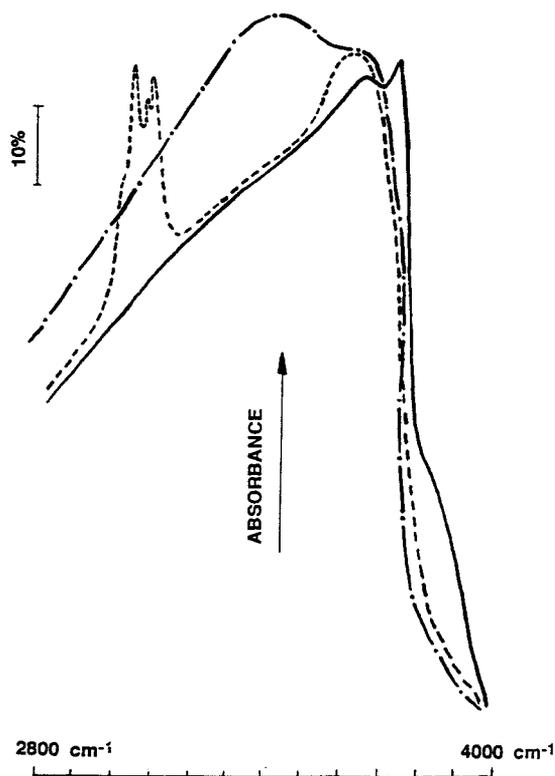


Figure 3. IR-spectra of Si-pillared montmorillonite pretreated at 770 K (—) and after adsorption of benzene (---) and CD<sub>3</sub>CN (-·-·-).

fundamental region, exhibit strong acidic properties comparable with those of zeolitic OH-groups. Indeed, for HZSM-5, HX, and HY zeolites the bands at 3610–3660 cm<sup>-1</sup>, attributed to the bridged OH-groups, are shifted after benzene adsorption to 3400–3250 cm<sup>-1</sup> (Kazansky *et al.*, 1983).

The conclusion about the existence in Al-pillared samples of Brønsted sites similar to those in zeolites finds a further much clearer support in the IR spectra recorded in the overtone region of OH stretching vibrations. Previously we have shown (Kustov *et al.*, 1981) that the investigation of the overtones of the stretching vibrations may give more profound or complementary information on the nature, localization, and properties of OH-groups in catalysts and adsorbents. The following characteristic features established earlier should be taken into account when the spectra in the region of the overtones are considered (Kustov *et al.*, 1981):

- 1) For different kinds of isolated OH-groups (terminal or bridged) in various oxides including zeolites, the fundamental ( $\nu_{0-1}$ ) and overtone ( $\nu_{0-2}$ ) frequencies are connected by the equation derived from the theory of an anharmonic oscillator, where the anharmonicity parameter  $X_e$  is equal to about  $2.1 \cdot 10^{-2}$ :

$$\nu_{0-1} = \nu_{0-2} (1 - 2X_e) / (2 - 6X_e) \quad (1)$$

Therefore the separation of the bands in the overtone region and their resolution is about twice as good as it is in the fundamental region.

- 2) In the overtone region the bands of the hydrogen

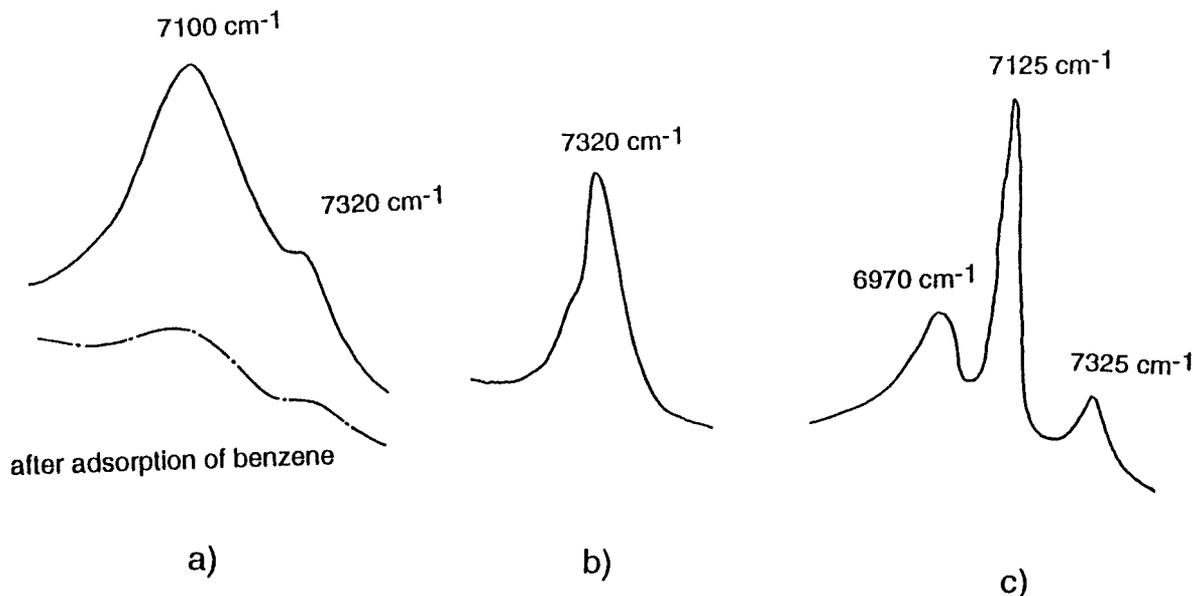


Figure 4. IR-spectra in overtone region: a) Al-pillared montmorillonite before and after adsorption of benzene; b) Si-pillared montmorillonite; and c) HY zeolite.

bonded hydroxyls are much broader. Therefore they cannot always be resolved from the background in the overtone region.

As one can see from the spectra represented in Figure 4, this is just the case of the overtone spectra of Al (a) and Si (b) pillared samples. (For the comparison spectrum (c) represents the overtone OH stretching region for LZ62-HY zeolite). Since the broad band from the hydrogen bonded hydroxyls is invisible, for the silicon pillared sample only a single band from terminal silanol groups at  $7320\text{ cm}^{-1}$  is observed (Figure 4b) that is practically identical to the similar band for HY zeolite at  $7325\text{ cm}^{-1}$  (Figure 4c). For the Al-pillared sample the intensity of this band is much weaker and it appears as an unresolved shoulder (Figure 4a).

Unlike the sample pillared by silicon, the overtone spectrum of Al-PILC (Figure 4a) contains another much stronger band with the maximum at  $7100\text{ cm}^{-1}$ , which should also be ascribed to isolated hydroxyls. Its position is close to that of the most intensive overtone band of HY zeolite at  $7125\text{ cm}^{-1}$  (Figure 4c). Thus, pillaring with Al apparently results in hydroxyl groups nearly as acidic as those in HY, whereas pillaring with Si results only in silanol groups.

This conclusion is also confirmed by adsorption of benzene resulting in the case of Al-pillared sample in the immediate disappearance of the overtone band at  $7100\text{ cm}^{-1}$ . Simultaneously, as already discussed above, a weak band at  $3300\text{--}3400\text{ cm}^{-1}$  appears in the fundamental region of the spectrum, which corresponds to H-bonded complexes with benzene molecules (Figure 2). Taking into account the Eq. (1), one may derive from the overtone frequency the value of  $\nu_{0-1} = 3640\text{ cm}^{-1}$ , close to the value of  $3630\text{ cm}^{-1}$  reported by Tennakoon *et al.* (1987). Therefore, the positions of the maxima of the corresponding narrow band and the broad line from hydrogen bonded hydroxyls in the fundamental region coincide, and the former is not resolved, being superimposed on the broad bands of the hydrogen-bonded hydroxyls ( $\nu = 3600\text{--}3660\text{ cm}^{-1}$ ). From the calculated  $\nu_{0-1}$  frequency, it becomes possible to evaluate the fundamental frequency shift due to interaction with benzene for which  $\Delta\nu = 250\text{--}300\text{ cm}^{-1}$ . This is close to the corresponding values reported earlier for zeolites. For example, the shift resulting from benzene adsorption on H-forms of X, Y, and ZSM-5 zeolites is equal to  $240\text{--}350\text{ cm}^{-1}$  (Kazansky *et al.*, 1983). Thus, pillaring of montmorillonite by  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  polyoxocations results in the appearance of isolated hydroxyl groups with the overtone band position as well as with the estimated fundamental frequency close to the corresponding values obtained for zeolites. The frequency shift arising after adsorption of benzene on these sites also seems to be close to the one reported earlier for zeolites.

Another argument confirming the appearance in Al-

pillared samples of strongly acidic hydroxyl groups stems from the spectroscopic investigation of ethylene adsorption on the Al-pillared samples. The interaction of  $\text{C}_2\text{H}_4$  with the strongly acidic bridged OH-groups of HZSM-5 type zeolites is known to result in olefin oligomerization, which proceeds even at room temperature (Van Hooff, 1980; Kustov *et al.*, 1984). Unlike high-silica containing zeolites, OH-groups of faujasites exhibiting a lower acidity are unable to catalyze this reaction at 300 K. Such an approach has been realized in the case of Al-PILC in order to evaluate the reactivity of the isolated acidic hydroxyl groups and to compare their properties with those of zeolitic OH-groups.

In Figure 5, the spectra of Al-PILC are presented in the region of the fundamental stretching vibrations of C-H bonds just after admission of ethylene and after contacting the sample with ethylene for 24 h. As seen from the figure, in addition to the  $\nu_{\text{as}}(\text{C-H})$  and  $\nu_{\text{s}}(\text{C-H})$  lines of adsorbed  $\text{C}_2\text{H}_4$  ( $3100$  and  $2990\text{ cm}^{-1}$ ) new bands at  $2970$ ,  $2930$ ,  $2870\text{ cm}^{-1}$  appear immediately after contact of the Al-PILC with ethylene. The intensities of the lines at  $2970\text{ cm}^{-1}$  show a tendency to increase with the contact time. Evacuation of the preadsorbed olefin at 300 K leads to the disappearance of the lines at  $3100$  and  $2990\text{ cm}^{-1}$ , whereas the bands at  $2970$ ,  $2930$ , and  $2870\text{ cm}^{-1}$  remain unchanged. They start to decrease in intensities only after heating the Al-PILC in vacuum up to  $400\text{--}500\text{ K}$ .

According to Kustov *et al.* (1984) the bands at  $2970$ ,  $2930$  and  $2870\text{ cm}^{-1}$  which appeared after adsorption of ethylene onto H-forms of zeolites should be assigned to the resulting oligomers containing both CH ( $\nu_{\text{as}} = 2970\text{ cm}^{-1}$ ,  $\nu_{\text{s}} = 2870\text{ cm}^{-1}$ ) and  $\text{CH}_2$ -fragments ( $\nu_{\text{as}} = 2930\text{ cm}^{-1}$ ,  $\nu_{\text{s}} = 2860\text{ cm}^{-1}$ ). Thus, we may conclude that acidic OH-groups of Al-PILC are able to catalyze the oligomerization of ethylene.

Since the intensities of the bands at  $\nu < 2970\text{ cm}^{-1}$  increased rather slowly with contact time, the reactivity of the acidic hydroxyl groups of Al-PILC could be estimated as intermediate between that of HZSM-5, which catalyzes ethylene oligomerization very quickly, and HY, which is inactive. Furthermore, whereas on HZSM-5 oligomerization is known to proceed shape-selectively resulting in preferential formation of linear polymer chains, Al-PILC, which is characterized by larger pores, catalyzes the formation of branched oligomers containing a high concentration of  $\text{CH}_3$  fragments. A similar pattern was observed earlier (Telbiz *et al.*, 1986) for ethylene oligomerization on strongly acidic OH-groups of partially dealuminated faujasites, which are also large-pore systems as compared with ZSM-5 zeolites.

Thus, the data obtained show that pillaring montmorillonites by aluminium hydroxy polycations results in the appearance of strongly acidic Brønsted sites capable of ethylene oligomerization. These protons are

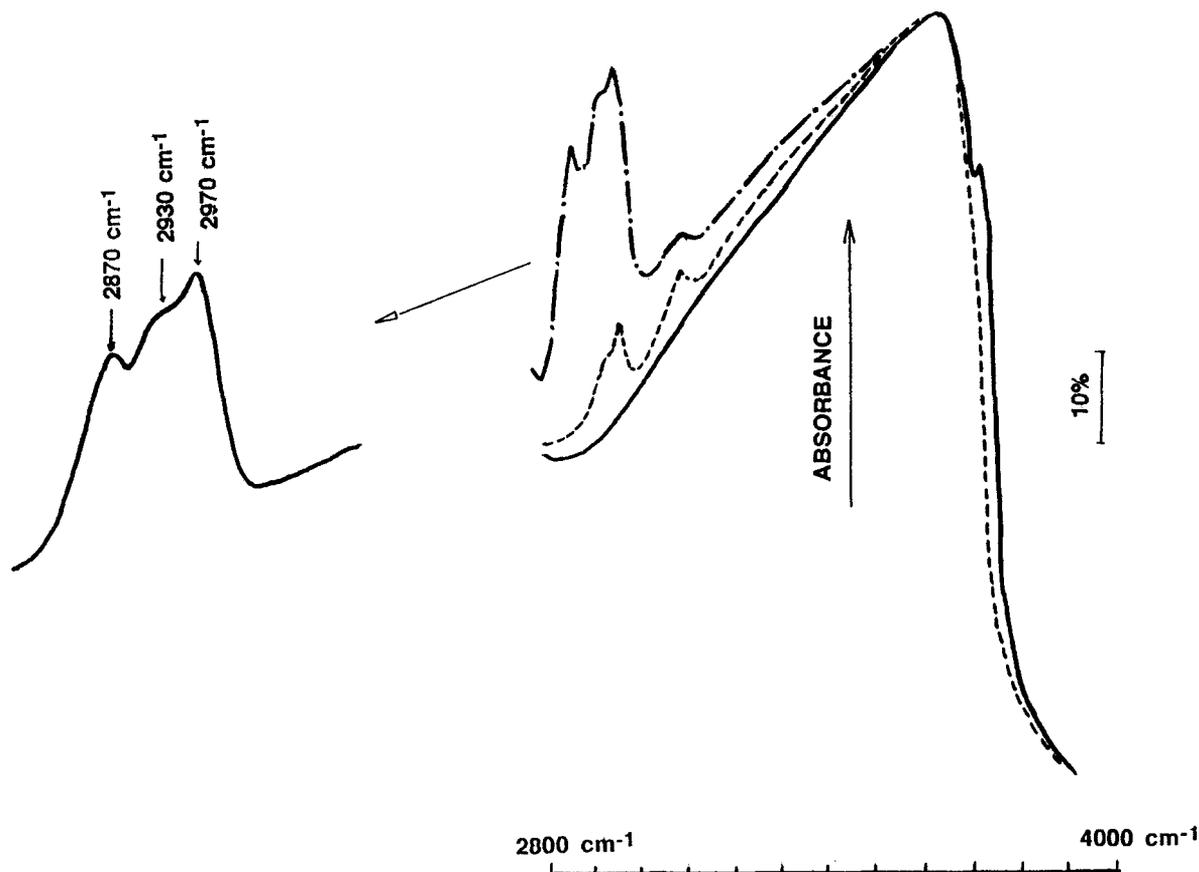


Figure 5. IR-spectra of Al-pillared montmorillonite pretreated at 770 K (—), just after (---), and after 24 h of ethylene adsorption (-·-·-).

not observed when the clay is pillared by silicon compounds and should then be associated with the Al pillars rather than the clay sheet. In their work, Lewis *et al.* (1985) also reported that, in spite of their good thermal stability, Si-pillared clays exhibited only poor performances for the cracking of gas oil with a high selectivity for coke. This behavior is also consistent with the results of the present study. These strong acid sites cannot be bridged due to the structure of the pillared clay, but could bear some analogy with those corresponding to extra framework aluminium species in zeolites as recently suggested by Bodoardo *et al.* (1994). This extra framework aluminium, the structure of which is not known, induces a high acidity in mildly steamed zeolites.

#### REFERENCES

- Bodoardo, S., Figueras, F., and Garrone, E. (1994) IR study of Brønsted acidity of Al-pillared montmorillonite: *J. Catal.*, **147**, 223–230.
- Fetter, G., Tichit, D., Massiani, P., Dutartre, R., and Figueras, F. (1990) Preparation and characterization of montmorillonite pillared by cationic silicon species: in *Proceedings 12th Ibero-American Symp. Catalysis, Rio de Janeiro (Brazil)*, 1990, Instituto Brasileiro Petroleo **2**, 448–457.
- Figueras, F. (1988) Pillared clays as catalysts: *Catal. Rev. Sci-Eng.* **30**, 457–499.
- Figueras, F., Klapysa, Z., Massiani, M., Mountassir, M., Tichit, D., Fajula, F., Gueguen, C., Bousquet, J., and Auroux, A. (1990) Use of competitive ion exchange for intercalation of montmorillonites with hydroxy-aluminium species: *Clays & Clay Minerals* **38**, p. 257.
- Hedge, S. G., Ratnasamy, P., Kustov, L. M., and Kazansky, V. B. (1988) Acidity and catalytic activity of SAPO-5 and AIPO-5 molecular sieves: *Zeolites* **8**: 137–141.
- He Ming-Yuan, Zhonghui, L., and Enze, M. (1988) Acidic and hydrocarbon catalytic properties of pillared clays: *Catal. Today* **2**, 321–338.
- Kazansky, V. B., Borovkov, V. Yu., and Kustov, L. M. (1984) IR diffuse reflectance study of oxide catalysts. Use of molecular hydrogen adsorption as a test for surface active sites: *Proceedings 8th Intern. Congr. on Catalysis, Berlin, 1984*, Verlag Chemie (Weinheim) **III**, 3–14.
- Kazansky, V. B., Kustov, L. M., and Borovkov, V. Yu. (1983) Infra-red diffuse reflectance study of high silica zeolites: *Zeolites* **3**, 77–81.
- Kazansky, V. B. (1984) The study of Brønsted and Lewis acidity of decationized and dealuminated zeolites by IR diffuse reflectance spectroscopy and quantum chemistry: in *Structure and Reactivity of Modified Zeolites*, P. A. Jacobs,

- P. Jiru, and V. Kazansky, eds., Elsevier, Amsterdam, 61–75.
- Kikuchi, E. and Matsuda, T. (1988) Shape selective acid catalysis by pillared clays: *Catal. Today* **2**, 297–307.
- Kustov, L. M., Borovkov, V. Yu., and Kazansky, V. B. (1981) Spectra of hydroxyl groups in zeolites in the near-infra red region: *J. Catal.* **72**, 149–159.
- Kustov, L. M., Borovkov, V. Yu., and Kazansky, V. B. (1984) Study of ethylene oligomerization on Brønsted and Lewis acidic sites of zeolites using diffuse reflectance IR spectroscopy: in *Structure and Reactivity of Modified Zeolites*, P. Jacobs, P. Jiru, and V. Kazansky, eds., Elsevier, Amsterdam, 241–247.
- Lewis, R. M., Ott, K. C., and Van Santen, R. A. (1985) Silica-clay complexes: *U.S. Patent 4,510,257*, 14 pp.
- Lussier, R. J., Magee, J. S., and Vaughan, D. E. W. (1980) Pillared interlayered clay cracking catalysts—Preparation and properties: *7th Canadian Symp. Catal., Edmonton, Alberta*, 88–95 (preprint).
- Ocelli, M. L. and Finseth, D. H. (1986) Surface and catalytic properties of some pillared hectorites: *J. Catal.* **99**, 316–326.
- Plee, D., Borg, F., Gatineau, L., and Fripiat, J. J. (1985) High resolution solid state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  nuclear magnetic resonance study of pillared clays: *J. Amer. Chem. Soc.* **107**, 2362–2369.
- Schoonheydt, R. A. (1991) Clays: From two to three dimensions: in *Introduction to Zeolites: Science and Practice*, H. Van Bekkum, E. M. Flanigen, and J. C. Jansen, eds., Elsevier, Amsterdam, 201–239.
- Sprung, R., Davis, M. E., Kauffman, J. S., and Dybowski, C. (1990) Pillaring of magadiite with silicate species: *Ind. Eng. Chem. Res.* **29**, 213–220.
- Telbiz, G. M., Galich, P. N., Kustov, P. N., Borovkov, V. Yu., and Kazansky, V. M. (1986) Possibilities of the existence of strongly acid hydroxyl groups in Polycation forms of zeolite X: *Kinetics and Catalysis* **27**, 405–408.
- Tennakoon, D. T. B., Jones, W., Thomas, J. M., Ballantine, J. H., and Purnell, J. H. (1987) Characterization of clay and pillared clay catalysts: *Solid State Ionics* **24**, 205–212.
- Thomas, J. M. (1988) Uniform heterogeneous catalysts: The role of solid state chemistry in their development and design: *Angew. Chem.* **27**, 1973–1991.
- Tichit, D., Fajula, F., Figueras, F., Gueguen, C., and Bousquet, J. (1988a) Influence of the conditions of preparation on the catalytic properties of Al-pillared montmorillonites: in *Advances in Fluid Catalytic Cracking, New Orleans, 1987*, ACS Symposium Series **375**, M. L. Ocelli, ed., American Chemical Society, Washington, D.C., 237–252.
- Tichit, D., Fajula, F., Figueras, F., Gueguen, C., and Bousquet, J. (1988b) Catalytic properties of Al-pillared clays in the cracking of heavy fuels: in *Proc. 9th Int. Cong. Catalysis, Calgary 1988, Vol. 1*, M. J. Phillips and M. Ternan, eds., Chemical Institute, Canada, 112–119.
- Van Hooff, J. H. C. (1980) The conversion of methanol to hydrocarbons using a new type of zeolite as catalyst (Mobil process): in *Chemistry and Chemical Engineering of Catalytic Processes*, R. Prins, G. C. A. Schuit, eds., NATO Advanced Study Institute Series E., **39**, 559–599.
- Ward, J. W. (1976) Infrared studies of zeolite surfaces and surface reactions: in *Zeolite Chemistry and Catalysis*, J. A. Rabo, ed., ACS Monograph **171**, Washington, D.C., 118–284.

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