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Physicochemical characteristics of pillared interlayered clays

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Abstract

A series of pillared interlayered clays (PILCs) including Al-, Ti- and Zr-PILCs have been prepared and characterized by X-ray diffraction, elemental and thermal analyses, N_2 adsorption, NH_3 temperature-programmed desorption and IR measurements after pyridine adsorption. It was found that Al-PILC relatively contained higher microporosity and surface acidity than Zr- and Ti-PILCs. However, Al-PILC reveals weaker thermal stability than the other PILCs. To overcome this drawback, the addition of lanthanum (La), cerium (Ce) or yttrium (Y) as the second metal component to Al-PILC has been attempted. The overall results of this study demonstrate that the addition of Y significantly enhances the thermal stability of the resulting PILC with little change in the acidity compared to that of the other second metals. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Al-PILCs; Second metal addition; Thermal stability; Pore structure; Acidity

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1. Introduction

Pillared interlayered clays (PILCs) represent a new class of microporous solids that have found a wide range of potential applications in catalytic, adsorption and separation processes [1–5]. Typically, the preparation of PILCs involves the introduction of bulky inorganic or organic clusters into the interlayer region of clays [6–8]. When the intercalated species are metal polyoxycations, in particular, they are converted after heating at elevated temperatures into the corresponding metal oxide clusters that are rigid enough not only to prevent the interlayer spaces from collapsing, but also to generate micropores larger than those of conventional zeolites. Due to their high surface areas and shape-selective nature, as a direct consequence, the synthesis of clays pillared with metal oxides, in many cases with mixed metal oxides, and their catalytic applications have been the subject of a number of previous studies [9–14]. To date, it has been shown that metal oxide PILCs exhibit high activity in numerous catalytic reactions including oil refining, methanol conversion, Friedel–Crafts reaction, photocatalytic decomposition of organic pollutants, selective catalytic reduction of NO, many acid catalyzed reactions, etc. [9–14].

Many important properties of metal oxide PILCs, most notably their acidity, thermal stability and microporosity are known to primarily depend on the nature of the pillaring species, as well as on the choice of host materials. The $Al_{13}{}^{7+}$ keggin ion is the most frequently used species for pillaring [15], although other inorganic polyoxocations made from the nitrate or chloride salts of various transition metals such as Ti and Zr are often used [2,3]. Al-PILCs have received much attention as new microporous materials

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replacing zeolites, especially in the catalytic cracking process [16] and selective reduction of NO by hydrocarbons [17], due to their superior catalytic activities. However, the application of Al-PILCs to commercial catalytic processes has been severely limited by their poor thermal stability. Thus, many attempts have been made to improve the thermal stability of Al-PILCs.

One appropriate way to overcome such a problem is the introduction of the second metal component to Al-PILC during the preparation process [18–21]. Since Ga is right below Al in the periodic table and has physicochemical properties similar to those of Al, for instance, this element has been recognized as an effective additive stabilizing Al-PILCs [18,19]. It has been speculated that the isomorphous replacement of Al by Ga at the tetrahedral site of the Al_{13}^{7+} keggin ion is closely related to the thermal tolerance for the resulting PILCs [19]. On the other hand, insertion of rare-earth ions such as La and Ce into the structure of Al-PILCs is reported to yield the formation of spinel-like structures in the interlayer region of clays, which may be responsible for the enhanced thermal resistance. However, little attention has been directed towards a comprehensive understanding of the physicochemical properties of PILCs with various metal mixed oxides.

In the present study, the synthesis and characterization of Al-, Ti- and Zr-PILCs have been examined to evaluate their applicability to commercial catalytic processes. In addition, the effects on the addition of the second metal component including La, Ce and Y to Al-PILC are investigated to improve the thermal stability of the resulting PILCs.

2. Experimental

2.1. Preparation of PILCs

The starting clay material, a purified montmorillonite with a particle size ≤2 μm, was obtained from Fisher. This bentonite contains a cation exchange capacity (CEC) of 76 meq/100 g clay. The chemical composition of the starting clay employed in the present study is given in Table 1. The aluminum hydroxy-oligomeric solution was prepared by dissolving aluminum chloride ($AlCl_3·6H_2O$, 99%, Aldrich) in deionized water to produce 0.2 M $AlCl_3$ solution. Then, 0.2 M NaOH was slowly added to 0.25-l of 0.2 M $AlCl_3$ in order to obtain oligomeric solutions with OH/Al molar ratios between 1.0 and 3.0. After aging at room temperature for 24 h, the appropriate amount of pillaring solutions, required for the Al/clay (mmol Al/g clay) ratio in the range from 3 to 20, was slowly added to 1.0 l of distilled water containing 10 g of clay. The final suspension was rigorously stirred at room temperature for 24 h, recovered by filtration, washed repeatedly with water, and then dried in air overnight at 110°C. The solids obtained were calcined at 300, 500 or 700°C for 5 h. The samples prepared in this way are referred to as Al-PILC(*n*), where *n* is the Al concentration per gram of clay used for their preparation. The sample prepared at 10 mmol Al/g clay, however, is simply denoted as Al-PILC.

Table 1
Chemical compositions of the parent clay and PILCs (the concentration of pillaring agent used for the PILC preparation was fixed to 10 mmol Al/g clay, where M is Al, Ti or Zr)

Sample	FB[a]	Al-PILC	Ti-PILC	Zr-PILC
Component (wt.%)				
SiO_2	58.52	54.23	34.81	53.62
Al_2O_3	18.41	28.54	9.14	16.34
MgO	2.31	1.56	1.21	1.54
Fe_2O_3	3.42	2.31	1.67	2.15
Na_2O	2.53	0.85	0.13	0.83
CaO	1.27	0.09	0.06	0.12
K_2O	0.39	0.23	0.21	0.18
TiO_2			39.40	
ZrO_2				12.20

[a] Fisher Bentonite.

For comparison, Ti- and Zr-PILCs were prepared with procedures similar to the Al-PILC preparation. The pillaring agent for Ti-PILC was prepared by adding $TiCl_4$ (99.9%, Aldrich) into 2.0 M HCl solutions, and diluted with distilled water to obtain the final Ti and HCl concentrations of 0.8 and 0.4 M, respectively. The pillaring solution was aged for 24 h at room temperature before use. A given amount of pillaring solution (10 mmol Ti/g clay) was slowly added to 1.0 l of deionized water containing 10 g of clay and rigorously stirred for 5 h. In the preparation of Zr-PILC, the zirconium hydroxy-oligomeric solution was prepared from $ZrOCl_2·8H_2O$ (98%, Aldrich). 0.2 M NaOH was added to the solution maintaining the molar ratio of OH/Zr between 1.0 and 3.0. The subsequent steps were the same as in the procedure given above.

The La-, Ce- and Y-doped Al-PILC samples were prepared by using partially hydrolyzed pillaring solutions containing the chloride salts of Al and the corresponding second metal. The OH/(Al + second metal) molar ratio of 2.0 and the Al/second metal molar ratios of 3, 5 and 10 were employed to prepare the optimal mixed oxide Al-PILC materials.

2.2. Characterization methods

X-ray powder diffraction (XRD) patterns were measured on an MAC Science M18XHF diffractometer (Cu Kα radiation). For routine analysis and identification of phases, the samples were analyzed at steps of 0.02° with scanning rate 2°/min in the 2θ range 3–40°. To precisely confirm the presence of the (0 0 1) reflection peak in each sample, the XRD patterns in the 2θ range 3–12° were also taken at steps of 0.02° with scanning rate 0.05°/min. The chemical compositions of the parent clay and PILCs with different oxide compositions prepared here were determined by a Spectro ICP-Flame-EOP inductively coupled plasma-optical emission spectrometer. The N_2 sorption isotherms were measured on a Micromeritics ASAP 2010 analyzer. Prior to measurements, all samples were outgassed at 150°C for 10 h. Specific surface area and microporosity were determined by using the BET equation and the *t*-plot method, respectively. The total pore volume was considered to be the volume of liquid N_2 adsorbed at $P/P_0 \leq 0.99$. Thermogravimetric analyses were performed under flowing Ar on a Perkin-Elmer TGS-2 thermal analyzer. Approximately, 15 mg of sample was used at a heating rate of $5°\mathrm{C\,min^{-1}}$.

Temperature-programed desorption (TPD) of ammonia was recorded on a fixed-bed, flow-type apparatus linked to a gas chromatograph and a quadruple mass spectrometer. Approximately, 50 mg of sample was activated in flowing He at 500°C for 3 h, then ammonia was passed over the sample at 100°C for 0.5 h. The sample was subsequently purged with He at the same temperature for 1 h to remove the physisorbed ammonia. Then, the TPD profiles were obtained in flowing He from 100 to 500°C at a ramping rate of $10°\mathrm{C\,min^{-1}}$. The IR spectra of adsorbed pyridine were recorded on a Perkin-Elmer 1800 FT-IR spectrophotometer, using self-supported pellets of PILCs prepared here, at a spectral resolution of $4\,\mathrm{cm^{-1}}$. The pellets were degassed by heating under vacuum at 400°C for 2 h before pyridine adsorption. The IR spectra were recorded after evacuation in the temperature range 25–400°C.

3. Results and discussion

3.1. Formation of PILCs

Fig. 1 shows the XRD patterns of Al-, Ti- and Zr-PILCs, which were prepared by using pillaring solutions with 10 mmol of the corresponding metal chloride salts per gram of the clay. The XRD pattern (not shown) of the parent clay (i.e., montmorillonite) exhibits three main X-ray peaks around 7°, 20° and 35°. The first peak is commonly assigned to the basal (0 0 1) reflection, while the second and third peaks are attributed to the two-dimensional (*h k*) planes. It has been observed that all the characteristic peaks of montmorillonite gradually decrease during the pillaring procedure. In particular, the (0 0 1) peak was found to shift towards the lower 2θ region, which is a clear indicative of the enlargement of the basal spacing of the clay. Fig. 1 also shows that the three metal oxide PILCs prepared here are distinct with respect to the type of metal used. For example, Al- and Zr-PILC samples give the (0 0 1) peak with a considerable intensity even after pillaring. However, this peak is hardly observed for Ti-PILC. It thus appears that the long-ranged layered structure of Ti-PILC may collapse during the pillaring process, revealing its poor microporosity. This is not unexpected because Ti-PILC is prepared from media that are much more acidic than those for the Al- or Zr-PILC preparation. Upon heating at a higher temperature, on the other hand, the (0 0 1) peaks of all PILCs become weaker and shift slightly to the higher 2θ region. As shown in Fig. 1, in particular, heating at 700°C results in a significant decrease in intensity of the basal (0 0 1) peak, which is more apparent to Al-PILC than to Zr-PILC. This reveals the poor thermal stability of Al-PILC that is detrimental to its catalytic applications.

The chemical compositions of the parent clay and Al-, Ti- and Zr-PILCs prepared in this study are given in Table 1. It is clear that the amount of the

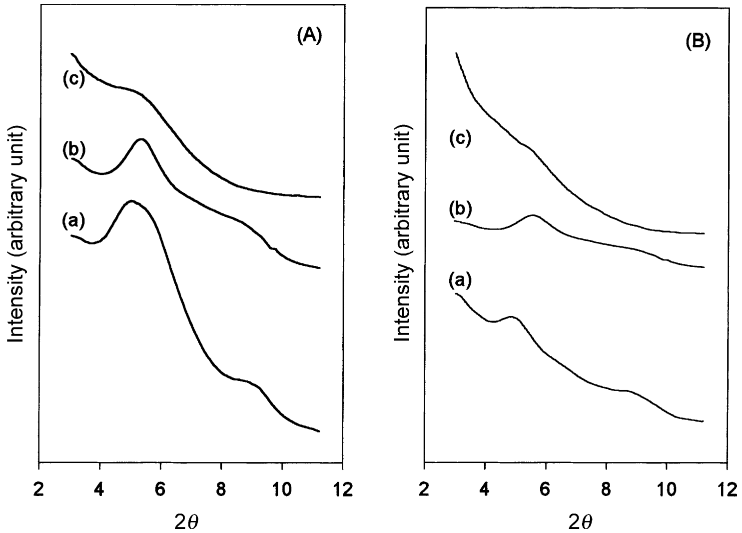

Fig. 1. XRD patterns of (a) Al-PILC, (b) Zr-PILC and (c) Ti-PILC in (A) as-synthesized and (B) calcined at 700°C for 5 h.

metal oxide introduced into the interlayer region of the clay differs according to the type of metal employed. For example, the amount of TiO_2 in Ti-PILC reaches values up to about 40 wt.% of the resulting PILC. In the case of Al-PILCs, however, the amount (~10 wt.%) of the Al_2O_3 intercalated is almost independent of the concentration of Al solutions used for their preparation at over 5 mmol Al/g clay, which can be further evidenced by the chemical composition data in Table 2. A similar result is also observed for Zr-PILC samples prepared using Zr-containing hydroxy-oligomeric solutions with different concentrations (3–10 mmol Zr/g clay).

Table 2
Amounts of the Al used for pillaring and the second metals added

Sample ID	Second metal component (wt.%)			
	Al_2O_3	Y_2O_3	La_2O_3	CeO_2
Al-PILC(5)[a]	8.5			
Al-PILC(10)[a]	10.1			
Al-PILC(20)[a]	9.8			
YAl-PILC	10.2	0.83		
LaAl-PILC	9.3		0.62	
CeAl-PILC	10.9			1.83

[a] The numbers in parentheses indicate the Al concentration (mmol Al/g clay) used for their preparation.

3.2. Thermal stability of PILCs

Al-PILC relatively reveals weaker thermal stability than that of the other PILC as examined in Fig. 1. In order to enhance the thermal stability of Al-PILC, LaAl-, CeAl- and YAl-PILC have been prepared by using mixed solutions of the chloride salts of Al and the corresponding second metal. Fig. 2 shows the XRD patterns of these second metal-doped Al-PILCs. The XRD pattern of Al-PILC is also compared in Fig. 2. No notable differences in the position and intensity of the basal (0 0 1) reflection are observed for these three mixed metal PILC materials in the as-synthesized form. However, it should be noted that the (0 0 1) reflection of each metal-doped Al-PILC is much stronger than that of Al-PILC. An interesting observation is that the addition of the second metal component including La and Y during the preparation process of Al-PILCs results in the considerable improvement of the thermal stability of the resulting materials. As seen in Fig. 2, in particular, YAl-PILC still shows the distinct (0 0 1) peak even after calcination at 700°C, which is in contrast to the result from Al-PILC. No studies have thus far focused on the ability of Y to enhance the thermal stability of Al-PILCs. Note that the thermal stability of YAl-PILC differs strongly according to the preparation method,

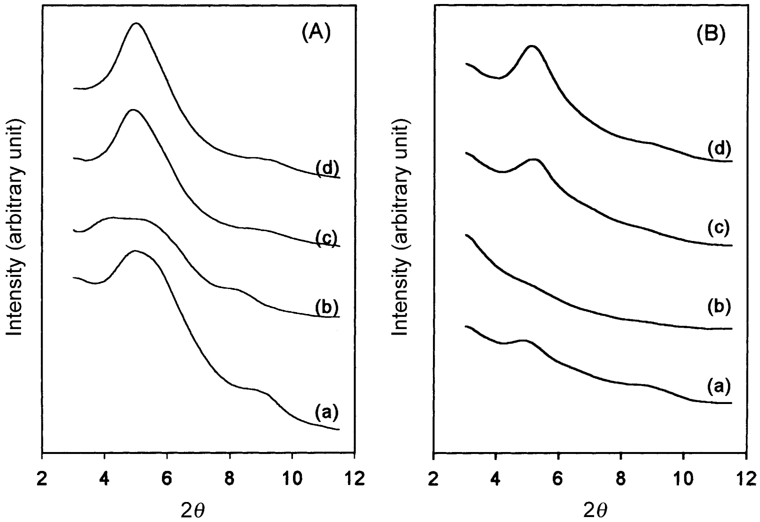

Fig. 2. XRD patterns of (a) Al-PILC, (b) AlCe-PILC, (c) AlLa-PILC and (d) AlY-PILC in (A) as-synthesized and (B) calcined at 700°C for 5 h.

which is the same as the trend commonly found in other metal or mixed metal oxide PILCs. When Y is independently introduced to Al-PILC, for example, no noticeable enhancement of the thermal stability of the resulting material is observed. This suggests that the use of a mixed solution of Al and Y (or the other second metal component) may be the critical factor enhancing the thermal stability of PILCs formed. Thus, it has been believed that most, if not all, of Y in YAl-PILC may be present as a certain mixed oxide form with Al, although further study is necessary to identify the exact state of this second metal.

The chemical compositions of LaAl-, CeAl- and YAl-PILC materials prepared in this study are given in Table 2. These data reveal that the amount of Al pillared during the intercalation process is nearly the same for these three mixed metal oxide PILCs, suggesting a similarity in the pillaring density. Table 2 also shows that the amount of the second metal in each PILC sample is considerably low compared to the amount of Al. This suggests that the second metal added is not separately pillared into the interlayer region of the parent clay, which is probably due to the poor polymerization ability.

Table 3 shows changes in the basal (0 0 1) spacing of all the materials prepared in this study. These data reveal that in the case of PILCs with a single metal component, the basal (0 0 1) spacing is in the order Al-, Ti- and Zr-PILC, which matches well with their thermal stability. It is commonly known that the higher the distance between the (0 0 1) planes the PILC has, the poorer the thermal stability. However, to develop PILCs with larger micropores, thermally stable PILCs with high basal distance is demanded. Al-PILCs with second metal including Y and La exhibited high intensity of (0 0 1) plane as well as basal (0 0 1) spacing even after the thermal aging at 700°C as shown in Table 3.

The advantage of PILCs over the conventional catalyst may be the variety of physical and structural characteristics with respect to the type of pillar and the method of preparation. In many catalytic processes, the catalyst pore structure plays a critical role for the features of catalyst, activity, selectivity and life. For example, for the selective catalytic reduction of NO, the modification of catalyst pore structure significantly improves the NO removal activity and the sulfur tolerance [22,23]. The variety of physical and structural characteristics of PILC with respect to the type of pillar and the method of preparation may offer the commercial application of PILC to catalytic processes.

The nitrogen adsorption–desorption isotherms of clay and PILCs with respect to the type of pillar were examined in Fig. 3. Although the raw clay employed

Table 3
Temperature dependence of basal spacing and N_2 adsorption results of PILCs

Sample[a]	$d(001)$ (Å)		BET surface area (m^2/g)			Micropore surface area[b] (m^2/g)			Total pore volume (cm^3/g)			Micropore volume[b] (cm^3/g)		
	300°C	700°C	300°C	500°C	700°C	300°C	500°C	700°C	300°C	500°C	700°C	300°C	500°C	700°C
Al-PILC(3)			188	142	93	128	93	49	0.16	0.15	0.12	0.06	0.05	0.02
Al-PILC(5)			208	164	108	140	116	69	0.17	0.15	0.12	0.06	0.05	0.03
Al-PILC(10)	17.8	17.6	220	196	126	160	143	87	0.17	0.15	0.13	0.07	0.06	0.03
Al-PILC(20)			205	161	97	135	105	62	0.17	0.15	0.12	0.06	0.05	0.02
Ti-PILC	16.9	16.6	246	228	195									
Zr-PILC	16.5	16.1	237	207	98	168	147	55	0.19	0.18	0.12	0.08	0.06	0.03
YAl-PILC	17.6	17.2	250	236	198	194	186	156	0.20	0.18	0.17	0.09	0.08	0.07
LaAl-PILC	17.8	16.8	225	203	144	161	145	93	0.18	0.15	0.14	0.07	0.06	0.04
CeAl-PILC			240	196	46	178	142	18	0.18	0.16	0.09	0.08	0.06	0.01

[a] Al-PILC(3), Al-PILC(5), Al-PILC(10) and Al-PILC(20) prepared by 3, 5, 10 and 20 mmol Al/g clay, respectively.
[b] Acquired by the *t*-plot method.

in the present study contains very low microporosity, the N_2 adsorption isotherm for the raw clay are mainly close to Type I isotherm, generally, observed for the solids containing micropores according to IUPAC classification. After pillaring, Ti-PILC reveals Type II or Type IV adsorption isotherms due to the mesopores formed in the pore structure, while Al-PILC and Zr-PILC still maintain Type I adsorption isotherms. This agrees with the XRD pattern with respect to the type of pillar. In addition, the hysteresis loop of PILCs exhibited H3 type, revealing the formation of slit-shaped pores in the pore structure, regardless of the type of pillar. Fig. 3 also exhibits the alteration of the isotherm after calcinations at 700°C. The thermal stability of PILCs also exhibits a great difference with respect to the type of pillar. Ti-PILC reveals higher thermal stability than Al-PILC and Zr-PILC as referred in Table 3. However, note that this may not be adequate as a microporous material. The effect of second metal on thermal stability of Al-PILC was also examined by the alteration of N_2 isotherm as shown in Fig. 4. Fig. 4 shows that the yttrium and lanthanum were effective for the stronger thermal tolerance of the clays comparing to cerium. Especially, Fig. 4 clearly reveals the addition of Y significantly enhances the structural tolerance of the clays by the thermal treatment, although the slight decrease of the basal spacing of AlY-PILC by XRD is observed. It may be elucidated due to stabilizing the pillar as forming complex with second metal.

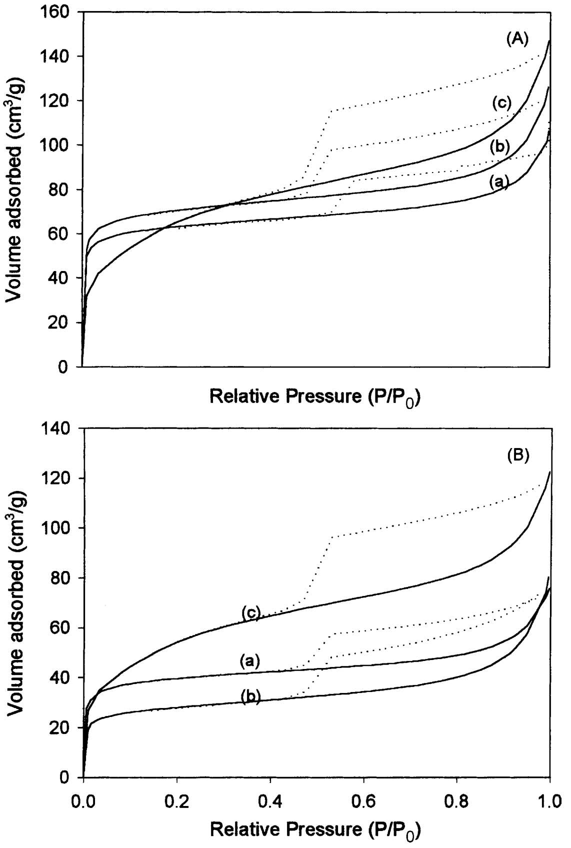

Fig. 3. N_2 isotherms of (a) Al-PILC, (b) Zr-PILC and (c) Ti-PILC after calcination at (A) 300 and (B) 700°C for 5 h. Solid and dotted lines indicate adsorption and desorption branches, respectively.

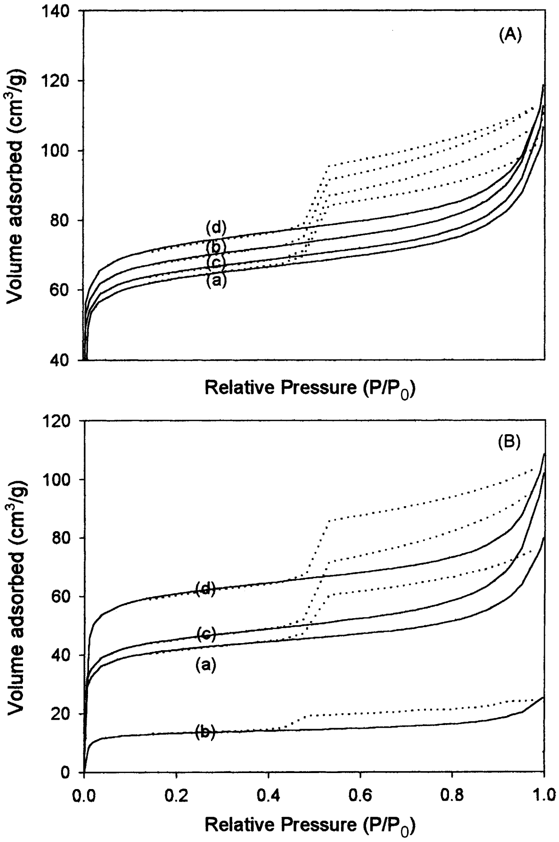

Fig. 4. N_2 isotherms of (a) Al-PILC, (b) AlCe-PILC, (c) AlLa-PILC and (d) AlY-PILC after calcination at (A) 300 and (B) 700°C for 5 h. Solid and dotted lines indicate adsorption and desorption branches, respectively.

Table 3 shows the results by N_2 adsorption of PILCs aged at the variety of temperatures from 300 to 700°C. The BET surface area (30 m^2/g) of the raw clay employed in the present study is quite low. As listed in Table 3, however, a remarkable increase in the surface area and pore volume is observed after pillaring, regardless of the type of the metal used. Note that Al-PILC and Zr-PILC exhibit a high degree of microporosity, while the opposite is observed for Ti-PILC. In the present study, the micropore volume and surface area of Ti-PILC could not be obtained by *t*-plot. It is due to the poor microporosity of Ti-PILC. This indicates that the microporosity generated during the pillaring procedure differs in the type of pillar, as evidenced by the XRD and N_2 isotherm results. The surface area of PILCs gradually reduced with respect to the thermal aging temperature. The sudden decrease of PILCs by sintering at 700°C is mainly caused by the destruction of micropores formed in the pore network of the clay. This is the reason that Ti-PILC reveals strong thermal stability in the surface area compared to Al- and Zr-PILCs as examined in Table 3. In addition, Table 3 reveals that the thermal stability could be slightly enhanced with respect to the density of pillar. However, Al-PILC prepared over 10 mmol Al/g clay, on the contrary, exhibited deterioration of the initial surface area as well as thermal stability. This may be due to the saturation of pillaring capacity of alumina at over 10 mmol Al/g clay as shown in Table 2. Table 3 also lists the alteration of surface area of Al-PILC modified by the second metals employed in the present study with respect to the aging temperatures. Al-PILCs with second metal, especially yttrium, maintain high surface area even after the thermal aging at 700°C as expected from the XRD and N_2 isotherm results.

The TGA/DTG curves for Al-, LaAl- and YAl-PILCs were also examined to identify the role of the second metals on the surface of the clays and are given in Fig. 5. All the materials give two stages of weight loss: 50–300 and 450–700°C. While the first step can be assigned to the desorption of water, the second step can be related to the dehydroxylation of OH groups on the internal and/or external surface of the PILCs. As shown in Fig. 5, however, there is a slight but visible dissimilarity in the DTG peak of each material. For example, Al-PILC gives the DTG peak at 580°C. However, the DTG peaks for LaAl- and YAl-PILCs are observed around 610 and 620°C, respectively. This suggests that the introduction of the second metal to the clay may lead to a shift of the dehydroxylation temperature to a higher temperature region, which can be related to the improvement of the thermal stability observed for the second metal-doped Al-PILC materials.

3.3. Surface acidity of PILCs

The acidity is one of the important properties required from PILCs. It was also investigated to evaluate the application of PILC to a commercial catalytic process. The acidity of PILC with respect to the type of pillar was observed by NH_3 TPD as shown in Fig. 6. All of the PILCs contained enormously high surface acidity compared to the original

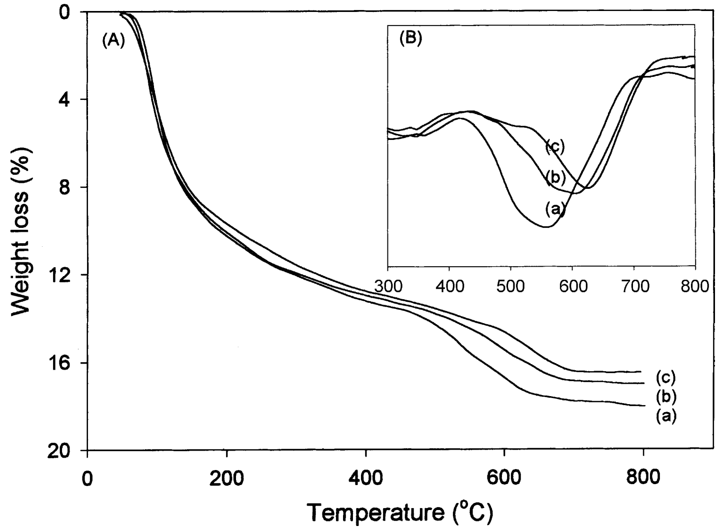

Fig. 5. TGA curves of as-synthesized: (a) Al-PILC; (b) AlLa-PILC; (c) AlY-PILC. The inset shows the DTG curves of the corresponding materials.

clay, montmorillonite. This simply indicates that the acidity of the clay is enhanced by pillaring the clay. The acid strength of PILC is basically identical before and after pillaring according to the comparison of the desorption temperature of NH_3 of the clay. Al-PILC exhibited relatively higher surface acidity than the other PILCs. The addition of the second metal may also have an effect on the surface acidity of PILCs. Thus, it is necessary to examine the effect of the second metal on acidity. As shown in Fig. 6, the addition of the second metals slightly decreases the amounts of NH_3 adsorption on the clay surface.

In addition, an IR study has been performed by the adsorption of pyridine on the clay surface to further identify the surface acidity of the clay along with NH_3 TPD. Fig. 7 shows the IR spectra of Al-PILC and YAl-PILC adsorbing pyridine in the region of IR band from 1400 to 1700 cm^{-1}. The clay evacuated

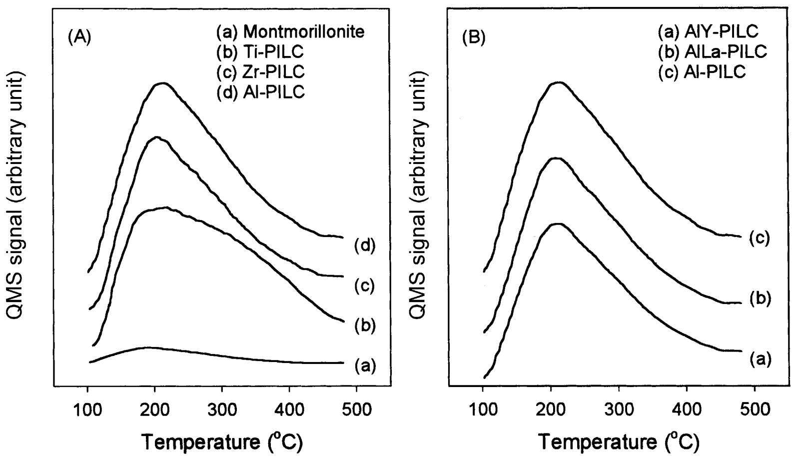

Fig. 6. NH_3 TPD curves of: (A) Al-, Ti- and Zr-PILCs; (B) various metal-doped Al-PILCs.

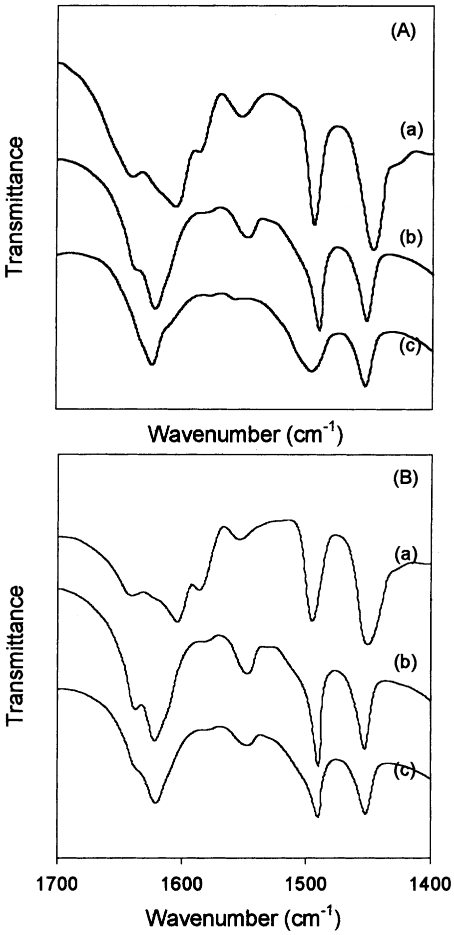

Fig. 7. IR spectra of pyridine adsorbed on (A) Al-PILCs and (B) AlY-PILCs followed by heating at: (a) 25; (b) 200; (c) 400°C.

at room temperature after pyridine adsorption exhibits IR bands at 1448, 1490, 1550, 1600, 1620 and 1638 cm^{-1}. The bands at 1448, 1600 and 1620 cm^{-1} are commonly assigned to a Lewis acid site [24]. The band at 1490 cm^{-1} is mainly attributed to both Lewis and Brönsted acid sites of the clay [24]. A small peak at 1550 cm^{-1} and a shoulder of the IR band at 1638 cm^{-1} are observed due to Brönsted acid sites on the clay surface [24]. The PILCs commonly contains both Brönsted and Lewis acid sites. Al-PILC, without a second metal, exhibited a stronger intensity of the bands corresponding to both Brönsted and Lewis acid sites. The intensities of the bands assigned to pyridine coordinated onto Lewis and Brönsted acid sites are reduced with respect to the evacuated temperature of the clay. Especially, the bands at 1550 and 1638 cm^{-1} of Al-PILC, assigned to Brönsted acid sites, nearly disappeared after the evacuation at a temperature of 400°C. However, for YAl-PILC evacuated at 400°C, the intensities of the bands at 1550 and 1638 cm^{-1} assigned to Brönsted acid sites are slightly reduced, although a significant loss of the intensity was observed for Al-PILC. YAl-PILC containing yttrium as the second metal maintains the high ratio of Brönsted and Lewis acid sites on the surface of the clay. This may also elucidate the strong thermal tolerance of YAl-PILC as discussed before.

4. Conclusions

A series of PILCs intercalated by a variety of metals have been prepared to investigate the physico-chemical characteristics. Al-PILC exhibited superior microporosity and surface acidity to Zr and Ti-PILCs. However, Al-PILC reveals weaker thermal stability than the other PILCs examined in the present study. The addition of the second metal component during the Al-PILC preparation process was found to significantly enhance the thermal stability of the resulting clay. In particular, the addition of Y was quite effective in improving the thermal stability of Al-PILC. Although the addition of Y into Al-PILC slightly reduced the total surface acidity, the ratio of B/L acidity on the clay surface, however, was enhanced. It may be one of the reasons elucidating the stronger thermal stability of YAl-PILC.

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