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Abstract

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THE INFLUENCE OF ELECTRONEGATIVE ELEMENTS ON THE CATALYTIC ACTION OF SILVER IN THE OXIDATION OF ETHYLENE

(Presented by Academician A. N. Frumkin, 21 VII 1958)

The process of catalytic oxidation of ethylene to ethylene oxide

$$C_2H_4 + \tfrac{1}{2}O_2 = C_2H_4O \qquad (1)$$

takes place on the surface of silver at 200–300°. Small additions of chlorine compounds increase the selectivity of the catalyst, i.e., decrease the relative role of the undesirable reaction

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O, \qquad (2)$$

without lowering the degree of conversion of ethylene. Somewhat larger amounts of chlorine cause poisoning of the catalyst ([1]). There are reports of an analogous action of sulfur ([1,2]). The interest that these phenomena present for the theory and practice of catalysis prompted us to investigate them in greater detail.

The procedure used for the kinetic measurements has been described earlier ([3]). The experiments were carried out in a flow-circulation apparatus at 1 atm. and 218°. The ethylene–air mixture entering the cycle contained 2.5±0.2 vol.% C_2H_4. Volumetric flow rates of about 1500 hr^{-1} were used; the degree of conversion of C_2H_4 on silver without additions of Cl and S was 50–60% of that passed. The concentrations of CO_2 and C_2H_4 were determined with an accuracy up to 0.05 vol.%, and C_2H_4O up to 0.01 vol.%.

In addition to the previously used ([3]) means of purifying the reaction gases, to remove traces of organic sulfur compounds the air was passed through a tube with ZnO at 400° ([4]).

Sulfur compounds labeled with the radioisotope S^{35} were used. This made it possible to determine very small amounts of sulfur and to observe the migration of sulfur in the catalyst. The procedure for preparing and dosing H_2S was similar

to that described ([5]). To determine S, a weighed sample was dissolved in nitric acid containing H_2O_2, after which a precipitate of $BaSO_4$ was obtained. The radioactivity of $BaSO_4$ was measured in a saturation layer with an end-window counter.

The catalyst was spongy silver obtained by thermal decomposition of Ag_2CO_3 in a stream of an ethylene–air mixture. The surface of the catalyst was measured by low-temperature adsorption of nitrogen. Most of the experiments were carried out with silver grains having a specific surface of about 1 m^2/g. Tablets 5×3 mm with a specific surface of 0.3 m^2/g were also used. The tablets, unlike the grains, contained traces of chlorine introduced during manufacture.

The activity of the catalyst will be characterized by the rate constant of reaction (1), k_1, calculated from equation (6):

$$\omega_1 = \frac{k_1[C_2H_4]}{[C_2H_4O] + 0.3[CO_2]}, \tag{3}$$

where ω_1 is the rate of reaction (1), measured as the ratio of the volume of C_2H_4O, in ml at 0° and 1 atm, formed in 1 sec, to the catalyst surface area in square meters. The selectivity s is defined as the ratio of the rate of reaction (1) to the sum of the rates of reactions (1) and (2).

Initially, experiments were carried out with a tableted catalyst, in which H_2S was continuously added to the reaction mixture for 20–30 hr. The H_2S concentrations in different experiments varied from 0.1 to 50 mg/m^3. A slight increase in catalyst activity was observed (by 10–20%) after the introduction onto the catalyst of from $3 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ at.% S (relative to Ag). This was accompanied by an increase in selectivity from $s = 0.70$ to $s = 0.77$. Regardless of the concentration of H_2S in the gas mixture, after amounts of sulfur of the order of 10^{-2} atomic % had been introduced onto the catalyst, the oxidation of ethylene almost ceased. At the same time, dark spots appeared on the pellets first encountered by the gas stream. A separate test of the catalytic activity of the silver layers showed that, despite the high linear velocity of the gas mixture in the flow-circulation system (about 1 m/sec in the reaction zone), predominantly the pellets first encountered by the gas stream were poisoned. Measurements of the radioactivity of the pellets confirmed this and showed that the sulfur initially captured by the outer surface of the pellet migrates inward under the reaction conditions. This can explain the slow changes in catalyst activity and selectivity observed after the supply of H_2S to the reaction mixture was stopped.

To achieve a uniform distribution of sulfur over the surface, the following methods were used:

1. Silver grains 0.1–0.2 mm in size were treated in a "fluidized bed" with hydrogen sulfide at room temperature (at 218°, the grains stuck together).
2. Ag_2CO_3 and Ag_2S were precipitated together, followed by washing with

hot water (after washing, only about 1/3 of the initial amount of S remains in the silver).

3. Carbonate silver was wetted with a solution of H_2SO_4.
4. Silver powder was wetted with a solution of Na_2SO_4 (particle size 0.05 mm).

Regardless of the method of introducing sulfur into the catalyst, after ethylene oxidation has been carried out on the latter for some time, most of the added sulfur can be washed off the catalyst with water at room temperature. From this it may be concluded that, during the catalytic process, most of the sulfur is present on the silver in the form of a surface sulfate. This makes it possible to calculate the degree of surface coverage θ from the total S content, assuming that all the sulfur is on the surface. The values calculated in this way are given below; evidently they may be overestimated, but not underestimated.

Figure 1 presents the results of determining the catalytic activity and selectivity of silver grains preliminarily treated with H_2S in a "fluidized bed." Since a logarithmic scale was used for the concentration of S in this and the following figures, the points corresponding to activity and selectivity without sulfur additions could not be plotted. The corresponding values are shown by dashed straight lines. The catalyst was tested for about 10 hr. The average performance indices of the catalyst during the test are given.

At sulfur contents up to $2 \cdot 10^{-3}$ at.%, which corresponds to $\theta \leq 0.025$, the catalyst activity is higher than the activity without sulfur additions, while at higher sulfur contents the activity falls below the initial activity. At $2 \cdot 10^{-2}$ at.% S, i.e. $\theta \simeq 0.25$, the activity is 0.04 of the initial value. The selectivity of silver without additions is $s = 0.46$. Upon introduction of sulfur, the selectiv-

···ness initially increased and reached its greatest value at $\theta \simeq 0.03$. At $\theta \simeq 0.1$ the selectivity again decreased to the initial value.

Figure 2 presents data characterizing catalysts obtained by the coprecipitation of Ag_2CO_3 and Ag_2S. The reported values of activity and selectivity were averaged over the period from the 44th to the 54th hour of catalyst operation. As in the experiments described above, small amounts of S increase the activity of the catalyst. The maximum activity was observed at $5.5 \cdot 10^{-5}$ at.% S and was 4 times higher than the activity of the unpromoted sample. With a further increase in the S content in the catalyst, the activity decreased, while nevertheless remaining above the activity of the initial sample up to $\sim 10^{-3}$ at.% S. Sulfur in an amount of 10^{-1} at.% practically completely poisoned the catalyst. The selectivity of the catalysts increased from $s = 0.57$ for the initial sample to $s = 0.71$ for a catalyst containing $4.2 \cdot 10^{-4}$ at.% S, and decreased with a further increase in the sulfur concentration.

Fig. 1 **Fig. 2**

Experiments with the introduction of sulfur in the form of Na_2SO_4 and H_2SO_4

Fig. 1 and Fig. 2: Selectivity s and $k \cdot 10^3$ versus $\lg[S]$; dashed reference lines labeled $[S] = 0$.

Figure 1: Fig. 1 and Fig. 2: Selectivity s and $k \cdot 10^3$ versus $\lg[S]$; dashed reference lines labeled $[S] = 0$.

gave results consistent with those described above, which makes it possible to attribute the activating and poisoning action to SO_4^{--} ions on the surface of silver.

Experiments on the effect of additions of Cl_2 and HCl to the reaction mixture were carried out with a tableted catalyst already containing an amount of chlorine close to the optimum. Therefore, in them only a decrease in catalyst activity could be observed. Additions of Cl_2 and HCl at concentrations of about 2 mg/m^3 reduced the activity of the catalyst by a factor of 5 after $0.5 \cdot 10^{-2}$ at.% Cl, relative to Ag, had been introduced into the reaction mixture. At the same time the selectivity increased from 0.70 to 0.76–0.80. The poisoning was partially reversible. Higher concentrations led to irreversible poisoning.

The data presented show that the increase in the selectivity of the catalytic action of silver upon introduction of sulfur (and also chlorine) cannot be explained by partial poisoning of the catalyst with respect to the undesirable reaction (2). Small amounts of sulfur increase both the rate of reaction (1) and the rate of reaction (2), but to different degrees.

An increase in the amount of sulfur leads to poisoning. Thus we have here an example of a phenomenon that was described by S. Z. Roginskii and called by him "modification of contacts" ([7,8]). Since the action of various negative ions, namely SO_4^{--} and Cl^-, is similar, it may be assumed that the modification of silver by these ions is due to a change in the electronic state of the surface.

A. Kh. Breger and A. A. Zhukhovitskii ([9]) demonstrated the fundamental possibility of the existence of long-range forces between adsorbed atoms. Taking into account the electronegativity of oxygen, it is natural to expect that SO_4^{--} or other negative ions should decrease the adsorption energy of oxygen. Apparently, there is an optimum value of the adsorption energy of oxygen at which the catalytic activity is maximal. On the clean surface of silver the adsorption energy of oxygen is greater than the optimum; as the surface concentration of negative ions increases, the adsorption energy of oxygen reaches the optimum value and then becomes smaller than it; this can explain the fact that the reaction rate passes through a maximum.

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