Catalysis Letters 15 (1992) 353–362

Study of elementary reactions of free radicals formed on oxide and platinum containing catalysts

Z.R. Ismagilov * and S.N. Pak

Institute of Catalysis, Prospekt Akademika Lavrentieva, 5, Novosibirsk 630090, Russia

Received 22 January 1992; accepted 12 June 1992

The formation of alkylperoxy radicals on catalysts $CuCr_2O_4/\gamma\text{-}Al_2O_3$, $Pt/\gamma\text{-}Al_2O_3$ and on alumina upon the interaction of amines and alcohols with oxygen has been observed applying the matrix isolation ESR technique. Surface-generated gas phase radicals are shown to initiate a radical chain reaction. The efficiency of the yield of radicals depends on the catalyst mass and its arrangement in a reactor: the desorption of radicals into the gas phase occurs primarily from the outer geometrical surface of catalyst granules.

Keywords: Oxide and platinum containing catalysts; surface-generated gas phase radicals; initiation of radical chain reaction

1. Introduction

At present it is well known that a solid surface traditionally considered as a radical decay site can take part in all elementary reactions of free radicals: radical generation, chain prolongation and branching. The formation of radicals on a catalyst surface is typical for reactions carried out under severe conditions, usually above 673 K, such as total oxidation, pyrolysis of organic compounds and methane coupling.

The reactions of desorbed radicals can considerably contribute to the total catalytic transformation of hydrocarbons. For instance, recombination reactions of radicals desorbed from the surface make the main contributions to the catalytic conversions of propylene to 1,5-hexadiene [1,2] and methane to ethane and ethylene [3,4]. Surface reactions of chain prolongation and branching are less studied. There are some experimental data based on IR spectroscopy which show the possibility of the transfer of free valency from a gas phase radical to an aldehyde adsorbed on SiO_2 [5] and to a surface $-OH$ group on MgO with the formation of $-O^-$ [6]. The data on the existence of surface chain branching have been mainly obtained by studying the reactor wall effect on the proceeding of gas phase radical-chain oxidation reactions [7]. The study of radicals and their

---

* To whom correspondence should be addressed.

reactions in the presence of catalysts allows one to obtain the confirmation of the radical mechanism of a catalytic reaction and to determine the kinetic parameters of the elementary steps of a chain reaction.

The possibility that gas phase radical reactions are initiated by the surface of catalysts for total combustion is studied insufficiently. Moreover, the very high activity of these catalysts, connected with the presence of active oxygen on the surface has led to the assumption, as e.g. in ref. [8], that the catalyst surface is a sufficiently strong inhibitor for the development of gas phase radical-chain reactions. In the present paper we report the results of the study of radical formation on oxide and platinum containing catalysts for total oxidation as well as the study of the conditions for the initiation of a gas phase chain oxidation reaction by the catalyst surface. Special attention is given to the elucidation of the influence of the geometrical parameters of the catalyst bed arrangement in the reactor and the structural parameters of the catalyst granules themselves on the generation of radicals by surface. Based on radical accumulation data the general regularities of catalytic reactions involving surface-generated gas phase radicals are discussed.

2. Experimental

One of the modern effective and versatile methods for the study of radicals desorbed from the surface is the so-called matrix isolation ESR technique which has proved to be useful in the study of gas phase radical reactions [9]. Using this method it is possible to study the structure of radicals desorbed from the surface and determine the kinetic parameters of their formation.

The schematic diagram of the experimental set-up for the study of radical formation is shown in fig. 1a. Reactions were carried out in a quartz flow reactor with 8 mm i.d. at total pressure $\leqslant 10$ Pa. Catalysts in a shape of spherical granules with 2 mm diameter were placed into the reactor in one layer. Reagents were fed to the reactor via fine control valves. The freezing unit installed into the ESR resonator cavity was a quartz Dewar flask cooled by liquid nitrogen to 77 K.

Catalysts 34% $CuCr_2O_4/\gamma\text{-}Al_2O_3$, $S_{BET} = 110$ m^2/g and 0.64% $Pt/\gamma\text{-}Al_2O_3$, $S_{BET} = 190$ m^2/g were used in the experiments. The kinetic parameters of radical formation from amines (C_1–C_4) and alcohols (C_1–C_6) of normal structure were studied.

The rates of radical formation in the experiments were determined from the accumulation curves – dependences of the intensity of frozen radical ESR signals on reaction time. Examples of various types of dependences are illustrated in fig. 2, which shows that these dependences are not always linear. The changes observed in the radical accumulation rates may be ascribed to changes of the catalyst state. Actually it has been previously mentioned [10] that the

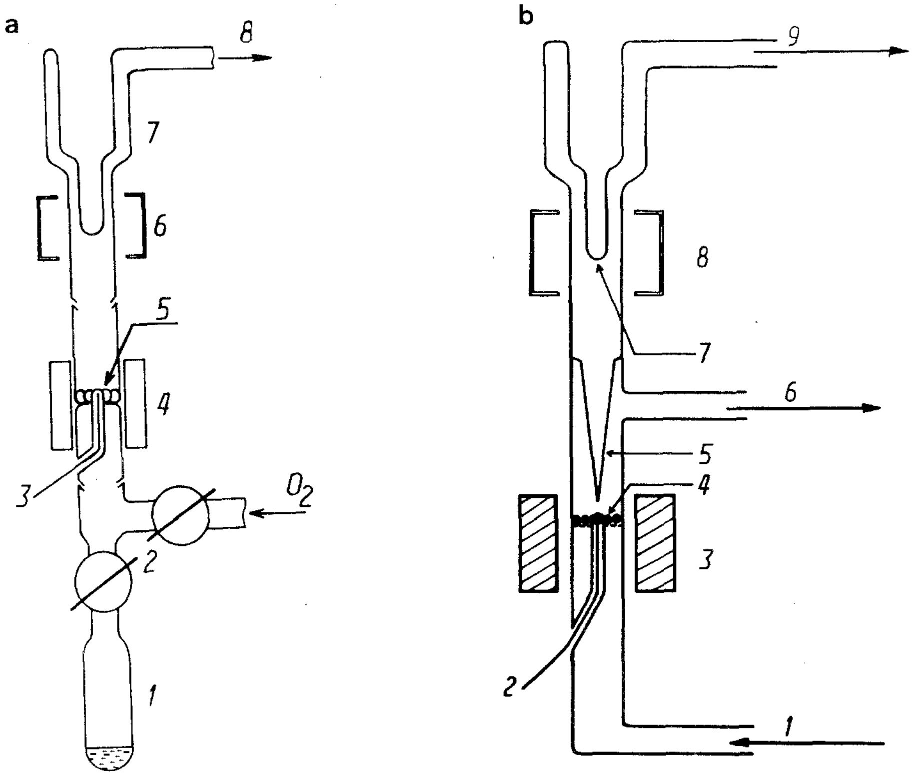

Fig. 1. (a) Experimental set-up for the study of radical formation on catalysts. (1) Flask with reagent, (2) valves, (3) thermocouple, (4) furnace, (5) catalyst layer, (6) ESR cavity, (7) Dewar flask, (8) to vacuum. (b) Schematic diagram of the apparatus for the study of heterogeneous–homogeneous reactions. (1) Reaction mixture feed, (2) thermocouple, (3) furnace, (4) catalyst layer, (5) calibrated capillary tubing, (6) reaction products outlet, (7) Dewar finger, (8) ESR cavity, (9) to vacuum system.

changes in the rates of radical formation in the reactions of alcohols on CuO (curve 2.3) were due to the reduction of the outer surface of catalyst granules. In the experiments with amines over alumina–platinum catalyst (curve 2.2) coking of the outer catalyst surface was observed. These experimental observations have shown that in order to make an accurate comparison of reactivity of reagents and catalysts in radical generation reactions a possible alteration of the state of a catalyst during the reaction should be taken into account. In the present paper the comparison of the rates in all the experiments was carried out only from radical accumulation data having linear type of dependence on the reaction time.

The chain reaction of the oxidation of *n*-propanol was studied at atmospheric pressure. GC analysis was applied to all stable reaction products. The concentration of free radicals in the gas phase over a catalyst was determined by ESR. The products were allowed to flow through a quartz capillary from the gas phase

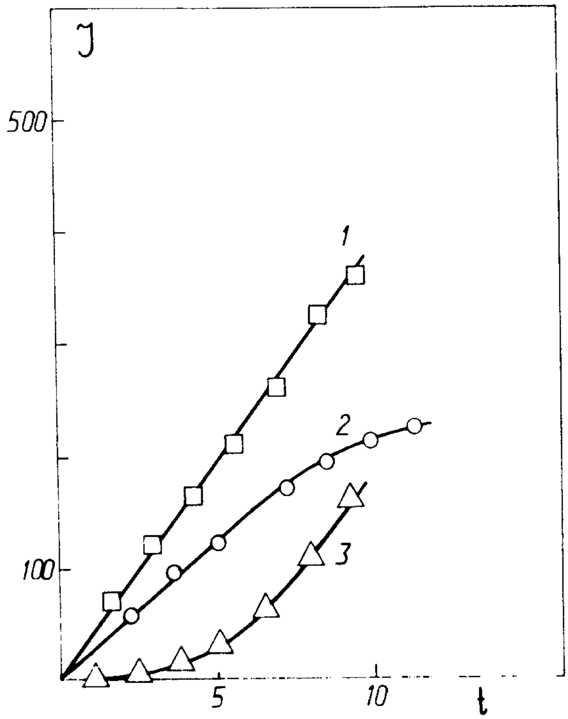

Fig. 2. Kinetic curves of accumulation of $R\dot{O}_2$ radicals (I (arb. units) versus time (min)) upon interaction of amines and alcohols with oxygen over various catalysts. (1) n-C_3H_7OH, $CuCr_2O_4/\gamma$-Al_2O_3, 781 K; (2) $(C_4H_9)_2NH$, Pt/γ-Al_2O_3, 773 K; (4) n-C_3H_7OH, CuO, 797 K.

to the low pressure region ($\leqslant$ 10 Pa) and further to the Dewar finger installed in the ESR resonator cavity (fig. 1b). The tip of the capillary was placed at a distance of $\approx$ 0.5 mm above the catalyst layer. Catalyst samples in the experiments were of 0.5–1.0 mm fraction with the mass $\approx$ 50 mg. They were placed in a thin layer of $\approx$ 1 mm in the reactor. Reactions were performed under flow condition, the residence time being equal to about 0.07 s.

3. Results and discussion

Data on radical formation in reactions of a great number of amines and alcohols were described in detail elsewhere [10,11]. The kinetic parameters measured and the study of alkylperoxy radicals observed in experiments made it possible to propose tentative mechanisms of their formation on oxide catalysts.

The highest rates of radical formation were observed in the oxygen deficient media at $P(O_2) \leqslant P(\text{ROH or RNH}_2)$. At larger values of oxygen partial pressure the efficiency of radical formation decreased; this was attributed to the

Table 1
Activation energy (E, kJ/mol) and reaction rate (W, particles/m^2 s at 133 Pa) of RO_2 formation in reactions of alcohols at $T = 760$ K on catalysts $CuCrO_4/\gamma\text{-}Al_2O_3$ and $Pt/\gamma\text{-}Al_2O_3$

Substance	$CuCr_2O_4/\gamma\text{-}Al_2O_3$		$Pt/\gamma\text{-}Al_2O_3$	
	E	W	E	W
CH_3OH	113	5.1×10^{11}	117	2.1×10^{11}
C_2H_5OH	126	4.3×10^{11}	92	5.4×10^{11}
$n\text{-}C_3H_7OH$	121	5.0×10^{11}	105	5.5×10^{11}
$n\text{-}C_4H_9OH$	121	5.0×10^{11}	117	4.5×10^{11}
$n\text{-}C_5H_{11}OH$	121	2.5×10^{11}	113	4.7×10^{11}
$n\text{-}C_6H_{13}OH$	117	1.8×10^{11}	121	1.9×10^{11}

effective oxidation both of initial molecules and intermediate species on a catalyst surface.

The kinetic parameters of radical formation in the reactions of amines and alcohols of normal structure are given in tables 1 and 2. The represented data make it possible to conclude that the number of radicals desorbed from the surface is sufficient for the initiation of a chain reaction in the gas phase. The least value of the radical formation rate is observed in the reactions of methylamine on $\gamma\text{-}Al_2O_3$. Under the experimental conditions at $T = 760$ K and $[RNH_2] \approx 10^{21}$ m^{-3} the concentration of free radicals over the catalyst, $[R\dot{O}_2]$, is equal to $\approx 10^{14}$ m^{-3}. Taking into account the predominating decay of radicals on the walls the length of the chain N, which is defined as the ratio of the rate of chain prolongation to that of radical decay, can be expressed as

$$N = \frac{k_p[R\dot{O}_2][RNH_2]}{k_d[R\dot{O}_2]} = \frac{10^{-16}\,e^{-33500/RT} \times 10^{14} \times 10^{21}}{10^5\,e^{-41900/RT} \times 10^{14}} \approx 70,$$

where $k_p = 10^{-16}\,e^{-33500/RT}$ m^3 s^{-1} is the value of the constant for chain prolongation [12], $k_d = 10^5\,e^{-41900/RT}$ s^{-1} is the constant of alkylperoxy radicals decay on the quartz surface [13]. Thus, if the temperature of a reactor is maintained close to that of a catalyst, a chain radical reaction can develop initiated by the radicals desorbed from the catalyst surface.

Table 2
Activation energy (E, kJ/mol) and reaction rate (W, particles/m^2 s at 133 Pa) of RO_2 formation in reactions of amines at $T = 760$ K on catalysts $Pt/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$

Substance	$Pt/\gamma\text{-}Al_2O_3$		$\gamma\text{-}Al_2O_3$	
	E	W	E	W
CH_3NH_2	125	1.3×10^{10}	85	1.4×10^{9}
$C_2H_5NH_2$	105	3.7×10^{11}	127	1.9×10^{10}
$n\text{-}C_4H_9NH_2$	105	4.2×10^{11}	117	2.6×10^{10}

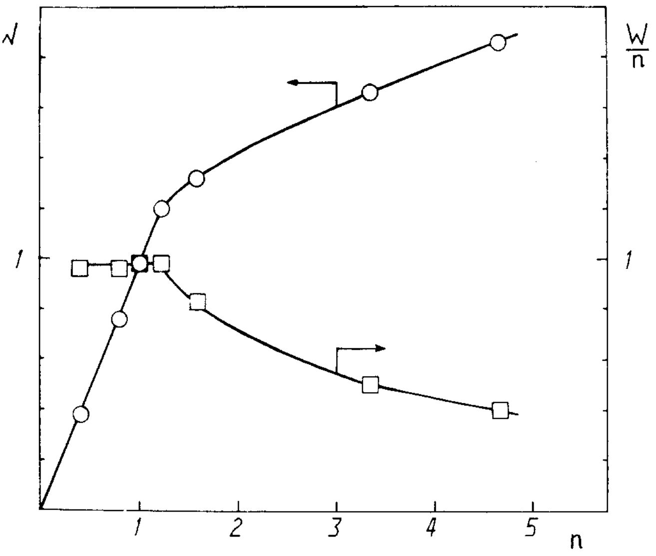

Fig. 3. Variation of radical accumulation rate *W* (arb. units) and efficiency of radical formation on one catalyst layer *W*/*n* with increasing the number of layers of $\gamma\text{-Al}_2\text{O}_3$ in the reactor.

One of the characteristic features of gas phase radical reactions is the dependence of kinetic parameters on reactor geometry. In the case of heterogeneous–homogeneous reactions, reactor geometry and the catalyst distribution in a reactor are expected to have a considerable effect since the concentration of radicals in the gas phase determined from the data on radical accumulation depends on the reactions of their formation and decay and on the change of the concentrations of the components of the reaction mixture on passing the catalyst bed.

Fig. 3 shows the experimental dependence of radical accumulation rate on the mass of a catalyst sample. The number of catalyst layers was defined as the ratio of the catalyst volume to the volume of one catalyst layer. If the number of catalyst granules placed into the reactor does not compose the whole layer, the value of *n* should be estimated as the ratio of this number to the quantity of granules in the complete layer. As can be seen from fig. 3, the contribution of secondary reactions and the change of the mixture composition is small at the initial linear part of the dependence of the reaction rate on the number of catalyst layers. The efficiency of surface generation of gas phase radicals decreases with the increase of the number of catalyst layers.

Thus, in experiments with one catalyst layer it is possible to relate the rates of radical formation to the mass of the catalyst sample used in an experiment. However, the problem of the determination of the specific rate of radical formation from the data on radical accumulation has still to be clarified. The experimental observation of the change of the rates of radical formation due to the change of the state of the outer catalyst surface described previously [10]

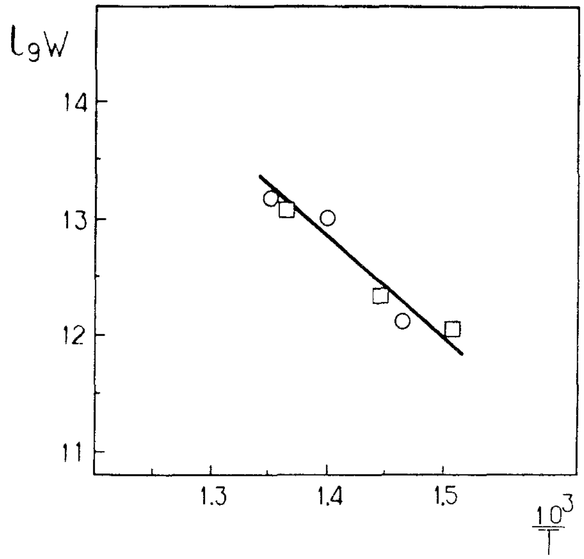

Fig. 4. Temperature dependences of accumulation of $R\dot{O}_2$ radicals W (particles/gs) at $P_{RNH_2} =$ 133.3 Pa) in reactions of $C_2H_5NH_2$ with O_2 over α-Al_2O_3 (○) and γ-Al_2O_3 (□).

allows the assumption that under the reaction conditions the outer geometrical surface of a catalyst is active in the formation of gas phase radicals. To verify this assumption a reaction with the formation of radicals was conducted using samples of alumina having the same geometrical dimension but different pore

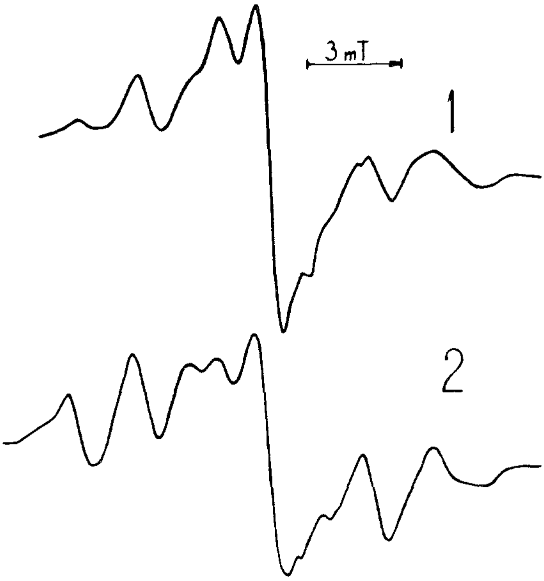

Fig. 5. ESR spectra of species produced in the photolysis of $R\dot{O}_2$ radicals formed upon interaction of $C_2H_5NH_2$ with oxygen over (1) γ-Al_2O_3, (2) α-Al_2O_3.

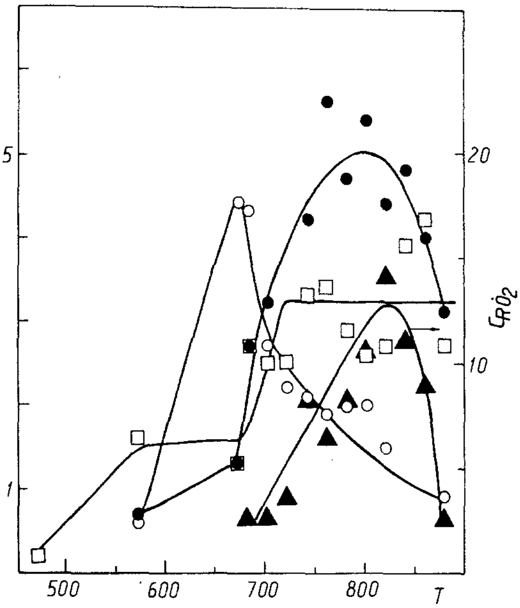

Fig. 6. The formation of radicals ($\times 10^{11}$ particles/ml) and stable products (vol%) of *n*-propanol oxidation over Pt/γ-Al_2O_3 versus temperature. $C_{ROH} = 20.0$ vol%, $C_{O_2} = 15.4$ vol%. (□) CH_3CH_2CHO, (○) $CH_2{=}CHCH_3$, (●) CO_2, (▲) $R\dot{O}_2$.

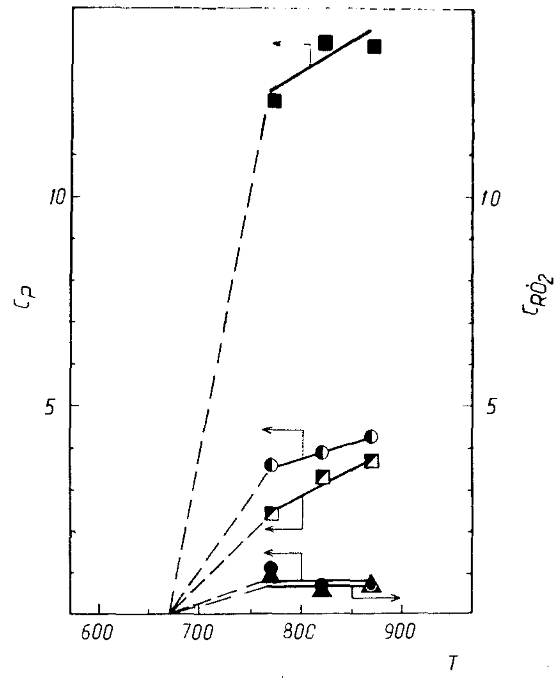

Fig. 7. The formation of radicals ($\times 10^{11}$ particles/ml) and stable products (vol%) of *n*-propanol oxidation in empty reactor versus temperature. $C_{ROH} = 20.2$ vol%, $C_{O_2} = 13.9$ vol%, (■) CO, (◐) C_2H_4, (▨) CH_4, (●) CO_2, (▲) $R\dot{O}_2$.

structure and S_{BET}: γ-Al_2O_3 with mean pore radius (r_m) 40–100 Å and $S_{BET} = 220$ m^2/g, and α-Al_2O_3 with $r_m = 1000$ Å and $S_{BET} = 7$ m^2/g. The reactor was loaded with equal number of catalyst granules. In the temperature range 673–773 K the rates of radical accumulation on these catalysts were found to be practically the same, with E_{eff} being 115 ± 10 kJ/mol (fig. 4).

Fig. 5 shows the spectra of radicals formed after the photolysis of alkylperoxy radicals obtained in the reactions of ethylamine with oxygen on γ-Al_2O_3 and α-Al_2O_3. The use of this technique for the study of the structure of peroxy radicals formed in the oxidation reactions of alcohols and amines over oxide catalysts was discussed previously in detail [10,11]. For ethylamine reactions both on γ-Al_2O_3 and α-Al_2O_3, after the irradiation the ESR spectra exhibit six components with 2.0–2.7 mT splitting with traces of hyperfine structure side components. These spectra can be assigned to ethyl radicals. The close values of effective activation energies of radical formation and close chemical composition of the oxides used as well as the data on radical photolysis make it possible to assume the similar mechanisms of radical formation on γ- and α-Al_2O_3.

The data on the dependence of radical formation rate on the mass of a catalyst sample and the evidence for the activity of outer catalyst surface in radical formation seem to be general for high temperature heterogeneous catalytic reactions with the participation of radicals. Taking into consideration the results obtained, the values of the rates given in the tables should be increased by a factor of $\approx 10^4$ and therefore the specific rates of radical formation at 760 K would be $\approx 10^{15}$ m^{-2} s^{-1} which is comparable to specific rates of catalytic oxidation.

The experimental confirmation of the possibility of the development of a gas phase chain reaction initiated by the surface of total oxidation catalysts is considered in detail in ref. [14]. Here we present as an example the data on the formation of free radicals and stable reaction products in the presence of a catalyst (fig. 6) and in an empty reactor (fig. 7) upon the variation of temperature. As can be seen from the figures a homogeneous radical reaction initiated by the surface starts at 650–700 K, and the radical formation in an empty reactor is observed only at 750–800 K. The compositions of reaction products are also quite different. The presence of a catalyst leads to the increase of the yield of oxidation products; the correlation of the change of the concentrations of radicals and CO_2 is observed which is typical for branched chain reactions of hydrocarbons oxidation.

4. Conclusion

The experimental data obtained show that on total oxidation catalysts and aluminas alkylperoxy radicals can be formed, their concentration being sufficient for the initiation of a gas phase chain reaction. At fairly high temperatures typical for heterogeneous–homogeneous reactions the catalyst pore structure and S_{BET} do not play a significant role in reactions of radical formation and decay. Apparently, the outer catalyst surface takes the main part in the desorption of radicals into the gas phase.

References

[1] W. Martir and J.H. Lunsford, J. Am. Chem. Soc. 103 (1981) 3728.
[2] A.A. Muradyan, K.G. Gazaryan, T.A. Garibyan and A.B. Nalbandyan, Oxid. Commun. 5 (1983) 463.
[3] D.J. Driscoll, W. Martir, J.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 58.
[4] K.D. Campbell, E. Morales and J.H. Lunsford, J. Am. Chem. Soc. 109 (1987) 7900.
[5] R.A. Bakhchadjan, I.A. Vardanyan and A.B. Nalbandyan, Khim. Fiz. 5 (1986) 393.
[6] N.A. Vasilieva, E.A. Paukshtis and R.A. Buyanov, Izv. SO Akad. Nauk SSSR ser. khim. 1 (1983) 97.
[7] V.V. Azatyan and R.G. Aivazyan, Kinet. Katal. 27 (1986) 1086.
[8] G.I. Golodets and V.M. Vorotyntsev, Kinet. Katal. 26 (1985) 879.
[9] A.B. Nalbandyan and A.A. Mantashyan, *Elementary Processes in Slow Gas Phase Reactions* (Yerevan, 1975) (in Russian).
[10] V.K. Yermolaev, S.N. Pak, L.G. Krishtopa, Z.R. Ismagilov and K.I. Zamaraev, Khim. Fiz. 7 (1988) 1141.
[11] Z.R. Ismagilov, S.N. Pak, V.K. Yermolaev and K.I. Zamaraev, Dokl. Akad. Nauk SSSR (phys. chem.) 298 (1988) 637.
[12] V.N. Kondratiev, *Rate Constants of Gas Phase Reactions* (Nauka, Moscow, 1970) (in Russian).
[13] E.G. Garibyan, A.A. Muradyan and T.A. Garibyan, Armyanskii Khim. Zh. 31 (1978) 466.
[14] Z.R. Ismagilov, S.N. Pak and V.K. Yermolaev, J. Catal., in press.