Adsorption 2, 227–235 (1996)

Adsorption and Characteristics of Base-Treated Pillared Clays

DANYUN LI AND ALFRED A. SCALA
Department of Chemistry, Worcester Polytechnic Institute, Worcester, MA 01609

YI HUA MA
Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609

Received November 8, 1995; Revised February 14, 1996; Accepted February 22, 1996

Abstract. The effect of base treatment on the cation exchange capacity (CEC) of pillared clays and their adsorption isotherms for Cu^{2+}, Cr^{3+} and Pb^{2+} have been investigated. Results indicate that although the CEC of pillared clays are only about 15% of that of the parent clays, a large fraction of the native clays CEC may be recovered by treatment with base. The fraction of the CEC recovered depends upon the base strength, its concentration, and the temperature. Contrary to previous suggestions the mechanism of recovery is related to the destruction of pillars which is accompanied by the loss of surface area. It is possible under conditions specified to prepare these base treated pillared clays as a new class of useful, regenerable adsorbent for heavy metal adsorption from aqueous solution.

Keywords: pillared clays, heavy metal ions, adsorption, cation exchange capacity

Introduction

Pillared interlayered clays (PILCs) were developed in the 1970's in a search for materials having larger pore sizes than zeolites. Pillared clays are an attractive class of acidic microporous solids because of their facile synthesis and structural adaptability. Their preparation and properties have been extensively investigated (Pinnavaia, 1983; Occelli and Tindwa, 1983; Figureas, 1988; Burch, 1988). Pillared clays are formed by direct ion-exchange of oligomer cations in aqueous solutions. These large cations function as pillars and prevent the collapse of the structure during outgassing. At elevated temperatures, dehydration and dehydroxylation occur, resulting in the oxide aggregates forming stable pillared clays with microporous structure. The most common ions used as pillaring agents are polycationic species of Al, Zr, Ti, Fe, and Cr which are prepared by hydrolysis of corresponding salts in solution. For example, a base hydrolyzed $AlCl_3$ solution at OH^-/Al^{3+} ratio in the range 1.0–2.5 which form the $Al_{13}O_4(OH)_{24}^{7+}$ ion. The clays that are usually intercalated are the natural and synthetic smectite clays. Smectite clays are readily pillared because of their low charge density, their swelling ability and transverse layer rigidity. Properties, such as acidity, surface area, pore size distribution and hydrothermal stability, depend on the method of synthesis, as well as on the nature of the host clay.

In addition to catalytic applications, the zeolite like micropore structure of pillared clays has potential application as molecular sieves. Because of the large surface, and micropore area in pillared clay, compared to natural clay, it is reasonable to expect that the adsorption capacity of pillared clay will be greater than that of the corresponding natural clay. Recently, pillared clays have been investigated as adsorbents. For example, pillared clays are considered promising adsorbents for flue gas cleanup because of their high equilibrium sorption capacities for SO_2 and NO, and high SO_2/CO_2 selectivity (Baksh and Yang, 1992). PILCs have been evaluated as selective adsorbents for gases.

Although cation modified PILC has shown a N_2/O_2 selectivity of 3.2 at 25°C and 1 atm, its capacity is only 20% that of the zeolite (Cheng and Yang, 1995). The adsorption characteristic of various pillared clays were found to depend on three structural properties of the pillared clay: the pillar height, the distribution of the pillars between the clay layers and the nature of the pillaring species (Molinard and Vansant, 1994, 1995). Water adsorption isotherms using alumina pillared clay exhibited hydrophobic characteristics (Malla and Komarneni, 1990; Yamanaka et al., 1990). For the purpose of adsorption, the pore size and pore size distribution of PILCs greatly affect their adsorption properties and separation efficiencies (Zhu et al., 1994). The pore size distribution of pillared clays has been controlled by interpillar spacing, rather the interlayer spacing (Baksh et al., 1992). Also, introducing cations into the interlayer spacing produces some interesting effects on the shape of the adsorption isotherm, the heat of sorption, and the total sorption capacity. These properties depend upon the ionic radius and polarizing ability of different cations (Cheng and Yang, 1995; Molinard and Vansant, 1995).

The cation exchange capacity (CEC) of pillared analogues decreases dramatically compared with unpillared clays. Only 10 to 15% of CEC remains after formation of a stabilized pillared structure. It has been reported that approximately 80% of the initial CEC of the clay could be restored by treating pillared clays with base, such as potassium carbonate or ammonia (Vaughan et al., 1981; Molinard et al., 1994a, b). The loss of CEC after pillaring is a major drawback to the use of pillared clays for heavy metal removal from aqueous solutions by cation adsorption. However, if the CEC can be at least partially restored, the pillared clays possess several advantages over the parent clays. The large particle size of pillared clay is easier to process and causes a smaller pressure drop in a fixed-bed operation compared to native clays. Under moderate conditions for regeneration the pillared structure is stable and the interlayer distance is maintained.

The objective of this study was to investigate the effects of pillaring on the cation exchange capacity of pillared clays. Also, factors affecting the recovery of the CEC of the pillared clays by treatment with base solution were examined. The results of this study have implication for the development of practical, efficient and economical adsorbents for pollution abatement, specifically, for heavy metal ion removal from aqueous solutions.

Experimental

1. Starting Materials

A natural Texas Ca^{2+} montmorillonite, STx-1, was obtained from the Source Clay Minerals Repository at the University of Missouri (Columbia, MO). Two other clays used in the preparation of alumina pillared clays were sodium beidellite and sodium rectorite obtained from China. All the starting clays (particle size < 2 μm) were exchanged to the sodium from before the pillaring reaction. The Ca^{2+} and Na^+ Texas montmorillonites were designated CaTM and TM, respectively. The Na^+ beidellite and Na^+ rectorite were designated CB and CR, respectively. The measured cation exchange capacities (CEC) were 87 meq/100 g clay for TM, 100 meq/100 g clay for CB and 70 meq/100 g for CR, all determined by the ammonia electrode method (Busenberg and Clemency, 1973).

2. Synthesis of Alumina Pillared Clays

Alumina pillared clays were prepared by intercalation of sodium clays with the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (Ge et al., 1994). The Pillaring solution was prepared by hydrolysis of 0.20 M $AlCl_3$ with 0.20 M NaOH. The OH^-/Al^{3+} ratio was 2.4. Sodium Clay (2 wt%) was added to the pillaring solution at 70°C. The Al^{3+}/clay ratio was maintained in the range 2.8–3.0 mmol/g. After aging for 2 h at 70°C, the mixture was centrifuged, and washed with deionized water until chloride free. The suspension was air dried, and the product was calcined by heating from 25°C, at a rate of 5°C/min, to a temperature of 350°C and the temperature maintained at 350°C for 10 h. AlTM, AlCB and AlCR refer to alumina pillared Texas montmorillonite, beidellite, and rectorite respectively.

3. Synthesis of Zirconium Pillared Clays

Zirconium intercalated clays were prepared from TM by reaction with zirconyl chloride solution. $ZrOCl_2$, 0.10 M was refluxed for 24 h to form the pillaring solution. The $[Zr(OH)_8(H_2O)_{16}]^{8+}$ ion is the pillaring precursor (Burch and Warburton, 1986; Figueras et al., 1989). TM (2 wt%), was added to the pillaring solution at 70°C and aged for 2 h. After separation by filtering and washing, the product was dried and calcined as described for AlTM above.

4. *Base Treatment of Pillared Clays*

4.1. Exposure to Ammonia Vapor. Approximately 4 g of calcined AlTM was finely ground and stored in a dessicator containing 150 mL of concentrated, 35 wt%, NH_4OH solution, in a 250 mL beaker. After the sample was exposed to ammonia vapor for 24 h, it was exchanged to the ammonium form by one of the following two methods:

a) [AlTM(NH_3)]: The sample was washed with large amounts of deionized water, until the pH reached 7, then separated by filtration. The sample was then treated with 100 mL of 1 M NH_4Cl solution. After washing, the NH_4^+ exchanged clay was obtained for CEC and Cu^{2+} adsorption measurements.
b) [AlTM(NH_3)(HCl)]: The ammonia treated sample was first washed with deionized water, then with dilute HCl (0.1 M), and then with water until the washes were chloride free. The NH_4^+ exchanged form was obtained by treating the clay with 100 mL of 1 M NH_4Cl as described in a) above.

4.2. Treatment by Ammonium Hydroxide Solution.

a) [AlTM(NH_4OH)(HCl)]: AlTM, 2 g, was added into 100 mL of 17 wt% NH_4OH solution, and stirred at room temperature for 1 h. After washing with water, followed by 0.10 M HCl, and again with water until the washes were chloride free, the sample was exchanged into the ammonium form as described in 1a) above.
b) [AlTM(NH_4OH)(R)(HCl)]: AlTM, 2 g, was added to 17 wt% NH_4OH solution. The mixture was refluxed for 1 h followed by washing as in 2a) above and subsequently converted to the ammonium form as described in 1a) above.

4.3. Treatment by Dilute NaOH Solution. [AlTM(NaOH)(HCl)] AlTM, 2 g, was mixed with 100 mL of 10^{-5} M sodium hydroxide solution (pH = 9), and stirred for 1 h at room temperature. Two other samples were treated with 0.02 M and 0.2 M NaOH solutions. All samples were washed with water and dilute HCl, then converted to the ammonium form as described in 1a) above.

5. *Characterization Methods*

X-ray diffraction (XRD) patterns were obtained for oriented powder samples using a Rigaku diffractometer, equipped with rotating anode, and using Ni-filtered, Cu Kα radiation. Surface area and pore size distributions were determined using nitrogen as the sorbate, at 77 K, on a Quanta Chrome (Auto Sorb-1) sorptometer. The samples were outgassed overnight at 150°C at a pressure of 10^{-5} torr. The BET surface areas were calculated in the range of $0 < P/P_0 < 0.1$. The t-plot method was used to determined microporous surface area (Boer et al., 1966). Cation exchange capacities (CEC) were determined according to the literature procedure (Busenberg and Clemency, 1973). The clays were exchanged with 1 M ammonium acetate, followed by 1 M ammonium chloride, washed until chloride free, then air dried. The amount of ammonia liberated from the ammonium exchanged clays when suspended in 5 M NaOH was measured with an ammonia electrode.

6. *Metal Ion Adsorption Isotherms*

Cu^{2+}, Cr^{3+}, and Pb^{2+} adsorption isotherms were used to characterized the adsorption of heavy metal ions on the montmorillonite, beidelite and rectorite, and their pillared derivatives. Adsorbent, 0.10 g, was added to 20 mL of solution containing from 60 to 300 ppm $CuCl_2$, $Cr(NO_3)_3$ or $Pb(NO_3)_2$. The mixtures were shaken for 24 h at 25°C, and then separated by centrifugation. The concentration of Cu^{2+}, Cr^{3+}, or Pb^{2+} remaining in the aqueous solution was measured using a Perkin Elmer 3100 Atomic Absorption Spectrometer. The quantity of the metal ion adsorbed was calculated from the difference between the initial concentration and the equilibrium concentration. Experiments which measured the adsorption as a function of time clearly demonstrated that twenty four hours was more than sufficient to establish equilibrium.

Results and Discussion

1. *The Structure of Pillared Montmorillonites*

When an expandable layer type clay, usually a smectite clay, is directly exchanged with pillaring reagent, and calcined, the interlayered metal complexes are converted into metal oxides. For aluminum pillared clay, the stabilized oxide pillars prop clay layers

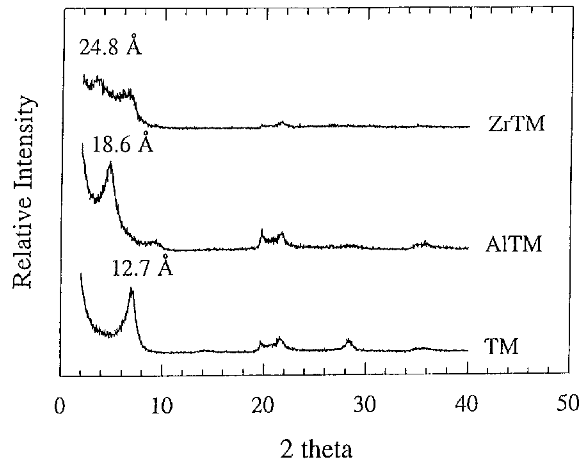

Figure 1. X-ray powder diffraction patterns (CuKα) for the sodium form of Texas montmorillonites (TM), alumina pillared TM (AlTM), calcined at 350°C, and zirconium intercalated TM (ZrTM) calcined at 350°C.

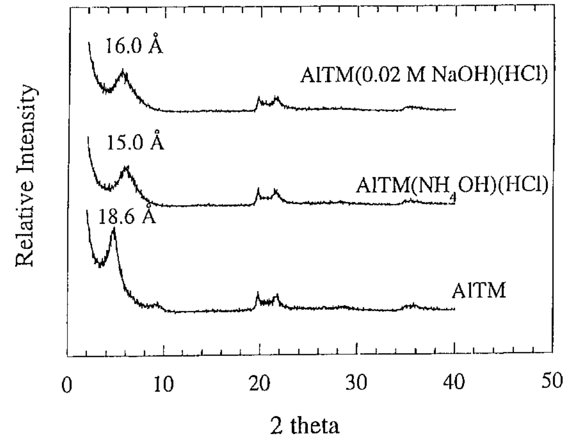

Figure 2. X-ray powder diffraction patterns (CuKα) for alumina pillared Texas montmorillonites, AlTM, alumina pillared TM calcined at 350°C. AlTM[(NH_4OH)(R)(HCl)], AlTM refluxed with NH_4OH, and AlTM[(0.02 M NaOH)(HCl)], AlTM treated by 0.02 M NaOH solution.

7–9 Å apart, and form micropores between the pillars. Figure 1 presents the x-ray powder diffraction patterns for Texas Montmorillonite (TM), Aluminum pillared TM (AlTM), and Zirconium pillared TM (ZrTM). The x-ray powder diffraction patterns shown in Fig. 1 clearly demonstrate that pillaring Texas Montmorillonite with either aluminum or zirconium does expand the clay structure. The basal spacing, 12.7 Å, of the natural clay is expanded to 18.6 Å for the aluminum pillared Texas Montmorillonite (AlTM) and to about 25 Å for the Zirconium pillared clay (ZrTM). Table 1 presents the basal spacing determined from the x-ray patterns along with the BET surface areas, micropore surface areas, and the CEC determined by the ammonia selective electrode method. Pillaring TM increases the surface area from 28 m^2/g to 307 m^2/g for AlTM and to 298 m^2/g for ZrTM. The data in Table 1 demonstrate that, the larger basal spacing is accompanied by increased BET surface area with a substantial increase in micropore surface area. More than 60% of the total surface area occurs in the micropore region. Figure 2 presents the x-ray diffraction data for three AlTM samples. The first is AlTM as prepared, the other two received treatment with ammonia or sodium hydroxide according to procedures 2b and 3(0.02 M) respectively. Tables 3 and 4 present the CEC data for a series of AlTM samples which were treated with base as indicated in the tables and described in the Experimental section.

Table 1. Basal spacings, surface areas and cation exchange characteristics of alumina pillared clays.

Sample	Basal spacing (Å)	BET surface area (m^2/g)	S_T (m^2/g)	S_{micro} (m^2/g)	CEC meq/100 g
[NaTM]	12.7	28	30	0	87
[AlTM]	18.6	307	311	206	13
[AlTM(NH_4OH)(R)(HCl)]	15.0	206	206	91	45
[AlTM(0.02 M NaOH)(HCl)]	16.0	219	222	110	36

These base treated AlTM samples were used in adsorption experiments, for solutions of $CuCl_2$, $Cr(NO_3)_3$, and $Pb(NO_3)_2$. The adsorption isotherms determined in these experiments are presented in

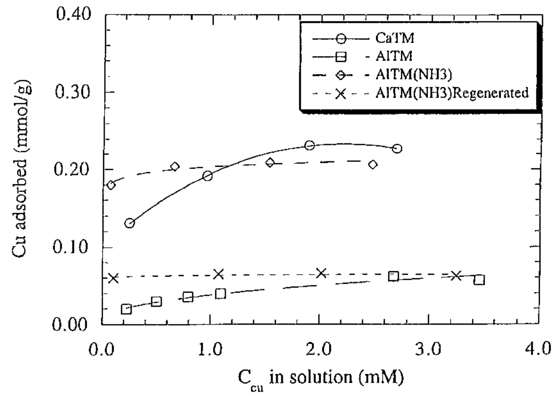

Figure 3. Adsorption of Cu^{2+} by unpillared clay and alumina pillared Texas montmorillonites.

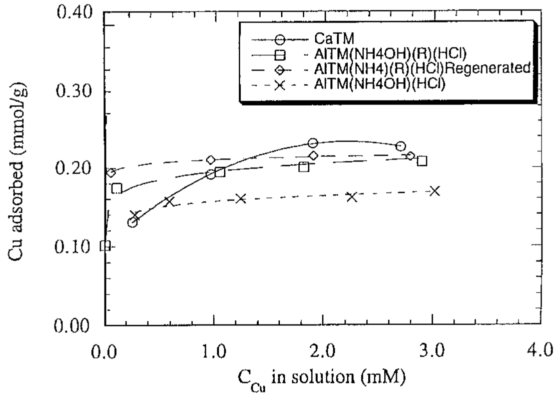

Figure 4. Adsorption of Cu^{2+} by alumina pillared Texas montmorillonites treated with NH_4OH solution.

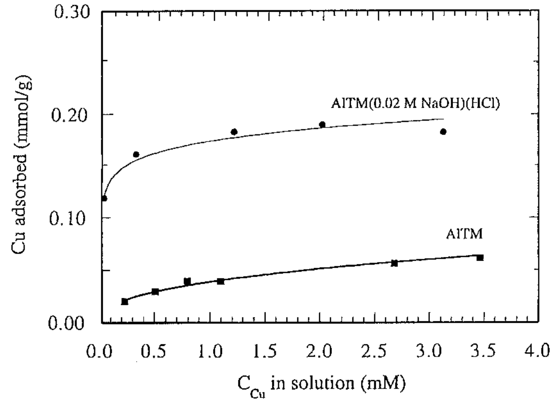

Figure 5. Adsorption of Cu^{2+} from $CuCl_2$ solution by alumina pillared Texas montmorillonites treated with NaOH solution.

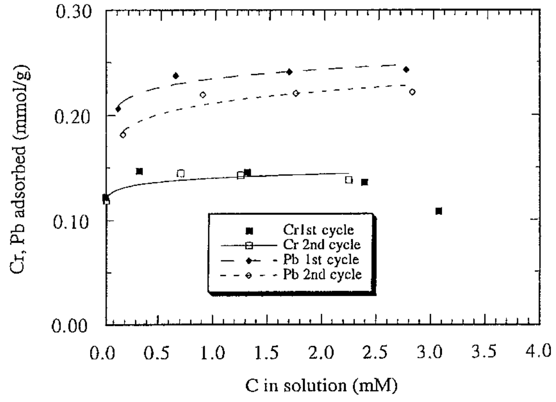

Figure 6. Adsorption Cr^{3+} from $Cr(NO_3)_3$ solution and Pb^{2+} from $Pb(NO_3)_2$ solution by AlTM [NH_4OH)(R)(HCl)].

Figs. 3–6. The CEC values, determined in this manner, are consistent with the CEC values determined by the ammonia electrode method.

2. *Cation Exchange Capacity (CEC) of Pillared Clays*

Table 1 indicates that the pillaring process, which results in the increase in accessible surface area of the clay, also consumes 85% of cation exchange capacity of the clay. The CEC of the pillared clays are only about 15% of those of the native clay. The CEC of TM is 87 meq/100 g while that of the aluminum and zirconium pillared TM are only 13 and 11 meq/100 g respectively. This well known phenomenon is the result of the pillaring process consuming some of the cation sites. As suggested by prior work it is believed that aluminum poly-cations mainly the Keggin ion under present conditions, are decomposed upon calcination to alumina, protons and water shown in reaction 1 and as described below (Vaughan et al., 1981).

$$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow 6.5\,Al_2O_3 + 20.5\,H_2O + 7\,H^+ \quad (1)$$

The protons balance the ion exchange capacity of the original clay which was satisfied by the positive charge of the aluminum oligomer. The released protons migrate into the clay octahedral layer, toward incompletely neutralized hydroxyl groups coordinated to magnesium, aluminum or other octahedral structural cations. Migration of protons into the clay octahedral layer is basically responsible for the low ion exchange capacity for calcined pillared products.

3. *Recovery of CEC of Pillared Clays*

3.1. Ammonia Vapor Treated Alumina Pillared Montmorillonites. For [AlTM(NH_3)] the CEC value measured by the ammonia electrode increases to 54 meq/100 g (Table 2). When, AlTM treated with ammonia gas was pumped for 24 h and converted to the ammonium form, [AlTM(NH_3)] was used to adsorb copper ions from aqueous solution it was found that despite washing the clay with copious amounts of water, prior to the introduction of the copper ion, copper hydroxide precipitated on the clay. The observed CEC using the ammonia electrode was 54 meq/100 g. The corresponding capacity for removal Cu^{2+} illustrated in Fig. 3 is very closed to that of the unpillared clay. At the low concentration edge, the pillared clays are more efficient than the parent clay. Attempts to regenerate this pillared clay to the sodium form and use it for another cycle of adsorption were unsuccessful. When the

Table 2. CEC values for ammonia altered alumina pillared Texas Montmorillonites.

Sample	CEC (meq/100 g pillared clay)
[AlTM] NH_4Cl exchanged AlTM	13
[AlTM(NH_3)] AlTM treated by NH_3, then exchanged by NH_4Cl	54
[AlTM(NH_3(HCl)] AlTM treated by NH_3, washed by dilute HCl, then exchanged by NH_4Cl	11
[AlTM(NH_4OH)(25°C)(HCl)] AlTM treated by NH_4OH solution for 1 h, then washed by dilute HCl, exchanged by NH_4Cl	31
[AlTM(NH_4OH)(R)(HCl)] AlTM refluxed with NH_4OH solution for 1 h, washed by dilute HCl, then exchanged by NH_4Cl	45

adsorbent was regenerated by exchange with NaCl, in a second cycle of Cu^{2+} adsorption, the amount of Cu^{2+} removed decreased dramatically. Figure 3 shows that the capacity for copper of AlTM(NH_3) in a second cycle is only at the level of the pillared clay (AlTM). To verify the ammonia effect, another sample of ammonia treated AlTM was washed with dilute hydrochloric acid, followed with water. After exchange into the ammonium form with ammonium chloride the CEC was only 11 meq/100 g (Table 2, AlTM(NH_3)(HCl), and the capacity for removal of Cu^{2+} was identical to that of untreated AlTM.

3.2. Ammonium Hydroxide Treated AlTM. For [AlTM(NH_4OH)(HCl)], the CEC value was 31 meq/100 g, increasing greatly compared with the initial value of 13 meq/100 g for untreated pillared clay. The capacity of removing Cu^{2+} from solution also increased correspondingly, as shown in the Fig. 4. Since optimized cation exchange capacity result in high metal ion adsorption, another base treatment using ammonia solution was carried out at reflux temperature, [AlTM(NH_4OH)(R)(HCl)]. As expected, the higher temperature treatment restored more of the CEC. The observed CEC was 45 meq/100 g. Figure 3 shows that the capacity of [AlTM(NH_4OH)(R)(HCl)] for removing Cu^{2+} is close to that of unpillared clay. The steep slope at low concentration indicates that at low concentration, the base treated pillared clays remove metal ions from solution more efficiently than the native CaTM, despite the slightly lower ultimate capacity. To regenerate the exchangeable sites, the adsorbents were exchanged by NaCl. After washing and filtering, the adsorbents were reused to adsorb Cu^{2+}. The second cycle adsorption is almost identical to that of the first cycle (Fig. 4).

3.3. Sodium Hydroxide Treated AlTM. That ammonia solution restores the exchange capacity is due to the basicity of ammonia. Other bases, such as K_2CO_3 may also be used to restore cation exchange capacity (Vaughan et al., 1981; Molinard et al., 1994a, b). Higher temperature creates more exchangeable sites. Similarly, higher base concentration creates more exchangeable sites. CEC of AlTM treated by very dilute NaOH ($pH = 9$) is 23 meq/100 g (Table 3). The CEC increases to 36 meq/100 g after treatment with 0.02 M NaOH. When 0.2 M NaOH was used, the CEC increased to 64 meq/100 g. However, the 0.2 M NaOH produces clay particles which are very fine, and behave in the filtration process similar to unpillared clay. Therefore, moderate concentration (0.02 M) is appropriate in terms of both efficient CEC recovery and ease of processing. The corresponding Cu^{2+} adsorption isotherms of AlTM treated with 0.02 M NaOH is shown in Fig. 5. It can be seen that the capacity for Cu^{2+} of this pillared clay is comparable to, but slightly lower than the ammonia treated AlTMs and CaTM shown in Fig. 4, and much greater than untreated AlTM.

Table 3. CEC values for sodium hydroxide altered alumina pillared Texas Montmorillonites.

Sample	CEC (meq/100 g pillared clay)
[AlTM] NH_4Cl exchanged AlTM	13
[AlTM(0.001 M NaOH)(HCl)] AlTM treated by 0.001 M NaOH, washed by dilute HCl, then exchanged by NH_4Cl	23
[AlTM(0.02 M NaOH)(HCl)] AlTM treated by 0.02 M NaOH solution for 1 h, then washed by dilute HCl, exchanged by NH_4Cl	36
[AlTM(0.2 M NaOH)(HCl)] AlTM treated by 0.2 M NaOH solution for 1 h, then washed by dilute HCl, exchanged by NH_4Cl	64

3.4. Mechanism of Restoring CEC by Treating with Base. Molinard et al. (1994a, b) reported that treatment of aluminum pillared montmorillonite with ammonia vapor, restores 79% of the original CEC by capturing the inaccessible protons in the octahedral layer of the clay as ammonium ions on the clay surface. The CEC was measured by a Kjeldahl analysis for nitrogen. This method measures total nitrogen i.e., NH_3 and NH_4^+. Because it is necessary to heat AlTM to 500°C before all of the NH_3 in the micropores is removed, it is probable that samples pumped at room temperature, even for extended periods of time still contain considerable quantities of ammonia (He et al., 1988). This is a reasonable phenomenon based on the structure and acidity of pillared clays. Pillared clays are a class of solid acid materials which contain both Brönsted and Lewis acid sites. The structural hydroxyl groups on the clay are suggested to be a major source of Brönsted acidity in calcined pillared product. The pillars are recognized as the major source of Lewis acidity. Ammonia adsorption was one of methods used to investigate Lewis acidity (Occelli and Tindwa, 1983; He et al., 1988). Therefore washing with water or removal under vacuum at low temperature can not remove chemically adsorbed ammonia. The NH_3 residue is however neturalized by washing with dilute HCl.

Since the retreat of protons into the octahedral layer of the calcined pillared clays has been suggested as the cause of the reduced CEC of pillared clays it seemed that this phenomenon might not occur when tetrahedral clays are pillared. When rectorite or beidellite, both tetrahedrally charged clays are pillared and calcined, they behave exactly like the octahedrally charged montmorillonite. For AlCB pillaring reduces the CEC from 100 to 15 meq/100 g. For AlCR pillaring reduces the CEC from 70 to 14 meq/100 g. In both cases treatment with ammonia restores the CEC to 23 meq/100 g. It is quite clear that the restoration of the CEC by ammonia cannot be the result of neutralization of protons buried in the octahedral layers of these clays, since the charges in these clays originate mainly in the tetrahedral layers. Because high CEC is a prerequisite for efficient ion adsorbents, methods of increasing the CEC of pillared clays were investigated.

For ammonia treated pillared clays, the CEC and adsorption results with AlTM(NH_3) and AlTM(NH_3)(HCl) indicate that the treatment with ammonia vapor does not create recoverable cation exchange sites. The Cu^{2+} removed after ammonia treatment is not due to exchangeable sites restored and is likely related to the small amount of ammonia trapped in the micropores of the pillared structure. This precipitates Cu^{2+} or other heavy metal ions as their insoluble hydroxides. The green color of the clay after the first cycle indicated that it contained copper hydroxide solid. The copper hydroxide precipitated on the clay could be dissolved in ammonia solution. The adsorption capacity of ammonia treated AlTM is not unreasonable for a practical adsorbent, however the capacity, results mainly from ammonia adsorbed in the micropores and, not from the recovery of cation exchange capacity. The disadvantage of this material is that it is not easily regenerable.

Unlike ammonia vapor, treatment with aqueous base restores the CEC sites on alumina pillared montmorillonites. The evidence suggests that base attacks the structure of the pillared clays. However, most of pillars may be retained under mild base treatment. The evidence for this is the XRD pattern in Fig. 2. After treatment of AlTM with base solution, the 001 reflection shifts from 18.6 to 16.0 Å for 0.02 M NaOH treatment, and to 15.0 Å after reflux with ammonia. At the same time the width of the line is increased, indicating a partial collapse of the pillared structure. The surface area data in Table 1 are also consistent with this interpretation. Both total surface area and microporous area decrease as a result of treatment with aqueous base. In the case of AlTM(NH_4OH)(R)(HCl), the total surface area is 206 m^2/g, and the microporous area is 91 m^2/g, only about 50 to 60% of that of the alumina pillared clay without any base treatment (AlTM). If we consider the process of calcination of pillared clays, pillar precursors are converted into γ-Al_2O_3, which is not the most stable phase of Al_2O_3. The most stable α-Al_2O_3 is formed at temperatures above 1000°C. Actually, the lack of thermal and hydrothermal stability are the major limiting factors for the commercial use of pillared clay as cracking catalysts. It has been suggested that pillars are less stable than clay sheets and collapse first (Vaughan, 1988). The CEC recovery in Table 3 also shows that more CEC sites are recovered by higher base concentration. One could therefore predict that zirconium pillars would, because of their greater stability, be less susceptible to treatment with base (Barley, 1988). For that reason stronger base and more severe conditions would be required to recover the same CEC for zirconium pillared clays. This can be seen in Table 4.

Table 4. Surface areas and cation exchange characteristics of zirconium pillared clays.

Sample	BET surface area (m^2/g)	S_T (m^2/g)	S_{micro} (m^2/g)	CEC meq/100 g
[ZrTM]	298	302	178	11
[ZrTM(NH$_4$OH)(R)(HCl)]	270	276	152	20
[ZrTM(0.2 M NaOH)(HCl)]	268	272	150	18

4. *Removal of Cr^{3+} and Pb^{2+} from Aqueous Solution by Base Treated Pillared Clays*

Figure 6 presents adsorption data for removal of Cr^{3+} and Pb^{2+} by AlTM(NH$_4$OH)(R)(HCl). The molar amount of Cr^{3+} removed is about 60% of the amount for Cu^{2+}. The molar amount of Pb^{2+} adsorbed is almost identical to that for Cu^{2+}, Fig. 4. These capacities are consistent with the two to three charge factor and the expectation that metal ion adsorption should be non-selective and depend only on the charge. Second cycles for both chromium and lead adsorption after the clay was exchanged with NaCl solution, are virtually indentical to the corresponding first cycles.

Recent studies have shown that clay, Na-bentonite and two zeolites, natural eronite and synthetic Y zeolite may be used as adsorbents for radioactive cobalt (Carrera et al., 1993). At equilibrium 0.79 meq/g was exchanged into Na-bentonite (CEC = 0.87 meq/g), 1.10 meq/g Co^{2+} into erionite (CEC = 1.51 meq/g), and 1.49 meq/g into Y-zeolite (CEC = 3.08 meq/g). Co^{2+} is more effectively adsorbed by Y zeolite because of its high CEC. The shapes of the adsorption/time curves of these adsorbents are different. The clay showed a slow uptake before the equilibrium, and the attaintment of equilibrium required as much as 100 h. This observation results from the slow interlayer diffusion in the natural clay. In contrast, base treated pillared clay improved the shape of the adsorption isotherm at low concentrations and shortened the equilibrium time. Up to 60% of the CEC of the unpillared clays was recovered in the base treated pillared clays.

5. *pH Effect in the Adsorption of Heavy Metal Ions*

Generally, the amount of heavy metal ion adsorbed by a clay or zeolite increases with increasing pH (Carrera et al., 1993; Farrah and Pickering, 1979). This effect is due to decreased competition from protons for cation adsorption sites at higher pH. Since the objective of the work is to investigate the basic ion exchange properties of pillared clays for the possible establishment of a practical process, using regenerable adsorbents, for the removal heavy metal ions from aqueous media, only metal ion concentrations have been controlled, not the pH of solution. However, the pH effect can still be seen. For example in Fig. 6 at the three highest concentration of Cr^{3+}, the amount of Cr^{3+} adsorbed decreased because of the lower pHs of the more concentrated Cr(NO$_3$)$_3$ solutions. The corresponding pH were 3.28, 3.20 and 3.14. In the more concentrated solutions at their lower pHs, the competition of protons for active sites increases and results in a decrease in the amount of Cr^{3+} adsorbed. The adsorption of protons can also result in a significant increase in the pH. If the pH increases, beyond a threshold of solubility of the metal hydroxides, the hydroxide will precipitate on the adsorbent. For this reason it is important that studies of heavy metal adsorption include pH control and monitoring. Although the pH was not controlled in this study, it changed minimally during adsorption experiments and hydroxide precipitation was not a problem, except as indicated in the ammonia gas treated AlTM, [AlTM (NH$_3$). In a subsequent paper, the pH effect and the distinction between adsorption by ion exchange, and hydroxide formation will be discussed.

Conclusion

The present attempts to recover the cation exchange capacity of AlTM were prompted by the observation that base i.e., OH$^-$ seemed to increase the CEC of pillared clay. All of the base treatments of AlTM used in this study result in recovery of some fraction of the CEC of the original clay, but at the expense of some fraction of the pillars and the associated surface area. The extent of recovery of the CEC is a function of the base concentration, the temperature, and the duration of the treatment. When AlTM is treated with 0.20 M NaOH it reverted to a material with the physical characteristics of native clay. The best recovery of CEC without totally destroying the pillars has been attained by refluxing in ammonia solution. 0.020 M sodium hydroxide at 25°C gives a reasonable CEC recovery, 36 meq/100 g, and still retains much of the pillared surface area. In both cases since the CEC is regenerable, these adsorbents have potential in process application.

Acknowledgment

This work was supported by the USEPA through RREL Cincinnati Grant No. CR 822728-01. The authors express sincere appreciation to Mr. Huai-Te Shu for his generous assistance throughout this work.

References

Baksh, M.S., E.S. Kikkinides, and R.T. Yang, "Characterization by Physisorption of a New Class of Microporous Adsorbent: Pillared Clays," *Ind. Eng. Chem. Res.*, **31**, 2181–2189 (1992).

Baksh, M.S.A. and R.T. Yang, "Unique Adsorption Properties and Potential Energy Profiles of Microporous Pillared Clays," *AIChE J.*, **38**(9), 1357–1368 (1992).

Barley, G.J.J., "Zirconium Pillared Clays," *Catalysis Today, Pillared Clays, Catalysis Today*, R. Burch (Ed.), Vol. 2, pp. 233–241, Elsevier, New York, 1988.

Boer, J.J., B.C. Lippens, B.G. Linsen, J.C.P. Broekhoff, A. van den Heuvel, and Th.J. Osinga, "The *t*-Curve of Multimolecular N_2-Adsorption," *J. Colloid Interface Sci.*, **21**, 405–414 (1966).

Burch, R. (Ed.), *Pillared Clays, Catalysis Today*, Vol. 2, Elsevier, New York (1988).

Burch, R. and C.I. Warburton, "Zr-Containing Pillared Interlayer Clays," *J. Catal.*, **97**, 503–510 (1986).

Busenberg, E. and C.V. Clemency, "Determination of the Cation Exchange Capacity of Clays and Soils Using an Ammonia Electrode," *Clays Clay Miner.*, **21**, 213–217 (1973).

Carrera, L.M., S.G.P. Bosch, and S. Bulbulian, "Removal of ^{60}Co by Zeolites and Clays," *Zeolites*, **13**, 622–625 (1993).

Cheng, L.S. and R.T. Yang, "A New Class of Non-Zeolitic Sorbents for Air Separation: Lithium Ion Exchanged Pillared Clays," *Ind. Eng. Chem. Res.*, **34**(6), 2021–2028 (1995).

Farrah, H. and W.F. Pickering, "pH Effects in the Adsorption of Heavy Metal Ions by Clays," *Chemical Geology*, **25**, 317–326 (1979).

Figueras, F., A. Mattrod-Bashi, G. Fetter, A. Thrierr, and J.V. Zanchetta, "Preparation and Thermal Properties of Zr-Intercalated Clays," *J. Catal.*, **119**, 91–96 (1989).

Figureas, F., "Pillared Clays as Catalysts," *Catal. Rev. Sci. Eng.*, **30**(3), 457–499 (1988).

Ge, A., D. Li, and T.J. Pinnavaia, "Preparation of Alumina-Pillared Montmorillonite with High Thermal Stability, Regular Microporosity and Lewis/Brönsted Acidity," *Microporous Mater.*, **3**, 165–175 (1994).

He, M., Z. Liu, and E. Min, "Acidic and Hydrocarbon Catalytic Properties of Pillared Clay," *Catalysis Today*, R. Burch (Ed.), vol. 2, pp. 321–338, Elsevier, New York, 1988.

Malla, P.B. and S. Komarneni, "Synthesis of Highly Microporous and Hydrophilic Alumina-Pillared Montmorillonite: Water-Sorption Properties," *Clays Clay Miner.*, **38**(4), 363–372 (1990).

Molinard, A., P. Cool, and E.F. Vansant, "Physicochemical Properties of Ammonia-Adsorbed Alumina-Pillared Montmorillonite and Structural Aspects of Deammoniation Process," *Microporous Mater.*, **3**, 149–158 (1994a).

Molinard, A., K.K. Peters, and E.F. Vansant, "Restoring the Cation Exchange Capacity of Alumina Pillared Montomorillonite through Modification with Ammonium," *Separation Technology*, E.F. Vansant (Ed.), pp. 445–454, Elsevier Science B.V., Amsterdam, 1994b.

Molinard, A. and E.F. Vansant, "Gas Adsorption Properties of Cation Modified Alumina Pillared Montmorillonite," *Separation Technology*, E.F. Vansant (Ed.), pp. 423–436, Elsevier Science B.V., Amsterdam, 1994.

Molinard, A. and E.F. Vansant, "Controlled Gas Adsorption Properties of Various Pillared Clays," *Adsorption*, **1**, 49–59 (1995).

Occelli, M.L. and R.M. Tindwa, "Physicochemical Properties of Montmorillonite Interlayered with Cationic Oxyaluminum Pillars," *Clays Clay Miner.*, **31**(1), 22–28 (1983).

Pinnavaia, T.J., "Intercalated Clay Catalysts," *Science*, **220**, 365–371 (1983).

Vaughan, D.E.W., "Pillared Clays—A Historical Perspective," *Pillared Clays, Catalysis Today*, R. Burch (Ed.), Vol. 2, pp. 187–198, Elsevier, New York, 1988.

Vaughan, D.E.W., R.J. Lussier, and J.S. Magee, "Pillared Interlayered Clay Product," U.S. Patent 4,176,043, 1981.

Yamanaka, S., P.B. Malla, and S. Komarneni, "Water Adsorption Properties of Alumina Pillared Clay," *J. Colloid Int. Sci.*, **134**(1), 51–58 (1990).

Zhu, H., Z. Hu, N. Maes, and E.F. Vansant, "Correlation between the Micropore Structure and the Adsorption of Benzene in Pillared Clays," *Separation Technology*, E.F. Vansant (Ed.), pp. 715–726, Elsevier Science B.V., Amsterdam, 1994.