EVALUATION OF TOLUENE ADSORPTIVITY OF POROUS PILLARED CLAYS IN COMPARISON WITH OTHER POROUS SILICAS

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ABSTRACT

Adsorption and desorption behaviors of toluene were investigated for porous pillared clays, such as organic-pillared clays (silica- or silica/alumina-pillared kanemite, and porous clay nanocomposites) and compared with those of silicalite, \( \beta \)-zeolite, ordered mesoporous silica, and silica aerogel to examine their abilities as adsorbents for volatile organic compounds (VOCs). Toluene adsorption isotherms of these materials showed that all the porous pillared clays adsorbed toluene in the relatively low pressure region \( (p/p_0 < 0.01) \) and much higher than the other porous materials, owing to the flat toluene molecule. No other significant differences were observed in the adsorption rates of the porous pillared clays. DTA-TG analyses of the porous pillared clays revealed a weak ability to entrap toluene up to 373 K. Lower retention of VOCs at raised temperatures allows the porous pillared clays to regenerate more easily for repeated use.

Key words: Pillared clays, Zeolites, Mesoporous silica, Aerogel, toluene, VOC, Adsorption, Desorption

INTRODUCTION

Emissions of VOCs such as toluene, xylene, \( p \)-dichlorobenzene and ethylbenzene have harmful impacts on the human body. Eye and throat irritation, as well as liver or central nervous system damage may occur due to prolonged exposure to VOCs from chemical products. Therefore, VOC emission control is an important issue for the environment and human health. There exist various VOC control techniques such as condensation, adsorption, catalytic oxidation and thermal oxidation (Ruddy, 1993). In these techniques, the adsorption of gaseous VOCs into porous adsorbents has been developed for the removal of VOCs in work places or newly-built buildings. The removal technology must be effective at low concentration levels (Gupta, 2002). The success of the adsorption process, dependent on the performance of adsorbents in terms of both equilibria and kinetics, requires large surface areas with pores suitable for VOCs and a viable pore network for quick transport. Inorganic porous materials such as alumina, silica gel, and zeolites are among the adsorbents with the potential to fulfill the performance criteria stated above. They have already been used as a constituent in architectural materials, wallpaper, coating materials and so on, in order to control the emission of VOCs in buildings and houses.

Porous pillared clays are one of the most widely studied materials among various inorganic porous materials. They are prepared by the intercalation of inorganic clusters or organic cations in the clay interlayers. The resultant modified clay materials have expanded interlayer spaces, leading to enhanced surface areas. In addition, the intercalation of inorganic clusters or organic cations brings about narrow spaces surrounded by silicate layers, forming slit-shaped micropores that show a shape-selectivity for aromatic compounds. Some research groups have demonstrated that organic pillared clays can be used as effective adsorbents to remove some aromatic compounds from their vapor phases or from aqueous solutions (Barrer, 1967, Barrer, 1989; Lee, 1989; Jaynes, 1991; Sheng, 1998; Meier, 2001; Okada, 2004). This suggests the possibility of successful application for the removal of VOCs by organic pillared clays as well as
other porous inorganic materials. However, there have been only limited investigations on the adsorptive and desorptive capabilities of VOCs by porous pillared clays in comparison with inorganic porous materials.

In this work, we report the adsorption and desorption behaviors of toluene by porous pillared materials in order to examine their ability to remove VOCs. Toluene was chosen as the model molecule for VOCs. We used a series of porous pillared clays that included tetraalkylammonium clays, silica- and silica/alumina-pillared clays, and organically modified clay nanocomposites (Ishii, 2005). For comparison, we examined the performance of porous inorganic materials: silicalite, \( \beta \)-zeolite, mesoporous silica (Folded Sheet Mesoporous material, abbreviated as FSM-22) and silica aerogel. In the first part of this study, the porous properties of the pillared clays were derived from nitrogen adsorption measurements. In the second part, toluene adsorption isotherms and the adsorption rates of the samples were investigated to evaluate the amount of VOCs adsorbed as well as their desorption behaviors at elevated temperatures.

**EXPERIMENTAL**

Tetra-alkylammonium (TMA) clays were prepared as follows: montmorillonite (2 g, Kunimipia-F, C.E.C. = 1.19 meq/g, Kunimine Co., Japan) was dispersed in 100 cm\(^3\) of tetramethylammonium chloride solution (0.3 mol 10\(^{-3}\) cm\(^{-3}\)) with stirring at 343 K. After stirring for 24 h, the obtained TMA-intercalated montmorillonite (TMA-Mnt) was washed with deionized water until Cl- ions were no longer detected in the filtrate. TMA-intercalated saponite (TMA-Smt) was prepared by the same procedure using synthetic saponite (Smepton SA, C.E.C. = 0.712 meq/g, Kunimine Co., Japan). After filtration, both TMA-Mnt and TMA-Smt were dried at 323 K overnight.

Silica- or silica/alumina-pillared clays were prepared by the following processes: \( \delta \)-sodium silicate (5 g, Tokuyama Siltech Co., Japan) was stirred in 50 cm\(^3\) of deionized water for 3 h and dried at 333 K overnight. The product (4 g) was stirred in 80 cm\(^3\) of cetyltrimethylammonium (CTA) chloride solution at 343 K for 3 h. While stirring, the pH of the solution was maintained at 8.59 by adding some drops of 2 mol 10\(^{-3}\) cm\(^{-3}\) of HCl solution. The suspension was centrifuged and washed with deionized water. This process was repeated 5 times and the product was dried at 333 K. The obtained TMA-intercalated kanemite was stirred with tetraethoxysilsilicate (TEOS) for 24 h at room temperature. After centrifugation, the white compound was dried at room temperature. The compound was stirred with 0.4 mol 10\(^{-3}\) cm\(^{-3}\) of HCl ethanol solution at room temperature for 1 h. After centrifuging and drying, the product was then calcined at 873 K for 6 h. This product was designated as SPK. Alumina was incorporated into SPK as follows: aluminumisopropoxide (0.01 g) was stirred in 15 g of isopropanol at 363 K for 48 h. SPK (0.07 g) was suspended in the solution for 3 h to adsorb alumina sol on the surfaces of the SPK. After filtration, the compound was calcined at 873 K for 6 h. This was designated as ASPK.

Pororous clay nanocomposites were prepared according to the method reported by Ishii et al. 2005, using commercial vermiculite (C.E.C. = 0.85 meq g\(^{-1}\), Australian Vermiculite Industries Co., Australia). The vermiculite (1 g) was suspended in 7 cm\(^3\) of 0.3 mol 10\(^{-3}\) cm\(^{-3}\) CTA chloride solution and stirred for 5 h at 323 K. The resulting compound was washed twice, first with deionized water and then with ethanol. The precipitate was dried at room temperature overnight and left in saturated humidity for 24 h. It was dispersed in phenyltrimethoxysilane (30 cm\(^3\)) at 363 K for 24 h and dried, first at room temperature overnight, then at 423 K for 2 h, after which it was stirred in 35 cm\(^3\) of 2 mol 10\(^{-3}\) cm\(^{-3}\) of HCl ethanol solution at 343 K for 24 h. After the acid treatment, the precipitate was centrifuged and washed with water and then with ethanol. The resultant product was designated as PIV(2), where the parenthesis indicates the HCl concentration. Methyl-incorporated clay nanocomposite was prepared by the same procedure as that of PIV(2) using methyltritylthoxysilane. The product was designated as MIV(2).

Silicalite and FSM-22 were prepared by the methods reported elsewhere (Persson, 1994; Inagaki, 1993). Silica aerogel (Aerosil200, Japan BEL Co., Japan) and BETA-type zeolite (HSZ-930NHA, Tosoh Co. Ltd., designated as \( \beta \)-zeolite) were used after calcination at 773 K for 6 h.

Powder X-ray diffraction (XRD) was measured using an M21X diffractometer (MAC Science Co., Japan) with curved graphite monochromator (Cu K\(_a\) radiation) operated at 45 kV and 250 mA. Nitrogen adsorption measurement at 77 K was carried out on a Belsorp-MAX (Japan BEL Co., Japan), for samples degassed at 423 K < 0.1 Pa for 4 h. The specific surface areas were calculated by the BET method using adsorption isotherms between \( p/p_0 = 0.05 \) and 0.1. Adsorption isotherms and adsorption rates of toluene at 298 K were collected by a Belsorp-18 (Japan BEL Co., Japan). The pretreatment of the samples was the same as for the nitrogen adsorption measurement. The DTA-TG curves of the samples were collected using a Thermo-Plus TG8120 thermal analyzer (Rigaku Co., Japan) at a heating rate of 10 K min\(^{-1}\). The desorption behavior of toluene molecules from the samples was also measured by DTA-TG analysis. The samples were degassed at 423 K < 0.1 Pa for > 2 h. The samples were dispersed in toluene overnight, followed by quick filtration. The wet samples were used for the DTA-TG measurements in order to derive their desorption behavior at elevated temperatures.

**RESULTS AND DISCUSSION**

XRD and DTA-TG measurements

The TMA-Mnt and TMA-Smt showed sharp peaks at 2\( \theta \) = 6.16 and 6.38° in their XRD patterns, corresponding to the (001) reflections with basal spacings of 1.39
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FIG. 1. (a) XRD patterns of (1) CTA-intercalated kanemite, (2) CTA-intercalated kanemite after TEOS treatment, (3) SPK and (4) ASPK. (b) XRD patterns of (1) CTA-intercalated vermiculite, (2) CTA-intercalated vermiculite after phenyltrimethoxysilane treatment, (3) PIV (2).

and 1.43 nm, respectively. The resultant interlayer distances can thus be estimated as 0.43 and 0.47 nm for TMA-Mnt and TMA-Smt, since the thickness of a silicate layer is known to be 0.96 nm.

The XRD patterns of CTA-intercalated kanemite, CTA-intercalated kanemite after TEOS treatment, SPK and ASPK are presented in Fig. 1 (a). The CTA-intercalated kanemite shows a peak at 2θ = 2.01°, corresponding to the (001) reflection with a basal spacing of 4.39 nm. The large basal spacing indicates the intercalation of CTA ions between the silicate layers. After TEOS treatment, the peak shifts to a higher 2θ value. The SPK and ASPK show peaks at 2θ = 2.20° (d = 4.01 nm) and 2.22° (d = 3.87 nm) respectively, indicating that the interlayer distance was retained after HCl/ethanol treatment followed by calcination. This is due to the presence of silica pillars in the interlayers, resulting from hydrolysis/condensation of TEOS molecules in the interlayers. Vermiculites after CTA intercalation followed by phenyltrimethoxysilane treatment are shown in Fig. 1 (b). The basal spacings of CTA-intercalated vermiculite before and after phenyltrimethoxysilane treatment are 3.72 and 4.53 nm, indicating the expansion of the interlayer spaces. The subsequent HCl/ethanol treatment, however, shifts to a higher value of 2θ with a decrease in intensity. MIV(5) showed the disappearance of the peak and the appearance of an amorphous halo in the XRD pattern after the HCl/ethanol treatment. The structural change is caused by the leaching of CTA and inorganic ions in the silicate layers under the acid condition, resulting in partial destruction of the layered structures.

The DTA-TG curves for the TMA-Mnt, TMA-Smt, PIV(2) and MIV(5) showed TG declines between 573 and 973 K due to the decomposition of the organic moieties in the products. The TG declines of TMA-Mnt and TMA-Smt were 6.9 and 4.8 mass%, calculated as 0.93 and 0.65 mmol/g of the TMA ion uptakes. The values correspond to 78 and 91% of total ion exchange sites for TMA-Mnt and TMA-Smt, respectively. The declines in the PIV(2) and MIV(5) were 18 and 7.2 mass%. Thus, the amounts of phenyl and methyl groups incorporated in the PIV(2) and MIV(5) are estimated as 2.3 and 4.8 mmol/g.

N2 adsorption isotherms

Nitrogen adsorption isotherms of TMA-Mnt, PIV(2), MIV(5), and SPK are presented in Fig. 2 (a). They show type-I isotherms except for SPK on the BDDT classification (Gregg and Sing, 1981), which correspond to microporous materials. The BET specific surface areas are listed together with those of TMA-Smt and ASPK in Table 1. The surface areas range from 180 to 1000 m² g⁻¹. The SPK and ASPK show large surface areas (~1000 m² g⁻¹) due to the successful pillaring between the silicate layers. The PIV(2) and MIV(5) have improved surface areas due to the pillaring and selective leaching of the layers. For comparison, nitrogen adsorption isotherms of silicalite, β-zeolite, FSM-22 and silica aerogel are given in Fig. 2 (b). Silicalite and β-zeolite belong to a type-I isotherm, while the others are a type-IV, which correspond to mesoporous materials. The BET surface areas were determined from their adsorp-
TABLE 1. Porous parameters for the porous clay materials and the other porous inorganic materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area/m² g⁻¹</th>
<th>Total surface area/m² g⁻¹</th>
<th>External surface area/m² g⁻¹</th>
<th>W₀⁺/cm³(liq.) g⁻¹</th>
<th>Pore width⁴/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIV(5)</td>
<td>685</td>
<td>692</td>
<td>80</td>
<td>0.301</td>
<td>0.98</td>
</tr>
<tr>
<td>PIV(2)</td>
<td>545</td>
<td>348</td>
<td>37</td>
<td>0.142</td>
<td>0.91</td>
</tr>
<tr>
<td>SPK</td>
<td>1007</td>
<td>1014</td>
<td>259</td>
<td>0.476</td>
<td>1.3</td>
</tr>
<tr>
<td>ASPK</td>
<td>908</td>
<td>899</td>
<td>385</td>
<td>0.331</td>
<td>1.3</td>
</tr>
<tr>
<td>TMA-Mnt</td>
<td>180</td>
<td>198</td>
<td>8</td>
<td>0.067</td>
<td>0.71</td>
</tr>
<tr>
<td>TMA-smecton</td>
<td>450</td>
<td>471</td>
<td>16</td>
<td>0.221</td>
<td>0.97</td>
</tr>
<tr>
<td>Silicalite</td>
<td>374</td>
<td>394</td>
<td>11</td>
<td>0.131</td>
<td>0.50⁴</td>
</tr>
<tr>
<td>β-zelite</td>
<td>690</td>
<td>623</td>
<td>106</td>
<td>0.331</td>
<td>0.70⁴</td>
</tr>
<tr>
<td>FSM-22</td>
<td>1068</td>
<td>1057</td>
<td>—</td>
<td>1.33</td>
<td>4.0⁶</td>
</tr>
<tr>
<td>Silica aerogel</td>
<td>208</td>
<td>213</td>
<td>—</td>
<td>—</td>
<td>30⁴</td>
</tr>
</tbody>
</table>

*W₀ represents pore volumes of the internal surface obtained by the αs plot.

1Pore width was calculated by the division of W₀ by the subtraction of the external surface area from the total surface one.

2The data were taken from Baerlocher et al., 2001.

3The pore widths calculated by the BJH method (Barret 1951).

The αs plots of the products were calculated using a standard curve of nonporous silica (Jacroniec, 1999). The plots consisted of two slopes that reflect the total and external surface areas. These surface areas are summarized in Table 1. The total surface areas are nearly equal to the corresponding BET surface areas. The pore widths of the porous pillared clays were calculated from the following formula, assuming a slit-shaped pore model:

$$\text{Pore width} = \left(\frac{(S_T - S_{EX})/W_0}{2}\right)$$

where $S_T$ and $S_{EX}$ are the total and external surface areas derived from the αs plots. $W_0$ is the intercept of the plot, corresponding to the pore volumes of the internal surface. The calculated pore widths are listed in Table 1, and all are around 1 nm in the pillared clays. The TMA-Mnt and TMA-Smt have pore widths reflecting a layered structure with interlayer height of 0.4–0.5 nm and the interval between TMA ions of 1 nm. The PIV(2), MIV(5), SPK, and ASPK have much smaller pore widths than the corresponding interlayer heights. This is because the widths reflect the interval distance corresponding to the pillars and not between the layers. The estimation of the pore widths suggests that the slit-shaped pore model reflects well the texture of porous pillared clays.

**Toluene adsorption isotherms**

Toluene adsorption isotherms of TMA-Mnt, PIV(2), MIV(5), and SPK are shown in Fig. 3 (a). The isotherms of TMA-Mnt, PIV(2), and MIV(5) fit the Langmuir model. By contrast, the isotherms for SPK and ASPK (data not shown) fit the Freundrich model. The isotherms on silicalite, β-zelite, FSM-22 and silica aerogel also show a similarity with SPK, as shown in Fig. 3 (b). The toluene uptake of the products at $p/p_0 = 0.01$ and 0.9 is plotted against their BET surface areas in Fig. 4. The uptake values at $p/p_0 = 0.9$ are almost proportional to the BET surface areas, indicating that the total toluene capacity of the products corresponds to their BET surface areas. On the other hand, the uptake values at $p/p_0 = 0.01$ do not show a proportional relationship with their BET surface areas. The MIV(5) has the highest uptake, and the other porous pillared clays (TMA-Mnt, TMA-Smt, PIV(2), SPK, and ASPK) show higher uptakes than those of silicalite, β-zelite, FSM-22 and silica aerogel. This suggests that the adsorption at low $p/p_0$ is not affected by porosity but affected by other factors such as the surface property and pore structure.

These isotherms show a good fit with the Langmuir-Freundrich isotherm model represented by the following formula (Newalkar, 2002; Newalkar, 2003).
Evaluation of Toluene Adsorptivity

**FIG. 4.** Toluene uptakes vs. the BET surface areas for the porous pillared clays and the other inorganic materials: the uptakes at $p/p_0=0.01$ (●) and at $p/p_0=0.9$ (○).

\[ q = q_m(b/p)^{1/n}(1+(b/p)^{1/n}) \]

where $q$ and $q_m$ are the adsorbed amount at equilibrium pressure $p$, and monolayer adsorption capacity respectively. Parameters $b$ and $n$ represent the sorbate-sorbent interaction and system heterogeneity, respectively. The fitted parameters are listed in Table 2. The $b$ values are divided into two groups: silicalite, TMA-Mnt, TMA-Smt and β-zeolite having high $b$ values of $>5 \times 10^{-3}$ Pa$^{-1}$, and the other materials having low $b$ values $<3 \times 10^{-3}$ Pa$^{-1}$. Their difference is related to the framework microporosity (Huang, 2006). Adsorbents with higher framework microporosity such as zeolites have a stronger interaction with aromatic carbon molecules than those with lower framework microporosity. Silicalite, TMA-Mnt, TMA-Smt and β-zeolite possess a crystalline framework with pore widths of $<1$ nm in size. The ordered pores in sub-nanometer size cause a strong interaction with toluene molecules, leading to the high $b$ values. The other materials, such as MIV(5) and SPK, have lower framework microporosity. This is due to amorphous frameworks with pore sizes around 1 nm, causing a weaker interaction with aromatic carbons.

Contrary to the $b$ values, the monolayer adsorption capacities, $q_m$, of the materials show different behaviors. The $q_m$ values are observed to increase in the sequence of SPK > ASPK > MIV(5) > FSM-22 > TMA-Smt, indicating that the porous pillared clays have higher $q_m$ values than the others. The higher $q_m$ values are related to the high toluene adsorptivity at $p/p_0=0.01$. The ratios of $q_m/q_N$, where $q_N$ represents the monolayer capacity derived from $N_2$ adsorption isotherm, are listed in Table 2. The $q_m/q_N$ ratios of all the pillared clays are $>0.6$ and higher than FSM-22, β-zeolite, silicalite and silica aerogel (0.3–0.5). This suggests shape-selective adsorption for a flat shape such as toluene by the porous pillared clays. The anisotropic shape and large cross-sectional area do not induce sufficient occupation on a surface having a specific pore-geometry at the monolayer adsorption stage. Silicalite and β-zeolite have a cylindrical-shaped channel of $<1$ nm in size, resulting in limited uptakes due to the insufficient structural compatibility between the toluene and the surface (there are some reports on the adsorption of critically sized molecules such as toluene and ethyl benzene into the micropores of the zeolites (Karsli, 1992; Huang, 2006; Vinh-Thang, 2006)). Consequently, the results indicate that the porous clay minerals are better suited to toluene adsorption in the low pressure region such as at the monolayer adsorption stage than are other inorganic materials such as zeolites having cylinder-shaped pores.

**Kinetic analyses on the adsorption and desorption processes**

In order to examine the adsorption rate of toluene molecules on the surface of the materials, uptake curves as function of time on the degassed materials were collected. The uptake curve, $u(t)$, is defined as follows:

\[ u(t) = (p_0 - p(t))/(p_0 - p_e) \]

where $p_0$, $p(t)$, and $p_e$ represent the initial pressure, pressure at time $t$ (s), and equilibrated pressure of toluene. When the toluene uptake reaches the equili-

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area/$\text{m}^2 \cdot \text{g}^{-1}$</th>
<th>$q_m$/mmol/g</th>
<th>$b/10^{-3}$ Pa$^{-1}$</th>
<th>$n$</th>
<th>$q_m/q_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIV(5)</td>
<td>1273</td>
<td>4.74</td>
<td>1.14</td>
<td>1.69</td>
<td>0.67</td>
</tr>
<tr>
<td>PIV(2)</td>
<td>331</td>
<td>2.30</td>
<td>1.58</td>
<td>2.02</td>
<td>0.65</td>
</tr>
<tr>
<td>SPK</td>
<td>3111</td>
<td>6.30</td>
<td>2.26</td>
<td>0.66</td>
<td>0.61</td>
</tr>
<tr>
<td>ASPK</td>
<td>1828</td>
<td>5.71</td>
<td>2.66</td>
<td>0.80</td>
<td>0.61</td>
</tr>
<tr>
<td>TMA-Mnt</td>
<td>245</td>
<td>1.24</td>
<td>7.39</td>
<td>1.60</td>
<td>0.68</td>
</tr>
<tr>
<td>TMA-Smecton</td>
<td>629</td>
<td>2.91</td>
<td>5.25</td>
<td>1.10</td>
<td>0.63</td>
</tr>
<tr>
<td>Silicalite</td>
<td>305</td>
<td>1.35</td>
<td>10.7</td>
<td>1.00</td>
<td>0.35</td>
</tr>
<tr>
<td>β-zeolite</td>
<td>646</td>
<td>2.89</td>
<td>5.25</td>
<td>0.67</td>
<td>0.41</td>
</tr>
<tr>
<td>FSM-22</td>
<td>1136</td>
<td>3.63</td>
<td>2.95</td>
<td>0.70</td>
<td>0.33</td>
</tr>
<tr>
<td>Silica aerogel</td>
<td>202</td>
<td>1.13</td>
<td>1.35</td>
<td>1.00</td>
<td>0.53</td>
</tr>
</tbody>
</table>

*The surface areas were calculated by the data on their toluene adsorption isotherms.*
brated uptake at \( t \) s, \( u(t) \) becomes unity. The \( u(t) \) curves are given in Figs. 5 (a) and (b). TMA-Mnt and SPK show a similar increase with the time-course. The times when \( u(t) = 0.8 \) are 266, 266 and 296 s for TMA-Mnt, TMA-Smt (data not shown), and SPK, respectively. PIV(2) and MIV(5) exhibit a slower increase than the others (\( t_{0.8} = 604 \) s and 545 s for PIV(2) and MIV(5), respectively). Similarly longer \( t_{0.8} \) values are observed in \( \beta \)-zeolite (486 s) and silica aerogel (552 s). These longer \( t_{0.8} \) values are caused by slow increases in the uptake when \( u(t) < 0.05 \). The slow increases might be due to time-consuming diffusion process in macropores in the materials. Silica aerogel and other materials such as PIV(2), MIV(5) and \( \beta \)-zeolite contain large amounts of the macropore that are formed by vacant spaces in their structures or between their particles. The macropore diffusion disturbs the prompt adsorption of toluene on the surfaces, resulting in the slow increases in the uptakes. On the other hand, silicalite and FSM-22 show \( u(t) \) curves similar to those of TMA-Mnt, TMA-Smt, and SPK, with \( t_{0.8} \) values of 292 and 236 s for silicalite and FSM-22, respectively. These \( t_{0.8} \) values are two times faster than those of silica aerogel and other materials. It suggests that they contain less macropore, leading to the faster \( t_{0.8} \) values. However, we could not obtain the details on the differences affecting the adsorption rates between the porous pillared clays and the others, e.g., the differences in pore geometry or the sorbate-sorbent interaction.

The dTG/dT curves of the porous pillared clays and the other materials are given in Figs. 6 (a) and (b). These curves have a peak below 373 K due to the desorption of toluene molecules from the micropores and the external surfaces. Fig. 6 (b) shows that silicalite has an additional peak around 413 K and \( \beta \)-zeolite has a shoulder around 417 K on their respective curves. These materials have high \( b \) values on the Langmuir-Freundrich isotherm model, indicating that the strong sorbate-sorbent interaction entraps toluene molecules in the micropores at higher temperatures. In addition, their complicated three-dimensional pore network may inhibit easy diffusion for desorption. On the other hand, TMA-Mnt and TMA-Smt do not exhibit a similar entrapment of toluene, although they also have high \( b \) values. The other porous pillared clays exhibit rapid decay of their dTG/dT up to 373 K similar with FSM-22 and silica aerogel. As a result, it is suggested that the porous pillared clays have a lower entrapment ability than those of zeolites at elevated temperatures. This would be not only due to the weak interaction between toluene molecules and the pores, but also due to their simpler, two-dimensional gallery structure of pore network, which enables toluene molecules to be easily desorbed.

The low entrapment ability of the porous pillared clays suggests their high sorption ability for VOC adsorbents. Ideal characteristics for adsorbents of VOC include not only a sufficient adsorption capacity for VOCs, but also a regeneration capability for reuse. The above-described low entrapment ability is necessary for the regeneration process and widens the range of possible applications for VOC removal. Consequently, the porous pillared clays have high advantages for practical use as well as high adsorptivity in comparison with the other inorganic materials.
CONCLUSION

We investigated toluene adsorption and desorption behavior of the porous pillared clays and the other porous silicas such as silicalite, β-zeolite, FSM-22, and silica aerogel in order to evaluate each as an adsorbent for volatile organic compounds (VOC). Toluene adsorption isotherms of the materials showed that the porous pillared clays had higher toluene uptake in the low relative pressure region \((p/p_0 < 0.01)\) while the uptake in the higher pressure region depends on their BET surface areas. The comparison of \(q_m/q_N\) values among the materials suggests that the porous pillared clays, having slit-shaped pores, facilitate the adsorption of flat-shaped molecules at the early adsorption stage owing to their shape-selectivity. The adsorption rates indicate that the porous pillared clays show no other advantage in their adsorption rate. The dTG/dT curves showed that the porous pillared clays released the adsorbed toluene at around 373 K, while silicalite and β-zeolite entrapped the molecules up to 413-417 K due to the strong sorbate-sorbent interaction. The low toluene entrap ability is considered to be suitable to enable reusage, suggesting good practical applications for adsorbents.

The results might be applicable to other VOC molecules such as xylene, \(p\)-dichlorobenzene and ethylbenzene, all of which are flat-shaped molecules. In addition, the low working concentration of the materials \((p/p_0 = 0.01)\) is estimated as \(\approx 1\) ppm, which corresponds to the upper limit for the risk of chemical exposure in factories or newly-built buildings (Foo, 1990; Donald, 1991; Ng, 1992). Consequently, porous pillared clays have good potential for application in the removal of VOC molecules.

REFERENCES


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