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Abstract

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On the Effect of the Composition of the Gas Mixture on the Yield of Carbonyl Compounds in the Oxidation Reaction of Propylene over a Copper Catalyst

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In recent years, the importance of acrolein as a starting material for the synthesis of various valuable products has sharply increased (1). This is connected with the discovery of a new method for obtaining acrolein by the direct oxidation of propylene over copper catalysts. However, despite the considerable number of patents, the scientific literature contains very few publications devoted to this reaction.

S. Z. Roginskii and co-workers (2) established the highly selective action of copper oxide on the oxidation process of propylene. We previously (3) studied the significance of the nature of supports for catalysts in this reaction. In the present work, in order to find the optimum conditions for obtaining acrolein, the effect of the oxygen concentration in the gas mixture on the oxidation reaction of propylene in the presence of copper catalysts was investigated.

The oxidation experiments were carried out in a reactor consisting of a glass U-shaped tube heated to 350° by a mixture of molten nitrates. The gas mixture was passed over the catalyst at a space velocity of 2000. The carbonyl compounds formed in the reaction were determined by means of 2,4-dinitrophenylhydrazones and by titration with hydroxylamine. Acrolein was determined by a photometric method developed by us, using the ultraviolet absorption spectra of aqueous solutions of carbonyl compounds. The gases formed as a result of the reaction were analyzed on a VTI apparatus. Carbon dioxide was determined in a separate sample by the baryta method. A catalyst of composition 1.5% CuO on silicon carbide was prepared by the method described earlier (2).

It is known (4) that in the study of oxidation reactions it is often difficult to obtain reproducible results because of the instability of the catalyst. In the case of the oxidation of propylene to acrolein, this circumstance is especially important to take into account, since the selective course of the reaction is ensured here by copper oxide, which is metastable at 350°. Therefore, in order to achieve reproducibility of the results, a gas mixture of definite composition was passed through the catalyst for an hour before samples were taken for analysis; after this, the temperature in the catalyst zone usually became constant. We conditionally called this operation "training" of the catalyst.

In some cases, during "training," a mixture of gases of a composition different from that used during the experiment was fed to the catalyst.

The results of the experiments presented in Table 1 showed that decreasing the oxygen concentration in the gas mixture being oxidized promotes an increase in the yield of carbonyl compounds (calculated on oxygen), but at the same time the stability of the catalyst decreases. Thus, for example, at a propylene-to-oxygen ratio of 13 : 1 (by volume), after the gases had been passed over the catalyst for three hours, the yield decreases.

by a factor of 2.5. It was observed that changing the gas ratio toward an increase in the oxygen concentration (for example, during "training" of the catalyst on a mixture propylene : oxygen = 6 : 1) restores the activity of the catalyst.

Table 1

Results of the oxidation of propylene over a catalyst of 1.5% CuO on silicon carbide at various concentrations of propylene and oxygen in the initial gas mixture

Ratio $C_3H_6 : O_2$ (by volume)	Yield of carbonyl compounds, % based on oxygen passed	Yield of carbonyl compounds, % based on propylene passed	Volume of carbonyl compounds, g/l per hour	CO_2, %	O_2, %	C_3H_6, %	CO, %
4 : 1	23.5	6.2	252.0	–	9.35	–	0.0
4.75 : 1	23.4	4.8	197.0	3.4	8.0	88.6	0.0
6 : 1	25.5	4.3	173.0	2.6	2.3	95.1	0.0
7.5 : 1	28.1	3.8	151.0	2.3	3.1	94.6	0.0
10 : 1	32.4	3.3	132.0	2.2	3.3	94.5	0.0
13 : 1	33.7	2.6	104.0	1.4	2.2	96.4	0.0

Ratio C_3H_6 : O_2 (by volume)	Yield of carbonyl compounds, % based on oxygen passed	Yield of carbonyl compounds, % based on propylene passed	Volume of carbonyl compounds, g/l per hour	CO_2, %	O_2, %	C_3H_6, %	CO, %
(“Training” of the catalyst on mixture 6 : 1) 30 : 1	40.6	3.1	126.0	2.0	1.9	96.1	0.0
(“Training” of the catalyst on mixture 6 : 1) 30 : 1	48.8	1.6	65.8	0.8	0.0	99.2	0.0
(after 2 hours of operation) 30 : 1	38.9	1.3	51.3	0.6	0.0	99.4	0.0

Ratio $C_3H_6 : O_2$ (by volume)	Yield of carbonyl compounds, % based on oxygen passed	Yield of carbonyl compounds, % based on propylene passed	Volume of carbonyl compounds, g/l per hour	CO_2, %	O_2, %	C_3H_6, %	CO, %
(after 3 hours of operation) 30 : 1	30.6	1.0	39.8	0.6	0.0	99.4	0.0
(after 5 hours of operation) 30 : 1	18.7	0.6	25.0	0.6	0.5	98.9	0.0

A more stable yield of carbonyl compounds is obtained in the oxidation of a gas mixture with a propylene-to-oxygen ratio of 10 : 1 or lower. Under these conditions the yield of carbonyl compounds varies from 25.5 to 32.4%, and the output from 104 to 252 g/l of catalyst per hour. In this case the catalyst operated without regeneration for 78 hours.

Analysis by the spectrophotometric method showed that the carbonyl compounds consist of 60–70% acrolein. For a more detailed study, the liquid reaction products were condensed and, after distillation of the propylene, were roughly fractionated from a Favorskii flask. Fractions boiling at 720 mm Hg were isolated in the following ranges:

	Yield, wt. %
I fraction 33–49°	8.0
II “49–50°	70.0
III “50–68.5°	4.2
Residue above 68.5°	15.8
Losses	2.0

Investigation by the spectrophotometric method established that fraction I consists mainly of acrolein (80%), water, and traces of acetone and formaldehyde. Fraction II, as is evident from Fig. 1, is acrolein. Fraction III contains acrolein and other higher-boiling carbonyl compounds. Because of the small quantities of this fraction, it was not possible to study it in detail. However, upon recrystallization of the 2,4-dinitrophenylhydrazones obtained from fraction III, it was possible to isolate a small

amount of osazones (a qualitative reaction with alcoholic alkali), which indicates the presence of methylglyoxal. The residue apparently consists of polymers of acrolein and methylglyoxal.

Fig. 1. Absorption curves in the ultraviolet region. **1**—absorption curve of the substance isolated during the oxidation of propylene (fraction II); **2**—absorption curve of pure acrolein.

Investigation of the fractions confirmed the data of S. Z. Roginskii and coworkers (2) on the highly selective action of a copper catalyst in the oxidation of propylene over it. An interesting fact is the presence of methylglyoxal among the products of propylene oxidation. It should be noted that, when acrolein was passed at 350° over the catalyst under study, no dioxy compounds were obtained (negative test for osazones). This indicates that methylglyoxal is not a product of the direct oxidation of acrolein, but is formed in the course of the oxidation of propylene. The formation of pyruvic and glyceraldehyde aldehydes was established by M. B. Neiman and F. A. Lukovnikov (5) in the cool-flame oxidation of propylene. The formation of one of these products in the catalytic oxidation of propylene indicates that this process can be used not only for the synthesis of acrolein, but also for obtaining other products.

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