JOURNAL OF CATALYSIS 43, 356–359 (1976)

Proton Magnetic Resonance Investigations on Benzene Molecules in Faujasite-Type Zeolites Containing Cations of Different Charge

The catalytic properties of zeolites are determined by the ability of special structures at cavity walls to cause the activation of molecules. However, the reactions catalyzed by zeolites are often diffusion-controlled, so the mobility of the participants of the reaction in the cavities must also be taken into account.

This Note reports an NMR study of the influence of ion exchange on the mobility of benzene molecules in synthetic zeolites of the faujasite type. The structure of faujasite (*1*, *2*) leaves large cavities of about 13 Å diameter connected by channels about 8 Å wide. In these cavities at least two kinds of singly charged ion can be found. One of these comprises the so-called S_2 ions, which are situated in front of the six-membered rings common to the cubooctahedra and the large cavities. The other ions have not so far been located by X-ray diffraction (*1–4*) and are designated as nonlocalizable ions. With increasing Si/Al ratio the number of nonlocalizable ions decreases. Above Si/Al = 2.43 only the S_2-sites should be occupied. At higher Si/Al ratios or after an exchange of the sample by doubly or triply charged ions, these sites become progressively unoccupied.

At room temperature and at low to intermediate coverages, benzene molecules have a fairly good mobility in the cavities of Na faujasites. At coverages higher than 4 molecules/cavity, there is a restriction of this mobility due apparently to a mutual disturbance caused by the limited space inside the cavities, which favors also molecular dipole–dipole interaction of the benzene protons. This effect grows with increasing Si/Al ratio. It has been explained, following calculations of the electric field distribution of Dempsey (*5*), by regarding the surface of the samples with low Si/Al ratios as consisting of relatively numerous flat potential wells, whereas at high ratios there are only a few deeper potential wells above the ions in the S_2-sites, and a wide range of results on dipole molecules of different size can be understood in this way (*6–8*). For Si/Al $>$ 2.43 in Na faujasite a superimposed NMR line can be observed at high coverages, indicating that a small number of benzene molecules sorbed inside the cavities have an increased mobility. The occurrence of this narrow line corresponds to the situation where the number of the ions at the walls of the large cavities is too low to fix at least four molecules. Similar effects have been observed in the case of dioxane (*9*).

The Si/Al ratios of the samples used were chosen on the following basis. First, two samples with low Si/Al ratios of 1.22 and 1.18 were selected, for which one may calculate almost complete occupation of the nonlocalizable sites by ions of unit charge. The third sample had Si/Al = 2.5, which is just above the value of 2.43 at which the nonlocalizable ions are no more needed to build up the structure.

Na ions were then exchanged for Ca ions. X-Ray data (*10*, *11*) imply that the sample with the lower Si/Al ratio should then contain about three S_2 ions in the large cage, and the nonlocalizable sites are again not needed. Such samples, therefore, should be well suited for studying the direct influence of S_2 ions on the molecular mobility. One sample was exchanged with rare earth ions. For this the Si/Al ratio was chosen as high as available, to be sure that as many ions as possible would be removed from the structure. According to X-ray data (*12*, *13*), the Si/Al = 2.7 sample should then contain not more than one Na ion in the large cavity, because the rare earth ions preferably move to the S_I- and the S_I'-sites inside the cubo-octahedra in the course of the dehydration procedure.

The exchanged samples used for the experiments had the final compositions:

1. $Na_{0.5}Ca_{5.1}(AlO_2)_{11.0}(SiO_2)_{13.0}$,
2. $Na_{0.8}Ca_{2.7}(AlO_2)_{6.9}(SiO_2)_{17.1}$,
3. $Na_{1.3}La_{1.7}(AlO_2)_{6.5}(SiO_2)_{17.5}$.

The paramagnetic impurities incorporated in the aluminosilicate framework should not exceed 100 ppm calculated as iron.

Ion exchange, dehydration and sorption of benzene were carried out following conventional procedures. The NMR measurements were made on the wide-line unit of a VARIAN DP 60 spectrometer. A frequency of 16 Mc and a modulation frequency of 20 c were used. The temperature was 25°C.

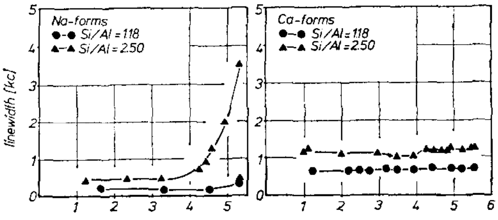

FIG. 1. Linewidths of the proton resonance spectra of benzene sorbed in Ca- and Na-faujasites.

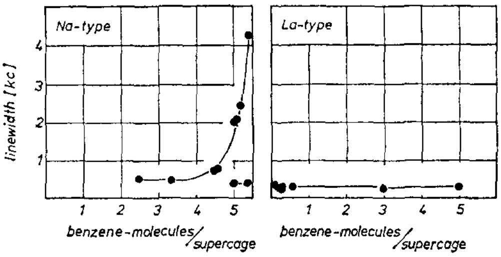

FIG. 2. Linewidths of the proton resonance spectra of benzene sorbed in the La and the Na form of a faujasite sample with Si/Al = 2.70.

The results of the linewidth measurements of the proton resonance of benzene molecules in the Ca forms of the two faujasite samples with Si/Al = 1.18 and 2.5 are compared with the results of the respective Na forms in Fig. 1. The linewidths in the Ca containing samples at low and intermediate coverages are distinctly increased in comparison to the Na faujasites. This indicates a stronger interaction with the surface, as can be expected from the model of the potential distribution outlined above.

A striking effect of the exchange of Na ions by Ca ions is the lack of the increase of the linewidth at high coverages for the sample with the high Si/Al ratio. A possible reason may be that in the Na form four benzene molecules in the large cavity are fixed to S_2 ions and the space inside the cavity is almost filled with these molecules of low mobility. In the Ca forms only two ions are left in this cavity, so that most of the molecules are no longer fixed to ions. The shape of the resonance lines gives no indication of the occurrence of two kinds of molecules with different mobility as has been observed in the Na forms.

In Fig. 2 the results obtained on the La-containing sample with Si/Al = 2.7 are compared with the respective Na forms. The linewidth in the rare earth sample is distinctly reduced compared with the samples containing Na ions and also to the sample with the Ca ions and Si/Al = 2.5. As in the sample with the Ca ions, the linewidth at high coverages shows no increase, and the shapes of the resonance lines indicate no occurrence of molecules with different mobility. The value of the widths of the resonance of the benzene protons in the La form nearly equals the width of the narrow lines at high coverages in the Na forms of high Si/Al ratio. As mentioned above, X-ray data (*12, 13*) imply that only about one Na ion should be expected in each large cavity. The observed linewidth, therefore, can be regarded as resulting from the mobility left by the interaction of the benzene molecules with the oxygen ions of the aluminosilicate framework or with one another.

Geschke and Pfeifer (*16*) have discussed the behavior of the relaxation times in a sample with Si/Al = 2.7 containing Ce ions. The high absolute value of the longitudinal relaxation time, as well as the temperature behavior and the apparently very low temperature of the T_1 minimum, seem to indicate a mobility undergoing only a quite weak restriction compared with the situation in the respective Na forms. The authors state, however, that the observed effects are due to a shortening of the electronic relaxation time of the paramagnetic impurity of the sample by the presence of the Ce ions. Supplementary measurements on our zeolite sample containing Ce and Pr ions do not lead to unambiguous results to clarify this difference.

Summarizing, it can be stated that the model of the potential distribution in the large cavities according to Dempsey (*5*) explains the results of the linewidth measurements at low and intermediate coverages of benzene as long as the Si/Al ratio is below 2.43, where the S_2-sites are occupied. The strong increase of the linewidths at high coverages can only be observed in the Na forms at high Si/Al ratios. At low ratios, the failure of this effect may be caused by the flat potential holes expected from the above model. At higher Si/Al ratios in the Ca-containing samples, the reduced number of only two ions in the large cavity leaves about three benzene molecules which are bound less tightly and which possibly change their sites with the molecules at the ions with a high rate.

In the La form, the low linewidth indicates a good mobility of the molecules inside the large cavities over the whole range of coverages. As La forms have catalytic activities exceeding by several orders of magnitude those of the other faujasite samples discussed above, it seems highly probable that this mobility, which is otherwise connected with the presence of large cavities with nearly no cations, is a decisive supposition for the activity, regardless of the question of the nature of the active centers.

ACKNOWLEDGMENTS

We thank Professor H. Pfeifer for providing details of work as yet unpublished. The support of our work by the "Deutsche Forschungsgemeinschaft" and the "Fonds der chemischen Industrie" is gratefully acknowledged.

REFERENCES

1. Eulenberger, G. R., Shoemaker, D. P., and Keil, J. G., *J. Phys. Chem.* **71**, 1812 (1967).
2. Smith, J. V., *Advan. Chem. Ser.* p. 171 (1971).
3. Olson, D. H., private communication.
4. Mortier, W. J., Bosmans, H. J., and Uytterhoeven, J. B., *J. Phys. Chem.* **76**, 650 (1972).
5. Dempsey, E., *SCI (Soc. Chem. Ind., London) Monogr.* p. 293 (1968).
6. Lechert, H., Hennig, H. J., and Mirtsch, S., *Surface Sci.* **43**, 88 (1974).
7. Lechert, H., and Hennig, H. J., *Z. Naturforsch.* **29a**, 1065 (1974).
8. Lechert, H., Habilitation thesis, University of Hamburg, 1974.
9. Lechert, H., Wittern, K. P., and Hennig, H. J., *Z. Naturforsch.* **30a**, 690 (1975).
10. Bennett, J. M., and Smith, J. V., *Mater. Res. Bull.* **3**, 633 (1968).
11. Pluth, J., and Smith, J. V., *Mater. Res. Bull.* **7**, 1311 (1972).

12. Bennett, J. M., and Smith J. V., *Mater. Res. Bull.* **3**, 865 (1968).
13. Hunter, F. D., and Scherzer, J., *J. Catal.* **20**, 264 (1971).
14. Lechert, H., Haupt, W., and Kacirek, H., *Z. Naturforsch.* **30a**, 1207 (1975).
15. Kacirek, H., and Lechert H., *J. Phys. Chem.* **79**, 1589 (1975).
16. Geschke, D., and Pfeifer, H., *Z. Phys. Chemie (Leipzig)*, in press.

H. Lechert
W. Haupt
K. P. Wittern

Institute of Physical Chemistry
University of Hamburg
Laufgraben 24
2 Hamburg 13, Germany

Received July 21, 1975; revised January 14, 1976