

The radicals generation in the methanol oxidation on a Pt-containing catalysts. Influence of support acidic properties

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Abstract

Gas phase radicals, formed during methanol oxidation, have been investigated for series of Pt-containing catalysts with different support acidic properties, using matrix isolation method. Generation rates and activation energies were determined. It was estimated that strength and concentration of active surface sites play an important role in radicals generation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methanol oxidation; Gas phase radicals; Pt-containing catalysts

1. Introduction

Surface intermediates, mechanisms of their formation and their role in free radicals generation attract research interest regarding the mechanisms of heterogeneous–homogeneous reactions. It is also important to estimate the contribution of gas phase radicals into the general scheme of reaction mechanism.

In order to distinguish the role of active component and support in radicals generation, we examined changing of the reaction kinetic parameters provided by catalysts on supports with different acidic properties. So we have studied the gas phase radicals formed during the methanol oxidation on Pt-containing catalysts for the series catalysts: pure support (SiO_2 or $\gamma\text{-Al}_2\text{O}_3$) → mechanical mixture of platinum

black and support → impregnated catalysts → pure Pt, using matrix isolation method with EPR spectra recording [1–3]. There are several reasons to study methanol oxidation. On the one hand, methanol is widely used as feedstock for formaldehyde and other chemicals production and for fuel cells. On the other hand, it is one of the main intermediates in methane and other light hydrocarbons oxidative processes. However, in spite of numerous works concerned with methanol adsorption, decomposition and oxidation, a fundamental understanding of mechanism is lacking.

2. Experimental

2.1. Samples

Pure Pt metal film was deposited on the quartz reactor walls from H_2PtCl_6 .

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Impregnated catalysts Pt/SiO₂ (InCatPt-1) and Pt/Al₂O₃ (InCatPt-2) were prepared in the Omsk Department of the Institute of Catalysis according to the standard EurPt procedure [4,5].

Alumina of the A-1 trademark ($S_{sp} = 186 \text{ m}^2/\text{g}$, $V_p = 0.51 \text{ cm}^3/\text{g}$) was used for the purpose. The same alumina was used for preparation of mechanical mixtures.

Silica of the KSKG trademark ($S_{sp} = 300 \text{ m}^2/\text{g}$, $V_p = 0.84 \text{ cm}^3/\text{g}$) was at first washed with concentrated nitric acid, then milled and pressed to tablets under 50 atm. The same silica was used for preparation of mixed catalyst.

Mixed catalysts were prepared by support mixing with platinum black, and then were pressed to tablets under 50 atm. Content of platinum in the catalysts being exactly the same as in the impregnated samples (InCatPt-1–3.1 wt.% Pt, InCatPt-2–2.6 wt.% Pt).

2.2. Methods

We have registered radicals desorbing from the catalyst surface during methanol oxidation by molecular oxygen (work pressure 3.7 Pa, reaction temperature 720–920 K). All experiments were carried out in kinetic region, when no reaction between radicals occurs in the gas phase.

The experimental setup was described in detail elsewhere [3]. Absolute methanol, trice degassed by recrystallization and pumping, being passed from evaporator into reactor. Oxygen was pre-dried. Oxygen and methanol pressures were finely regulated by a flow meter. Catalyst was disposed over reactor grid as a one-grain layer. Radicals together with other reaction products were frozen out in the side arm of Dewar vessel installed in the EPR resonator and connected to the flow vacuum system. Radicals photolysis was done with the full light of mercury lamp (DRSh-500, Russia).

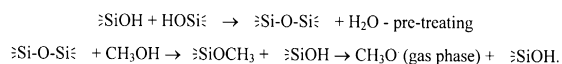
Reaction was performed at different methanol/oxygen ratios, ranging from 10 to 0.1, component pressures being $\sim 1.3 \text{ Pa}$. Silica

based samples were pre-treated at 940 K in a oxygen flow ($\sim 2000 \text{ Pa}$) during 1 h. Alumina based catalysts were then treated at other conditions (see below for the data obtained).

3. Results and discussion

In the course of our previous study we suggested special method to identify radicals, which is based on the different resistance of radicals to photolysis under the full light of high pressure mercury lamp [3]. Recently our data were confirmed by Applegate et al. [6].

We have found radicals CH₃O ($\sim 80\%$) and CH₃O₂ ($\sim 20\%$) to form simultaneously on catalytic systems Pt + SiO₂ and SiO₂, and activation energies for radicals generation are 7 and 38.4 kcal/mol, respectively. Activation energy value for SiO₂ sample well agrees with reported IRS data [7,8] revealing the mechanism of methanol adsorption and decomposition on silica. Dehydroxylation on silica surface produces surface sites with silicon in different configurations. Methanol adsorption gives >SiOCH_3 species independently on the active site configuration, only adsorption mechanism changes. Assuming that surface intermediates are responsible for radicals evolution into the gas phase, we may write their generation process as



This scheme explains why no OH-radicals are registered by the EPR. Obviously, OH radicals are strongly adsorbed on the silica surface.

Situation changes, however, when catalyst is Pt⁰ or Pt/SiO₂ and Pt/Al₂O₃ (impregnation catalysts). No radicals are registered over pure platinum at any temperatures and inlet reaction mixture compositions. Pressure periodically changes in the system most likely due to CO oxidation, as in study [9]. Catalyst Pt/SiO₂

behaves similarly, though beside oscillations pressure progressively grows to values more than 13 Pa (outside of work region). According to EXAFS data [10], deposited Pt is stabilized in the silica lattice as Pt⁰. According to IRS studies [7,8], methoxy groups decomposing on the silica surface at elevated temperatures (873 K) produce radical like structures $\geq\text{SiH}_x$ species ($x = 1, 2$), which are able to produce the partial methanol oxidation products: CO and hydrogen. So CO oxidation on Pt⁰ causes the pressure oscillations while hydrogen production causes the pressure increasing.

On catalyst Pt/Al₂O₃ radicals are also not registered during 215 min of accumulation for all temperatures and mixture compositions. Pressure, though growing in the first 15–20 min from 0.8 to 1.3 Pa, then stabilizes till the run end. According to EXAFS data for supported Pt/Al₂O₃ [10], there are three types of platinum compounds on the surface: (1) small clusters of metal platinum, where inter-atomic distances Pt–Pt are noticeably shorter than in the bulk platinum, (2) surface platinum oxides PtO_x, and (3) isolated platinum ions stabilized in the tetrahedron cation vacancies of alumina. Relative contribution of these compounds and surface oxide structure are sensitive to storage conditions and catalyst activation procedure. Since we were unable to distinguish the contribution of different surface sites into reaction mechanism using our method, we began experiments with pure support.

At first we failed to register radicals on γ -Al₂O₃. As we know from the literature [11], γ -Al₂O₃ surface hydroxylation produces various strength acid sites. Sites concentration versus calcination temperature goes through two maxima at 773 and 1073 K (see Fig. 7.5, p. 197, Ref. [11]). Since at 940 K (standard conditions for samples pre-treatment) acid sites concentration is minimum, we changes the temperature of samples treatment to 773 K, other conditions being the same.

As a result we registered radicals at 723, 753, and 773 K reaction temperatures. The radicals

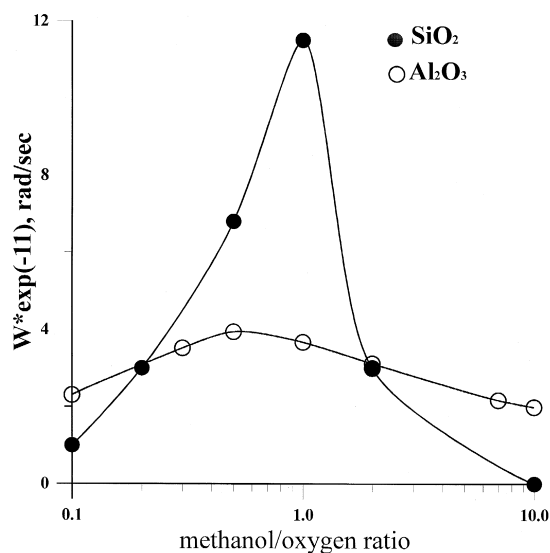
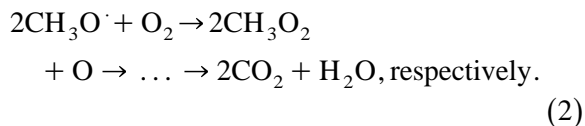
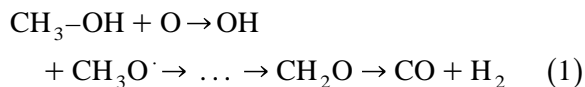


Fig. 1. Dependencies of radicals generation rates (rad/s) vs. methanol/oxygen ratio in methanol oxidation for pure supports at $T_{\text{exp}} = 773$ K. (●) SiO₂, (○) Al₂O₃.

spectrum parameters are $g_{\parallel} = 2.03$, $g_{\perp} = 2.008$, $A_{\perp} = 8.7$ G, similar to those of radicals, generated in methanol oxidation on silica [3] and we ascribe them to sum of CH₃O and CH₃O₂.

Radicals formation rate on alumina is by an order of magnitude less than that on pure silica, and insignificantly depends on the temperature. This is most likely provided by a low concentration of sites responsible for radicals generation, and thus by a lower value of pre-exponent factor in the Arrhenius equation.

Fig. 1 shows how radicals generation rate depends on the methanol/oxygen ratio for various support materials. The extreme character of these dependencies supports our assumption that methoxy radicals are the main intermediates in methanol oxidation. Most likely, methanol dehydrogenation competes with deep oxidation according to a formal scheme:



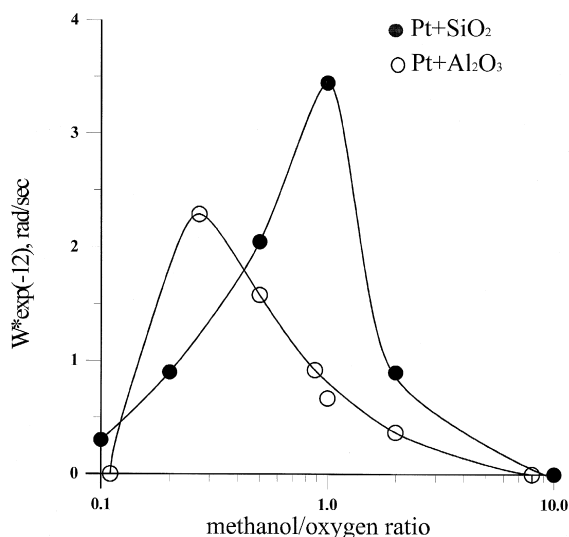


Fig. 2. Dependencies of radicals generation rates (rad/s) vs. methanol/oxygen ratio in methanol oxidation for mixture catalysts at $T_{\text{exp}} = 773$ K. (●) Pt + SiO₂, (○) Pt + Al₂O₃.

Fig. 2 shows radical formation rate versus catalyst composition for mixed catalysts. Platinum introduction increases radicals formation rate by a factor of 4–6 on both supports. Platinum effect on the activation of radicals formation is ambiguous. On the one hand, platinum opens additional ways for methoxy radicals to form. On the other hand, activation energy determined for Pt + SiO₂ is three times lower than that reported by Zum Mallen and Schmidt [9] for platinum foil (20 kcal/mol). Such a difference may be explained if we assume that radical desorption limits radical generation. Taking into account that catalyst is a mechanical mixture of platinum and support, we expect that methoxy radicals form on platinum, as for HO· radicals, and then spill over to platinum/support interface, where desorption is easier with respect to energy. Pretreatment effect on the rate of radicals generation confirms this idea indirectly. Indeed, pretreatment in oxygen at $T_{\text{tr}} = 940$ K and $P(\text{O}_2) = 2000$ Pa increases radicals generation rate by a factor of 2–2.5 on silica and 4–4.5 on alumina.

The observed shift of maximum rates for various type supports is most likely caused by the different concentration of surface active sites and their strength. The effect on pre-treatment temperature on radicals generation over alumina supported catalysts indirectly confirms this assumption.

4. Conclusion

Serial approach to studying the radicals generation in the system «support → active component» shows that not only active component but both support and platinum/support interface origin play important role in radicals evolution into the gas phase.

Based on experimental data, we suggest that strength and concentration of acid sites determine methanol adsorption, and thus reaction route.

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