

Research Note

CECE 触媒用疎水性シリカビーズの細孔構造及び水蒸気吸着特性

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Porosity and water vapor sorption property of new hydrophobic silica beads
for CECE catalyst support

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(Received December 17, 2013; May 23, 2014)

Abstract

The porosity and water vapor sorption property of commercially available hydrophobic SiO₂ beads were investigated. The hydrophobic SiO₂ beads, the surface of which has been modified by trimethylsilyl functional groups, with a surface area of 70.7 m²/g, a mesopore diameter of about 36 nm and a mesopore volume of about 0.91 cm³/g showed lower water vapor sorption property as compared to the unmodified SiO₂ beads; the amount of monolayer water adsorbed were estimated to be 2.94×10^{-3} and 5.12×10^{-3} g(H₂O)/g(adsorbent) for hydrophobic and unmodified SiO₂ beads, respectively. The evaluation of the heat of water vapor sorption suggests that the suppression of water cluster formation by trimethylsilyl groups is attributed to the hydrophobic property.

Research note

The combined electrolysis catalytic exchange (CECE) method is a practical process for the enrichment of heavy water and the extraction of tritium from light and heavy water mixtures.[1-3] From the development of the CECE process and afterwards, much effort has been devoted to improve the catalytic activity, design of the catalyst bed, and operation parameters.[1,4,5] One of the CECE catalysts commercially available at the present is the styrene-divinylbenzene copolymer supported Pt catalyst which has been known as the Kogel catalyst.[1,3-5] Although the superior activity and life time with satisfactory operating results of the Kogel catalyst have been well known, one problem is the difficulty in its mass production and hence a high price. Therefore, the development of a new preparation method with improved activity is still an interesting task.

From these backgrounds, we started our attempt at preparing a new CECE catalyst from commercially available, relatively cheap materials such as SiO₂, Al₂O₃ and activated carbon. Among the several physical and chemical properties required for a CECE catalyst support, such as porosity, water resistance, and hardness, one of the most important properties is hydrophobicity.[1,4,5] Although the hydrophobic/hydrophilic property is difficult to define quantitatively [6], it has been known that hydrophilic CECE catalysts easily cause pore blocking due to the condensation of water vapor, resulting in the decrease in catalytic activity.[1,4,5] We

have chosen hydrophobic SiO₂ beads (Fuji Silysia Chemical Ltd., Aichi), denoted as SiO₂B, for use as the catalyst support in a new CECE catalyst system. In this note, we report some fundamental properties of SiO₂B, especially focusing on water vapor sorption properties in addition to other pore structural properties. As a reference material, SiO₂ beads (CARiACT-Q50, Fuji Silysia, denoted as SiO₂B_{H2O}) were used in this study. This SiO₂B_{H2O} was the parent material for SiO₂B, which had trimethylsilyl functional groups grafted on the surface (grafting density of 1.2 – 1.8 groups/nm² in catalog). It should be noted that SiO₂B_{H2O} also shows hydrophobicity, since it is composed of pure silica [6], which excludes Al³⁺ or related counter-cations of Na⁺ or Ca²⁺ as is the case with hydrophilic silica gel or zeolite molecular sieves.

Fig. 1 shows the SEM image of SiO₂B and the optical photo of SiO₂B and SiO₂B_{H2O}.

The color of these beads was white and the diameter was about 2.4 – 4.1 mm (Fig.1 inset). The SEM measurements (JSM-6701F, JEOL) revealed that SiO₂B possessed textural pores with the diameter of several tens of nanometers. These pores existed as continuous wormhole-like structures in a SiO₂ framework.

Nitrogen sorption isotherms were measured by using Autosorb-1MP (Quantachrome) at -196 °C. The samples were evacuated previously at 200 °C for more than 12 h. Brunauer–Emmett–Teller surface area (S.A.) were found to be 70.7 and 76.2 m²/g for SiO₂B and SiO₂B_{H2O}, respectively. Both SiO₂B and SiO₂B_{H2O} showed a type V isotherm as shown in Fig. 2 [7]; the sorption capacity was small in low and middle P/P₀ ranges, and then suddenly increased at higher P/P₀. This suggested that unrestricted monolayer-multilayer adsorption could occur.[7,8] Indeed, the micropore volumes (V_{p_{micro}}) below a P/P₀ of 0.205, corresponding to the pore

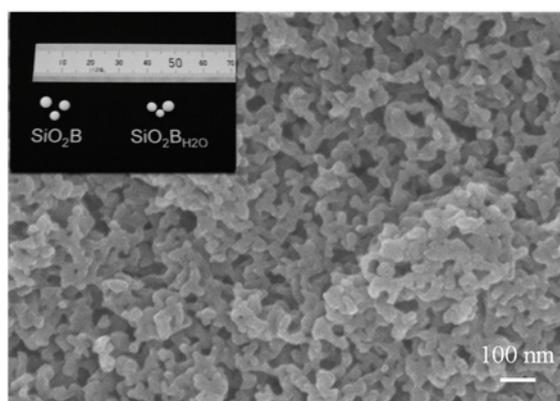


Fig.1 SEM image of SiO₂B. Inset: Appearance of SiO₂B and SiO₂B_{H2O}.

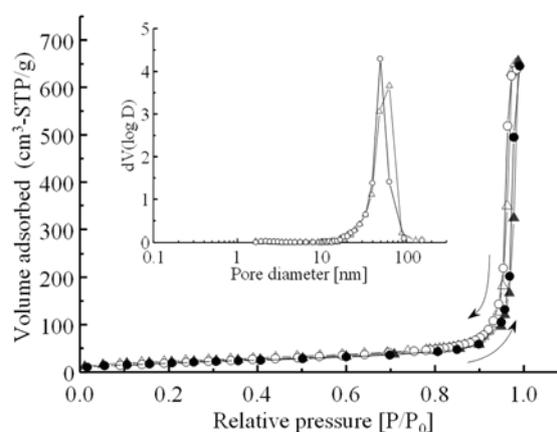


Fig. 2 N₂ sorption isotherm of SiO₂B and SiO₂B_{H2O}. Inset: Barrett-Joyner-Halenda (BJH) pore size distribution of SiO₂B and SiO₂B_{H2O} evaluated from the desorption branch. Symbols are circle for SiO₂B and triangle for SiO₂B_{H2O}, respectively.

Table 1 Summary of sorption study of SiO₂B and SiO₂B_{H2O}.

	N ₂ sorption				Hg porosimetry			H ₂ O vapor sorption 25 °C (BET constant)	
	<i>S.A.</i> [m ² /g]	<i>D_p</i> [nm]	<i>V_{p, micro}</i> [cm ³ /g]	<i>V_{p, meso}</i> [cm ³ /g]	<i>D_p</i> [nm]	<i>V_{p, meso}</i> [cm ³ /g]	<i>V_{p, macro}</i> [cm ³ /g]	<i>w_m</i> [g _(H₂O) /g]	<i>C</i> [–]
SiO ₂ B	70.7	49.0	0.030	0.176	36	0.909	0.059	2.94 × 10 ⁻³	7.67
SiO ₂ B _{H2O}	76.2	63.3	0.034	0.187	37	0.934	0.050	5.12 × 10 ⁻³	5.36

diameter of 2.1 nm, were 0.030 and 0.034 cm³/g for SiO₂B and SiO₂B_{H2O}, respectively (Table 1). On the other hand, the pore volume in the region between 0.205 and 0.957, corresponding to the mesopore diameter of 2.1 to 47 nm (*V_{p, meso}*), were found to be 0.176 and 0.187 cm³/g, respectively, and larger than *V_{p, micro}*. The Barrett-Joyner-Halenda (BJH) pore size distribution curve (desorption branch) also revealed that most of the pores had sizes in the range of 30 – 60 nm (Fig. 2,

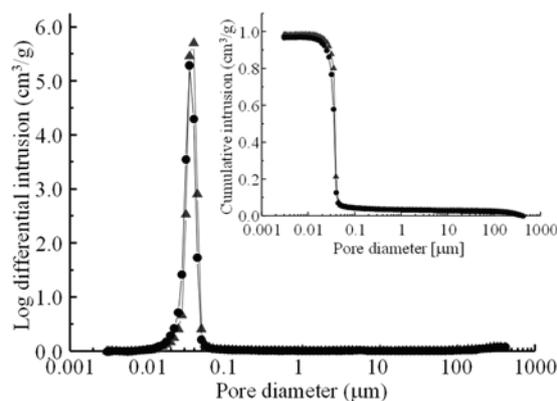


Fig. 3 Pore size distribution of (circle) SiO₂B and (triangle) SiO₂B_{H2O} obtained by mercury porosimetry. Inset: cumulative intrusion of Hg.

inset), which was consistent with SEM measurements. The pore diameter (*D_p*) was found to be 49.0 and 63.3 nm for SiO₂B and SiO₂B_{H2O}, respectively. However, these high *P/P₀* region is excluded from the applicability of the N₂ sorption study [8]. Therefore, we investigated the pore size distribution using mercury porosimetry (AutoPore IV 9510, Micromeritics). Fig. 3 shows the pore size distribution curves of SiO₂B and SiO₂B_{H2O} and the cumulative intrusion of Hg (inset). It is clearly seen that both SiO₂B and SiO₂B_{H2O} possess mesopores with the pore diameter of 36 and 37 nm, respectively, which are smaller than the ones from the BJH pore size distribution [8]. The pore volumes of the mesopore (*V_{p, meso}*, 2.0 – 50 nm) and macropore (*V_{p, macro}*, 50 – 414 nm) regions were listed in Table 1. It was revealed that both SiO₂B and SiO₂B_{H2O} were mesopore-rich materials. This finding is consistent with the SEM image (Fig. 1). From these data, we have determined the *S.A.*, *D_p* and *V_{p, meso}* of SiO₂B were 70.7 m²/g, 36 nm, and 0.909 cm³/g, respectively.

Water vapor sorption isotherms were measured with Hydrosorb1000 (Quantachrome). The samples were previously heated in vacuum at 200 °C for more than 12 h. Water vapor sorption isotherms (25 °C) are shown in Fig. 4 and corresponding BET plots are shown in Fig. 4 inset. The adsorption capacity close to saturation was about 0.50 mmol/g for SiO₂B, while it was

more than 1.94 mmol/g for SiO₂BH₂O. For SiO₂BH₂O, the amount of water vapor increased gradually at $P/P_0 < 0.7$, and the amount adsorbed steeply increased at P/P_0 larger than 0.8. Such a steep increase can be attributed to the formation of water clusters as will discuss below. Also, substantial hysteresis was observed in the desorption branch of SiO₂BH₂O. The presence of hysteresis suggests an interaction between the adsorbent (SiO₂BH₂O) and water molecules.

The silica surface mainly consists of siloxane

bridges (Si-O-Si) and fewer silanol groups.[6,9] These surface siloxane bridges are hydrolyzed by adsorbed water molecules to form silanols, which are considered to cause the decrease in water molecules desorbed.

On the other hand, for SiO₂B, the amount of water vapor adsorption is limited; the water adsorption ability was lower than that of SiO₂BH₂O over the whole range of P/P_0 , and the steep increase at high P/P_0 was absent. The amount of water adsorbed at $P/P_0 = 0.99$ was less than one-fourth of that for SiO₂BH₂O. These findings demonstrated the hydrophobicity of SiO₂B as expected. The decrease in water adsorption property was also confirmed by the significant reduction of the hysteresis loop in the desorption branch. These data clearly shows the hydrophobic property of SiO₂B.

The surface property on water vapor sorption was evaluated using the BET plots (Fig. 4 inset). The amount of monolayer water adsorbed (w_m) can be estimated to be 2.94×10^{-3} and 5.12×10^{-3} (g(H₂O)/g(adsorbent)) for SiO₂B and SiO₂BH₂O, corresponding to 0.163 and 0.284 mmol/g, respectively (Table 1). The BET constant (C) of SiO₂B was slightly larger than that of SiO₂BH₂O, suggesting an interaction in this early stage. By using the surface area ($S.A.$) evaluated from N₂ sorption study (Table 1) and Avogadro's number (N_A), the number of water molecule per unit surface area (N_{water}) can be calculated from the following equation:

$$N_{\text{water}} = \frac{w_m \times N_A}{18.015 \times S.A.}$$

The N_{water} for SiO₂B and SiO₂BH₂O was 1.39 and 2.24 (molecules/nm²), respectively. Assuming the geometrical closest packing of H₂O molecules (0.125 nm²/molecule), corresponding to 8 molecules/nm², it seems that the surface coverage by water molecules was low.

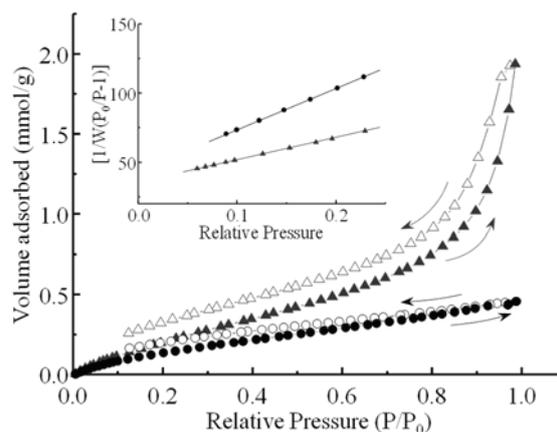


Fig. 4 Water vapor sorption isotherm of SiO₂B and SiO₂BH₂O. Inset; BET plots by water sorption. Symbols are circle for SiO₂B and triangle for SiO₂BH₂O, respectively.

The differential heat of water vapor adsorption was shown in Fig. 5. For SiO₂B, a high heat evolution (about 60 kJ/mol) was seen in the initial stage of water adsorption, and then it decreased to less than 44 kJ/mol, which is the heat of liquefaction of water [10], at the adsorption amount of 0.05 mmol/g. This large exothermic effect is probably due to the strong interaction between water and unreacted silanol groups (Si-OH), which were

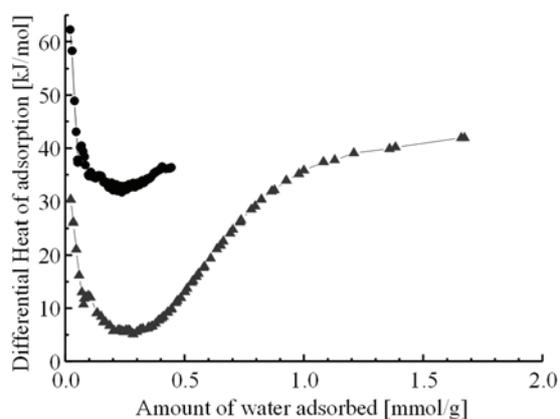


Fig. 5 Differential heat of adsorption of water vapor on (circle) SiO₂B and (triangle) SiO₂BH₂O.

left during the grafting of bulky trimethylsilane.[9,11,12] The heat of adsorption reached a minimum at around 0.2 - 0.3 mmol/g, which is close to the value of w_m (0.163). Then, the heat of adsorption slightly increased with an increase in the adsorption amount. However, the formation of water clusters was not detectable (below 44 kJ/mol), obviously preventing the additional adsorption of water molecules to grow the water clusters. On the other hand, for SiO₂BH₂O, the heat of adsorption was low at the initial stage, indicating less interaction between siloxane and water molecules and hence suggesting the hydrophobic character of the surface.[6,9] The minimum value of the heat of adsorption was observed at the adsorption amount of around 0.20 – 0.30 mmol/g, which is close to the w_m (0.284 mmol/g). Then, the released heat increased gradually as the adsorption proceeded, attaining about 44 kJ/mol at the adsorption amount of about 1.65 mmol/g. These findings support the idea that after formation of monolayers, additional water molecules coordinate to the water molecules to form water clusters in the pores. The hydrolysis of siloxane bonds to generate silanol groups probably takes place during water uptake, which may explain the large hysteresis in the desorption isotherm. An FT-IR study may help us obtain more detailed understanding of the hydrolysis process, but it would be out of the scope of this paper.

In conclusion, we have investigated the porosity and water vapor sorption properties of trimethylsilane grafted hydrophobic silica beads (SiO₂B), which we have chosen as a catalyst support for CECE reaction. The low water vapor sorption capacity and restricted interaction for water cluster formation of this SiO₂B demonstrated a desired feature for a catalyst support: prevention of pore blocking due to water condensation. Preparation and characterization of Pt-loaded catalysts and the CECE reaction activity of resultant catalysts will be reported elsewhere.

Acknowledgement

The authors thank to Fuji Silysia Chemical Ltd., Aichi, for their kindly supply of SiO₂ beads. This work is performed with the support and under the auspices of the NIFS Collaboration Research program (NIFS13KOBA029).

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