J. Chem. Soc., Faraday Trans. 1, 1984, **80**, 3135–3145

Fine Control of the Pore-opening Size of the Zeolite Mordenite by Chemical Vapour Deposition of Silicon Alkoxide

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Received 24*th February*, 1984

Chemical vapour deposition (c.v.d.) of $Si(OCH_3)_4$ on the H form of mordenite has been carried out in order to control the pore-opening size without affecting its acidic properties. It has been shown that $Si(OCH_3)_4$ is deposited irreversibly on the zeolite. Because the molecular size of the alkoxide is larger than the pore size, the alkoxide does not enter the pore and the silicon compound is deposited on the external surface. The alkoxide may be deposited by reaction with hydroxide, thus covering the external surface of zeolite crystal after subsequent reactions. Calcination with oxygen removes the hydrocarbon residue and produces silica-coated H-mordenite (SiHM). The SiHM thus obtained has been characterized by temperature-programmed desorption (t.p.d.) of NH_3, adsorption experiments and X-ray photoelectron spectroscopy. The deposition of the alkoxide does not change the acidity but reduces the size of pore opening. Enrichment of Si on the external surface of the zeolite is confirmed. One can therefore conclude that SiO_2 covers the external surface of the zeolite, thus reducing the effective size of the pore opening. The pore size is effectively reduced by *ca.* 0.1 and 0.2 nm upon formation of 1–2 and 3 molecular layers of silicon oxide, respectively.

Acidity and pore size are the main characteristics of zeolites as catalysts or adsorbents. Their acidic properties have been extensively studied[1] since the discovery of the unique catalytic activity of ZSM-5.[2-4] Because ZSM-5 zeolites possess a broad range of silicon:aluminium ratios, the acidity distribution may be complex, and it is difficult to make a comparison with other zeolites such as mordenite. Generally speaking, the acidity of zeolites is dependent on the components or impurities they contain, and therefore must be carefully controlled. On the other hand, the size of the pores or channels is determined by the zeolite's structure and is thereby strictly controlled.

On the basis of these fundamental data one can select the appropriate zeolite species to achieve activity for a desired reaction. However, in many cases it is insufficient to use the zeolite in its natural form, since selectivity is often limited. For industrial use the material must be modified by appropriate methods to control its physicochemical properties.

We have considered acidity and pore size as parameters which independently influence catalytic properties. First we have investigated controlling the acidity of H-mordenite by cation exchange and dealumination;[1] secondly we have examined the influence of acidity distribution on methanol conversion.[5] According to our previous study, cation exchange poisons the strong acid sites preferentially, while dealumination reduces acid sites over a whole region. Therefore, the acid distribution may be changed by using these methods. Control of the acid–base properties of zeolites has been reported by Itoh *et al.*[6] and exemplified by the side-chain alkylation of toluene with methanol. On the other hand, the method of pore-size control has not yet been established. Only cation exchange has been used for this purpose,[7] although silanation using SiH_4 has recently been suggested for pore-size modification.[8] However, these methods modify the acidity as well as the pore structure, so an undesired change in catalytic activity may be introduced.

Based on these considerations, the possibility of controlling the pore size without affecting the acid sites should be investigated. As reported in a preliminary communication,[9] the chemical vapour deposition (c.v.d.) of $Si(OCH_3)_4$ on H-mordenite has been effective in reducing the pore size with no change in acidity. Furthermore, we have shown the extremely high shape-selectivity of SiO_2-coated H-mordenite in the cracking of paraffins.[10] The catalyst was used to sieve an octane mixture, and only the smaller molecules were converted into lower hydrocarbons. Shape selectivity was controlled to an accuracy of ångströms by adjusting the extent of deposition. The purpose of the present study was to reveal the characteristics of the c.v.d. of this compound and also to characterize the material obtained.

EXPERIMENTAL

MATERIALS AND DEPOSITION

H-mordenite (hereafter termed HM), supplied by Norton as 100-H, was used without further purification. The external surface area was 3.6 $m^2\ g^{-1}$, a value obtained by the flow-type B.E.T. method on the hydrated sample.[11] The pore volume was measured by nitrogen adsorption at 77 K to be 0.192 $cm^3\ g^{-1}$. The mean radius of the zeolite crystal was thus 0.16 μm. The powder was compressed and crushed into pellets of 28–48 mesh. $Si(OCH_3)_4$, obtained from the Shin-etsu Chemical Co. Ltd, was purified by vacuum distillation.

Deposition was performed using a vacuum system. The vacuum line consisted of 8 mm i.d. Pyrex glass and a 32 mm i.d. cylindrical vessel was used for the microbalance. The vessel was heated with an electric furnace, and its upper part was warmed at 350 K by boiling CCl_4 vapour in a doubly sealed outer glass jacket in order to maintain the quartz spring constant. HM was set in a quartz basket hung on the microspring, and the alkoxide was kept in a liquid reservoir. Before deposition of the alkoxide, the HM was evacuated at 423 K for 1 h and successively at 593 K for 1 h. $Si(OCH_3)_4$ vapour was then admitted to the dried HM at the vapour pressure of the alkoxide, which was left at room temperature or 273 K. The liquid reservoir was kept open to the vacuum system during deposition. The resultant increase in weight was measured *in situ* by the quartz microbalance. The degree of deposition was varied by changing the amounts of HM and alkoxide. The weight increase upon deposition (in wt %) is used to show the extent of modification, *e.g.* SiHM (1.4 wt %). Materials thus deposited were calcined in flowing oxygen at 673 K to remove carbonaceous residues.

In the present study non-zeolitic oxides were used as a comparison. γ-Al_2O_3 (surface area, 169 $m^2\ g^{-1}$) was a reference catalyst JRC-ALO-1 which was supplied by the Catalysis Society of Japan.[12] SiO_2 (353 $m^2\ g^{-1}$) and SiO_2–Al_2O_3 (425 $m^2\ g^{-1}$) were obtained commercially from Fuji–Davison and Nikki Chemical Industries, respectively.

Products evolved in the gas phase during the deposition were analysed by gas chromatography. Squalane on Al_2O_3 at 343 K and Porapak S at 323–423 K were used for the separation.

I.R. AND E.S.R. SPECTROSCOPIES

In situ spectra were recorded on a Jasco IR-G spectrophotometer. The i.r. cell was connected to a vacuum line which was used to evacuate the mordenite and to admit the organic vapour. E.s.r. spectra were measured by a Jeol JES-ME-1X instrument operating in the X-band to measure the relative amount of coke radicals produced.

TEMPERATURE-PROGRAMMED DESORPTION (T.P.D.)[1]

T.p.d. spectra were measured with conventional apparatus. The detection of desorbed molecules was made using a thermal-conductivity detector. *Ca.* 0.25 g of the sample was evacuated in a quartz cell at 773 K for 1 h, exposed to ammonia (which was used as a probe base at 373 K for 45 min at an equilibrium pressure of 7.3 kPa) and then evacuated at 373 K for 45 min. T.p.d. measurements were made from 373 to 773 K at a heating rate of 2.5 K min^{-1} and with helium as carrier gas having a flow rate of 60 cm^3 min^{-1}.

ADSORPTION EXPERIMENTS

Sorption measurements were made at 293 K using water, hexane and *p*- and *o*-xylenes with kinetic diameters[13] of 0.265, 0.43, 0.58 and 0.63 nm, respectively. Experiments were carried out using a quartz microbalance whose extension was followed using a cathetometer. HM and SiHM were evacuated at 593 K before adsorption, and the partial pressure of the adsorbent was kept constant at its vapour pressure at 293 K.

X.P.S. AND SEM

The X-ray photoelectron spectra (X.p.s.) were obtained with a Vacuum Generator ESCA LAB-5 spectrometer. The powder was pressed onto a grid and introduced into the chamber. The atomic ratio of Si to Al was determined by the peak intensities of Si 2*s* and Al 2*p*, these cross-sections[14] being assumed to be 0.855 and 0.5735, respectively.

Scanning electron microscope (SEM) images for HM were taken using Jeol JSM-T20 instrument before and after deposition.

RESULTS

CHEMICAL VAPOUR DEPOSITION

DEPOSITION OF $Si(OCH_3)_4$ ON HM

Before deposition HM was evacuated at 593 K to remove water. *Ca.* 12 wt% of water was removed, and no further significant decrease in weight was observed. Because this amount corresponds to the water content in the usual formula of mordenite, all sorbed H_2O should be removed to obtain dried HM. Methyl orthosilicate was then admitted from the liquid reservoir and the weight increase was noted. Examples of the change in sample weight during deposition at 593 K are shown in fig. 1. The weight increased rapidly in the initial state, becoming saturated 2–3 h later. The gas phase was then evacuated, but only a small decrease of weight was observed. The alkoxide was thus irreversibly deposited on HM by this method.

The gaseous products evolved during deposition were analysed by gas chromatography. At 593 K lower hydrocarbons such as ethylene and propane were detected in the products. However, hydrocarbons having more than four carbon atoms were not observed. On the other hand, at 493 K methanol and dimethylether were detected but other hydrocarbons were not observed. This suggests that some sort of methanol conversion, primarily the formation of lower hydrocarbons, occurred at 593 K during deposition. It has been reported[15] that methanol is converted into hydrocarbons at temperatures > 573 K.

CALCINING THE DEPOSITED LAYER WITH OXYGEN

The colour of the modified zeolites was brown–black, thus indicating the formation of coke or some carbonaceous material. The e.s.r. spectra of these materials showed the coke radical at $g = 2.00$. Carbonaceous materials were removed by calcining with oxygen. Calcining the c.v.d. zeolite *in situ* in the microbalance decreased the mordenite weight very gradually, indicating the slow formation of carbon oxides. The weight

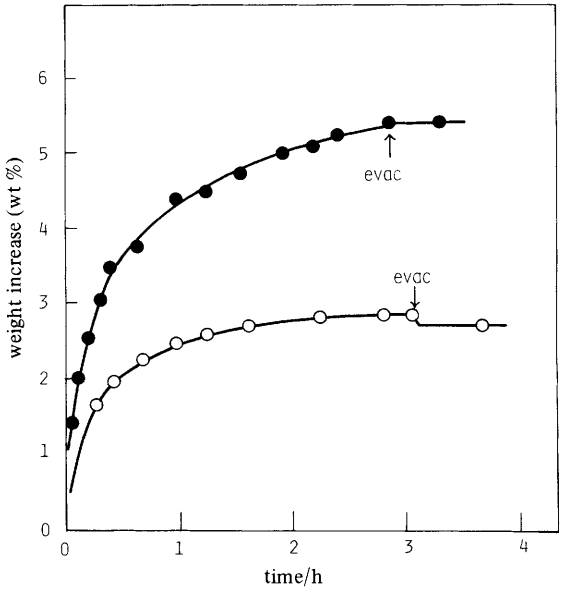


Fig. 1. Deposition of the alkoxide (1.2 kPa) at 593 K on 0.5 (●) or 1.0 (○) g of HM: evac indicates evacuation of the gas phase.

of SiHM modified at 593 K decreased by 50% on calcination at 673 K for 16 h. The SiHM thus obtained showed no coke radicals and returned to its original colour (white). The SiO_2 content of the SiHM finally obtained could thus be regarded as 50% of the weight increase at 593 K.

I.R. STUDIES

The layer deposited on HM was studied by i.r. spectroscopy. Deposition of $Si(OCH_3)_4$ at 473 K revealed the CH stretching absorption at 2900 cm^{-1} as well as those at 1600, 1480 and 1370 cm^{-1}, as shown in fig. 2(*b*). The band corresponding to the hydroxide of HM at *ca.* 3600 cm^{-1} became broad upon deposition. The deposited layer was then evacuated successively at 538, 588, 643 and 673 K. Evacuation at 538 K did not change the i.r. spectrum, while at 588 K the CH stretching vibration at 2900 cm^{-1} was removed. Simultaneously, the 1480 cm^{-1} band diminished and the hydroxide band at 3600 cm^{-1} was restored [fig. 2(*c*)]. After this was evacuated at 673 K, the disc was finally exposed to oxygen at 673 K, followed by evacuation. The spectrum thus obtained was approximately the same as that of the background. The absorptions at 1600 and 1370 cm^{-1} may be ascribed to carboxylate or carbonate ions. These were removed from the mordenite only by calcination. The results obtained by i.r. spectroscopy support the consideration of the deposition process mentioned above, since the adsorbed residue was desorbed above 573 K, and irreversibly deposited carbonaceous material was removed by the calcination. Furthermore, Brönsted-acid sites were not altered by the deposition of SiO_2, although they were affected by the adsorbed organic molecules at relatively low temperatures.

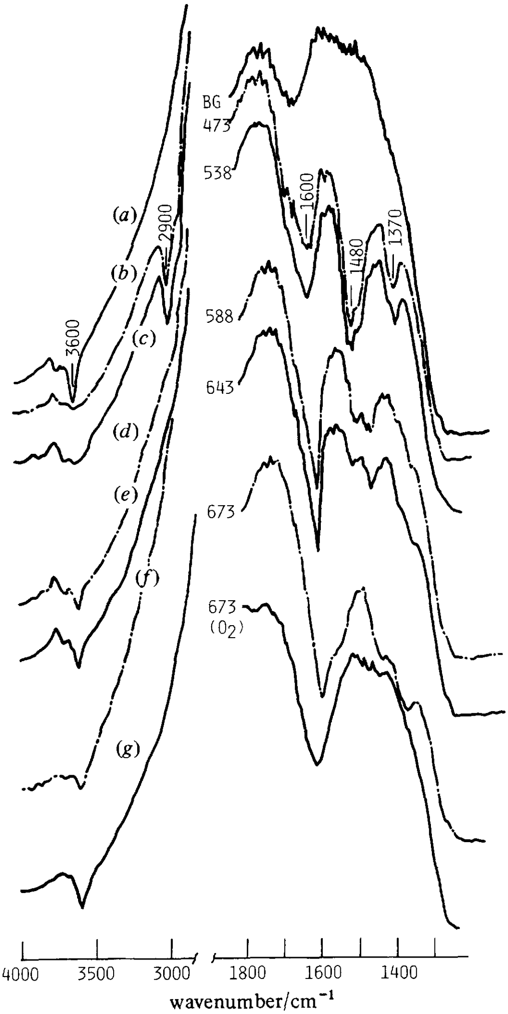


Fig. 2. Infrared spectra of HM: (*a*) background evacuated at 593 K; (*b*) after admission of the alkoxide, followed by evacuation at 473 K; (*c*)–(*f*) samples evacuated at (*c*) 538, (*d*) 588, (*e*) 643 and (*f*) 673 K; (*g*) after calcination by oxygen at 673 K.

DEPOSITION ON SiO_2, Al_2O_3 AND SiO_2–Al_2O_3

Non-zeolitic oxides were used for deposition in order to check the influence of surface properties on the process. The alkoxide was deposited irreversibly on these solids also. Variations in weight increase upon deposition were similar to those obtained in HM shown in fig. 1.

CHARACTERIZATION OF SiHM

TEMPERATURE-PROGRAMMED DESORPTION OF AMMONIA

It has been reported[1] that the amount and strength of acid sites can be measured by the t.p.d. of NH_3. On increasing the temperature from 373 to 773 K two desorption

Table 1. Amount and strength of acidity measured by t.p.d. of ammonia

catalyst	deposition temp./K	weight increase (wt %)	amount of acid/mmol g^{-1}		
			low (T_M/K)	high (T_M/K)	total
HM	untreated	0.0	0.41 (425)	0.93 (675)	1.34
SiHM	593	2.2	0.33 (420)	0.87 (675)	1.20
	593	4.8	0.41 (423)	0.92 (685)	1.33
	693	4.9	0.42 (430)	0.91 (673)	1.33
	643	6.1	0.38 (428)	0.81 (689)	1.19
	543	8.6[a]	0.36 (428)	0.87 (683)	1.23
	493	8.9[a]	0.32 (428)	0.86 (683)	1.18

[a] About 60% corresponds to the weight increase of other materials, since these included hydrocarbon fractions removable above 573 K.

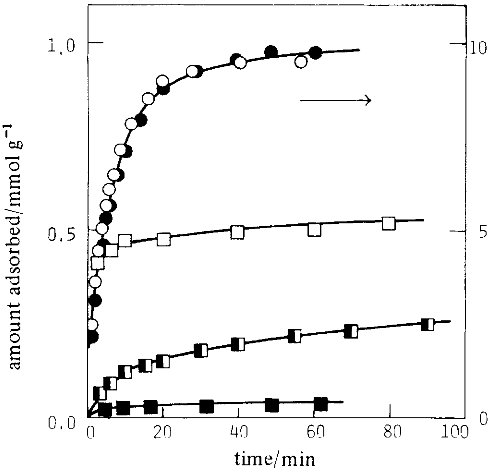


Fig. 3. Adsorption of H_2O (○, ●) and *o*-xylene (□, ■, ◧) on HM (○, □), SiHM (1.4 wt %) (◧) and SiHM (2.7 wt %) (■).

peaks were observed at 420 and 680 K which were termed *l* and *h* peaks, respectively. These absorptions were ascribable to weak and strong acid sites. By using this method the acidity of SiHM was measured.

As shown in table 1, neither the amount of desorbed ammonia nor the temperature at peak maximum of HM was changed by this modification. It was therefore concluded that the acidity of HM was not changed by the deposition of silica, even when the mordenite was modified at different temperatures ranging from 493 to 593 K, or with different amounts of deposition.

ADSORPTION EXPERIMENTS

In order to know the effective size of the pore opening, adsorption experiments have been carried out using various adsorbates with different kinetic diameters. Fig. 3–5 show the adsorption behaviour of H_2O, *o*- and *p*-xylenes and hexane on HM and SiHM at various degrees of deposition.

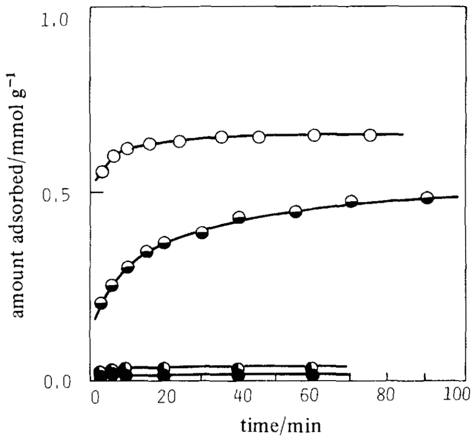


Fig. 4. Adsorption of *p*-xylene on HM (○), SiHM (1.4 wt%) (◒), SiHM (2.7 wt %) (◐) and SiHM (4.8 wt %) (●).

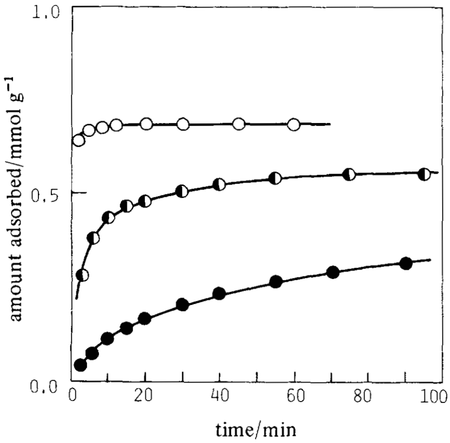


Fig. 5. Adsorption of hexane on HM (○), SiHM (2.7 wt %) (◐) and SiHM (4.8 wt %) (●).

For the adsorption of water, no significant difference was observed between HM and SiHM (2.7 wt%), as shown in fig. 3. One can see that the internal surface of HM is conserved by the deposition of SiO_2, in agreement with the t.p.d. results. On the other hand, the sorption of larger molecules was suppressed, depending on the degree of deposition. The adsorption of *o*- and *p*-xylenes was limited on SiHM (1.4 wt %) and strongly inhibited on SiHM (> 2.7 wt %). On the other hand, hexane was still adsorbed on SiHM (2.7 wt %) and to some degree even on SiHM (4.8 wt %).

In order to understand quantitatively these adsorption profiles, the kinetics of adsorption was analysed based on the so-called root-*t* law. The kinetics of diffusion is described as follows:[16]

$$\frac{Q}{Q_e} = \frac{6}{r}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

where Q and Q_e denote amounts adsorbed at time t and at equilibrium, respectively, r is the radius of the zeolite crystal and D is the diffusion constant. Table 2 lists

Table 2. Diffusion constants on SiHM (in 10^{-16} cm^2 s^{-1})

adsorbate	hexane	*p*-xylene	*o*-xylene
SiHM (1.4 wt %)	—	2.1	0.28
SiHM (2.7 wt %)	3.4	< 0.01	< 0.01
SiHM (4.8 wt %)	0.18	< 0.01	—

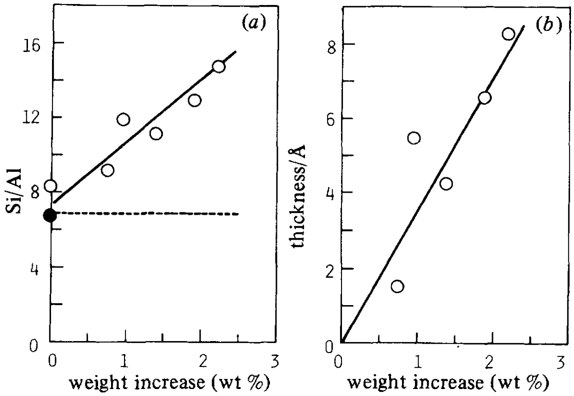


Fig. 6. (*a*) Si/Al ratio obtained from X.p.s. plotted against the weight increase upon deposition at 593 K. The dotted line represents the calculated values when the Si compound is deposited uniformly in the zeolite bulk. ●, Experimental result obtained by X-ray fluorescence spectroscopy.

diffusion constants thus obtained for various adsorbates on SiHM. Diffusion constants greatly varied with the extent of deposition. However, adsorption on HM was so fast that its analysis based on this equation was impractical. Measuring the diffusion constant using a small mordenite crystal of < 1 μm diameter was extremely difficult because adsorption reached equilibrium very rapidly. Satterfield *et al.*[17] measured precisely the diffusion constants of hydrocarbons on Na-mordenite with a large crystal size. Their values were *ca.* 10^{-10} cm^2 s^{-1} and were much greater than those obtained on SiHM. Consequently it was considered that the rates of hydrocarbon adsorption on SiHM were limited in comparison with that on HM.

X.P.S. MEASUREMENTS

SiHM (0.9–2.2 wt %) deposited at 593 K was used for the X.p.s. study in order to measure the Si/Al ratio in the surface layer. No change in the Si_{2s} peak at 161 eV was observable, but in contrast the Al_{2p} peak intensity at 82 eV decreased on deposition. As shown in fig. 6(*a*), the ratio of Si to Al measured by peak intensities increased with increasing degree of deposition. As shown by the dotted line, the Si/Al ratio calculated by assuming a uniform deposition of alkoxide within the zeolite crystal changed little. Therefore one can conclude that the silicon compound is not deposited uniformly in the zeolite bulk but is enriched on the external surface.

The Si/Al ratio of HM measured by X.p.s. was in agreement with that obtained by X-ray fluorescence spectroscopy, thus justifying its accuracy.

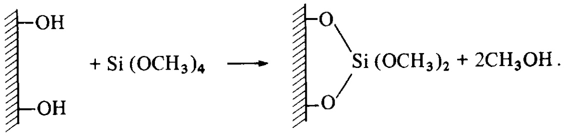
SEM pictures were taken before and after modification. No significant change was observed. It was therefore confirmed that the large compound seen in the SEM picture was not formed upon deposition. The size of the mordenite crystal seemed to be *ca.* < 1 μm, although the resolution was insufficient to confirm this.

DISCUSSION

It was observed in the present study that methyl orthosilicate is deposited easily on the zeolite. Because the alkoxide is deposited irreversibly it may be converted into other molecules or fractions. Infrared spectra of the surface layer at temperatures > 573 K show no absorption ascribable to the C—H bond, thus suggesting the complete conversion of the alkoxide. Also, below 573 K the alkoxide may be converted significantly, because the product in the gas phase contains dimethylether as well as methanol, and the i.r. spectra of the adsorbed layer show absorptions of carbonate or carboxylates at 473 K. Therefore various kinds of surface reactions may be taking place.

The isolated, vicinal or geminal silanol has been regarded as a target surface group for the modification of existing[18] or the preparation of new[19] catalysts. However, $Si(OCH_3)_4$ was deposited even on non-zeolitic oxides such as SiO_2, Al_2O_3 and SiO_2–Al_2O_3. Therefore, so far as the present study is concerned, any kind of surface hydroxide may be available for deposition. The initial reaction step is, probably, hydrolysis of the alkoxide as follows:

$$Z{-}OH + Si(OCH_3)_4 \longrightarrow Z{-}OSi(OCH_3)_3 + CH_3OH \qquad (1)$$



(2)

Similar reaction steps were reported by Hertl[20] for the reaction of $(H_3CO)_3SiCH_3$ with a silica surface. Methanol formed may be converted on the acidic sites of mordenite; a previous study by Ono *et al.*[15] reported that methanol is converted into dimethylether and hydrocarbons at temperatures below and above 573 K, respectively. Products in the gas phase contained these compounds:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (3)$$

$$m CH_3OH \rightarrow \text{hydrocarbons} + m H_2O. \qquad (4)$$

However, the infrared spectra of the deposited layer indicate the complete removal of hydrocarbon residues above 573 K, thus suggesting surface reactions between deposited materials as well as the desorption of organic materials (fig. 2). Therefore, the deposited materials could react with each other to form a two-dimensional compound possessing siloxane bonds. However, the surface reactions occurring during deposition remain unknown. One may only state that the alkoxide was strongly deposited on the zeolite surface rather than forming a large Si-containing compound, because the pore size was uniformly controlled as mentioned below.

Silicon compounds and carbonaceous materials were the final products upon deposition of $Si(OCH_3)_4$. The carbonaceous material, which showed an e.s.r. signal, was only removed by calcining in oxygen. About half of the weight gained was thus lost again to obtain SiHM. The silicon compound was completely oxidized by the final calcination and was stabilized on the external surface of the zeolites.

The SiHM thus obtained was characterized by various methods. From the t.p.d. profile it was concluded that the acidity was not altered by the deposition of $Si(OCH_3)_4$.

Adsorption of water also indicated the conservation of the internal surface, because the sorption capacity of H_2O was not affected. Therefore one can conclude that the $Si(OCH_3)_4$ does not interact with the inside surface of the pores, but is deposited only on the external surface of the zeolite. This is because the alkoxide is too large to enter the pore; its kinetic diameter is estimated to be 0.89 ± 0.02 nm, which is larger than the pore channel in mordenite, 0.67×0.70 nm.

On the other hand, the size of pore was reduced by the alkoxide deposition, as observed by experiments with various adsorbates. The diffusion constants of adsorbates varied greatly with the extent of deposition. Because the inside of the pore was not altered, the adsorption experiment indicates that only the pore opening decreases in size.

As judged from the different diffusion constants (table 2), separation of *o*- and *p*-xylenes is possible on SiHM (1.4 wt %), thus providing a means of estimating the size of its pore opening. Because of the kinetic diameters, 0.63 and 0.59 nm for *o*- and *p*-xylene, respectively, the size of the pore opening of SiHM (1.4 wt %) is estimated to be *ca.* 0.6 nm. The adsorption of these xylene isomers was almost inhibited, but hexane was adsorbed on SiHM (2.7 wt%). The pore size is further narrowed to *ca.* 0.5 nm at this extent of deposition because hexane, whose kinetic diameter is 0.43 nm, can just enter the pore. Finally, the adsorption of hexane was strongly suppressed by supporting the alkoxide as much as 4.8 wt %. The size of the pore opening of SiHM decreases on increasing the extent of deposition. Furthermore, the adsorption behaviour is strongly dependent on the size of the adsorbate and the degree of deposition. Therefore, it is suggested that the size of the pore opening is uniformly controlled by deposition. Such a sharp distribution of pore-opening sizes could be effective in shape-selective catalytic reactions and separation processes, as has been reported.[10]

Silica enrichment is clearly confirmed by X.p.s. measurements. Because X.p.s. supplies information about the surface layer, the thickness of the SiO_2 compound formed can be estimated by assuming the electron escape depth. The Si/Al ratio of SiHM can be correlated with the thickness (t) of the SiO_2 layer and the electron escape depth (d) as follows:

$$\mathrm{Si/Al} = t(n+1)/(d-t)+n$$

where n denotes the Si/Al ratio of HM, 6.8. Fig. 6(*b*) shows the thickness of SiO_2 layer thus estimated, the electron escape depth being taken as 2.0 nm.[21] Therefore one can estimate the SiO_2 layer formed to be 0.2–0.8 nm in thickness.

On the other hand, the thickness of the SiO_2 layer can be estimated from the deposition density of SiO_2 and the cation site density of the mordenite. The deposition density is calculated from the amount of SiO_2 deposited and the external surface area; it is 12.2 nm^{-2} for an increase of 1 wt %. On the other hand, the cation surface density of mordenite is 8.61 nm^{-2}, since 32 sites exist on the unit square 1.81×2.05 nm^2 normal to the pore.[22] A comparison of these values clearly indicates that 1.4 layers of silica are formed by the deposition of 1 wt %. This estimate is in good agreement with that made on the basis of the study, because a monolayer of SiO_2 is estimated to be *ca.* 0.3 nm in thickness, while 0.4 nm is suggested for this extent of deposition.

Results on the characterization of SiHM can therefore be summarized from the viewpoint of the structure of the silica layer and the pore-opening size. The pore-opening size is narrowed by 0.1 nm upon formation of 1–2 layers of SiO_2. Because the thickness seems to be proportional to the degree of deposition, it is considered that 2–3 layers of SiO_2 are formed when 2 wt % is deposited, which reduces the pore opening by *ca.* 0.2 nm.

Silica deposited on the external surface is inactive to catalytic reactions. In other words, the silica layer inactivates the external surface by poisoning the acidic sites. Such a deactivation of the external surface will probably enhance the shape selectivity, because the non-selective reaction is strongly inhibited upon formation of a silica layer. Therefore, silica on the external surface not only reduces the effective pore-opening size but also inactivates the external surface, thus enhancing shape selectivity.

The characteristics of the SiHM obtained in this study are clearly discriminated from those of the silanated zeolites prepared using SiH_4 previously studied by Barrer *et al.*[16] The latter study reported that the whole zeolite surface could be silanated. Although the acidity was not measured, it is expected that the acidity of H-mordenite silanated by SiH_4 should be altered significantly. Also, in the P-modified ZSM-5 both the acidity and the pore-opening size were modified, as reported previously.[23] Therefore, only the present method modifies the pore-opening size without changing the acidity. The pore-opening size obtained is finely controlled, as judged from adsorption studies and the enhanced shape selectivity for paraffin cracking. It seems that the size of the pore opening can be controlled to an accuracy of 1 Å by choosing the deposition conditions. Therefore, various applications of this method may be developed, especially in the fields of shape-selective catalytic reactions and sorption. Utilization of the method may also be anticipated for metal-loaded zeolites.

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