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1960

SovietRxiv

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PHYSICAL CHEMISTRY

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CATALYTIC OXIDATION OF PROPYLENE AND ACROLEIN ON A COPPER CONTACT*

(Presented by Academician A. A. Balandin, February 15, 1960)

In the mild catalytic oxidation of hydrocarbons, along with the target oxygen-containing compound, products of complete combustion—carbon dioxide and water—are usually formed. In the selective oxidation of ethylene to ethylene oxide ([1,2]), of naphthalene to phthalic anhydride ([3]), and in a number of other cases, CO_2 is formed not through the target product, but by a parallel independent route. A limited number of works ([4,5]) have been devoted to the mechanism of the oxidation of propylene to acrolein, from which it was not possible to draw a conclusion about the pathways of formation of carbon dioxide in this process.

Table 1

Oxidation of propylene and acrolein in an empty glass reactor and on a carborundum support. Reactor diameter 16 mm, height of the heated zone 80 mm, flow rate of the mixture 121-133 cm^3/min.

Experimental conditions	Propylene oxidation: temp., °C	Propylene oxidation: gases after reactor, % C_3H_4O	Propylene oxidation: gases after reactor, % CO_2	Propylene oxidation: gases after reactor, % O_2	Degree of O_2 conversion, %	Acrolein oxidation: temp., °C	Acrolein oxidation: gases after reactor, % C_3H_4O	Acrolein oxidation: gases after reactor, % CO_2	Degree of C_3H_4O conversion, %
Empty reactor	380	traces	–	5.0	0	300	1.61	0.00	0
Empty reactor	380	traces	–	5.0	0	350	1.53	0.05	1

Experimental conditions	Propylene oxidation: temp., °C	Propylene oxidation: gases after reactor, % C_3H_4O	Propylene oxidation: gases after reactor, % CO_2	Propylene oxidation: gases after reactor, % O_2	Degree of O_2 conversion, %	Acrolein oxidation: temp., °C	Acrolein oxidation: gases after reactor, % C_3H_4O	Acrolein oxidation: gases after reactor, % CO_2	Degree of C_3H_4O conversion, %
Empty reactor	380	traces	–	5.0	0	400	1.55		7*
Empty reactor	380	traces	–	5.0	0	430	1.24	0.54	17
On carborundum support	381	traces	–	4.8	0	349	1.50	0.03	1
On carborundum support	419	0.04	–	5.0	0	400	1.50		8*
On carborundum support	419	0.04	–	5.0	0	431	1.20	0.48	19

* Calculated values.

To clarify this question, the dependence of the concentrations of the substances formed during the oxidation of C_3H_6 on the contact time was investigated, and the oxidation of acrolein and propylene under similar conditions on the same catalyst samples was also studied. The catalyst was prepared by depositing $Cu(NO_3)_2$ from solution onto pieces of carborundum (grain size 2–3 mm) and subsequently calcining it at 400–450° in a stream of air. The study was carried

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

out by the flow method under conditions free from diffusion inhibition, as was established by special experiments. In the oxidation of propylene, the initial mixture used contained 4.8-5.1% O_2, 20-21% C_3H_6, and 74-75% N_2 at $\tau = 0.4–0.8$ sec.; in the gases leaving after contact, the acrolein content reached 0.4-0.6%, and the oxygen concentration decreased by 1-3%. In the oxidation of acrolein, the initial mixtures used were 1.4-1.6% C_3H_4O, 3.2-3.6%

[*] The work was reported at the All-Union Conference on Organic Catalysis, November 19, 1959.

O_2 and 95% N_2. Acrolein was determined by the bromide-bromate method; carbon dioxide, when present in small amounts in the mixture, was determined by absorption with a titrated $Ba(OH)_2$ solution, and, when present in larger amounts, by gas analysis; C_3H_6, O_2, and CO were also determined with a VTI-2 gas analyzer.

From the data presented in Table 1 it is evident that in the empty reactor used by us and on the support, in the range 300-400°, neither propylene nor acrolein was practically oxidized, although acrolein proved to be less stable than propylene.

Fig. 1. Dependence of the concentration of the acrolein and carbon dioxide formed on contact time.
1 –C_3H_4O, 320°; 2 –$CO_2/3$, 320°; 3 –C_3H_4O, 380°; 4 –$CO_2/3$, 380°.

Effect of contact time. The contact time τ was varied by changing the flow rate of the reaction mixture and the amount of catalyst. When working with a large amount of contact, the first 2 cm^3 of it were diluted with the support, as a result of which the temperature drop across the bed, even at high degrees of conversion, did not exceed 3-4°. From the data in Fig. 1 on the dependence of the concentrations of the C_3H_4O and CO_2 formed on τ at 320 and 380°, it is seen that at the lower temperature, with increasing τ, the amounts of C_3H_4O and CO_2 continuously increase. At the same time the selectivity changes very little over a wide interval of τ (0.28-3.87 sec) (Fig. 2). This indicates the predominantly parallel formation of acrolein and carbon dioxide from propylene by mutually independent pathways at 320°:

$$C_3H_6 + O_2 \begin{array}{l} \nearrow C_3H_4O \\ \searrow CO_2 + H_2O \end{array}$$

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

Fig. 2. Dependence of the selectivity of propylene oxidation to acrolein on contact time at 320° (1) and 380° (2).

At 380° the curve for the change in acrolein concentration at $\tau = 1.2$ sec passes through a maximum; the amount of carbon dioxide increases continuously, and the selectivity decreases; all this unambiguously indicates oxidation of the acrolein formed. At this temperature carbon dioxide is formed according to a parallel-consecutive scheme:

$$\begin{array}{ll} C_2H_6 + O_2 \nearrow & C_3H_4O \xrightarrow{+O_2} CO_2 + H_2O \\ & \quad \searrow CO_2 + H_2O \end{array}$$

Oxidation of acrolein. The oxidation of acrolein was studied on several catalyst samples containing different amounts of copper per unit volume; the oxidation of propylene was investigated on the same samples. As a rule, on samples containing a larger amount of copper (9 g Cu per 1 l of catalyst), the process began already at temperatures below 300°; at 310-320° and $\tau = 0.8$ sec, the amount of CO_2 in the reaction products was 0.3-0.4% (Fig. 3). On contacts with a lower content

of copper (2.5 g Cu per 1 l), oxidation of acrolein began only above 310-320° (Fig. 4). A decrease in the contact time significantly reduced the rate of the process. Thus, at $\tau = 0.8$ sec on a catalyst containing 9 g Cu/l, more than 30% was oxidized at 360°, and at 380° half of the initial acrolein (Fig. 3). At $\tau = 0.4$ sec on a similar contact (10 g/l), the amount of acrolein oxidized at 355° was only 10%, and at 385°—30% of the initial amount.

Thus, at the usual temperatures for the catalytic synthesis of acrolein (330-370°), the latter can undergo partial oxidation. However, as our experiments have shown, on the same contacts

Fig. 3. Dependence of acrolein oxidation on temperature on a catalyst containing 9 g Cu/l. 1 $-CO_2$; 2 $-C_3H_4O$; 3 —degree of conversion of C_3H_4O (X)

Fig. 4. Dependence of acrolein oxidation and CO_2 formation during propylene oxidation on temperature on a catalyst containing 2.5 g Cu/l. 1 —formation of CO_2 during oxidation of C_3H_6; 2 —formation of CO_2 during oxidation of C_3H_4O; 3 —decrease in the concentration of C_3H_4O during its oxidation; 4 —degree of oxidation of $[C_3H_4O]$ (X)

oxidation of propylene and the formation of a noticeable amount of carbon dioxide usually began at lower temperatures than the conversion of acrolein. In Fig. 4, 1 the amount of CO_2 formed during oxidation of C_3H_6 is shown under the same conditions as for C_3H_4O. It is evident that at a given temperature more CO_2 is obtained from propylene than during oxidation of C_3H_4O. This cannot be explained if one assumes that all carbon monoxide is formed through acrolein.

The data on the oxidation of propylene and acrolein confirm the conclusion made above concerning the parallel formation of C_3H_4O and CO_2 at low temperatures (300–325°) and the parallel-consecutive course of the process at higher temperatures.

In one of the recently published papers[6] it is asserted that the oxidation of propylene on copper contacts proceeds according to a parallel-consecutive scheme, with the share of the consecutive reaction being greater than that of the parallel one. The authors of that work carried out the process at long contact times ($\tau = 1.2$ sec) and high temperature (396°), at which oxidation proceeds nonselectively. As follows from our data, at such temperatures and contact times CO_2 is indeed formed both in parallel with the formation of acrolein and through its oxidation, with oxidation of C_3H_4O occurring to a large extent. Under selective conditions for carrying out the oxidation of propylene, however, there occurs chiefly parallel formation of C_3H_4O and CO_2. The decisive factor,

determining the proportions of the parallel and consecutive processes is the catalysis temperature. It is difficult to determine the exact temperature boundary for the onset of noticeable further oxidation of acrolein, since it depends on the amount of copper on the support and on the contact time.

As has been shown in a number of works ([7], [8]), the initial copper oxide is reduced during catalysis to the suboxide, on which the oxidation of propylene to acrolein takes place. It was of interest to determine the activity of different phases with respect to the acrolein oxidation reaction. For this purpose the catalyst was preliminarily treated either with hydrogen, in order to reduce it, or with oxygen, in order to oxidize it to CuO, after which its activity was tested. It is not possible to draw a quantitative conclusion about the occurrence of oxidation on one or another isolated phase (CuO, Cu_2O, or Cu), since upon admission of the mixture the catalyst surface immediately begins to change its chemical composition under its influence. However, from Table 2 it is seen that in all cases after

Table 2

Oxidation of acrolein on a reduced or oxidized copper catalyst

Experiment no.	Catalyst treatment conditions	Experimental temp., °C	Composition of off-gases, % C_3H_4O	Composition of off-gases, % CO_2	Composition of off-gases, % O_2	Conversion of C_3H_4O, %
1	O_2; 345°; 2 h	347	1.27	0.71	2.12	16
2	H_2; 345°; 2½ h	345	1.31	0.30	2.45	7
3	H_2; 345°; 2 h	344	1.45	0.20	2.70	5
5	O_2; 345°; 2½ h	345	1.29	0.48	2.30	11
6	O_2; 345°; 5 h	346	1.19	0.64	2.10	14
7	H_2; 346°; 3½ h	346	1.35	0.38	2.70	9
9	Decomposition at 420° $Cu(NO_3)_2$	377	1.10	1.17	1.6	26
10	H_2; 380°; 4 h	380	1.25	0.69	2.0	15
11	O_2; 375°; 3 h	380	1.16	1.15	1.35	25
12	H_2; 375°; 5 h	377	1.35	0.68	2.10	15

preliminary reduction of the contact the degree of acrolein oxidation was lower than after heating in an O_2 atmosphere; i.e., with increasing degree of oxidation of the catalyst, its activity with respect to acrolein oxidation increases.

In light of these data, the increase in the selectivity of the contact observed with time in the process of propylene oxidation, in comparison with the initial selectivity, becomes understandable. At the beginning of operation, when the catalyst contains much copper oxide, more rapid oxidation of acrolein occurs on it. As the catalyst is reduced, the amount of CuO decreases, acrolein oxidation becomes more difficult, and the selectivity increases. Thus, the composition of the contact is regulated, favoring the formation and greater stability of acrolein.

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Received
11 II 1960

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