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Adsorptivity Control and Microcalorimetric Characterization of Silanized Ordered Porous Silica

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Abstract. Microporous silica (PS) with an ordered pore array of two-dimensional hexagonal symmetry was successfully prepared by regulated hydrolysis and co-condensation of tetramethoxysilane in decyltrimethylammonium bromide solution. The porous silica, PS, was silanized by 2-(3,4 epoxycyclohexyl) ethyltriethoxysilane to control hydrophilicity of the surface (PS-echx). The pore size of PS-echx was 0.8 nm, which is intermediate size between those of microporous aluminosilicate zeolites and conventional mesoporous silica, MCM-41 and MCM-48. PCS-echx exhibited significant water adsorptivity at low relative pressure region ($P/P_0 = 0.2$), and low differential heats (44 and 50 kJ/mol, for the first and the second adsorption runs, respectively).

Keywords: adsorption, heat of adsorption, mesopore, micropore, silica, water

1. Introduction

Mesoporous silica materials with regular pore structures (Beck et al., 1992; Kregse et al., 1992), have large specific surface areas and high pore volumes. Because of their unique pore characteristics, the ordered mesoporous silica materials have attracted interest as model mesoporous materials in adsorption science (Kruk, 1996; Matsumoto et al, 2001, 2002a, 2002b; Ravikovitch et al, 1995; Zhu, 1996), packing materials in selective separation (Grün et al., 1996), and catalysis (Corma, 1997). Recently, an application of the silica materials to desiccants for heat pump and air conditioning systems has been studied. In this case, lowering the pore size to micropore region (less than 1 nm) and controlling hydrophilicity of the surface are necessary to impart an efficient sorptivity towards water at an appropriate humidity. However, the pore size controlling of the porous silica to less than 2 nm was difficult and their porosity decreased by hydrolysis of surface siloxane (Si─O─Si) to silanol (Si─OH) by adsorbed water.

This paper reports an attempt to prepare a microporous silica with regular pore arrays, control the hydrophilicity and stabilization against hydrolysis of the surface by silanization. The adsorption characteristics of water on the silica material was also elucidated by adsorption microcalorimetry.

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2. Experimental

2.1. Preparation of Microporous Silica and Surface Tailoring by Silanization

Microporous silica with regular pore arrays was prepared by hydrolysis and co-condensation of tetramethoxysilane (TMOS) in a water-methanol mixed solution (water/methanol = 75/25 w/w) of *n*-decyltrimethylammonium bromide at pH > 11, which was the similar to the procedure reported by Yano et al, (2001). The prepared sample was designated as PS (abbreviation of Porous Silica). A conventional ordered mesoporous silica, MCM-41, was also prepared and examined for comparison (Grün et al., 1999).

2-(3,4 Epoxycyclohexyl) ethyltriethoxysilane (Azmax, 98%) was as a silanization reagent. Freshly calcined PS was dried for 24 h at 423 K in vacuo. And then, the sample was refluxed in the silanization reagent dissolved in anhydrous toluene (Kanto Chemical, 99.5%)

at 313 K for 4 h. The tailored silica (designated as PS-echx) was then suction filtered and thoroughly washed with toluene and dried at 423 K for 12 h.

2.2. *Physicochemical Characterization and Water Adsorption*

X-ray diffraction (XRD) patterns were measured by using CuKα radiation (Rigaku RINT2000). Nitrogen adsorption isotherms were measured volumetrically at 77 K (Quantachrome Autosorb 6B). Solid-state MAS NMR spectra for ^{29}Si and ^{13}C atoms were measured by a single pulse technique (Varian VNMR400P). The concentration of anchored groups was determined by elemental analysis (Yanaco CHN corder NT-6).

Differential heats of adsorption of water and adsorption isotherms were measured at 298 K by a twin conduction type microcalorimeter (Tokyo Riko) equipped with a volumetric adsorption apparatus. Each sample was pretreated at 423 K and 1 mPa for 12 h before the adsorption measurements.

3. Results and Discussion

3.1. *Characterization of Pore Structure and Surface Chemical Structure*

X-ray diffraction patterns of PS, PS-echx and MCM-41 indicated that these materials had the pore array of the two-dimensional hexagonal (2DH) symmetry. A sharp Bragg peak of the reflection from the (100) plane of the 2DH structure was observed at $2\theta = 3.62^\circ$ and 3.70° for PS and PS-echx, respectively, indicating the pore widths of PS and PS-echx are narrower than those of MCM-41.

The nitrogen adsorption isotherm of MCM-41 exhibited type IV character, as shown in Fig. 1. On the other hand, those of PS and PS-echx were of type Ib, suggesting the presence of micropores in these materials. The pore characteristics determined by the nitrogen adsorption measurements were shown in Table 1. The concentration of the 2-(3,4 epoxycyclohexyl) groups (ECHX groups) on PS-echx was 0.19 groups/nm^2 or 0.45 mmol/g.

^{29}Si NMR spectrum of PS exhibited a sharp resonance signal at –110 ppm and a shoulder at –100 ppm, which can be assigned to the Q^4 and Q^3 units, respectively (Vansant et al, 1995). After the ECHX modification, the intensity of the Q^3 signal decreased and a new signal due to silicon in an anchored ECHX group appeared at −52 ppm (Vansant et al, 1995), suggesting successful anchoring of ECHX groups by the silanization

Table 1. Pore characteristics of samples.

Sample	Surface area [a]/ $m^2\ g^{-1}$	Pore volume [a]/ $mL\ g^{-1}$	Pore size (2r)/ nm	Wall thickness [c]/ nm
PS	1450	0.48	0.8[a]	2.0
PS-echx	1160	0.37	0.8[a]	2.0
MCM-41	1200	0.67	2.3 [b]	1.7

[a]Determined by *t*-plot; [b] median pore diameter by the Dollimore-Heal method; [c] estimated by $2d_{100}/\sqrt{3} - 2r$.

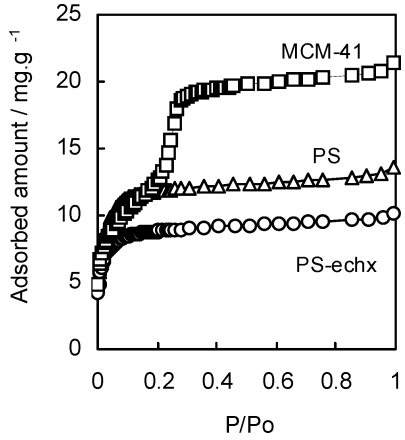

Figure 1. Nitrogen adsorption isotherms of PS, PS-echx and MCM-41.

3.2. *Water Adsorption*

The water adsorption isotherm of a conventional ordered mesoporous silica, MCM-41, was of type V for the first adsorption run, indicating hydrophobicity at low P/P_0 region (Fig. 2). However, the adsorption isotherm exhibited a hydrophilic character in the second and the third runs, where a condensation step shifted to a lower P/P_0 value ($P/P_0 = 0.42$) due to decreasing of an effective pore diameter by adsorbed water (Matsumoto et al, 2001, 2002b). The saturated adsorption amount was reduced in the second adsorption rum by partial collapse of pore structure by adsorbed water (Zhao, 1998; Carrot, 1999).

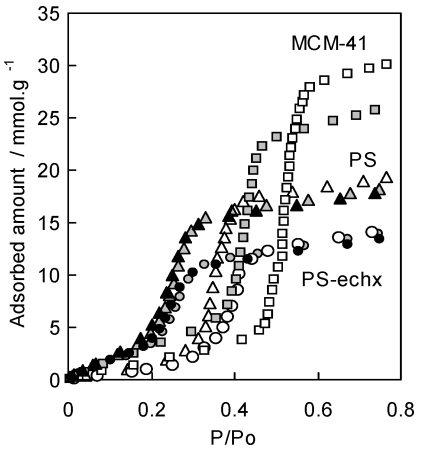

Figure 2. Changes in water adsorption isotherms by repetition of adsorption. Opened, shadowed and closed symbols denote the first, the second and the third adsorption runs, respectively.

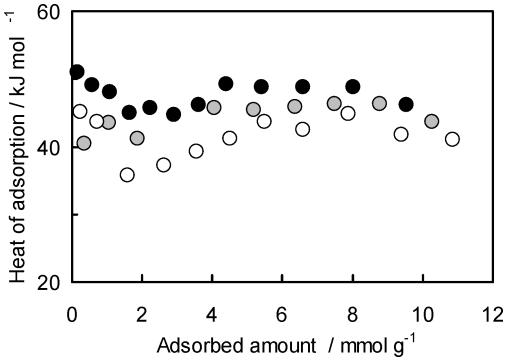

Figure 3. Differential heats of water adsorption on PS-echx. Opened, shadowed and closed symbols denote the first, the second and the third adsorption runs, respectively.

In the case of PS, the adsorption isotherm showed hydrophobic character in the first adsorption run, however, the surface became hydrophilic by water adsorption (Fig. 2). Although the adsorbed amount at high P/P_0 region also decreased for some extent by the iteration of water adsorption, the attrition rate of the water uptake for PS (7% at $P/P_0 = 0.8$) was less than that for MCM-41 (14%). It suggests that the pore structure of PS is more stable than that of MCM-41. The stability would arise from a thicker pore wall of PS (Table 1).

The water adsorption isotherm of the mesoporous silica with anchored alkyl group never exhibits a condensation step (Matsumoto, 2002b). But the isotherm of PS-echx exhibited a condensation step, indicating some hydrophilicity of PS-echx. PS-echx became more hydrophilic in the second adsorption run. This hydrophilic change is not due to surface silanol groups as observed in PS but diol formed by hydrolysis of epoxy group in the anchored ECHX groups, because ^{13}C NMR results for PS-echx showed that a strong signal assigned to carbon attached to epoxy group in ECHX group (51 ppm) disappeared and a new one due to carbon of diol was appeared (74 ppm) by water adsorption. In the cases of mesoporous silica and PS, the water adsorptivity decreased by a partial disorder of the pore structure by water sorption. However, the water adsorptivity of PS-echx did not change at all by repeated adsorption. These results suggest that the pore structure of PS-epoxy was very stable for water adsorption.

The differential heats of water adsorption (DHA) on PS-echx for the first adsorption run were 45 kJ/mol at the initial stage of adsorption and immediately decreased to 35 kJ/mol, and then, it reached constant at ca. 43 kJ/mol (Fig. 3). The initial heat evolution would be due to a direct interaction between water and silanol on the silica surface or the ECHX groups. Whereas, the surface covered with the ECHX groups is rather hydrophobic so that DHA decreased. On the other hand, the initial heat increased by iteration of water adsorption, and it became 52 kJ/mol for the third run. The initial heat is still lower than that of conventional mesoporous silicas, showing a weak interaction between surface and water molecules, and such a weak interaction enables easy removal of adsorbed water at a mild temperature condition.

4. Conclusion

Preparation procedure of mesoporous silica was successfully applied to a synthesis of microporous silica with two-dimensional hexagonal pore structure. The relative pressure at which a capillary condensation of water took place was lowered ($P/P_0 = 0.25$) by regulating the pore size to microporous region (0.3 nm). The silanization with 2-(3,4 epoxycyclohexyl) ethyltriethoxysilane brought about hydrophilicity to the surface of microporous silica. The pore structure of the silanized silica was stable against hydrolysis of siloxane on pore wall. Because of the hydrophilic nature and stability of the surface, an application of this material as a desiccant air-conditioning and heat-pump systems is expected.

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References

Corma, A. *Chem. Rev*., **97**, 2373–2420 (1997).
Beck, J. et al., *J. Amer. Chem. Soc*., **114**, 10834–1083 (1992).
Grü n, M. et al., *J. Chromatogr. A*, **740**, 1–9 (1996).
Grün, M. et al., *Microporous Mesoporous Mater.*, **27**, 207–216 (1999).
Kregse, C.T. et al., *Nature*, **359**, 710–712 (1992).
Kruk, M et al., *Langmuir*, **15**, 5279–5284 (1999).
Matsumoto, A. et al., *Langmuir*, **17**, 47–51 (2001).
Matsumoto, A. et al., *Colloids Surf. A*, **203**, 185–193 (2002a).
Matsumoto, A. et al., *Langmuir*, **18**, 4014–4019 (2002b).
Ravikovitch, P. et al., *Langmuir*, **11**, 4765–4772 (1995).
Ribeiro Carrot, M. et al., *Langmuir*, **15**, 8895–8901 (1999).
van Blaaderen, A. and Vrij, A. *The Colloid Chemistry of Silica, Adv. Chem. Ser. 234*, H.E., Bergna (Ed.), *Amer. Chem. Soc.* Washington D.C., Chapter 4, 1994.
Vansant, E. et al., *Characterization and Chemical Modification of the Silica Surface*, Elsevier, Amsterdam, 1995.
Yano, K. Japanese Patent, J2001–157815A (2001).
Zhao, X. S. et al., *J. Phys. Chem. B*, **102**, 4143–4146 (1998).
Zhu, H. et al., *Langmuir,* **12**, 6513–6517 (1996).