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## Abstract

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# THE INFLUENCE OF SELENIUM AND TELLURIUM ON THE CATALYTIC ACTION OF SILVER IN THE OXIDATION OF ETHYLENE

*(Presented by Academician S. S. Medvedev on 28 III 1960)*

Earlier, the modifying action ([1]) of sulfur compounds upon their introduction into a silver catalyst for the oxidation of ethylene ([2]) was investigated. In the patent literature there is an indication that additions of selenium and tellurium compounds increased the selectivity of a silver catalyst, i.e., directed the reaction to a greater extent toward the formation of ethylene oxide; at the same time, however, the activity of the catalyst decreased considerably ([3]). Below are set forth the results of a study of the influence of sulfur analogues on a silver catalyst.

Catalyst samples were tested in a flow-circulation system at 219°C. The concentration of ethylene in the ethylene–air mixture fed was maintained at 2.5 to 3.0%. The method of kinetic measurements and the air-purification system have been described earlier ([2,4]). Ethylene, obtained by dehydration of ethanol, was purified by passing it successively through activated charcoal AG-3 and AS, a trap at a temperature of −78°, a furnace with copper oxide at 150°, and columns with soda lime and silica gel. The purification system used made it possible to work with a catalyst sample for more than 300 hours without a decrease in stationary activity. Selenium and tellurium compounds labeled with the radioisotopes $Se^{75}$ and $Te^{127}$ were used, which made it possible to monitor very small concentrations of the additive in the catalyst, to observe migration of additives toward the surface, and to establish the absence of carryover of additives from the surface during the catalytic process.

The catalyst was sponge silver, obtained by coprecipitation of silver carbonate and silver selenate or tellurate, followed by reduction in an ethylene–air mixture at 219°.

Selenic acid was prepared by oxidation of elemental selenium with hydrogen peroxide on heating ([5]); telluric acid, by oxidation of elemental tellurium with hydrogen peroxide in an alkaline solution on heating ([6]). The surface area of the catalyst samples was measured by low-temperature adsorption of nitrogen and was, for the series with selenium additions, $0.95 \pm 0.15$ m$^2$/g, and for the series with tellurium additions, $0.75 \pm 0.1$ m$^2$/g.

Fig. 1

Figure 1: Fig. 1

We shall characterize catalytic activity by the rate constant of the reaction of formation of ethylene oxide, $k_1$, expressed in relative units. The unit was taken to be the rate constant of the reaction on a sample without additive with a specific surface area equal to the corresponding value for catalysts of the given series. The rate constant was calculated from the equation ($^7$)

$$\omega_1 = \frac{k_1[\mathrm{C_2H_4}]}{[\mathrm{C_2H_4O}] + 0.3[\mathrm{CO_2}]},$$

where $\omega_1$ is the rate of the reaction of formation of ethylene oxide, and $[\mathrm{C_2H_4}]$, $[\mathrm{C_2H_4O}]$, $[\mathrm{CO_2}]$ are the concentrations of the corresponding gases in the reacting mixture. The selectivity $S$ is defined as the percentage ratio of the rate of reaction

of ethylene oxide formation to the sum of the rates of the reaction of ethylene oxide formation and the reaction of ethylene oxidation to $CO_2$ and $H_2O$. The change in selectivity is $\Delta S = S - S_0$, where $S$ is the selectivity of the catalyst with an additive, and $S_0$ is the selectivity of the catalyst without an additive. On average $S_0 \simeq 50\%$.

The catalysts were tested for no less than 55 h; for purposes of comparison, the mean values of $k_1$ and $\Delta S$ used are those corresponding to the interval from the 44th to the 54th hour of catalyst operation. Figure 1 presents the dependence of the quantities $k_1$ and $S$ for the catalysts on the concentration in them of selenium (curves I) and tellurium (curves II). The dashed straight lines refer to the catalyst without additives. As will be shown below, the greater part of the selenium or tellurium is located at the catalyst surface. The fraction of the silver surface covered with selenium or tellurium was calculated conventionally as the ratio of the number of Se or Te atoms in the catalyst to the number of Ag atoms on the surface. As is seen from Fig. 1, addition of selenium at a concentration of $10^{-4} \div 5 \cdot 10^{-3}$ at. % (0.1-5% surface coverage) increases the catalytic activity by approximately a factor of 3.5. A further increase in the selenium concentration leads to poisoning of the catalyst. At a content of $7.8 \cdot 10^{-2}$ at. % Se (coverage of about one monolayer), the catalyst is 9 times less active than the catalyst without an additive. Introduction of tellurium does not lead to a substantial increase in catalytic activity. Tellurium concentrations greater than $10^{-2}$ at. % (about 12% surface coverage) poison the catalyst. The activity of a catalyst with $3.3 \cdot 10^{-2}$ at. % Te (about 40% surface coverage) is 15 times lower than the activity of the catalyst without an additive.

**Fig. 1**

A significant increase in selectivity is observed only at those Se or Te contents for which the catalytic activity is decreased.

The initial concentration of the additive in the catalysts was calculated from the radioactivity of a solution of silver carbonate in nitric acid. The radioactivity was determined with an MS-4 Geiger-Müller counter; the solution was placed in a shielded double-walled glass cuvette (8). After completion of the kinetic measurements, catalysts with selenium additives were washed with hot water and with a 2% hot NaOH solution; catalysts with tellurium additives were washed with hot water, a 2% hot NaOH solution, concentrated ammonia solution, and a 2% $HNO_3$ solution. The catalysts were then dissolved in $HNO_3$. The radioactivity of all solutions was determined. Selenium was not washed off the catalysts by water; a 2% NaOH solution washed off 40-80% of the selenium, while dissolving no more than one monolayer of silver. Tellurium was not washed off by water; a 2% NaOH solution and a saturated aqueous ammonia solution washed off part of the tellurium only from catalysts containing $3.3 \cdot 10^{-2}$ at. % Te (about 40% surface coverage) and more. A 2% $HNO_3$ solution washed off 55-90% of the tellurium, while dissolving no more than two monolayers of silver.

Thus, selenium and tellurium added during preparation of the catalysts are located in the near-surface layer of the working catalyst. It was found earlier (2) that, when sulfur is added to the catalyst, 80-90% of it can be washed off the working catalyst with water. The maximum catalytic activity was observed at a concentration of about $5 \cdot 10^{-5}$ at. % S and was approximately 3.5 times greater than the activity of the sample without additives.

Apparently, when small amounts of elements of Group VI of the D. I. Mendeleev periodic system are added to a silver catalyst, two effects occur, due to impurities on the surface or in the near-surface layer of the catalyst. The first of these effects is caused by the formation on the surface of negative ions, such as $SO_4''$ or $SeO_3''$, which cause a decrease in the adsorption energy of oxygen; this slows the adsorption of oxygen and accelerates the reaction of adsorbed oxygen with ethylene*. As a result, at some optimal bond energy, the reaction rate passes through a maximum.

The second effect consists in the blocking of the silver surface by foreign atoms and can lead only to a decrease in the activity of the catalyst. To achieve maximum catalyst activity, a smaller amount of sulfur is required than of selenium. In the case of introducing tellurium into the catalyst, only the second effect is observed, since the affinity of tellurium for oxygen is considerably lower than the affinity of sulfur or selenium for oxygen.

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* The decrease in the bond energy of oxygen on silver and the slowing of oxygen adsorption upon addition of sulfur in amounts corresponding to small surface coverages have been established in experiments that will be described in another communication.

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