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N. I. Popova, V. P. Latyshev

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## Abstract

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**N. I. Popova, V. P. Latyshev**

# Investigation of the Mechanism of Propylene Oxidation on Copper Catalysts by the Method of Separate Calorimetry

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The application of Koval' skii' s method of separate calorimetry to the study of catalytic oxidation processes of hydrocarbons ($^1$) made it possible to establish that, in the cases of catalysts of "mild" and deep oxidation, different oxidation mechanisms operate: in the first case a purely heterogeneous mechanism, and in the second a heterogeneous-homogeneous one ($^{2,3}$). At the same time it is known that catalytic processes of "mild" oxidation are always accompanied by parallel reactions of deep oxidation of hydrocarbons. For selective conduct of these processes it is very important to know the laws governing the formation of carbon dioxide on these catalysts. In the study of the oxidation of propylene to acrolein on copper catalysts by Rubanik and co-workers ($^4$), on the basis of kinetic measurements it was proposed that at low temperatures, of the order of 320°, parallel formation of acrolein and carbon dioxide takes place, whereas at high temperatures (380—400°) carbon dioxide is formed according to a parallel-consecutive scheme. Margolis and co-workers ($^5$), using the tracer-atom method, demonstrated a parallel-consecutive scheme for the oxidation of propylene to acrolein (at 396°).

The aim of the present work was to study the mechanism of propylene oxidation on copper catalysts by Koval'skii's method of separate calorimetry and to clarify the reasons for the different character of carbon dioxide formation at low and high temperatures under the conditions of this process.

## Experimental Procedure

The layout of the apparatus is shown in Fig. 1. The reaction vessel was made according to the type proposed by Butyagin ($^{2,3}$). To determine the magnitude of heating ($\Delta t$), a three-junction differential thermocouple (copper—constantan), with wire diameter 0.1 mm, was used.

The use of a triple differential thermocouple makes it possible to measure the following temperature differences: $\Delta t_1$—between the catalyst surface and the volume of the reactor, $\Delta t_2$—between the catalyst surface and the furnace, $\Delta t_3$—

Fig. 1. Diagram of the apparatus: 1 —reactor; 2, 3, 5 —traps; 4 —diffusion pump; 6 —electric furnace; 7 —burette; 8 —manometer (up to 760 mm Hg); 9 —manometric lamp; 10 —MacLeod manometer; 11 —ballast vessel; 12 —cylinders for gas storage

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between the volume of the reactor and the furnace. This method of measurement makes it easy to detect the presence of homogeneous oxidation in the case of the simultaneous occurrence of a heterogeneous process.

Measurements of $\Delta t$ were carried out with the aid of a mirror galvanometer with a current sensitivity of $1 \cdot 10^{-9}$ A. The measuring scale was placed 4 m away from it, which made it possible to measure temperature differences down to 0.01°. The catalyst was applied to the wall of a tube made of molybdenum glass (diameter 10 mm, length 50 mm), which was placed in the reactor. The distance between the thermocouple junctions was 5 mm, one of them passing strictly through the center of the tube, and the second immediately next to the tube wall. The reactor was heated by means of an electric furnace filled with copper filings for more uniform heating; the current supplying the furnace was stabilized.

**Starting gases.** Oxygen was obtained by decomposition of $KMnO_4$ (chemically pure), and propylene by the dehydration of isopropyl alcohol over $Al_2O_3$ at 350°, followed by purification from low-boiling impurities by repeated freezing with liquid nitrogen and evacuation under vacuum. Traces of water vapor and high-boiling impurities were removed by prolonged freezing at the freezing temperature of mercury.

**Catalyst.** Preparation of the catalyst and its deposition on the walls of the vessel were carried out as follows.

A certain amount of a hot aqueous solution of copper nitrate was poured into the reaction tube, which was then placed in a slowly rotating tubular furnace heated to 100-110°. The water evaporated, and an even layer of copper nitrate formed on the inner surface of the tube. After this the furnace temperature was raised to 250°. Pre-dried air was drawn through the tube by means of a water-jet pump. As a result, a thin layer of copper oxide was formed on the walls of the reactor. Before each experiment the catalyst was conditioned for one hour in a mixture of propylene and oxygen in order to bring it to a steady state.

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Fig. 2. Change in the temperature difference between the surface and the volume ($\Delta t_1$) during the oxidation of propylene and acrolein on a copper catalyst. a –oxidation of propylene: I $-T = 370°$, II $-T = 340°$, III $-T = 300°$, IV $-T = 400°$. $C_3H_6 : O_2 = 4 : 1$, $p =$ 25-26 mm; b –oxidation of acrolein: I $-T = 390°$, II $-T = 360°$, III $-T = 325°$. Acrolein : $O_2 = 4 : 1$, $p = 23$ mm

Figure 2: Fig. 2. Change in the temperature difference between the surface and the volume ($\Delta t_1$) during the oxidation of propylene and acrolein on a copper catalyst. a –oxidation of propylene: I $-T = 370°$, II $-T = 340°$, III $-T = 300°$, IV $-T = 400°$. $C_3H_6 : O_2 = 4 : 1$, $p =$ 25-26 mm; b –oxidation of acrolein: I $-T = 390°$, II $-T = 360°$, III $-T = 325°$. Acrolein : $O_2 = 4 : 1$, $p = 23$ mm

Fig. 3

Figure 3: Fig. 3

for gas storage.

**Investigation of the oxidation of propylene and acrolein.** To check the operation of the apparatus, model experiments were carried out on the oxidation of metallic copper to copper oxide (a purely heterogeneous process) and the oxidation of propylene by oxygen on platinum deposited on $BaSO_4$ (a heterogeneous-homogeneous process). The heating curves obtained corresponded to the literature data (1-3). Preliminary experiments established that without a catalyst in the apparatus used–

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*b* –oxidation of acrolein: I $-T = 390°$, II $-T = 360°$, III $-T = 325°$. Acrolein : $O_2 = 4 : 1$, $p = 23$ mm.

···volume reactor the process of homogeneous oxidation of propylene and acrolein at a temperature of 300-400° does not occur.

**Fig. 3.** Change in the temperature difference ($\Delta t_1$) between the surface and the volume on a copper catalyst during oxidation of propylene ($I$) and of a mixture of propylene and 2-3% acrolein ($II$). $I$–$T = 350°$, $p = 26$ mm; $II$–$T = 350°$, $p = 27$ mm

Figure 2a gives the heating curves during oxidation of propylene by oxygen on a copper catalyst. As is seen from Fig. 2a, the change in $\Delta t_1$ with time has a qualitatively different character at temperatures of 300-370° and 400°. At low and moderate temperatures (300-370°) the oxidation of propylene occurs only heterogeneously. This is also confirmed by the fact that $\Delta t_3$, measured in parallel and characterizing the temperature difference between the volume and the furnace, was initially equal to 0 in these experiments.

Fig. 4

Figure 4: Fig. 4

Raising the temperature to 400° changed the character of the heating curve $\Delta t_1$ (curve IV). The oxidation process partly passed from the surface into the volume. The small value of $\Delta t_1$ on this curve is explained by the fact that, under these conditions, the reaction proceeds simultaneously on the surface and in the volume, while the value of $\Delta t_3$ measured in parallel reached about 1-1.5°, which indicates a significant development of homogeneous oxidation processes. These data quite clearly show that on a copper catalyst the overall process of propylene oxidation at 400° proceeds heterogeneously-homogeneously, with predominance of the homogeneous stage.

In the oxidation of a mixture of propylene and 2-3% acrolein (Fig. 3), the value of $\Delta t_1$ at 350-370° decreased somewhat, probably as a result of poisoning of the catalyst by products of acrolein decomposition, but in general the heterogeneous character of the process was retained. Oxidation of acrolein (see Fig. 2b) on a copper catalyst in all the temperature ranges investigated (from 300 to 400°) proceeds by a heterogeneous-homogeneous mechanism.

## On the mechanism of propylene oxidation.

The results of the present study make it possible to establish the reasons for the difference in the mechanism of propylene oxidation at comparatively low (300-370°) and high temperatures (400° and above). At low temperatures, the process of formation of acrolein and carbon dioxide proceeds mainly on the catalyst surface. Under these conditions, apparently, inhibition of the process of acrolein oxidation in the volume takes place owing to chain termination by propylene. At high temperature, however, the rate of chain oxidation acrolein in the bulk exceeds the rate of chain termination, as a result of which the oxidation process of propylene as a whole assumes a heterogeneous-homogeneous character (see Fig. 2). In reality, the oxidation of propylene to acrolein at this temperature also proceeds heterogeneously, while the further oxidation of acrolein is heterogeneous-homogeneous. Under these conditions the rate of formation of carbon dioxide increases considerably, since, in addition to the formation of this gas on the catalyst surface (a process occurring at all temperatures), it is also produced as a result of the very rapidly proceeding heterogeneous-homogeneous oxidation of acrolein.

**Fig. 4.** Scheme of propylene oxidation on a copper catalyst. $I$—according to literature data; $II$—according to the authors' results. $R$ and $R_1$—unidentified products

Isaev, Margolis, and Sazonova [5], as a result of an investigation using labeled atoms, proposed a scheme for the oxidation of propylene on copper catalysts (see Fig. 4). The data of the present study make it possible to refine this scheme (see Fig. 4). According to this scheme, carbon dioxide is formed in the following ways: 1) by direct oxidation of propylene on the catalyst (through the formation of unknown intermediate products); 2) by oxidation of the organic film on the catalyst, which is apparently formed not only from acrolein but also from propylene, since the process of formation of an organic film from hydrocarbons has repeatedly been established for a wide variety of catalysts and processes [6]; 3) by heterogeneous-homogeneous oxidation of acrolein. This process is manifested mainly at high temperatures.

Institute of Chemistryof the Siberian Branch of the Academy of Sciences of the USSR

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