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Fine Control of the Pore-Opening Size of Zeolite ZSM-5 by Chemical Vapor Deposition of Silicon Methoxide

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The pore-opening size of ZSM-5 was finely controlled by the chemical vapor deposition (CVD) of silicon methoxide. The silicon compound vapor was deposited, and the deposited material was calcined by oxygen, finally forming a silica-coated zeolite (SiHZSM-5). This was characterized by temperature-programmed desorption of ammonia and adsorption experiments using various molecules. It was found that the silica was deposited only on the external surface and narrowed the pore-opening size effectively with the internal structure unaltered. The fine control of the pore-opening size was tested, exemplified by the conversion of methanol. Hydrocarbon product distribution shifted to smaller molecules over the SiHZSM-5: the formation of smaller olefins such as ethylene and propylene increased in place of the complementary decrease of large aromatics. Enhancement of the product shape selectivity was remarkable in xylene isomers and larger aromatics, which indicated the fine controls of the pore-opening size according to the deposition extent. Structures of the CVD zeolite and the enhanced shape selectivity in the methanol conversion were discussed.

Introduction

The pore size of zeolite is determined primarily by the number of oxygens in the ring of zeolite pore, and the distribution of pore sizes is intermittent, depending on six-, eight-, ten-, and twelve-membered rings. In other words, the pore sizes of zeolites are not distributed continuously, and the selection of a zeolite species in a desired reaction or sorption is restricted. From this point of view, zeolite ZSM-5 is an important species to fill the vacancies in pore size distribution of zeolites, since the ten-membered ring of the synthesized structure forms a pore of an intermediate size, larger than those of zeolite A and erionite, and smaller than those of mordenite- and faujasite-type zeolites. The pore size 0.5–0.6 nm would be suitable for sieving organic molecules, and therefore the ZSM-5 could be vastly utilized for the reaction and the sorption of hydrocarbons. Even though the unique property of the ZSM-5 species is now available,[1] it may be insufficient to use the zeolite species only in a native form. In order to overcome this drawback, therefore, a method to precisely control the pore size would be required.

We have previously proposed the CVD (chemical vapor deposition) of silicon alkoxide to control the pore-opening size of zeolite mordenite.[2–4] With this method, the pore-opening size of mordenite was controlled uniformly and precisely without affecting acidic sites. Mono- to trilayers of silica deposited on the external surface of mordenite narrowed the size of the pore opening effectively, and the selectivity of such a catalytic reaction as cracking was drastically enhanced. However, neither the CVD reaction nor the structure of deposited silica is understood exactly. Furthermore, it is not yet known whether the present method is applicable to other kinds of zeolite, since only the acid-type mordenite was utilized. Therefore, the CVD method has to be extended to various zeolites in order to know the whole aspect.

In recent years, the ZSM-5 zeolite has been extensively studied from various viewpoints, owing to its unique structure and catalytic activity.[5] Stability against coke deposition and high shape selectivity are attributed to the structure as well as to the acidic property. Because ZSM-5 possesses a cross-linked structure that is different from the mordenite of linear pore, the structure of ZSM-5 seems to result in a different way of controlling the pore-opening size by the deposited silica. Not only the structure of the deposited silica but also the deposition reaction should be different from on the mordenite because the deposition may be affected by the composition of Si and Al or by the strength and/or amount of acid sites of zeolites. Therefore, it is extremely important to check the influence of these different conditions on the formed zeolites. Obviously, the ZSM-5 zeolite with a controlled pore-opening size could enhance its significance in zeolite chemistry. Furthermore, the characteristics of the CVD method could be identified, since various methods for modifying the ZSM-5 with additives,[6–8], organic molecules,[9] or large silicon compounds[10] have already been proposed.

The purpose of the present paper is therefore to study the applicability of the CVD method to the ZSM-5 zeolite: moreover, the deposition reaction and the structure of the deposited silica on the ZSM-5 will be studied. The conversion of methanol into hydrocarbons is selected as a test reaction for the shape selectivity, because the methanol conversion is one of the typical acid-catalyzed reactions on the ZSM-5 zeolite. The mechanism of the enhanced product shape selectivity will be discussed.

Experimental Method

Zeolite ZSM-5 was prepared by the method described in the Mobil patent.[13] This was ion-exchanged in an ammonium nitrate solution 3 times, and the ammonium form of ZSM-5 was converted into the decationized H form (HZSM-5) by calcining at 673 K in flowing nitrogen. The SiO_2 to Al_2O_3 molar ratio of the HZSM-5 was 38. The unit cell composition of the fully hydrated sample was $Si_{91.2}Al_{4.8}Na_{0.04}H_{4.8}O_{192}\cdot 43.7H_2O$. The external surface area (determined by the benzene-filled pore method[14]) was 19.2 m^2/g.

CVD has been carried out by the method described elsewhere.[2,3] Deposition was performed with a vacuum system. The vacuum

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[1] (a) Derouane, E. G. *Catalysis by Zeolite*; Imelik, B. et al., Eds.; Elsevier: Amsterdam, 1980; p 5. (b) Weisz, P. B. *Proc. Int. Congr. Catal., 7th* **1981**, 57.

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[3] Niwa; M., Kato; S.; Hattori, T.; Murakami, Y. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 3135.

[4] Niwa, M.; Kawashima, Y.; Murakami, Y. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2757.

[5] For example: (a) Vedrine, J. C. et al. *J. Catal.* **1979**, *59*, 248. (b) Topsoe, N.-Y.; Pedersen, K.; Derouane, E. G. *J. Catal.* **1981**, *70*, 41. (c) Haag, W. O.; Lago, R. M.; Weisz, P. B. *Faraday Discuss. Chem. Soc.* **1981**, *No. 72*, 318.

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[10] Rodewald, P. G. U.S. Patents 4060563, 4090981, 4100219, 4127616.

[11] Plank, C. J.; Rosinski, E. J.; Schwartz, A. B. U.S. Patent 1402981, 1974.

[12] Chang, C. D. *Catal. Rev.—Sci. Eng.* **1983**, *25*, 1.

[13] Argauer, R. J.; Landolt, C. R. U.S. Patent 3702886, 1972.

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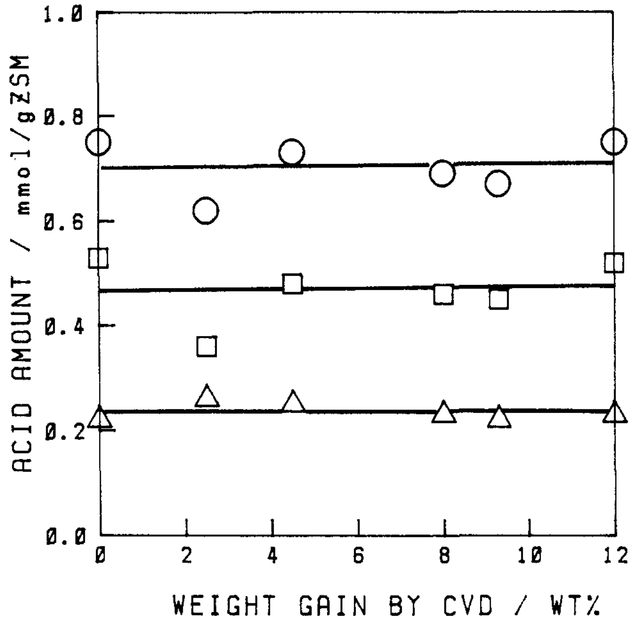

Figure 1. Dependence of acid amount as determined by TPD of ammonia on the weight gain by CVD: l (△), h (□) peaks and total (○) amount.

line consisted of an 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 vapor in a doubly sealed outer glass jacket in order to maintain the quartz spring constant. HZSM-5 was set in a quartz basket hung on the microspring, and the alkoxide was kept in a liquid reservoir. Zeolite material was evacuated fully at 593 K, and $Si(OCH_3)_4$ vapor was deposited at this temperature. The profile of the deposition was followed gravimetrically with a quartz spring balance. The weight gain upon deposition (composed of silica and other residues[15]) was used to show the extent of the modification, e.g., SiHZSM-5 (12.0 wt %). The deposition amount was controlled by choosing experimental conditions such as catalyst weight and pressure of the alkoxide. For the highly deposited sample, the CVD were repeated after the evacuation of the gas phase (7 times at most). The sample became gray after the deposition because of coke deposition. The deposited sample was then calcined in flowing oxygen at 673 K to remove the carbonaceous deposit.

Sorption studies were carried out with a gravimetric or volumetric apparatus. The temperature-programmed desorption (TPD) of ammonia was measured by the method used previously.[16] Zeolite was evacuated at 773 K, and ammonia was adsorbed at 373 K. The temperature of the zeolite bed was linearly increased from 373 K at a rate of 2.5 K/min. Infrared spectra were recorded on a Jasco IR-G spectrophotometer. Behaviors of the deposited species and of the zeolite surface condition upon deposition and subsequent treatment were measured in situ.

Conversion of methanol into hydrocarbons was treated by the continuous-flow method. The reaction was performed at 623 K over the catalyst pretreated at 773 K for 1 h. Methanol vapor was fed into a reactor through a saturator connected with condenser at 273 K. The partial pressure of methanol was then 30 Torr (1 Torr = 133.3 Pa). Liquid and gas products were analyzed by gas chromatography with silicon OV 101 and squalane on alumina columns, respectively. The xylene and ethyltoluene isomer distribution was analyzed with a Benton 34 column.

Results

Characterization of SiHZSM-5. TPD spectra of ammonia were obtained on HZSM-5 and modified ones. The spectrum on the HZSM-5 was characterized of double peaks at peak maximum temperature 428 and 613 K, which were named l and h peaks, as reported previously.[16] Also on SiHZSM-5, similar spectra were obtained on not only the temperature maxima of peaks but also the desorbed amount (Figure 1). One could conclude therefore that neither strength nor amount of the acidity was changed by the deposition of the silica compound.

TABLE I: Rate Constant k and Adsorption Amount at Equilibrium v_e for Adsorption of *o*-Xylene on HZSM-5 and SiHZSM-5[a]

adsorbent	10^3k, mmol/min gZSM	v_e, mmol/gZSM
HZSM-5	6.1	1.08
SiHZSM-5 (4.5 wt %)	1.4	1.11
SiHZSM-5 (8.0 wt %)	1.3	1.02
SiHZSM-5 (12.0 wt %)	0.55[b]	

[a] Partial pressure of *o*-xylene was 0.64 kPa. [b] v_e was assumed to be 1.05 mmol/gZSM.

TABLE II: Product Yield of Hydrocarbons in the Methanol Conversion[a]

	% yield[b]				
		wt % SiHZSM5			
catalyst	HZSM5	4.5	8.0	9.3	12.0
C_2	0.2	0.1	0.1	0.1	0.2
$C_2^=$	8.1	9.7	14.0	14.1	15.2
C_3	4.6	4.6	4.5	5.0	5.2
$C_3^=$	10.0	11.2	12.4	12.8	12.6
i-C_4	14.2	13.3	9.5	10.3	9.4
C_4	1.7	1.6	1.3	1.6	1.6
$C_4^=$	4.3	4.6	6.5	7.6	5.8
C_5^+	18.6	19.2	16.4	16.9	13.6
A_6, A_7	4.6	4.7	4.4	5.3	4.5
A_8	15.5	16.3	14.6	16.2	13.9
Ag	14.5	11.8	3.9	2.9	1.6
A_{10}^+	3.5	2.6	1.1	0.6	0.2
hydrocarbon yield, %	100	99.7	89.5	93.3	84.2[c]

[a] Reaction conditions: reaction temperature, 623 K; catalyst weight, 0.2 g; total flow rate, 40 mL/min; partial pressure of methanol, 0.039 atm. [b] (=) indicates olefin; i, isobutane; unless otherwise described, paraffin or aromatics. [c] The decreased yield was increased by using the larger amount.

Adsorption studies were performed with various molecules of different sizes. Results using such small molecules as water (kinetic diameter,[17] 0.265 nm) and nitrogen (kinetic diameter, 0.364 nm) indicated conservation of the adsorption capacities because neither the rate nor the isotherm of the adsorption was changed by deposition of the silicon alkoxide (Figure 2).

On the other hand, the rate of adsorption of *o*-xylene (kinetic diameter, 0.63 nm) was suppressed significantly by the modification. It was found that the rate of adsorption could be expressed by the following equation:

$$dv/dt = k(v_e - v)/v \quad (1)$$

where v and v_e are the adsorption amounts at time t and at equilibrium, and k denotes the rate constant of adsorption. This could be reformed by integrating with respect to time, i.e.

$$v_e \ln (v_e/(v_e - v)) - v = kt \quad (2)$$

Linear plots of eq 2 are shown in Figure 3. The rate constant (k) was determined by the slope, as shown in Table I. By the deposition of silica compound, the rate constant (k) for *o*-xylene adsorption decreased greatly, while the adsorption amount at equilibrium (v_e) changed little.

Conversion of Methanol. The conversion of methanol into hydrocarbons was carried out over HZSM-5 and SiHZSM-5. Products included hydrocarbons of C_2 (hydrocarbon with 2 carbons) to C_{10}, as shown in Table II. Increasing the deposition

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[15] It was found experimentally that the deposited layer contained 87 wt % SiO_2.

[16] Hidalgo, C. V.; Itoh, H.; Hattori, T.; Niwa, M.; Murakami, Y. *J. Catal.* **1984**, *85*, 362.

[17] Breck, D. W. *Zeolite Molecular Sieves*; Wiley: London, 1974; p 636.

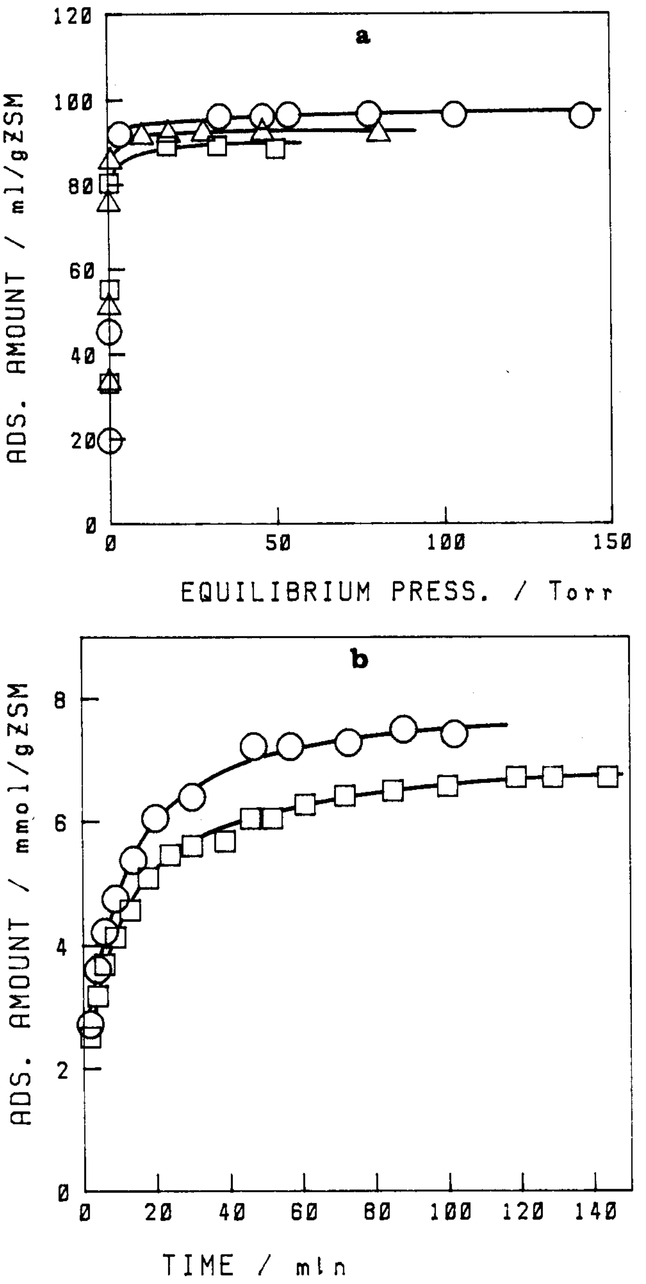

Figure 2. (a) Adsorption isotherm of nitrogen at 77 K; (b) adsorption of water at room temperature (293 K) on HZSM-5 (○), SiHZSM-5 (9.3 wt %) (△), and (12.0 wt %) (□).

amount decreased the yields of such large molecules as A_9 (aromatic compound with 9 carbons) and A_{10} significantly. Likewise, the formation of isobutane and C_5^+ (hydrocarbons with more than 5 carbons) also decreased by small degrees. On the other hand, the yields of small olefins (ethylene, propylene, and butene) were increased by the deposition. Especially, the variation of ethylene formation was remarkable. The formation of other molecules seemed to remain almost constant. In other words, the modification resulted in the decrease of large molecules and the complementary increase of small olefins.

Details of the product aromatic distribution are summarized in Table III. The remarkable change of xylene distribution is shown in Figure 4. The distribution of xylene isomers on the HZSM-5 was in good agreement with that predicted from thermodynamics (at 623 K, *o*-xylene 23.1%, *m*-xylene 53.1%, *p*-xylene 23.8%), but it changed significantly by the deposition of silica: *p*-xylene, the smallest isomer, was enhanced, while other larger isomers were suppressed. It was found that *p*-xylene was formed selectively on the SiHZSM-5 (12.0 wt %). Similar trends were observed for ethyltoluene isomers: *p*-ethyltoluene was formed on the SiHZSM-5 more selectively than *o*- and *m*-ethyltoluenes.

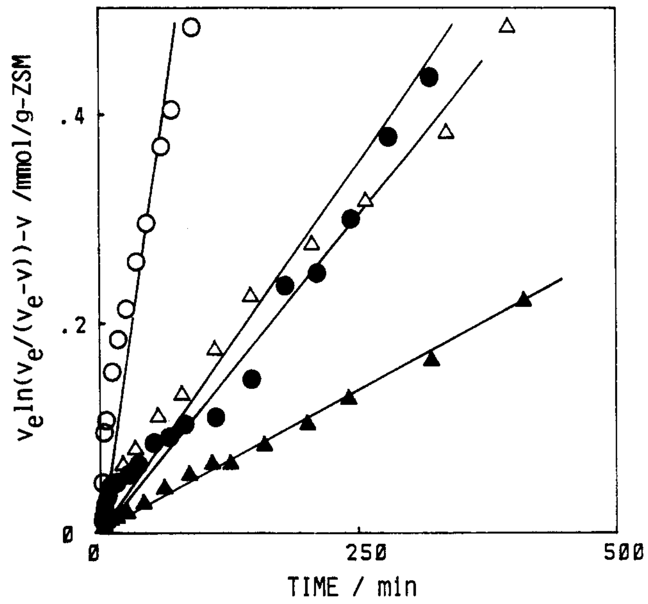

Figure 3. Plots for rate of adsorption of *o*-xylene derived from eq 2 over HZSM-5 (○), SiHZSM-5 (4.5 wt %) (△), SiHZSM-5 (8.0 wt %) (●), and SiHZSM-5 (12.0 wt %) (▲).

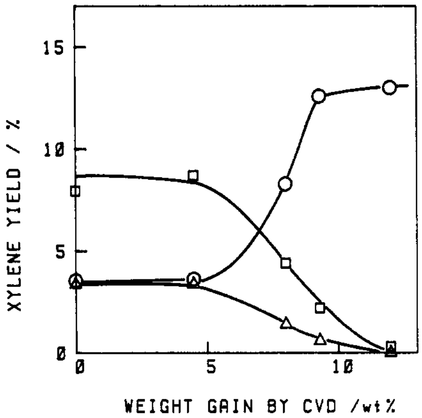

Figure 4. Change of product xylene distribution with increasing deposition extent (weight gain by CVD): *o*-xylene (△), *m*-xylene (□), and *p*-xylene (○).

TABLE III: Change of Aromatics Yield with Extent of CVD Deposition

	% yield				
		wt % SiHZSM5			
catalyst	HZSM5	4.5	8.0	9.3	12.0
o-xylene	3.4	3.4	1.4	0.6	0.0
m-xylene	8.0	8.7	4.4	2.2	0.3
p-xylene	3.6	3.6	8.3	12.6	13.0
o-ethyltoluene	0.2	0.2	0.0	0.0	0.0
m-ethyltoluene	1.4	1.9	0.7	0.3	0.0
p-ethyltoluene	0.6	0.7	1.1	1.4	1.3
1,2,4-trialkylbenzene	10.7	8.1	1.9	1.0	0.1
1,2,4,5- and 1,2,3,4-tetraalkylbenzene	1.9	1.3	0.3	0.1	0.0
ethylbenzene	0.6	0.7	0.6	0.7	0.6
1,3,5-trialkylbenzene	0.5	0.1	0.0	0.0	0.0

Among A_9 aromatics, furthermore, 1,3,5-trimethylbenzene was suppressed initially and 1,2,4-trimethylbenzene was then inhibited. Likewise, the formation of 1,2,4,5-tetramethylbenzene was suppressed on the SiHZSM-5 (more than 9.3 wt %). On the other hand, the formation of ethylbenzene did not change greatly. After all, *p*-xylene, *p*-ethyltoluene, and ethylbenzene were formed on the SiHZSM-5 (12.0 wt %) which was modified in the highest degree. In conclusion, the shape selectivity of product aromatics was discretely found according to the molecular size and the extent of the modification.

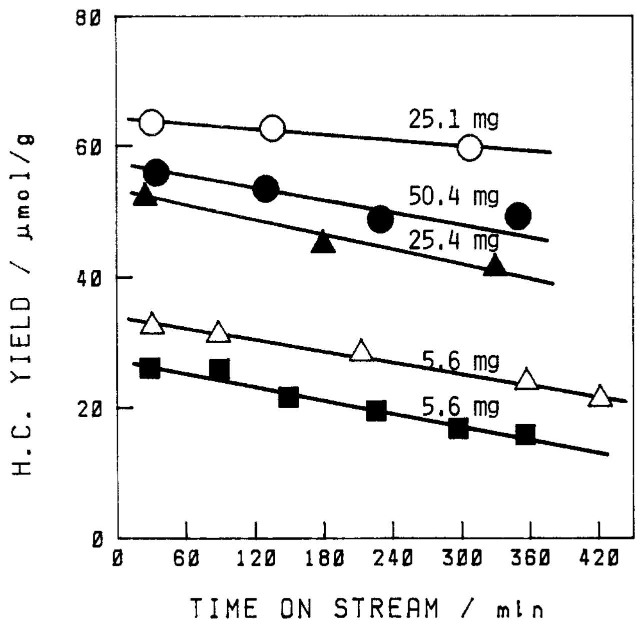

Figure 5. Activity changes with time on stream over SiHZSM-5 (12.0 wt %) (closed symbol) is compared with those of HZSM-5 (open symbol) at various conditions of charged catalyst amount.

The above findings were obtained under the experimental condition of almost 100% methanol conversion so that the activity decline was not found. Because the activity decline was reported to occur from the top to the bottom along the catalyst bed,[4] the catalyst life was then measured by using smaller amounts of zeolites. As shown in Figure 5, the conversion of methanol declined gradually with time on stream in similar degrees over both SiHZSM-5 (12.0 wt %) and HZSM-5 catalysts. The extent of deactivation was therefore independent of the kind of catalyst.

Infrared Study of the Deposited Layer. The deposition reaction was followed by an infrared measurement. The deposition of $Si(OCH_3)_4$ at 473 K revealed C–H stretching vibrations at 2950 and 2850 cm^{-1} as well as small shoulder peaks at 1700–1400 cm^{-1} (Figure 6). These decreased gradually upon evacuation at temperatures above 593 K and removed only by oxygen calcination at 673 K. On the other hand, hydroxide bands at 3740 and 3600 cm^{-1} were perturbed upon deposition of the alkoxide. The intensity of the 3600-cm^{-1} band was restored by the evacuation, while the 3740-cm^{-1} band was not completely. In other words, acid sites of zeolite at 3600 cm^{-1} were not changed by the deposition, while the isolated Si–OH at 3740 cm^{-1} varied significantly. It was therefore concluded that the silanol was significantly altered by the deposition.

Discussion

CVD on the HZSM-5. TPD of ammonia and sorption experiments showed conservation of the internal zeolite structure and narrowing of the pore-opening size by the CVD of $Si(OCH_3)_4$. This is simply because the size of the alkoxide is too large to enter the pore of HZSM-5. The kinetic diameter of the silicon alkoxide is supposed to be 0.89 ± 0.02 nm, much larger than that of HZSM-5 pore, 0.54–0.56 nm. It has to deposit on the external surface of the zeolite as silica.

The deposition only on the external surface of the zeolite seems to be confirmed by the infrared measurement of the deposited layer, since the isolated Si–OH, which was reported to exist on the external surface of zeolites,[9] was altered significantly by the CVD of the alkoxide. Probably, the isolated Si–OH may become vicinal or geminal hydroxide, unobservable by infrared spectroscopy. On the other hand, the infrared study indicated also the conservation of acid sites in the pore, since acidic hydroxide was hardly varied.

This behavior of the hydroxide groups suggests that the nonacidic Si–OH, at least, is available for deposition as active sites. The conclusion seems to be in agreement with the former observation by Hertl about the reaction of $Si(OCH_3)(CH_3)_3$ on the surface of SiO_2, because he claimed the preferential reactivity of the nonacidic hydroxide to the hydrogen-bonded hydroxide.[18] However, no substantial information was obtained as to the reactivity of the acid sites on the external surface of ZSM-5, as far as IR observations were concerned.

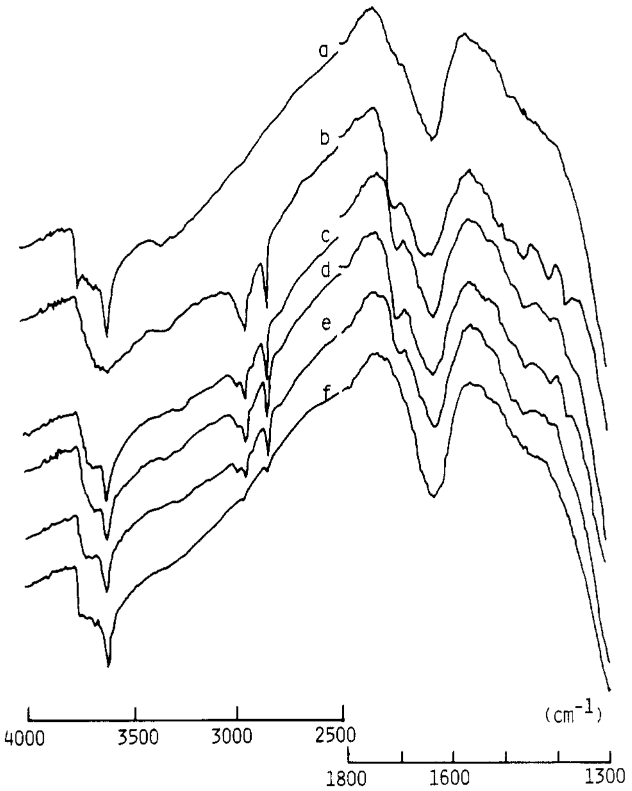

Figure 6. Infrared spectra of HZSM-5: (a) background evacuated, 593 K; (b) after admission of the alkoxide, followed by evacuation at 473 K; (c) evacuated at 593 K; (d) evacuated at 633 K; (e) evacuated at 673 K; (f) after calcination by oxygen at 673 K.

The activity of acid sites on the external surface should be neglected in the highly modified sample, because the formation of *o*- and *m*-xylenes was inhibited completely. As is easily understood, acid sites on the external surface, if existed, could contribute only to a non-shape-selective reaction. Therefore, fine controlling of the pore-opening size and deactivation of the external surface may indicate that the deposited silica makes a structure of the layer that covers the external surface. In other words, zeolites may be coated with the silica layer. Therefore, all the hydroxides on the external surface seem to be available for the deposition of the alkoxide.

If the deposited silica formed a layer structure, the number of layers could be evaluated from the deposited amount of silica and the cation surface density on ZSM-5. Since the cation site density on the external surface of ZSM-5 is regarded to be 8.91 nm^{-2},[19] the number of silica layers over the modified ZSM-5 is therefore about six on the SiHZSM-5 (12.0 wt %) and four to six on the shape-selectivity improved SiHZSM-5. On the other hand, mono- to trilayers are enough for the modification of mordenite[2,3] and platinum-loaded mordenite.[4] In other words, a thicker layer is required to narrow the smaller ZSM-5 pore. These are probably based on the difference in the structure of silica deposited on the external surface. Furthermore, the structure of the silica may be related to the mechanism of the surface reaction or to the zeolite structure.

Methanol Conversion on the SiHZSM-5. The rate of methanol conversion decreases due to the narrowing of the pore-opening

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[18] Hertl, W. *J. Phys. Chem.* **1968**, *72*, 1248; **1968**, *72*, 3993.

[19] It was reported that 24 cation sites existed on the unit square 2.01 × 1.34 nm^2 normal to the *y* axis. See: Olson, D. H. Kokotailo, G. K.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238.

size, while the reaction of methanol on active sites is believed to proceed on the mechanism that is almost the same as before the modification. The enhancement of product shape selectivity therefore should be caused by the diffusion control of molecules within the pore and the subsequent surface reactions but not by the primary reaction about the methanol activation. The deposition of coke is not stimulated on the SiHZSM-5, however, because the activity decline was not fastened even in highly modified SiHZSM-5 (12.0 wt %). This may be supported by a former study[20] claiming that the coke was deposited only on the external surface of ZSM-5. We could indicate some possible reactions responsible for the high shape selectivity on the SiHZSM-5.

Isomerization into small-size molecules is one of the significant reactions, and it is exemplified by the increase of *p*-xylene and *p*-ethyltoluene formation. Because on the zeolite with a small pore opening only the para isomer could diffuse out from the ZSM-5 pore, deviation from the thermodynamic equilibrium in the pore enhanced isomerization from the ortho and meta isomers to the para isomer.

A complementary increase of small olefins in place of large compounds is also indicative of the reaction within the pore. Although it seems that large compounds such as A_9 and A_{10} decompose into small olefins as ethylene and propylene, the direct conversion is unfavorable to the thermodynamics. It has been reported[21-23] that such hydrocarbons as propylene and butene are converted readily into various hydrocarbons, of which product distribution is similar to that observed in the methanol conversion. Depending on the method of catalyst activation,[24] ethylene is also converted into various hydrocarbon products. In other words, olefins once formed in the zeolite pore are converted rapidly into products, including aromatic compounds. From that viewpoint, olefinic residues are regarded as adsorbed intermediates in this reaction.[25] In orer to explain the higher reactivities of olefins and the resultant similar product distribution, therefore, it may be supposed that these hydrocarbon residues are converted to each other by gaining or losing skeletal carbons.

In the small-size pore, smaller molecules should diffuse out easily and the exit of larger compounds may be suppressed. Under these conditions, the formation of small molecules should be relatively stimulated, since residues of larger compounds have to be converted into those for small molecules. One could therefore indicate the interconversion between hydrocarbon residues as a plausible idea in explaining the suppression of large aromatics and the complementary increase of small olefins.

Registry No. $Si(OCH_3)_4$, 681-84-5; ammonia, 7664-41-7; water, 7732-18-5; nitrogen, 7727-37-9; *o*-xylene, 95-47-6.

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[25] Dessau, R. M.; LaPierre, R. B. *J. Catal.* **1982**, *78*, 136.

Chemical Reactivity in Monolayers: Study of an Amphiphilic Tetrapyridinoporphyrazine in Langmuir–Blodgett Films

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This paper reports on the synthesis, association in solution, monomolecular layer formation, and Langmuir–Blodgett (LB) homolayer and alternate layer properties of an amphiphilic copper tetrapyridinoporphyrazine. The high conjugation of the four pyridinium rings with the central porphyrazine core has a great influence on the chemical properties in solution and in a monolayer. The degree of association is dependent on the Lewis acidity of the solvent, the oligomeric forms—stable in pure chloroform solution—being broken by any donor–acceptor interaction between the porphyrazine ring and Lewis acids such as acetic acid, nitrogen dioxide, or iodine. The amphiphilic porphyrazine forms stable monomolecular layers to film pressure up to 35 mN·m^{-1}. The aromatic ring reacts with water, giving rise to a virtually two-electron-reduced porphyrazine through a donor–acceptor complex. This complex can be transferred onto solid substrates and is indefinitely stable in LB films. It is characterized by infrared, electronic, and ESR spectroscopy. The chemical reduction in the monolayer state is inhibited by Lewis acids present either in the bath or in the monolayer. ESR studies on homolayers and alternate layers built from mixtures of the amphiphilic porphyrazine and ω-tricosenoic acid show that the porphyrazine rings lie flat on the substrate, and provide an estimation of the plane-to-plane and in-plane coupling between the copper ions.

Numerous studies on physical and chemical properties of substituted phthalocyanines have recently appeared in the literature.[1-12] The increasing use of phthalocyanines in photovoltaic cells,[13] semiconductors,[14,15] organic metals,[16,17] or sensitive coating films[18-20] leads scientists to search how to modify the features of

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