Reports of the Academy of Sciences of the USSR

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1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958, Vol. 119, No. 1

PHYSICAL CHEMISTRY

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ON A COPPER CATALYST FOR THE OXIDATION OF PROPYLENE TO ACROLEIN

(Presented by Academician V. N. Kondrat' ev, 6 VIII 1957)

The study of the oxidation of propylene to acrolein on a series of transition-metal oxides ([1]) showed that, on cuprous oxide, the introduction of oxygen into the hydrocarbon molecule can occur without rupture of the double bond, with formation of the unsaturated aldehyde–acrolein.

It is known that cuprous oxide is a typical hole semiconductor, whose impurity electrical conductivity in the temperature range from 0° to 250° varies from 10^{-9} to $10^2\ \Omega^{-1}\text{cm}^{-1}$, depending on its oxygen content ([2]). Comparison of the electrical properties of cuprous oxide with its adsorption properties toward propylene showed that the less oxygen there is in cuprous oxide, the more propylene is sorbed on the catalyst. It is probable that the catalytic activity of cuprous oxide also changes when its oxygen content changes.

A number of foreign patents ([3,4]) give data on the preparation of active catalysts for this process, based both on cuprous oxide and on copper oxide. One of the patents ([4]) states that copper oxide is not active for this reaction. Nevertheless, later patents recommend using copper oxide deposited on various supports. It remained unclear what the phase composition of the copper contacts is, what happens to the catalyst during the reaction, and which of the oxides is catalytically active.

To clarify these questions, three series of experiments were carried out, in which the following catalysts were chosen: 1) copper oxide CuO, 2) cuprous oxide Cu_2O, and 3) metallic copper, deposited on pumice.

Copper oxide was prepared by impregnating pumice with a solution of $Cu(NO_3)_2$ and subsequent calcination at 500°. Cuprous oxide was prepared by the method proposed by D. N. Finkelstein ([5]), and after washing was deposited on pumice from an aqueous suspension. Metallic copper was obtained by reduction of the oxides deposited on pumice in a stream of hydrogen at 300–350°C.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The phase composition of the catalysts before and after operation was studied by X-ray diffraction. The X-ray patterns were recorded in a Debye camera 57.3 mm in diameter using iron K_α radiation.

The catalysts were tested in a dynamic apparatus at atmospheric pressure on a mixture of propylene with air containing 10—12% propylene and about 20% oxygen, in the temperature range 300—400°, for 40 minutes.

Figure 1 presents the results of identification of the X-ray patterns of the three catalysts, where the abscissa gives the interplanar spacings d in the crystal lattice, and the ordinate gives the line intensities in the X-ray patterns, determined visually.

Treatment of copper oxide with an air-propylene mixture at 300° does not change the phase composition of the catalyst. Raising the temperature to 400° leads to reduction of the copper oxide both to cuprous oxide and to the metal.

The initial cuprous oxide under these conditions is always partially reduced to copper. Passing an air-propylene mixture over copper at 300° leads to its partial oxidation to Cu_2O.

Additional X-ray investigation of these catalysts showed that, after their treatment with a propylene-air mixture, the surface of all the samples studied is covered with a layer of cuprous oxide.

Fig. 1. Change in the phase composition of a copper catalyst during oxidation of propylene with oxygen in air. **1**—initial cupric oxide, **2**—cupric oxide after reaction at 300°, **3**—cupric oxide after reaction at 400°, **4**—initial cuprous oxide, **5**—cuprous oxide after reaction at 350°, **6**—initial metallic copper, **7**—copper after reaction at 300°.

Thus, in the presence of a propylene-air mixture, cupric oxide is reduced to the $Cu_2O + Cu$ system, and copper is oxidized to cuprous oxide. The reaction of propylene oxidation to acrolein proceeds in the presence of cuprous oxide. The appearance of the metallic phase in this system may be due to reduction of Cu_2O to the metal. Analysis of the off-gases

Fig. 2. Change in the phase composition of a copper oxide catalyst during its reduction with a propylene-nitrogen mixture. **1**—initial cupric oxide, **2**—cupric oxide after reduction at 300°, **3**—cupric oxide after reduction at 400°, **4**—initial cuprous oxide, **5**—cuprous oxide after reduction at 200°, **6**—cuprous oxide after reduction at 350°.

formed during the oxidation of propylene shows the almost complete absence of oxygen in them. Consequently, during the reaction the catalyst operates in a reducing medium, and therefore the transition $Cu_2O \rightarrow Cu$ is possible. To study this phase transformation, the catalyst was treated at a temperature of 200–400° with a mixture of propylene and nitrogen containing 10% propylene and less than 1% oxygen. The results of the X-ray analysis are shown in Fig. 2. Significant reduction of cuprous oxide to copper is observed

is achieved at 350°. Passing the mixture over copper oxide at 300° leads to partial reduction of the oxide to the metal. Raising the temperature to 400° results in rapid and complete reduction of copper oxide to copper. The introduction of oxygen into the reaction mixture, however, as stated above (see Fig. 1), again leads to partial oxidation of metallic copper to cuprous oxide. Copper oxide is not detected in this case by X-ray analysis.

Thus, by changing the propylene:oxygen ratio in the reaction mixture, it is possible to suppress or intensify the process of reduction of cuprous oxide.

From what has been said above it follows that the composition of the catalyst is self-regulated by the presence of a reversible process of reduction of Cu_2O to Cu and oxidation of Cu to Cu_2O. Depending on the composition of the reaction mixture and the temperature conditions of the catalytic process, the phase composition of the catalyst changes, and either enrichment of cuprous oxide with copper occurs, or the oxygen content in cuprous oxide increases. In both cases the catalytic activity with respect to the oxidation of propylene to acrolein changes. The introduction, in one case, of oxygen, and in the other of propylene, leads to an increase in the activity of the catalyst, which is consistent with the data of a number of patents ([6]–[8]), in which it is recommended that regeneration of the copper catalyst be carried out by stopping the feed of propylene or oxygen.

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Received
25 VII 1957

CITED LITERATURE

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