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Kinetics of Free Radical Generation in the Catalytic Oxidation of Methanol

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Abstract—The formation of free radicals over the surface of platinum-containing catalysts in the methanol oxidation reaction depending on the temperature, the composition of the reaction mixture, and the procedure used for introducing platinum was studied by the matrix isolation method technique. The nature and transformations of surface intermediates depending on the temperature and the presence of oxygen in the gas phase were studied by Fourier transform IR spectroscopy. The main surface intermediate was the methoxy group. The following three types of these groups were stabilized in alumina-based catalysts: (I) $CH_3O–Al_{oct}$ (ν_s(C–H) = 2806 cm^{-1}), (II) $CH_3O–Al_{tetr}$ (ν_s(C–H) = 2825 cm^{-1}), and (III) $CH_3O < (Al)_2$ (ν_S(C–H) = 2845 cm^{-1}, δ_{as}(C–H) = 1460 cm^{-1}, δ_s(C–H) = 1440 cm^{-1}, $r_{\parallel}$ (CH_3) = 1185 cm^{-1}, and ν(C–O) = 1095 cm^{-1}). At the same time, isolated methoxy groups (ν_{as}(C–H) = 2997 cm^{-1}, ν_{as}(C–H) = 2959 cm^{-1}, ν_s(C–H) = 2857 cm^{-1}, and δ(CH_3) = 1450 cm^{-1}) and hydrogen-bonded groups (ν(O–H) = 3400–3550 cm^{-1}), which resulted from chemisorption at siloxane bridges, were stabilized in silica gel–based catalysts. It was found that $CH_3O^\bullet$ and $CH_3OO^\bullet$ radicals were formed only over the surfaces of pure supports (SiO_2 and Al_2O_3) and their mechanical mixtures with platinum. The total concentration of radicals was described by an extremal function of the composition of reactants, whereas the relative concentration depends on the nature of the support. This is conceivably due to the effect of coordinatively unsaturated cations of the support, which are formed by dehydroxylation in the course of catalyst pretreatment. An increase in the rate of formation of gas-phase radicals on mixed catalysts was explained by special properties of the platinum/support interface region, at which surface intermediates were formed in superequilibrium concentrations under reaction conditions.

INTRODUCTION

The high-temperature transformations of hydrocarbons often include homogeneous reactions initiated by free radicals, which are desorbed from the surface of a catalyst. In the mechanistic studies of heterogeneous and homogeneous reactions, it is of importance to correlate the formation of surface intermediates with the role of these intermediates in the formation of free radicals and to determine the contribution of these free radicals to the overall reaction mechanism.

The freezing of radicals in the matrix of products of a test reaction at 77 K followed by the recording of the EPR spectra of the condensate (the matrix isolation method technique) is an instrumental technique for studying the composition of radicals in a gas phase and the kinetics of radical generation and decay over wide temperature, pressure, and concentration ranges. This technique was proposed by V.N. Panfilov and developed under the supervision of A.B. Nalbandyan at the Institute of Chemical Physics in the Armenian Soviet Socialist Republic [1, 2]. Matrix isolation method has received wide acceptance in the analysis of mechanisms of the gas-phase oxidation of hydrocarbons from different classes [2–5]. Presumably, peroxide radicals ($RO_2^\bullet$) were frozen in these reactions. Because of their low chemical activity, these radicals were transferred without considerable concentration changes from the reaction zone to a condensate-freezing unit. In this case, it is assumed *a priori* that the frozen radical can be identified by the EPR spectrum.

However, when a reaction results in the formation of a few radicals with close parameters of the EPR spectra (for example, $HO^\bullet$ and $HO_2^\bullet$ [5, 6] or $CH_3O^\bullet$ and $CH_3O_2^\bullet$ [7]), the spectrum of the condensate is a superposition of the spectra of individual radicals. Because of this, their relative concentrations are difficult to evaluate. To solve this problem, a special method was proposed for determining the nature of frozen radicals ($RO_2^\bullet$ or $RO^\bullet$). This method is based on the assumption that methoxy and methylperoxy radicals exhibit different stability to photolysis with the full light of high-pressure mercury lamps [7].

With the use of photolysis for the identification of radicals, we found that $CH_3O^\bullet$ and $CH_3O_2^\bullet$ radicals were formed in the methanol oxidation reaction on a catalyst that was a mechanical mixture of platinum black and silica gel at a 1 : 1 ratio between the reactants

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† Deceased.

and at T = 770–920 K with an activation energy of 7 kcal/mol [7].

Nonadditive effects of an increase in the catalytic activity of Pt(Pd) + oxide mechanical mixtures were reported in publications on the catalytic oxidation of H_2 and light hydrocarbons [9–11]. These effects were explained assuming the development of a radical chain mechanism. Thus, it was of interest to us to perform a comparative study of the generation of free radicals in catalytic systems with active components introduced by different procedures in order to understand the mechanism of radical generation and the overall reaction mechanism.

To determine the effects of the active component, the procedure of introducing it, and the nature of the support on the generation of radicals in methanol oxidation, we performed experiments in the order pure support $\longrightarrow$ active component for the most commonly used supports (SiO_2 and γ-Al_2O_3), their mechanical mixtures with platinum, and supported platinum catalysts. The methanol oxidation reaction was studied for several reasons. On the one hand, methanol is one of the main intermediates in the oxidation of methane and light hydrocarbons. On the other hand, methanol belongs to the main products of organic synthesis with continually expanding areas of application. The main areas of methanol application are the production of formaldehyde and the use as an effective component of alcohol fuels. However, although many publications were devoted to the adsorption, decomposition, and oxidation of methanol, the reaction mechanism is still understood incompletely. Moreover, Krishtopa *et al.* [3] found that the rates of radical generation in the oxidation of hydrocarbons and their oxygenates on oxide catalysts in the order hydrocarbon $\longrightarrow$ alcohol $\longrightarrow$ aldehyde $\longrightarrow$ carboxylic acid are in a ratio of 1 : 10 : 5 : 5. This suggests that the contribution of a homogeneous component to the oxidation of alcohols is considerable.

In this work, we studied the reactions of surface intermediates formed under conditions of methanol oxidation with the use of Fourier transform IR spectroscopy.

EXPERIMENTAL

Radical products in the methanol oxidation reaction at 720–920 K were studied by matrix isolation method in the following series of catalysts: pure support (SiO_2 or γ-Al_2O_3) $\longrightarrow$ mechanical mixture (Pt + support) $\longrightarrow$ impregnated catalyst (Pt/SiO_2 or Pt/Al_2O_3) $\longrightarrow$ pure Pt.

Catalysts

Pure Pt^0 was a metal film deposited from H_2PtCl_6 on the walls of a quartz reactor.

The impregnated catalysts Pt/SiO_2 (InCatPt-1) and Pt/Al_2O_3 (InCatPt-2) were prepared in accordance with a standard procedure [12, 13] at the Omsk Branch of the Boreskov Institute of Catalysis.

Commercial A-1 alumina (S_{sp} = 186 m^2/g; V_{pore} = 0.51 cm^3/g) and KSKG silica gel from the Ryazan refinery (S_{sp} = 280 m^2/g; V_{pore} = 0.84 cm^3/g) were used as catalyst supports. The silica gel was prewashed with concentrated nitric acid, ground by attrition, and pelleted at a pressure of ~50 atm. The above SiO_2 and Al_2O_3 were used for preparing mixed catalysts.

Platinum black was prepared according to Zelinskii [14]. A solution of H_2PtCl_6 (~100 ml) was treated with a formaldehyde solution (10 ml) at 288 K; after cooling the mixture in an ice bath to 273 K, a KOH solution (~20 g in 50 ml of H_2O) was added in small portions. Platinum black began to precipitate at pH 8–9. The precipitate was heated to 323–333 K and settled at room temperature for several hours. The platinum black was filtered off using a glass filter and washed with water to remove the alkali. The resulting black was dried at 303–393 K for 6 h. After calcination (at 773 K for 6 h), S_{sp} was ~6 m^2/g.

Mixed catalysts were mechanical mixtures of a support and platinum black, which were ground by attrition and pelleted. The weight concentrations of Pt were equal to that in the impregnated catalysts (3.1 and 2.6 wt % Pt in InCatPt-1 and InCatPt-2, respectively).

To retain the geometry of samples, all the catalysts were ground by attrition in an agate mortar and pelleted at a pressure of ~50 atm. The average dimensions of working samples were 5 × 5 × 2 mm.

Matrix Isolation Method with the Recording of EPR Spectra

The setup was described elsewhere [7]. Absolute methanol triply degassed by recrystallization and evacuation before each experiment was supplied from an evaporator to a reactor equipped with an electric furnace. The catalyst was put over the grid of the reactor (d_{int} = 16 mm) as a one-grain layer. The temperature in the catalytic bed zone was maintained to within 0.5 K. The flow rates of methanol vapor and oxygen, which was supplied from a gas cylinder after the removal of water vapor impurities, were controlled using fine control valves. The resulting radicals together with reaction products and unreacted methanol were frozen at 77 K in the side arm of a Dewar vessel, which was placed in the resonator of an EPR spectrometer and connected to a flow vacuum system. The photolysis of radicals in the matrix of reaction products was performed with full light from a DRSh-500 lamp, which was focused by a quartz lens to the end of the side arm of the Dewar vessel. Previously [4], it was found that, under the experimental conditions specified, the height of a condensate layer was 2–3 mm from the bottom of the arm, and the condensate distribution did not increase errors in the determination of the concentration of paramagnetic centers.

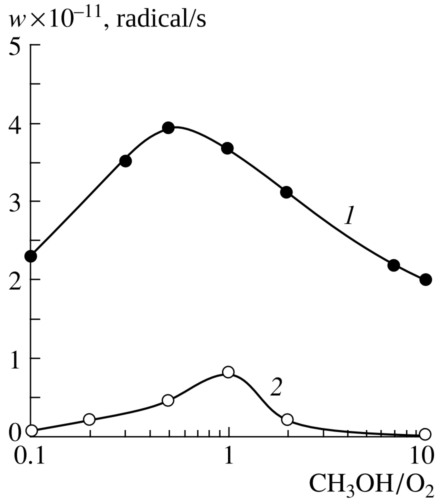


Fig. 1. Dependence of the rates of radical generation in the methanol oxidation reaction (T_{expt} = 773 K) on the composition of the reaction mixture for pure supports: (*1*) γ-Al_2O_3 (T_{tr} = 773 K) and (*2*) SiO_2 (T_{tr} = 940 K).

The experiments were performed at methanol/oxygen ratios of 0.1 : 10 under the following pretreatment conditions: T_{tr} = 943 K; oxygen pressure, ~2000 Pa; and treatment time t_{tr} = 1 h. In some experiments, the treatment temperature was changed for catalysts based on Al_2O_3 as specified below.

All the experiments were performed in the kinetic region when radical reactions did not occur in a gas phase (working pressure of 3.7 Pa). An upper pressure limit of the technique was ~13 Pa, which corresponds to the breakdown of a diffusion pump. The sensitivity of the EPR spectrometer was ~5×10^{10} paramagnetic centers under standard measurement conditions.

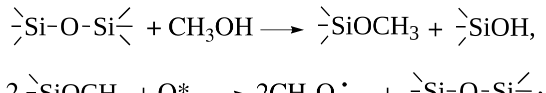
IR Spectroscopic Experiments

The IR spectra of samples in the region 400–5000 cm^{-1} were measured on a Shimadzu FTIR-8300 spectrometer with a resolution of 4 cm^{-1} in a cell suitable for high-temperature spectroscopic measurements (up to 773 K). The catalyst samples were pressed in pellets 10–15 mg/cm^2 in thickness before measuring the spectra. Next, they were placed in the cell ($V \approx 500$ cm^3) and pretreated in oxygen and then in a vacuum at 773 K with the freezing of volatile oxidation products for 1 h. Surface methoxy groups were obtained by the treatment of a catalyst sample with the vapor of absolute methanol (~6 Torr) at 523 K for 1 h followed by evacuation at the specified temperature for 1 h (to remove alcohol molecules bound to the surface by hydrogen or coordination bonds). The resulting methoxy groups were decomposed by holding the samples at 573, 673, and 773 K for 30 min. The spectra were measured at 7-min intervals. The experiments were performed both in the absence and in the presence of oxygen. In the latter case, oxygen (1–2 Torr) was added to the cell before measuring the spectra at 523 K. The treatment of experimental data included the decomposition of the resulting absorption spectra into individual Gaussian components.

RESULTS AND DISCUSSION

Matrix-Isolation Study of Radical Generation in the Gas Phase

With the use of photolysis for the identification of radicals, we found that $CH_3O^{\bullet}$ and $CH_3O_2^{\bullet}$ radicals were formed in the methanol oxidation reaction on silica gel at T = 720–920 K (the parameters of the EPR spectra of these radicals $g_{\parallel}$ = 2.03, $g_{\perp}$ = 2.008, and $A_{\perp}$ = 8.7 G were consistent with those reported previously [7]). The maximum rate of radical generation on silica gel at the reactant ratio methanol/oxygen = 1 : 1 was lower than that on a mechanical mixture of Pt + SiO_2 by a factor of 25 (Figs. 1, 2), and the apparent activation energy of the overall formation of $CH_3O^{\bullet}$ and $CH_3O_2^{\bullet}$ radicals on SiO_2 was 38.4 kcal/mol. The value of the activation energy of radical generation on the support is almost equal to the activation energy of methanol oxidation on silica gel (40 kcal/mol) determined in [17]. This agreement in activation energies suggests that the formation of the adsorption centers of methanol molecules is a rate-limiting step in the formation of radicals over the surface of silica gel. According to IR-spectroscopic data [17, 18], the adsorption of methanol resulted in the formation of $\geqslant SiOCH_3$ regardless of the structure of the adsorption center; only the mechanism of adsorption was changed. Assuming that surface intermediates are responsible for the yield of radicals to a gas phase, the heterogeneous process of radical generation can be written as



$$\geqslant Si\text{–}O\text{–}Si\leqslant + CH_3OH \longrightarrow \geqslant SiOCH_3 + \geqslant SiOH,$$

$$2\geqslant SiOCH_3 + O^* \longrightarrow 2CH_3O^{\bullet}_{(gas)} + \geqslant Si\text{–}O\text{–}Si\leqslant,$$

where O* is the active surface oxygen, which resulted from the pretreatment with oxygen.

The situation changed when Pt^0 (metal film deposited from H_2PtCl_6) or Pt/SiO_2 and Pt/Al_2O_3 (supported by impregnation) were used as catalysts. In the case of pure platinum, radicals were not detected (the rate of formation was $\ll 10^8$ radical/s) at all the tested reactant compositions and temperatures. In this case, the pressure in the system periodically changed at the ratio $MeOH/O_2$ = 1 : 1 and 873 and 893 K. It is evident that these changes were due to the oxidation of the carbon oxide formed on platinum, as described previously [19]. The Pt/SiO_2 catalyst exhibited an analogous behavior. However, in this case, along with oscillations, the pressure gradually increased to values that did not allowed us to perform experiments using this procedure. According to EXAFS data [20], deposited platinum was stabilized as Pt^0 in the lattice of silica gel. At the same time, according to IR-spectroscopic data [18], the $\geqslant SiH_x$ structures ($x = 1, 2$) and the partial oxidation products of methanol (CO and hydrogen) were formed upon the degradation of methoxy groups on the surface of silica gel at elevated temperatures (873 K). Thus, we believe that in the case of the Pt/SiO_2 catalyst the following reactions of methanol oxidation take place:

on platinum

$$CH_3OH + 1/2O_2 \longrightarrow CO + H_2O + H_2,$$

$$CO + 1/2O_2 \longrightarrow CO_2,$$

on silica gel

$$Si{-}OCH_3 \longrightarrow CO + H_2 + \geqslant Si{-}H_x.$$

In this case, a temperature shift of the oscillation regime, as compared with published data [19], was due to the effect of the support, which, in turn, can result in the formation of CO and hydrogen; this explains the increase in the pressure in the system.

Radicals were also not detected over the Pt/Al_2O_3 catalyst (the rate of formation was $\leqslant 10^8$ radical/s). The pressure in the system increased from 6×10^{-3} to 10^{-2} Torr in the first 20 min of reaction; however, it subsequently stabilized and remained constant (~10^{-2} Torr) up to the end of the experiment. According to EXAFS data [20] for supported Pt/Al_2O_3 catalysts, three types of platinum compounds can be recognized: (1) platinum metal clusters, in which Pt–Pt interatomic distances are noticeably shorter than that in the bulk metal; (2) PtO_x surface oxides; and (3) isolated platinum ions stabilized at tetrahedral cationic vacancies in γ-Al_2O_3. Because of the complicated overall behavior of active component centers, their contributions to the reaction cannot be distinguished under the conditions of our procedure. Therefore, we performed experiments for studying the reaction on a pure support.

Early attempts to detect radicals on pure γ-Al_2O_3 were unsuccessful. It is well known [21] that acid sites of different strengths are formed on the surface dehydroxylation of γ-Al_2O_3. The dependence of the concentration of acid sites on the temperature of calcination exhibited two maximums at 773 and 1073 K [21 (Fig. 7.5, p. 197)]. Because the concentrations of acid sites were minimum at 940 K (standard sample treatment conditions), we chose another temperature of 773 K as the pretreatment temperature. The other conditions remained unchanged.

As a result of a change in treatment conditions, we detected radicals on the pure support (γ-Al_2O_3) and its mechanical mixture at reaction temperatures of 723, 753, and 773 K. The EPR spectra of the radicals were analogous to the spectra of radicals formed in the methanol oxidation reaction on silica gel; they appeared as an asymmetric line typical of paramagnetic species with an axial anisotropy of the g-tensor. The corresponding main values were equal to $g_{\parallel} = 2.03$, $g_{\perp} = 2.008$, and $A_{\perp} = 8.7$ G; we attributed them to the sum of $CH_3O^{\bullet}$ and $CH_3O_2^{\bullet}$ radicals.

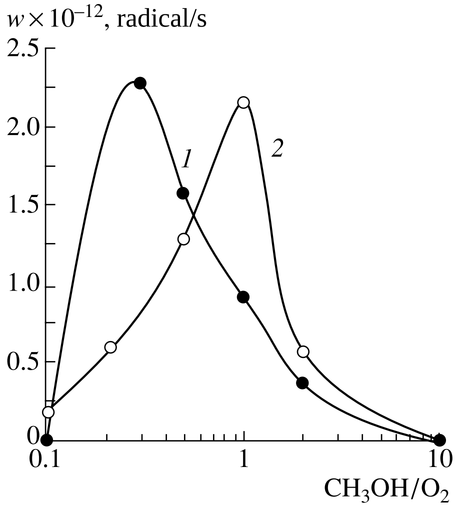


Fig. 2. Dependence of the rates of radical generation in the methanol oxidation reaction (T_{expt} = 773 K) on the composition of the reaction mixture for mixed catalysts: (*1*) Pt + Al_2O_3 (T_{tr} = 773 K) and (*2*) Pt + SiO_2 (T_{tr} = 940 K).

In repeated experiments with the supported Pt/Al_2O_3 sample, whose treatment temperature was changed to 773 K, radicals were not detected at all the test reactant compositions. Radicals were not formed in the case of the impregnated catalyst; this fact allowed us to make an assumption about the nature of active centers responsible for radical generation on the surface. In a study of the acceptor properties of an alumina surface by the paramagnetic probe method [22], it was found that the formation of Al^{3+} ions in a tetrahedral environment in the structure of the oxide and coordinatively unsaturated ions on the surface are characteristic of pure alumina. The introduction of platinum dramatically decreased the concentration of coordinatively unsaturated aluminum ions; in this case, the number of "disappeared" centers was commensurable with the number of supported platinum atoms. According to Lunina [22], a decrease in the acceptor properties of alumina is associated with the injection of electrons from the metal to the support. Because of electron transfer, the alumina surface adjacent to a metal crystallite acquires a negative charge. In this case, the depth of acceptor traps (the strength of acceptor sites) near crystallites decreases so that they cease to be acceptor sites. This approach can explain an apparent contradiction between our results and data obtained by Pak [23], who reported the formation of methylperoxy radicals in the oxidation of methanol on a Pt/Al_2O_3 (0.64 wt % Pt) supported catalyst. According to Lunina [22], the concentration of acceptor sites at this platinum content decreased by a factor of ~2.3 as compared with the concentration of acceptor sites on pure alumina. The ratio

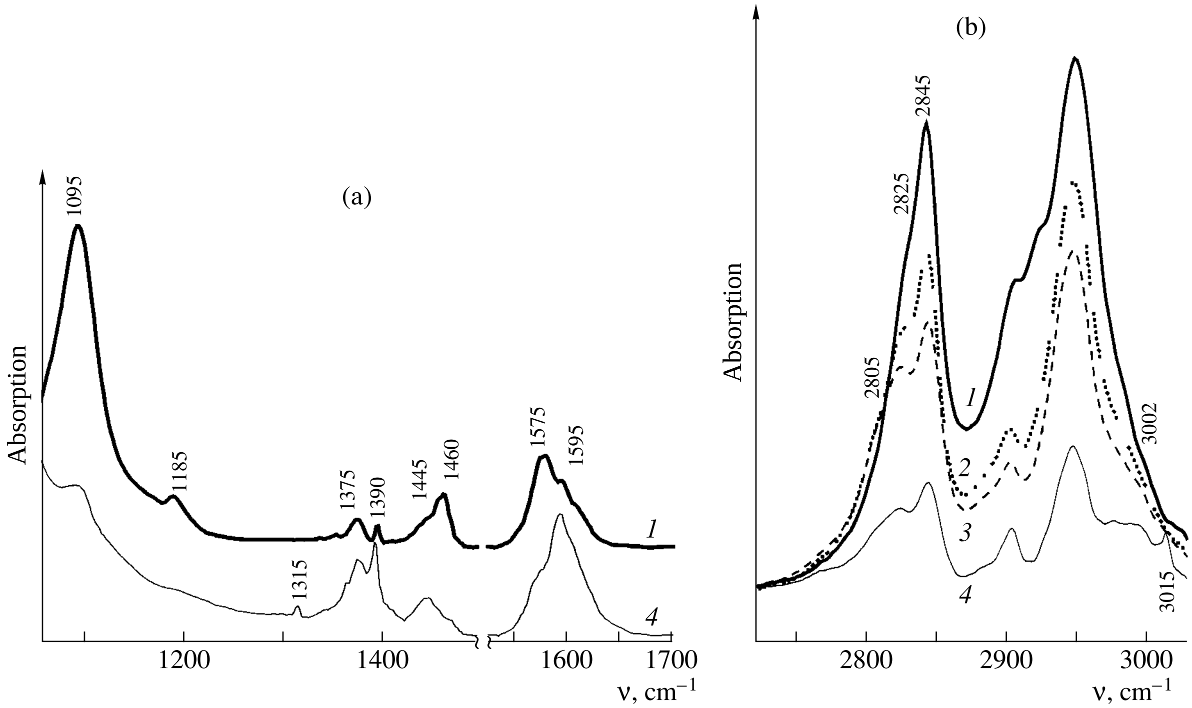


Fig. 3. Changes in the IR spectra of a sample of 2.6 wt % Pt + γ-Al_2O_3 (treated with methanol vapor at 523 K with the subsequent evacuation at T = 523 K) (a) at 1050–1700 cm^{-1} and (b) in the region of CH vibrations depending on the temperature of heating (K): (*1*) 523, (*2*) 573, (*3*) 673, and (*4*) 773.

between the rates of radical generation found in this work for the pure support and reported by Pak [23] for Pt/Al_2O_3 (0.64 wt % Pt) under identical conditions was the same (a factor of 2.32). It is likely that, as the weight concentration of Pt was increased up to 2.6 wt % in our experiments, platinum blocked centers at which the formation of surface intermediates responsible for the generation of gas-phase radicals took place.

Thus, in the order support ⟶ active component, we detected radical products only in the case of pure supports and their mechanical mixtures with platinum.

Figure 1 demonstrates the dependence of the rates of radical generation on the methanol/oxygen ratio for different supports.

The rates of radical generation on pure alumina were higher than those on pure SiO_2 by almost one order of magnitude, and they insignificantly depended on temperature.

Figure 2 demonstrates the effect of the composition of a reaction mixture on the rate of radical generation for mixed catalysts. The maximal rates of radical generation upon the addition of platinum to SiO_2 or Al_2O_3 increased in both supports (by a factor of 6 or 25, respectively). According to published data [19], in the oxidation of methanol on platinum foil, hydroxyl and methoxy radicals were formed with E_a = 20 kcal/mol. One might assume that the increase in the rate of radical generation resulted from their additional desorption from the surface of platinum. In this case, the apparent activation energy of radical generation in our experiments should be equal to E_{app} for platinum metal. However, the activation energy of $CH_3O^{\bullet}$ formation found for a Pt + SiO_2 catalyst [7] is lower than the value reported by Zum Mallen and Schmidt [19] by a factor of 3. In our opinion, the platinum–support interface plays a priority role in the case of mixed catalysts. This difference in activation energies can be explained on the assumption that the desorption of radicals from the catalyst surface is a rate-limiting step in radical generation. Taking into account that the catalyst was a mechanical mixture of a support and platinum in our experiments, we believe that a methoxy radical was formed on the platinum. Next, it migrated to the platinum–support interface, where the desorption of $CH_3O^{\bullet}$ is energetically favored, because of a spillover. The effect of pretreatment on the rate of radical generation is indirect evidence for the above consideration. Thus, the pretreatment in the presence of oxygen increased the rate of radical generation by a factor of 2–2.5 for both supports.

We obtained additional corroboration of the hypothesis that the support plays a crucial role in the generation of radicals by analysis of the composition of resulting radicals. We found that the nature of radicals desorbed from the surface of a pure support or its mechanical mixture with platinum remained practically unchanged. At the same time, the composition of radicals strongly depended on the initial reactant concentrations. Thus, ~80% $CH_3O^{\bullet}$ and 20% $CH_3O_2^{\bullet}$ radicals were formed on SiO_2 and Pt + SiO_2 catalysts at the composition methanol/oxygen = 1 : 1. As the concentration of oxygen was increased, the concentration of methylperoxy radicals somewhat increased, whereas the methylperoxy radical was not detected in reducing mixtures (where the alcohol concentration was higher than the oxygen concentration); however, the $CHO^{\bullet}$ radical with proton splitting of ~127 G appeared. The methylperoxy radicals were practically not detected in catalysts based on γ-Al_2O_3, whereas the formyl radical was formed in an excess of methanol. The table summarizes changes in the composition of frozen radicals depending on the alcohol/oxygen ratio in the initial reaction mixture.[1]

In Situ IR Spectroscopic Study of Surface Groups

The treatment of samples based on Al_2O_3 with methanol at 523 K followed by evacuation at the above temperature resulted in the formation of three types of surface methoxy groups (two terminal and one bridging group). These groups can be identified by the following absorption bands observed in the IR spectra (Fig. 3, spectrum *1*): (I) $CH_3O{-}Al_{oct}$ (ν_s(C–H) = 2806 cm^{-1}), (II) $CH_3O{-}Al_{tetr}$ (ν_s(C–H) = 2825 cm^{-1}), and (III) $CH_3O < (Al)_2$ (ν_S(C–H) = 2845 cm^{-1}, δ_{as}(C–H) = 1460 cm^{-1}, δ_s(C–H) = 1440 cm^{-1}, $r_{\|}$ (CH_3) = 1185 cm^{-1}, and ν(C–O) = 1095 cm^{-1}) [24], which form hydrogen bonds with the neighboring OH groups of alumina (ν(O··H) = 3450–3565 cm^{-1}). The composition of the sample influenced the formation and conversion of surface groups in the course of thermal treatment. Only methoxy groups were formed on the surface of alumina at 523 K; other surface groups, which will be considered below, were also formed upon the treatment of Pt-containing catalysts.

An increase in the cell temperature to 573 K in the absence of oxygen resulted in a decrease in the intensities of absorption bands at 2845 and 2825 cm^{-1} and an increase in the intensity of an absorption band at 2805 cm^{-1} in the IR spectra of the pure support (Fig. 4a). This corresponds to the decrease in the concentrations of bridging and terminal methoxyls (types III and II) and the increase in the concentration of terminal methoxy groups (type I). According to Moravek *et al.* [25], the conversion of methoxy complexes $CH_3O< \longleftrightarrow CH_3O-$ can occur by an associative mechanism of catalytic dehydration via bimolecular substitution with the participation of two neighboring surface sites. An increase in the temperature to 673 K resulted in a decrease in the concentrations of all types of methoxyls (Fig. 4a) and the formation of new surface compounds, which are characterized by the absorption bands ν(C–H) = 3002, ν_{as}(C–O) = 1595, ν_S(C–O) = 1390, and δ(C–H) = 1375 cm^{-1} in the IR spectra. According to Matyshak *et al.* [26], they are due to the formation of HCOO– formate structures. The concentration of

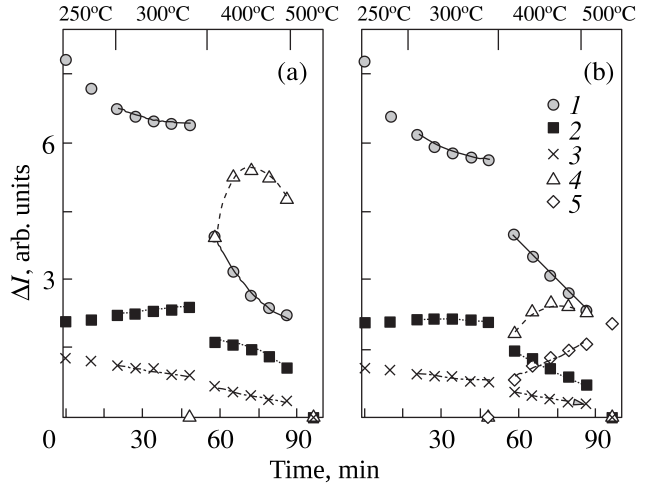


Fig. 4. Changes in the absorption band intensities of surface groups and gas-phase methane on heating a γ-Al_2O_3 sample: (a) without oxygen and (b) on the addition of oxygen (1 Torr) at the beginning of heating. (*1*) ν_s(C–H) ($CH_3O <(Al)_2$), 2845 cm^{-1}; (*2*) ν_s(C–H) ($CH_3O - Al_{oct}$), 2805 cm^{-1}; (*3*) ν_s(C–H) ($CH_3O - Al_{tetr}$), 2825 cm^{-1}; (*4*) ν_s(C–O) (HCOO–), 1390 cm^{-1}; and (*5*) ν_s(C–H) (CH_4), 3015 cm^{-1}. The temperatures of heating over the corresponding time intervals are specified at the top of the figure.

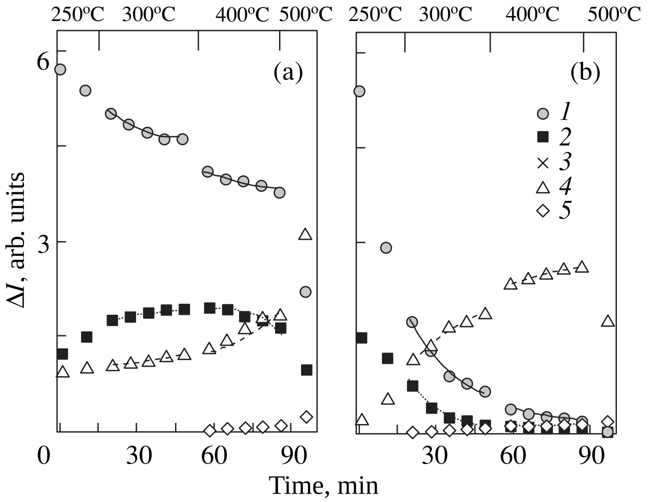


Fig. 5. Changes in the absorption band intensities of surface groups and gas-phase methane on heating a Pt + γ-Al_2O_3 sample (see Fig. 4 for notation): (a) without oxygen and (b) on the addition of oxygen (1 Torr) at the beginning of heating.

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[1] We compared the compositions of radicals only for mechanical mixtures. Because the rates of radical generation in the mixed systems were considerably higher, errors in the relative radical concentrations decreased with the use of photolysis for identification.

Composition of radical products in the methanol oxidation reaction on mixed catalysts at a reaction temperature of 773 K

Methanol/oxygen ratio	Radical composition	
	Pt + SiO_2	Pt + Al_2O_3
10 : 1	2.2% $HC^\bullet O$, 97.8% $CH_3O^\bullet$	Not detected
5 : 1	94% $CH_3O^\bullet$, 4% $CH_3O_2^\bullet$, 2% $HC^\bullet O$	~100% $CH_3O^\bullet$, trace $HC^\bullet O$
2 : 1	93% $CH_3O^\bullet$, 7% $CH_3O_2^\bullet$	100% $CH_3O^\bullet$
1 : 1	80% $CH_3O^\bullet$, 20% $CH_3O_2^\bullet$	91% $CH_3O^\bullet$, 9% $CH_3O_2^\bullet$
1 : 2	76% $CH_3O^\bullet$, 24% $CH_3O_2^\bullet$	88% $CH_3O^\bullet$, 12% $CH_3O_2^\bullet$
1 : 10	Not detected	Not detected

HCOO– passed through a maximum in the course of the decomposition of methoxy groups at 673 K. Yamashita *et al.* [27] studied the behavior of surface formates in the decomposition of methanol on Cr_2O_3; they explained an analogous effect that was manifested as the extremal dependence of formate concentrations by the formation of methoxy–formate complexes. It is likely that such complexes are also formed on the surface of alumina to increase the rate of formate decomposition at temperatures higher than 673 K. At 773 K, the complete decomposition of formate and methoxy structures occurred with the release of CO_2 and water, which were readsorbed with the formation of surface ammonium bicarbonate on cooling the sample to 298 K (absorption bands at 1230, 1445, and 1650 cm^{-1}) [28]. Moreover, the IR spectrum of the sample heated at 673 K exhibited the appearance of a weak absorption band at 1690 cm^{-1}, which can be attributed to the absorption of adsorbed formaldehyde. Thus, we can assume the occurrence of the following surface reactions:

$$CH_3O{<}(Al)_2 \longleftrightarrow CH_3O\text{–}Al,$$

$$CH_3O\text{–}Al \xrightarrow{400°C} HCOO\text{–}Al \xrightarrow{500°C} CO_{2(gas)} + H_2O_{(gas)},$$

$$CH_3O\text{–}Al \xrightarrow{400°C} CH_2O_{ads}$$

$$+ HO\text{–}Al \xrightarrow{500°C} CO_{2(gas)} + H_2O_{(gas)}.$$

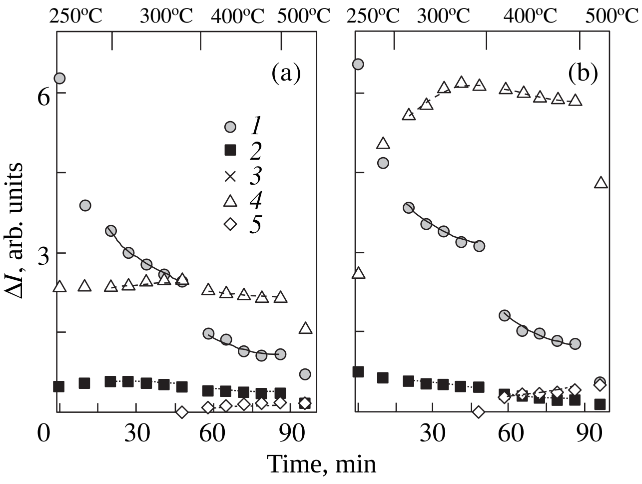


Fig. 6. Changes in the absorption band intensities of surface groups and gas-phase methane on heating a Pt/γ-Al_2O_3 sample (see Fig. 4 for notation): (a) without oxygen and (b) on the addition of oxygen (1 Torr) at the beginning of heating.

In this case, formates are formed with the participation of neighboring lattice oxygen atoms of the support.

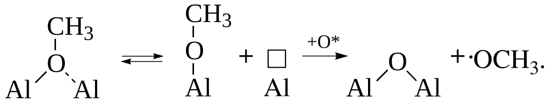
In accordance with Fig. 4, the addition of gaseous oxygen to the system did not change the rate and temperature of decomposition of bridging and terminal methoxyls; however, differences in the products of their reactions were observed. According to IR-spectroscopic data, the formation of carboxylate–carbonate surface structures, which are characterized by absorption bands at 1445, 1530–1550, and 1575 cm^{-1}, was observed on heating to 673 K. Methane (ν(C–H) = 3015 and δ(C–H) = 1305 cm^{-1}) and CO (broad absorption band at 2110–2165 cm^{-1} with a minimum at 2140 cm^{-1}) appeared in the gas phase. Carbon monoxide may be a decomposition product of formaldehyde. The concentration of surface formate structures formed at 673 K was lower than that in the absence of gaseous oxygen by a factor of ~2. This is likely due to the rapid final oxidation of these structures to the gaseous products of deep oxidation. Thus, in the presence of gas-phase oxygen, the conversion of methoxy groups occurred via an additional reaction path to form surface carbonate–carboxylate complexes and CH_4, and CO in the gas phase. The mechanism of methane formation is unclear; probably, it is formed by the decomposition of formate–methoxy complexes

$$[HCOO^{-}\cdots CH_3O^{-}] \longrightarrow CH_{4(gas)} + CO_3^{2-}.$$

An analysis of the IR spectra of γ-Al_2O_3 and its mechanical mixture with platinum suggests that differences in the behavior of reaction intermediates were observed even when catalyst surfaces were treated with methanol vapor at 523 K followed by evacuation at the specified temperature. In the sample of a mechanical mixture of Pt + γ-Al_2O_3, three types of methoxy groups, which were described above, as well as formate and carboxylate (ν_{as}(C–O) = 1575 and ν_S(C–O) = 1440 cm^{-1}) surface complexes, were identified using IR-spectroscopic data (Fig. 3b, spectrum *1*). The lower temperature of the formation of HCOO– and RCOO– structures on the addition of platinum to alumina can result from the formation (on the oxidative treatment of the sample) of chemisorbed oxygen, which is active in the oxidation of methanol or methoxyls, on the platinum at the step of the initial treatment. Endo *et al.* [29] observed the formation of formates in the oxidation of methanol with molecular oxygen on Pt(111) under conditions of a high vacuum. They found that formate degradation at temperatures higher than 420 K resulted in the formation of deep oxidation products: carbon dioxide and water. Figures 3 and 5 illustrate the decomposition of the resulting surface groups in the absence and presence of gaseous oxygen, respectively (a change in the intensity of the absorption band ν_s(C–H) = 2825 cm^{-1}, which characterizes the terminal methoxy groups CH_3O–Al_{tetr}, is not shown in Fig. 5; the decrease in the concentration of these groups upon decomposition is proportional to the decrease in the concentration of bridging methoxy groups). The decomposition of all the types of methoxy groups on the sample of a mechanical mixture under oxygen-free conditions occurred similarly to the decomposition of methoxyls on pure alumina but at a lower rate: the IR spectra exhibited the absorption bands of the three types of methoxy groups even at 773 K (Fig. 3, spectrum *4* and Fig. 5a). The resulting surface formate complexes did not degrade with the formation of $CO_{2(gas)} + H_2O_{(gas)}$. Methane traces were detected in the gas phase upon heating above 673 K. In the presence of oxygen, the decomposition of all the types of surface methoxyl complexes on the sample of a mechanical mixture of Pt + γ-Al_2O_3 was considerably accelerated (Fig. 5b). The heating of the sample to 773 K decreased the concentration of bridging methoxyls by a factor of ~15 (proportionally to a change in the intensity of the absorption band ν_s(C–H) = 2845 cm^{-1}), as compared with a decrease in the concentration of $CH_3O<$ by a factor of ~1.5 under oxygen-free conditions. A portion of the resulting formate structures was oxidized at 773 K with the release of CO_2 and water into the gas phase. In the gas phase, methane traces were detected at 573 K or higher.

A comparison between the rates of decomposition of methoxyl complexes for γ-Al_2O_3 and its mechanical mixture with platinum suggests (Figs. 4b, 5b) that the rate was much higher in the latter case in the presence of gas-phase oxygen. In kinetic experiments with the use of matrix isolation method, we found that the amount of the resulting methoxy radicals in the mechanical mixture of Pt + γ-Al_2O_3 was several times greater than that in the case of pure alumina. Assuming that methoxy radicals appeared in the gas phase because of the decomposition of surface methoxyl complexes, we can conclude that the role of Pt consists in the activation of oxygen. It is likely that oxygen is of first importance in the formation of methoxy radicals. The following reaction scheme can be proposed for radical generation on the mechanical mixture of Pt + γ-Al_2O_3:

$$\mathrm{Pt} + 1/2\mathrm{O}_{2(\mathrm{gas})} \longrightarrow \mathrm{O}^*,$$



$$\underset{\mathrm{Al}\quad\mathrm{Al}}{\overset{\mathrm{CH_3}}{\mathrm{O}}} \rightleftarrows \underset{\mathrm{Al}}{\overset{\mathrm{CH_3}}{\mathrm{O}}} + \square \xrightarrow{+\mathrm{O}^*} \underset{\mathrm{Al}\quad\mathrm{Al}}{\mathrm{O}} + {}^{\cdot}\mathrm{OCH_3}.$$

$$\underset{\mathrm{Al}}{} \quad \mathrm{Al}$$

This reaction path can lead to the formation of additional free radicals from the support, along with radicals formed by a spillover. It is likely that radical generation on the γ-Al_2O_3 surface occurs analogously, but in this case activated oxygen is formed in the process of surface dehydration.

As demonstrated above, along with methoxy radicals, peroxy and formyl radicals were detected in the oxidation of methanol. We believe that they are formed in the secondary reactions of methoxyl with activated oxygen:

$$\mathrm{CH_3O^{\bullet}} + \mathrm{O}^* \longrightarrow \mathrm{CH_3O_2^{\bullet}}^* \longrightarrow \mathrm{CH_3O^{\bullet}_{2(gas)}},$$

$$\mathrm{CH_3O_2^{\bullet}}^* \longrightarrow \mathrm{CH_3O_2^{\bullet}};\ \mathrm{CH_3O_2^{\bullet}}^* \longrightarrow \mathrm{HCO^{\bullet}} + \mathrm{H_2O}.$$

Here, $CH_3O_2^{\bullet}*$ (ads) is the peroxy radical resulting from the interaction with oxygen in the coordination sphere of Al^{+3}, usually in the electronically excited state. As evidenced by the results of photolysis, one of the reaction paths of this species consists in the formation of the formyl radical.

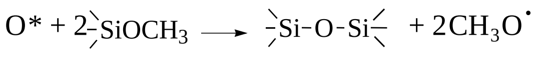
In the study of the supported catalysts by kinetic experiments using matrix isolation method, the formation of radicals was not detected at all the tested compositions of the reaction mixtures. This finding was supported by IR-spectroscopic data. The treatment of the surface of supported platinum catalysts with methanol vapor at 523 K followed by evacuation at the specified temperature resulted in the formation of not only the three types of surface methoxy groups and surface formate complexes, which were described for the mechanical mixture of Pt + γ-Al_2O_3, but also platinum carbonyls. The IR spectra exhibited intense absorption bands at 1790, 2025, 2060, 2080, and 2110 cm^{-1}, which characterize bridging and terminal CO complexes on Pt^0 platinum metal clusters of different sizes and $Pt^{\delta+}$ [30, 31]. It is likely that CO and hydrogen are the main decomposition products of methoxyl complexes formed on the surface of supported samples under oxygen-free conditions at 523–573 K. The IR spectra exhibited a considerable increase in the absorption band intensities of platinum carbonyls. At 673–773 K, only the products of full oxidation were detected among the decomposition products of methoxyls. The introduction of oxygen into the system at 523 K decomposed carbonyls on platinum metal. On heating above

573 K, the IR spectra exhibited a continuous increase in absorption bands due to CO in the gas phase. Moreover, a considerable increase in the intensities of absorption bands due to formate structures was observed, which is indicative of the rapid oxidation of methoxyl complexes by oxygen activated on dispersed platinum metal (Fig. 6). In the absence of oxygen, methoxyl complexes on the surface of supported catalysts decomposed with the release of CO; in an excess of oxygen, the mechanism of rapid oxidation to formates came into play. Thus, the absence of radicals from the gas phase in the case of supported platinum catalysts is likely due to a low steady-sate concentration of surface intermediates because of their rapid conversion into nonparamagnetic stable decomposition products. According to published data, the rate of methanol decomposition on the Pt/Al_2O_3 and Ni/Al_2O_3 supported metal catalysts is higher than the rate of methanol decomposition on the support by a factor of ~10^6 [32]. Correspondingly, both the steady-state concentration of intermediates and the rate of radical desorption into the gas phase should decrease to the same extent.

The treatment of samples based on silica gel with absolute methanol at 523 K followed by evacuation at the specified temperature resulted in the formation of surface methoxy groups with the simultaneous degradation of methanol to CO and H_2O. The IR spectra exhibited the absorption bands $\nu_{as}(C–H) = 2997$, $\nu_{as}(C–H) = 2959$, $\nu_s(C–H) = 2857$, and $\delta(CH_3) = 1450$ cm^{-1}, which characterize isolated methoxy groups formed in the reaction of methanol with isolated hydroxyl groups of silica gel, and an absorption band with $\nu(O–H) = 3400–3550$ cm^{-1}, which characterizes hydrogen-bonded methoxy groups formed by the chemisorption of methanol at siloxane bridges [17]. The isolated methoxy groups exhibit enhanced thermal stability: they underwent no degradation or oxidation on heating the samples to 800 K [33] (the temperature range of radical detection).

An increase in the concentration of methoxy groups on the surface of a mixed catalyst increased the rate of radical generation due to the adsorption substitution

$$Pt + 1/2O_2 \longrightarrow O^*,$$



$$O^* + 2\equiv SiOCH_3 \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + 2CH_3O^{\bullet}$$

and/or the spillover of methoxy radicals from platinum.

Radical Stop Effect

An interesting effect was found on the Pt + γ-Al_2O_3 catalyst at the ratio methanol/oxygen = 10 : 1 with the use of matrix isolation method. Because the pressure in the system increased from 10^{-4} to 10^{-1} Torr (beyond the working range of a diffusion pump; the signal intensity of radicals remained at a noise level) after radical accumulation for ~45 min, the supply of methanol was terminated, whereas the flow of oxygen remained unchanged. In this case, the pressure in the system decreased to 4×10^{-2} Torr in 3 min, whereas the signal intensity increased by a factor of ~6. That is, the rate of radical desorption after the termination of supplying methanol increased by almost two orders of magnitude. After 10 min, the pressure in the system increased again and stabilized at a value of ~2×10^{-2} Torr after 35 min with a slow increase in the signal intensity. The repeated supply of methanol to the reactor resulted in an increase in the pressure to limiting values in 3 min, and the signal intensity continued to increase for 50 min after stopping the flows of methanol and oxygen.

An analogous so-called stop effect was described [34–36] for the heterogeneous oxidation reactions of alcohols and amines on amphoteric metal oxides, when the termination of the flow of a reactant resulted in a considerable change in the rate of formation of final products. The appearance of the stop effect for radical products is indicative of a significant contribution of radical reactions under conditions of a nonstationary state of the catalyst surface; this opens up the way to the determination of elementary steps in the reaction mechanism of methanol oxidation. Because the composition of the gas phase smoothly changed (from the ratio methanol/oxygen = 10 : 1 to 1 : 10) when the flow of methanol was terminated, we actually observed the formation of radicals over the entire range of concentrations.

CONCLUSIONS

A comparison between experimental conditions in the studies of methanol oxidation using Fourier transform IR spectroscopy and matrix isolation method indicates that the initial conditions (catalysts, catalyst treatment conditions, temperature regions, and reactant compositions) were identical or overlapping, whereas the modes of reactant supply to the catalyst surface were different. Flow conditions with a varied composition of the reactants in a flow were used (methanol/oxygen = 0.1–10) in the matrix isolation method technique, whereas the stationary conditions of methanol chemisorption at 523 K were used in the IR-spectroscopic experiments, and the reactions of surface intermediates in the presence or in the absence of oxygen in the gas phase were studied over the temperature region of radical detection. In the case of the IR-spectroscopic experiments, the ratio between the reactants (the amount of chemisorbed methanol/the amount of oxygen in the gas phase) was 4 : 1, which corresponded to the center of the range of compositions studied by matrix isolation method.

As demonstrated above, methoxy and formate groups (main intermediates in the catalytic reactions of methanol oxidation) were detected on the surfaces of catalysts based on γ-Al_2O_3 in all the test systems. It would be expected that the detected surface species are the precursors of gas-phase radicals, which were detected in the matrix isolation method experiments.

The chemisorption of the methanol molecule on alumina resulted in the methoxy anion stabilized on the Al^{3+} cation and a proton, which reacted with the neighboring basic O^{2-} to form the hydroxyl group. Methoxy groups on the surface of γ-Al_2O_3 are mobile and reactive. This manifests itself in the rearrangement of the species of types II and III into the methoxy groups of type I and in the formation of formate structures with the simultaneous consumption of methoxyls. In the case of silica gel, chemisorbed methanol is the methoxy group stabilized at isolated silicon cations (at the sites of isolated hydroxyl groups) or hydrogen-bonded methoxyls formed on the chemisorption of methanol at siloxane bridges. Because the methoxy group stabilized at isolated silicon cations are thermally stable up to 800 K [18], it is likely that in this temperature region methoxyls that are desorbed from siloxane bridges contribute to the formation of gas-phase radicals. As estimated previously [37], the number of active surface sites on silica gel after treatment at 973 K was ~1.5×10^{-4} mol/g, and the concentration ratio was [SiOH]/[SiOSi] = 2 : 1. At the same time, according to published data [38], the concentration of active surface sites for various aluminum modifications was ~10^{18} site/m^2, which gave a value of ~3×10^{-3} mol/g based on the surface area of the support used in this work. Thus, the contribution of surface methoxyls to the formation of gas-phase radicals on alumina should be at least one order of magnitude higher than that on silica gel. These estimated values are consistent with the results of matrix isolation method experiments (Fig. 1), when the rates of formation of total $CH_3O^{\bullet}$ and $CH_3OO^{\bullet}$ radicals on the pure supports were compared.

The introduction of platinum changed the structure of active surface sites. According to published data [20], supported catalysts based on alumina contained a set of PtO_n mixed oxides (where $n \geq 1$), PtO_xCl_y incorporated into the oxygen sublattice of Al_2O_3, and Pt^0 metal clusters of different size. In supported platinum catalysts based on silica gel, Pt^0 clusters with a size of ~10–15 Å were formed. The amount of oxidized platinum in the catalyst increased after high-temperature pretreatment in oxygen; in this case, finely dispersed Pt^0 clusters (up to 15 Å in size) disappeared, but the metal core of large clusters (> 60 Å) was retained [20]. The disappeared clusters were converted into PtO_2; it is likely that they were also incorporated into the lattice of the support. Based on the experimental results (see Fig. 6), we believe that the inclusion sites and/or boundaries serve as the sites of formation (stabilization) of formate structures and, consequently, regions where the deep oxidation of methanol occurs.

It is likely that the size of Pt aggregates in mixed catalysts remained unchanged (according to optical microscopic data, the characteristic size of these aggregates is 0.8–70 μm). Under reaction conditions, the surface of aggregates was covered with chemisorbed oxygen atoms, which formed a boundary layer near Pt^0 aggregates. It is likely that this boundary layer exhibits special properties. The special properties of this boundary layer can be due to a superequilibrium amount of methoxy groups under reaction conditions. Methoxy particles that were formed on platinum, which tend to stabilize on the support by the spillover mechanism, and methoxy groups that migrated by the reverse spillover mechanism from the support to the active component simultaneously diffused to the platinum–support interface. When the surface sites of the support near the interface are blocked by chemisorbed methanol, the methoxy particles that tend to the interface from platinum can provide an additional reaction path for the formation of gas-phase radicals. In terms of this reaction scheme, we can explain the lower activation energy of the formation of gas-phase radicals for the SiO_2 + Pt catalyst, as compared with the energies of radical generation on the support and the active component.

The absence of data on the molar absorption coefficients of methoxy and formate groups on catalyst surfaces does not allow us to quantitatively compare the rates of conversion of surface groups and the rates of formation of gas-phase radicals; this comparison will be the subject matter of further studies.

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