INVESTIGATION OF THE PATHWAYS OF INITIATION OF
THE LIQUID-PHASE OXIDATION OF CUMENE IN THE
PRESENCE OF PLATINUM AND PALLADIUM CATALYSTS

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The generation of radicals under conditions of catalyzed liquid-phase oxidation of hydrocarbons may be accomplished on account of the following reactions with the participation of a heterogeneous catalyst:

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\begin{align*}
S + O_2 & \rightarrow [S ... O_2] \rightarrow R' + [O_2H ... S] & (1) \\
S + RH & \rightarrow [S ... RH] \rightarrow R' + [H ... S] & (2) \\
S + ROOH & \rightarrow [S ... ROOH] \rightarrow RO' + [OH ... S] & (3) \\
S + ROOH & \rightarrow [S ... ROOH] \rightarrow RO_2' + [H ... S] & (4)
\end{align*}
\]

where \([S ... O_2]\), etc. is the symbol of an adsorbed molecule or radical on the surface of the catalyst.

The formation of radicals with the participation of hydroperoxide lies at the basis of the mechanism of the catalytic conversion of hydrocarbons in liquid-phase oxidation [1, 2]. In an investigation of the influence of donor-acceptor modification of a heterogeneous catalyst on the liquid-phase oxidation of cumene [2], it was shown that the formation of radicals on the surface of the catalyst is preceded by the appearance of negatively charged forms of the adsorbed reagents — oxygen [reaction (1)] and hydroperoxide [reactions (3), (4)]. The literature also discusses the possibility of the generation of radicals in the liquid-phase oxidation of hydrocarbons by stripping of a H atom from the hydrocarbon molecule on the catalyst [reaction (2)] [3]. In this case the role of \(O_2\) consists of the removal of \(H_2\) from the surface of the catalyst (Pt and Pd). The copper-initiated liquid-phase oxidation of cumene is explained on the basis of such a mechanism of generation of radicals in [4].

In [3] no data are cited on the influence of oxygen adsorbed by palladium and platinum on the process of oxidation. Nor are there any data on the absence of hydroperoxide in the initial hydrocarbons. However, the presence of oxygen on the surface of the catalyst studied or the presence of hydroperoxide in the hydrocarbon solution in the initial period of oxidation leads to the formation of radicals according to reactions (1), (3), and (4). Therefore, on the basis of [3, 4], it is impossible to arrive at an unambiguous conclusion on the predominant role of reaction (2) in the formation of radicals even on such dehydrogenating catalysts as Pt and Pd.

To determine the possible pathways of formation of radicals under the conditions of liquid-phase oxidation, we studied the influence of preliminary treatment of Pt- and Pd-catalysts with oxygen (before contact of the catalyst with hydrocarbon), as well as the influence of hydroperoxide on the liquid-phase oxidation of cumene.

EXPERIMENTAL METHOD

The oxidation of cumene was conducted on a manometric setup in the reactor described in [5] at 73°C and an \(O_2\) pressure 760 mm Hg. The products of oxidation were analyzed by the method of gas-liquid
Fig. 1. Kinetic curves of the adsorption of O₂ in the liquid-phase oxidation of cumene in the presence of catalysts Pd- (a), Pt-black (b), 10% Pd/Al₂O₃ (c), treated with: 1) O₂; 2) Ar; 3) H₂; 4) CO₂; 5) CO; 6) cumene vapors. The arrows mark the time of introduction of hydroperoxide into the reaction mixture; 7) oxidation of cumene with traces of hydroperoxide (10⁻⁴ M).

**DISCUSSION OF RESULTS**

The purpose of preliminary treatment of the catalyst with various gases was to exclude contact of O₂ with the catalyst when it was introduced into the reactor, and also so that the adsorption of the hydrocarbon would precede the adsorption of O₂ on the catalyst. Experiments were conducted, in which cumene vapors were adsorbed on Pt and Pd under vacuum conditions at 20° (Fig. 1c, curve 6).

On a catalyst preliminarily treated with argon (curve 2), the oxidation of cumene begins to proceed at an appreciable rate only after the introduction of a definite amount of hydroperoxide into the reaction mixture. The same effect is observed in the case of treatment of the catalyst with other gases: H₂ (curve 3), CO₂ (curve 4), and CO (curve 5). Pd is characterized by a greater sensitivity to the presence of hydroperoxide in the hydrocarbon. The amount of hydroperoxide that must be introduced into cumene undergoing oxidation for the reaction to begin is ~10⁻⁴ M.

On a catalyst that has preliminarily adsorbed O₂ (curve 1), the oxidation of cumene containing no hydroperoxide begins immediately. It should be noted that the rates of oxidation of cumene, both in the presence of a catalyst containing O₂ and in the presence of traces of hydroperoxide (10⁻⁴ M) are practically equal. The data obtained on the influence of a catalyst with O₂ adsorbed on it on the oxidation of cumene are evidence that the initiation of the oxidation process in the presence of Pt and Pd occurs first in reactions of adsorbed (activated) oxygen with the hydrocarbon [reaction (1)]. The stimulation of the process of oxidation by hydroperoxide present in solution is explained by decomposition of the hydroperoxide on the surface of the heterogeneous catalyst [reactions (3), (4)]. In this case, in the

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**Fig. 2.** Kinetic curves of the adsorption of oxygen (1), formation of hydroperoxide (2), 1,4-dimethylphenylcarbinol (3), acetophenone (4) in the oxidation of cumene in the presence of catalysts: a) 5% Pd/Al₂O₃; b) 5% Pt/SiO₂.