Yu. N. Stepanov, L. Ya. Margolis, and Corresponding Member of the USSR Academy of Sciences S. Z. Roginskii

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Yu. N. Stepanov, L. Ya. Margolis, and Corresponding Member of the USSR Academy of Sciences S. Z. Roginskii

Mobility of Modifying Additives in Silver

Studies on the gas modification of metals ([1–5]) have shown the possibility of a significant change in the catalytic activity of solids under the action of small amounts of introduced metalloids (oxygen, nitrogen, etc.). In this connection, with respect to the ethylene hydrogenation reaction, sharp maxima of activity are observed at a definite concentration of additives in the metal (1 atom of metalloid per 100 atoms of metal). The introduction of sulfur ions into nickel ([6]), and of phosphate ion into palladium ([7]), also had a modifying effect on hydrogenation reactions.

Fig. 1. Change in the specific radioactivity of a silver catalyst after heating at 300° in various gaseous media:
1 –in nitrogen (without oxygen), 2 –in air, 3 –in an air mixture + 3% C_2H_4.

In subsequent studies ([8]) on the action of additives on metals and oxide catalysts, it was shown that gas promotion is a special case of catalyst modification, which is the principal method for regulating their activity and selectivity. The use of sensitive radioactive isotopic methods of investigation broadened the range of observations on the modifying action of metalloid additives on metals and showed the high effectiveness of halides ([9,10]). As follows from measurements of the work function and electrical conductivity of various metals and semiconductors, one of the main reasons for the modifying action is a change in the activation energy of chemisorption and of the catalytic process under the influence of charging of the surface ([11]). However, there are also other kinetic cases of modification, in which the main change in activity is due to a large change in the pre-exponential factor K_0 ([12]).

In analyzing the phenomenon of modification it is customary to consider additives that are irreversibly fixed in the solid. These may be solid solutions or mixed phases. However, as applied to modifying metalloid additives, such a concept is too categorical, since migration of metalloid additives in the solid is observed ([4,13]). In this connection, it was of interest to study the mobility of metalloid additives introduced into a silver catalyst during the catalytic process.

The problem of the present work is divided into two more particular questions: migration through the layer and release into the bulk of metalloids introduced into the solid, and capture of metalloids from gas molecules and their behavior in the layer (next communication).

Additives of metalloids labeled with isotopes (Cl^{36}, J^{131}, S^{35}) were introduced into silver powder, with intensive stirring, by adsorption from

solutions of salts (NaCl, KJ, Na_2SO_4). The silver powder was pressed into tablets 10 mm in diameter and 5 mm high, after which the radioactivity of the surface was determined with an end-window counter with a mica window of 1.5 mg/cm^2.

The uniformity of distribution of the additive over the tablet was checked radiometrically. The silver tablets obtained in this way were placed in a glass reactor heated by an electric coil, through which a gas mixture was passed at various rates; the temperature in the catalyst layer was measured with a thermocouple. The specific radioactivity (per 1 cm^2 of geometric surface) was determined after every 5 hr of heating the tablets in various gas media.

Figure 1 gives data on the change in the specific radioactivity of silver containing the chlorine ion after heating at 300°C in nitrogen purified of oxygen, in air, and in a mixture of air with 3% ethylene.

Table 1

Influence of various reducing agents on the change in the specific radioactivity of silver

Composition of gas mixture	Initial average specific radioactivity of catalyst, imp/(min·cm^2)	Average specific radioactivity of catalyst after heating, imp/(min·cm^2)	Rate of chlorine removal, min^{-1}	Chlorine content in silver, %: initial, determined nephelometrically	Chlorine content in silver, %: after heating, determined nephelometrically	Chlorine content in silver, %: determined radiometrically after heating
Hydrogen	260	48*	$0.68 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$	$1.6 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Ethylene	360	100	$0.24 \cdot 10^{-2}$	–	–	–

Composition of gas mixture	Initial average specific radioactivity of catalyst, imp/(min·cm^2)	Average specific radioactivity of catalyst after heating, imp/(min·cm^2)	Rate of chlorine removal, min^{-1}	Chlorine content in silver, %: initial, determined nephelometrically	Chlorine content in silver, %: after heating, determined nephelometrically	Chlorine content in silver, %: determined radiometrically after heating
Nitrogen + 5.3% isopropyl alcohol	330	56	$0.27 \cdot 10^{-2}$	$7.7 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$
Nitrogen + 2% ethylene oxide	330	88	$0.25 \cdot 10^{-2}$	$7.7 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$
Carbon monoxide	330	340	0.0	$7.7 \cdot 10^{-3}$	$7.9 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$

* Specific radioactivity after 2 hr of heating.

In nitrogen and in air, no migration of chlorine in the silver catalyst was detected over the course of 15 hr. Raising the temperature to 400–450°C also had no effect on the movement of the additive in these media. In the presence of a 3% ethylene–air mixture at the temperature of catalysis, a slow decrease in radioactivity is observed. Probably, on the surface of the silver grains a reduction reaction of the chlorine ion takes place under the action of ethylene, as a result of which hydrogen chloride should form. If this assumption is correct, all reducing agents containing hydrogen atoms should promote the removal of chlorine from the silver surface. Table 1 gives data on the influence of various reducing agents on the process of chlorine removal from silver at 300°, a heating time of 5 hr, and a flow rate of 16 l/hr.

Chlorine is removed from the surface of silver most rapidly in hydrogen, and also under the action of reducing agents containing a hydrogen atom in the molecule. It is known that carbon monoxide has reducing properties and readily interacts with halides. Treatment of chlorine-containing silver with carbon monoxide did not lead to a change in the radioactivity of the catalyst. Nephelometric analysis of the silver for its chlorine content after treatment with carbon monoxide con-

Figure 2 and Figure 3

Figure 2: Figure 2 and Figure 3

firmed the radiometric data on the complete absence of halide removal in this case. Specially arranged experiments made it possible to determine the content of hydrogen chloride in the reaction products. In the reactor, at a distance of 15 cm from the layer of silver tablets containing Cl^{36} and heated to 300°, there was placed a silver-

a silver plate, whose temperature did not exceed 40° because the walls of the upper part of the reactor were cooled with water.

After heating at 300° in ethylene for 5 h, radioactivity was detected on the silver plate, exceeding the initial background value of this plate by a factor of 10. A significant increase in the radioactivity of the silver plate placed above the catalyst layer was also observed when $S^{35}O_4^{2-}$ was introduced into the silver. In a number of experiments, instead of a silver plate, a trap containing

Fig. 2. Change in the specific radioactivity of silver during heating in ethylene-nitrogen mixtures at 300°: 1 —in a 3% ethylene-nitrogen mixture, 2 —in a 10% ethylene-nitrogen mixture, 3 —in a 35-60% ethylene-nitrogen mixture, 4 —in ethylene

Fig. 3. Dependence of the logarithm of the initial rate of chlorine removal from silver on reciprocal temperature: 1 —in a 3% ethylene-air mixture, 2 —in a 35% ethylene-air mixture

distilled water with an indicator (methyl red) was placed at the reactor outlet. When gases were passed through such a trap, it was found that the reaction products of hydrogen or ethylene with the chlorine ion contained in silver possess appreciable acidity. When the water in the trap was replaced by a solution of silver nitrate, the amount of chlorine removed from the catalyst was determined nephelometrically. These results indicate that the reaction forming hydrogen chloride takes place on the surface of the silver.

To determine the variation of radioactivity through the volume of the pellet, sections of silver 0.2 mm thick were made. Measurement of the radioactivity of the surfaces of the sections showed that the reduction reaction proceeds throughout the entire volume of the pellet. The possibility of diffusion of the chlorine ion through the silver lattice was studied on a silver single crystal. On the surface of a cylindrical single crystal 5 mm thick and 11 mm in diameter, a hole 5 mm in diameter was drilled, into which a small amount of potassium chloride labeled with Cl^{36} was pressed. The single crystal was heated in hydrogen at 300° for 5 h. Measurement of the radioactivity of sections of the silver single crystal at a distance of 3 mm from the plane containing Cl^{36} showed the absence of noticeable diffusion of the chlorine ion through the silver lattice under the experimental conditions ($T = 300^{\circ}$, gas flow rate 8 l/h).

Thus, the metalloid is removed from silver as a result of a reduction reaction that proceeds on the surface of silver grains. The effect of the concentration of ethylene in a mixture with nitrogen on the rate of change in the radioactivity of silver, i.e., on the rate of removal of chlorine from the surface, is presented in Fig. 2. With an increase in the ethylene concentration in the gas mixture, the rate of removal of the additive increases. Raising the concentration above 35% changes the rate of chlorine removal from silver only slightly. Figure 3 shows the dependence of the logarithm of the initial rate of the process of chlorine removal from

of silver on the reciprocal temperature in 3% and 35% mixtures of ethylene with air. The activation energy of the process is about 15 kcal/mole. It is of interest to trace the rate of the reduction process in silver of additives of sulfur labeled with the isotope S^{35} (in the form of SO_4^{2-}) and iodine labeled with J^{131}.

Table 2

Rate of removal of various halide additives from a silver catalyst. Medium: C_2H_4

Additive introduced into silver	Amount of introduced additive, wt. %	Initial specific radioactivity, imp/min · cm^2	Specific radioactivity after heating, imp/min · cm^2	Rate of additive removal, min^{-1}	Amount of removed additive, %
J^-	$8 \cdot 10^{-3}$	2000	630	$0.23 \cdot 10^{-2}$	70
Cl^-	$8 \cdot 10^{-3}$	385	135	$0.22 \cdot 10^{-2}$	65
SO_4^{2-}	$9 \cdot 10^{-2}$	277	180	$0.12 \cdot 10^{-2}$	35

Table 2 presents the change in the radioactivity of silver, with labeled additives introduced into it, after heating in ethylene at 300° for 5 h. As can be seen, for iodine and sulfur a reduction reaction is also observed.

Under the conditions of the catalytic process of ethylene oxidation to ethylene oxide, the concentration of the metalloid additive introduced into the silver to increase the selectivity of the oxidation process gradually decreases as a result of reduction of the additive by ethylene with subsequent removal of the products of this reaction.

An increase in the concentration of ethylene in the mixture leads to a significant increase in the rate of reduction of chlorine and, consequently, to a more rapid fall in the selectivity of the catalyst. Therefore, a more rational method of introducing metalloids into silver is the method of continuously adding them to the gaseous reaction mixture.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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