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Heterogeneous–Homogeneous Reactions Involving Free Radicals in Processes of Total Catalytic Oxidation

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Using a modified matrix isolation ESR technique conditions for initiation of a heterogeneous–homogeneous reaction by total oxidation catalysts $CuCr_2O_4/\gamma\text{-}Al_2O_3$ and 0.64% $Pt/\gamma\text{-}Al_2O_3$ and reaction dependences at atmospheric pressure have been studied. The dependences of homogeneous component contribution into the total conversion on the concentration and the ratio of reactants and catalyst temperature have been established. © 1992 Academic Press, Inc.

INTRODUCTION

One of the specific features of total catalytic oxidation reactions is a possibility to initiate gas-phase homogeneous radical reactions by the catalyst surface (*1, 2*). Numerous studies of the formation steps of radicals on solid contacts were discussed in Review (*3*). Direct detection of surface generated gas-phase radicals allows us to perform more detailed mechanistic studies of catalytic reactions on the level of active intermediates and to obtain data on the steps of initiating homogeneous radical reactions.

At the same time the character of catalyst contribution to these reactions has been studied insufficiently. The known high activities of total oxidation catalysts due to the presence of highly reactive surface oxygen suggest that the surface of oxide catalysts can be a strong inhibitor for radical-chain oxidation (*4*).

On the surface of both oxide and Pt-containing catalysts free radicals can be formed and desorbed into the gas phase (*5–7*). Effective formation of radicals was observed at relatively low temperatures (673–773 K) compared to flame combustion temperatures. The formation of surface radicals was the most efficient in the conditions of oxygen deficiency. Kinetic parameters for the formation of radicals were determined from the kinetic dependences of their accumulation. It permitted us to propose formation mechanisms of radicals for catalytic transformation of alcohols and amines. These experiments were carried out at low pressures, $P \leqslant 10$ Pa, and in conditions for the detection of radicals selected so that after the desorption of radicals from the catalyst the contribution of secondary transformations of radicals would be minimal. With increasing the concentration of reactants and rising the total pressure up to 1 atm. (i.e., reaction conditions approach real oxidation processes) secondary reactions of radicals in the gas phase become possible. Hence one could expect principle changes in the observed dependences. The aim of the present study was to examine a possibility for the formation of radicals on total oxidation catalysts and for the realization of heterogeneous–homogeneous reactions at atmospheric pressure.

METHODS

The object of our study was the reaction of *n*-propanol oxidation over 34% $CuCr_2O_4/\gamma\text{-}Al_2O_3$ and 0.64% $Pt/\gamma\text{-}Al_2O_3$ catalysts at atmospheric pressure. A thin layer of catalyst samples ≅50 mg, 0.5–1.0 mm fraction were placed into a quartz reactor with inner diameter 12 mm. Standard pretreatment of catalysts before experiments was their heat-

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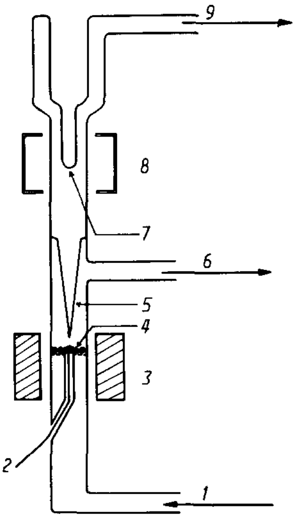

FIG. 1. Experimental setup: (1) feed of reaction mixture into the reactor; (2) thermocouple; (3) furnace; (4) catalyst layer; (5) quartz capillary; (6) outlet of reaction products; (7) freezing finger; (8) ESR spectrometer cavity; (9) to vacuum system.

ing for an hour in flowing oxygen at 773 K and then treatment in helium.

Experiments were carried out in a flow reactor with the residence time $\tau \cong 0.06$ s. Reaction mixtures were prepared from commercially available gases: analytical grade O_2 and He. To supply alcohol to the reaction mixture and control ROH concentrations a saturator was used.

Stable reaction products were analyzed using a gas chromatographic method. Carbon dioxide and organic compounds were separated in a 2-m long Porapak Q column in the linear temperature programmed mode. CO, O_2, and CH_4 were separated in a 1-m long column packed with molecular sieves NaX at $T = 25°C$.

Concentrations of radicals in the gas phase over a catalyst were determined using a modified matrix isolation ESR technique (*8*). The experimental setup is schematically represented in Fig. 1. Part of the products from the reaction zone at atmospheric pressure were fed through a capillary placed at a distance 0.5 mm above the catalyst into the low-pressure ($\leq$10 Pa) region, and then to the Dewar finger cooled to 77 K and localized in the cavity of the ESR spectrometer.

RESULTS AND DISCUSSION

Preliminary experiments were carried out without catalyst. Noticeable conversions of *n*-propanol in an empty reactor were observed only above 770 K. Composition of reaction products (CO, methane, ethylene) suggests that in this case alcohol pyrolysis takes place. In the presence of catalysts the reaction started at much lower temperatures (473 K for platinum and 573 K for aluminium–copperchromium catalysts). The main reaction products were propionaldehyde and CO_2. During *n*-propanol oxidation radicals were detected over catalysts.

At 723 K for the mixture with $C_{O_2} = 15$ vol.% and $C_{ROH} = 20$ vol.% and for the observed reaction order with respect to an alcohol equal to unity (*6*, *7*) the estimated value of radical concentration is about 10^{14} ml^{-1}. Experimental concentration of radicals is equal to $\cong 10^{11}$ ml^{-1}. The consideration of the reaction of chain propagation: $R\dot{O}_2 + ROH \rightarrow ROOH + R'\dot{C}HOH$ with taking into account experimental data $C_{R\dot{O}_2} \cong 10^{11}$ ml^{-1} and $C_{ROH} = 2.0 \times 10^{18}$ ml^{-1} has shown that the lifetime of surface radicals desorbed into the gas phase equals $\tau = 1/(k\ C_{ROH}) \cong 10^{-9}$ s, where $k \cong 10^{-10}$ ml s for bimolecular reactions, and is by seven orders of magnitude lower than the residence time of reaction mixtures in the volume between the catalyst surface and the capillary tip (3.6×10^{-2} s). It means that under experimental conditions practically all initial radicals have enough time to take part in the reaction of chain propagation.

The comparison of ESR spectra of radicals with those obtained previously at low pressures indicates that the nature of radicals accumulated changes. It means that the radicals registered during reactions at atmospheric pressure are products of secondary reactions in free volume. ESR spectra of radicals frozen out from the gas phase in experiments with oxide and alumina–platinum catalysts are presented in Fig. 2. Unlike

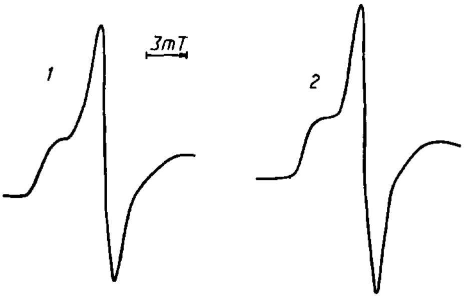

FIG. 2. ESR spectra of radical frozen out from gas phase at 77 K after oxidation of *n*-propanol over $CuCr_2O_4/\gamma\text{-}Al_2O_3$ (1) and $Pt/\gamma\text{-}Al_2O_3$ (2).

alkylperoxy radicals observed in experiments with the formation of radicals at low pressures, at atmospheric pressure one can observe the predominant accumulation of radicals whose spectra are mixtures of the intensive singlet and of the alkylperoxy signal having typical axial anisotropy of *g*-factor. Apparently, paramagnetic centers with an unshared electron localized on the oxygen atom or delocalized over several oxygen atoms dominate among the radicals accumulated (e.g., $R\dot{C}O$, $R\dot{C}O_3$), whose formation is typical for branched chain oxidation reactions.

Comparative studies of the temperature dependence of the concentrations of stable reaction products and radicals show that the appearance of radicals in the gas phase is accompanied by drastic changes in the yield of oxidation products: propionaldehyde and CO_2 (Fig. 3). The shape of the plotted temperature dependence of the yield of radicals and stable products is practically the same for oxide and alumina–platinum catalyst. The observed bell-shaped curves for the concentration of radicals and CO_2 are similar to the known temperature dependence of the rate for the gas-phase chain degenerated-branched reaction (*9*).

The initial rise in the rate of gas-phase total oxidation reactions can be due to the increase in the rates of chain propagation and branching, which leads to the growing number of active centers. Chain branching is usually ascribed to the reactions involving acetyl radicals, which is in agreement with the interpretation of experimental ESR spectra. The observed negative sign of the temperature coefficient for the rate of gas-phase oxidation can be due to the change in the transformation route of acetyl radicals (*9*):

$$R\dot{C}O + O_2 \rightarrow R\dot{C}O_3 \qquad (1)$$

$$R\dot{C}O_3 + RH \rightarrow RCO_3H + \dot{R} \qquad (2)$$

$$RCO_3H \rightarrow R\dot{C}O_2 + \dot{O}H \qquad (3)$$

$$R\dot{C}O \rightarrow \dot{R} + CO. \qquad (4)$$

With increasing temperature, reaction (4) becomes prevailing, hence the branching rate decreases. Further transformations of formed radicals diminish the concentration of radicals in the gas phase (*10*):

$$\dot{R} + O_2 \rightarrow \text{olefin} + H\dot{O}_2$$

$$H\dot{O}_2 \xrightarrow{\text{wall}} \text{decay}.$$

Our experiments showed that with decreasing the concentration of RO_2 those of CO and ethylene actually rise.

ESR spectra of the radicals accumulated at atmospheric pressure and the type of changes in the formation of oxidation products and in the concentrations of gas-phase radicals evidence in favor of the development of a branched chain reaction initiated by catalysts. In this connection one should expect that with varying the concentrations and the ratio of reactants, the dependences in the accumulation of radicals to the data on their formation at low pressures (*5–7*) would change.

The formation of stable products and radicals with varying the oxygen content in the reaction mixture and $C_{O_2} < C_{ROH}$ is illustrated in Fig. 4. It has been shown previously (*6, 7*) that the desorption rate of radicals at $P_{O_2} < P_{ROH}$ is independent of the partial pressure of oxygen. The rise in the concentration of radicals with increasing the oxygen concentration (Fig. 4) can be due to the branching reaction in the gas phase.

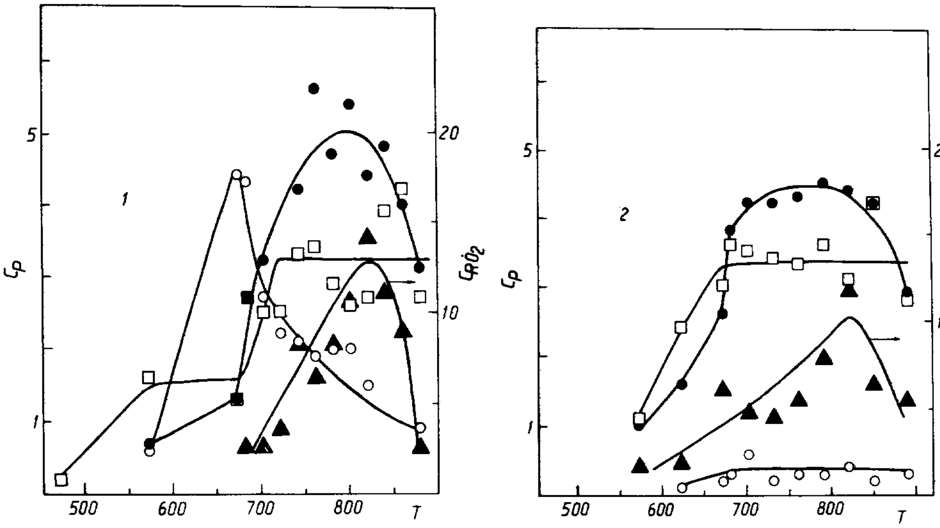

FIG. 3. Temperature dependences of concentrations of radicals ($C_{R\dot{O}_2}$ × 10^{11} ml^{-1}) and stable reaction products (C_p, vol.%) after oxidation of *n*-propanol over catalysts: (1) Pt/γ-Al_2O_3, C_{ROH} + 20.0 vol.%, C_{O_2} = 15.4 vol.%; (2) $CuCr_2O_4$/γ-Al_2O_3, C_{ROH} = 20.5 vol.%, C_{O_2} = 10.8 vol.%; (□) CH_3CH_2CHO, (○) $CH_2{=}CHCH_3$, (●) CO_2, (▲) $R\dot{O}_2$.

With further increasing the oxygen concentration up to its stoichiometric value, periodic flashes spreading opposite to the flow of reactants were observed, and apparently that is why no radicals above catalysts were detected in these conditions. Reaction products were CO_2 and water. It should be noted that at lower concentrations of reactants in the stoichiometric mixtures of ROH (3.5 vol.%) and O_2 (17.2 vol.%) purely heterogeneous oxidation was observed. The formation of oxidation products and radicals with varying the alcohol concentration in the reaction mixture is illustrated in Fig. 5. For intermediate concentrations (e.g., C_{ROH} = 11 vol.%) under the lack of oxygen the concentrations of radicals in the gas phase were stationary.

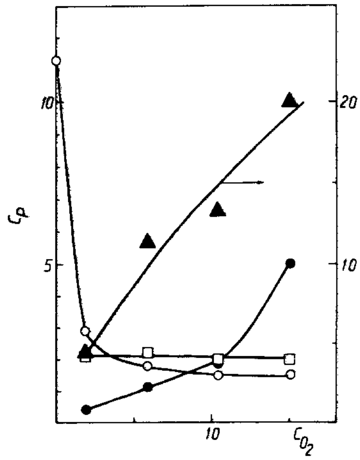

FIG. 4. Effect of oxygen concentration in initial mixture on accumulation radicals ($C_{R\dot{O}_2}$ × 10^{11} ml^{-1}) and stable products (C_p, vol.%) in oxidation of *n*-propanol over Pt/γ-Al_2O_3, C_{ROH} = 27.6 vol.%, T = 823 K. (□) CH_3CH_2CHO, (○) $CH_2{=}CHCH_3$, (●) CO_2, (▲) $R\dot{O}_2$.

As mentioned above, heterogeneous–homogeneous oxidation of stoichiometric mixtures proceeds with periodic ignitions of the reaction mixture. When oxidation reactions in stoichiometric mixtures were carried out at lower concentrations of reactants, these flashes were less intensive,which permitted to record periodic changes in the catalyst temperature (Fig. 6).

It should be noted that heterogeneous–homogeneous reactions initiated by catalysts are observed at relatively lower temperatures (600–700 K) compared to the combustion of organic compounds in the presence of catalysts (>1000 K) (*1*). The data of (*1*) show that at such high temperatures the nature of an active component exerts almost no effect on the generation of active radicals that are likely to be cracking products of the molecules oxidated. In our study species participating in heterogeneous–homogeneous reactions are the oxygen-containing organic radicals and the reactions develop at temperatures lower than those necessary for the cracking-directed reactions. It has been shown previously (*5–7*) that in these conditions the generation of radicals depends on the nature of catalyst active components and the nature and the chemical structure of reactants.

CONCLUSIONS

The results indicate that at atmospheric pressure in the presence of typical total oxidation catalysts a branched chain oxidation reaction initiated by the surface can develop. The contribution of the homogeneous component into the total conversion depends on the concentration and the ratio of reactants in the gas phase. At low concentrations of reactants the oxidation is purely heterogeneous and takes place on the surface. At high alcohol concentrations in the mixture heterogeneous–homogeneous, oxidation can take place. In this case the contribution of the homogeneous route rises with increasing the ratio O_2/ROH.

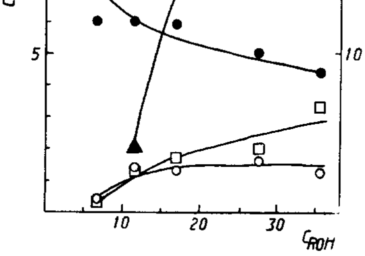

FIG. 5. Effect of alcohol concentration in initial mixture on accumulation of radicals ($C_{R\dot{O}_2} \times 10^{11}$ ml^{-1}) and stable products (C_p, vol.%) in oxidation of *n*-propanol over Pt/γ-Al_2O_3, C_{O_2} = 15.0 vol.%, T = 823 K. (□) CH_3CH_2CHO, (○) $CH_2{=}CHCH_3$, (●) CO_2, (▲) $R\dot{O}_2$.

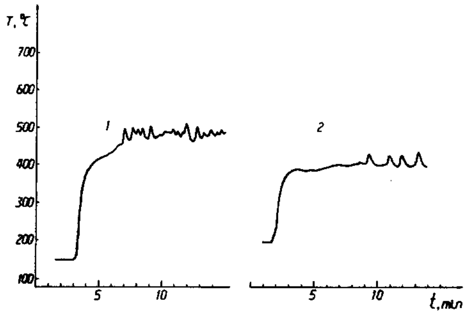

FIG. 6. Periodic changes of catalyst temperature in oxidation of *n*-propanol (11.2 vol.%) by stoichiometric amount of oxygen (50.7 vol.%) over catalysts: (1) Pt/γ-Al_2O_3, (2) $CuCr_2O_4$/γ-Al_2O_3.

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