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Abstract

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STUDY OF THE RADIOLYSIS OF AMMONIA ADSORBED ON SOLID SURFACES BY THE E.P.R. METHOD

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From the point of view of increasing the efficiency of using the energy of nuclear radiation for carrying out chemical reactions, the use of solid sorbents may be of great interest. A number of studies have shown that a distinct sensitization of radiation processes takes place. However, the mechanism of these phenomena has as yet been little clarified. A number of data indicate that energy is transferred from the sorbent to the sorbate. Along with this there are also other effects, associated with adsorption of radiolysis products and with changes in the conditions of their interaction with one another and with adsorbed molecules. To elucidate the nature of these effects, it is essential to determine the nature of the particles formed under the action of radiation both in the sorbent and in the sorbate, and also to obtain information on the fate of defects formed in the solid during the course of the radiation-catalytic reaction.

For this purpose we investigated the processes occurring during γ-irradiation of ammonia adsorbed on zeolite. The results of this investigation are given in the present communication.

Samples of type 4A zeolites, calcined in vacuum at 10^{-4}–10^{-5} mm Hg at 350°, were filled with ammonia and irradiated with a Co^{60} source at the temperature of liquid nitrogen. The dose rate of the γ-irradiation was 200 rad/sec. The e.p.r. spectra were recorded on an RE-1301 instrument. The paramagnetic centers of the quartz were annealed beforehand. The relative accuracy of measuring the concentration of paramagnetic centers was 10–15%.

The e.p.r. spectrum of irradiated zeolite is shown in Fig. 1, *a*. It is a weakly anisotropic singlet with a width $H = 30.5$ G and a g-factor equal to 2.0122.

Fig. 1. Change in the e.p.r. spectrum as a function of the amount of ammonia adsorbed on the zeolite surface: *a* –0 wt.%; *b* –0.05; *c* –0.11; *d* –0.8; *e* –1.8 wt.% (dotted line shows the e.p.r. spectrum of an aqueous ammonia solution).

When zeolite with ammonia adsorbed on it is irradiated, the spectra shown in Fig. 1, *b, c, d* are observed. It is seen that the initial singlet of the zeolite is

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Figure 1: Fig. 1. Change in the e.p.r. spectrum as a function of the amount of ammonia adsorbed on the zeolite surface: a –0 wt.%; b –0.05; c –0.11; d –0.8; e –1.8 wt.% (dotted line shows the e.p.r. spectrum of an aqueous ammonia solution)

Fig. 2

Figure 2: Fig. 2

distorted by the appearance of hyperfine structure. As the amount of adsorbed ammonia is increased, these distortions gradually increase, and the initial singlet disappears. In the irradiated zeolite on which about 1.8 wt.% ammonia is adsorbed, which corresponds to complete coverage of the zeolite surface, the e.p.r. spectrum is a well-resolved quintet with a width of the central component of about 6 G and a spacing between components of 24 G; the g-factor of the quintet is 2.005. The intensities of the components of the quintet, measured from the amplitudes

taking into account the width of each, are in the ratio $1 : 5.6 : 9.7 : 3.3 : 0.33$. The total width of the spectrum, measured between the extrema of the outer h.f.s. lines, is 117 G.

In Fig. 1,d this spectrum is compared with the e.p.r. spectrum of an irradiated solution of ammonia in water ([1,3]), shown by the dashed line. As can be seen from the figure, these spectra coincide almost completely. The complete coincidence of the spectra gives grounds for considering that the e.p.r. spectrum observed in irradiated zeolite with adsorbed ammonia belongs to the NH_2 radical stabilized on the surface of the zeolite.

The e.p.r. spectrum of the NH_2 radical in an inert argon matrix consists of three fully resolved triplets ([2]). In an ammonia matrix the spectrum of this radical consists of seven clearly resolved lines. The other two components are poorly resolved ([3]). In addition, there are differences in the total width of the spectrum, which is 68.5 G in the argon matrix and 85 G in the solid-ammonia matrix. In aqueous ammonia solutions and in the adsorbed state, the spectrum of this radical consists of 5 h.f.s. components, and the total width of the spectrum is 117 G.

Fig. 2. Effect of surface coverage on the concentration of radicals: **1**—total; **2** —NH_2 radicals; **3**—paramagnetic centers of the zeolite

These differences between the spectra of one and the same radical in different matrices can be associated with "hindering" of the rotational degrees of freedom of the NH_2 radical. It is known that in an argon matrix the NH_3 molecule

Figure 3

Figure 3: Figure 3

rotates freely even at a temperature of 4.2 K ([4]). In solid ammonia, hydrogen bonds $N-H\cdots N$ restrict rotation of the molecule, and in aqueous solution this restriction is still greater because of the larger energy of the hydrogen bond with the oxygen atom. Study of microwave absorption ([5]) and i.r. spectra ([6]) of adsorbed ammonia has shown that the rotational motion of the NH_3 molecule is completely "hindered." Evidently, analogous hindering of rotation may also be expected for the NH_2 radical.

In the absence of rotation, the anisotropic h.f.s. interaction is not averaged, or is not averaged completely, which should lead to changes in the e.p.r. spectra in different matrices. As is known ([7]), the influence of the anisotropic h.f.s. interaction is manifested in changes in the width of the components, the total width of the spectrum, and the shape of the outer components of the spectrum, whose anisotropy is visible in Fig. 1,d. When added to the isotropic splitting, the anisotropic splitting changes the overall splitting on the nitrogen nucleus. The change in the widths of the components and in the ratio of the splitting on the protons to the splitting on the nitrogen nuclei leads to the merging of individual components of the spectrum. At the same time, the number of observed resolved components of the hyperfine structure changes.

From the total width of the e.p.r. spectrum of radicals adsorbed on the surface of the zeolite, an approximate value of the anisotropic splitting was calculated. The value of the isotropic splitting was taken to be 23.9 G on the protons and 10.3 G on the nitrogen nuclei ([2]). The obtained value of the anisotropic interaction is 12 G and agrees with literature data ([8]).

By superposing the e.p.r. spectra of paramagnetic centers in irradiated zeolite and of the NH_2 radical in aqueous solution, the spectra shown in Fig. 1,b,c were obtained. With the aid of such superposition, parameters characterizing the relative concentrations of radicals were determined

NH_2 in the total spectrum. This made it possible to determine the dependence of the concentration of adsorbed NH_2 radicals on the degree of filling of the zeolite surface with ammonia. This dependence is shown in Fig. 2. As the filling of the adsorbent surface with ammonia increases, as is seen in the figure, the total concentration of unpaired spins first increases and then decreases, becoming approximately three times smaller than the initial concentration of paramagnetic centers in the irradiated zeolite. The same figure shows the change in the concentration of NH_2 radicals and paramagnetic centers formed in the zeolite (Fig. 2, 3). When the surface is filled,

Fig. 3. *a*—Dependence of the concentration of NH_2 radicals on the heating temperature at different degrees of filling: 1—11 wt.%; 2—3.8; 3—1.8; 4—1.5; 5—0.8; 6—0.11; 7—0.05 wt.%. *b*—Dependence of the recombination temperature

$T_{1/2}$ on the filling of the surface with ammonia

approximately equal to a monolayer, the yield of NH_2 radicals, measured from the slope of the linear section of the dependence of concentration on irradiation time, is approximately equal to the yield of paramagnetic centers upon irradiation of the zeolite, while the EPR spectrum contains no signal from the paramagnetic centers of the zeolite.

From this it may be concluded that the formation of NH_2 radicals occurs not only as a result of direct radiolysis of ammonia molecules, but also as a result of transfer of the energy absorbed by the zeolite, which, in the absence of ammonia molecules adsorbed on the surface, leads to the formation of paramagnetic centers in the zeolite itself.

As the filling of the zeolite surface with ammonia increases above $\sim$ 1.5 wt.%, which corresponds to a monolayer, the yield of NH_2 radicals decreases. At the same time, as was already stated above, the EPR spectrum contains no signal from paramagnetic centers of the zeolite. It follows from this that the probability of transfer of the absorbed radiation energy from the zeolite to the adsorbed molecules does not decrease. To clarify the reason for the decrease in the concentration of NH_2 radicals with increasing filling of the zeolite surface with ammonia, the temperature dependence of the concentration of adsorbed radicals was measured at different degrees of surface filling. These dependences are presented in Fig. 3, *a*, where it is seen that, with an increase in the filling of the surface above a monolayer, recombination of radicals is observed at lower temperatures (the heating time at all temperatures was constant). Fig. 3, *b* gives the dependence of the temperature at which the concentration of NH_2 radicals decreases by a factor of two on the filling of the zeolite surface with ammonia. At a surface filling of about 10 wt.%, the dependence of the concentration of adsorbed radicals on the heating temperature coincides with the ana-

with a logical dependence in solid ammonia. It follows from this that the presence of several layers of adsorbed ammonia molecules promotes recombination of the NH_2 radicals located on the surface of the zeolite (the conclusion that the NH_2 radicals are located on the surface follows from the fact that the EPR spectrum of this radical does not change as the coverage of the surface with ammonia increases). Since the presence of several layers cannot facilitate diffusion of radicals over the zeolite surface, it should be assumed that the nature of this phenomenon is not connected with simple diffusion. It is possible that interaction of a radical located on the surface with molecules of the upper layers causes the transition of the radical from the surface into the upper layer of adsorbed molecules (for example, by a free-valence migration mechanism).

Regardless of the mechanism, the dependence of the recombination temperature on surface coverage makes it possible to explain the decrease in the yield of radicals upon irradiation as the coverage of the surface with ammonia increases (see Fig. 2). Since, after irradiation, recombination of radicals at liquid-nitrogen temperature is not observed, it must be assumed that during the irradiation

process there exist regions of local heating in which some fraction of the radicals recombines. This fraction is the larger, the more ammonia is adsorbed on the surface of the zeolite.

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REFERENCES CITED

1. Yu. A. Sorokin, V. I. Tsivenko, S. Ya. Pshezhetskii, ZhFKh, **37**, 1870 (1963).

2. S. N. Foner, E. L. Cochran et al., Phys. Rev. Letters, **1**, 91 (1958).

3. V. I. Tupikov, V. I. Tsivenko et al., ZhFKh, **37**, 138 (1963).

4. H. McConnel, J. Chem. Phys., **29**, 1422 (1956); D. E. Milligan, R. M. Hexter, K. Dressler, J. Chem. Phys., **34**, 1009 (1961); W. H. Flygare, J. Chem. Phys., **39**, 2263 (1963).

5. Ch. Schonfeld, V. Feldman, M. Foilman, Bull. Rés. Counsil. Israel., **A11**, 229 (1962).

6. C. B. Blyholder, E. A. Richardson, J. Phys. Chem., **66**, 2597 (1962).

7. S. M. Blinder, J. Chem. Phys., **33**, 748 (1960); N. W. Sord, S. M. Blinder, J. Chem. Phys., **34**, 1693 (1961).

8. J. R. Rowlands, D. H. Whiffen, Nature, **193**, 81 (1962).

Note: Figure translations are in progress. See original paper for figures.