JOURNAL OF CATALYSIS **114**, 186–189 (1988)

NOTES

The Influence of Chemisorbed Molecules on Mass Transfer in H-ZSM-5-Type Zeolites and the Location of Brønsted Acid Sites

Heterogeneous catalysis is one of the most important applications of zeolites. Therefore, various methods have been developed to determine the strength and concentration of Brønsted acid sites in zeolites. Among them, in the last few years, ^{1}H MAS NMR has become a powerful tool (*1–3*). In addition to the accessibility of the acid sites probed by chemisorption of N-bases (*2, 3*), the steric environment of these catalytically active sites is of importance since it imposes constraints on the geometry of the transition state. However, only a few studies have been reported on this topic. Information was obtained from quantum chemical calculations (*4*), catalytic experiments (*5–8*), I.R. spectroscopy (*9*), and the arrangement of guest molecules (*10*). From these investigations it has been concluded that in H-ZSM-5 the channel intersections should be preferential location centers for the Brønsted acid sites.

In adsorption technology, in the use of zeolites as shape-selective adsorbents, modification of the molecular sieve properties by chemisorption of nitrogen-containing bases (N-compounds) has become a common technique [e.g., (*11–13*)]. We have applied the NMR pulsed field gradient technique (*14*) to study the influence of chemisorbed N-compounds on transport properties of molecular sieves, considering the chemisorbed compounds as transport obstacles.

Evidently, such influence must be expected to depend on the location of the N-compound considered within the channel network. If the obstacles are localized within the pore segments of ZSM-5 between channel intersections, the passage of molecules through only these segments is reduced or prohibited. On the contrary, occupation of the channel intersections by chemisorbed molecules should affect the passage through all four adjacent pore segments. Hence, depending on the location of the given sorption sites, the N-compounds will lead to different reductions of translational mobility within the channel network. Comparison of the experimentally observed dependences with computer simulations of molecular mobility in ZSM-5-type channel networks with statistically distributed obstacles may provide an estimate of the most probable locations of the N-compounds and, thus, of the Brønsted acid site positions within the H-ZSM-5-type zeolites investigated.

ZSM-5 specimens of different Si/Al ratios were synthesized with TPABr as template. After calcination (6 h at 600°C) the zeolites were ion-exchanged by means of 0.1 *M* HCl. The concentration of Brønsted acid sites was determined by ^{1}H MAS NMR after sample activation at 400°C and 10^{-2} Pa. The ^{1}H MAS NMR spectra were measured with the homemade pulse spectrometer HFS-270 (Leipzig, Sektion Physik) operating at 270 MHz and at a spinning frequency of 3 kHz using sealed glass ampoules. The proton spectra consist of three lines: line a at 1.8 . . . 2.3 ppm caused by nonacidic OH groups (silanol groups), line b at 4.3 ppm representing the Brønsted acid OH groups, line d at 6.7 ppm attributed to ammonium ions [cf. (*1–3*)].

For the ^{1}H NMR self-diffusion measurements of methane, the samples were modified by quantitative chemisorption of ammonia or pyridine in the following way.

0021-9517/88 $3.00

After sample activation at 400°C and 10^{-2} Pa, an amount of ammonia or pyridine corresponding to approximately 80% of the equivalent number of Brønsted acid protons (as determined by the ^{1}H MAS NMR) was sorbed on the activated zeolite via vacuum distillation. Sealed glass ampoules with the zeolites and the N-compounds chemisorbed were tempered at 300°C for 5 h to distribute the N-compounds over the zeolite crystal homogeneously. It can be concluded from the significant reduction in the intensity of line b in the ^{1}H MAS NMR spectra that all of the N-compounds introduced had reacted with the Brønsted acid sites (*2*, *3*).

Then the zeolites containing different amounts of chemisorbed N-compounds were loaded with methane. The self-diffusion coefficients of methane were measured by means of the NMR pulsed field gradient technique (*14*) at 60 MHz on the homemade pulse spectrometer FEGRIS (Leipzig, Sektion Physik). Applying two intense and sufficiently short field gradient pulses of separation time t, the precessional phases of the nuclear spins are used to monitor the differences $r(t)$ in the positions of the individual spins (and hence of the atoms and molecules to which they belong) at the time of generation of the two gradient pulses. In homogeneous systems, by the Einstein equation

$$D = \frac{\langle r^2(t) \rangle}{6t} \tag{1}$$

the resultant molecular mean square displacement $\langle r^2(t) \rangle$ may be applied to determine the self-diffusion coefficient D of the molecules under consideration.

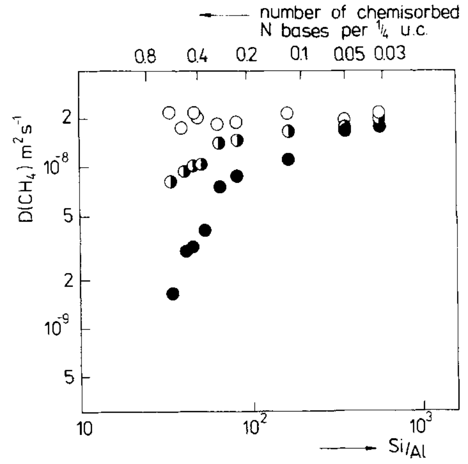

FIG. 1. Intracrystalline self-diffusion coefficients of methane (loading approximately 2 molecules per ¼ unit cell, 27°C) in H-ZSM-5 of different Si/Al ratios containing molecules of chemisorbed N-compounds covering approximately 80% of the equivalent number of Brønsted acid sites: ◑, ammonia; ●, pyridine. For comparison, the self-diffusivities in the parent H-ZSM-5 without any N-bases (○) are included.

Figure 1 shows the self-diffusion coefficients of methane at 27°C and at a loading of approximately two molecules per channel cross section (¼ unit cell) sorbed on H-ZSM-5 specimens of different Si/Al ratios without and with chemisorbed N-compounds. In agreement with previous investigations (*15–17*), methane self-diffusion in the unmodified H-ZSM-5 specimens is found to be independent of the Si/Al ratio. On the contrary, chemisorption of N-compounds leads to a significant reduction in the self-diffusion coefficients. This effect becomes more pronounced with increasing number of chemisorbed N-bases corresponding to a decreasing Si/Al ratio.

Evidently, the chemisorbed N-compounds represent significant obstacles for the self-diffusion of methane molecules. Even in the case of ammonia, the reduction of the mobility of the probe molecule methane exceeds by a factor of more than 2 the expectations derived from the dependence of the methane mobility on the pore filling of the ZSM-5 structure (*17*).

This microdynamical model is supported by the results of a comparison between the mean lifetimes τ_j on sorption sites of the methane molecules and N-bases, respectively. Correlating the self-diffusion coefficients D of the methane molecules with the diffusion path l between adjacent channel segments by an expression similar to Eq. (1), with $l \sim 1$ nm and $D \sim 10^{-8}$ m^2 s^{-1}, τ_j is

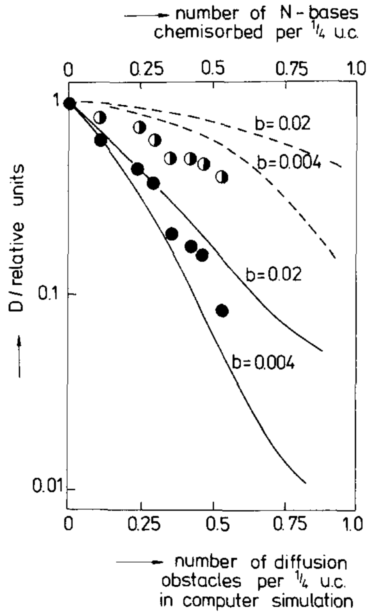

FIG. 2. Results of the computer simulation of a random walk in a two-dimensional channel network with statistically distributed obstacles of different transition probability (*b*) over the channel intersections (—) and over the pore segments (---). Comparison with the experimental values (cf. Fig. 1) of methane self-diffusion in H-ZSM-5 containing ammonium (◑) and pyridinium (●) ions.

estimated to be on the order of 10^{-9} s. On the other hand, from ^{1}H NMR studies of the interaction of pyridine molecules with the Brønsted OH groups of HY (*1*), it follows that the correlation times of pyridinium ions are on the order of 10^{-6} s. Therefore, with respect to the highly mobile methane molecules, the chemisorbed N-bases may be regarded as rigid obstacles in the channel network of H-ZSM-5.

The influence of statistically distributed obstacles on the self-diffusion of molecular species sorbed in ZSM-5-type channel networks has been determined under the condition that the obstacles are distributed over either the channel intersections or the connecting segments (*18, 19*).

Figure 2 shows the results of these computer simulations. The parameter *b* denotes the ratio between the probabilities of molecular jumps between adjacent intersections with and without an obstacle situated in the channel segment between them. It becomes evident from Fig. 2 that the shape of the logarithmic plot of the self-diffusion coefficient (ln *D*) versus the number (*n*) of obstacles is typical of the given type of obstacle distribution; i.e., there is no possibility of transfer of the ln *D* versus *n* plots of one limiting case to those of the other by a simple change in the transition probability across the obstacles (*18, 19*).

The experimental results for the influence of chemisorbed ammonia and pyridine on methane self-diffusivity are also shown in Fig. 2. It turns out that in the case of pyridine, the self-diffusion data are in satisfactory agreement with the theoretical prediction for the case that the obstacles are distributed over the channel intersections. In agreement with suggestions of previous work (*4–10*) one has to conclude, therefore, that the chemisorbed pyridine molecules and, thus, the Brønsted acid sites are most likely to be localized in the channel intersections.

A similarly strict conclusion cannot be drawn from the experimental data for chemisorbed ammonia, which give rise to a behavior intermediate between those of the two limiting cases. One should take into account, however, that due to the smaller size of ammonia molecules (in contrast to the assumptions of the computer experiments) an ammonium ion probably does not lead to a simultaneous blockage of all adjacent channel segments when it is situated at one channel intersection. Thus, complete agreement of these experimental data with those of the computer simulations cannot be expected.

ACKNOWLEDGMENTS

The authors thank Dr. M. Hunger for providing the ^{1}H MAS NMR results and Dr. W. Heink for assistance in the self-diffusion measurements.

REFERENCES

1. Pfeifer, H., Freude, D., and Hunger, M., *Zeolites* **5**, 274 (1985).

2. Freude, D., Hunger, M., Pfeifer, H., and Schwieger, W., *Chem. Phys. Lett.* **128,** 62 (1986).
3. Hunger, M., Freude, D., Fröhlich, T., Pfeifer, H., and Schwieger, W., *Zeolites* **7,** 108 (1987).
4. Fripiat, J. G., Berger-André, F., André, J. M., and Derouane, E. G., *Zeolites* **3,** 306 (1983).
5. Derouane, E. G., and Védrine, J. C., *J. Mol. Catal.* **8,** 479 (1980).
6. Topsøe, N. Y., Pedersen, K., and Derouane, E. G., *J. Catal.* **70,** 41 (1981).
7. Lercher, J. A., and Rumplmayr, G., *Z. Phys. Chem.* (*NF*) **146,** 113 (1985).
8. Anderson, J. R., Mole, T., and Christov, V., *J. Catal.* **61,** 477 (1980).
9. Jacobs, P. A., and von Ballmoos, R., *J. Phys. Chem.* **86,** 3050 (1982).
10. Narasimhan, C. S., Narayana, M., and Kevan, L., *J. Phys. Chem.* **87,** 984 (1983).
11. Rosbach, D. H., U.S. Patent 4,283,587 (1981).
12. Smolin, W., U.S. Patent 4,351,981 (1982).
13. Nayak, V. S., and Riekert, L., Proceedings, International Symposium on Zeolite Catalysis, Siófok (Hungary), 1985, p. 157.
14. Kärger, J., and Pfeifer, H., *Zeoites* **7,** 90 (1987).
15. Caro, J., Hočevar, Kärger J., and Riekert, L., *Zeolites* **6,** 213 (1986).
16. Caro, J., Bülow, M., and Kärger, J., *Chem. Eng. Sci.* **40,** 2169 (1985).
17. Caro, J., Bülow, M., Schirmer, W., Kärger, J., Heink, W., Pfeifer, H., and Ždanov, S. P., *J. Chem. Soc. Faraday Trans. 1* **81,** 2541 (1985).
18. Förste, C., Germanus, A., Kärger, J., Pfeifer, H., Caro, J., Pilz, W., and Zikánová, A., *J. Chem. Soc. Faraday Trans. 1* **84,** 2347 (1987).
19. Germanus, A., Ph.D. thesis, Karl-Marx-Universität, Leipzig, Sektion Physik, 1986.

J. CARO
M. BÜLOW

Zentralinstitut für physikalische Chemie der AdW der DDR,
Rudower Chaussee 5, DDR-1199 Berlin
German Democratic Republic

J. KÄRGER
H. PFEIFER

Sektion Physik der Karl-Marx-Universität Leipzig
Linnéstrasse 5, DDR-7010 Leipzig
German Democratic Republic

Received October 27, 1986; revised May 19, 1988