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Abstract

Full Text

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, CO₂ 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 cm³/min.

	Propylene					Acrolein			Degree of conversion, %
	Propylene oxidation: gases after reaction, °C	Propylene oxidation: gases after reaction, % C ₃ H ₄ O	Propylene oxidation: gases after reaction, % CO ₂	Propylene oxidation: gases after reaction, % O ₂	Degree of conversion, %	Acrolein oxidation: gases after reaction, °C	Acrolein oxidation: gases after reaction, % C ₃ H ₄ O	Acrolein oxidation: gases after reaction, % CO ₂	
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					Acrolein			
	oxidation: after reaction, temp., °C	gases after reactor, % C ₃ H ₄ O	gases after reactor, % CO ₂	oxidation: after reaction, % O ₂	Degree of conversion, %	oxidation: after reaction, temp., °C	gases after reactor, % C ₃ H ₄ O	gases after reactor, % CO ₂	Degree of 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 C₃H₆ 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(NO₃)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% O₂, 20-21% C₃H₆, and 74-75% N₂ 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% C₃H₄O, 3.2-3.6%

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

O₂ and 95% N₂. 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; C₃H₆, O₂, 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 -C₃H₄O, 320°; 2 -CO₂/3, 320°; 3 -C₃H₄O, 380°; 4 -CO₂/3, 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 cm³ 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 C₃H₄O and CO₂ formed on τ at 320 and 380°, it is seen that at the lower temperature, with increasing τ , the amounts of C₃H₄O and CO₂ 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°:

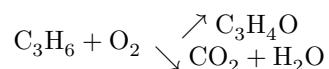
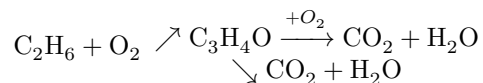


Fig. 3 and Fig. 4

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:



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 CO₂ 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 —CO₂; 2 —C₃H₄O; 3 —degree of conversion of C₃H₄O (*X*)

Fig. 4. Dependence of acrolein oxidation and CO₂ formation during propylene oxidation on temperature on a catalyst containing 2.5 g Cu/l. 1 —formation of CO₂ during oxidation of C₃H₆; 2 —formation of CO₂ during oxidation of C₃H₄O; 3 —decrease in the concentration of C₃H₄O during its oxidation; 4 —degree of oxidation of [C₃H₄O] (*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 CO₂ formed during oxidation of C₃H₆ is shown under the same conditions as for C₃H₄O. It is evident that at a given temperature

more CO_2 is obtained from propylene than during oxidation of $\text{C}_3\text{H}_4\text{O}$. 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 $\text{C}_3\text{H}_4\text{O}$ and CO_2 at low temperatures ($300\text{--}325^\circ$) and the parallel-consecutive course of the process at higher temperatures.

In one of the recently published papers⁶ 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 $\text{C}_3\text{H}_4\text{O}$ occurring to a large extent. Under selective conditions for carrying out the oxidation of propylene, however, there occurs chiefly parallel formation of $\text{C}_3\text{H}_4\text{O}$ 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,			Conversion of C ₃ H ₄ O, %
			% C ₃ H ₄ O	% CO ₂	% O ₂	
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 O₂ 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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