Korean J. Chem. Eng., **20**(1), 77-82 (2003)

Pore Structures and Acidities of Al-Pillared Montmorillonite

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(*Received 14 October 2002 • accepted 18 November 2002*)

Abstract−Korean montmorillonite was intercalated with Al-hydroxypolycation solution aged for 1, 4 and 7 days and then calcined at 400 °C, 600 °C and 760 °C, respectively. Basal spacings by XRD, pore structure (micro- and mesopore distributions and surface areas) by nitrogen (or argon) adsorption at liquid nitrogen (or argon) temperature and acidity (distribution and acid-amount) by NH_3-TPD were investigated for the samples. The basal spacing formed by intercalation appeared at about 17 Å and decreased with the heating temperature for the sample intercalated with the Al-hydroxypolycation solution aged for 1 day. However, for the one aged for 7 days, the spacing remained constant. The total surface area and pore-volume also increased with aging time of the Al-solution, in which micro-pore area increased more rapidly. Argon adsorption indicated that three modal distributions of 3.3, 3.7 and 4.3 Å in micropore radius appeared, in which 3.3 Å readily was reduced by heating. NH_3-TPD showed that two ammonia-desorption peaks appeared at 230 °C and 430 °C, respectively. The maximum acid-amount for the intercalated sample appeared as 86 meq./100 g-solid, and the values decreased with the heating temperature, especially for the peak at 430 °C.

Key words: Korean Montmorillonite, Al-intercalation, Micro/Mesopore Structure, NH_3-TPD/Acid Amount

INTRODUCTION

Refiners want more efficient catalysts for the processing of fluid catalytic cracking. The problems encountered in zeolite-use are the small pore size of the zeolites and the large amount of non-selective pre-cracking that occurs before large residual molecules are reduced to a size capable of diffusing into the very active and selective zeolite component of the catalyst. Therefore, an approach to synthesizing large pore zeolites is to seek another material that has an ideal distribution in micro- and meso-pores of the material for the reaction of the large molecules.

The synthesis of pillared clay such as Al-pillared montmorillonite has grown with the advances in intercalation chemistry [Sawhney, 1968; Tichit et al., 1988; Jones, 1988; Monila, 1992; Figueras et al., 1990; Vaccari, 1998; Storato et al., 1996], which offers the possibility of making them potential catalysts for fluidized catalytic cracking [Jones, 1988] if thermal stability is improved [Jones, 1988; Khalaf, 1997; Mishra, 1998; Trillo et al., 1993].

However, few studies have been found for the pore structure and the acidities of this intercalated montmorillonite, especially with natural Ca- and Mg-Montmorillonite. No study was found for the micropore structure of the Al-intercalated clay, although some information was found for the acidity of the pillared clay. In this study we are interested in intercalation in the use of Korean Ca-montmorillonite (Yunil area in Korea) as a starting material in preparing Al-pillared clays because the acidic properties depend strongly on the natural sources. Therefore, the main objective of this study was to determine the pore structure by the adsorption of nitrogen and argon at their boiling temperatures and the acidity through ammonia-TPD for the Al-pillared Korean montmorillonite to discover the potentiality as an adsorbent and catalyst.

EXPERIMENTAL

1. Starting Material

1-1. Clay

The starting clay was a montmorillonite from a deposit in the Yunil area located in the southeastern region of the Korean peninsula. The enriched montmorillonite (<270 mesh) was separated by sieving through a water suspension of the raw montmorillonite. The separated product was dried at 105 °C for 16 hours.

1-2. Al-Hydroxypolycation Solution

0.2 M aluminum chloride (Junsei G.R.) solution was added with strong agitation to 0.5 M NaOH (Tedia G.R.) solution. The added amounts of the aluminum chloride were determined to be obtained as 2.0 molar ratio of OH/Al, which was the optimum [Sawhney, 1968]. This solution was aged for 1, 4 and 7 days, respectively. Parker et al. [1995] reported that a maximum amount of Keggin ion Al_{13} is largely transformed into $Al_{24}O_{72}$(Al_{13} dimer) for the Al-solution aged more than 1 day. Therefore, it is supposed that the Al-solution aged for 4 and 7 days contains the dimer of the Keggin ion, Al_{13} form. Keggin formation was identified as becoming clear by mixing a turbid solution of $AlCl_3$ and NaOH after a period of time [Park, 1999]. The clearing period was about 8 hours.

1-3. Preparation of Al-Hydroxy Pillared Montmorillonites

Al-hydroxy intercalated montmorillonites were prepared by slow addition, with stirring, of corresponding amounts of Al-hydroxypolycationic solution to a suspension of purified montmorillonite for 24 hours. The solid was separated by filtration, washed with distilled water and dried at 105 °C. The dried samples were calcined for 3 hours at 400 °C, 600 °C and 760 °C, respectively.

2. Characterizations of the Samples

X-Ray powder diffraction pattern was obtained by using a Rigaku

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‡This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

Geigerflux M-3A with CuKα radiation (1.540 Å) to determine basal spacing of the clay.

Nitrogen and argon adsorption was carried out to measure isotherms at their liquid temperatures by using Micromeritics ASAP-2000E, from which surface area, micro-pore (t-plot) (determined pore size (Å) by argon adsorption) and meso-pore (determined pore size (nm) by nitrogen adsorption) diameter distribution (BJH), and pore volumes were determined. The samples (0.15-0.2 g) were degassed in a vacuum at 200 °C for 4 hours before the measurement.

The acidity was determined by NH_3-TPD. The evolved ammonia from the TPD was trapped in an aqueous solution and volumetrically titrated with 0.01 HCl solution with the titration intervals of 50 °C. The ammonia was adsorbed on the samples at 100 °C for 1 hour and flushed with He gas for 2 hours at the same temperature. Ammonia was desorbed by temperature-programming at 10 °C/min from 50 °C to 850 °C. The water vapor fraction desorbed from the samples in a vent stream was eliminated at an NaOH-trap.

RESULTS AND DISCUSSION

1. XRD

XRD measurements were performed to investigate the variation of basal spacing d(001) formed from the pillaring procedure and the modified diffraction patterns of the samples by thermal treatment. Figs. 1, 2 and 3 show the evolution of d(001) lines of raw montmorillonite and the samples of intercalated with Al-hydroxy-polycation solution of molar ratio (OH/Al) of 2 for the aging period of 1, 4 and 7 days, respectively. The intercalated products obtained with Al-solution aged for 1 day were calcined at 400 °C, 600 °C and 760 °C, respectively. d(001) reflections upon heating decreased up to 600 °C and then disappeared at 760 °C. The spacings are presented in Table 1 with a function of calcination temperature.

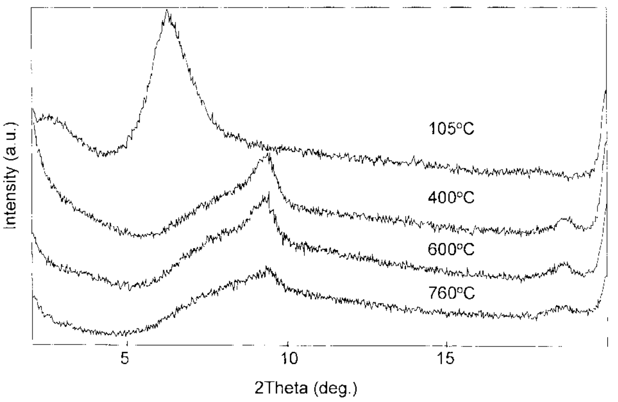

Fig. 1. XRD patterns of raw montmorillonites calcined at 105 °C, 400 °C, 600 °C and 760 °C.

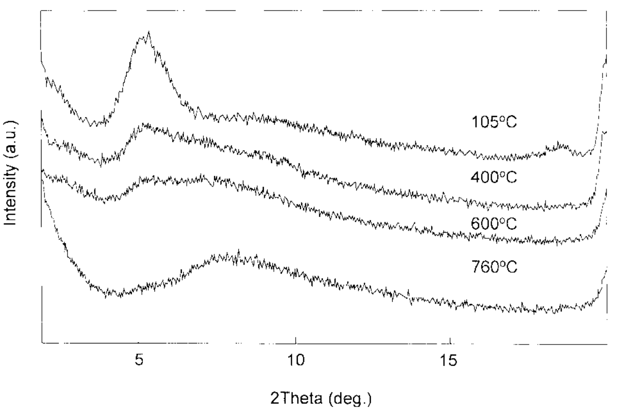

Fig. 2. XRD patterns of samples intercalated with Al-solution aged for 1 day. Calcination temperatures: 105 °C, 400 °C, 600 °C and 760 °C.

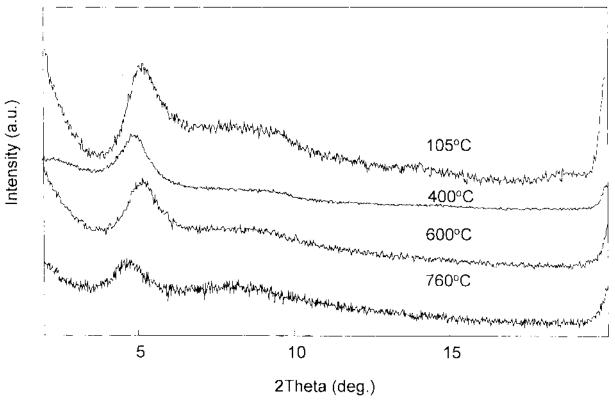

Fig. 3. XRD patterns of samples intercalated with Al-solution aged for 7 days. Calcination temperatures: 105 °C, 400 °C, 600 °C and 760 °C.

Table 1. d(001) values obtained after calcination for raw Ca-montmorillonite and the samples intercalated with Al-solution (OH/Al=2)

Calcination temperature (°C)	Raw montmorillonite	Intercalated montmorillonites with Al-solution aged for		
		1 day	4 days	7 days
105	14.2	17.2	17.1	17.1
400	9.4	16.8	17.1	18.3
600	9.4	15.9	17.0	17.0
760	9.5	10.6	16.8	17.4

The raw montmorillonite shows 14.2 Å of basal spacing, but the heating reduces the value to 9.4-9.5 Å that is the minimum value for the montmorillonite. However, intercalated montmorillonite with Al-solution aged for 1 day and dried at 105 °C has 17.2 Å, which means that an intercalated bridge was formed. However, the basal spacing decreased with the calcination temperature up to 10.6 Å. The intercalated montmorillonite with 4 and 7 days aged Al-solution retained a spacing of about 17 Å. The intercalated sample with the 7 days aged Al-solution has more good stability. This indicates that the intercalation with the dimer of Al_{13} form increased the stability of the pillared clay due to its large size of Al-hydroxypolycation [Parker et al., 1995].

2. N_2- and Ar-adsorption Studies

The specific surface areas, the pore volumes and mesopore size distribution (3-70 nm) of the raw montmorillonite and the samples intercalated with the Al-solution aged for 1, 4 and 7 days were determined by nitrogen adsorption at liquid nitrogen temperature. Argon adsorption was also performed to determine the distribution of micro-pore diameter (6-10 Å).

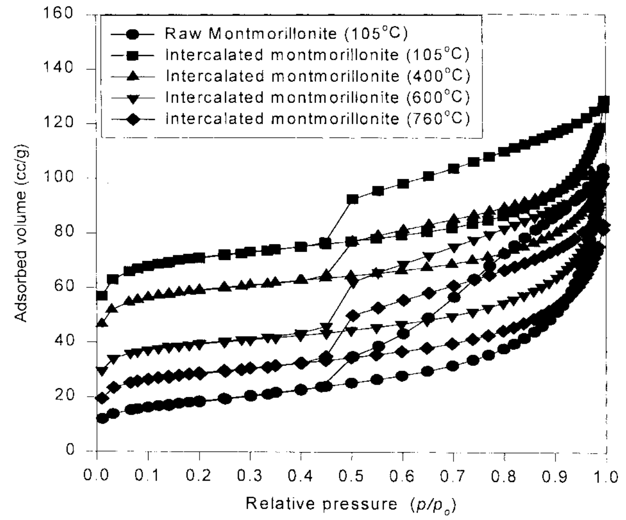

Fig. 4. N_2 isotherms of raw montmorillonite and intercalated samples with Al-solution aged for 1 day. Calcination temperature: 105 °C, 400 °C, 600 °C and 760 °C.

The isotherms of nitrogen are presented in Fig. 4 for the raw montmorillonite and the intercalated samples with solution aged for 1 day, in which samples were treated at 105 °C, 400 °C, 600 °C and 760 °C, respectively.

The montmorillnite shows isotherms with hysteresis, but the intercalation transforms the isotherm in the desorption branch as he adsorption capacity is increased, which means that intercalation forms the micropores between the layers of the basal sheets. The samples intercalated with the 7 days aged Al-solution show a higher adsorption capacity than those of the samples intercalated with 1 day aged Al-solution even though the isotherm does not appear on the figure. As observed in the XRD study, a treatment with Al-solution aged for more than two days may intercalate a stronger bridge between the basal sheets.

Table 2 presents the surface areas obtained for the raw montmorillonite and the intercalated samples. The raw montmorillonite has 65 m^2/g of the total surface area in which the 51 m^2/g (78%) is for the mesopores. The intercalation increased the total surface area up to 269 m^2/g in which the micropore area is 199 m^2/g (74% based on total area). The longer time of aging of the Al-solution increased the surface area of micropore up to 329 m^2/g, whereas the mesopore area actually remained unchanged [Sterte, 1987].

Table 2. Surface areas (m^2/g) for the raw montmorillonite and the intercalated samples

Calcination temperature (°C)		Raw montmorillonite	Intercalated samples with Al-solution aged for		
			1 day	4 days	7 days
105	Total	65.5	268.9	321.6	328.8
	Micro	14.2	199.7	239.4	245.4
	Meso	51.3	69.2	82.2	83.4
400	Total	67.6	223.9	282.9	290.4
	Micro	20.0	163.6	208.7	215.0
	Meso	47.6	60.3	74.2	75.4
600	Total	64.2	148.2	253.4	263.0
	Micro	16.2	101.0	173.9	179.0
	Meso	47.9	47.2	79.5	84.0
760	Total	33.0	106.5	190.9	210.7
	Micro	4.8	54.4	115.5	133.4
	Meso	28.2	52.1	75.4	77.3

The surface area decreased as the calcination temperature increased. About 50% of the area dropped at 760 °C compared to the samples treated at 105 °C. The samples intercalated with the 7 days aged Al-solution have 133 m^2/g of the micro-surface, which is a large value compared to that of the 1 day sample.

The pore volumes for raw montmorillonite and the intercalated samples are shown in Table 3. Raw montmorillonite has a total pore volume of 0.14 ml/g, which is increased by the intercalation up to 0.18-0.19 ml/g due to increases of both the micro- and meso-pore volumes. However, the heating reduced the pore volumes due to

Table 3. Pore volumes (ml/g) for the raw montmorillonite and the intercalated samples

Calcination temperature (°C)		Raw montmorillonite	Intercalated samples with Al-solution aged for		
			1 day	4 days	7 days
105	Total	0.14	0.18	0.19	0.19
	Micro	0.00	0.08	0.09	0.09
	Meso	0.14	0.10	0.10	0.10
400	Total	0.13	0.15	0.18	0.18
	Micro	0.01	0.06	0.08	0.08
	Meso	0.12	0.08	0.09	0.09
600	Total	0.13	0.13	0.17	0.17
	Micro	0.01	0.04	0.07	0.07
	Meso	0.13	0.09	0.10	0.10
760	Total	0.12	0.11	0.15	0.15
	Micro	0.00	0.02	0.04	0.05
	Meso	0.12	0.09	0.10	0.10

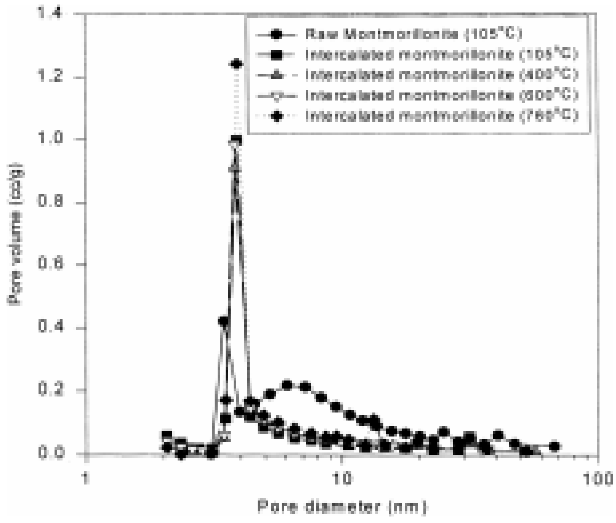

Fig. 5. Pore size distributions of the intercalated samples with Al-solution calcined at different temperatures. Calculation method: BJH method. Source: N_2 adsorption isotherm.

the main decrease of micropore volumes.

The mesopore size distributions determined from the desorption isotherm branches are presented in Fig. 5 for the samples intercalated with Al-solution aged for 7 days and raw montmorillonite. Raw sample has two modes of distribution of about 3.5 and broad 6-7 nm, whereas the intercalated samples have unique peaks at 4 nm. The samples intercalated with the 1 day aged Al-solution appear to be the same as the Fig. 3, although data do not appear in the figure.

Argon adsorption was studied in order to understand the micropore distribution formed for the intercalated samples with the Al-solution aged for 1 day and 7 days. The results are shown in Figs. 6 and 7, respectively. The figures indicate that the intercalated samples have three modal micro-pore distribution of 3.3, 3.7 and 4.3 Å in radius in which 3.7 and 4.4 Å appear more clearly for the sample intercalated with Al-solution aged for 7 days. The heating reduces mainly the first and second pores, especially for the samples intercalated with the aged Al-solution for 1 day. For the sample intercalated with the 1 day aged Al-solution, the heating at 760 °C completely removed 3.3 Å pore radius; however, for the sample intercalated with the Al-solution aged for 7 days the pore of 3.3 Å radius did not disappear. It indicates that the improved stability for the samples intercalated with the 7 days aged Al-solution is due to enlarged Al-hydroxypolycation through the dimerization of the Keggin ion as already mentioned above [Parker et al., 1995].

3. Acidities by NH_3-TPD

NH_3-TPD was done to determine the acidity distribution and the acid amount of the intercalated samples. The acid amount of the sample was determined by volumetric HCl-titration for the trapped ammonia evolved from the TPD apparatus confirming the desorbed ammonia. Ammonia TPD patterns are presented in Figs. 8, 9 and 10, respectively. The desorption curve of ammonia for the raw mont-

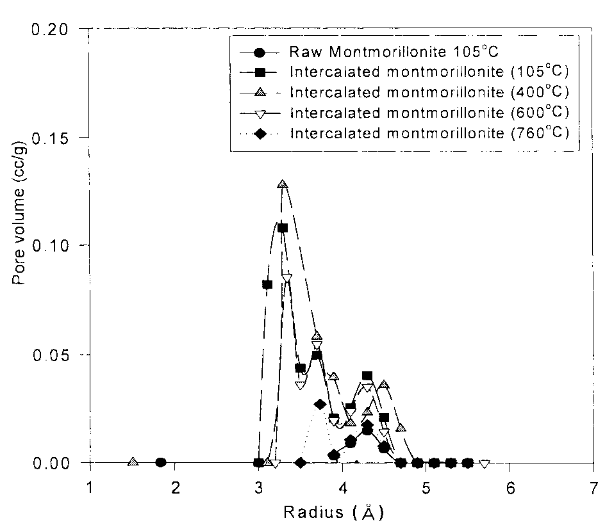

Fig. 6. Micropore size distributions (MP method of Ar adsorption) for the samples intercalated with the Al-solution aged for 1 day.

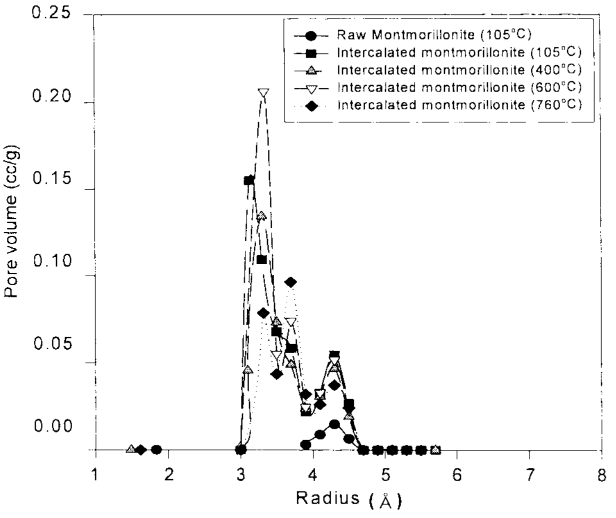

Fig. 7. Micropore size distributions (MP method of Ar adsorption) for the samples intercalated with the Al-solution aged for 7 days.

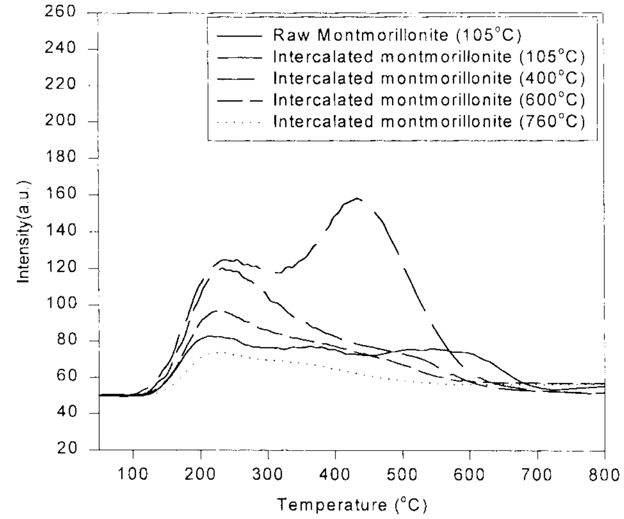

Fig. 8. NH_3-TPD spectra of raw montmorillonite and intercalated samples with Al-solution aged for 1 day. Calcination temperature: 105 °C, 400 °C, 600 °C and 760 °C.

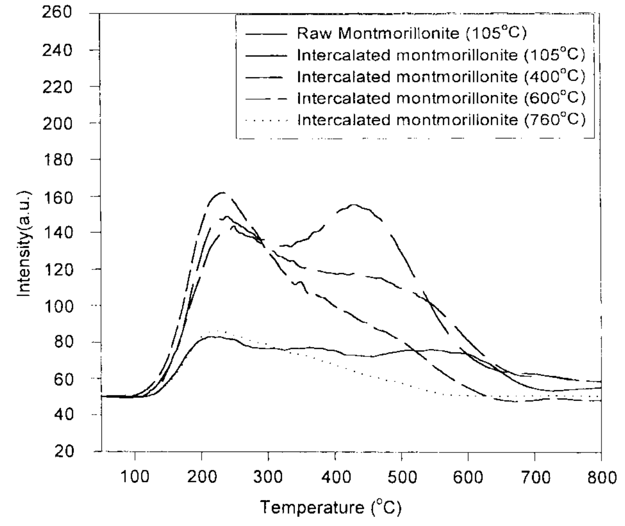

Fig. 9. NH_3-TPD spectra of intercalated samples with Al-solution aged for 4 days. Calcination temperature: 105 °C, 400 °C, 600 °C and 760 °C.

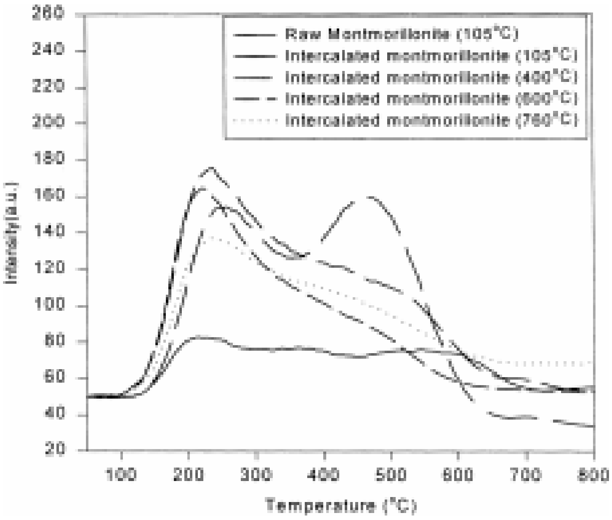

Fig. 10. NH_3-TPD spectra of intercalated samples with Al-solution aged for 7 days. Calcination temperature: 105 °C, 400 °C, 600 °C and 760 °C.

Table 4. Acid amounts for the intercalated samples with the Al-solution aged for 1, 4 and 7 days (unit: meq./100 g solid)

Calcination temperature (°C)	Raw montmorillonite	Intercalated samples with the aged Al-solution for		
		1 day	4 days	7 days
105	33.5	77.8	84.3	86.0
400	29.1	45.6	64.9	72.7
600	9.1	33.5	56.4	57.0
760	5.8	13.9	41.3	47.0

morillonite shows a broad peak ranging between 150-700 °C. The desorption curve for montmorillonite is considered to consist of several acid site distributions such as peak temperatures at ~200 °C, ~350 °C and ~550 °C. However, the intercalation created two distinct desorption peaks at around 230 °C and 430 °C over the sample intercalated with Al-solution aged for 1 day and dried at 105 °C. However, the calcination reduces only the strong acid site that appears at 430 °C. Further heating reduces two peaks together as the second peak is reduced. However, a strong acid site reduces more rapidly. The second peak is assumed to originate from the intercalated alumina bridge, and the reduction of this site by calcination is caused by the corruption of the acid site due to the solid-reaction between the layer sheet and the Al-hydroxypolycation.

The acid amounts determined by HCl-titration are presented in Table 4 with the heating temperature. The acid amount increased with the aging time for the Al-hydroxypolycation in the solution due to dimer formation as mentioned above [Parker et al., 1995]. However, the heating reduced the acid amount.

CONCLUSION

1. The basal spacing by intercalation of Al-hydroxypolycation for montmorillonite appeared to be about 17 Å and decreased with the heating temperature for the sample intercalated with the Al-solution aged for 1 day, but for the one aged for 7 days, the spacing actually remained constant.

2. The total surface area and pore-volume increased also with the aging time of the Al-solution, in which micropore area increased more rapidly. Argon adsorption indicated that three modal distributions of 3.3, 3.7 and 4.3 Å in micropore radius appeared. However, the heating preferentially removed 3.3 Å of the micropore.

3. NH_3-TPD indicates that two desorption peaks of ammonia appeared at 230 °C and 430 °C, respectively. The heating preferencially reduced the strong acid site. The maximum acid-amount for the intercalated sample with Al-solution aged for 7 days appeared to be 86 meq./100 g-solid, which is large compared to the raw material.

4. Therefore, this intercalated clay catalyst could be used as an acid-catalyzed reaction at low temperature, and also the thermal treatment could control the acidity distribution depending on the reaction.

ACKNOWLEDGEMENT

This study was financially supported by Hanyang University (2000).

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