

High benzene selectivity of uniform sub-nanometre pores of self-ordered mesoporous silicate

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The high benzene gas selectivity of mesoporous silicate (SBA-15) was observed in the sub-nanometre micropore condensation region. The benzene/toluene ratios of the adsorbed amount were > 100 and > 6 in ideal and pseudo-atmospheric environments, respectively.

Molecular recognition using a nano-sized pore is a significant subject in relation to such industrial uses as separation technology, shape-selective catalysis, and polymerization.¹ Recently, mesoporous silicates have attracted attention due to the possibility of controlling their pore size, and so they are expected to have further potential for practical applications such as precisely controlled molecular recognition. Newalkar *et al.* described the separation of light hydrocarbons such as ethylene/ethane by using mesoporous silicate.² However, it is more important to detect aromatic hydrocarbons selectively than to realize light hydrocarbon separation since the former has a larger number of applications including drug delivery systems and sensors for various environmental pollutants.³ As an example of aromatic hydrocarbon separation by using nano-sized pores, we developed a microfluidic device to detect and identify ppb levels of environmental pollutant gases, namely, benzene, toluene, and xylenes (BTX). The aromatic hydrocarbon is separated by using the time difference between the thermal desorption of each gas from silicate material with meso and micropores as a gas adsorbent.⁴ The micropore structure of the porous silicate may be the most important factor determining the gas sensitivity, which can be expected even when the molecular structures of the target and coexisting molecules are similar. However, the relationship between the micropore structure and the adsorbate molecules has not been investigated even as regards light hydrocarbon selectivity.² Here, we report (1) highly selective molecular recognition based on a mesoporous silicate that adsorbs at least hundred times more benzene than toluene, (2) the mechanism of the high benzene selectivity, which we analyzed by carefully studying various kinds of mesoporous silicate.

Since the variation in the micropore size of microporous silicates has been investigated in relation to such synthesis conditions as synthesis temperature,⁵ calcination temperature,⁶ and chemical treatment after calcination, we were able to obtain the desired structure for our study. We used (1) SBA-15, (2) SBA-16, (3) SBA-15-acid, and (4) SDP† in order to study the effects of micropore size on gas selectivity. We characterized the micropore size of each silicate by using conventional nitrogen adsorption measurement and with the positron annihilation technique.^{7‡} Fig. 1 shows the micropore diameter ($2r_p$) distributions from 0.3 to 0.8 nm obtained from positron annihilation spectra. The median values of $2r_p$ were 0.60 and 0.63 nm for SBA-15 and SBA-15-acid, respectively. SBA-16 and SDP show twin peaks at 0.45 and 0.90 nm, and 0.46 and 0.83 nm, respectively. The small-angle XRD patterns of SBA-15 and SBA-15-acid were almost similar and show well-resolved peaks associated with hexagonal symmetry, while that of SBA-16 also shows well-resolved peaks associated with cubic symmetry. Those results corresponded well with the results reported elsewhere.⁸ The patterns of SDP shows almost no peak.

We then studied the benzene selectivity over toluene for each silicate by using detailed benzene and toluene isotherms in the lower P/P_0 region (Fig. 2).§ In the large P/P_0 region, the adsorption

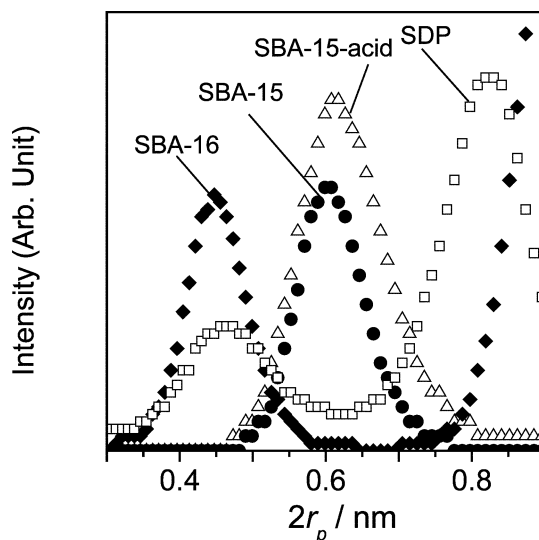


Fig. 1 Micropore distribution calculated using the positron annihilation spectrum of SBA-15 (●), SBA-16 (◆), SBA-15-acid (△), and SDP (□).

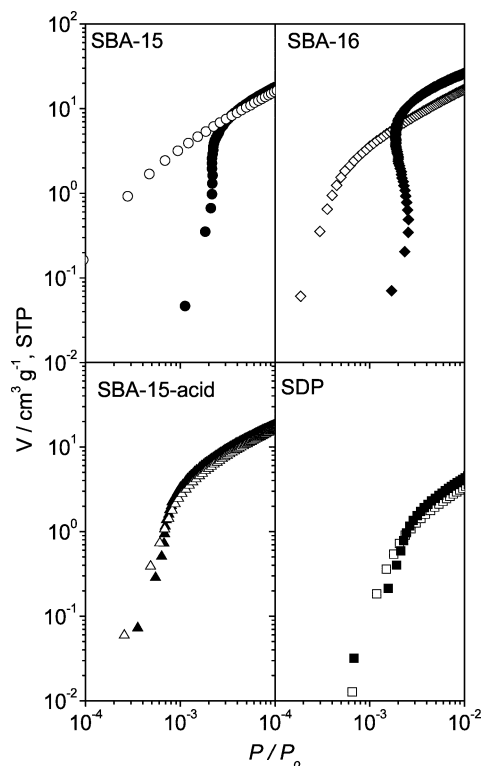


Fig. 2 Isotherm of SBA-15 (circles), SBA-16 (diamonds), SBA-15-acid (triangles), and SDP (squares). The unfilled and filled symbols correspond to benzene and toluene adsorption, respectively.

volumes of toluene (V_{tl}) were always larger than those of benzene (V_{bz}). This was because toluene has a higher boiling point and lower saturation pressure than benzene. However, with SBA-15 and SBA-16, V_{tl} was particularly small in the $P/P_0 < 2 \times 10^{-3}$ region. We first compared the results of SBA-15 and SBA-16 to analyze the micropore size effect. The estimated V_{bz} and V_{tl} values in the micropore condensation region, for example, at $P/P_0 = 8 \times 10^{-4}$ (extrapolated for toluene), were about 2.8 and 0.03 [$\text{cm}^3 \text{g}^{-1}$ at STP] for SBA-15 and 2.9 and 0.02 [$\text{cm}^3 \text{g}^{-1}$ at STP] for SBA-16, respectively. The degrees of benzene selectivity estimated from $V_{\text{bz}}/V_{\text{tl}}$ were 93 and 145 for SBA-15 and SBA-16, respectively. The negative slope observed at the part of toluene isotherm of SBA-16 was reproducible with different measurements and was not observed with other silicates. We believe that this is not due to systematic errors of measurement but this matter requires further study for an explanation. To confirm whether pore size is really important as regards the benzene selectivity, we mainly studied the benzene selectivity of SDP, which has larger micropores. V_{bz} and V_{tl} at $P/P_0 = 8 \times 10^{-4}$ were both about 0.07 [$\text{cm}^3 \text{g}^{-1}$ at STP] and $V_{\text{bz}}/V_{\text{tl}}$ was 1. However, SDP has two types of micropore and there is some doubt as to the contribution from each type. We then studied the benzene selectivity of SBA-15-acid that has a $2r_p$ distribution over a larger size region than SBA-15. The median of the difference between the distribution curves of SBA-15 and SBA-15-acid was about 0.67 nm and thus the difference between SBA-15 and SBA-15-acid must be represented by the adsorption around $2r_p = 0.67$ nm. V_{bz} and V_{tl} at $P/P_0 = 7 \times 10^{-4}$ were both about 1.2 [$\text{cm}^3 \text{g}^{-1}$ at STP] and $V_{\text{bz}}/V_{\text{tl}}$ was about 1. This indicates that it is important to limit $2r_p$ to a wider diameter region, which may allow toluene adsorption, in order to increase the benzene selectivity. This led us to a reasonable explanation of how to generate a high benzene selectivity over toluene. The primary condition involves adjusting $2r_p$ to the size of a benzene molecule, namely, smaller than ~ 0.6 nm. The secondary condition is to limit $2r_p$ to a wider diameter region, which may increase V_{tl} . Other factors such as surface silanol groups and their density may affect the benzene selectivity. We also confirmed that porous silicates without the silanol group have little selectivity for any gas. This is also an important issue that should be investigated in the near future.

Moreover, to confirm whether or not the benzene selectivity of SBA-15 and SBA-16 is practically available, we measured the adsorption volumes of benzene and toluene in a pseudo-atmospheric environment. We measured the FT-IR microscope reflectance spectra of each silicate before and after they had been exposed for 10 min to mixture gases containing 50 ppm each of benzene and toluene diluted in nitrogen at atmospheric pressure with a flow rate of $0.18 \text{ cm}^3 \text{ s}^{-1}$. The P/P_0 values that correspond to a partial pressure of 50 ppm for benzene and toluene in air at atmospheric pressure are 4×10^{-4} and 1×10^{-3} , respectively. We calculated the peak areas of benzene and toluene in the spectra by fitting the corresponding peak to a Gaussian curve. We observed that the ratios of benzene/toluene adsorbed in SBA-15 and SBA-16 were more than 2.0 and 6.3, respectively, while that adsorbed in SBA-15-acid was around 1.5. Although the benzene/toluene ratio of SBA-15/SBA-16 was much smaller than the value estimated from the isotherm measurement due to the difference in the total pressure or the fluidic measurement, the qualitative trends of the benzene selectivity of SBA-15/SBA-16 were demonstrated in a pseudo-atmospheric environment.

We succeeded in observing the benzene selectivity of SBA-15/SBA-16 from toluene and found that it is improved by (1)

adjusting the pore diameter to an appropriate size and (2) limiting the diameter of the distribution to a wider diameter region. These conclusions result from careful measurements of isotherm curves and a detailed analysis of the micropore size and distribution. We also confirmed the benzene selectivity of SBA-15/SBA-16 in a pseudo-atmospheric environment. We thus showed that control of the micropore structures is the key to realizing an ideal gas-selective mesoporous silicate for a given gas.

Notes and references

† SBA-15 was synthesized by using the method developed by Zhao *et al.*⁸ except that we controlled the temperature more precisely. Dissolve P123 (EO₂₀-PO₇₀-EO₂₀, BASF Corporation: Pluronic P123; $M_w = 5750$) in dilute aqueous HCl at 45 °C and stir the solution for 1 h. Add TEOS to the above solution at the same temperature and stir it for 20 h. Age the mixture solution and the accompanying precipitated products at 80 °C for another 24 h. Filter the products, and wash and air-dry them at room temperature. Finally, calcinate the products by slowly increasing the temperature from room temperature to 500 °C over 8 h, heating them at 500 °C for 6 h, and then reducing the temperature from 500 °C to 100 °C over 8 h. The mole ratio of the chemicals is 1 TEOS : 0.017 P123 : 5.7 HCl : 193 H₂O. SBA-16 was synthesized similarly to SBA-15 except that we used F127 (EO₁₀₀-PO₆₅-EO₁₀₀, BASF Corporation: Pluronic F127; $M_w = 12600$) instead of P123. SBA-15-acid: SBA-15 treated with 0.1 M hydrochloric acid after calcination. SDP: Commercially obtained amorphous silicon dioxide powder (Kanto Chemical).

‡ Measured with a positron annihilation lifetime spectrometer located at AIST, Japan. The positron source and the detector were ²²NaCl (about 1.85 MBq) and a plastic scintillator combined with a photomultiplier, respectively. The data were analysed using the maximum entropy lifetime analysis (MELT) computer program.⁹

§ We used Belsorp 18 plus (BEL Japan, Inc.) for the adsorption measurement. We heated each sample for 12 hours at 500 °C under a pressure of around 10 Pa prior to the measurements.

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