THE ACTION OF FUNCTIONAL GROUPS OF AN ION EXCHANGER DURING ITS USE AS A SOLID CATALYST

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Macroporous and standard sulphonated styrene–divinylbenzene ion exchangers were partially neutralized by ammonia and organic basic compounds in the gaseous phase and by inorganic basic ions in the aqueous phase. Their catalytic activity for dehydration of methanol was investigated in a static microreactor connected to a mass spectrometer. From a decrease in the catalytic activity during the partial neutralization it was possible to estimate the distribution of neutralized catalyst functional groups as well as the location of functional catalyst groups which take part in the catalytic reaction.

One of characteristic properties of ion exchangers as solid catalysts consists in the fact that not only their surface functional groups take part in the catalytic reaction, but also those which are inside the polymer mass. The fraction of the latter groups from the total amount depends on several parameters. We have succeeded in characterizing some of these parameters through purposefully controlled poisonings and by following their effect on the catalytic activity.

The relation between partial neutralization of ion exchangers and their activity has been examined by several authors[1-5]. Their results are mostly exploited for discussing the mechanism of catalytic reactions. The effect of the character of the neutralizing ion on the catalytic activity has been also established[3]. Usmanov and Rustamov[6] have investigated the accessibility of functional groups of an ion exchanger by varying the magnitude of its particles. Several papers[7-12] have been devoted to a study of relations between the accessibility of functional groups of ion exchangers and the dimension, resp. character, of sorbate molecules during adsorption from liquid and gaseous phases.

EXPERIMENTAL

Catalysts. Two forms of a sulphonated styrene–divinylbenzene ion exchanger catalyst containing 25% divinylbenzene were examined: a standard gel form (SS-25) with exchange capacity 3·72 mequiv./g, specific surface $S < 0.1$ m^2/g, helium density 1·42 g/cm^3, porosity 0·02% and a macroporous form (MS-25) with exchange capacity 3·8 mequiv./g, specific surface 44 m^2/g, helium density 1·45 g/cm^3, porosity 58%. The catalysts were transformed by ion exchange firstly to the Na^+-form, then to H^+-form and before use they were dried in vacuum (1 Torr) for 6 h at 105°C.

Apparatus. The experiments were performed in a glass static microreactor connected directly to a mass spectrometer (Finnigan, Model 3000), which made it possible to follow quantitatively the time dependence of composition in the gaseous part of the reaction system. Gaseous basic adsorbates and methanol were sampled by measuring their volume and pressure before contacting the evacuated catalyst.

Catalytic activity. The catalytic activity of the ion exchange catalyst was being determined by measuring the degree of conversion of methanol in its dehydration to dimethyl ether at a given temperature and selected time.

Working procedure. The catalyst in the amount of 0·2 g was being heated for 3 h at 100°C and a final pressure of 10^{-3} Torr. The corresponding amount of the base prepared in the measuring part of the apparatus contaminated subsequently the catalyst at 100°C. In all cases, after a 10 min lasting adsorption of the base, the pressure decreased below 0·1 Torr. The measuring part of the apparatus was filled with methanol at 93·2 Torr and the temperature of the microreactor was adjusted to the temperature of the catalytic reaction. The moment of interconnection of the measuring part and the reactor space was taken to be the beginning of the reaction. Composition of the gaseous phase was being analyzed at selected time intervals.

RESULTS AND DISCUSSION

The effect of adsorption of ammonia from the gaseous phase on the catalytic activity of the MS-25 catalyst is illustrated on Fig. 1, curve *1*, that of the SS-25 catalyst on Fig. 2, curve *2*. Obviously, the courses of both curves differ considerably. Since adsorption conditions were identical in both cases, the difference may be due only to differences in texture between the standard and macroporous catalyst. It follows from results published in our preceding works[12-14] that amounts of adsorbed bases at saturation are practically identical for both catalysts. The course of the catalytic activity of the standard or macroporous catalyst during adsorption of ammonia from the gaseous phase must be consequently determined by the distribution of ammonia molecules in the catalyst. It is probable that during the adsorption from the gaseous phase the occupation of sulphonic acid groups by ammonia starts on the catalyst surface and proceeds subsequently towards the inside of the particles. During the catalytic reaction methanol must overcome this catalytically inactive layer so that it may become adsorbed on free sulphonic acid groups. In the MS-25 catalyst, which was prepared by polymerization in suspension and which is composed of very fine beads of the macromolecular substance with interstices constituting the porosity of the particle, ammonia is spread onto a large surface and the neutralized layer is consequently thin, hindering thus the permeation of methanol only slightly. On the other hand, the same amount of ammonia on the standard catalyst with the small surface forms much thicker layer, which represents a considerable barrier for methanol during its permeation towards the sulphonic acid groups. Due to this reason, the catalytic activity of the standard samples decreases rapidly already at small amounts of adsorbed ammonia, whereas the activity of the macroporous catalysts remains

proportional to the number of free unoccupied sulphonic acid groups till they are practically fully neutralized.

To confirm the above ideas, we have examined — at the same conditions — the catalytic activity of catalysts which were partially neutralized by alkali hydroxide in aqueous solution. It has been established in our preceding works[5] and by Frenkel[15] that the neutralization in aqueous media leads to a regular distribution of neutralized ions in the catalyst body. The dependence of the catalytic activity on the degree of neutralization in the aqueous phase is illustrated in Fig. 1, curve *3* for MS-25 and in Fig. 2, curve *1* for SS-25. The steep nonlinear decrease in the catalytic activity during neutralization of sulphonic acid groups in aqueous media has been explained by a two--centre mechanism of the catalytic reaction. Similarly, the dehydratation of methanol is a reaction requiring two active centres[16] and the decrease in the catalytic activity proceeds analogously. A different course of the decrease in the catalytic activity
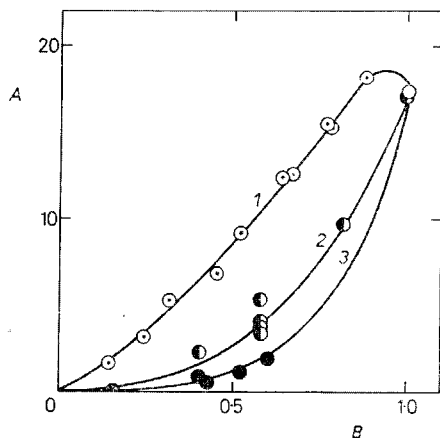

FIG. 1

Catalytic Activity of Partially Neutralized MS-25 Catalysts

A Catalytic activity expressed as the degree of conversion of methanol to dimethyl ether at the reaction time of 5 min and 100°C; *B* Fraction of acid centres from their total amount; curve *1* activity of samples after the adsorption of ammonia from the gaseous phase; *2* activity of samples measured 48 h after the adsorption of ammonia from the gaseous phase; *3* activity of samples neutralized with an inorganic ion in an aqueous medium for 12 h.
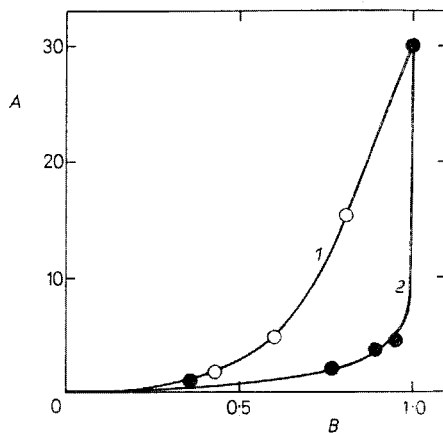
FIG. 2

Catalytic Activity of Partially Neutralized SS-25 Catalysts

A Catalytic activity expressed as the degree of conversion of methanol to dimethyl ether at the reaction time of 25 min and 100°C; *B cf.* the caption to Fig. 1; curve *1* activity of samples neutralized with an inorganic ion in an aqueous medium for 12 h; *2* activity of samples after the adsorption of ammonia from the gaseous phase.

during the adsorption of ammonia from the gaseous phase confirms differences in the distribution of neutralized functional groups in the bulk of the polymer material.

It follows from our preceding works[13,14] that ammonia which is bonded to a part of sulphonic acid groups of the styrene–divinylbenzene copolymer can permeate at higher temperatures through all sulphonic acid groups of the copolymer, with a distinct trend to a regular distribution. We have prepared several MS-25 samples partially neutralized by ammonia in the gaseous phase; the samples were being heated in the microreactor for 48 h at 100°C and their activity after the thermal treatment was determined. The results are on Fig. 1, curve 2. The observed values differ from those on curve *1* and approach the values on curve *3*. It seems probable that molecules of ammonia adsorbed from the gaseous phase on the surface have spread during the 48-h period in the bulk of the catalyst by migration, which shifted the catalytic activity towards the values found for samples partially neutralized in aqueous media. This effect has not been observed with the SS-25 catalyst, since the desiccated macro-molecular substance in large gel particles is so compact, that the migration cannot proceed so rapidly as in the loose dispersion structure of macroporous samples.

In a manner similar to ammonia, the adsorption from the gaseous phase has been performed with other organic bases, which had similar basicities as ammonia but
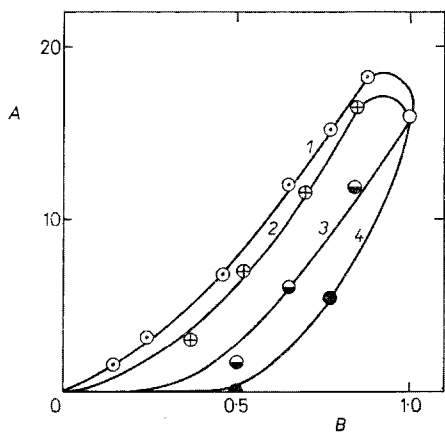

FIG. 3

Catalytic Activity of MS-25 Catalysts Partially Neutralized with Organic Amines from the Gaseous Phase

Cf. the caption to Fig. 1; curve *1* adsorption of ammonia; *2* adsorption of methyl-amine; *3* adsorption of trimethylamine; *4* adsorption of pyridine.
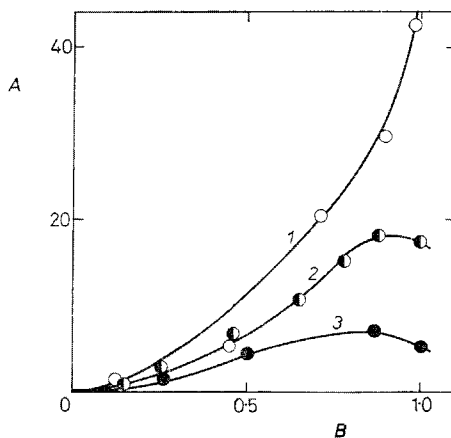

FIG. 4

The Temperature Dependence of the Catalytic Activity of the MS-25 Catalyst Partially Neutralized with Ammonia from the Gaseous Phase

Cf. the caption to Fig. 1; curve *1* dehydration of methanol at 150°C; *2* dehydration of methanol at 100°C; *3* dehydration of methanol at 75°C.

which differed from it by the magnitude of their molecules. It may be seen from Fig. 3 that the larger is the molecule of the adsorbed base, the higher is the rate of decrease of the catalytic activity of MS-25. It means that larger molecules neutralize sulphonic acid groups on the catalyst surface and simultaneously their larger volume prevents methanol from permeation through this desactivated layer. The shape of this desactivation curve in the case of the pyridine adsorption (curve 4) is analogous to that obtained during neutralization of the catalyst in aqueous media (Fig. 1, curve 3); however, the desactivation mechanisms are different. In the first case the reaction is retarded by large pyridine molecules chemisorbed on the catalyst surface, in the second one by a decrease in the number of pairs of active centres suitable for the reaction.

Desactivation curves obtained with the MS-25 catalyst after the adsorption of ammonia from the gaseous phase at 100°C and dehydratation of methanol at three different temperatures are depicted on Fig. 4. At lower reaction temperatures the catalyst activity slowly decreases with increasing amount of adsorbed ammonia, whereas at higher temperatures this decrease is considerably rapid. It means that at lower temperatures, when the catalytic reaction proceeds slowly, the rate of mass transfer of methanol through the neutralized surface layer is sufficient and does not affect the dehydration, whereas at higher temperatures and, consequently, expected higher dehydration rates, this dehydration is slowed down considerably by the mass transfer. At temperatures of 100 and 75°C, the desactivation curve of the macroporous catalyst displays a distinct maximum in the activity for the adsorption of ammonia and methylamine from the gaseous phase. This shows that small amounts of these bases adsorbed on the catalyst surface either improve the accessibility of functional groups in deeper layers of the macromolecular substance or contribute by another mechanism to the acceleration of the catalytic reaction (*e.g.* by accelerating the chemisorption of methanol on free sulphonic acid groups).

The texture of the investigated ion exchangers has proved to be the decisive factor determining their catalytic properties. As it has been stated above, particles of macroporous catalysts are formed by small beads of macromolecular material, whose diameter in the case of MS-25 is approximately 0.05 μm. This figure was calculated from the helium density, porosity, and a simplified geometric representation of the beads as a system of close-packed spheres. Even though this representation may be far from reality, it bears some resemblance to the real structure of macroporous samples determined microscopically. During the interaction of reacting substances with functional groups of a copolymer, steric mobility of macromolecules may appear. Particles of standard gel ion exchange catalysts with the particle size in the range 0.1 − 0.8 mm display some steric mobility only in a relatively thin surface layer, whereas in a desiccated state the inside of the particles is extremely compact and steric mobility of macromolecules is excluded.

REFERENCES

1. Tartarelli R., Lucchesi A., Stoppato B.: J. Catal. *19*, 310 (1970).
2. McGovern T. J., Dranoff J. S.: AICHE J. *16*, 536 (1970).
3. Davini P., Tartarelli R.: Chim. Ind. (Milan) *53*, 1119 (1971).
4. Teshima H., Sumi T., Morita N.: Nippon Kagaku Kaishi *1972*, 2045.
5. Jeřábek K., Bažant V., Beránek L., Setínek K.: *Proc. V. Int. Congr. Catal., Miami Beach, 1972,* Vol. II. 1193. North-Holland Publ., Amsterdam 1973.
6. Usmanov R. U., Rustamov Ch. R.: Uzb. Khim. Zh. *1964*, 82.
7. Kressman T. R. E.: J. Phys. Chem. *56*, 118 (1952).
8. Hale D. K., Packham D. I., Pepper J. W.: J. Chem. Soc. *1953*, 844.
9. Watkins S. R., Walton H. F.: Anal. Chim. Acta *24*, 334 (1961).
10. Davydov A. T., Nagornaya N. A.: Kolloid. Zh. *26*, 174 (1964).
11. Donskaya N. G., Libinson G. S.: Zh. Fiz. Khim. *44*, 1561 (1970).
12. Prokop Z., Setínek K.: This Journal *39*, 1253 (1974).
13. Prokop Z., Setínek K.: J. Polym. Sci. *12*, 2535 (1974).
14. Prokop Z., Setínek K.: J. Polym. Sci. *12*, 2545 (1974).
15. Frankel L. S.: Anal. Chem. *42*, 1638 (1970).
16. Thanh L. N., Setínek K., Beránek L.: This Journal *37*, 3878 (1972).

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