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1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE NATURE OF ACTIVE CENTERS IN THE REACTION OF ISOTOPIC HYDROGEN EXCHANGE ON γ-IRRADIATED SILICA GEL

In a number of works carried out recently, an increase has been observed in the catalytic activity and adsorption capacity of catalysts as a result of their preliminary irradiation (see, for example, the review by Barru ([1])). The effect of radiation on adsorption and catalytic properties is manifested most strikingly in the case of silica gel. Kohn and Taylor ([2–6]) established that after preliminary irradiation the catalytic activity of SiO_2 in the reaction of H_2—D_2 exchange and ethylene hydrogenation, as well as its adsorption capacity with respect to hydrogen, increases sharply. Hydrogen adsorption is accompanied by disappearance of the coloration formed under the action of irradiation. The authors associate the adsorption and catalytic properties of the irradiated samples with the presence in them of aluminum impurities. They believe that under the action of irradiation electrons and holes are formed, part of which is localized on impurity atoms. The centers responsible for the catalytic and adsorption properties of SiO_2, in their opinion, are of different nature.

In the present work the nature of the color centers in irradiated silica gel was investigated by optical and radiospectroscopic methods, and their role in the processes of irreversible hydrogen adsorption and catalytic activity was clarified.

We used four types of silica gel, the characteristics of which are given in Table 1 (the amount of impurities was determined spectrometrically).

Table 1

Type of silica gel and method of its preparation	Al	Fe	Cu	Mg	Mn	Sum of alkali metals	S, m^2/g
Silica gel K-5*, hydrolysis of $SiCl_4$ (⁷)	$8 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$< 5 \cdot 10^{-5}$	not determined	700±50
Ethylate silica gel, hydrolysis of ethyl silicate	$3.4 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	$7 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	$< 5 \cdot 10^{-5}$	$2.8 \cdot 10^{-1}$	
Silicate silica gel 1, action of sulfuric acid on a sodium silicate solution	$8.7 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$< 5 \cdot 10^{-5}$	$1.4 \cdot 10^{-1}$	300±50

Type of silica gel and method of its preparation	Al	Fe	Cu	Mg	Mn	Sum of alkali metals	S, m^2/g
Silicate silica gel 2, action of sulfuric acid on a sodium silicate solution	$7.3 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	$2 \cdot 10^{-4}$	$8.9 \cdot 10^{-3}$	$< 5 \cdot 10^{-5}$	$1 \cdot 10^{-1}$	300±50

* Silica gel K-5 was kindly provided to us by V. F. Kiselev.

Before irradiation, the silica gel samples were evacuated for 24 hours at temperatures of 400, 500, or 600°C and a final pressure of 10^{-5}—10^{-6} mm Hg. After completion of the treatment, the ampoules with the samples were sealed off under pumping and irradiated with γ-rays from a Co^{60} source at the temperature of liquid nitrogen or at room temperature. The irradiation dose in different experiments varied from $2 \cdot 10^5$ to $2 \cdot 10^7$ r. The catalytic activity of silica gel in the reaction of H_2—D_2 exchange was measured at an equimolecular mixture composition, a temperature of 77°K, and a pressure of 0.7 mm Hg. The isotopic composition of hydrogen during the reaction was measured from the thermal conductivity of the mixture ([8]). Adsorption measurements were performed at room temperature and hydrogen pressures

from $5 \cdot 10^{-3}$ to 5 mm Hg. The absorption spectra in diffuse scattered light were recorded at room temperature on an SF-4 spectrophotometer modified for this purpose according to the method described in ([9]). The EPR spectra were recorded on an EPR-2 radiospectrometer ([10]) at 77°K. Before measurement the samples were kept for a long time at this temperature.

The results obtained by us confirmed the conclusions of Kohn and Taylor that

Fig. 1. Optical spectra of silicate silica gel 2 before (a) and after (b) adsorption of hydrogen at room temperature

Figure 1: Fig. 1. Optical spectra of silicate silica gel 2 before (a) and after (b) adsorption of hydrogen at room temperature

the specific catalytic activity of samples subjected to the same preliminary treatment and irradiated with the same dose increases with increasing aluminum content in them. The least active with respect to the isotopic exchange of hydrogen proved to be the purest silica gel K-5; the most active was silicate silica gel 2, containing the largest amount of aluminum. Measurements carried out on silicate silica gel 2 showed that the specific catalytic activity is the higher, the longer the duration and the higher the temperature of its preliminary thermal treatment. The specific catalytic activity of silica gel also increases with increasing irradiation dose.

Fig. 1. Optical spectra of silicate silica gel 2 before (*a*) and after (*b*) adsorption of hydrogen at room temperature

At the temperature of liquid nitrogen the catalytic activity of irradiated silica gel remains unchanged for a practically unlimited period of time. It begins to decrease only after heating the samples in vacuum for one hour at 200°C and practically completely disappears at temperatures above 350°C.

Table 2

Annealing in hydrogen	Annealing in hydrogen	Annealing in hydrogen	Annealing in vacuum	Annealing in vacuum	Annealing in vacuum
t-ra, °C	duration, h	K, $1/\text{min} \cdot \text{m}^2$	*t*-ra, °C	duration, h	K, $1/\text{min} \cdot \text{m}^2$
−196	300	$4.02 \cdot 10^{-4}$	−196	300	$2.5 \cdot 10^{-4}$
−78	0.1	$1.8 \cdot 10^{-4}$	0	1	$2.2 \cdot 10^{-4}$
0	1	$0.74 \cdot 10^{-4}$	+100	1	$2.3 \cdot 10^{-4}$
+100	1	$7 \cdot 10^{-7}$			

A different picture is observed if the irradiated samples are heated in the presence of hydrogen and their catalytic activity is likewise measured at the temperature of liquid nitrogen. A noticeable decrease in activity is observed in this case already at −78°, i.e., at a temperature approximately 200° lower than in vacuum (see Table 2, which gives the results for silicate silica gel 2, evacuated at 500°C for 24 h and irradiated with a dose of $1.5 \cdot 10^7$ r at 77°K). The more rapid annealing of catalytic activity in a hydrogen atmosphere, as compared with annealing in vacuum, can be explained by irreversible adsorption of hydrogen on the active centers of the catalyst.

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

Thus, in contrast to Kohn and Taylor, we come to the conclusion that both the adsorption of hydrogen and the reaction of its catalytic isotopic exchange occur in irradiated silica gel on the same surface defects formed under the action of ionizing radiation. We succeeded in establishing the nature of these defects by studying irradiated silica gel by optical and radiospectroscopic methods.

It was shown in (11,12) that, upon irradiation of quartz containing aluminum impurities and of aluminosilicate glasses, centers are formed

color centers, which are positively charged holes stabilized on an oxygen atom adjacent to an aluminum atom. This radiation defect gives, in fused quartz, an absorption maximum in the visible region of the spectrum at 545 mμ (^13) and a characteristic EPR spectrum consisting of six components caused by hyperfine splitting of the unpaired electron on the nucleus of the aluminum atom ($I = 5/2$). A quantum-mechanical calculation of the structure of this center, performed by O' Brien, showed that the unpaired hole electron is 97% localized on the oxygen atom and only 3% on the aluminum atom (^14).

Fig. 2. Spectra of irradiated silicate silica gel before (*a*) and after (*b*) adsorption of hydrogen on it

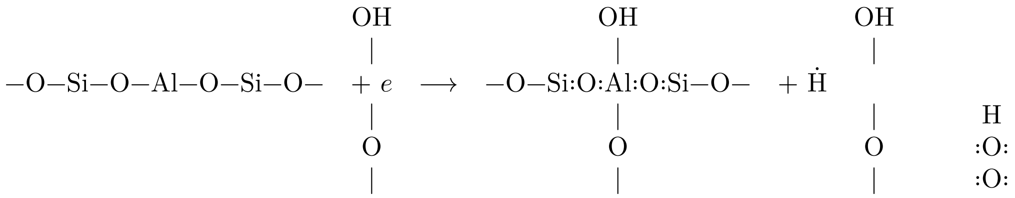
We were able to observe the same defects also in the case of irradiated silica gel. Fig. 1*a* presents the optical spectrum of irradiated silica gel, which has two absorption maxima (reflection minima) at 350 and 500–550 mμ. The position of one of them corresponds to defects associated with an aluminum impurity. We were also able to observe EPR spectra from these defects. During prolonged storage (~24 hours) of irradiated silica gel at the temperature of liquid nitrogen, apparently, some ordering of its structure occurs, as a result of which the lines characterizing the defect associated with the aluminum impurity become narrower. At the same time, in the EPR spectra, in addition to the previously observed (^15, ^16) narrow lines ($g = 2.0006 \pm 0.0004$) from color centers caused by electrons trapped at oxygen vacancies, there is also observed a poorly resolved sextet with splittings between neighboring components of ~8.5 Oe (see Fig. 2*a*). The intensity of this signal correlates well with the aluminum content in the samples. It, like the catalytic activity, increases with increasing duration and temperature of the preliminary vacuum treatment and with increasing irradiation dose.

Fig. 3. Dependence of the catalytic activity (*1*), the intensity of the sextet in the EPR spectra (*2*), and the adsorption capacity (*3*) of irradiated silica gel, in

relative units, on the temperature of heating the samples in vacuum (heating duration 1 hour)

Adsorption of hydrogen at room temperature is accompanied by the disappearance of the maximum at 500-550 mμ in the optical spectrum and of the sextet in the EPR spectrum (Figs. 1*b*, 2*b*). The amount of adsorbed hydrogen is, in order of magnitude, equal in this case to the initial intensity of the signal.

Heating the samples in vacuum to temperatures above 200°C leads both to a decrease in the intensity of the sextet in the EPR spectrum and to a weakening of their coloration. Figure 3 presents the dependence of the decrease in the intensity of the EPR signal on temperature when the samples are heated in vacuum for one hour. For comparison, the same figure also gives data on the change in adsorption capacity and catalytic activity of the same samples. The parallel change in these quantities once again confirms that the centers of catalysis and adsorption in irradiated silica gel are surface color centers associated with an aluminum impurity. The mechanism of their formation may be represented as follows. It is known that impurity aluminum atoms can form acidic centers in the surface layer of silica gel (^{17}). Upon irradiation of solids, as is known, free electrons and holes are formed. Some of these electrons can be captured by protons of acidic centers, leading to the formation of hydrogen atoms (^{16}). They, however, do not play the role of active intermediates in the reaction of isotopic exchange of hydrogen on the surface of silica gel, since they recombine at a temperature much lower than that at which a noticeable annealing of its catalytic activity is observed. After the departure of a hydrogen atom, an uncompensated negative charge remains on the aluminum atom, which can be neutralized when a hole is stabilized on an oxygen atom adjacent to aluminum. This process may be depicted by the following scheme:



$$\begin{array}{ccccccc}
 & \text{OH} & & \text{OH} & & \text{OH} & \\
 & | & & | & & | & \\
-\text{O}-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}- & +\,e & \longrightarrow & -\text{O}-\text{Si}{:}\text{O}{:}\text{Al}{:}\text{O}{:}\text{Si}-\text{O}- & +\,\dot{\text{H}} & & \\
 & | & & | & & | & \text{H} \\
 & \text{O} & & \text{O} & & \text{O} & {:}\text{O}{:} \\
 & | & & | & & | & {:}\text{O}{:}
\end{array}$$

In the irreversible adsorption of hydrogen molecules, observed above −100°, their dissociation takes place, the electrons pass from the hydrogen atoms to the holes, and the initial structure of the acidic centers in the unirradiated silica gel is restored. Since this process requires activation energy, it does not proceed at the temperature of liquid nitrogen. The isotopic exchange of hydrogen with deuterium at −196° occurs on these same centers; however, adsorption of the molecule in this case is not accompanied by dissociation, but leads only to a weakening of the bond between the atoms composing it. With increasing temperature, the rate of dissociative adsorption increases, which leads to the destruction of the active centers and to a more rapid annealing of the catalytic activity in an atmosphere of hydrogen than in vacuum. The energetic inhomogeneity of the radiation defects leads to the fact that even at room temperature a portion of them is not destroyed by irreversible adsorption of hydrogen, but is preserved as catalytically active centers.

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Received
29 III 1964

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

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