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Abstract

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INVESTIGATION OF THE MECHANISM OF TOLUENE OXIDATION ON COPPER CATALYSTS WITH ADDITIONS OF OXIDES OF HEAVY METALS BY THE TRACER-ATOM METHOD

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Selective conduct of the processes of "mild" oxidation of hydrocarbons requires knowledge of the mechanism of "deep" oxidation of hydrocarbons to carbon dioxide and water. As a result of studying the kinetics of toluene oxidation ([1]) and of other hydrocarbons ([2]) on copper catalysts, a parallel scheme for the formation of aldehydes and CO_2 at short contact times was established.

The mechanism of propylene oxidation has been studied in especially great detail by the kinetic method ([3]) and with the use of tracer atoms ([4], [5]). It was observed that different methods give results that are not entirely consistent with one another: kinetic measurements established the parallel formation of acrolein and CO_2 at low temperature (about 320°) and a parallel-successive one at a higher temperature (380°), whereas radioactive indicators showed predominantly (by 90-95%) a successive course of the process over a fairly wide temperature range (340-400°). In the opinion of some authors ([6]), oxidation of benzene homologues on vanadium catalysts proceeds according to a successive scheme with formation of the alcohol as one of the intermediate products. The purpose of the present investigation was to study the mechanism of toluene oxidation on copper catalysts by the tracer-atom method under conditions in which kinetic measurements led to the conclusion that the process under study follows a parallel scheme. An attempt was also made to clarify the role of benzyl alcohol as a possible intermediate product in this reaction.

Toluene-1C^{14}, benzyl alcohol-7C^{14}, and benzaldehyde-7C^{14} were used as labeled compounds.

A gas mixture in the ratio $C_7H_8 : O_2 : N_2 = 10 : 15 : 75$ was passed in a flow apparatus through 2.5 ml of catalyst of the initial composition 1.5% CuO on silica gel with additions of molybdenum and tungsten oxides at a temperature of 390 ± 2°. The experiments were carried out at different contact times (0.09-0.45 sec), with addition of benzyl alcohol or benzaldehyde in amounts below 2%, i.e., below the limit of their formation during oxidation of toluene under the indicated conditions.

The specific activity of the initial and resulting components was determined in the form of $BaCO_3$ on an end-window counter; the specific activity of benzaldehyde was determined, in addition, in precipitates of 2,4-dinitrophenylhydrazones. Material and radioactive balances were obtained with satisfactory results.

Data on the composition of the initial and resulting products and the results of radiometric measurements are presented in Table 1. It should be noted that experiments Nos. 1–7 and 8–11 were carried out on two batches of catalyst of somewhat different activity. Table 1 gives the results of analyses of samples taken at the same time after the start of the experiments.

In the case of a completely parallel process of toluene oxidation in experiments with introduction of labeled benzaldehyde (experiments Nos. 1–3), the formation of inactive carbon dioxide should be expected; in the case of ···

Table 1

Composition and specific radioactivity of the oxidation products of toluene-C^{14} on copper catalysts

No. of experiments	Initial $C_6H_5CH_3$, wt. %	Initial C_6H_5CHO, imp/min · mg	Initial C_6H_5CHO, %	Initial $C_6H_5CH(OH)_2$, imp/min · mg	Initial $C_6H_5CH(OH)_2$, %	Initial $(C_6H_5CO)_2O$, imp/min · mg	Initial $(C_6H_5CO)_2O$, %	Obtained $C_6H_5CH_3$, imp/min · mg	Obtained $C_6H_5CH_3$, %	Obtained C_6H_5CHO, mg	Obtained C_6H_5CHO, % of initial activity	Obtained CO_2, wt. %	Obtained CO_2, % of initial activity	a_1/a_2
										a_2			a_1	
1	98.5	—	1.5	2097	—	—	96.30	—	2.40	1103	53.3	1.30	567	27.1	0.51
2	99.5	—	0.5	1707	—	—	97.08	—	1.71	579	33.4	1.07	203	11.9	0.35
3	99.5	—	0.5	1275	—	—	98.45	—	0.91	747	48.6	0.64	185	14.5	0.25
4	98.5	—	—	—	1.5	7664	96.14	—	2.33	3838	50.2	1.59	2766	36.1	0.72
5	99.5	—	—	—	0.5	7664	97.77	—	1.01	2485	32.5	1.33	1035	13.5	0.41
6	98.5	588	1.5	—	—	—	96.30	588*	2.31	367	62.5	1.30	420	71.5	—
7	99.5	588	—	—	0.5	—	97.54	588*	1.24	321	54.5	1.22	466	77.7	—
8	99.5	—	0.5	8427	—	—	98.33	—	0.84	4511	53.5	0.83	832	9.89	0.18
9	99.5	—	0.5	8427	—	—	97.17	—	1.29	2856	33.9	1.54	906	10.75	0.32
10	99.5	—	0.5	8497	—	—	96.80	—	1.18	2622	31.2	2.02	922	10.92	0.35
11	99.5	—	0.5	8427	—	—	95.58	—	0.95	2487	29.5	3.47	1056	12.52	0.42

* The specific activity of the toluene obtained was taken as equal to the specific activity of the initial toluene, since it was proved that there was no transfer of specific activity from benzaldehyde to toluene.

for a consecutive process, the specific activity of CO_2 should have proved to be higher than the specific activity of the benzaldehyde obtained, since the first

portions of this gas would be obtained from undiluted labeled benzaldehyde. Meanwhile, in experiments Nos. 1-3 the specific activity of CO_2 is considerably lower than that of the benzaldehyde obtained, which indicates a parallel-consecutive scheme of CO_2 formation. When larger amounts of benzaldehyde are introduced (1.5%), the activity of the CO_2 obtained increases, which indicates an increase in the share of the consecutive process. These same propositions are also confirmed by the experiments with labeled toluene (experiments Nos. 6, 7).

It should be noted that in all experiments with labeled benzaldehyde the ratio of the specific activity of CO_2 to the specific activity of the benzaldehyde formed (a_1/a_2) is less than unity, which indicates a significant share of the parallel path at short contact times ([5]).

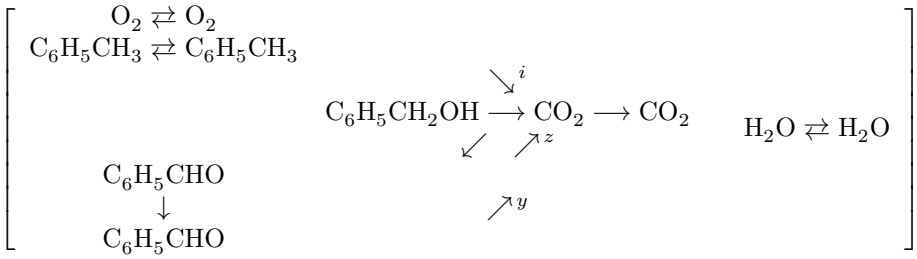
Fig. 1. Dependence of the rate of formation of benzaldehyde w_1 (1), CO_2 from toluene w_2 (3), and CO_2 from benzaldehyde W_3 (4) on the contact time τ, as well as of $\lg w_1$ on $\lg \tau$ (2).

The data on the oxidation of benzyl alcohol seem to speak in favor of the possibility of its formation as an intermediate product in the oxidation of toluene, since the distribution of radioactivities of benzaldehyde and CO_2 in experiments carried out under identical conditions, with the introduction of labeled benzaldehyde and benzyl alcohol (experiments Nos. 1, 2 and 4, 5), is close.

The somewhat higher activities of CO_2 in experiments Nos. 2 and 5 are apparently due to the fact that benzyl alcohol under these conditions is capable, to an in-

to a much greater extent than benzaldehyde, be oxidized homogeneously. It should be noted that in all experiments with the introduction of benzyl alcohol it was completely converted into benzaldehyde and CO_2 and was not detected in the reaction products. Consequently, if benzyl alcohol is formed during the oxidation of toluene, then the rate of its conversion into benzaldehyde many times exceeds the rate of its desorption from the catalyst. It is known that in this case the radiometric method cannot give unambiguous results ([6]), and therefore, on the basis of the data of Table 1, it is not possible to draw a reliable conclusion regarding the formation of benzyl alcohol as an intermediate product in the oxidation of toluene on copper catalysts.

The mechanism of toluene oxidation may be represented as follows:



In square brackets are shown the processes occurring on the catalyst surface; outside the brackets, those in the gas phase.

On the basis of the material and radioactive balance data, the intensities of the reactions proceeding along the directions x, y, z, and i were calculated (see Table 2). The data of Table 2 well explain the reasons for the discrepancy between the results of the study of the mechanism obtained by kinetic and radiometric methods. As is evident from the data of Table 2, the selectivity of the processes $(x/(x+z+i))$ when the contact time is changed from 0.304 to 0.91 sec varies within considerably smaller limits than the fraction of parallel processes of CO_2 formation from toluene $(i/(z+i))$ at the same contact times.

Table 2

Intensities of reactions in the oxidation process, expressed in moles of converted toluene

Experiment Nos.	τ, sec	x	y	z	i	$i/(z+i)$	$x/(x+z+i)$
1	0.30	100	11.8	8.7	19.2	69	78
2	0.31	100	2.5	5.7	21.3	79	79
3	0.18	100	6.5	5.4	35.9	87	71
4	0.30	100	11.1	8.7	19.1	69	78
5	0.30	100	5.8	13.7	51.8	75	61
6	0.29	100	12.3	8.4	22.6	73	76
7	0.30	100	4.3	9.7	34.4	78	69
8	0.09	157	10	5	98	95	60
9	0.15	151	9	16	62	80	66
10	0.30	109	10	19	52	73	61
11	0.45	83	13	28	60	68	48

Note: x and i are the number of moles of toluene converted respectively into benzaldehyde and into CO_2; y is the number of moles of benzaldehyde oxidized to CO_2 added as benzaldehyde introduced into the gas phase; and z is benzaldehyde formed as a result of toluene oxidation and converted into CO_2 without a desorption stage.

Fig. 2

Figure 1: Fig. 2

Figure 1 gives the dependences of the changes, with contact duration, in the rates of formation of benzaldehyde (w_1) and CO_2 (w_2) from toluene and of CO_2 from benzaldehyde (w_3), calculated by means of the kinetic method of Neiman ([7]). As is evident from Fig. 1, the dependences of the changes in w_1, w_2, and w_3 have a completely different character, which indicates different mechanisms for the course of all three processes on copper catalysts. The rate of formation of benzaldehyde w_1 falls from 65 at $\tau = 0.091$ to 3.5 (in arbitrary units) at $\tau = 0.304$ and thereafter remains approximately constant. The curve of change of w_1 is straightened in logarithmic coordinates (see Fig. 1, curve 2) and, consequently, is described by the equation $w_1 = At^{-1/n}$.

This indicates that the decrease in the rate of benzaldehyde formation is associated with a decrease in the sorption rate of one of the reaction products of toluene or oxygen, owing to blocking of the heterogeneous surface of the catalyst, since the equation $w = At^{1/n}$ (Benham' s equation) expresses the rate of sorption on a heterogeneous surface [8]. It is known that the oxidation reaction of toluene on copper catalysts [1] is of zero order with respect to the hydrocarbon and first order with respect to oxygen. On this basis, it should be assumed that the limiting stage of the reaction of toluene oxidation to benzaldehyde is the adsorption of oxygen by the catalyst.

Fig. 2. Dependence of the rate of benzaldehyde formation w_1 on the number of moles of benzaldehyde (z) adsorbed on the catalyst (1), and $\lg w_1$ on z (2)

With the aid of kinetic studies [9] it had previously been established that the oxidation reaction of hydrocarbons is inhibited by reaction products—in the present case by water, and especially strongly by benzaldehyde. The data in Fig. 2 confirm this proposition, since the curve of the dependence of the decrease in the rate w_1 on the concentration of benzaldehyde on the catalyst z is expressed by the equation $w_1 = Ae^{-nz}$ and becomes linear in semilogarithmic coordinates (see Fig. 2). Apparently, the benzaldehyde and water formed at short contact times (0.091 sec) are almost completely (see Table 2) desorbed from the catalyst, and the process of toluene oxidation is carried out by the most active surface sites, which become blocked at longer contact times owing to a decrease in the rate of desorption of the reaction products.

The linear character of the decrease in the rate of formation of CO_2 from toluene indicates that in this case the process proceeds on other, energetically more homogeneous surface sites and probably has a different limiting stage than the reaction of oxidation of toluene to benzaldehyde. The change in the rate of oxidation of benzaldehyde to CO_2 (w_3) with contact time is linear in character and increases with increasing contact duration. Probably, for this process the limiting stage is the rate of desorption of benzaldehyde from the catalyst, which

decreases with increasing contact time. At a certain contact duration the rate of oxidation of benzaldehyde to CO_2 (w_3) begins to exceed the rate of its formation from toluene (w_1), and the process changes from parallel-consecutive with predominance of the parallel route to consecutive-parallel with predominance of the consecutive route.

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