

A Comparative Study of the Acidity toward the Aqueous Phase and Adsorptive Properties of Al₁₃-Pillared Montmorillonite and Al₁₃-Pillared Saponite

Latifa Bergaoui,[†] Ihlen Mrad,[†] Jean-François Lambert,^{*,‡} and Abdelhamid Ghorbel[‡]

Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, 1060 le Belvédère, Tunis, Tunisia, and Laboratoire de réactivité de surface, UMR 7609 CNRS, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

Received: October 8, 1998; In Final Form: February 5, 1999

The selectivity of an Al₁₃-pillared saponite and an Al₁₃-pillared montmorillonite for Cd²⁺ and Cu²⁺ adsorption was studied. The quantity of metal adsorbed on both pillared clays depends on the pH of the solution and the pillars density. Adsorption equilibria are regulated by the protonation equilibria of the amphoteric sites on the pillars. Pillared clays adsorb more cadmium and copper than classic aluminum hydroxides which is simply attributable to a higher density of surface aluminum groups. Significant differences in behavior are observed between pillared montmorillonite and pillared saponite. Pillared montmorillonite appears to be more acidic, which is correlated with a more advanced degree of structural modification of the pillars on calcination. We propose a tentative, partial structural model of pillar transformation compatible with these differences. At the same time, both pillared clays have similar affinities for cadmium II at low pH (5–6), but pillared montmorillonite seems to be a more efficient cadmium trap at pH = 8 when its surface groups are negatively ionized. Thus, the nature of the clay layers conditions the structural modifications of the intercalated [Al₁₃] polycations, which in turn determine adsorptive behavior.

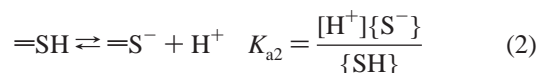
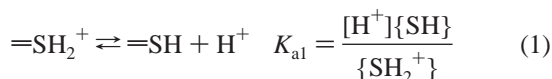
Introduction

Recently, we became interested in the adsorptive properties of pillared clays and their exploitation for the removal of metal cation pollutants such as Cu²⁺ and Cd²⁺.

Our previous investigations have indicated that copper and cadmium adsorption on aluminum pillared clay occurs through a mechanism essentially different from cation exchange.^{1–4} The adsorption reaction involves specific groups on the pillars surface and can be written as an inner-sphere complex formation with the divalent metal ion, accompanied by proton release. Therefore, it is strongly pH-dependent.

The aim of the present work is to compare the acido–basic properties of two aluminum-pillared smectites, as well as their aptitude to adsorb copper and cadmium, and to determine if these two characteristics are correlated.

Thus, acid–base titration results are used to understand the cation adsorption mechanism. Many studies have been carried out on the acido–basic properties of oxide surface groups. The commonly adopted approach (1 site, 2 pK⁵) is to consider that the oxide has only one type of surface amphoteric group (noted SH) for which one writes a first deprotonation characterized by an equilibrium constant K_{a1} and then a second deprotonation characterized by K_{a2} :⁵



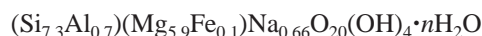
Here the {} and [] symbols represent a concentration of adsorbed

species in the solid phase (mol/g) and a concentration in solution (mol/L), respectively. In this model, a simple acid–base titration gives access to the intrinsic values of the acidity constants.

In fact, the surface groups of an oxide are not homogeneous. For instance, the hydrolyzable groups of the oxide surface can be terminal, geminal, or bridging. Every OH type is expected to have a different acido–basic behavior. The so-called “multisite, 1 pK” model was recently proposed to account for these differences.^{6,7} In the present work, we will make use of the classic “1 site, 2 pK” model, reserving discussion of surface heterogeneity for a later publication.

Experimental Section

Sample Preparation. The saponite used in this work came from Ballarat. It was obtained from the Source Clay Minerals Repository. Saponite is a trioctahedral clay where all octahedral cavities are occupied by Mg²⁺ and substitution occurs exclusively in the tetrahedral sheet. The following formula of Ballarat saponite may be written:⁸



The purification and pillaring of this clay have been described elsewhere.^{9,10}

The second clay used in this work is a Greek montmorillonite provided by Expansia (France). It is a dioctahedral clay where 2/3 of the octahedral cavities are occupied by Al³⁺. Substitution occurs in both the octahedral and the tetrahedral layer, and the

* To whom correspondence should be addressed. E-mail: lambert@ccr.jussieu.fr. Fax: (33) 1 44 27 60 33.

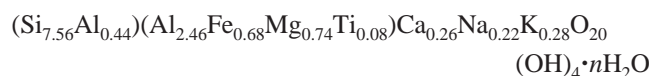
[†] Campus Universitaire.

[‡] Université Pierre et Marie Curie.

TABLE 1: Basal Distances and BET Surface Areas of Sodium-Exchanged and Pillared (Calcined at 500 °C) Clays

sample	d_{001} (Å)	S_{BET} (m ² /g)	sample	d_{001} (Å)	S_{BET} (m ² /g)
Na-saponite	12.4	35	Na-montmorillonite	12.6	67
pillared saponite	18.1	270	pillared montmorillonite	18.0	204

formula is¹¹



The optimization of Al polycation pillaring of this clay has been discussed elsewhere.¹²

Table 1 summarizes the most important characteristics of both clays and pillared materials derived from them.

In the procedure we used, the intercalation solution mainly contains the $[\text{Al}_{13}]$ polycations $[\text{Al}_{13}\text{O}_4(\text{OH})_{24+x}(\text{H}_2\text{O})_{12-x}]^{(7-x)+}$. For saponite the quantity of intercalated aluminum is about 4.3 g of Al/100 g of clay. For montmorillonite, it is about 5.2 g of Al/100 g of clay.

Acid–Base Titration. Titration measurements were performed with a TT-2 (Taccussel) automatic pH-meter equipped with a combination glass electrode. We have followed the same procedure that was used to measure the acidity constant of the ALOH surface groups in alumina.¹³ Before the start of the titration, the suspension was stirred at 20 °C for 20 h. In this way the surface is rehydrated and protonation/deprotonation equilibria are reached. A small quantity of concentrated acid or base (0.1 mol/L) was added to shift the pH to the initial value chosen for the titration. The titration was started after a 20 min equilibration time. A minimum temporization of 2 s and variable maximum temporizations and pH stability criteria (maximum rates of pH drift) were applied for each volume increment. We have studied the influence of clay concentration, ion strength, stability criterion, and maximum temporization (5–20 mn). In every case, the titration has been repeated under the same conditions but in the absence of the mineral matrix. Between pH = 3 and pH = 9, no spurious effects were manifested on these blanks.

For each titration point, the pH first changes rapidly after base (or acid) addition. This rapid variation may be followed by a slower drift. Such a slow drift of the pH during the titration is, in general, observed for Al_2O_3 ,⁶ Fe_2O_3 ,¹⁴ TiO_2 ,¹⁵ and ZnO ¹⁶ suspensions. However, only the rapid variation of the pH after adding the increment is attributed to the H^+/OH^- exchanges at the solid/liquid interface.¹⁶

This slow pH drift is most probably due to the dissolution of the aluminum-containing pillars. To check this, we have analyzed the solution for dissolved aluminum after each titration. As could be expected, aluminum dissolution is more important when the maximum temporization is higher and when the stability criterion is more severe (both of which imply a slower rate of titration). For instance, changing the stability criterion from 0.01 to 0.001 pH units/min increased the amount of dissolved Al from 6 to 90 mg/L; changing the maximum temporization from 5 to 20 mn increased it from 6 to 47 mg/L. The amount of dissolution also depends of course on the two extreme values of the pH reached during titration. Finally, it is preferable to bring first the pH of the suspension to the basic limit and titrate with HCl rather than the opposite: the pillared clay is more stable in basic than in acidic solutions.

Data treatments are based on titrations obtained under the following conditions: [pillared saponite] = 8 g/L and [pillared montmorillonite] = 16 g/L; before titration pH brought to value

of 9 by a 0.1 M solution of NaOH; titration by a 0.1 M HCl solution down to pH = 3; stability criterion 0.01 pH/min; maximum temporization 5 min; ion strength = 0.02 mol/L, with indifferent electrolyte NaNO_3 .

If we suppose that the hydrolysis of one Al^{3+} necessitates 3 protons, the quantity of protons consumed by the dissolution of pillars, in the pH range where dissolution is observed, does not exceed 0.67 mequiv/L. This is less than what corresponds to the probable error on pH reading as shown by Perdue.¹⁷

Taking into account that the activities of the ions in solution (γ) depend on the ion strength (I) along $\log \gamma = -0.5115[I^{1/2}/(1 + I^{1/2}) - 0.3I]$, it is possible to calculate the concentrations of H^+ and OH^- from the pH values:

$$[\text{H}^+] = \frac{10^{(-\text{pH})}}{\gamma} \quad [\text{OH}^-] = \frac{10^{(\text{pH}-14)}}{\gamma}$$

From the equation

$$Q = \frac{C_A - C_B + [\text{OH}^-] - [\text{H}^+]}{a}$$

where Q is the surface charge (mol/g), C_A is the concentration of the strong acid (mol/L), C_B is the concentration of the strong base (mol/L), and a is the concentration of pillared saponite (g/L), we can then calculate the value of Q as a function of pH. In a second step, the apparent $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ values are plotted as a function of Q . These plots should be linear in suitable pH intervals. An extrapolation of the straight lines to zero surface charge ($Q = 0$) gives the intrinsic values of $\text{pK}_{\text{a}1}^{\text{int}}$ and $\text{pK}_{\text{a}2}^{\text{int}}$.

Cd^{2+} and Cu^{2+} Adsorption. M^{2+} ($\text{M} = \text{Cu}, \text{Cd}$) adsorption isotherms were recorded as follows: The pH of the pillared clay suspensions (16 g/L) was equilibrated by shaking the clay overnight at 20 °C in a 2×10^{-2} mol/L NaNO_3 solution. At the same time, solutions with different $\text{M}^{2+}/\text{Na}^+$ ratios but with constant values of the amount $(2[\text{M}^{2+}] + [\text{Na}^+]) = 2 \times 10^{-2}$ mol/L were separately brought to the desired pH. Then, 5 mL of the suspension and 15 mL of the $\text{M}^{2+}/\text{Na}^+$ solution were mixed. The clay concentration in the final solution was thus 4 g/L. For the isotherm at pH = 8, experiments were carried under exclusion of atmospheric CO_2 . After 7 days of equilibration at 20 °C in closed flasks, the suspensions were centrifuged at 10 000 rpm during 10 min. The supernatant solution was then analyzed for M^{2+} by atomic adsorption for copper and by isotopic dilution for cadmium (^{109}Cd isotope).

Results and Discussion

Acid–Base Titration. After titration and data processing, we found the following average values of $\text{pK}_{\text{a}1}^{\text{int}}$ and $\text{pK}_{\text{a}2}^{\text{int}}$: for pillared saponite $\text{pK}_{\text{a}1}^{\text{int}} = 4.3$ and $\text{pK}_{\text{a}2}^{\text{int}} = 8.0$, which corresponds to $\text{pH}_{\text{PZC}} = 6.2$; for pillared montmorillonite $\text{pK}_{\text{a}1}^{\text{int}} = 5.0$ and $\text{pK}_{\text{a}2}^{\text{int}} = 6.5$, which corresponds to $\text{pH}_{\text{PZC}} = 5.8$. We notice that the $\text{pK}_{\text{a}2}^{\text{int}}$ values are significantly different.

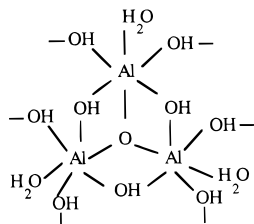
We can compare the values obtained with those found in the literature for aluminum oxides and hydroxides of known structure. The following table presents the published pH_{PZC}

values of different aluminum oxides and hydroxide:

materials	pH _{PZC}	ref
α-Al ₂ O ₃	9.1	5
γ-Al ₂ O ₃	8.4	13
α-Al(OH) ₃	5.0	5
γ-Al(OH) ₃ (bayerite)	6.7	18
γ-AlOOH	8.2	5

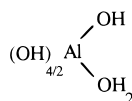
The pH_{PZC} values of pillared clays lie close to those published for Al(OH)₃ and are markedly different from those for Al₂O₃ polymorphs. The pK_a^{int} values of pillared clays are also different from those of γ-AlOOH. The pK_{a1}^{int} and the pK_{a2}^{int} values of γ-Al₂O₃ given by Hohland Stumm¹³ are 7.2 and 9.5, respectively. This is in contradiction with the often formulated supposition that, after calcination, the pillars constitute an “Al₂O₃ phase”;¹⁹ apparently, the surface groups exposed in pillared clays are significantly different from those on an alumina surface.

In the pillared clay, if the pillars are not modified by calcination, they only expose octahedrally coordinated aluminums on their surface. The coordination sphere of these aluminums consists of a terminal H₂O group, 4 bridging OH groups, and one μ₄-oxygen shared with the central tetrahedral aluminum:



Thus, there is only one type of OH group: bridging, or μ₂, between two 6-coordinated Al³⁺ ions. In the terminology of Knözinger and Ratnasamy,²⁰ they are “type II b”, and in the terminology of Tsyganenko and Mardilovich, they are “66” type OH groups.²¹ This situation is simpler than what is encountered even on a single crystal plane of a hydroxylated alumina. For instance, plane C of the (110) face that predominates in γ-alumina²² exhibits two different kinds of OH groups; taking into account all of exposed planes, at least 6 types of OH are present.²¹ In contrast, on [Al₁₃] pillars, only one type of OH is present.

No data unambiguously related to the same configuration of the Al surface have been reported in the literature for model compounds. However, the reactive surface groups of γ-Al(OH)₃ have been presented (for a neutral surface) as¹⁸



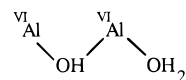
In this structure, the aluminum ion is octahedrally coordinated. Four of its coordinates are in the bulk of the lattice, shared with other aluminum atoms, and two are exposed at the surface. The acidity constants pK_{a1}^{int} and pK_{a2}^{int} of this hydroxide are 5.24 and 8.08, respectively,¹⁸ and are supposed to correspond to the successive deprotonation of the two geminal ligands shown.

The pK_a^{int} values of the pillared saponite and of γ-Al(OH)₃ are quite close. For pillared saponite, we can suggest by analogy that the value of pK_{a2}^{int} of 8.0 corresponds to the deprotonation of the terminal aqua groups present on each octahedral Al and that the value of pK_{a1}^{int} corresponds to the deprotonation of the bridging OH groups (which are geminal to the aqua ligands, as

in the case of γ-Al(OH)₃). The value of pK_{a1}^{int} is somewhat inferior to that for γ-Al(OH)₃, because in the case of the pillared saponite the groups responsible for pK_{a1}^{int} are bridging and therefore expected to be more acidic than the terminal groups of γ-Al(OH)₃.

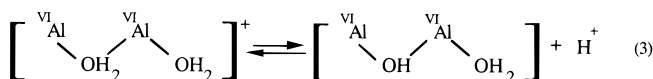
On the other hand, no direct comparison is possible with the estimates of deprotonation constants provided by Contescu et al.⁶ for γ-Al₂O₃, because of the lack of geminal groups in the latter (at least in the model used by the authors).

In our hypothesis, then, the surface sites of pillars in saponites in their “neutral form”²⁸ can be presented as



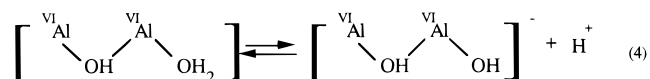
and will be denoted as AlOH(OH₂) for short (note that v₁Al denotes the coordination number of the Al ion and has nothing to do with its oxidation number).

The acid–base equilibria for pillars in saponites may then be written as follows:



$$K_{a1} = \frac{[\text{AlOH(OH}_2\text{)}][\text{H}^+]}{[\text{Al(OH}_2\text{)}^{2+}]}$$

For pillared montmorillonite, pK_a values are significantly



$$K_{a2} = \frac{[\text{Al(OH)}_2^-][\text{H}^+]}{[\text{AlOH(OH}_2\text{)}]}$$

different which calls for an alternate explanation. The available structural data, although limited, allow us to put forward some hypotheses.

It has been demonstrated by several investigators, including ourselves,^{9,23,24} that heating intercalated clays causes the release of protons from the [Al₁₃] polycations. In pillared saponite, these protons attack siloxane bridges in the clay sheets, preferentially forming bridging Si–OH–Al, which makes the tetrahedral sheets more fragile. This is the first step in the formation of layer-pillared covalent bonds involving inversion of (AlO₄) [and/or (SiO₄)] tetrahedra. Apart from this bonding, only moderate modifications of the [Al₁₃] structure occur up to 500 °C: some of the terminal H₂O groups on the six-coordinated Al's are eliminated to give five-coordinated Al's, but this reaction is reversible upon exposure to water at room temperature. Under room humidity, the sample shows essentially the same ²⁷Al solid-state NMR spectrum before and after calcination at 500 °C^{10,23} (Figure 1a,b).

On the other hand, calcination of pillared montmorillonite to 500 °C has an irreversible effect on the ²⁷Al solid-state NMR spectrum under room humidity; the intensity of the peak assigned to tetrahedral aluminum (61 ppm) increases at the expense of the octahedral aluminum peak (4 ppm, Figure 2).

When heated to 750 °C, a pillared saponite shows the same behavior as montmorillonite²⁵ does at 500 °C (Figure 1c; note that the peak assigned to tetrahedral aluminum was initially more important in saponite than in montmorillonite due to the contribution of substitutional Al³⁺ in the tetrahedral sheet).

On the basis of available structural information, it may not be too far-fetched to suggest that two successive transformations

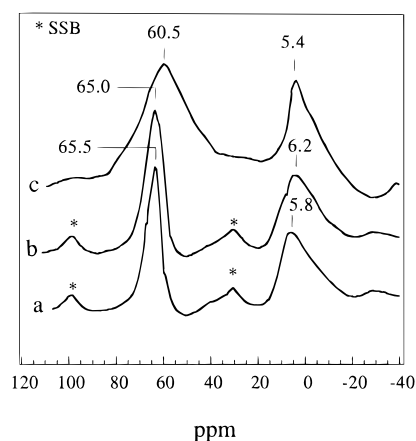


Figure 1. ^{27}Al NMR-MAS spectrum of the Al_{13} -intercalated saponite after drying (a) and of the Al_{13} -pillared saponite after calcination at 500 °C (b) and after calcination at 750 °C (c). Asterisk indicates SSB.

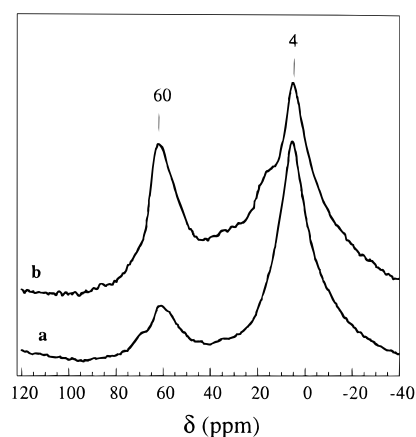


Figure 2. ^{27}Al NMR-MAS spectrum of the Al_{13} -intercalated montmorillonite after drying (a) and of the Al_{13} -pillared montmorillonite after calcination at 500 °C (b).

have occurred in pillared montmorillonite calcined at 500 °C. First, some of the terminal H_2O groups on the six-coordinate Al's are eliminated to give five-coordinated Al's as was shown to occur for saponite.^{9,10} Second, an oxolation reaction occurs between two Al's belonging to different 3-groups to give two tetrahedral aluminums (Figure 3).

The most straightforward consequence of this reaction scheme would be the appearance of an $^{\text{IV}}\text{Al}-\text{OH}-^{\text{IV}}\text{Al}$ group in the position denoted **A** in the figure. However, the (dehydration + ololation) sequence that we have postulated in pillared montmorillonite has another consequence: the sites that we have noted as **B** now consist of an $^{\text{IV}}\text{Al}-\text{OH}-^{\text{VI}}\text{Al}-\text{OH}_2$ arrangement, instead of $^{\text{VI}}\text{Al}-\text{OH}-^{\text{VI}}\text{Al}-\text{OH}_2$ (as the coordination of one of the Al's implied has changed from 6 to 4). This modification is expected to have a significant impact on the $\text{p}K_{\text{a}}$ values.⁶

Note that four **B** sites would be produced for each **A** site. If we assume for the sake of simplicity that **B** sites are chiefly responsible for the acidic properties of pillared montmorillonite, we can keep the same formal denomination as for pillared saponite, simply dropping the indication of coordination.

For both pillared clays, we have by definition

$$\{\text{AlO}_{\text{total}}\} = \{\text{Al}(\text{OH})_2^+\} + \{\text{AlOH}(\text{OH}_2)\} + \{\text{Al}(\text{OH})_2^-\} \quad (\text{I})$$

It is possible to calculate $\{\text{Al}(\text{OH})_2^+\}$, $\{\text{Al}(\text{OH})_2\text{OH}\}$, and $\{\text{Al}(\text{OH})_2^-\}$ as a function of pH ($K_{\text{a1}}^{\text{int}}$ and $K_{\text{a2}}^{\text{int}}$ will be noted

K_{a1} and K_{a2}):

$$\{\text{Al}(\text{OH})_2^+\} = \frac{\{\text{AlO}_{\text{total}}\}}{1 + \frac{K_{\text{a1}}}{[\text{H}^+]} + \frac{K_{\text{a1}}K_{\text{a2}}}{[\text{H}^+]^2}} \quad (\text{II})$$

$$\{\text{Al}(\text{OH})_2\text{OH}\} = \frac{\{\text{AlO}_{\text{total}}\}}{1 + \frac{[\text{H}^+]}{K_{\text{a1}}} + \frac{K_{\text{a2}}}{[\text{H}^+]}} \quad (\text{III})$$

$$\{\text{Al}(\text{OH})_2^-\} = \frac{\{\text{AlO}_{\text{total}}\}}{1 + \frac{[\text{H}^+]}{K_{\text{a2}}} + \frac{[\text{H}^+]^2}{K_{\text{a1}}K_{\text{a2}}}} \quad (\text{IV})$$

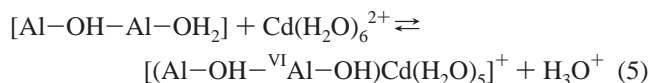
Equations II–IV permit one to estimate the distribution of different species vs pH. The calculated distributions of different surface groups for both pillared clays are presented on Figure 4.

Adsorption Isotherms. Adsorption isotherms are presented on a bilogarithmic scale: logarithm of the quantity of adsorbed cadmium $\{\text{Cd}^{2+}\}$ (mol/g) vs logarithm of the equilibrium concentration of cadmium in solution $[\text{Cd}^{2+}]$ (mol/L). When this presentation is linear, the adsorption is said to obey a Freundlich-type isotherm.

Cadmium adsorption isotherms on pillared montmorillonite and on pillared saponite at pH = 5, 6, and 8 are presented in Figures 5–7, respectively.

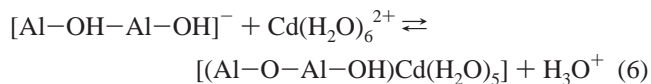
The mechanisms of cadmium and copper adsorption have been discussed elsewhere.^{1–4} We have shown that the adsorption of one cadmium ion is accompanied by the release of one proton. Assuming this mechanism to be correct, we may try to compare the behaviors of the two clays. At pH = 5 and pH = 6 the adsorption isotherms on pillared montmorillonite and pillared saponite are close to each other. At these pH values, the predominant surface groups on pillars should be $\text{Al}_2(\text{OH})\text{OH}_2$ for both pillared clays as shown in Figure 4.

In our model the adsorption reaction is written as



This reaction seems to have very close equilibrium constants for both pillared clays.

In contrast, at pH = 8 pillared montmorillonite adsorbs more cadmium than pillared saponite. At this pH the predominant surface groups on the pillars are $[\text{Al}-\text{OH}-\text{Al}-\text{OH}]^-$ in pillared montmorillonite while there are equal numbers of $[\text{Al}-\text{OH}-\text{Al}-\text{OH}_2]$ and $[\text{Al}-\text{OH}-\text{Al}-\text{OH}]^-$ in pillared saponite. Then, for pillared saponite, there is competition between adsorption on the neutral and the negative groups while for pillared montmorillonite the adsorption occurs only on negative groups:



The observed behavior would be expected if the constant for Cd^{2+} adsorption on negatively charged surface groups was higher than on neutral groups, since, at pH = 8, pillared montmorillonite has most of its surface groups negatively ionized while pillared saponite does not. Indeed reaction 6 causes a decrease of both surface charges ($-1 \rightarrow 0$) and free charge in solution ($+2 \rightarrow +1$) and, therefore, should correspond

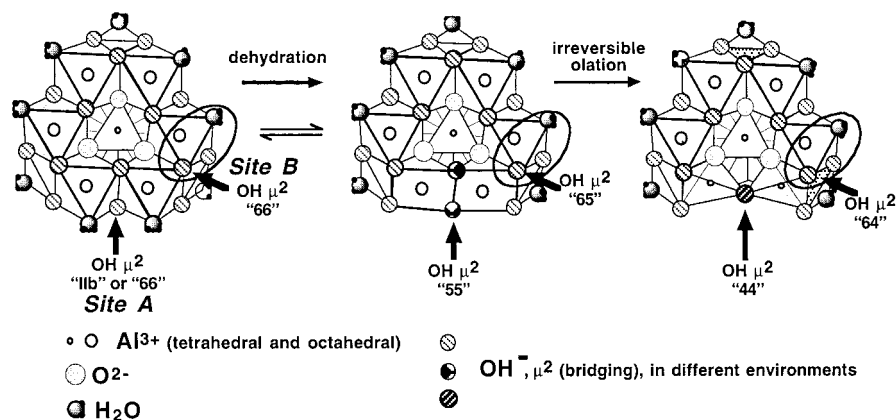


Figure 3. Possible mechanism for the initial steps of thermal transformation of Al₁₃ pillars in pillared clays: left, initial structure after intercalation, indicating the Al coordination polyhedra and the (OH⁻) and (H₂O) ligands; center, after loss of terminal (H₂O) ligands from two neighboring Al octahedra; right, after olation.

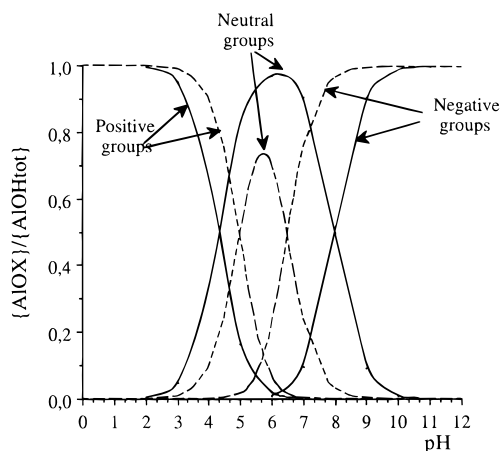


Figure 4. Distribution of charged and neutral amphoteric sites on the pillars surface vs pH: (—) pillared saponite; (---) pillared montmorillonite.

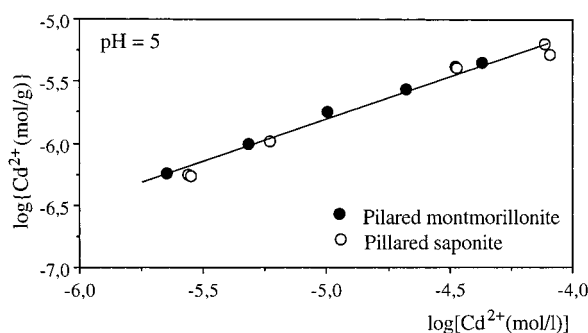


Figure 5. Cd adsorption isotherms on pillared clays, measured at pH = 5.

to decreased solution structuring and be entropically favored. The charge decrease is not so clear in reaction 5 for adsorption on neutral groups: surface charge increases while the charge in solution decreases. Therefore, it is reasonable to postulate that $K_6^{\text{ads}} > K_5^{\text{ads}}$.

Figure 8 presents the quantity of adsorbed cadmium vs the initial cadmium concentration at pH = 6, a presentation which may be of more significance for practical applications. For the same initial cadmium concentration, the pillared montmorillonite adsorbs more cadmium than the pillared saponite. This is due to the higher quantity of inserted aluminum in the case of montmorillonite.

At this point, it is interesting to compare the adsorption capacities of pillared clay and Al(OH)₃. For an initial cadmium

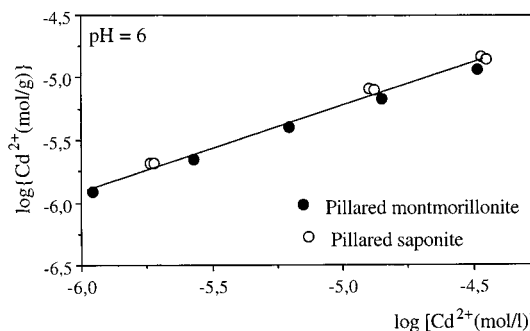


Figure 6. Cd adsorption isotherms on pillared clays, measured at pH = 6.

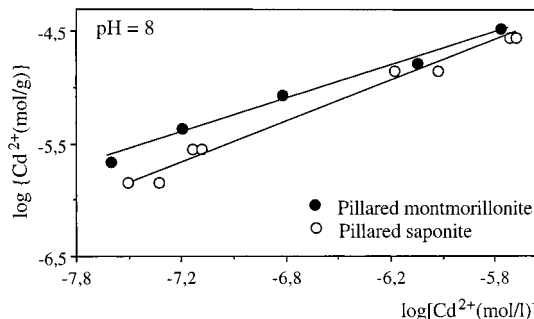


Figure 7. Cd adsorption isotherms on pillared clays, measured at pH = 8.

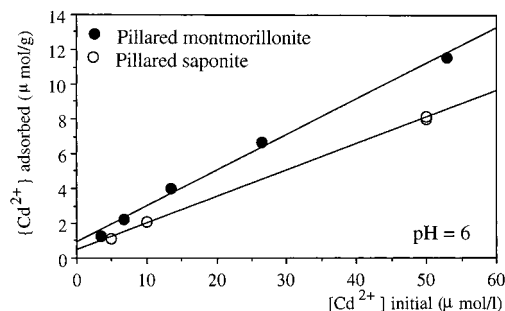


Figure 8. Variation of the quantity of adsorbed cadmium as a function of the initial cadmium concentration at pH = 6.

concentration of 10⁻⁴ mol/L and a pH = 6, pillared montmorillonite and pillared saponite respectively adsorb 78% and 65% of the total cadmium in solution. Aluminum hydroxide only adsorbs 2.7% of the total cadmium²⁷ in the same conditions. This is not unexpected since in the [Al₁₃] pillars almost all the Al's are exposed at the surface and available for adsorption

TABLE 2: Magnetic Parameters of Copper Adsorbed on Pillared Saponite and Pillared Montmorillonite ($A_{||}$ in G)

pillared saponite ¹			pillared montmorillonite ⁴		
$g_{ }$	g_{\perp}	$A_{ }$	$g_{ }$	g_{\perp}	$A_{ }$
2.375	2.097	148	2.325	2.050	147

while this is the case for only a small fraction of the Al's in alumina and Al(OH)₃. In fact, this is the basis for the practical interest of pillared clays as sorbent.

In the case of copper adsorption we found the same behavior for pillared saponite and pillared montmorillonite when the adsorption occurs at pH = 5. When the equilibrium copper concentration is above 3×10^{-3} mol/L, precipitation of Cu(OH)₂ occurs on the surface of the clay.¹

At lower concentrations, we have shown that Cu²⁺ adsorbs on the [Al₁₃] pillars through an inner-sphere mechanism, with the formation of grafted [Cu^{II}(AlO)_n(H₂O)_{4-n}]^{x+} and/or [Cu^{II}-(AlO)_n(H₂O)_{6-n}]^{x+} complexes that give rise to an anisotropic EPR signal under all humidity conditions.¹

Magnetic parameters of the EPR signals of copper adsorbed on pillared saponite and pillared montmorillonite are presented in Table 2. While the g values are somewhat different, the hyperfine splitting constants are in close agreement. In both pillared clays the copper is chemisorbed and seems to be adsorbed on similar surface groups. Thus, the behavior of both clays for Cu^{II} sorption is very similar; this is not surprising since copper adsorption experiments are necessarily carried out at low pH values (to avoid bulk hydroxide precipitation), where no differences were detected in Cd^{II} sorption either.

Conclusion

In this work, two different aluminum-pillared smectites (a saponite and a montmorillonite) were characterized. The acid–base titration data results are probably related to the different degrees of pillar transformation upon heating at 500 °C. For saponite, all the surface aluminum of pillars remain octahedral. At the opposite, some of these aluminums become tetrahedral in montmorillonite.

We have proposed a tentative model for the thermal transformations of pillars. While its details are still open to doubt, we believe that increased surface acidity is due to the ^{VI}Al ↔ ^VAl → ^{IV}Al transformation, which takes place at variable temperature according to the particular clay.

At pH 5 and 6 the adsorption mechanism of cadmium and copper are similar on the two pillared clays. For the same initial cadmium concentration, the pillared montmorillonite adsorbs more cadmium than the pillared saponite because the density of pillars is higher for the montmorillonite.

At pH 8 the surface groups in montmorillonite are almost totally ionized, while for pillared saponite only 50% of those

groups are ionized. Adsorption on negatively ionized groups seems to be favored for entropic reasons.

In this paper, we have established a correlation between technologically important properties of pillared clays (heavy metal adsorption), surface acidity, and the structural evolution of [Al₁₃] pillars on calcination. This underlines the necessity of a more precise characterization of [Al₁₃] transformations to gain in-depth understanding of pillared clay materials. We hope to draw the attention of the scientific community to this often overlooked question.

References and Notes

- (1) Bergaoui, L.; Lambert, J.-F.; Suquet, H.; Che, M. *J. Phys. Chem.* **1995**, *99*, 2155.
- (2) Bergaoui, L.; Lambert, J.-F.; Suquet, H. *J. Chim. Phys.* **1995**, *92*, 1486.
- (3) Mrad, I.; Ghorbel, A.; Lambert, J.-F.; Che, M. *J. Chim. Phys.* **1997**, *94*, 1883.
- (4) Mrad, I. Ph.D. Thesis, Université de Tunis II, Faculté des sciences de Tunis, 1997.
- (5) Stumm, W. *Chemistry of the Solid-Water interface*; John Wiley & Sons: New York, 1992; p 20.
- (6) Contescu, C.; Jagiello, J.; Schwarz, J. A. *Langmuir* **1993**, *9*, 1754.
- (7) Bandosz, T. J.; Jagiello, J.; Putyera, K.; Schwarz, J. A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3573.
- (8) Post, J. L. *Clays Clay Miner.* **1984**, *32*, 147.
- (9) Bergaoui, L.; Lambert, J.-F.; Franck, R.; Suquet, H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2229.
- (10) Chevalier, S.; Lambert, J.-F.; Franck, R.; Suquet, H.; Barthomeuf, D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 667.
- (11) Tichit, D. Ph.D. Thesis, University of Montpellier, 1986.
- (12) Mrad, I.; Ghorbel, A.; Tichit, D.; Lambert, J.-F. *Appl. Clay Sci.* **1997**, *12*, 349.
- (13) Hohl, H.; Stumm, W. *J. Colloid Interface Sci.* **1976**, *55*, 281.
- (14) Onada, G. Y., Jr.; DeBruyn, P. L. *Surface Sci.* **1966**, *4*, 48.
- (15) James, R. O.; Healy, T. W. *J. Colloid Interface Sci.* **1972**, *40*, 42.
- (16) Forbes, E. A.; Posner, A. M.; Quirk, J. P. *J. Soil Sci.* **1976**, *27*, 155.
- (17) Perdue, E. M. *Organic Acids in Aquatic Ecosystems*; John Wiley & Sons Ltd.: New York, 1990; p 111.
- (18) Pulfer, K.; Schindler, P. W.; Westall, J. C.; Grauer, R. *J. Colloid Interface Sci.* **1984**, *101*, 554.
- (19) Vaughan, D. E. W. *Catal. Today* **1988**, *2*, 187.
- (20) Knözinger, H.; Ratnasamy, P. *Catal. Rev. Sci. Eng.* **1978**, *17*, 31.
- (21) Tsyganenko, A. A.; Mardilovich, P. P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4843.
- (22) Reller, A.; Cocke, D. L. *Catal. Lett.* **1989**, *2*, 91.
- (23) Lambert, J.-F.; Chevalier, S.; Franck, R.; Suquet, H.; Barthomeuf, D. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 675.
- (24) Lambert, L.; Poncelet, G. *Top. Catal.* **1997**, *4*, 43.
- (25) Chevalier, S. Ph.D. Thesis, University Pierre et Marie Curie, 1992.
- (26) Almgren, M.; Johannsson, R.; Eriksson, J. C. *J. Phys. Chem.* **1993**, *97*, 8590.
- (27) Kinniburgh, M. L.; Syers, J. K. *Soil Sci. Soc. Am. J.* **1976**, *40*, 796.
- (28) It may be objected that an [Al₁₃] pillar having all of its surface groups in what we have called the “neutral” form has a charge of 7+. However, the bulk of the material (clay and pillars) is electrically neutral. What we mean by “neutral form” is only that the considered groups play the same role as SH in eq 1.