

Controlled Doping of Transition Metal Cations in Alumina Pillared Clays

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A two-step method of loading controlled amounts of transition metal cations into alumina pillared clays (Al-PILCs) is proposed. First, calcined Al-PILC was dispersed into an aqueous solution of sodium or ammonium ions. Increasing the pH of the dispersion resulted in an increase in the amount of cations loaded into the clay. The ion-doped Al-PILC was then exchanged with an aqueous solution of transition metal salt at a pH of ~ 4.5 to replace Na^+ or NH_4^+ ions by transition metal cations. Analytical techniques such as atomic absorption spectroscopy, X-ray diffraction, diffuse reflectance–ultraviolet–visible spectroscopy, as well as N_2 adsorption were used to characterize the PILC products with and without the loading of metal ions. The introduced transition metal species exist in the forms of hydrated ions in the PILC hosts. The content of transition metal ions in the final product increased with the amount of Na^+ or NH_4^+ loaded in the first step so that by controlling the pH of the dispersion in the first step, one can control the doping amounts of transition metal cations into Al-PILCs. A sample containing 0.125 mmol/g of nickel was thus obtained, which is ~ 3 times of that obtained by directly exchanging Al-PILC with $\text{Ni}(\text{NO}_3)_2$ solution, while the pillared layered structures of the Al-PILC remained. The porosity analysis using N_2 adsorption data indicated that most of the doped transition metal ions dispersed homogeneously in the micropores of the Al-PILC, significantly affecting the micropore structure.

Introduction

Cation-doped pillared clays have attracted great interest in academia and industry. Researchers in several groups have found that the catalytic performance of pillared clays can be greatly enhanced by doping a small amount of transition metal ions.^{1–6} It is expected, similar to the case of zeolite, that catalysts with superior properties can be developed from pillared clays by introducing transition metal ions. All methods proposed to date for loading transition metal ions into pillared clays (in most cases they are alumina pillared clay, Al-PILC) can be classified into two types: introducing the metal ions before or after the pillaring process. Generally, a Na^+ -exchanged clay is used as the starting material for the preparation of PILCs. After calcination at $>400^\circ\text{C}$, a rigid microporous system forms. The calcined PILCs are then exchanged with solution containing the desired cations. However, the calcined PILCs have poor cation-exchange ability.^{7,8} During the calcination, as the pillaring precursors are converted to rigid oxide pillars, protons are released. This process for Al-PILC can be expressed as



The liberated protons, with a positive charge and small volume, supposedly migrate into the silicate layers, and are hardly accessible to succeeding cation-exchange processes.⁹ As shown later in our study, the amount of transition metal ions doped on an Al-PILC by a direct cation-exchange procedure could be <5 meq/100 g clay.

If the migrated protons are drawn back from the clay layers and replaced by cations that cannot penetrate into the clay sheets, the calcined PILCs will exhibit a significant cation-exchange capacity (CEC). Indeed, it has been found that treating a calcined

PILC with a base, like K_2CO_3 , NaOH , KOH , and ammonia solutions, can increase its CEC greatly.^{11–18} The migrated protons are drawn back from the clay layer by the bases and react with the hydroxyl groups to form water. Accordingly, the metal cations or NH_4^+ ions are left as the charge balance cations between the clay layers of the PILC. In our previous work,^{10,18} we found that the amount of Ca^{2+} or Na^+ cations doped into an alumina pillared montmorillonite (Al-PILM) increased as the pH of the cation-exchange solution increased. These cations were introduced into Al-PILM without obvious damage to the pillared layered structures of the host when the pH was controlled below a value of 10.

There is, however, a great difficulty in introducing transition metal ions into Al-PILC by controlling the pH. In a neutral or basic environment, transition metal cations will precipitate on the external surface of the particles rather than diffuse into the micropores of Al-PILC.

It is also possible to exchange sodium cations with the cations of interest before the pillaring process. This new M^{n+} -clay is then pillared in a controlled way, and some M^{n+} cations remain in the pores of the final porous material.^{1–4} The amount of cations loaded on the PILCs by this approach may be greater, compared with that loaded by a direct postexchange. However, a product of low porosity may result, and it is quite difficult to adjust the amount of cations loaded in such a product.

Another factor of equal importance is the location and environment of cations in the PILCs. It is most desired that the transition metal species be in an ionic form and homogeneously dispersed in the micropore system of the PILC without precipitation outside the micropores and migration of the cations into the clay layers. It is believed that the cations of transition elements doped on PILC are responsible for catalytic reduction of NO ,¹⁹ but we found that the oxide of hydroxide precipitates of the transition elements is inactive. Some detailed studies on the location and environment of transition metal species have

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been conducted with various surface analysis techniques,^{4,20,21} which reflect the importance of introducing transition metal cations into the micropores of PILCs.

In this study, we propose a two-step cation-exchange approach. By such an approach, one can load a large and controllable amount of various transition cations on Al-PILCs without causing precipitation. The doped cations disperse homogeneously in the micropores of the clays. The moderate experimental conditions and the simplicity of the procedure offer a promising technique for preparing effective transition metal catalysts based on PILCs.

Experimental Section

Materials. Sodium bentonite, supplied by Commercial Minerals Ltd., Australia, was used as starting clay material to prepare Cu²⁺-doped Al-PILC samples. More than 90% of the bentonite powder has particle sizes of <2 μm , and the CEC is 75 meq/100 g of clay. Sodium montmorillonite was used as the starting clay for Ni²⁺-doped Al-PILC samples. The CEC of this clay is 100 meq/100 g of clay. A commercial solution of aluminum hydroxylchloride (Locron L from Hoechst, Germany) was used as the alumina source. This solution contains polyoxocations of aluminum hydrate, with an Al₂O₃ content of 23.5 \pm 0.5 wt %, an OH/Al ratio of 2.5, and a pH of \sim 3.5–3.7.

Preparation of Alumina Pillared Clays. The commercial Locron L solution was diluted with deionized water. Then, 10 g of sodium montmorillonite or sodium bentonite was dispersed into 375 mL of the pillaring solution with stirring. The ratio of Al (mmol) to clay (g) is 10 mmol Al/g clay. The clay suspension was stirred at room temperature for 4 h, and the Na⁺ ions of the clay were exchanged with the Keggin ions [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺. The solid was then separated by filtration, followed by washing with deionized water until Cl[−] free, and by drying in air at room temperature. The intercalated product was calcined at a heating rate of 5 K/min and held for 2 h at 773 K. The pillared montmorillonite thus obtained was labeled as Al-PILM and the pillared bentonite was labeled as Al-PILB.

Loading of Cations into the Pillared Clay. First, 2.0 g of calcined Al-PILM powder was dispersed into an aqueous solution of NaNO₃ (100 mL, 0.1 M). The suspension was stirred for \sim 12 h, while the pH value of the system was adjusted by addition of a dilute solution of NaOH (0.02 M). The solid was separated by filtration, washed with deionized water, and dried at 323 K overnight. The Al-PILM powder was treated at three different pH values, 5.5, 8.5, and 9.5, in the present study, and the products were designated as Na-Al-PILM-5.5, Na-Al-PILM-8.5, and Na-Al-PILM-9.5, respectively. Subsequently, 0.5 g of each Na-Al-PILM sample was dispersed into 50 mL of 0.2 M Ni(NO₃)₂, and the stirring was prolonged overnight. The pH values of all the suspensions in this stage were \sim 4.5. The solids were then separated and washed and dried in the same manner as for Na-Al-PILM samples, and the products were labeled as Ni-Al-PILM-5.5, -8.5, and -9.5, where the numbers indicate the pH values of the previous treatment with sodium solution. A 0.5-g aliquot of the parent Al-PILM sample was directly treated with the Ni(NO₃)₂ solution under the same experimental conditions and was named Ni-Al-PILM-4.5.

A similar procedure was employed to load Cu²⁺ ions into alumina pillared bentonite (Al-PILB). In this procedure, Al-PILB powder was dispersed into an aqueous solution of NH₄Cl, instead of NaNO₃, and a dilute solution of ammonia was used to adjust the pH. The Al-PILB samples doped with various amounts of NH₄⁺ ions were then exchanged with a 0.2 M Cu(NO₃)₂ solution. The pH of the suspension for Cu²⁺ ion

exchange is stable at \sim 4.5, similar to the situation for Ni²⁺ ion exchange. Also, 0.5 g of the parent Al-PILB sample was directly treated with the Cu(NO₃)₂ solution and named Cu-Al-PILB-4.5.

In another approach of doping Ni²⁺ into Al-PILM, Al-PILM was equilibrated with pyridine vapor, and the pores in Al-PILM were filled with pyridine by adsorption. The resultant Al-PILM was subsequently exchanged with Ni²⁺ as already described for Na-Al-PILM. In this way, Ni²⁺ cations were introduced into the pores by formation of Ni²⁺–pyridine complexes, and the sample thus obtained was labeled as Ni-pyridine-Al-PILM.

Characterization. The content of transition metals (Ni, Cu, and Na) in the samples was determined by atomic absorption spectrometry (AAS), with an AA-845 spectrometer (Nippon Jarrell Ash Company Ltd.). A fusion method²² was used to prepare the samples and references. The ammonia ion contents were derived from the nitrogen content in the samples, whereas the latter was experimentally determined. The samples doped with transition metal ions (Mⁿ⁺) were treated with hydrogen fluoride (HF) solution, and the content of Mⁿ⁺ in the liquor was analyzed. X-ray diffraction patterns of powder samples were recorded on a Philips PW 1840 powder diffractometer with cobalt K α radiation at 40 mA and 100 kV and a nickel filter. Nitrogen ads-desorption isotherms were measured at liquid nitrogen temperature with a gas sorption analyzer (Quantachrome, NOVA 1200). The samples were degassed at 323 K and a vacuum $<10^{-3}$ Torr for 16 h prior to the measurement. The surface area was calculated by the BET equation, and the external and micropore surface areas were determined by the *t*-plot method of Lippens and De Boer.²³ The ads-desorption isotherms of water were measured at 295 K using a gravimetric rig with quartz springs as the microbalance elements. Diffuse reflectance spectra in the ultraviolet–visible (UV–vis) range (DR–UV/VIS), 200–900 nm, were recorded with a JASCO 550 UV–vis spectrophotometer equipped with a JASCO ISV-469 integrating sphere attachment. The absolute remittance R_{∞} from the sample was measured. Relative remittance quantity $R'_{\infty} = R'_{\infty}(\text{sample})/R'_{\infty}(\text{reference})$ is used to calculate the Kubelka–Munk function defined as $F(R_{\infty})$:²⁴

$$F(R_{\infty}) = (1 - R)^2/2R_{\infty} \quad (2)$$

The parent Al-PILCs are used as references for the clays loaded with nickel and copper.

Results and Discussions

Cation Loading. In Figure 1, the content of Na⁺ in Na-Al-PILM samples is plotted against the pH values of the suspensions of calcined Al-PILM and NaNO₃. The Na⁺ amount is expressed in meq/100 g of sample.

The pH of an Al-PILM aqueous suspension is \sim 4.5, which is also illustrated in Figure 1. A low Na⁺ content was found for Al-PILM, reflecting a small amount of sodium residual remaining in the sample. The amount of Na⁺ cation loaded into the Al-PILM should be the difference between the Na⁺ content of Na-Al-PILM samples and that of Al-PILM. This amount increases with the pH of the suspension, which is similar to the behavior of Ca²⁺, as previously reported.^{10,18}

For the NH₄⁺-Al-PILB samples, a similar trend was observed (Figure 2), although lower CECs were observed compared with those of Na⁺-Al-PILM obtained at the same pH. The CEC of bentonite clay we used is lower than that of montmorillonite and this could be a reason for the lower cation content of NH₄⁺-Al-PILB samples.

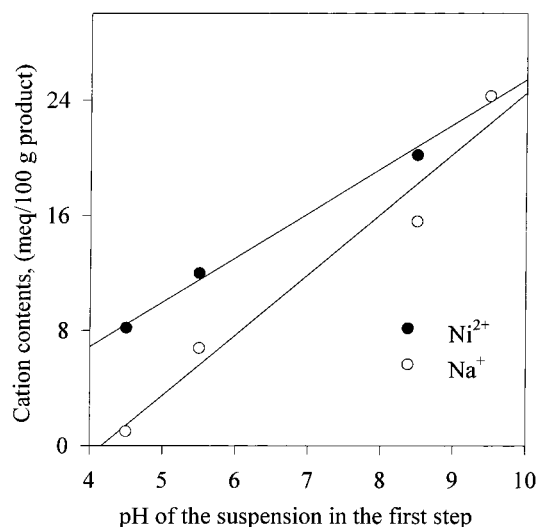


Figure 1. Relationship between the cation content of Na-Al-PILM-*n* and Ni-Al-PILM-*n* and the pH of the suspensions of calcined Al-PILM and NaNO₃.

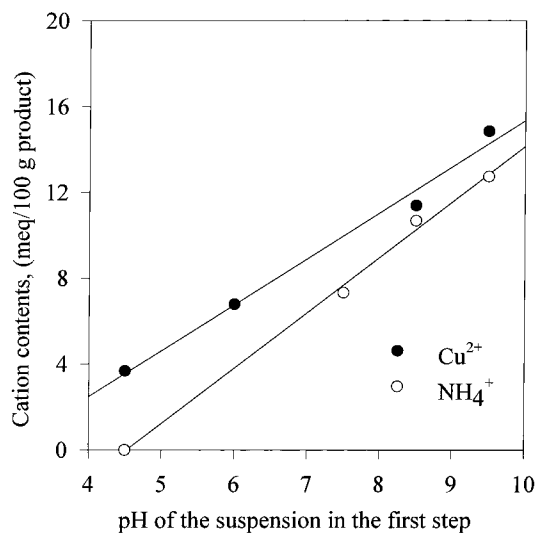


Figure 2. Relationship between the cation content of NH₄-Al-PILB-*n* and Cu-Al-PILB-*n* and the pH of the suspensions of calcined Al-PILB and NH₄OH-NH₄Cl.

The nickel content of Ni-Al-PILM-*n* samples obtained by exchanging Na-Al-PILM-*n* with of 0.2 M Ni(NO₃)₂ solution is also illustrated in Figure 1. This procedure was conducted at a constant pH between 4 and 5. Therefore, the sole factor influencing the amount of Ni²⁺ cations doped in the pillared clays is the content of Na⁺ cations in the Na-Al-PILM-*n* samples. Evidently, the amount of Ni²⁺ cations doped in the pillared clays increases with the content of Na⁺ cations. This general trend is confirmed by the results of Cu²⁺ loading in Al-PILB (Figure 2). For Cu²⁺ loading in Al-PILB, we used diluted ammonia solution to adjust the pH of the suspension in the first step. This trend indicates that transition metal cations are doped onto the pillared clays mainly by cation exchange with Na⁺ or NH₄⁺ ions.

The role of the first step appears to be to restore the CEC of calcined Al-PILC. In a suspension of a higher pH value, a greater CEC of Al-PILM is restored. Treating the calcined pillared clays with basic substances can draw the migrated protons back to the interlayer space from the silicate layer of the clay.^{7,9–12,17} We observed that after an addition of a small amount of dilute base solution, the pH value of the suspension

decreased gradually, reflecting a consumption of OH[−]. This consumption is attributed to the reaction with protons, whereas the cations of the bases, Na⁺ or NH₄⁺ ions, remain in the interlayer space, maintaining the balance of electrical charges. To maintain the pH at a certain value for a certain period, the base solution was added in small dosages several times. The second step should be mainly a cation exchange reaction in which Na⁺ or NH₄⁺ ions are replaced by Mⁿ⁺ ions in a slightly acidic environment (pH ~4.5), according to the data shown in Figures 1 and 2.

On the other hand, it is found in Figure 1 that the amount of nickel in Ni-Al-PILM is always above that of sodium in their parent Na-Al-PILM samples. A similar trend is also observed in Figure 2, although it is not as significant as that in Figure 1. Part of the transition metal ions loading cannot be attributed to the exchange with Na⁺ or NH₄⁺ ions. This result appears more important when the Na⁺ or NH₄⁺ loading is low. When Al-PILM was treated directly with Ni(NO₃)₂ solution, the content of Ni²⁺ cations in the product was ~8 meq/100 g. This result cannot be explained by a cation exchange mechanism. Comets et al.^{19,20} suggested that Cu²⁺ ions exchanged in Al-PILC possibly coordinate directly to the oxygen on the alumina pillars rather than attaching to clay sheets. This phenomenon could be a common one for other transition metal cations when loaded into Al-PILC. As the amount of loaded cation increases, the difference between the amounts of Na⁺ or NH₄⁺ and transition metal ions visibly decreases (Figures 1 and 2), reflecting that the fraction of transition metal ions doped by cation exchange become prevailing.

Because the cation exchange with transition metal ions (in the second step) is conducted in a slightly acidic environment (pH ~4.5), the proposed two-step procedure allows us introduce a significant amount of desired transition metal ions into the pillared clays but avoid the precipitation of transition metal cations, which generally occurs in a neutral or slightly basic environment. It is noteworthy that the nickel content of Ni-Al-PILM-9.5 and Ni-Al-PILM-4.5 (the sample obtained by exchanging Al-PILM directly with Ni²⁺) differs by a factor of ~3. The copper content of Cu-Al-PILB-9.5 is nearly 4 times of that in Cu-Al-PILM-4.5, the direct-exchanged sample. Even larger amounts of the cations could be doped at a pH value >9.5, however, a possible expense is a partial damage to the pore texture. The damage increases gradually as the pH is raised.¹⁵

Pyridine molecules can form complexes readily with Ni²⁺ ions. If the complexes are formed in the pores, a loss of pore volume resulting from the pyridine treatment is expected. The N₂ adsorption of Ni-pyridine-Al-PILM is obviously lower compared with that of Ni-Al-PILM-4.5 (Figure 3). The amount of Ni²⁺ cations introduced into Al-PILM by such a process is ~13.6 meq/100 g. This amount is ~55% of the content in Ni-Al-PILM-9.5, but much greater than that in Ni-Al-PILM-4.5, the sample obtained by exchanging directly with Ni²⁺ solution. The extra loading of the Ni²⁺ cations is attributed to the restored CEC by pyridine, which is a base. The introduction of Pd²⁺ species via an ion exchanging Al-PILM with Pd(NH₃)₄²⁺ has been reported by Luca et al.¹⁷ The function of the NH₃ molecules could be explained as similar to pyridine in the present study.

Chemical State of the Doped Transition Metals. The chemical state of the transition metals introduced into the host pillared clays is an important factor that greatly influences their performance when the solids are used as catalysts. No phases of transition metal oxides can be observed from the XRD

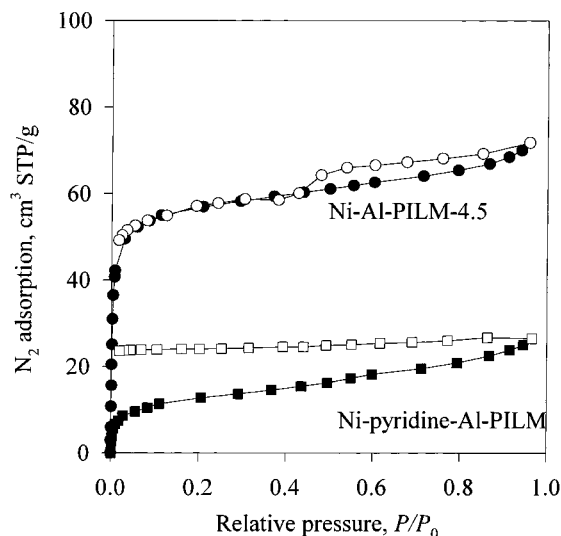


Figure 3. N_2 adsorption isotherms of Ni-pyridine-Al-PILM and Ni-Al-PILM-4.5 samples.

patterns. The patterns of parent Al-PILCs and the clays doped with transition metals are almost identical. This similarity means that the doped transition metals species do not form bulk precipitates of oxide or hydroxide but exist in a highly dispersed phase. This result is anticipated because these species were introduced into the pillared clays mainly by an ion-exchange mechanism in slightly acidic environment.

The spectroscopic technique, DR-UV/VIS, is generally applied to determine the chemical state of transition metals in solids. The results obtained by this technique for two Ni-Al-PILM-*n* and Cu-Al-PILB-7.5 are shown in Figures 4a and 4b, respectively.

The main bands of Ni-Al-PILM-9.5 and -7.5 are double bands at 13 600 and 14 500 cm^{-1} and the strongest band at 25 500 cm^{-1} . These bands are close to those of octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in zeolite Y and in nickel phyllosilicate,²⁵ and to those of Ni^{2+} on montmorillonite.²⁶ The band at 25 500 cm^{-1} is for ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, the band at 13 700 cm^{-1} is for ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, and band at 15 500 cm^{-1} is for ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{E}_g(\text{D})$. Thus, the nickel in this clay is present as hydrated cations with a 6-fold coordination. The shape of the spectrum for Cu-Al-PILB-7.5 is similar to that of the hydrate of Cu^{2+} on montmorillonite reported by Velghe et al.²⁶ The strongest band is at 12 700 cm^{-1} , close to 13 100 cm^{-1} they reported, and is regarded as a composite band that can be decomposed to three bands at 10 550, 13 100, and 15 200 cm^{-1} . The doped copper in Al-PILB should also exist in the form of hydrate ions, $\text{Cu}(\text{H}_2\text{O})_4^{2+}$, following the argument of Velghe et al.²⁶

Influence of the Cation Loading on the Host Structure.

The micropore structure of Al-PILC, formed by intercalation with alumina pillars, is stable in a slightly basic environment.^{10,15,18} Nevertheless, it has been reported that some bases may react with the pillars,¹⁵ in particular when the bases are not dilute, causing damage to the pillared layered structure of the host. The intercalated structure of Al-PILM can be examined by the d_{001} peak in the XRD patterns.^{8,9,27,28} In this work, the most basic environment to which the pillared clay was subjected was at a pH value of 9.5. As shown in Figure 5, the d_{001} peaks of the XRD patterns of Al-PILB and Cu-Al-PILB-9.5 had similar shapes and positions. This result indicates that the intercalated structure of Al-PILB is maintained during the treatment. A similar behavior is observed for Ni^{2+} -Al-PILM-*n* samples (not shown). The d_{001} peak in Figure 5 corresponds to

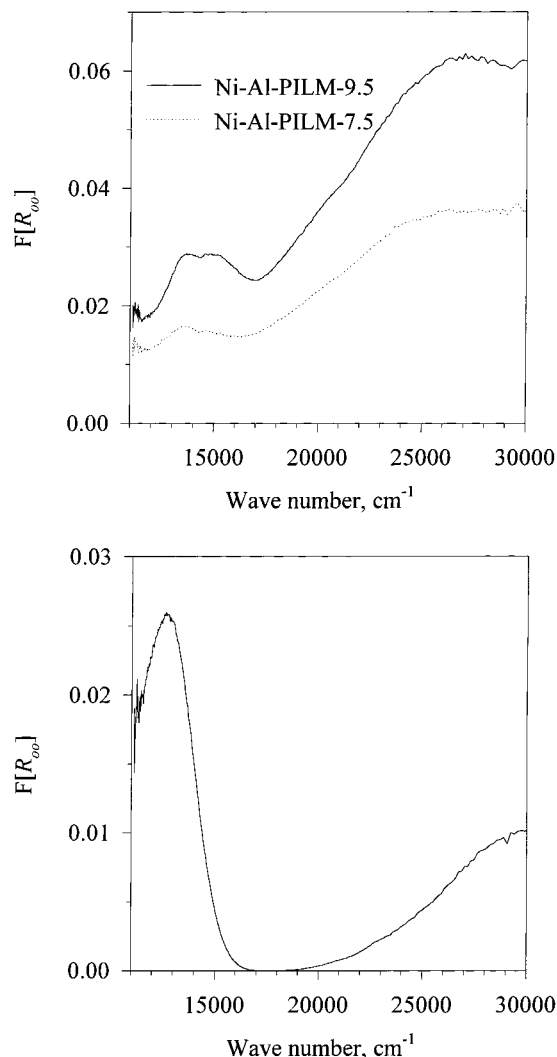


Figure 4. DR-UV/VIS spectra of the Al-PILCs doped with transition metal cations, expressed in Kubelka-Munk function $F(R_\infty)$ against wavelength. (a) Ni-Al-PILM-7.5 and -9.5, and (b) Cu-Al-PILB-7.5.

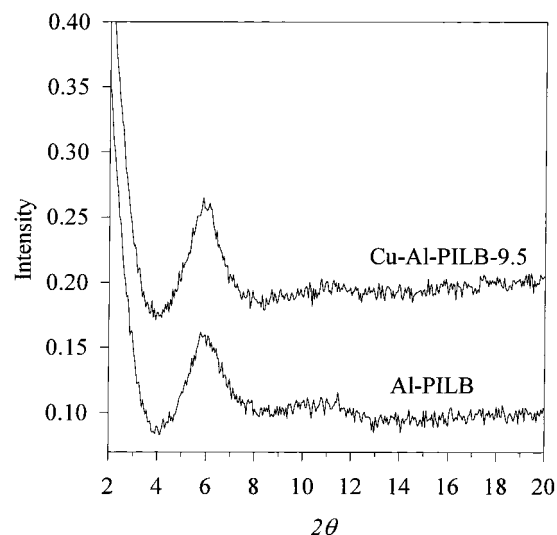


Figure 5. XRD patterns of Al-PILB and Cu-Al-PILM-9.5 samples.

a basal spacing of 1.67 nm and the free spacing between the clay sheets (which is usually regarded as the size of the micropores in the clay) is 0.71 nm, which is the difference between the basal spacing and the thickness of a single sheet

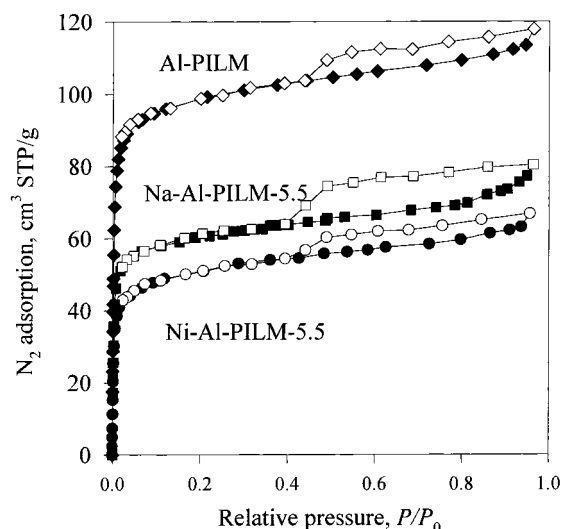


Figure 6. N_2 adsorption and desorption isotherms of Al-PILM, Na-Al-PILM-5.5, and Ni-Al-PILM-5.5.

of montmorillonite clay (0.96 nm). This result means that the prevailing pore structure in the pillared clays are slit-shaped micropores with a pore width of ~ 0.73 nm. The interlayer spacing of Al-PILM sample is ~ 0.73 nm, which is slightly above that of Al-PILB sample, but both values are consistent with those reported in the literature.^{8,9,23,24}

Location of the Doped Cations. Analysis of the porosity of the pillared clays using N_2 adsorption data can provide useful information about the location of the doped ions. The N_2 adsorption and desorption isotherms of Al-PILM, Na-Al-PILM-5.5, and Ni-Al-PILM-5.5 in Figure 6, have a typical Langmuir-type shape, or Type I, according to the B. D. D. T. classification,²⁹ also suggesting that these solids are microporous.

The adsorption reaches a plateau at a very low relative pressure, <0.1 , reflecting that these solids contain primarily small micropores and ultramicropores.³⁰ It appears that loading of cations, both Na^+ and Ni^{2+} , into the Al-PILM, always results in a decrease in N_2 adsorption capacity, which reflects a reduction in pore volume. The loss of pore volume is evidence that the doped cations entered into the micropores.

Quantitative data of surface areas, pore volumes, and mean pore widths of micropores and mesopores in these samples were derived from the N_2 adsorption isotherms.³¹ Detailed information of the pore textures of the solids is provided by these porosity parameters. The micropore volume, V_{mic} , and the surface area of mesopores, A_{mes} , were derived from the t -plot of Lippens and De Boer,²³ with data between the relative pressure of 0.5 and 0.8. The Brunauer–Emmett–Teller (BET) specific surface area, A_{tot} , was calculated with data in a relative pressure range from 0.01 to 0.1. The surface area of the micropores, A_{mic} , was obtained by subtracting A_{mes} from A_{tot} .

The ratio of the pore volume and surface area has the dimension of the mean pore size (hydraulic radius). Because the micropores in Al-PILMs have a slit shape, this ratio for micropores is half of the mean micropore width, d_{mic} . The mean micropore width for Al-PILM was found to be 0.84 nm and that for Al-PILB was 0.82 nm, which is slightly greater than the pore width calculated from the XRD measurements. The data of surface areas and micropore volume are summarized in Table 1.

According to the data in Table 1, most of the surface area of Al-PILCs is contributed by micropores. As already discussed, the introduced transition metals exist in hydrate cations. There

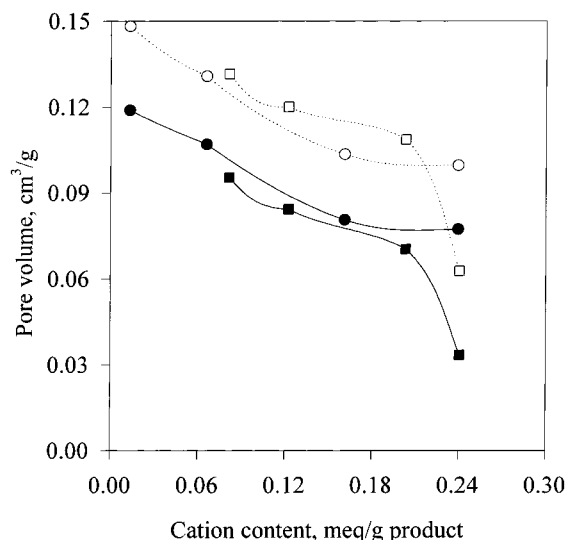


Figure 7. Total pore volume (V_{tot} , empty symbols) and micropore volume (V_{mic} , solid symbols) of Na-Al-PILM- n (represented by circles) and Ni-Al-PILM- n (represented by squares) as a function of the cation content.

TABLE 1: Surface Area, Pore Volume, and Pore Width in Alumina Pillared Clays and Ions-Doped Alumina Pillared Clay Samples

samples	A_{tot} (m^2/g)	V_{mic} (cc/g)	A_{mic} (m^2/g)	d_{mic} (nm)
Al-PILM	304.8	0.1189	284.6	0.84
Na-PILM-5.5	233.0	0.1011	218.3	0.93
Ni-PILM-5.5	191.3	0.0700	164.2	0.85
Ni-PILM-9.5	72.9	0.0261	50.4	1.04
Al-PILB	204.6	0.0657	159.7	0.82
Cu-Al-PILB-4.5	173.4	0.0597	140.5	0.85
Cu-Al-PILB-7.5	168.0	0.0594	140.3	0.85
Cu-Al-PILB-9.5	151.5	0.0527	123.1	0.86

are repulsive forces between the cations so that these cations must distribute homogeneously over the pore surface. Therefore, most of the exchangeable cations should be located in the micropores. Naturally, the micropore volume of the cation-doped samples decreases as the cation content increases. This phenomenon is also clearly demonstrated in Figure 7.

In Figure 7 the total pore volume, V_{tot} and micropore volume, V_{mic} , of Na-Al-PILM- n and Ni-Al-PILM- n samples are plotted against the cation content. It is observed that V_{tot} and V_{mic} vary inversely with the cation content. Loss of the pore volume is due to loading of cations because the cations occupy part of the space in the micropores. In addition, the difference between the two pore volumes is essentially constant. The loss of pore volume is mainly from micropores, which also means that the doped cations primarily locate in the micropores of the Al-PILM host.

Replacing Na^+ ions by transition metal ions M^{2+} occurs in concomitance with a further loss of micropore volume, as can be seen in Figures 6 and 7. There are possibly more coordinated water molecules in the M^{2+} -form samples than in the Na^+ -form samples because of the high hydration heat of Ni^{2+} and Cu^{2+} ions.

However, the micropore volume of Ni-Al-PILM-9.5 is too low (0.026 cm^3/g) to be attributed solely to the amount of the coordinating water molecules remaining in the sample. Considering the free interlayer spacing of the Al-PILM host, the dimension of most micropores is ~ 0.73 nm. If doped cations locate in the space of these micropores, free space around the cations coordinated with water molecules has a dimension quite close to or even below the kinetic diameter of N_2 molecules

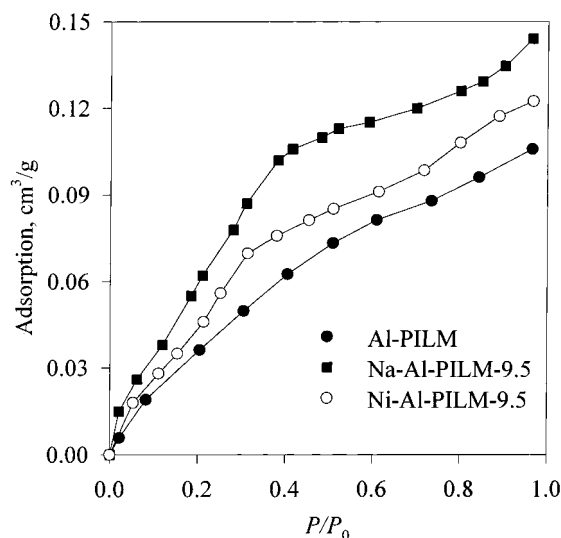


Figure 8. Water adsorption isotherms of Al-PILM, Na-Al-PILM-9.5, and Ni-Al-PILM-9.5.

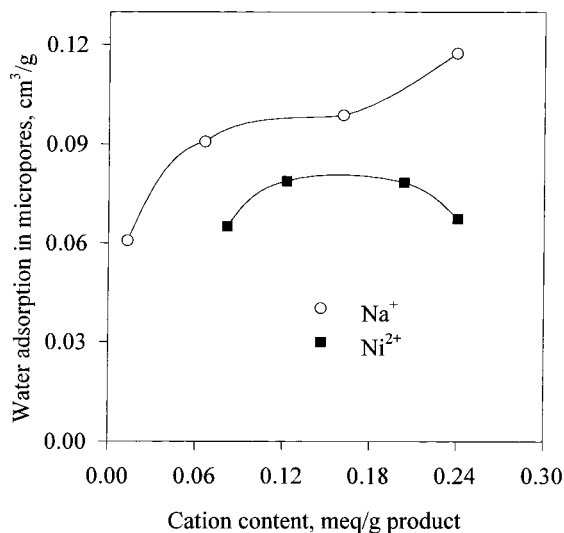


Figure 9. Correlation between the cation content and water uptake in micropores of Na-Al-PILM and Ni-Al-PILM samples.

(0.364 nm). At a high cation population, passages of the micropore system can be substantially narrowed.¹⁸ Part of the micropore space becomes inaccessible to N_2 molecules, resulting in a low N_2 adsorption. A low micropore volume is thus derived from the N_2 adsorption data. We also found that hysteresis on the N_2 isotherm of the Ni-Al-PILM-9.5 sample extends to very low relative pressures. Usually, the hysteresis of the nitrogen isotherm for Al-PILC samples ended at a relative pressure of ~ 0.45 . The interpretation for the hysteresis observed for Ni-Al-PILM-9.5 is that the micropores or the pore entrances in the solid are of a dimension close to that of nitrogen molecules.³⁰

Water molecules can diffuse into some micropores with a narrowed entrance that N_2 molecules cannot pass through because they have a smaller kinetic diameter and because water adsorption was conducted at higher temperature. In addition, changes in surface hydrophilicity of the pore walls can be examined at the same time. Evidently, the doped cations located on the surface of pore walls strongly affect the hydrophilicity. Figure 8 shows the water adsorption isotherms of Al-PILM, Na-Al-PILM-9.5, and Ni-Al-PILM-9.5. In Figure 9 the water uptake in micropores of Na-Al-PILM and Ni-Al-PILM samples are correlated with cations content.

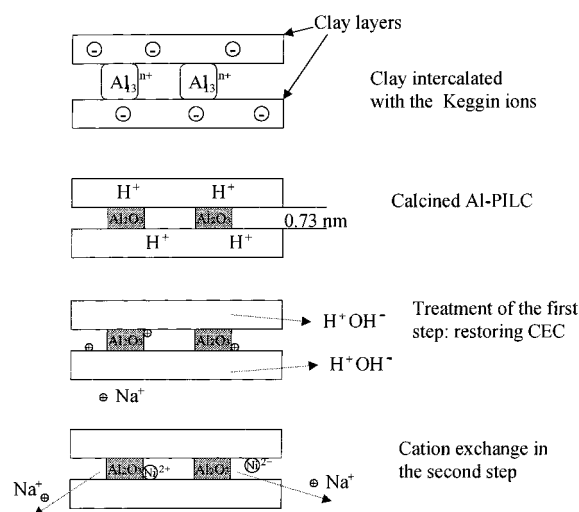


Figure 10. A schematic diagram of the pillaring mechanism involved in the two-step procedure. Al-PILM, Na-Al-PILM- n and Ni-Al-PILM- n samples are used as examples.

The water adsorption on Al-PILM in the low-pressure region (below a P/P_0 of 0.5) is quite low (Figure 8), indicating that the surface of Al-PILM is hydrophobic.^{10,16} In the micropores with hydrophobic pore walls, water exhibits a lower density than in its bulk liquid phase.²⁶ The cation-doped samples exhibit features of a hydrophilic surface; that is, the enhanced adsorption in the low vapor pressure region. To bring about such a significant change of surface nature from hydrophobic to hydrophilic, the cations must have dispersed homogeneously all over the pore surface of the solid. Water molecules are readily adsorbed directly on the cations or through hydrogen bonding with the water molecules coordinated to the cations. Because most of surface area of the samples arises from micropores, the cations must be dispersed mainly in the micropores. The water uptake in the micropores of Na-Al-PILM- n samples increases with the Na^+ content (Figure 9). It means that no serious loss in porosity has resulted.

The relationship between amount of Ni^{2+} cations and uptake of water in the micropores of Ni-Al-PILM is more complicated (Figure 9). The initial increase in water uptake could be attributed to the change of the surface nature from hydrophobic to hydrophilic. The subsequent decrease is due to the increasing occupation of the pore volume by the Ni^{2+} ions and their coordinating water. Also, water adsorption in the micropores of Ni-Al-PILM-9.5 is obviously higher (0.062 cm^3/g) than its micropore volume calculated from N_2 adsorption data (~ 0.03 cm^3/g in Figure 7), showing that a considerable part of pore volume in this sample is inaccessible to N_2 . This result conforms to our earlier explanation of the micropore narrowing due to the existence of a large amount of Ni^{2+} ions and their coordination water.

The results of adsorption experiments suggest that the doped Ni^{2+} cations are mainly distributed in the micropores. The reactions involved in the suggested two-step procedure are summarized schematically in Figure 10. The cations doped could seriously affect the micropore geometry of the pillared clay, depending on the type and quantity of the cations. This effect can have a strong influence on the accessibility of the active sites in the micropores to the molecules of adsorbates and reactants when the solids are used as adsorbents or catalysts. Small molecules can penetrate through to reach the sites in the micropores, whereas large molecules will be rejected. Evidently, these cation-doped solids are limited to small molecules.

Nevertheless, the variation of the accessibility with the cation content can be utilized to control or improve the performance of the solids for certain reactions.

Conclusion

Large amount of transition cations M^{n+} (Ni^{2+} and Cu^{2+} ions in the present study) can be doped into the calcined Al-PILC by the two-step method proposed in this work. The process consists of two stages. The objective of the first stage is to restore the CEC of calcined Al-PILC through a treatment with a basic solution. The extent of the restored CEC can be controlled by maintaining the suspension at various pH values. In the second stage transition metal ions M^{n+} are introduced by cation exchange, where M^{n+} (Ni^{2+} and Cu^{2+} ions in this study) replaces Na^+ or NH_4^+ ions. The amount of M^{n+} loaded onto Al-PILC depends on the amount of Na^+ or NH_4^+ ions previously loaded into the sample, especially when the amount loaded is large. Thus, the amount of M^{n+} loaded can be well controlled. It could be much higher than that resulted from a direct exchange with an M^{n+} solution and that obtained by forming complexes of pyridine and M^{n+} .

The micropore texture of Al-PILCs is maintained during the basic treatment, but loss in micropore volume is observed due to the doped cations. The introduced transition metal species exist in the form of hydrate ions that are distributed homogeneously in the micropores of Al-PILC. These ions can significantly affect the accessibility of these pores. The experimental conditions of the proposed method are relatively mild so that the strategy of the two-step method could be applied for doping various amounts of desired cations to Al-PILCs as well as other pillared clays. The method offers an effective and simple means for tailoring the pore structure as well as surface chemistry of pillared clays for adsorption and catalytic applications.

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