 

# Formation of Selective Adsorption Cavity by Chemical Vapor Deposition of Molecular Sieving Silica Overlayer on Alumina using Molecular Template in the Presence of Acetic Acid

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Chemical vapor deposition (CVD) of tetramethoxysilane was carried out on alumina after the pre-adsorption of aldehyde as the molecular template, in order to form a molecular-sieving silica overlayer with controlled cavities. The adsorption of a molecule (1-naphthaldehyde) larger than the template was almost completely suppressed when acetic acid was added during CVD, showing a high selectivity based upon the shapes of the controlled cavity and the adsorbed molecule, while the selectivity was low when acetic acid was not used. The infrared (IR) spectrum and nuclear magnetic resonance (NMR) of $^{29}$Si showed that the acetic acid enhanced the oligomerization of Si alkoxide via hydrolysis, probably by acid catalysis, resulting in the formation of a dense network of siloxane. Such a dense wall of silica is speculated to determine the shape of the adsorption cavity precisely, and to generate high selectivity.

The design and formation of reaction cavities on a solid surface with the size and shape controlled on the atomic dimension is one of the targets of modern chemistry. A molecular imprinting technique has been developed on organic polymers to construct an adsorption cavity using a molecule as a template.[1] On the other hand, some attempts have been made on inorganic metal oxide surfaces using silica,[2–8] because inorganic metal oxides have various functions, such as catalysis, semiconductivity, sensing function and selective adsorption properties. We have proposed a method of chemical vapor deposition (CVD) of tetramethoxysilane [$Si(OCH_3)_4$] using a molecular template on such basic metal oxides as alumina and tin oxide; we called the obtained material "molecular-sieving silica overlayer" (Fig. 1).[7,9] This strategy is based on the formation of a surface thin layer of silica with the thickness controlled on the atomic scale by the CVD[10] and strong chemisorption of such an aldehyde as benzaldehyde[11] on these basic surfaces. The obtained $SiO_2/SnO_2$ showed a chemisorption capacity,[12] a sensing property,[13] and oxidation catalysis[14] with specific selectivities probably based upon the shapes of the cavities and the reactant molecules.

However, these studies (the pioneering works[1–6] and ours[12–14]) could not achieve high selectivity, or could achieve it in very limited areas, and have not been developed well.[9] In our case, on a sample of $SiO_2/SnO_2$ prepared using benzaldehyde, the chemisorption properties of aldehydes with different sizes were measured in order to evaluate the shape selectivity; benzaldehyde was adsorbed well, while the adsorption of 1-naphthaldehyde, which was a larger molecule than the template, was suppressed. However, the degree of suppression

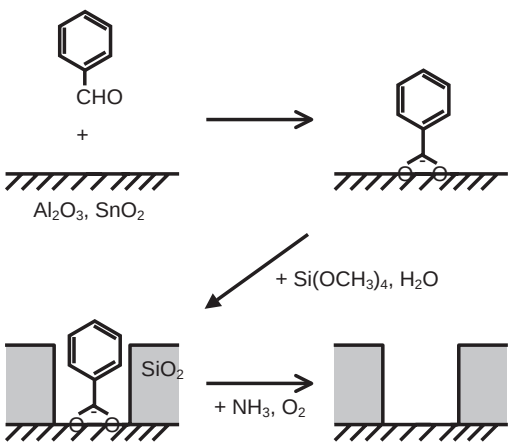


Fig. 1. Schematic drawing of CVD of silica using benzaldehyde as template.

was not high,[12] as shown in the following section. One possible reason for the low selectivity is the presence of micropores probably formed in the silica layer, because the hydrolysis of silicate precursors (sodium silicate,[2,3] silica gel surface,[4] or silicon alkoxide[6,12–14]), utilized in most of these studies, is known to form a microporous silica gel.

In order to overcome this disadvantage, we added a volatile acid (acetic acid) during the CVD process to enhance the oligomerization of Si alkoxide so as to develop a siloxane (SiOSi) network. The deposition rate was enhanced, and the yielded $SiO_2/SnO_2$ sample showed a high selectivity in the chemisorption of aldehydes; the adsorption of 1-naphthalde-

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hyde was almost completely suppressed.[15]

The purpose of the present study is to clarify the role of the added acetic acid. For this purpose, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) of $^{29}Si$ are promising tools. However, the application of these methods to $SiO_2/SnO_2$ is difficult, because both methods show a low sensitivity on the tin oxide-based material. For IR spectroscopy, tin oxide has a problem in that the transmittance for the IR beam is quite low. For NMR, the low Si content was a problem, because silica was deposited on the surface with a controlled density, and the surface area was low (only 20 $m^2 g^{-1}$). Therefore, we here utilized a $\gamma$-alumina support with a high IR transmittance and a high surface area (151 $m^2 g^{-1}$). The use of alumina as a support of the molecular-sieving silica overlayer has been reported.[16] In the present paper, we show the improvement in the chemisorption selectivity by the addition of acetic acid and spectroscopic findings on the $SiO_2/Al_2O_3$ samples.

## Experimental

**IR.** For an in situ observation of the CVD process, alumina (10 mg, JRC-ALO4, 151 $m^2 g^{-1}$, a reference catalyst supplied by Catalysis Society of Japan) was molded into a self-supporting disk (13 mm i.d.). It was evacuated in an in situ IR cell at 673 K for 1 h using a rotary pump, a diffusion pump and a liquid nitrogen trap; vapor of benzaldehyde (ca. 120 Pa) was admitted onto the disk at 323 K for 15 min; the adsorption temperature 323 K was chosen based on the previous study[16] to cover about 1/3–1/2 of the surface. After evacuation for 2 h, the introduction of tetramethoxysilane vapor (ca. 3 kPa, 5 min) and evacuation (20 min) were repeated 5 times at 523 K. The sample was then exposed to the vapor of a mixed liquid of acetic acid and water (1:1 in molar ratio, total pressure ca. 1.9 kPa) at 523 K for 5 min, followed by evacuation for 20 min. Again the introduction of benzaldehyde (ca. 120 Pa, 15 min) and evacuation (2 h) were carried out at 323 K, in order to avoid any loss of the template during these procedures. Further introduction of tetramethoxysilane (ca. 3 kPa, 5 min) and evacuation (20 min) were repeated 3 times at 523 K. During these procedures, the IR spectrum was collected by a Perkin Elmer Spectrum One spectrometer.

In order to analyze the microstructure of $SiO_2/Al_2O_3$ prepared by the following pulse method, about 10 mg of the sample was molded into a self-supporting disk, and evacuated at 673 K for 1 h. IR measurements were carried out as above. The spectrum in the OH stretching region (2000–4000 $cm^{-1}$) could be measured by this method, but the measurement in the skeletal region (<1200 $cm^{-1}$) was difficult because of a significant absorption by the SiO bonds. Therefore, the $SiO_2/Al_2O_3$ was crushed, mixed with KBr (1:20 in weight ratio), molded into a disk (total weight 10 mg) and measured in order to observe the spectrum in the skeletal vibration region.

**CVD by Pulse Method.** Alumina (0.1 g) was set in a Pyrex tube (4 mm i.d.) connected to a GC (gas chromatograph) with a column of silicone SE-30 (4 mm i.d., 2 m) operated at 313–373 K to analyze the reaction product. After pretreatment at 673 K for 1 h in a helium flow (50 $cm^3 min^{-1}$), purified by passing through a liquid nitrogen trap, a template material (benzaldehyde or 1-naphthaldehyde, 5 $mm^3$) was repeatedly injected at 323 K from an inlet with a septum installed before the reactor, followed by the injections of tetramethoxysilane (5 $mm^3$) at 523 K until the deposition was saturated, as described in the following section. An additional reagent (water or acetic acid/water with 1:1 molar ratio, 25 $mm^3$) was then repeatedly injected at 523 K until no hydrolysis product (methanol and/or dimethylether) was detected. Subsequently, ammonia (10 $cm^3$) was repeatedly injected to remove the adsorbed benzoate species as benzonitrile at 673 K until no product was detected. Finally, oxygen (50 $cm^3 min^{-1}$) was fed at 673 K for 1 h to remove the organic residue.

In most cases, the introduction of tetramethoxysilane was repeated until 6 Si atoms were deposited on 1 $nm^2$ of the surface area. On the assumption that half of the surface had been covered by the template, the uncovered surface should be blocked by silica at 6 Si atoms $nm^{-2}$, because the surface density of Si atoms on the silica monolayer was 12 $nm^{-2}$.[10] In some cases, the injection number was varied in order to study the effect of an increase of silica. On the other hand, some other samples were prepared without using a template as a comparison. In some cases, the introduction of tetramethoxysilane and the additional reagent was carried out at 423 K. The preparation conditions are summarized in Table 1.

**XPS.** In order to analyze the atomic composition on the surface, an X-ray photoelectron spectrum (XPS) was measured using a PHI Quantera SXM spectrometer. The sample was pasted onto a sticking tape, and the spectrum was collected at ambient temperature under 1487 eV of X-ray radiation from a source operated at 94 W. The molar ratio of Si/Al was calculated from the peak

Table 1. Adsorption Capacity of Aldehyde on $SiO_2/Al_2O_3$ Samples

| Entry | Template[a)] | Additional reagent[b)] | Deposition temperature/K | Amount of Si /atoms $nm^{-2}$ | Si/Al molar ratio on surface determined by XPS | Adsorption capacity/molecules $nm^{-2}$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | Benzaldehyde | 1-Naphthaldehyde |
| 1 | none | — | — | 0 | 0.00 | 2.3 | 1.0 |
| 2 | none | A | 523 | 12 | 0.30 | 0.02 | <0.001 |
| 3 | B | W | 523 | 6 | 0.13 | 0.45 | 0.06 |
| 4 | B | A | 523 | 6 | 0.11 | 0.76 | 0.02 |
| 5 | B | A | 523 | 6 | 0.12 | 1.0 | 0.02 |
| 6 | B | A | 423 | 6 | | 0.43 | 0.13 |
| 7 | B | A | 523 | 25[c)] | 0.20 | 1.0 | <0.001 |
| 8 | N | A | 523 | 6 | | 0.94 | 0.13 |
| 9 | N | A | 523 | 25[c)] | | 1.1 | 0.21 |

a) B = benzaldehyde, N = 1-naphthaldehyde. b) A = acetic acid + water, W = water. c) The amount of silica was estimated by extrapolation of the relationship against the pulse number at <6 Si $nm^{-2}$.

intensities at 103 and 75 eV ($Si_{2p}$ and $Al_{2p}$, respectively) while taking into account the cross-sectional areas of these orbitals.[17]

**$^{29}$Si NMR.** An NMR spectrum was collected in a single-pulse mode by a JEOL JNM-ECP 300 spectrometer (magnetic field of 7 T and 59.7 MHz, spinning rate of 4 kHz, the 40° pulse width of 4.0 μs, and sampling interval of 15 s). About 20000 integrations were required to detect the signal; the signal/noise ratio was quite low, probably because of the serious quadrupolar nature of Al, so it is noteworthy that the conditions were not optimized. The chemical shift was shown with polydimethylsilane as a reference at 34 ppm.

**Chemisorption Measurements by Pulse Method.** A $SiO_2/Al_2O_3$ sample (15 mg) was packed into a Pyrex tube (4 mm i.d.) connected with a GC. After a pretreatment in an oxygen flow (50 $cm^3\,min^{-1}$) at 673 K for 1 h, aldehyde (1 $mm^3$, benzaldehyde or 1-naphthaldehyde) was repeatedly injected at 573 K. The eluted aldehyde was quantified by GC. After saturation of adsorption was observed, ammonia was repeatedly injected at 673 K to form the corresponding nitrile (benzonitrile or 1-naphthonitrile). The injections of ammonia were repeated until no product was observed. We assumed that all of the adsorbed carboxylate anion was converted into nitrile on the basis of a previous study,[11] so the chemisorption capacity is shown by the amount of the formed nitrile.

## Results and Discussion

**In situ IR Observation of CVD Process.** The IR spectrum of support alumina after evacuation at 673 K is shown in Fig. 2(a). In the hydroxyl region (A), bands ascribed to AlOH groups with different environments[18] were observed at 3765, 3720, 3680, and 3600 $cm^{-1}$, and a broad absorption ascribed to the AlO vibration was observed at $<1200$ $cm^{-1}$. The AlOH bands were modified by the adsorption of benzaldehyde. After the adsorption of benzaldehyde, the benzoate anion was identified by the following bands: 3072 (CH on an aromatic ring), 1603, 1501, 1456 (CC in a substituted aromatic ring), 1555, and 1439 $cm^{-1}$ (CO in carboxylate species). A band ascribed to CO of free carbonyl groups, probably in physically adsorbed benzaldehyde, was also observed at 1654 $cm^{-1}$, but disappeared after the deposition of tetramethoxysilane (c). The formation of surface silicon alkoxide by the deposition of tetramethoxysilane was shown by new bands at 2955, 2854 (CH in methoxy groups), and 1000–1200 $cm^{-1}$ (SiOAl and SiOSi). These spectra are in agreement with our previous paper.[16] Then, a mixture of acetic acid and water vapor was introduced (d), resulting in a decrease of methoxy groups (2955 and 2854 $cm^{-1}$) and the generation of acetate anions (1580 and 1480 $cm^{-1}$ ascribed to CO in acetate species). A small shoulder due to the CO vibration in physically adsorbed acetic acid was also observed at 1714 $cm^{-1}$; it was diminished by a further introduction of tetramethoxysilane (e). When tetramethoxysilane was introduced again, benzoate anions (3072, 1603, 1555, 1501, 1456, and 1439 $cm^{-1}$), acetate anions (1580 and 1480 $cm^{-1}$) and silicon alkoxide (2955 and 2854 $cm^{-1}$) were observed. Thus, the co-existence of benzoate anion (template), silicon alkoxide (deposit) and acetate anion (additional reagent) was found.

**Deposition Behavior.** Figure 3 shows the increase of the surface density of Si atoms deposited on the alumina surface after the pre-adsorption of benzaldehyde by a stepwise introduction of tetramethoxysilane vapor in pulse experiments.

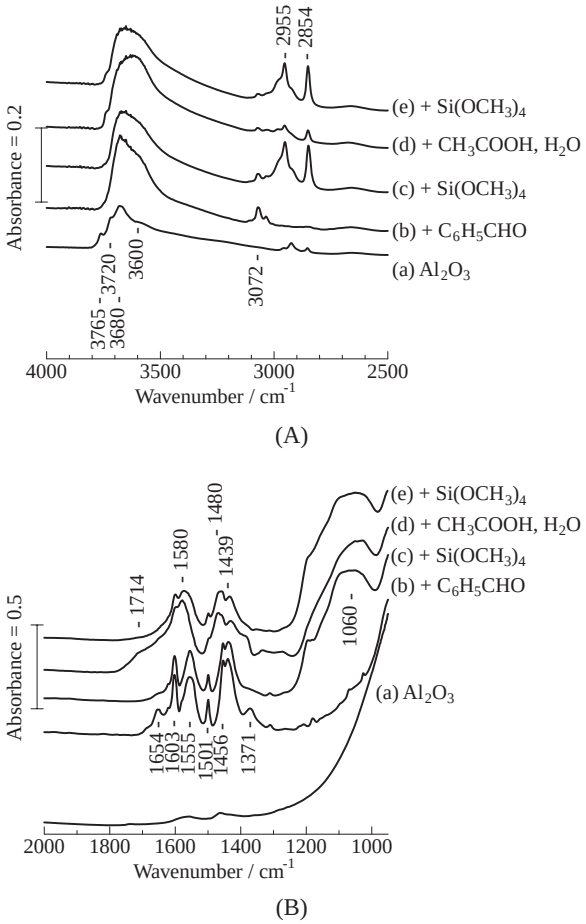


Fig. 2. IR spectra (A, 2500–4000 $cm^{-1}$ and B, 950–2000 $cm^{-1}$) of alumina after evacuation at 673 K (a) followed by adsorption of benzaldehyde (b) deposition of $Si(OCH_3)_4$ (c), addition of acetic acid and water (d) and further deposition of $Si(OCH_3)_4$ (e). The adsorption of benzaldehyde was carried out at 423 K followed by evacuation at 523 K. The deposition of $Si(OCH_3)_4$ and addition of acetic acid and water were carried out at 523 K. All the spectra were collected after cooling the sample to ambient temperature in vacuo following to these treatments.

By the first several pulses, Si species were readily deposited, but the deposition rate decreased during 7–8 pulses in both experiments (△ and ●, Entries 3 and 4, respectively, in Table 1). In the experiment shown by △, water vapor was introduced after the 8th pulse, in order to hydrolyze the surface alkoxide and to recover the deposition rate. As a result, a recovery of the deposition was observed, but the deposition rate again became slow with several more pulses. In the experiment indicated by ●, a mixture of acetic acid and water was admitted in place of water after the 8th pulse. The deposition rate was significantly enhanced, and continuous deposition was observed within the experimental conditions. Thus, an enhancement of deposition rate of Si alkoxide by acetic acid was observed on alumina, as already found on tin oxide.[15]

As described above, the co-existing of template (benzaldehyde), deposit (Si alkoxide) and acetate species was found, suggesting a catalytic enhancement for deposition by the acetate species. We observed that water was necessary for an en-

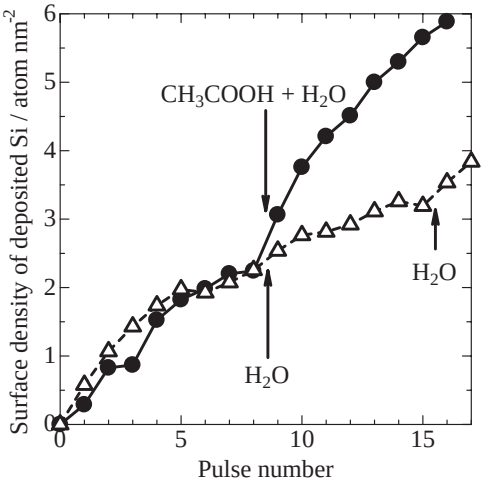


Fig. 3. Deposition behavior of Si on alumina by introduction of $Si(OCH_3)_4$ at 523 K. The experiments were done twice, and the first 8 pulses were carried out under the same conditions. In the experiment show by ●, a mixture of acetic acid and water (1:1 molar ratio) was introduced at the point shown by "$CH_3COOH + H_2O$", while water was introduced at the points shown by "$H_2O$" in the experiment △.

hancement on tin oxide; the deposition was not enhanced by the addition of pure acetic acid, and the co-feed of acetic acid and water was required to enhance the deposition on tin oxide.[19] Therefore, we can conclude that the added acetic acid catalyzed the hydrolysis of Si alkoxide probably by acid catalysis, resulting in a subsequent deposition, as follows:

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+, \quad (1)$$

$$\equiv Si\text{–}OCH_3 + H_3O^+ \rightarrow \equiv Si\text{–}OH + CH_3O^+H_2, \quad (2)$$

$$\equiv Si\text{–}OH + H_3CO\text{–}Si\equiv \rightarrow \equiv Si\text{–}O\text{–}Si\equiv + CH_3OH, \quad (3)$$

$$CH_3OH_2^+ + H_2O \rightarrow CH_3OH + H_3O^+. \quad (4)$$

Equations (1) and (2) show the hydrolysis of surface silicon alkoxide catalyzed by acetic acid and water. The thus-formed silanol and another methoxy group (in gaseous tetramethoxysilane or in another anchored silicon alkoxide) are supposed to react readily to form a siloxane bond as (3). By the decomposition of the intermediate $CH_3OH_2^+$ (probably transient species) (4), reactions (1) to (3) can be repeated. It is speculated that step (2) was slow in the absence of acid, resulting in the slow rate of the whole deposition process.

On the other hand, the color of the sample was white after the final calcination at 673 K in oxygen in all cases, showing that the deposited material was converted into silica with no carbonaceous material. From these results, the selective adsorption behavior shown below is considered to be generated by the deposited silica species with a specific microstructure.

**Adsorption Property.** Table 1 gives the adsorption capacities of aldehydes with different molecular sizes (benzaldehyde and 1-naphthaldehyde) on $SiO_2/Al_2O_3$ samples prepared using different templates (benzaldehyde and 1-naphthaldehyde) and additional reagents (water and acetic acid). On pure alumina (Entry 1), benzaldehyde and 1-naphthaldehyde were adsorbed at 2.3 and 1.0 molecules nm$^{-2}$, respectively, showing that the surface was almost completely covered by these molecules.[14] The deposition of silica decreased the adsorption capacity in all cases. Entry 2 shows the capacities on silica deposited on an alumina surface without a template at 523 K. The low adsorption capacities for both aldehydes indicate a complete coverage of the alumina surface by silica at 12 Si nm$^{-2}$ (= density of Si on the silica monolayer[10]), and that the aldehydes were not adsorbed on the silica surface.

As shown in Entry 3, the deposition of silica using the benzaldehyde template decreased the adsorption capacity for benzaldehyde (the template itself) down to 0.45 nm$^{-2}$, ca. 1/5 of the value on alumina (2.3 nm$^{-2}$), whereas the capacity for 1-naphthaldehyde (larger molecule than the template) was more significantly decreased down to 0.06 nm$^{-2}$ (ca. 1/17 of 1.0 nm$^{-2}$, the capacity on alumina). This difference was achieved by using water as an addition reagent. The use of acetic acid made the difference in the adsorption capacities for benzaldehyde and 1-naphthaldehyde larger, as shown in Entries 4 and 5; the preparation of these two samples was carried out under the same conditions in order to confirm the reproducibility. The adsorption capacity for benzaldehyde was 0.8–1 nm$^{-2}$, about 1/3–1/2 of the capacity on alumina, while the adsorption capacity for 1-naphthaldehyde was quite low, 0.02 nm$^{-2}$, ca. 1/50 of that on alumina. Thus, the adsorption of a molecule larger than the template was selectively blocked by adding acetic acid during the CVD of silica.

The template was then changed into a larger molecule, 1-naphthaldehyde, in Entry 8. The adsorption capacity of the smaller molecule, benzaldehyde, was high, and the capacity of the template, itself, 1-naphthaldehyde, was still high (0.13 nm$^{-2}$). In summary, the adsorption of a molecule larger than the template was selectively blocked, while the template molecule, itself, and a smaller molecule were adsorbed with the high capacities. The selective adsorption indicates that the size of adsorption site was controlled by the template molecule.

The surface density of silica was increased by increasing the number of tetramethoxysilane injections in Entries 7 and 9. In these entries, the addition of acetic acid was carried out after the 8th pulses, and further injections of tetramethoxysilane was made without any further addition of acetic acid. The surface density of silica was not directly determined by the GC connected with the pulse reactor, but was estimated from exploring the relationship between the amount of Si and the pulse number at <6 Si nm$^{-2}$, shown in Fig. 3 (●). The number of injections was 80 in Entries 7 and 9. At about 15–20 pulses in Fig. 3 (●), about a 1 nm$^{-2}$ increase was observed by 3 pulses. Therefore, an additional 60 (=80–20) pulses were estimated to induce 20 nm$^{-2}$ (=60/3) of the deposition, and therefore the final amount of Si should be ca. 25 ($\approx 6 + 20$) nm$^{-2}$. The surface density of Si atoms is thus estimated to be ca. 25 nm$^{-2}$, but it is noteworthy that the value should have a relatively large estimation error. Therefore, we show here the effect of an increase of the silica qualitatively; the effect and mechanism of accumulation of a silica layer on the monolayer is not simple, and are being studied.[20] In the case of a benzaldehyde template, increasing silica from 6 (Entries 4 and 5) to 25 Si nm$^{-2}$ (Entry 7) did not change the adsorption capacity of benzaldehyde, itself, while the adsorption of 1-naphthaldehyde was completely prohibited by increasing silica. In the case of

the 1-naphthaldehyde template, the adsorption capacity of benzaldehyde was maintained, whereas the capacity of 1-naphthaldehyde was not decreased (Entries 8 and 9). Thus, complete selectivity was generated by increasing silica.

Entry 6 shows the effect of the deposition temperature. Deposition at a low temperature (423 K) resulted in low selectivity; the adsorption capacities of benzaldehyde and 1-naphthaldehyde were 0.43 and 0.13 $nm^{-2}$, ca. 1/5 and 1/8 of those on alumina, respectively, and therefore the difference was small. This suggests that a highly enhanced deposition rate, which should be obtained only at such a high temperature as 523 K, is required to generate high selectivity.

**Structure in Nanometric Scale.** Table 1 gives the Si/Al molar ratio on a surface determined by the XPS analysis. The Si/Al ratio was 0.30 in Entry 2, where a monolayer of silica was speculated to cover the surface completely, as above mentioned. The XPS can detect atoms on the surface layer with ca. 2 nm of the thickness, corresponding to 4–6 cation layers of such metal oxides as silica and alumina. The surface density of Al atoms on the alumina surface is 9–14 $nm^{-2}$ (averagely ca. 12 $nm^{-2}$).[18] On the other hand, the density of Si atoms on a silica monolayer is estimated to be 12 $nm^{-2}$, because the CVD of silica forms a monolayer with 1:1 bonding between Si and the surface cation.[10] The numbers of Si and Al atoms detectable by the XPS on the covered surface should be 12 and 48 ($=12 \times 4$), respectively, based on the assumption that the first 5 layers from the surface, among which the 1st layer was silica and the other 4 were alumina, were detectable. The Si/Al ratio would be $12/48 = 0.25$, close to the observed value (0.30). This agreement indicates that all of the deposited silicon atoms were located on the surface within the escape depth of the electron detectable by the XPS, and hence strongly supports the formation of a monolayer.

An XPS analysis of the samples with 6 Si atoms $nm^{-2}$ deposited in the presence of template (Entries 3, 4, and 5) showed lower Si/Al ratios (0.11–0.13) than that in Entry 1, being consistent with the exposure of a fraction of the surface as a cavity formed by the template. The observed values are also in agreement with the structure predicted from the surface density of Si atoms (6 $nm^{-2}$) as follows. If half of the surface was covered by silica, the number of Si atoms on 1 $nm^2$ of the surface should be 6, and all these atoms were detectable by XPS. The number of Al atoms detectable by XPS on the covered surface should be $6 \times 4 = 24$, based on the assumption that the first 5 layers from the surface, among which the 1st layer was silica and the other 4 were alumina, were detectable. The number of Al atoms detectable by the XPS on the uncovered surface should be $6 \times 5 = 30$, and hence all of the Al atoms should be $24 + 30 = 54$. The Si/Al ratio would be $6/54 = 0.11$, in good agreement with the observed values (0.11–0.13). If a bulky silica particle was formed, the Si/Al ratio should be lower than these estimated values.

The increase of silica from 6 to 25 Si atoms $nm^{-2}$ (from Entries 4 and 5 to In Entry 7) increased the Si/Al ratio on the surface. From the surface density of Si 25 atom $nm^{-2}$, it is estimated that 4 ($=25/6$) layers of silica covered half of the surface uncovered by the template, and the other half of the surface was exposed. On the covered surface, 25 Si atoms and 6 Al atoms should be detected by XPS, because the first 5 layers, among which 4 were silica and the other 1 was alumina, are considered to be detectable. On the surface uncovered by silica, 30 ($=6 \times 5$) Al atoms should be detected. Therefore, the Si/Al ratio should be 0.69. However, the observed value 0.20 was obviously lower than the predicted value.

This disagreement is speculated to be due to an overestimation of the amount of silica in Entry 7. In this case, the amount of deposited silica was not analyzed because of an experimental problem, but it was estimated by extrapolation of the relationship between the amount of deposited silica and the pulse number at $<6$ Si $nm^{-2}$. It is reasonable that the accumulation of the silica layer was slower than the formation of monolayer. In addition, it is also possible that the 1st layer of silica covered homogeneously on the surface, but a further deposition of silica formed a layer of silica with a heterogeneous thickness and/or a particle of silica which did not cover the alumina surface.

Thus, although the structure of silica layer at a high silicon density can be heterogeneous, it is strongly supported that a thin layer of silica was formed on alumina by the CVD in the presence of a template, at least in a low silicon density region (Entries 3, 4, and 5).

Here we go back to the purpose of this study, in order to compare the structures of $SiO_2/Al_2O_3$ samples prepared at 523 K using acetic acid (Entries 4 and 5 in Table 1) and of the sample prepared without acetic acid (Entry 3). The addition of acetic acid hardly affected the Si/Al ratio analyzed by the XPS as above, indicating that the structure of silica layer was not modified by acetic acid on the nanometric scale. Figure 4(A) shows the IR spectrum of a $SiO_2/Al_2O_3$ sample prepared at 523 K without acetic acid (Entry 3 in Table 1, prepared with water only) after evacuation at 673 K. Small bands due to organic material (2928 and 2855 $cm^{-1}$) and carboxylate

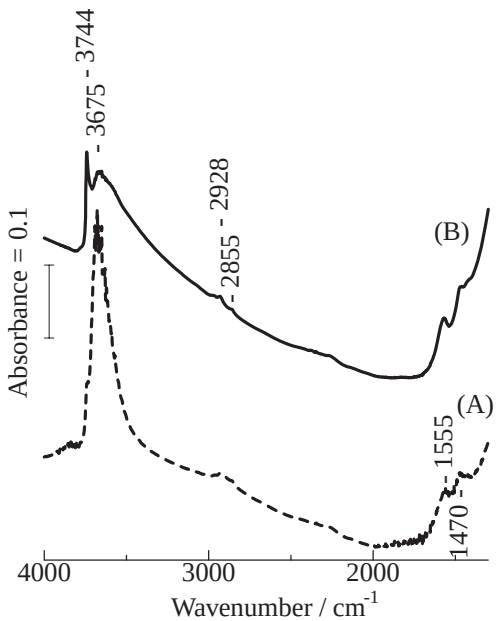


Fig. 4. IR spectra of self-supporting disks of $SiO_2/Al_2O_3$ [6 Si atoms $nm^{-2}$, deposited at 523 K using benzaldehyde template: prepared using water (A) and acetic acid + water (B) as additional reagents] evacuated at 673 K.

species (1555 and 1470 $cm^{-1}$) were observed. Because the band intensities were generally low, it can be interpreted that almost all of the organic materials were removed by calcination of the sample in oxygen at 673 K. These bands were also observed on a sample prepared with acetic acid (B, Entry 4 in Table 1). The amount of remaining organic residue was not affected by acetic acid addition.

From these findings, we conclude that the silica thin layers covered the surfaces of the samples (Entries 3 and 4) with 6 Si atoms $nm^{-2}$ uniformly on the nanometric scale, and the different adsorption properties of these samples (shown in the last section) should be due to the different microstructures on the atomic dimension, as shown by the following results.

**Microstructure.** As described in the previous section, the AlOH groups were observed on the alumina support by the IR, as shown in Fig. 2(A, a) after an evacuation at 673 K. As shown in Fig. 4(A), a large band was observed at 3675 $cm^{-1}$ on the $SiO_2/Al_2O_3$ sample prepared at 523 K without acetic acid (Entry 3). This band is attributed to the stretching of AlOH or SiOH groups hydrogen-bonded to other OH groups. This implies that the density of OH groups was high on this sample.

On the contrary, the OH band at 3675 $cm^{-1}$ was obviously small, and a sharp band ascribed to isolated SiOH groups was observed at 3744 $cm^{-1}$ on a sample prepared using acetic acid (Entry 4 in Table 1), as shown in Fig. 4(B). This indicates that the density of OH was decreased by the addition of acetic acid, probably because oligomerization via hydrolysis of the surface Si alkoxide was catalytically enhanced by the acid.

We therefore conclude that the surface layer had many pores consisting of OH nests on the sample prepared in the presence of water, while a network of SiOSi was developed well via the oligomerization of Si alkoxides in the presence of acetic acid. It is speculated that the former porous structure allowed the adsorption of molecules larger than the template. The dense structure of the silica wall formed by the addition of acetic acid is considered to realize the high selectivity of the adsorption site based on the shapes of the cavity and the adsorbed molecule.

We have presented the IR[10] and $^{29}Si$ NMR[21] spectra of the $SiO_2/Al_2O_3$ samples, which were covered by a monolayer of silica, prepared without a template. The CVD of silica was carried out at a high temperature (593 K) in these studies. The IR spectrum was similar to Fig. 4(B), consisting of a relatively small band at 3675 $cm^{-1}$ and a band at 3745 $cm^{-1}$,[10] suggesting the low density of OH groups on these samples. The NMR showed a spectrum mainly consisting of $Si(OSi)_3(OAl)$ species at $-103$ ppm,[21] suggesting a two-dimensional network structure of siloxane. In these cases, the density of OH groups was directly measured by means of titration with $CH_3MgBr$.[22] It was confirmed that the density of OH groups was quite low, ca. 1.5 $nm^{-2}$, on the silica monolayer fully covering the alumina surface. These findings indicate that the content of OH groups is quite low in a silica layer consisting of a well-developed network of siloxane, and that such a layer can be obtained by a simple deposition of tetramethoxysilane at 593 K.

However, we analyzed the deposition rate of tetramethoxysilane on alumina, and concluded that the reaction between the alumina surface and $Si(OCH_3)_4$ into the $AlOSi(OCH_3)_3$ species was quite fast, even at such a low temperature as 373 K, while the oligomerization of Si alkoxides to form a siloxane bond was slow.[23] In the present study, the CVD temperature should be kept below ca. 523 K in order to avoid decomposition of the template molecule. The role of acetic acid was therefore important in the present study to develop a siloxane network at 523 K.

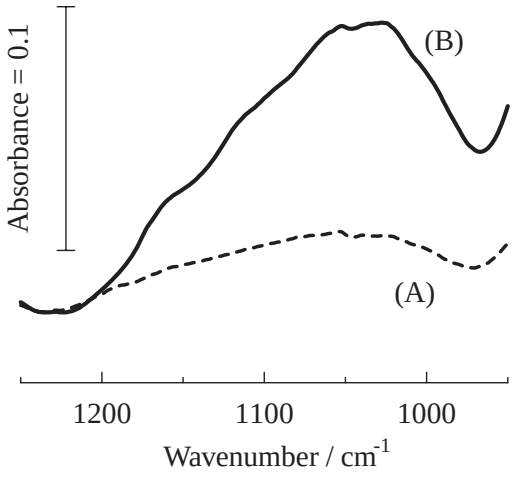


Fig. 5. IR spectra of $SiO_2/Al_2O_3$ [6 Si atoms $nm^{-2}$, deposited at 523 K using benzaldehyde template: prepared using water (A) and acetic acid + water (B) as additional reagents] diluted with KBr.

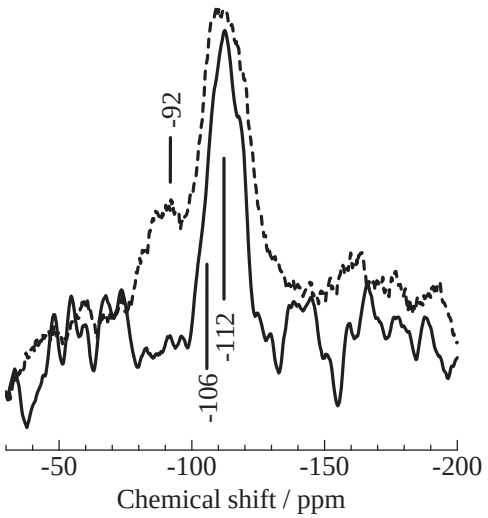


Fig. 6. $^{29}Si$ NMR spectra of $SiO_2/Al_2O_3$ [6 Si atoms $nm^{-2}$, deposited at 523 K using benzaldehyde template: prepared using water (dotted line) and acetic acid + water (solid line) as additional reagents].

Finally, the IR spectrum in the SiO region (Fig. 5, 1000–1200 $cm^{-1}$) and $^{29}Si$ NMR (Fig. 6) are shown. Although the accuracy of these spectra seems to be low, they were consistent with the above conclusions, as follows.

On a self-supporting disk of $SiO_2/Al_2O_3$, the spectrum in the SiO region could not be measured because of too strong absorption. Therefore, the sample was diluted with KBr, and the spectrum was collected under atmospheric conditions, as shown in Fig. 5. The intensity of the SiO band (SiOSi and

SiOAl, a broad band at 1000–1200 $cm^{-1}$) was significantly higher on a sample prepared with acetic acid (B, Entry 4 in Table 1) than that on a sample prepared without acetic acid (A, Entry 3 in Table 1).

The $^{29}Si$ NMR spectrum is shown in Fig. 6. On the sample prepared using acetic acid (solid line, Entry 5 in Table 1), a peak attributed to $Si(OSi)_4$ species was observed at $-112$ ppm. In addition, probably there was a shoulder due to $Si(OSi)_3(OAl)$ species at $-106$ ppm, because the replacement of one Si atom by one Al atom usually shifts the peak position $+6$ ppm.[24] The deconvolution of these fragments was impossible because of the broad peak shape. In addition, because the measurement parameters, especially the sampling interval, were not optimized, as described above, quantitative analysis was difficult. Apart from this, we can conclude that the silica layer formed in the presence of acetic acid consisted of these two species, $Si(OSi)_3(OAl)$ and $Si(OSi)_4$. In addition to these species, the sample prepared without acetic acid (dotted line, Entry 3 in Table 1) showed a tail at ca. $-90$ ppm, which should be ascribed to some silanol species, e.g., $Si(OSi)_2(OH)_2$.

## Conclusion

The IR study showed that acetic acid (additional reagent), benzoate anion (template) and Si alkoxide co-existed on alumina surface during the CVD process. The added acetic acid catalyzed the oligomerization of Si alkoxide via hydrolysis. The thus-prepared $SiO_2/Al_2O_3$ had a well-developed network of SiOSi and a low density of OH groups, as shown by the IR and NMR analyses. This means that a dense wall mainly consisting of Si and O atoms was formed. This $SiO_2/Al_2O_3$ sample showed a quite low adsorption capacity for a molecule larger than the template, while the template, itself, was adsorbed in the high capacity. Such a high selectivity was obtained by adding acetic acid, showing that a dense silica wall is required to realize shape-selective adsorption by the surface cavity.

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