Molecular Sieving Silica Overlayer on Tin Oxide prepared using an Organic Template

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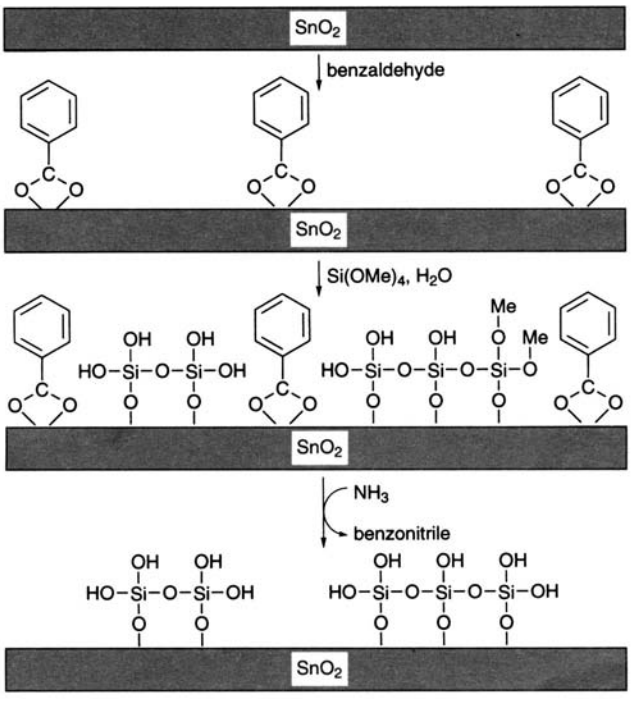
A silica overlayer prepared on tin oxide by a method of chemical vapour deposition (CVD) of silicon alkoxide using pre-adsorbed benzoate anion as a template molecule, has molecular sieving properties due to the created vacancy.

Currently much attention is focused on the preparation of materials with novel functions on the nanoscale. We now report on surface modification technology using an organic template and chemical vapour deposition on a metal oxide, the resulting silica overlayer is a molecular sieving material.

We have already reported that the deposition of silicon alkoxide on supports such as Al_2O_3, TiO_2, ZrO_2 and SnO_2 at *ca.* 600 K form a monoatomic layer of silica.[1,2] On the other hand, benzaldehyde is adsorbed readily on these metal oxides as a benzoate anion which covers the surface almost completely, and the adsorbed benzoate can be removed easily by treatment with ammonia.[3,4] Based on these findings, we have developed a new method to prepare a molecular sieving silica overlayer. In this investigation SnO_2 was used because it would be available as semiconductor gas sensors.

The procedure for the preparation consists of preadsorption of benzaldehyde, deposition of silicon alkoxide and removal of the adsorbed benzoate, as shown in Scheme 1. First, in order to incompletely cover the surface by the benzoate anion, the temperature for benzaldehyde adsorption on SnO_2 was selected from the dependence of the saturated surface concentration upon adsorption temperature. Saturated surface concentration of the benzoate species increased with increasing the adsorption temperature with a maximum value of 2.38 benzoates nm^{-2} at 523 K. At this temperature, the surface was estimated to be fully covered with the adsorbed species.† Benzaldehyde was therefore adsorbed at 423 or 498 K to cover the surface by 42 or 66%, respectively. $Si(OMe)_4$ vapour was then deposited on the surface at 473 K where the benzoate had been adsorbed.



Scheme 1 Procedure for the preparation of a silica overlayer on SnO_2 using benzoate anions as the organic template molecule

Because the surface of tin oxide became saturated with the silicon compounds after several injections of benzaldehyde, the deposition could not be continued; however, it was possible after the surface was treated by water at 473 K. The amount of deposited silica thus increased step-wise by repeating the deposition and hydrolysis. Finally, ammonia was reacted with the benzoate anion to remove it from the surface as benzonitrile. The adsorption sites from which the benzoate anion template was removed thus remained unoccupied. In other words, the vacancy sites were created on the surface of tin oxide. We prepared some modified samples with different deposited amounts of silica. All the procedures used the pulse method with FID gas chromatography. The tin oxide sample (30 to 50 mesh) was set in a 6 mm o.d. Pyrex glass tube.

Adsorption on the silica-controlled SnO_2 was then studied; benzaldehyde (7.06), 2-methycyclohexanol (7.90), *o*-chlorobenzaldehyde (8.08), 2,6-dichlorobenzaldehyde (9.12) and α-naphthaldehyde (9.71 Å) were selected as adsorbates, because the molecular sizes as shown in parentheses were equal to or larger than that of the template molecule. Fig. 1. shows the ratio of amount of adsorbate on the treated sample to that on unmodified SnO_2. The amounts of adsorbate on unmodified SnO_2 were 0.99, 1.21, 0.86, 0.58 and 1.19 nm^{-2}, respectively. BA423 and BA498 are samples prepared by the preadsorption of benzaldehyde at 423 and 498 K, respectively. As shown in Fig. 1, the adsorption behaviour was controlled gradually by increasing the amount of deposited silica. The difference in the adsorption amount ratio showed no pattern for BA423 (0.6 or 2.5 Si nm^{-2}), but it was clear for BA423 (4.5 Si nm^{-2}); the adsorbate ratio decreased, as the size of adsorbate molecule increased. Similar control of the adsorbate ratio due to the molecular size was also observed with BA498 (2.7 Si nm^{-2}). Because the cation density of the tin oxide surface is 9.4 cations nm^{-2} on the (110) plane, 4.5 and 2.7 Si nm^{-2} silicon density corresponds to 48 and 29% of coverage by the silica monoatomic layer, respectively. The sum of the coverage by silicon and benzoate is thus 90 and 95% on these samples. In other words, a distinction function of adsorption was obtained, when the surface of tin oxide was covered almost completely by both the template molecule and deposited silicon.

On the other hand, the samples prepared without the template, termed non-template in the Fig. 1, did not show such adsorption properties when the amount of silica deposited was 4.3 Si nm^{-2}, which was similar to that of the BA423 controlled sample, or 12.8 Si nm^{-2}, which was enough to cover the surface. Therefore, we proved that the silica overlayer on SnO_2 prepared using the organic template could discriminate between molecules based on the molecular size, *i.e.* molecular sieving properties.

It is well known that zeolites are synthesized in the presence of template molecules under the hydrothermal conditions; however, the role of the template molecule in the synthetic procedure is not known exactly. A recent investigation reported the method of preparation of mesoporous materials MCM41 using surfactant templates.[5] Folded sheet mesoporous materials (FSM) prepared from kanemite using template molecules has also been reported.[6] From these investigations, one can identify the utilizatioin of organic template molecules to adjust the size of mesopores in inorganic materials. On the other hand, in the present investigation, the template molecule is utilized in the surface modification. Because the simple molecular sieving

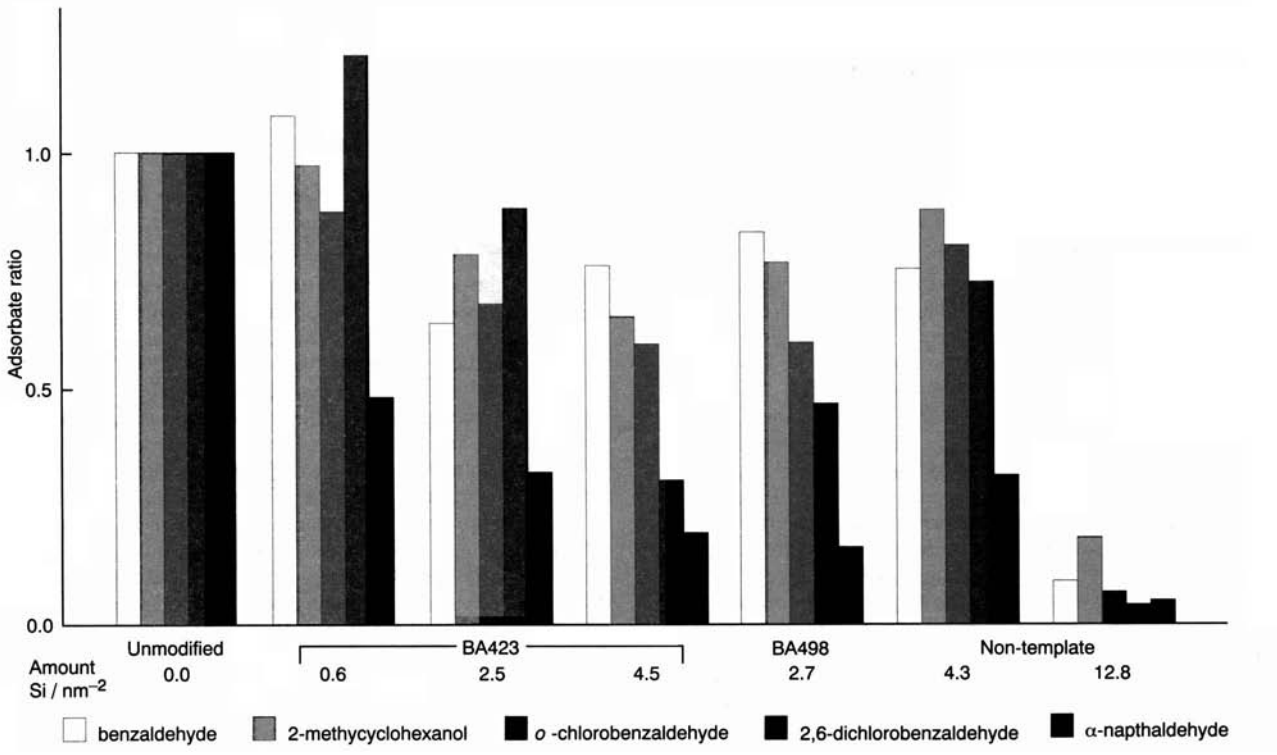


Fig. 1 Adsorption behaviour of silica-controlled SnO_2. Adsorption experiments used the pulse method, and the amount of aldehyde and alcohol adsorbed was measured by the amount of nitrile compounds formed upon injection of ammonia at 673 K and from the difference between injected and eluted amounts of alcohol at 373 K.

property was obtained with a silica overlayer, one can conclude that the monoatomic layer of silica is enough to distinguish between molecules, and it is based on the size of the created vacancy site. We have a broad possibility to produce vacancy sites with different sizes by using template molecules of different molecular size. Such weak basic metal oxides as Al_2O_3, TiO_2 and ZrO_2 could be used in place of SnO_2. It is also possible that the molecular sieving function of the silica overlayer on these metal oxides could have applications in heterogeneous catalysts as well as sensing materials.

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Footnote

† The occupied surface area by the benzoate anion was estimated as 0.39 nm^2 based on the structure of the adsorbed species; the benzoate species may be stabilized without interaction with the surface of SnO_2, because no change of IR intensity was observed.

References

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