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Study of the Joint Action of Radiation and Oxide Catalysts on the Dehydrogenation Reaction of Cyclohexane

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At the present time a comparatively small number of studies have been published on the joint action of radiation and catalysts at low temperatures, at which ordinary thermal catalytic processes practically do not occur. The observed effects are entirely due to the specific action of radiation on one or another catalytic system. When such processes are carried out at sufficiently low temperatures, it apparently becomes possible to preserve in the catalyst all disturbances of a structural and electronic character that arise under the action of radiation.

We shall mention here studies on the radiolysis of various kinds of alkanes on oxide catalysts ([1–4]). In some of them the conclusion was drawn that transfer of the absorbed energy can occur from the catalyst only to a single adsorbed layer ([1]). In works ([2–4]) the authors applied the semiconductor concept to the course of radiation-catalytic processes on oxide catalysts. Attempts to use electronic concepts to explain the mechanism of the action of ionizing radiation on catalysts are entirely natural in view of the establishment of a number of experimental facts concerning the influence of radiation on the electrical conductivity of semiconductor materials ([5]).

For understanding the mechanism of the action of radiation on catalytic processes, it is essential to compare the catalytic properties of irradiated catalysts with changes in their physical characteristics under the influence of irradiation. The appearance of paramagnetic centers, detected by the method of electron paramagnetic resonance, proves to be very sensitive to the action of radiation on a solid. The parallelism in the disappearance of the increased catalytic activity upon annealing and in the disappearance of the paramagnetic resonance signal makes it possible to suppose that this signal is associated with centers responsible for the increase in catalytic activity under the action of radiation ([6,7]). This has so far been established only with respect to one of the simplest reactions: isotopic exchange of hydrogen with deuterium. It was also shown by EPR methods that, during radiolysis and photolysis of adsorbed molecules, radicals stabilized on the surface can be formed ([9]).

Fig. 1. Dependence of the percentage conversion of cyclohexane on silica gel on the dose of absorbed energy

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In the present work an attempt was made to approach the elucidation of the possible mechanism of the influence of radiation on catalytic systems by comparing the action of radiation on catalysts possessing different electronic properties. The reaction chosen for study was the dehydrogenation of cyclohexane. Simultaneously with the study of changes in the catalytic properties of catalyst samples under the action of radiation, their magnetic properties were studied by the EPR method. As the catalysts investigated, oxides of the insulator type (SiO_2), semiconductors with low conductivity (Al_2O_3, MgO, ZrO_2, aluminosilicate), and n- and p-type semiconductors with appreciable conductivity (ZnO, NiO) were selected.

Most of the samples were prepared by precipitation of nitrate salts in the form of hydroxides, followed by conversion into oxides by calcination.

at such temperatures as ensured the production of a sufficiently well-developed specific surface. The magnitude of the specific surface was determined by adsorption of cyclohexane at 18° according to BET. Irradiation was carried out with accelerated electrons of energy 0.8 MeV and with γ-radiation on a Co^60 unit (3200 mCi), with a dose rate of 400 rad/sec.

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Experiments were carried out in Pyrex-glass cuvettes with a thin window (~100 μ), through which the electron beam passed. The amount of energy absorbed by the specimen was determined in the same way as in work (10). Before the start of an experiment, the cuvette with the catalyst sample placed in it was connected through a ground joint to the vacuum apparatus, and the catalyst was thoroughly trained at 400° with subsequent cooling to room temperature. Vapors of dehydrated cyclohexane were admitted onto the samples prepared in this way. The surface coverage for all samples was 25–35% of a monolayer. The cuvettes with the samples were disconnected from the vacuum apparatus by means of a stopcock and placed under the accelerator window in a special holder—refrigerator cooled with running water. The dose of absorbed energy in most experiments was $1.4 \cdot 10^9$ rad; the dose rate was $2.4 \cdot 10^6$ rad/sec. As was established by special experiments, the temperature in the middle of the catalyst powder layer during irradiation did not exceed 75–100°. After irradiation the cuvettes were connected by means of the ground joint to the apparatus; the vapors of organic compounds formed and of unreacted cyclohexane were frozen out in a trap cooled with liquid nitrogen. The noncondensable gas was analyzed for hydrogen by passage through a heated palladium capillary. The

liquid condensate was analyzed chromatographically.

Table 1

Data on the radiation-catalytic activity of various oxide catalysts

No.	Catalyst	Specific surface, m^2/g	Amount of adsorbed C_6H_{12}, mg/g	Amount of H_2 evolved, mg/g	Mol. H_2 per 100 eV
1	Silica gel	650	89	0.53	0.20
2	Aluminum oxide	300	36.8	0.565	0.19
3	Aluminosilicate	170	24.4	0.405	0.14
4	Zirconium dioxide	270	56	0.14	0.048
5	Magnesium oxide	250	30.2	0.073	0.025
6	Zinc oxide	50	14.6	0.039	0.014
7	Nickel oxide	60	16.5	0	0
8	Without catalyst	(P = 200 mm Hg)	0	0	0

Note. After adsorption of cyclohexane at 20° the pressure above the samples was 7 mm Hg. The dose was $1.4 \cdot 10^9$ rad. Mean values from 2–3 experiments carried out under identical conditions are given.

In parallel with the study of the catalytic properties of these oxides under irradiation, their paramagnetic properties were investigated by the EPR method.

Since paramagnetic surface centers, as a rule, are stable only in the region of low temperatures, irradiation in this case was carried out at the temperature of liquid nitrogen with Co⁀60 γ-radiation. The dose of absorbed energy in these experiments ranged from $5 \cdot 10^6$ to $1 \cdot 10^8$ rad. The conditions for preparing the samples were the same as for the catalytic experiments. After irradiation, EPR spectra were also recorded at the temperature of liquid nitrogen on an EPR spectrometer with high-frequency modulation of the magnetic field.

It was established that, upon exposure of the catalysts studied to irradiation, low-temperature dehydrogenation of cyclohexane occurs.

(see Table 1). Dehydrogenation of cyclohexane vapors without a catalyst did not occur under these conditions. Chromatographic analysis of the radiolysis products showed that they consist mainly of benzene and unreacted cy-

Fig. 2. EPR spectra of compounds irradiated at −196° (dose $3.3 \cdot 10^7$ rad): a −silica gel with cyclohexane adsorbed on the surface, b −pure silica gel (in vacuum), c −frozen benzene, d −frozen cyclohexane. Spectra a, b, d were recorded at −196°, c −at −50°

Figure 2: Fig. 2. EPR spectra of compounds irradiated at −196° (dose $3.3 \cdot 10^7$ rad): a −silica gel with cyclohexane adsorbed on the surface, b −pure silica gel (in vacuum), c −frozen benzene, d −frozen cyclohexane. Spectra a, b, d were recorded at −196°, c −at −50°

clohexane, with a small admixture (in the case of SiO_2) of lighter hydrocarbons. The conversion percentage, calculated as benzene and determined from the chromatographic-analysis data, practically coincided with the conversion percentage based on hydrogen.

As follows from the data given in Table 1, the oxides of the type of insulators and semiconductors with low conductivity (SiO_2, Al_2O_3, aluminosilicate catalyst) are characterized by the greatest activity under the action of radiation (the highest radiation yield). As was established for silica gel, the conversion percentage increases with increasing dose (Fig. 1). Oxides of the type of *n*-semiconductors with considerable conductivity (ZnO) have very low radiation activity. Finally, the "good" *p*-semiconductor NiO practically has no radiation-catalytic activity. Magnesium oxide and zirconium dioxide occupy an intermediate position. It should be noted that, as was established, thermal dehydrogenation of cyclohexane on SiO_2, aluminosilicate, Al_2O_3, MgO, and ZrO_2 does not occur even at high temperatures (500-550°). On ZnO and NiO, dehydrogenation begins at 300-350°.

Fig. 2. EPR spectra of compounds irradiated at −196° (dose $3.3 \cdot 10^7$ rad): **a** −silica gel with cyclohexane adsorbed on the surface, **b** −pure silica gel (in vacuum), **c** −frozen benzene, **d** −frozen cyclohexane. Spectra **a**, **b**, **d** were recorded at −196°, **c** −at −50°.

Thus, under the combined action of radiation and catalysts, the most active oxides are those that practically do not function in the usual catalytic process, even at fairly high temperatures. Conversely, oxides possessing considerable activity in the thermal process have either very low activity in the low-temperature radiation process, or practically do not accelerate the course of the reaction under study.

The study of the paramagnetic properties of irradiated catalysts by the EPR method showed that, in the spectra of some irradiated catalysts with cyclohexane adsorbed on the surface, additional free lines appear that can be associated with the formation of adsorbed free radicals. This effect is most pronounced in the case of silica gel. Figure 2a shows the spectrum of silica gel on whose surface cyclohexane had been adsorbed, irradiated at liquid-nitrogen temperature with a dose of $2.8 \cdot 10^7$ rad. Figure 2b shows the spectrum of silica gel irradiated with-

out an adsorbed substance; Fig. 2c, d shows the EPR spectra of benzene and cyclohexane frozen at −196° and irradiated. Comparison of spectra 2a and 2b shows that, during the radiolysis of adsorbed cyclohexane, an additional broad signal with well-resolved hyperfine structure appears in the spectrum, the intensity of which increases with the irradiation dose. Comparison of spectra 2a, 2b, and 2c shows that this signal can be associated with C_6H_7 radicals adsorbed on the surface of silica gel, which, as is known, are formed upon irradiation of benzene [11]. Spectra analogous to those shown in Fig. 2a were observed for aluminosilicate and aluminum oxide with cyclohexane adsorbed on the surface, irradiated at liquid-nitrogen temperature.

In irradiated magnesium oxide and zirconium dioxide, signals of complex form were observed. The presence of adsorbed cyclohexane molecules causes the appearance of weak additional lines; however, we cannot associate them with any free radicals. Upon irradiation of ZnO and NiO, both with cyclohexane adsorbed on the surface and without it, no EPR signals are observed. Thus, the appearance of C_6H_7 radicals was characteristic only of oxides possessing significant radiation-catalytic activity with respect to the reaction of dehydrogenation of cyclohexane to benzene.

It should be noted that the greater radiation-catalytic activity at low temperatures of oxide catalysts of the dielectric and "poor" semiconductor types, compared with "good" semiconductors active in the thermal conduct of the catalytic process, is apparently connected with the difference in the action of radiation on materials with different electronic properties. In dielectrics, ionization processes caused by the action of radiation play a more significant role than in semiconductors, owing to the possibility of longer capture of the secondary current carriers formed (electrons and holes). This point of view is also confirmed by the fact established by us of the complete absence of EPR signals in irradiated samples of ZnO and NiO, which is apparently due to the high rate of destruction of paramagnetic centers. In irradiated dielectric SiO_2, and also in "poor" semiconductors Al_2O_3, MgO, ZrO_2, and aluminosilicate, these centers are stable at low temperatures and appear in the EPR spectra.

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