The Effect of Water Vapor on the Oxidation of Propylene on a Copper Catalyst

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E. N. Popova and Ya. B. Gorokhovatskii

The Effect of Water Vapor on the Oxidation of Propylene on a Copper Catalyst

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The oxidation of propylene to acrolein on a copper contact is always accompanied by the formation of carbon dioxide. At low temperatures acrolein and carbon dioxide are formed by parallel pathways; with increasing temperature, the reaction of further oxidation of acrolein comes into play (1). The selectivity of this process can be increased by introducing promoting additives into the catalyst (2), or into the gas mixture (3). In many patents it is recommended to dilute the propylene-oxygen or propylene-air mixture with water vapor (4), along with other inert diluents (nitrogen, CO_2). From data previously obtained in our laboratory (5), as well as from data of A. G. Polkovnikova and co-workers (6), it follows that water is not an inert component, but has an inhibiting and selectivizing effect on the rate of oxidation of propylene. It is therefore of interest to study quantitatively the effect of water vapor at high contents of it in the reaction mixture. The present investigation is devoted to this question.

The investigation was carried out by the flow-circulation method, using a gradientless reactor with a piston turbulizer of the Korneichuk-Rubanik system (7), under conditions free from diffusion retardation. Approximately constant concentrations of propylene (30-32%) and oxygen (7.6-8.6%) were maintained in the catalyst zone. Dilution was carried out with nitrogen and water vapor. When the vapor concentration was changed, the amount of nitrogen introduced was correspondingly decreased or increased. The mixture of propylene with nitrogen was saturated with vapor by passing through the system: boiler, condenser, superheater. The specified amount of vapor was regulated by the temperature of the condenser placed in a thermostat. Fluctuation of the condenser temperature did not exceed $±$0.1°. Oxygen was introduced into the saturated and superheated mixture before the entrance to the reactor. Dilution of the mixture with oxygen was taken into account in calculating the amount of vapor supplied. In the final calculation of the water concentration in the catalyst zone, the water formed as a result of the reaction was also taken into account. The reaction products and unreacted components were analyzed by the methods described earlier (1).

The study of the influence of vapor concentration on the rate of formation of acrolein and carbon dioxide and on the selectivity of the process was carried out on two catalyst samples differing in the amount of deposited copper oxide and

Fig. 1

Figure 1: Fig. 1

in the type of support. Sample No. 1 contained 2.5 g of copper per 1 liter of nonporous (globular) silicon carbide, or 0.19% by weight of the support. Sample No. 2 contained 13.2 g or 1.53% copper on porous (thermosilicate) silicon carbide with a grain size of 2-3 mm. In all cases 5 cm^3 of catalyst was charged into the reactor.

From the data shown in Fig. 1 it is evident that, with increasing water concentration, at temperatures of 380 and 420° the rate of formation of carbon dioxide decreases sharply. The rate of formation of acrolein passes through a maximum as the vapor content increases. Accordingly, with an increase in the amount of water, the selectivity of propylene oxidation to acrolein increases. A similar form of the dependences of rate and selectivity on the conten—

of water is also observed on the more active catalyst sample No. 2, which contains a larger amount of copper, but at a considerably lower temperature, equal to 350° (Fig. 2).

The data presented indicate that water vapor is not an inert diluent, but actively affects the course of oxidation.

Fig. 1. Dependence of the rates of formation of acrolein and carbon dioxide and of selectivity on the concentration of water vapor on sample No. 1 at 380° (A) and at 420° (B). 1 —CO_2; 2 —C_3H_4O

The dependences we observed of the reaction rate on the vapor content in the mixture cannot be explained by uniform blocking or poisoning of the active surface of the catalyst by vapor, since in that case we would observe a decrease in both rates over the entire range of variation of H_2O concentrations. If only those surface sites on which deep oxidation of propylene occurs were blocked, the rate of formation of acrolein would not change. Evidently, the water vapor present in the reactant mixture competes with them for the surface. We suppose that on the surface of the copper-oxide contact there are two types of active centers, on some of which mild oxidation of propylene occurs, and on others deep oxidation occurs. Vapor, being adsorbed on the surface, lowers the rate of oxidation of propylene at both types of sites, as follows from (5). At the same time, the rate of further oxidation of acrolein also decreases. Therefore, with the clear presence of a stage of acrolein oxidation in the absence of vapor, the introduction of H_2O into the mixture leads to an increase in the acrolein concentration, despite the fact that the true rate of its formation is inhibited by vapor. As can be seen from Fig. 1B, up to a vapor concentration of 10-20% the inhibition of the true rate of oxidation of propylene to acrolein is largely offset by the decrease in further oxidation of acrolein; at larger amounts of vapor (above 30%) the mild oxidation of propylene decreases so much that the observed rate of formation of acrolein decreases appreciably. At a smaller fraction of the oxidation reaction

Fig. 2

Figure 2: Fig. 2

Fig. 2. Dependence of the rates of formation of acrolein and carbon dioxide and of selectivity on the concentration of water vapor at 350° on sample No. 2. 1 $-CO_2$; 2 $-C_3H_4O$

of acrolein in the absence of steam, the decrease in the true and observed rates of its formation occurs to a greater extent.

Thus, the results of the present study confirm the conclusion made earlier ([5]) that water vapor inhibits the rates of formation of carbon dioxide and acrolein and increases the selectivity ([6]). In the presence of a stage of oxidation of the acrolein formed, steam inhibits this process much more strongly than the oxidation of propylene. Therefore, a greater increase in selectivity in the presence of steam is obtained at higher temperatures and on more active catalysts.

The data we obtained on the dependence of the rates of the reactions forming acrolein (W_1) and carbon dioxide (W_2) on the concentration of water vapor, at constant contents of oxygen and propylene in the reaction mixture, are satisfactorily described by the following equations:

$$W_1 = k_1 \frac{(1 + C_{\mathrm{H_2O}})^{0.5}}{1 + b_1 C_{\mathrm{H_2O}}} \quad \text{and} \quad W_2 = k_2 \frac{1}{1 + b_2 C_{\mathrm{H_2O}}},$$

where b_1 and b_2 are empirical constants.

The value of b_1 for the catalyst with a copper content of 2.5 g/l at temperatures of 380 and 420° was 0.08, and for the contact containing Cu 13.2 g/l, at 350°, it was 0.05. The value of b_2 increases with temperature: for specimen No. 2 at 350° it was 0.015; for specimen No. 1 at temperatures of 380 and 420°, respectively, 0.02 and 0.04.

In the figures, the experimental data are represented by points, and the curves are calculated from the equations given above. It can be seen that the calculated curves agree fairly well with the experimental data.

The active participation of water vapor in the process of propylene oxidation is also confirmed by the fact that, at substantial water contents in the reaction mixture, the rate of oxidation of C_3H_6 increases strongly with increasing propylene concentration, whereas upon dilution of the mixture with nitrogen alone, or without a diluent, no such dependence was observed ([5,8]). These data will be considered in more detail in the following communication.

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Institute of Physical Chemistry named after L. V. Pisarzhevskii
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