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The Formation of Benzene Dimer Cations on Synthetic Mordenite

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Extensive studies have been carried out on the formation of cation radicals from aromatic hydrocarbons on silica-alumina or synthetic zeolites, since the electron-transfer process seems to be closely relevant to the acid-base properties of the surfaces.[1-6] It has been established that the heat treatment of the catalyst and the presence of adsorbed oxygen have a marked effect on the formation of cation radicals. Recently, Kurita and co-workers[7] reported that benzene dimer cations were formed when synthetic mordenite was contacted with benzene in carbon tetrachloride. The effects of catalyst pretreatment and of adsorbed oxygen on the formation of dimer cations over the ammonium form of synthetic mordenite were investigated by means of ESR spectroscopy and the mechanism of the formation of the dimer cations is discussed in this paper.

Experimental

The Na form of mordenite was furnished by Nippon Kagaku and NH_4^+ form was prepared by the conventional cation-exchange procedures with ammonium chloride. The degree of ion exchange was found to be 32% by the gravimetric analysis of the eluted Na^+ ions. For easy introduction and evacuation of gases the adsorption of benzene was carried out from vapor phase no solvents being used. The zeolite (600 mg) was placed in an ESR sample tube (o.d. 10 mm) and evacuated at an appropriate temperature for 3 hr and then exposed to benzene vapor at room temperature. ESR measurements were carried out with a JEOL X-band spectrometer with a modulation frequency of 100 kHz. Radical ion concentrations expressed in terms of spins per gram of dry zeolite were determined by double integration using a benzene solution of 1,1-diphenyl-2-picrylhydrazyl.

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4) R. P. Porter and W. K. Hall, *J. Catal.*, **5**, 366 (1966).

5) D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, **86**, 749 (1964).

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Results and Discussion

Assignment of ESR Signals. The ammonium mordenite showed no ESR absorption when it was evacuated at 600 °C. A well-resolved spectrum was obtained when it was exposed to benzene vapor of 50 Torr for 5 min. The hyperfine coupling constant of 2.2 Oe agrees with that of benzene dimer cations in sulfuric acid.8) The intensity distribution of lines was also in good agreement with that expected from radicals with 12 equivalent protons. Thus, the spectrum was unambiguously assigned to benzene dimer cations. The intensity of the spectrum decreased with time, the line shape being changed. The spectrum after 7 days was the same as that obtained on biphenyl adsorption on the mordenite. The results we obtained from the vapor phase adsorption of benzene are concluded to be essentially the same as those obtained by Kurita and co-workers7) from the adsorption of benzene in carbon tetrachloride. The adsorption of benzene on the ammonium mordenite leads to the formation of benzene dimer cations which are converted into biphenyl cation on the surface.

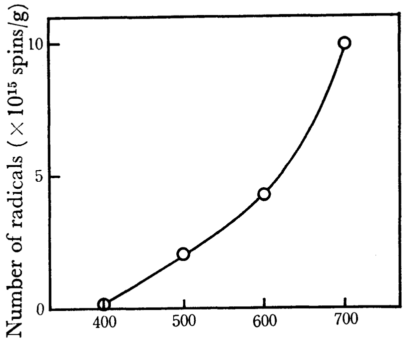

Fig. 1. Effect of pretreatment temperature on the number of benzene dimer cations.

Effect of Calcination Temperature. The effect of the temperature of zeolite activation on the generation of benzene dimer cation radicals on NH_4^+ mordenite is illustrated in Fig. 1. Generation of the radicals was observed only for samples evacuated above 500 °C, the radical amount increasing drastically with the rise in the activation temperature. It was reported9) that the dehydroxylation of H mordenite starts at 450 °C. Since the activation temperature of the mordenite giving dimer cations corresponds to the temperature of the dehydroxylation which results in the formation of the three-coordinated aluminium, it is concluded that the dimer cations are formed by the transfer of an electron from two benzene molecules to the three-coordinated aluminium atoms. The same mechanism of the charge transfer was proposed by Stamires and Turkevich5) for the formation of triphenylamine cation radicals on ammonium Y-zeolite.

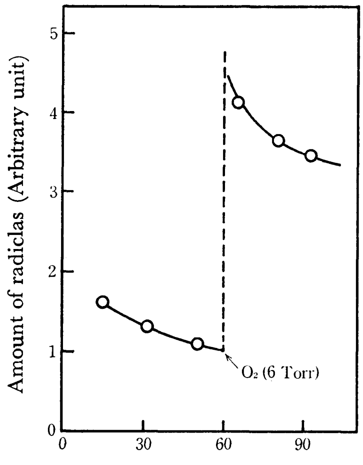

Fig. 2. Change in the radical amount on introduction of 6 Torr of oxygen.

Effect of Adsorbed Oxygen. *(a) Effect of the Introduction of Gaseous Oxygen*: Ammonium mordenite evacuated at 700 °C for 3 hr was exposed to benzene vapor for 5 min and evacuated for 2 min. The intensity of spectrum was then monitored with time. It decreased slowly with time. After 60 min, 6 Torr of oxygen was introduced into the system. This caused about five-time increase in ESR intensity as shown in Fig. 2. It was confirmed that this is not caused by the removal of the saturation of the ESR signal. It is thus concluded that the presence of oxygen enhances the dimer radical formation.

(b) Effect of Oxygen Pretreatment: When ammonium mordenite treated at 700 °C was exposed to 25 Torr of oxygen and evacuated at room temperature for 5 min prior to adsorption of benzene, the ESR intensity of dimer cations was 1.5 times larger than that from the sample without oxygen treatment. When oxygen pretreatment was carried out at elevated temperatures (200 and 400 °C), the enhancement of the ESR intensity was enormous, as shown in Fig. 3. These results show that the adsorbed oxygen has an important role in the formation of the dimer cations as it does for monomer cation radical formation.3,4,6) The adsorption of oxygen might be an activated process since the radical amount

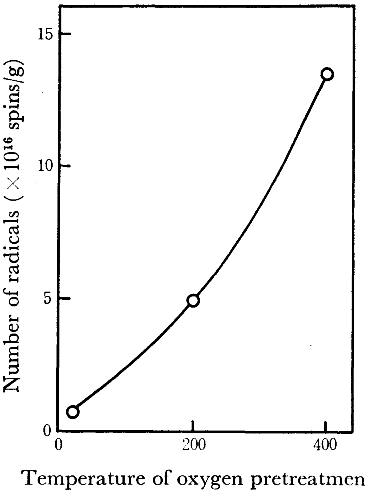

Fig. 3. Effect of oxygen pretreatment temperature on the number of benzene dimer cations.

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9) H. Karge, *Z. Physik. Chem.* (Neue Folge), **76**, 133 (1971).

increases with the temperature of oxygen pretreatment.

Enhancement of the radical formation by adsorbed oxygen could be caused by either or both of the following.

a) An increase in the electron-withdrawing power of the aluminium atoms due to the inductive effect of adsorbed oxygen. In this case, a negative charge would be shared by an aluminium atom and an adsorbed oxygen molecule.

b) The chemical reaction of benzene with chemisorbed oxygen. Actually, perylene in liquid $SbCl_3$ is stoichiometrically oxidized to the radical ion on the addition of oxygen according to[10]

$$O_2 + 4C_{20}H_{12} + 6SbCl_3 \longrightarrow 4C_{20}H_{12}^{+} + 4SbCl_4^{-} + 2SbOCl$$

The following experiments were carried out. When sulfur dioxide, instead of oxygen, was introduced into the catalyst with preadsorbed benzene at room temperature, a large increase in ESR signal of benzene dimer cations and, at the same time, the signal due to SO_2^- were observed. The ESR signal of SO_2^- (g_{xx}=2.0012, g_{yy}=2.0025, g_{zz}=2.0071) was observed even in the absence of preadsorbed benzene, the amount depending considerably on the adsorption temperature. The temperature dependence was similar to the dependence of amount of benzene dimer cations on the temperature of the oxygen pretreatment. The results indicate that the role of oxygen and sulfur dioxide on the formation of dimer cations is similar. Thus, the possibility of chemical reaction with adsorbed oxygen can be eliminated since sulfur dioxide as well as oxygen enhance the formation. The formation of benzene dimer cations and sulfur dioxide anions at the same time on the same catalyst strongly suggests the important role of the inductive effect on the electron transfer process on the mordenite.

It is demonstrated that the radical amount increases with the activation temperature of the zeolite, the presence of the adsorbed oxygen drastically enhancing the formation of the benzene dimer cations. It is concluded that the three-coordinated aluminium atoms are responsible for the dimer cation formation, the role of oxygen being to increase the electronegativity of aluminium atoms by its inductive effect.

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[10] J. R. Atkinson, T. P. Jone, and C. E. Baughan, *J. Chem. Soc.*, **1964**, 5808.