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Selected Paper

Shape-Selective Adsorption of Substituted Benzaldehyde Isomers by a Molecular Sieving Silica Overlayer Prepared by the Chemical Vapor Deposition Method Using Organic Template on Tin Oxide

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The chemical vapor deposition of a silica overlayer in the presence of template molecules was examined on tin oxide in order to construct surface cavities with a molecular sieving property. On a SiO_2/SnO_2 sample prepared using a benzaldehyde template, 4-chlorobenzaldehyde and 4-methylbenzaldehyde were adsorbed, while 2-chlorobenzaldehyde and 2-methylbenzaldehyde were not adsorbed. The adsorption of 3-chlorobenzaldehyde was controlled by the thickness of the layer, i.e., the depth of the cavity. It was adsorbed by a shallow cavity, but not by a deep cavity. Thus the shape selectivity due to the shapes of the adsorbate molecule and the cavity was obtained.

The precise design of a reaction field on a solid surface is one of the important targets of modern chemistry. For this purpose, a molecular imprinting technique has been developed mainly on organic polymers[1] and on inorganic solids using organic modifiers,[2–6] while attempts on purely inorganic metal oxide surfaces have been relatively few.[7–14] We have proposed a method of chemical vapor deposition (CVD) of tetramethoxysilane [$Si(OCH_3)_4$] using a molecular template on tin oxide. As postulated in Fig. 1, aldehyde (e.g., benzaldehyde) is adsorbed as a template (B) on the tin oxide surface (A). The surface density of the template should be adjusted so as to remain a part of the surface for the deposition of silica. Then, CVD of tetramethoxysilane is carried out to cover the surface (C). The template is removed by a reaction with ammonia to form nitrile (this step can be omitted). Finally, the organic residue is removed by calcination in oxygen to form surface cavities (D).[12,15] On the thus-modified surface, the adsorption capacities of aldehyde compounds with different molecular sizes were measured to evaluate the size of formed cavities. However, the selectivity for the adsorption, e.g., the ratio of the adsorption capacities of benzaldehyde (BA, template itself)/1-naphthaldehyde (1-NA, larger molecule), was low at first.[12] The reason was that the formed silica layer possessed dense silanol (SiOH) groups, indicating the presence of many cracks on the atomic scale. Recently, this method was significantly improved by the introduction of acetic acid during CVD. The SiO_2/SnO_2 prepared in the presence of BA template and acetic acid adsorbed the template aldehyde, itself (BA), at a high density, while the adsorption of a larger molecule (1-NA) was almost completely prohibited.[16] A highly dense silica layer consisting of a well-developed siloxane (SiOSi) network was suggested to be formed via acid-catalyzed oligomerization of silicon alkoxides,[17] giving high selectivity to distinguish between the benzene ring and the naphthalene ring of the tested adsorbates. Here, we applied the thus-obtained SiO_2/SnO_2 to the selective adsorption of substituted benzaldehyde isomers, mainly, chlorobenzaldehyde (CBA) isomers, in which the molecular sizes are same, but the shapes are different.

Experimental

Sample Preparation.[16] Tin oxide (0.1 g, prepared by the hydrolysis of $SnCl_2 \cdot 2H_2O$, followed by calcination in air at 773 K; surface area, 20 $m^2\,g^{-1}$) was set in a Pyrex tube (4 mm i.d.) and pretreated in an oxygen flow (50 $cm^3\,min^{-1}$) at 673 K for 1 h. Then, aldehyde (1 mm^3 as liquid) was repeatedly injected in a helium flow (50 $cm^3\,min^{-1}$) that had been purified by passing a liquid nitrogen trap. The eluted aldehyde was analyzed using a gas chromatograph (GC) with a flame ionization detector (FID) connected with the outlet of the reactor. The temperature was 423 and 313 K for the adsorption of BA and 1-NA, respectively; the adsorption density can be controlled by the temperature, and these temperatures were selected to result in covering the surface partly based on preliminary experiments.[15] The injections of aldehyde were repeated at least 7 times until the adsorption was saturated. The temperature was then adjusted to 473 K, and tetramethoxysilane (1 mm^3 as liquid) was repeatedly injected. By the first several injections, deposition of the silicon compound was observed, but the deposition rate gradually decreased with the repetition of injections. The injections were repeated at least 7 times until no deposition was observed. Then, 5 mm^3 of an aqueous solution of acetic acid (50 mol %) was 5 times repeatedly injected, and the injection of tetramethoxysilane was again carried out. The amount of silica was adjusted by varying the number of injections. Subsequently, ammonia (10 cm^3) was repeatedly injected at 673 K in order to evolve the corresponding nitrile compound [benzonitrile and 1-naphthonitrile (1-cyanonaphthalene) for BA and 1-NA, re-

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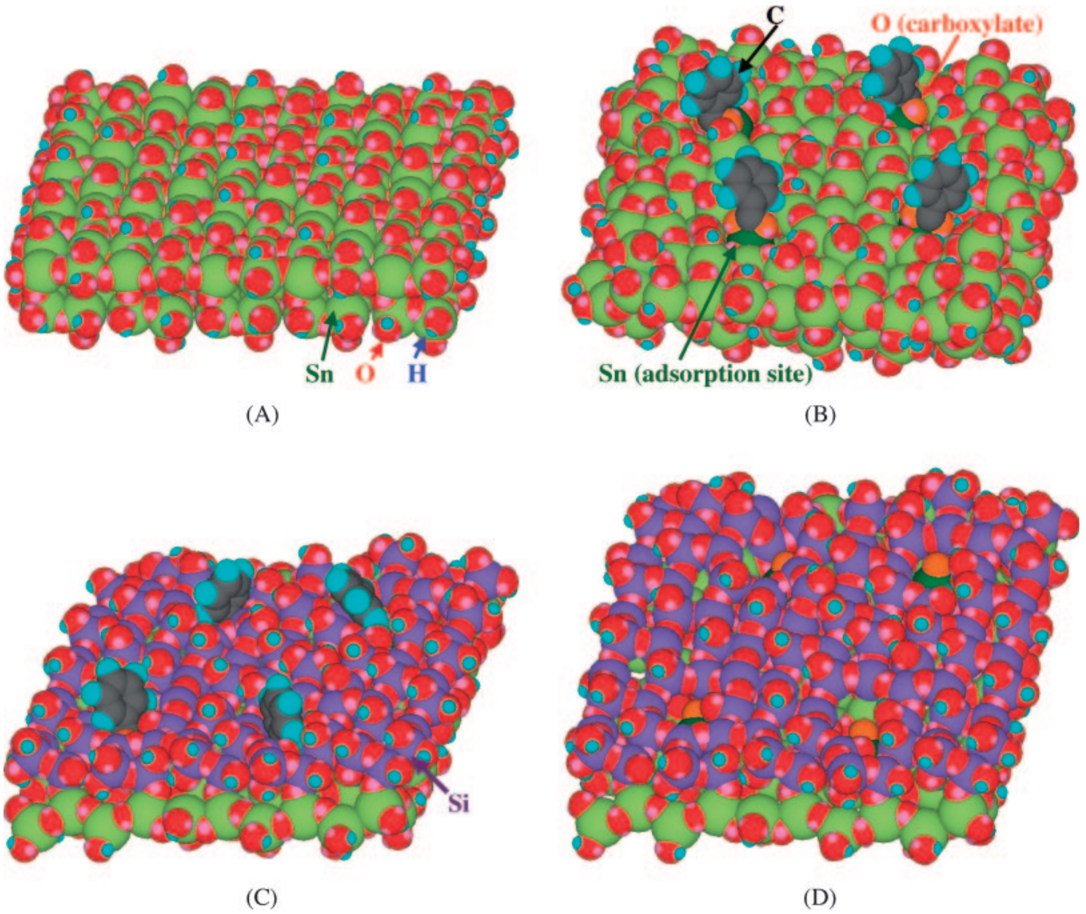


Fig. 1. Models of tin oxide surface (A, ca. 3.6 × 2.8 nm^2), adsorption of benzaldehyde (B, 0.4 molecules nm^{-2}), followed by CVD of silica (C, 9 Si atoms nm^{-2}), and cavities after removal of template (D) drawn by MM2 program.

spectively] by the reaction between the ammonia and the adsorbed template molecule.[18] Until no products were detected, the injections were repeated, and the amount of nitrile was quantified by the GC. The final calcination was carried out in an oxygen flow at 673 K for 1 h in order to remove all organic materials, namely, carboxylate anion, methoxy group of tetramethoxysilane, and hydrolysis reagent. The surface density of the deposited silica was calculated from the amount of eluted tetramethoxysilane, which was measured by the GC.

Adsorption Measurements. The physical adsorption capacity of nitrogen was measured at 77 K and $P/P_0 = 0.3$ after evacuation of the sample at 673 K for 1 h. The surface area was determined by the Brunauer–Emmett–Teller (BET) method.

Measurements of the chemisorption capacities for aldehydes [BA, 4-CBA (4-chlorobenzaldehyde), 3-CBA (3-chlorobenzaldehyde), 2-CBA (2-chlorobenzaldehyde), 4-TA (4-tolualdehyde, i.e., 4-methylbenzaldehyde), 2-TA (2-tolualdehyde), and 1-NA] on the thus-prepared SiO_2/SnO_2 were carried out by a pulse method.[12] After the pretreatment of 10 mg of the sample at 673 K in an oxygen flow (50 $\text{cm}^3\,\text{min}^{-1}$) for 1 h, aldehyde (1 mm^3 as liquid) was repeatedly injected at 573 K in a helium flow (50 $\text{cm}^3\,\text{min}^{-1}$) that had been purified by passing a liquid nitrogen trap. The injections of aldehyde were repeated with monitoring the eluted aldehyde by a GC connected to the outlet of the reactor at least 7 times until the adsorption was saturated; the amount of adsorbed aldehyde could be determined from the difference between the amounts of injected and detected (eluted) aldehyde, but the accuracy was not sufficient because most of the injected aldehyde was eluted. This was due to the small amount of used SiO_2/SnO_2 sample, limited by the experimental problem that only 0.1 g of the sample could be prepared by one experiment, as mentioned above. For accurate quantification, the reaction of carboxylate anion with ammonia was utilized as follows. After the adsorption of aldehyde, ammonia (10 cm^3) was repeatedly injected at 673 K, in order to evolve the corresponding nitrile compound.[18] Until no products were detected, the injections were repeated, and the amount of nitrile was quantified.

Model Drawing. Models of surface species were constructed using Chem3D software supported by an MM2 energy minimizing program.

Results

The total (BET) surface area of tin oxide (data not shown) was not changed by the modification, resulting in a surface area in the range of the experimental error (±1 $\text{m}^2\,\text{g}^{-1}$). Table 1 shows that all of the tested aldehyde compounds were adsorbed at 573 K on unmodified tin oxide (Entry 1). The adsorption capacities varied from 0.3 to 2.1 molecules nm^{-2}.

By the simple deposition of silica without a template (Entries 2 and 3), the adsorption capacities of all the tested aldehydes were decreased. At ca. 6 nm^{-2} of the Si atom density (Entry 2), the adsorption capacities of BA and CBA isomers were 0.2–0.4 nm^{-2}, while that of 1-NA was obviously low

Table 1. Adsorption Capacities of SiO_2/SnO_2 Samples Prepared Using Different Template Compounds

Entry	Template	Surface density of Si atom/nm^{-2}	Surface density of benzonitrile formed after CVD/nm^{-2}	Adsorption capacity/molecules nm^{-2}						
				BA	4-CBA	3-CBA	2-CBA	4-TA	2-TA	1-NA
1	no	0	—	2.1	0.64	1.3	0.28	1.5	0.23	1.1
2	no	5.7	—	0.40	0.32	0.32	0.21	*	*	0.06
3	no	34	—	0.01	<0.001	<0.001	<0.001	*	*	<0.001
4	BA	5.7	0.48	0.51	0.55	0.18	0.003	0.17	0.004	0.004
5	BA	10.5	0.30	0.26	0.064	0.18	*	*	*	*
6	BA	14.6	0.45	0.30	0.28	0.099	*	*	*	*
7	BA	17.4	0.1–0.3	0.31	0.11	<0.001	0.002	*	*	<0.001
8	1-NA	5.7	0.43	0.31	0.39	0.31	0.22	*	*	0.32

*: Not measured.

($0.06\ nm^{-2}$). By increasing silica up to $34\ nm^{-2}$ (Entry 3), the adsorption of aldehydes was almost completely prohibited ($<0.01\ nm^{-2}$).

In Entry 4, on samples prepared using the BA template, the density of cavities formed by the template molecules is speculated to be ca. $0.5\ nm^{-2}$, because the density of benzonitrile formed by the reaction with ammonia after the CVD, which should show the density of the template during the CVD, was ca. $0.5\ nm^{-2}$. BA, itself, was adsorbed on this sample with ca. $0.5\ nm^{-2}$ of the density after removal of the template. In Entries 5–7, the density of the cavities are estimated to be $0.1–0.5\ nm^{-2}$, or average $0.3\ nm^{-2}$, based on the density of the formed benzonitrile. BA was adsorbed on these samples (Entries 4–6) with $0.2–0.3\ nm^{-2}$ of the densities.

The adsorption capacity of 4-CBA was similar to, or lower ($0.06–0.6\ nm^{-2}$) than, those of BA in Entries 3–7. The adsorption capacity of 3-CBA in Entries 4 and 5 (ca. $0.2\ nm^{-2}$) was smaller than that of BA, decreased down to ca. $0.1\ nm^{-2}$ with a further increase of silica to 15 Si atoms nm^{-2} (Entry 6), and reached zero at 17 Si atoms nm^{-2} (Entry 7). The adsorption capacity of 4-TA was decreased by the deposition of silica at 6 Si atoms nm^{-2} (Entry 4), but it was still adsorbed in this entry (ca. $0.2\ nm^{-2}$).

The adsorption of 2-CBA, 2-TA, and 1-NA was completely prohibited by the deposition of silica at >6 Si atoms nm^{-2} (Entries 4–7).

In place of BA, 1-NA was utilized as the template in Entry 8. The density of formed 1-naphthonitrile after CVD, namely the estimated density of the cavities, was ca. 0.4 nm^{-2}. All of the BA, CBA isomers, and 1-NA were adsorbed on the thus-prepared SiO_2/SnO_2. The adsorption capacities ($0.2–0.4\ nm^{-2}$) were similar to the density of the cavities.

Discussion

Adsorption of Aldehydes on Tin Oxide. In Entry 1, the adsorption capacity of BA on tin oxide (2.1 molecules nm^{-2}) is consistent with the assumption that the surface was almost completely covered by molecules with benzene rings.[19] The capacity of 1-NA ($1.1\ nm^{-2}$) was also consistent with the assumption that the surface was almost completely covered by molecules with naphthalene rings.[19] However, the capacities of the CBA isomers ($0.3–1.3\ nm^{-2}$) were low, suggesting that the substitution of hydrogen by chlorine on the aromatic ring resulted in the weak adsorption of these compounds on tin oxide. Especially, the adsorption capacities of 4-CBA and 2-CBA were obviously low, suggesting a negative effect of chlorine substitution at the *para*- and *ortho*-positions on the chemisorption property. In addition, it is possible that the quite low capacity of 2-CBA was due to a steric hindrance between the chlorine atom at the *ortho*-position and the surface. The adsorption capacities of TA isomers were also lower than that of BA, and especially that of 2-TA was quite low. The latter was also ascribable to a steric hindrance caused by the methyl group at the *ortho*-position.

Here, we have to note another possible reason for the low capacities. We have confirmed by means of infrared (IR) spectroscopy that BA is adsorbed to form the benzoate anion on such basic metal oxides as alumina and tin oxide.[18] The formed anion is almost completely converted to benzonitrile by the reaction with ammonia at 673 K.[20] In addition, the surface density of adsorbed BA was consistent with the assumption that the species covered the surface, as described above. From these facts, we can conclude that BA covered the surface of tin oxide almost completely under the experimental conditions. However, the stoichiometric conversion of substituted benzoate anions formed from CBA and TA isomers has not been confirmed. It is possible that the amount of adsorbed CBA and TA isomers was higher than the observed amount of nitrile, but a fraction of them were not reacted with ammonia, and therefore not detected.

Therefore, it can be summarized that the adsorption and/or reactivity toward the reaction with ammonia of CBA and TA isomers was relatively weak compared to BA; this seems to be due to the chemical nature induced by chlorine or the methyl group. In addition, *ortho*-substitution caused the steric hindrance to decrease the adsorption capacity. An important conclusion for the following discussion concerning the generation of shape selectivity is, however, that all of the examined aldehydes were adsorbed on the tin oxide surface with considerably high densities ($>0.3\ nm^{-2}$).

Effect of Silica Deposition without a Template on the Adsorption Property. By simple deposition of silica without a template (Entries 2 and 3), which has been shown to form a silica overlayer homogeneously covering the surface,[21] the adsorption capacities of aldehydes were decreased, and finally diminished at 34 Si nm^{-2} (Entry 3). This indicates that the aldehydes were not adsorbed on the silica layer under the experimental conditions. Therefore, the adsorption capacities on the SiO_2/SnO_2 samples prepared using the template shown below should be ascribed to the uncovered surface of tin oxide.

In Entry 2 (6 Si atoms nm^{-2}), it is roughly estimated that half of the tin oxide surface was covered by silica, based on the surface density of Si (12 nm^{-2}) on a silica monolayer fully covering the surface.[22] In Entry 2, the adsorption capacity of BA (ca. 0.4 nm^{-2}) was only 1/5 of that on the unmodified tin oxide. This suggests that CVD without a template formed isolated islands of silica with cavities whose sizes were uncontrolled, and BA could not penetrate into some of the small cavities. The isolate structure and the prohibition of adsorption of BA by CVD of tetramethoxysilane without a template at <473 K have been found.[23] Only 1-NA showed a lower adsorption capacity, suggesting that the adsorption of this large molecule was more significantly affected by the isolated silica. However, the prohibition of 1-NA adsorption was not complete compared with the complete prohibition shown in Entry 4, as below, where the density of Si was the same as that in Entry 2, but a molecule (BA) smaller than 1-NA was utilized as the template.

Shape-Selective Adsorption Property of SiO_2/SnO_2 Prepared Using a Template at 6 Si atoms nm^{-2}. In Entry 4, on the sample prepared using the BA template, the density of cavities formed by the template molecules is estimated to be ca. 0.5 nm^{-2}. It seems that one cavity could adsorb one BA, namely the template, itself, because the adsorption capacity of BA was ca. 0.5 nm^{-2}.

The adsorption capacity of 4-CBA on this sample was also similar to the density of the cavity. This is consistent with the assumption that the aldehyde group of 4-CBA reacts with the surface, and therefore the substitution of hydrogen by chlorine at the *para*-position does not induce a steric hindrance around the adsorption site. The adsorption of 4-TA was also observed, although the adsorption capacity was lower than the density of the cavity.

The adsorption of 2-CBA, 2-TA, and 1-NA was negligible in Entry 4. Compared with the simple deposition of silica without a template (Entry 2), the effect of deposition with the BA template on the adsorption of these *ortho*-substituted aldehydes was clear. The complete prohibition for 1-NA adsorption has been reported.[16] Here, we emphasize that the present silica layer thus detected the substitution of hydrogen at the *ortho*-position by chlorine or a methyl group with high selectivity.

The selectivity should be principally due to the shape of the adsorbate molecule, but not by the chemical nature, because the adsorption of both 2-CBA and 2-TA was suppressed in spite of the difference of the substituted group. This selectivity was not observed on SiO_2/SnO_2 prepared using 1-NA template, namely a large molecule (Entry 8). In this entry, all of the examined aldehydes were adsorbed in similar capacities, suggesting that one cavity formed by the 1-NA template could adsorb one aldehyde molecule, and a steric hindrance did not occur because of the large size of cavity. From these observations, we can conclude that the clear shape selectivity for the chemisorption of aldehyde was generated by CVD of silica using the molecular template based on the shapes of the adsorbate and the formed cavity.

Change in Selectivity by Increasing Silica. The amount of silica was increased from Entry 4 to Entry 7 in the presence of the BA template. First we have to mention uncertainties observed in the density of the cavities (density of formed benzonitrile after the CVD) and the adsorption capacities of aldehydes, especially 4-CBA. The density of the cavities varied from 0.3 to 0.5 nm^{-2} with increasing silica from 6 to 15 Si atoms nm^{-2} (Entries 4–6). In Entry 7, experiments were repeated under the same conditions, but the density of the cavity varied from 0.1 to 0.3 nm^{-2}. As mentioned above, the BA template was adsorbed at a relatively low temperature (423 K) in order to disperse the template. We have shown that the density of benzoate anion on tin oxide at 423 K was ca. 1 nm^{-2}.[19] The density of the cavities (density of formed benzonitrile after CVD) was 0.1–0.5 nm^{-2}, indicating that a fraction of the benzoate anion was eliminated during CVD. Tetramethoxysilane, acetic acid, water (materials introduced during CVD), and methanol (formed during CVD by the reaction between tetramethoxysilane and surface hydroxyl group[17]) can react with the template to form such a volatile material as methylbenzoate. The decrease of the template during CVD was ascribable to these reactions, and the density of the cavities should be directly affected by the kinetics of these reactions. In the present study, the injections of tetramethoxysilane were repeated while monitoring the silicon density, in order to increase the amount of silica, as explained in the Experimental section. While other experimental variables were kept, as shown in Experimental section, the interval between injections was not controlled at high silicon density. This was because the required number of injections was huge (e.g., 80 times for Entry 7), and hence, it was practically impossible to maintain a constant time interval. Probably the variation of the time interval, i.e., the reaction time, affected the density of template during the CVD. The variation of adsorption capacity of 4-CBA, which complicatedly changed from 0.6 to 0.1 nm^{-2} at 6 to 17 Si atoms nm^{-2}, is also considered to be uncertainty ascribed to the experimental shortage. Throughout the study, the adsorption behavior could be affected by such a problem where the density of silicon was high. However, even taking account into these uncertainties, a clear change in the adsorption property with increasing silica was observed as follows.

The density of the cavities and the adsorption capacity of BA were generally similar throughout Entries 4–7, where silica was deposited in the presence of the BA template with increasing silica up to 17 Si atoms nm^{-2}. This similarity supports the above finding that one cavity could adsorb one molecule of the template, itself. Entry 6 exceptionally showed an adsorption capacity of BA lower than the density of the cavity. In addition to the uncertainty mentioned above, it is possible that a fraction of the cavity was blocked by the movement of atoms in the silica layer after removing the template. 4-CBA was also adsorbed, although the adsorption capacity was lower than that of BA in some cases.

The adsorption capacities of 3-CBA in Entries 4 and 5 were 0.18 nm^{-2}, smaller than that of BA; this is considered to be due to a weak adsorption property and/or a steric hindrance between the chlorine atom and the silica wall. However, it is obvious that the contribution of the steric hindrance was small in Entries 4 and 5, in which the density of Si atoms was 6–11 nm^{-2}; the adsorption capacity of 3-CBA decreased to 0.099

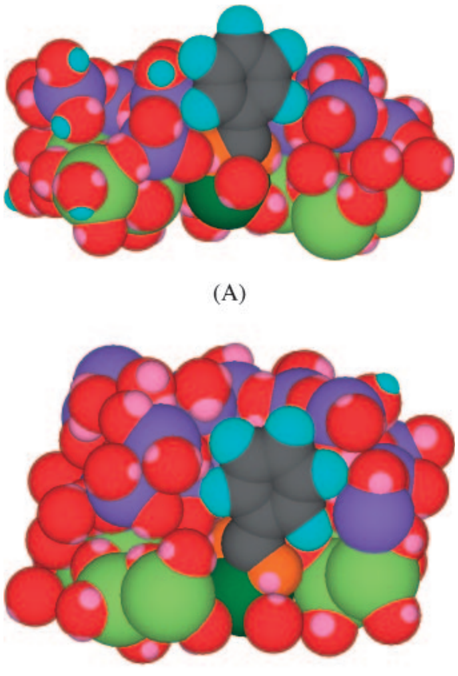
nm^{-2} with a further increase of silica to 15 Si atoms nm^{-2} (Entry 6), and reached zero at 17 Si atoms nm^{-2} (Entry 7). In Entry 7, a lack of adsorption ability for 2-CBA and 1-NA was confirmed. These results suggest that the adsorption of 2-CBA was strongly prohibited by the thin silica layer; 3-CBA with a chlorine atom at the *meta*-position could be adsorbed by the cavities in the silica layer with a small thickness, and increasing the thickness hindered the adsorption of 3-CBA; the adsorption of 4-CBA was possible, even after the thick layer was deposited.

Estimation of Thickness of Silica. Here, we speculate on the thickness of the silica layer on these samples. The density of template BA during CVD in Entry 4 was 0.5 molecules nm^{-2}, as above, while 2.1 molecules nm^{-2} of BA were adsorbed on pure tin oxide. It is considered that 24% (=0.5/2.1) of the surface was covered by the template, and the other 76% could be covered by silica. On the other hand, it has been found that the density of Si atoms in the silica monolayer fully covering the surface was ca. 12 nm^{-2}.[22] The silica monolayer covering 76% of the surface should have 9 nm^{-2} of Si atoms ($=12 \times 0.76$); hence, it is estimated that the sample in Entry 4 (ca. 6 Si atoms nm^{-2}) was covered by a silica monolayer covering most (2/3) of the surface. In Entries 5–7, the density of the template was ca. 0.3 molecules nm^{-2}. Therefore, 14% (=0.3/2.1) of the surface was covered by the template, and the other 86% could be covered by silica, where 10 Si atoms nm^{-2} ($=12 \times 0.86$) was the monolayer density. Therefore, the sample in Entry 5 (ca. 11 Si atoms nm^{-2}) should have a silica monolayer with controlled cavities.

Figure 1(B) shows a surface model of tin oxide adsorbing 0.4 nm^{-2} of BA, representing an image of the preparation step of these samples. Figure 1(C) shows an image of the surface after the CVD of silica with 9 Si atoms nm^{-2}. It can be seen that the cavities can exist individually, and a network of siloxane (SiOSi) can be deposited to form a monolayer roughly covering the surface. Figure 1(D) represents a model of $\mathrm{SiO_2/SnO_2}$, on which the densities of Si and the cavities are close to those in Entries 4 and 5. From Fig. 1(B), a cross-sectional view of the cavity and the template is cut and shown in Fig. 2(A). The silica wall is constructed to fit the van der Waals radii of the atoms in the benzoate anion.

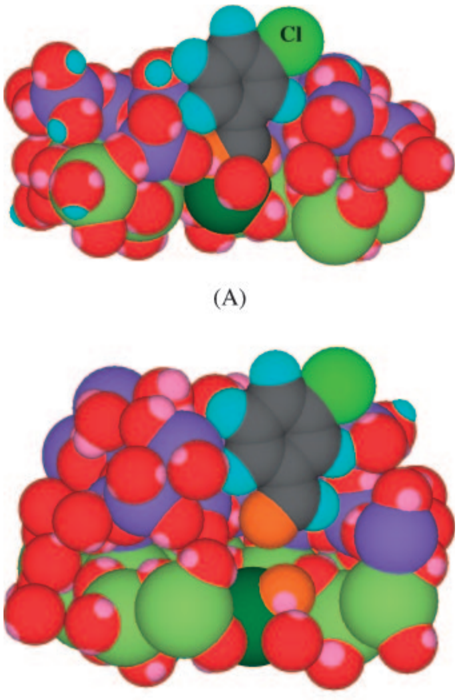
Entry 6 (ca. 15 Si atoms nm^{-2}) should show the effect of a 1.5 monolayer. The sample Entry 7 (ca. 17 Si atoms nm^{-2}) is estimated to be covered mainly by a doubly accumulated layer of silica. The model of the cavity and the template in Entry 7 with a doubly accumulated layer is shown in Fig. 2(B).

Therefore, it is concluded that 3-CBA was adsorbed on the samples covered by the silica monolayer with the cavities formed by the BA template (Entries 4 and 5). Figure 3(A) shows a model of a monolayer with cavities adsorbing 3-CBA, showing that the presence of chlorine at the *meta*-position does not induce a steric hindrance. The adsorption capacity of 3-CBA was decreased by increasing the thickness of silica from the mono- to double-layer. The adsorption was completely blocked by the double layer with the cavities (Entry 7). Figure 3(B) agrees well with the experimental observation; because of the presence of a chlorine atom at the *meta*-position, the aldehyde molecule could not penetrate into the deep cavity formed in the double-layer.


(A)

(B)

Fig. 2. Cross sectional view of formation of 1(A) and 2(B) layer of silica in the presence of BA template drawn by MM2 program.



(A)

(B)

Fig. 3. Cross sectional view of adsorption of 3-CBA on $\mathrm{SiO_2/SnO_2}$ shown in Fig. 2(A) and (B) drawn by MM2 program.

The adsorption of 2-CBA was almost completely diminished, even at ca. 6 Si atoms nm^{-2}, where the monolayer with the cavities was formed (Entry 4). Figure 4 indicates that the steric

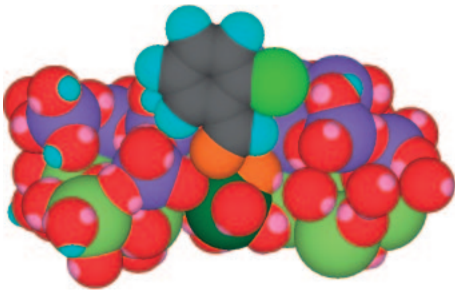


Fig. 4. Cross sectional view of adsorption of 2-CBA on SiO_2/SnO_2 shown in Fig. 2(A) drawn by MM2 program.

hindrance occurs between the wall of silica monolayer and the chlorine atom at the *ortho*-position. Also, the adsorption of 1-NA was almost completely suppressed in Entry 4, as already reported.[16]

Conclusion

On SiO_2/SnO_2 prepared by CVD using the BA template, the adsorption of BA and 4-CBA was not diminished. The adsorption of 3-CBA was completely suppressed by the formation of a double layer. The adsorption of 2-CBA, 2-TA, and 1-NA was almost completely blocked by the formation of a monolayer. These observations are in agreement with the assumption of a cavity whose shape was controlled by the template molecule. Thus, shape selectivity due to the shapes of the adsorbate molecule and the cavity was obtained. The presence and position of the chlorine atom was detected.

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