Reactions of peroxide radicals with the surface of heterogeneous catalysts in homolytic and heterolytic processes

A. L. Smirnova,* T. V. Filippova, and E. A. Blyumberg

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: +7 (095) 938 2156

An interrelation between homolytic and heterolytic stages is found for olefin epoxidation by hydroperoxides and cumene hydroperoxide decomposition in the presence of a heterogeneous catalyst (molybdenum selenide). Peroxide radicals that are formed in homolytic decomposition of the hydroperoxide interact with the catalyst surface. As a result, molybdenum atoms are oxidized to the highest valence state, and new reaction sites are created, on which heterolytic reactions occur. It is shown that olefin, as an electron donor, decreases the catalyst activity in the heterolytic reactions. The limited value for the olefin epoxidation rate, which is independent of the amount of the catalyst used, is explained by the disappearance of active sites on the catalyst surface due to their interaction with the neighboring sites containing adsorbed olefin molecules.

Key words: peroxide radicals; heterogeneous catalysts; epoxidation; heterolytic reactions; molybdenum selenide.

Liquid-phase oxidation of hydrocarbons and decomposition of hydroperoxides in the presence of heterogeneous catalysts are homogeneous—heterogeneous reactions.¹ One of the stages of these reactions is linear chain termination as a result of the interaction of peroxide radicals with the surface. It was shown that for cyclohexene oxidation in the presence of metal selenides (Cu, Mo, and W), in addition to chain termination, these catalysts can participate in other stages of the oxidation process, *i.e.*, in chain propagation² and branching.³

The interaction of radicals with the surface of metal selenides modifies the catalyst surface. For example, partial dissolving of copper selenide under the action of peroxide radicals is found to occur during cyclohexene oxidation.⁴ When the concentration of copper selenide is high enough, oxidation is completely inhibited, whereas when the amount of CuSe is slightly reduced, the reaction proceeds very fast. Thus, critical phenomena which are associated with homogeneous catalytic degenerate chain branching and heterogeneous (linear) chain termination on CuSe are characteristic of this system.

On the basis of the experimental data obtained in this work, we discuss the formation mechanism of reaction sites on the surface of molybdenum selenide, which involves peroxide radicals.

Experimental

Epoxidation of cyclohexene and styrene by cumene hydroperoxide (CHP) and CHP decomposition were carried out at 50 and 70 °C in an argon atmosphere in a thermostatically controlled glass reactor equipped with a device for sampling and with a magnetic stirrer. The spinning rate of the stirrer $(>1000 \text{ rev. min}^{-1})$ was high enough to provide the reaction occurrence in the kinetic regime. MoSe₂ produced by selfpropagating high-temperature synthesis (SPHTS)⁵ was used as a heterogeneous catalyst. CuSe was employed as a heterogeneous inhibitor. Specific surface areas of MoSe, and CuSe were 1 and 17 m^2 g⁻¹, respectively. Surface areas of the heterogeneous contacts were measured by the BET method using thermal desorption of Ar. Reaction products and CHP were analyzed by gas-liquid chromatography using a glass column filled with a fixed liquid phase - dinonylphthalate (15 %) on Chromatone.

Results and Discussion

The kinetics of cyclohexene and styrene epoxidation by CHP and that of CHP decomposition to phenol in the presence of $MoSe_2$ are of an autocatalytic type (Figs. 1 and 2). According to the literature data,⁶ these reactions proceed by a heterolytic mechanism, which involves no free radicals, *i.e.*, the reactions are not chain reactions with degenerate chain branching. Therefore, we can draw the conclusion that the autocatalysis is associated with the catalyst activation by one or several components of the reaction mixture.



Fig. 1. Kinetic curves for cyclohexene oxide (a) and styrene oxide (b) production in the course of olefin epoxidation by cumene hydroperoxide: in the presence of $10 \text{ g L}^{-1} \text{ MoSe}_2$ at 50 °C, $[\text{CHP}]_0 = 0.1 \text{ M}$, Ar (I); 2 g L⁻¹ MoSe₂ at 70 °C, $[\text{CHP}]_0 = 0.5 \text{ M}$, Ar (b); with the additive of 15 g L⁻¹ CuSe (2).

Molybdenum selenide produced by SPHTS is a mixed-valence compound, which contains molybdenum atoms in various oxidation states. We can assume that, during olefin epoxidation and CHP decomposition, mo-



Fig. 2. *a.* Kinetic curves for phenol production (1, 2) in the course of cumene hydroperoxide decomposition in the presence of 10 g L⁻¹ MoSe₂ at 70 °C, $[CHP]_0 = 0.18 M$, chlorobenzene as a solvent, Ar (1) and with the additive of 10 g L⁻¹ CuSe (2). *b.* The rate of phenol production as a function of CuSe concentration in the course of cumene hydroperoxide decomposition under the same conditions.

lybdenum atoms are oxidized on the catalyst surface, *i.e.*, molybdenum in the lowest oxidation state is converted to the highest oxidation state. Hydroperoxide molecules and RO_2 radicals can play the role of oxidizing agents. In order to elucidate whether MoS_2 is activated by a molecular or radical route, experiments with a heterogeneous inhibitor of free-radical reactions, *i.e.*, with copper selenide, were carried out. We did not use homogeneous inhibitors, because this might result in surface modification.

As one can see from Fig. 1, cyclohexene epoxidation in the presence of CuSe is completely inhibited. This fact can be explained in the following way. There are no molybdenum atoms in the highest oxidation state on the catalyst surface under the conditions of epoxidation. The hydroperoxide does not oxidize Mo atoms of the active sites, since the presence of the inhibitor should not slow down molecular stages of the process. Hence, RO_2^{\cdot} radicals that are known to be strong oxidizers take part in the formation of the active sites.

The rate of phenol production during CHP decomposition also decreases after addition of CuSe (see Fig. 2). However, in contrast to olefin epoxidation, the rate of CHP decomposition decreases only by about 50 %, i.e., hydroperoxide decomposition is not completely inhibited. Upon further increase in the amount of the inhibitor, the decomposition rate remains unchanged (see Fig. 2). The sharp difference in the inhibiting effect of copper selenide in these two heterolytic reactions can be explained if we assume that one of the reaction components in the epoxidation process, namely, the olefin, which is an electron donor, is adsorbed on the surface, thereby reducing the accepting ability of the reaction sites. This results in partial reduction of the surface and in the appearance of a new reaction site $Z_{R'H^*}$, which incorporates the olefin molecule: $Z^{m} + R'H \rightarrow Z^{n}_{R'H^{*}}$, where R'H is the olefin. Thus, in the course of CHP decomposition in chlo-

Thus, in the course of CHP decomposition in chlorobenzene, peroxide radicals interact with primary sites Z^n , whereas during olefin epoxidation, these radicals interact with $Z^n_{R'H^+}$ yielding the reaction sites which appear to contain RO_2^- anion-radicals:

$$Z^n (Z^n_{B'H^+}) + RO_2^{\cdot} \rightarrow Z^m_{RO_2^{-}}, n \le 5, m = 6.$$

In order to prove the effect of olefins on the catalytic activity of MoSe₂ in the heterolytic reactions, the kinetics of CHP conversion in the presence of molybdenum selenide and variable amounts of cyclohexene is studied. As one can see from Fig. 3, even small additives of cyclohexene drastically decrease the rate of phenol production, i.e., the rate of CHP decomposition via the heterolytic route. As the cyclohexene concentration increases, the rate of CHP consumption reaches a minimum and then starts to grow. The growth is related to the opening of a new route for CHP consumption, *i.e.*, cyclohexene epoxidation. The rate of cyclohexene oxide formation increases with growing olefin concentration, but it remains lower than the rate of dimethylphenylcarbinol (DMPC) formation because of parallel CHP decomposition by the homolytic reaction. At $[C_6H_{10}] < 0.02 \ M$, the rate of the homolytic DMPC production (the difference between the rates of DMPC and cyclohexene oxide production) and the accumulation rate of the products arising from the RO₂ radical disappearance increase with growing olefin concentration (see Fig. 3). This increase appears to be a result of the growth in the concentration of $Z^n_{\text{R'H}}$ reaction sites on the surface of MoSe₂ capable of inducing CHP decomposition to radicals. The maximum on curve 6 (see Fig. 3), which demonstrates the dependence of the formation rate of the products arising from RO₂ radical decay as a function of [R'H], is associated with the fact that the mechanism of heterogeneous termination of RO₂ radicals changes as the olefin concentration increases. In the absence of olefin, RO₂ radicals interact with the active sites on the MoSe₂ surface. However, as



Fig. 3. Rates of cumene hydroperoxide consumption (1) and rates of formation of phenol (2), cyclohexene oxide (3), dimethylphenylcarbinol (4), DMPC by the homolytic route (5), and accumulation of molecular products of RO₂ conversion (6) as a function of cyclohexene concentration in the presence of 50 g L⁻¹ of MoSe₂ at 50 °C, Ar, benzene as a solvent, [CHP]₀ = 0.1 *M*, the extent of CHP conversion is 10 mol: %.

the cyclohexene concentration grows, another route for radical decay, which is associated with RO_2 interaction with cyclohexene molecules adsorbed on the catalyst surface, becomes dominant:

$$Z_{R'H} + RO_2^{:} \rightarrow Z_{R'} + ROOH$$

 $Z_{R'} + RO_2^{:} \rightarrow Z + ROOR.$

A characteristic feature of the mechanism for olefin epoxidation in the presence of MoSe₂ is the involvement of the surface active sites containing $\overline{RO_2}^-$ anion-radical and olefin. Figure 4, a demonstrates an anomalous dependence of the cyclohexene epoxidation rate on the amount of MoSe₂. Initially, the rate of cyclohexene formation grows with increasing amount of MoSe₂, and then it no longer depends on the amount of the catalyst in the reaction mixture. The dependence of the rate of styrene oxide formation during styrene epoxidation by CHP in the presence of molybdenum selenide is analogous. The rate of DMPC formation by the homolytic route linearly increases with increasing amount of MoSe₂ (see Fig. 4). It is proved experimentally that the independence of the epoxidation rate from the amount of the catalyst used is not related to the coarsening (aggregation) of catalyst grains or to the transfer of the process



Fig. 4. *a.* Rates of formation of cyclohexene oxide (1) and dimethylphenylcarbinol (2), rates of cumene hydroperoxide consumption (3) and of DMPC production by the homolytic route (4) as a function of $MoSe_2$ amount during cyclohexene epoxidation by cumene hydroperoxide at 50 °C, $[CHP]_0 = 0.1 M$, [R'H] = 9.9 M, Ar. *b.* Rates of phenol formation (1) and cumene hydroperoxide decomposition (2) as a function of $MoSe_2$ amount during cumene hydroperoxide decomposition (0.1 M) at 70 °C in chlorobenzene, Ar.

from the kinetic to the diffusion regime and to the influence of the reaction products. Within the framework of the generally accepted mechanisms for catalytic heterolytic transformations of hydroperoxides, the reaction rate should increase as the amount of the catalyst used grows. This is actually observed during heterolytic CHP decomposition (see Fig. 4, b). The independence of the epoxidation rates from the amount of the catalyst within a certain range can be accounted for by the achievement of the steady-state concentration of the $Z^{m}_{RO_{2}}$ - reaction sites involved in epoxidation. In this case, the decay of $Z^m_{RO_2^-}$ reaction sites must proceed with the participation of a neighboring reaction site. The interaction of neighboring sites was considered in terms of the concept of electron-hole recombination on the surface of semiconductors,⁷ to which molybdenum selenide produced by SPHTS belongs. It is known that an electron and a hole can interact not directly, but with different surface groups, which are adsorbed on neighboring sites. In the catalytic system under study, RO₂. radicals accept electrons from the active surface sites to yield $Z^{m}_{RO_{2}}$ hole, *i.e.*, a reaction site, on which olefin epoxidation² and heterolytic CHP decomposition occur. The hole disappearance involves the olefin that is adsorbed on a neighboring surface site (Scheme 1).

This reaction allows us to explain why the dependences of the rates of olefin oxide and phenol formation on the amount of $MoSe_2$ differ. In the reaction media with no olefin, there are no $Z^n_{R'H'}$ sites that are involved in the consumption of the reaction sites for heterolytic hydroperoxide conversion. As a result, the rate of phenol



production is proportional to the catalyst amount (see Fig. 4, b).

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