

Ultra-fine Tuning of Microporous Opening Size in Zeolite by CVD

Daling Lu,[†] Junko N. Kondo,[‡] Kazunari Domen,^{*,†,‡} Hosne A. Begum,^{§,||} and Miki Niwa[§]

Core Research for Evolutional Science and Technology, Japan Science and Technology Corporation, 2-1-13, Higashiueno, Taito-ku, Tokyo, 110-0015 Japan, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503 Japan, and Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-cho, Tottori, 680-8552 Japan

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The porous structure of a CVD (chemical vapor deposition) layer on silicalite zeolite was studied in detailed by TEM (transmission electron microscopy). The pore mouth of silicalite was suggested to be narrowed by CVD on the basis of the adsorption results, where the rate of 1-methylpentane adsorption decreased as the amount of CVD is increased, while that of the isomer, *n*-hexane, was not affected. The CVD layer was observed as amorphous in TEM images and distinguished from silicalite when the focus was adjusted so that zeolite pores were clearly observable. The CVD layer was found to uniformly cover all faces of crystals. The thickness of the CVD layer increased as more silicon alkoxide was deposited, and the observed thickness in TEM images was in agreement with that estimated from the amount of deposition. The lattice fringe pattern was observed continuing from silicalite to the edge of a particle through the CVD layer, which seemed amorphous at the just-focus point for the observation of zeolite pores. Therefore, one-dimensional channels were considered to exist in the CVD layer, and we suggest that the opening size of the micropore in the CVD layer can be tuned in the region of 0.1 nm, which is quite important on the shape-selectivity.

Introduction

The importance of nanotechnology has recently become apparent in many fields, and the ultra-fine tuning of catalyst structures at dimensions smaller than 0.1 nm has attracted the interest of many scientists and manufacturers. Zeolites are applied extensively in catalytic reactions, and offer shape-selectivity as an important feature that is used for molecular organization.^{1–4} However, the distribution of pore size in crystalline zeolite is usually discontinuous because the pore size is predominantly determined by the number of oxygen atoms in the pore rim. This makes it difficult to achieve a desired shape-selectivity for an as-synthesized zeolite. Chemical vapor deposition (CVD) of a silicon alkoxide such as Si(OCH₃)₄ is an effective method for tuning the pore-opening size of zeolite, and is a technique that is capable of controlling the pore size of zeolite at scales that allow accurate molecular separation. Barrer et al. first studied the silylation to control the pore size of zeolite by using SiH₄, which can penetrate into the pore of zeolite.⁵ Then, Niwa et al. adopted silicon alkoxide, such as Si(OCH₃)₄, in the CVD method.^{6,7} Because the silicon alkoxide is larger than the pore-opening of zeolite with an MFI structure, it only locates on the external surface of the zeolite to modify the size of the pore-opening. Bülow also utilized the silanation to alter the external surface structure of a 5A-zeolite crystal in order to change the sorption availability for hydrocarbon gases.⁸ The preparation method, characterization, and molecular shape-selectivity of the CVD zeolite in the early stage of the study are summarized in review articles.^{9,10} The pore size engineering

in zeolites was also extensively reviewed by Vansant, which comprises all kinds of measures to modify the external and/or internal surface of zeolite crystallites.¹¹ Hydroconversion of methylcyclohexane on HZSM-5 zeolite modified by tetraethoxysilane (TEOS) of CVD was studied very recently¹² in addition to the transformation of 1,2,4-trimethylbenzene on the CVD-modified HZSM-5 crystals.^{13,14} It should be added that Halgeri and Das modified zeolites with 16 wt % of CVD silica and used them for dealkylation and realkylation of ethylbenzene,¹⁵ toluene disproportionation,¹⁶ para-disubstituted aromatics.¹⁷ Some of these applications are commercialized by Indian Petrochemicals Corporation.¹⁸ A method similar to CVD, chemical liquid deposition (CLD), was recently developed to modify the external surface of zeolite, and the decrease of the pore mouth of zeolites in size was also reported.^{19–24}

Although the CVD-modified zeolites were investigated and applied on sorption and reaction, it has been unclear what kind of CVD silica layer is formed on the zeolite by this method. According to reactions and adsorption results, some authors proposed that a part of the pore mouth was blocked by the CVD silica, which results in longer diffusion pathways, and hence a higher tortuosity of the pore system.^{14,25,26} The present report shows for the first time that a homogeneous and amorphous CVD silica layer having a straight microporous channel structure is formed on the external surface of zeolite by this technique.

Experimental Section

The synthesis of sample⁹ and adsorption experiment²⁷ were described in detail elsewhere. Briefly, for preparing silicalite, an aqueous solution of Ludox HS40 colloidal silica and an aqueous solution of tetra-*n*-propylammonium bromide in H₂-SO₄ were added dropwise into an aqueous solution of sodium chloride followed by adjusting the pH of the solution to 10.3. The mixed solution was stirred and heated at 443 K for 24 h.

* Author to whom correspondence should be addressed. E-mail: kdomen@res.titech.ac.jp.

[†] Japan Science and Technology Corporation.

[‡] Tokyo Institute of Technology.

[§] Tottori University.

^{||} Present address: Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh.

The product was filtered, washed with deionized water, and dried overnight at 373 K. The solid product was at last calcined in air at 803 K for 3 h. The silicalite crystal was set in a quartz basket hung on a quartz spring, and $\text{Si}(\text{OCH}_3)_4$ was kept in a liquid reservoir. Before deposition of $\text{Si}(\text{OCH}_3)_4$, the silicalite was evacuated at 673 K for 2 h until no weight change was observed. The vapor of $\text{Si}(\text{OCH}_3)_4$ was admitted onto the crystal at 773 K. The vapor pressure was kept at ≈ 2.5 Torr by chilling the reservoir with an ice bath and the degree of evacuation was $\approx 10^{-3}$ Torr. The gas phase was then evacuated for removing the reaction product (methanol). This process was repeated several times, and then the material was calcined and oxidized by oxygen under 200 Torr at 673 K to remove carbonaceous residues. The system was evacuated and the weight gain of the material was measured in situ by a quartz microbalance.

The prepared CVD silicalite crystals were observed by a high-resolution field-emission transmission electron microscope (TEM) (JEM-2010F, JEOL) operating at 200 keV. Because the microporous structures of both silicalite and CVD silica are easily damaged by the electron beam during normal TEM observation,^{28,29} a television and camera system was employed to obtain a quite weak incident electron beam for observation. A digital photograph system attached to the JEM-2010F, in which the sensitivity of digital films is 10 times higher than that of normal TEM films, was used to obtain TEM images. The photographs were captured at 1/10 of the shutter time used for normal films.

Results and Discussion

Silicalite, an aluminum-free ZSM-5 zeolite having an MFI structure, is a hydrophobic crystalline silica molecular sieve with a pore size of 0.53–0.56 nm.³⁰ The structure of this silicalite is orthorhombic, and the straight channels are oriented parallel to the [010] direction. This zeolite has excellent adsorbing, catalyzing, and shape-selecting properties. An adsorption experiment using silicalite modified with CVD silica revealed that there is a negligible difference on the adsorption rate of linear hexane (cross-section: 0.36×0.48 nm) on silicalite with a different amount of CVD silica (Figure 1a). On the other hand, the adsorption rate of 2-methylpentane (cross-section: 0.51×0.57 nm) decreased remarkably with increasing the amount of deposited CVD silica (Figure 1b). This is obvious with the CVD silica at 2.7 wt %, at which the rate of adsorption of the branched alkane (2-methylpentane) was drastically restricted, while that of linear alkane (*n*-hexane) was identical with those on the silicalite free from the CVD silica. 2-Methylpropane and *n*-butane were also used in the adsorption experiment on the CVD silica-coated silicalite:²⁷ the adsorption rate of 2-methylpropane was reduced with increasing the amount of CVD silica, while that of *n*-butane was not affected by CVD. If a part of the pore mouths of the silicalite was plugged by the deposited CVD silica, the adsorption rate of linear alkanes should be also affected on the CVD-modified surface of silicalite. Our adsorption results showed a contradictory conclusion against the above hypothesis. That is, only branched alkanes are hindered in the adsorption process when the amount of CVD silica on zeolite increases, while linear alkanes are not. Therefore, it can be suggested that the pores are not plugged but the pore-opening size on the CVD silica layer should be gradually decreased as the silica layer becomes thicker.

Figure 2a is a TEM image of a silicalite crystal coated with 1.9 wt % CVD silica. The crystal was slightly tilted from the [010] direction. Figure 2b–i are the TEM images taken at the corresponding parts indicated by the black circles around the

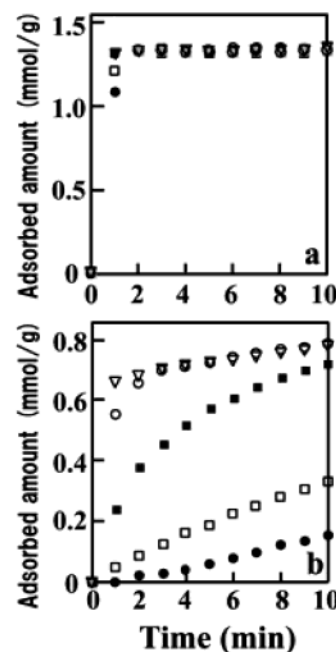


Figure 1. Adsorption of hexane (a) and 2-methylpentane (b) on CVD silica-coated silicalite with different amount of CVD silica. ∇ : 0 wt %, \circ : 0.75 wt %, \blacksquare : 1.3 wt %, \square : 1.9 wt %, \bullet : 2.7 wt %.

crystal shown in Figure 2a. The diagonal lines inside the particle are interference fringes of the silicalite crystal, and the outer parts correspond to the deposited layer of CVD silica. The CVD-silica layer was found to uniformly cover the surface of the silicalite crystal to a thickness of 5–8 nm on all faces of the crystal. We also observed the silicalite crystals covered uniformly with 2.7 wt % of CVD silica, and the thickness of the 2.7 wt % CVD silica layer was 6.5–10 nm. The measured thickness of the CVD silica layer from TEM images coincides with the estimated thickness from the deposited silica; 5.5 nm for 1.9 wt % silica, and 7.8 nm for 2.7 wt %.³¹

Figure 3a shows a CVDsilica-coated silicalite crystal observed along the [100] direction, which was determined by an electron diffraction pattern shown in the inset of Figure 3a. TEM images of Figure 3b–d are the magnified parts of this crystal, corresponding to the marked areas in Figure 3a. The boundary between the silicalite crystal and the CVD layer formed along the [001] and [010] directions can be seen clearly, and the ordered microporous structure of the silicalite crystal along the [100] direction can also be observed. The formation of the CVD layer on this crystal is consistent with above result, that is, the CVD silica layer uniformly grew on all faces of silicalite crystals. This phenomenon is different from the intergrowth of silica on zeolite in solution, in which silica preferentially nucleates and grows on (010) faces of the zeolite crystal.^{32–34}

We observed over one hundred silicalite crystals with different amounts of CVD silica and found that all faces of these crystals were covered by a homogeneous CVD layer and the thickness of CVD layer depends on the amount of CVD silica. Therefore, we can conclude that the CVD silica unselectively covers the all faces of the silicalite crystals and grows to a homogeneous film.

Figure 4a shows a silicalite crystal with a 1.9 wt % CVD silica layer, viewed along the [100] direction, with an electron diffraction pattern in inset. Figure 4b is a magnification of the upper left corner of the crystal in Figure 4a. Figure 4b shows that the silicalite crystal has a clear pore structure (TEM set to “just-focus”), whereas no crystal structure can be seen in the CVD silica layer. However, as shown in Figure 4c, if the focus

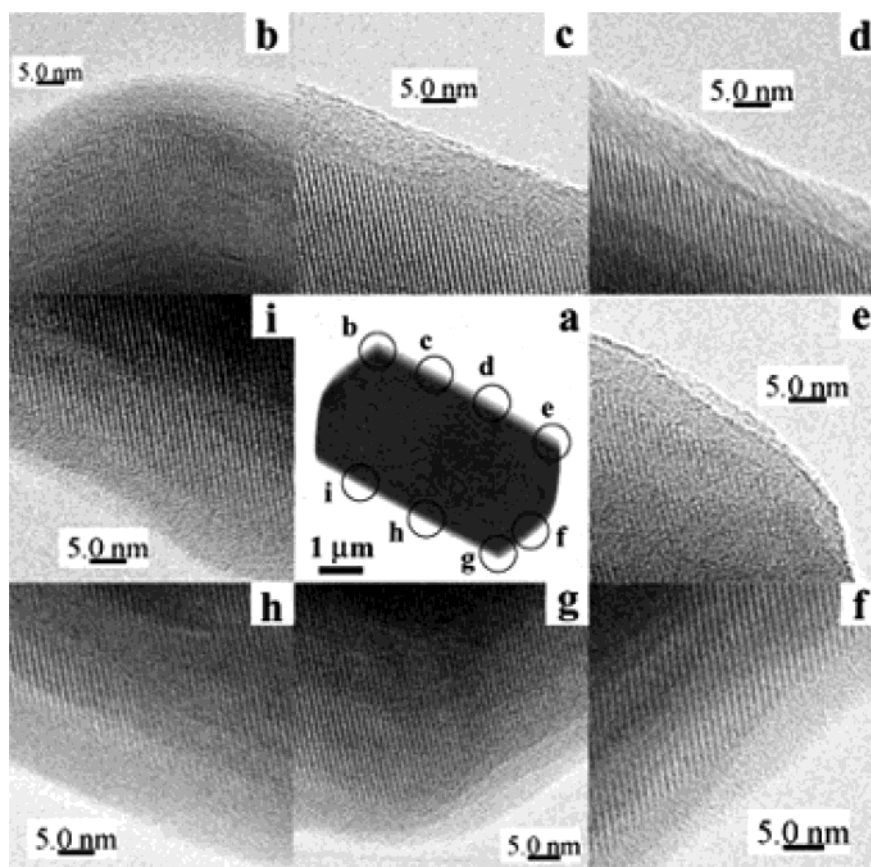


Figure 2. (a) 1.9 wt % CVD silica-coated silicalite crystal; (b–i) are enlarged sections of corresponding areas in (a).

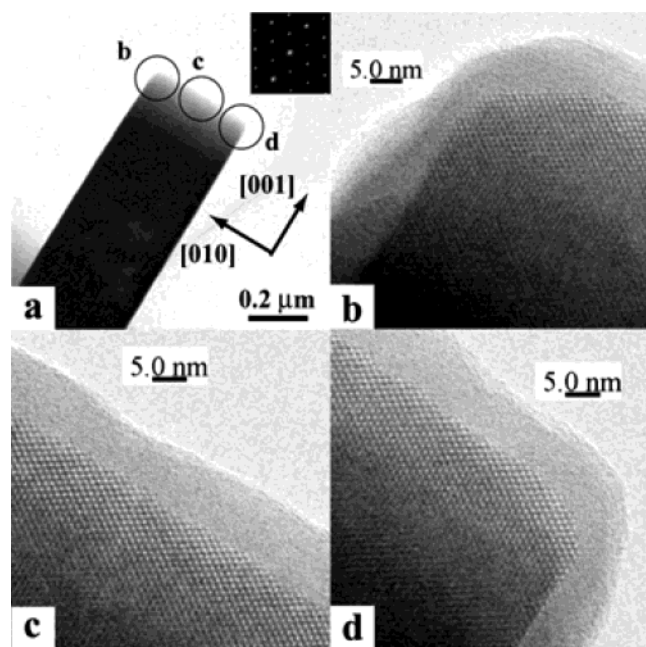


Figure 3. (a) 1.9 wt % CVD silica-coated silicalite crystal viewed along the [100] direction with diffraction pattern inset; (b–d) are enlarged sections of corresponding areas in (a).

is changed slightly from the just-focus point at the same position, the pore image in Figure 4b becomes an interference fringe image, and the fringes stretch into the CVD layer, which grew in parallel to the [001] direction. Figure 4d is a TEM image of the upper right corner of the crystal in Figure 4a, and the focus in this image is also varied slightly from the just-focus. The CVD silica layer on the (010) face of the crystal has no apparent crystal structure with a clear demarcation, and can be regarded

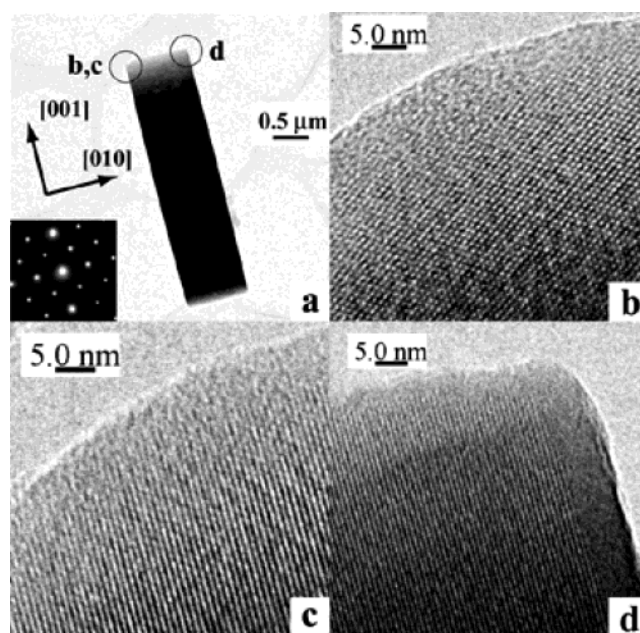


Figure 4. (a) 1.9 wt % CVD silica-coated silicalite crystal viewed along the [100] direction, with diffraction pattern inset. (b) Enlarged section of upper left corner of crystal in (a). (c) Same position as in (b) but with slightly different focus. (d) Enlarged section of upper right corner of crystal in (a).

as amorphous. However, the extension of the fringes along the [001] direction from the inner silicalite to the edge of the crystal indicates the presence of an ordered structure in the CVD layer that extends continuously from the silicalite. The same phenomenon was also observed on both (100) and (010) faces of the CVD silica-coated silicalite crystals.

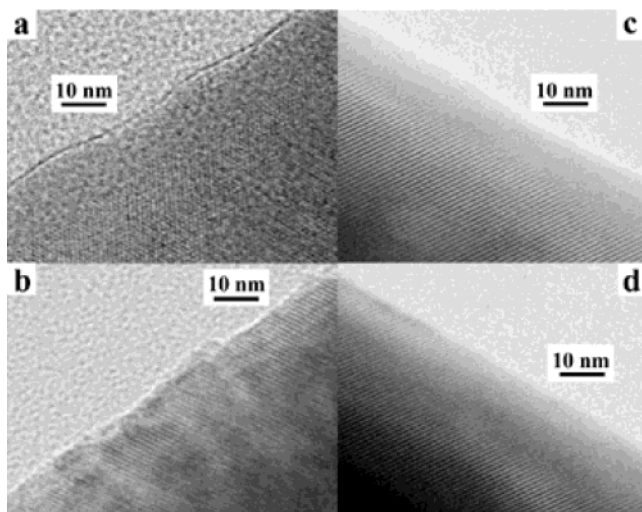


Figure 5. (a) A TEM image of a CVD silica-coated silicalite crystal observed under just-focus. (b) The same crystal of (a), but the focus deviated from the just-focus. (c) Another CVD silica-coated silicalite crystal under just-focus. (d) The same crystal of (c), but the focus varied from the just-focus.

In Figure 5 we represent two other silicalite crystals covered with the CVD silica layer. When the crystals were observed under just-focus condition, only the interference fringe images inside the silicalite crystals are quite clear, and there is nothing to be seen in the CVD silica layer (Figure 5a and 5c). However, if the focus deviates from the just-focus, the interference fringe images inside the crystals became slightly unclear, but they stretched into the CVD silica layer (Figure 5b and 5d). The interference fringes in the CVD layer are parallel to those inside the crystal, and they were continuously observed in the CVD layer. This phenomenon is the same as that shown in Figure 4. In other words, it can be explained that one-dimensional channel structure of micropores are formed in the CVD silica layer and that these micropores link to those micropores inside the silicalite crystals. Consequently, the adsorbent molecules can enter the micropores of silicalite through the channels in the CVD silica layer.

In the TEM images, where zeolite pores are clearly visible, the CVD layer is always observed to be free from any structural regularity, indicating that the CVD layer is essentially amorphous, and is not epitaxially grown. This is quite natural because there is no force that would drive the CVD layer to form the same three-dimensionally ordered porous structure that exists in the MFI zeolite. As indicated by the absorption results, the mouths of the zeolite pores are not closed but continue from the silicalite through the CVD layer, despite the homogeneity of the CVD coating. Therefore, zeolite pores run through the CVD layer, gradually decreasing in pore size as the thickness of the CVD layer increases. This is clearly evidenced by the observation of the continuous lattice fringe pattern from the silicalite to the CVD layer on the face orthogonal to the fringe direction (Figures 4 and 5). Therefore, straight channels, which extend from and parallel to microporous channels in the silicalite, spread through the CVD layer without a supporting two-dimensional orthogonal network.

Because the CVD layer is formed by the reaction between $\text{Si}(\text{OCH}_3)_4$ molecules and the surface silanol groups on silicalite, no layer would be accumulated on the micropores, where silanol groups are absent. In addition, the diameter of $\text{Si}(\text{OCH}_3)_4$ that is larger than the pore mouth of silicalite (MFI structure) prevents the incorporation of $\text{Si}(\text{OCH}_3)_4$ molecules inside the silicalite particle. As a result, the micropores extend from silicalite crystals through the CVD layer. We can deduce that the deposited silica has the structure, similar to but different from the MFI structure, in which, for example, a one-dimensional array of pore exists; due to the structure, the adsorption of larger hydrocarbon is suppressed to enhance the selectivity in the adsorption. However, the clear interpretation for the decrease in pore size in accordance with the increase in thickness of CVD layer is not given at present.

A schematic model of the straight channel structure in the CVD layer on the (010) surface of the silicalite crystal is shown in Figure 6. The straight channels in the CVD layer, orthogonal to the (010) surfaces of the crystal, become gradually narrower from the bottom upward. The opening size of the channels is smaller than that of the original micropores in the silicalite, as

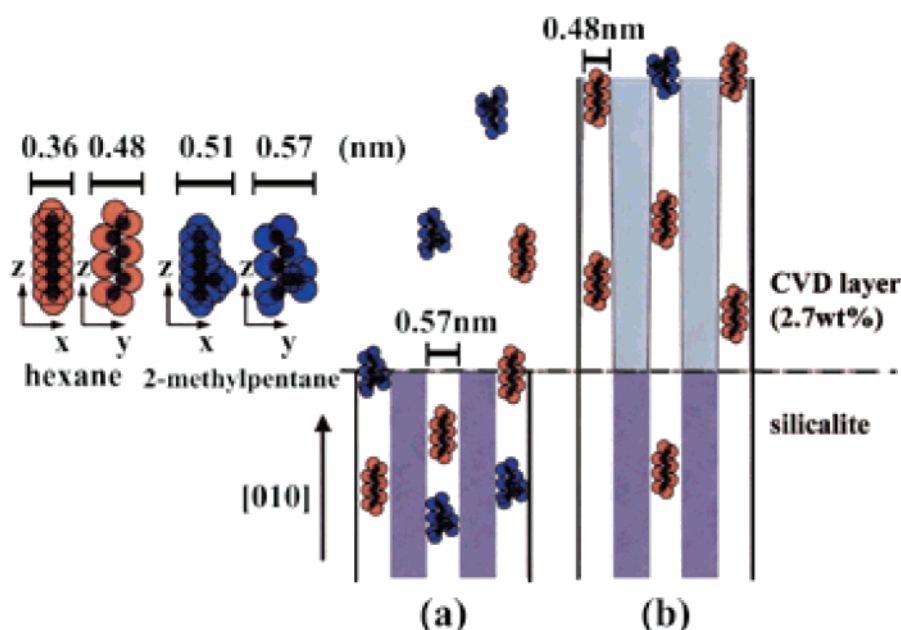


Figure 6. Schematic diagram of linear hexane and 2-methylpentane molecules entering micropores of silicalite (a) and CVD silica-coated silicalite (b). After the thickness of the CVD layer exceeds a limiting size, the pore-opening size of micropores in the CVD layer becomes too small to allow molecules larger than 2-methylpentane into the micropores.

found in the adsorption experiments (Figure 1). The molecules of linear hexane can enter freely into the silicalite either with or without the deposited CVD silica layer. However, 2-methylpentane molecules can enter into the micropores of CVD-free silicalite, but the rate of adsorption is gradually suppressed as the CVD layer becomes thicker.

Generally, it is quite difficult to tune the pore-opening size of zeolite in the range of 10^{-11} m, even though tuning at this level is necessary for separating molecules. The CVD method is commonly used for this purpose to prepare membranes and epitaxial layers. The reason for the availability of tuning of the pore-opening size below 0.1 nm (1 nm of CVD silica on silicalite reduces the micropore mouth of silicalite by 0.012 nm)³⁵ is clarified with the fine structure observed in this study.

Conclusion

We found for the first time by using TEM that there is a one-dimensional channel structure of micropore existing in the CVD silica layer formed on the surface of silicalite crystal. The micropores in the CVD silica layer are parallel to those micropores inside the silicalite crystal, and they continuously stretch from inside of the silicalite through the CVD layer to the opening mouth on the surface of CVD layer. Thus, adsorbent molecules can enter the micropores inside of silicalite from outside. The adsorption results support the finding that the size of the opening mouth is gradually decreased, not plugged, when the amount of CVD silica increases.

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References and Notes

- (1) *Catalysis and Zeolites: Fundamentals and Applications*; Weitkamp, J., Puppe, L., Eds.; Springer-Verlag: Berlin Heidelberg, 1999.
- (2) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304.
- (3) Davis, M. E. *Nature* **2002**, *417*, 813.
- (4) Corma, A.; Diaz-Cabanas, M. J.; Martinez-Triguero, J.; Rey, F.; Rius, J. *Nature* **2002**, *418*, 514.
- (5) Barrer, R. M.; Vansant, E. F.; Peeters, G. *J. Chem. Soc., Faraday I* **1978**, *74*, 1871.
- (6) Niwa, M.; Itoh, H.; Kato, S.; Hattori, T.; Murakami, Y. *J. Chem. Soc. Chem. Commun.* **1982**, 819.
- (7) Hibino, T.; Niwa, M.; Murakami, Y. *J. Catal.* **1991**, *128*, 551.
- (8) Bülow, M. *Z. Chem.* **1985**, *25*, 81–88.
- (9) Niwa, M.; Murakami, Y. *J. Phys. Chem. Solids* **1989**, *50*, 487.
- (10) Murakami, Y. *Stud. Surf. Sci. Catal.* **1989**, *44*, 177.
- (11) Vansant, E. F. *Pore size engineering in zeolites*; John Wiley: Chichester, 1990.
- (12) Berger, C.; Raichle, A.; Rakoczy, R. A.; Traa, Y.; Weitkamp, J. *Microporous Mesoporous Mater.* **2003**, *59*, 1.

- (13) Röger, H. P.; Möller, K. P.; O'Connor, C. T. *Microporous Mater.* **1997**, *8*, 151.
- (14) Röger, H. P.; Kräner, M.; Möller, K. P.; O'Connor, C. T. *Microporous Mesoporous Mater.* **1998**, *21*, 607.
- (15) Das, J.; Bhat, Y. S.; Halgeri, A. B. *Ind. Eng. Chem. Res.* **1993**, *32*, 2525.
- (16) Das, J.; Bhat, Y. S.; Halgeri, A. B. *Ind. Eng. Chem. Res.* **1994**, *33*, 246.
- (17) Halgeri, A. B.; Das, J. *Catal. Today* **2002**, *73*, 65.
- (18) Das, J.; Halgeri, A. B. *Catal. Surveys Asia* **2003**, *7*, 3.
- (19) Yue, Y. H.; Tang, Y.; Liu, Y.; Gao, Z. *Ind. Eng. Chem. Res.* **1996**, *35*, 430.
- (20) Weber, R. W.; Möller, K. P.; Unger, M.; O'Connor, C. T. *Microporous Mesoporous Mater.* **1998**, *23*, 179.
- (21) Weber, R. W.; Möller, K. P.; O'Connor, C. T. *Microporous Mesoporous Mater.* **2000**, *35–36*, 533.
- (22) Zheng, S.; Heydenrych, H. R.; Röger, H. P.; Jentys, A.; Lercher, J. A. *Stud. Surf. Sci. Catal.* **2001**, *135*, 1772.
- (23) Guo, H. C.; Wang, X. S.; Wang, G. R. *Stud. Surf. Sci. Catal.* **2001**, *135*, 4550.
- (24) Zheng, S.; Heydenrych, H. R.; Röger, H. P.; Jentys, A.; Lercher, J. A. *Top. Catal.* **2003**, *22*, 101.
- (25) Röger, H. P.; Manstein, H.; Böhringer, W.; Möller, K. P.; O'Connor, C. T. *Stud. Surf. Sci. Catal.* **2001**, *135*, 1602.
- (26) O'Connor, C. T.; Möller, K. P.; Manstein, H. *J. Mol. Catal. A: Chem.* **2002**, *181*, 15.
- (27) Begum, H. A.; Katada, N.; Niwa, M. *Microporous Mesoporous Mater.* **2001**, *46*, 13.
- (28) Treacy, M. M. J.; Newsam, J. M. *Ultramicroscopy* **1987**, *23*, 411.
- (29) Csencsits, R.; Gronsky, R. *Ultramicroscopy* **1987**, *23*, 421.
- (30) Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature* **1978**, *271*, 512.
- (31) The thickness (D) of the CVD silica layer deposited on the surface of a silicalite crystal was estimated using the following formula. D (nm) = $(N/SD) \times L$ where SD is the cation site density of zeolite ($SD = 8.61$ Si atom/nm²),³² L (= 0.32 nm) is the distance between neighboring silicon atoms in an SiO₂ crystal, and N is the surface concentration of deposited silica. N is obtained from the expression N (Si atom/nm²) = $[(W/100) \times A]/(M \times ES)$ $\div 10^{18}$ where W (wt %) is the amount of deposited silica, A is Avogadro's number, M (g/mol) is the molecular weight, it is 60 for SiO₂ in this case, and ES is the external surface area ($ES = 1.3$ m²/g).²⁷
- (32) Barrer, R. M. *Zeolite and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, 1978; p 289.
- (33) Feoktistova, N. N.; Zhdanov, S. P.; Lutz, W.; Bülow, M. *Zeolites* **1989**, *9*, 136.
- (34) Hay, D. G.; Jaeger, H.; Wilshier, K. G. *Zeolites* **1990**, *10*, 571.
- (35) Estimation of the CVD efficiency for controlling the pore opening size should be based on the kinetic diameters of both the adsorbing molecules (linear hexane and 2-methylpentane) and the micropore size in the CVD layers of the silicalite. However, the latter has not been reported. Molecules of size similar to that of the pores in zeolite, which cannot infiltrate the pores at room temperature, may enter the pores at higher temperatures. The vibrational excitation of the breathing mode (one of the Si–O stretching vibrations) of the pore mouths of zeolites is therefore regarded as an important factor for determining the adsorption behavior of molecules, in addition to the dynamic behavior of molecules. Therefore, the well-known static size, i.e., the van der Waals radii, are used in this study. The cross-section of 2-methylpentane (0.57 nm) is 0.09 nm larger than that of linear hexane (0.48 nm). Hence, the pore mouth closes by 0.09 nm on a rough assumption that both linear hexane and 2-methylpentane can migrate into micropores of bare silicalite, while only the former can enter the pores when 2.7 wt % of CVD silica is deposited. Considering that the thickness of the 2.7 wt % CVD layer is estimated to be 7.8 nm (7.5 ± 1.5 nm observed), 1 nm CVD deposition on silicalite reduces the pore mouth of the silicalite by 0.012 nm (0.009–0.013 nm).