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Concerning the Deep Catalytic Oxidation of Methanol in Aqueous Media

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Abstract

Deep methanol oxidation in aqueous solutions with the methanol concentration lower than 2.0 mass % within temperature range 250–450 °C is considered. Experiments were carried out with industrial catalysts based on aluminum oxide with active components such as platinum as well as copper, chromium, iron, and magnesium oxides. The minimum concentration of methanol after oxidation ($\leq 3 \text{ mg/dm}^3$) was achieved for $\text{CuO/Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Most likely, the methanol oxidation on the catalysts of this type proceeds according to the Mars–van Krevelen mechanism, wherein reactive oxygen species responsible for deep oxidation are presented by the lattice oxygen of the catalyst. TPD spectra were obtained for oxygen, methanol, water, as well as for methanol and water in simultaneous presence, within the temperature range of 100–950 °C.

Key words: catalysis, deep oxidation, methanol, water, gas condensate deposits

INTRODUCTION

In studying the issues of methanol oxidation into industrial products, the deep oxidation is often considered a side and undesirable process [1]. There are almost no data available from the literature concerning the deep oxidation of methyl alcohol in water.

Meanwhile, there are a number of industrial processes, wherein the formation or the presence of methanol and its partial oxidation products result in the contamination. In particular, after the stage of regeneration of water-methanol solution (WMS) at gas condensate fields (GCF) the residual methanol content in the waste solutions ranges within 1.5–2 mass %. This requires reducing the residual methanol concentration in the waste solution to the MPC level (3 mg/dm^3).

One of the most efficient destructive methods recommended for this purpose consists in deep catalytic oxidation of organic pollutants, in particular methanol. This process was profoundly studied in catalysis. However, the issue connected with the efficiency of deep methanol oxidation at the concentration aqueous solution lower than 2 mass %, as well as with the role of water in the process, remains still open.

The effect of water on the kinetics of methanol oxidation on silver catalysts was studied in [2]. It was demonstrated that water can react with the catalyst to oxidize the silver by oxygen formed in the course of its decomposition, exerting a significant influence upon the formation of formaldehyde on the catalyst surface *via* blocking the synthesis of formic acid in the volume above the surface. It was found that with increasing water content up to

50 mass % the yield of formaldehyde reaches 93.8 mass % in an alcohol mixture methanol/ethanol. The products of the oxidation reaction are presented within the temperature range of 520–620 °C only by CO, CO₂, hydrogen and the traces of formic acid.

According to [3], the water promotes to reduce the reaction rate of the rate-determining stage of the process such as the oxidation strongly adsorbed formate structures. Furthermore, water facilitates the breakage of homogeneously proceeding stages of formaldehyde oxidation into formic acid that is considered to be a homogeneous reaction product on the catalyst surface. This fact explains the absence of formic acid among the reaction products. However the appearance of intermediate products in the reaction of methanol oxidation is dependent not only on the water content but also on the amount and nature of oxygen species involved in the reaction of methanol oxidation, as well as on the nature of active sites of the catalyst and the conditions of the process.

There are two fundamentally different ways to convert methanol on the surface of catalysts. The first way consists in the oxidation of methanol occurring through the formation of formaldehyde and formic acid, the second one is presented its dehydration accompanied by the formation of dimethyl ether, methylal, and acetaldehyde [1].

According to the foregoing, and in accordance with [4], the catalytic systems with chromium and magnesium oxides under our investigation exhibit a high catalytic activity and selectivity with respect to complete methanol oxidation. Copper catalysts behave in a similar manner. In these cases, the oxidation of methanol occurs via the first pathway, *i. e.* through the formation of formaldehyde [3]. The second pathway is inherent in alumina, the catalyst of methanol dehydration into dimethyl ether [5].

Consequently, the catalytic oxidation of methanol in the presence of water could occur through the Mars–van Krevelen mechanism which is based on the interaction between strongly bound oxygen (to all appearance, lattice oxygen) and the catalyst. The process takes place in the case of alternating oxidation and reduction of the catalyst, the interaction be-

tween reactants and the catalyst proceeds step-by-step [6].

The authors of [4] also indicated that the deep oxidation of organic compounds at a high temperature occurs at the expense of active lattice oxygen.

Owing to the absence of carbon-carbon bond in the molecule of methanol, the latter exhibits the highest reactivity within a homologous series of aliphatic primary alcohols [3, 7]. In the case of the presence of water that coats the surface of the catalyst, the decomposition of intermediate products formed during the oxidation of adsorbed methanol, proceeds quite rapidly at elevated temperature values even in the absence of gas phase oxygen [4]. To all appearance, in these cases, the water itself serves as a supplier of oxygen that embedding into the lattice of the catalyst thereafter takes part in the oxidation process [4]. However, until now the issues connected with the possibility of deep catalytic methanol oxidation in systems with water content equal to about 90 mass % as well as choosing the catalytic systems those can efficiently operate under the mentioned conditions remain obscure.

The analysis of experimental available from the literature [1, 3, 7] demonstrates that different variants of copper-chromium, cobalt-chromium, and iron-chromium catalysts as well as Mn, Ni, Zn, Mg chromites and their ternary mixtures are most widely used as the catalyst systems for the deep oxidation of organic substances (including methanol). Typically, the systems of metals or metal oxides are applied onto refractory carriers such as Al₂O₃, ZrO₂, aluminosilicates, and silica. Such catalysts exhibit a higher heat resistance, durability and mechanical strength as compared to the metal catalysts. The Al₂O₃ carrier (γ -phase) is also remarkable for the fact that it is immediately involved in catalysis providing acidic sites. However, the use of catalytic systems under consideration in an aqueous system (1.5–2 mass % of the alcohol and 98 mass % of water) could be restricted or impossible due to an abrupt decrease of the rate of methanol oxidation.

The aim of this work consisted in studying the process of the deep catalytic oxidation of methanol on supported oxide catalysts in aque-

ous solutions containing methanol in the amounts lower than 2 mass %. In order to achieve this goal it was necessary to choose a catalyst of deep selective methanol oxidation in aqueous medium, to find out optimal conditions for its efficient operation, to consider the behaviour of oxygen, water and methanol in simultaneous presence on the catalyst surface.

In the course of the implementation of this technology one should take into account the value of energy consumption required for the efficient oxidation of methanol. At the GCF the mixtures with such a low concentration is usually supplied to a flare system, whereto the combustible wastes are also directed providing thus the required heat.

EXPERIMENTAL

In order to investigate the process of deep methanol oxidation in aqueous solutions we chose the samples of industrial catalysts (Table 1) obtained at the IC of the SB RAS (Novosibirsk).

The experiments were performed using an apparatus with a fixed bed catalyst. An initial aqueous solution with methanol content amounting to 1.5 mass % (15.0 g/dm³) and air (carrier and oxygen source) were supplied through an evaporator heated up to a temperature of 250 °C into a catalytic reactor. The flow rate of the liquid was equal to 40 cm³/h, the contact time for the catalyst bed and the mixture depending on the purpose of the experiment ranged from 0.49 to 2.38 s, the process temperature ranged from 250 to 450 °C with increments of 50 °C. At the outlet of the reactor the vapour mixture was cooled and separated into two phases, liquid and gas one; those were subjected to gas chromatographic analysis. The analysis of the reaction products was performed with the

use of Crystal-2000 M and Crystal-5000 M gas chromatographs with a flame ionization detector and a thermal conductivity detector, columns packed with a Porapaq-Q sorbent for the registration of organic compounds as well as with a NaX sorbent for the registration of inorganic compounds.

In order to understand the behaviour of oxygen, water and methanol on the catalyst surface we studied a reoxidation process for copper-chromium catalyst (the initial sample and the sample after operation) that was chosen for the industrial realizing the process. As a research method, we chose a thermal programmed oxidation (TPO) technique in a chromatographic mode, with the use of a Chemisorb 2750 chemisorption analyzer. Basing on the character of thermal desorption spectra we studied the state of oxygen on the catalyst surface.

Before the thermal desorption measurements a weighed sample portion (1 g) was placed in a U-shaped quartz reactor that was mounted to place into a gradientless furnace. The surface of a sample was preliminary treated *via* thermal heating up to 600 °C at a rate of 10 °C/min in a flow of helium. The sample temperature and the composition of the exhaust gases were permanently monitored. Further we performed the adsorption of oxygen onto the surface of the catalyst in the course of cooling in a flow of a mixture O₂ (5 vol. %)/He at the temperature values ranging from 25 to 500 °C at a rate of 10 °C/min. The oxygen desorption was registered with the help of a thermal conductivity detector. The presence of a trap before the detector, which trap was cooled by frozen isopropyl alcohol, excluded entering water into the detector.

The thermal desorption of water and methanol, as well as of oxygen, water, and methanol under simultaneous presence of them was investigated with the help of a TPD automatic

TABLE 1

Parameters of the catalysts under investigation (carrier: γ -Al₂O₃ (80 %) and α -Al₂O₃ (20 %))

Parameters	Active components				
	FeO	CuO/Cr ₂ O ₃ /MgO	MgO/Cr ₂ O ₃	CuO/Cr ₂ O ₃	Pt
Mass fraction, %	≤5.5	13–67–7.7	3.0–12.0	5.0–11.3	≤1
Specific surface area, m ² /g	150	127	135	123	87
Bulk density, g/cm ³	1.09	1.09	1.14	1.10	0.65

TABLE 2

Activity parameters for catalysts (concerning CH₃OH) in the reaction of deep methanol oxidation

Temperature, °C	CH ₃ OH concentration after the reactor in the aqueous phase, mg/dm ³				
	Active components				
	FeO	CuO/Cr ₂ O ₃ /MgO	MgO/Cr ₂ O ₃	CuO/Cr ₂ O ₃	Pt
300	6249±249.9	3921±156.8	1991±79.6	1043±41.7	44±6.6
350	2136±85.4	869±78.2	1608±64.3	527±47.3	30±4.5
400	65±7.1	277±24.9	232±20.8	216±19.4	19±2.9
450	5±1.1	≤3±0.7	≤3±0.7	≤3±0.7	9±2.1

thermal desorption unit. The TPD spectra were registered with the use of a QMS-300 quadrupole mass spectrometer.

The experimental technique was similar to the mentioned above. The difference consists in the fact that the procedure of adsorption was carried out at 80 °C, whereas the desorption process was performed within in the temperature range from 80 to 500 °C.

RESULTS AND DISCUSSION

The results of testing the catalysts in the reaction of deep methanol oxidation in aqueous solution are presented in Table 2. It can be seen that at the temperature ≥300 °C, methanol in the gas phase is not detected. Formaldehyde, formic acid, and dimethyl ether are absent throughout the entire range of temperature under investigation, both in the liquid and in the gas phases.

From Table 2 one can see that the maximum methanol conversion could be achieved using systems CuO/Cr₂O₃/MgO/Al₂O₃, Cr₂O₃/MgO/Al₂O₃, CuO/Cr₂O₃/Al₂O₃ at 400–450 °C. An almost complete oxidation of methanol to produce water occurs at 450 °C (the methanol concentration being reduced to a level of MPC). In this case, the platinum catalyst which operates efficiently within the entire temperature range cannot be used for the oxidation of methanol in aqueous mixtures due to exceeding the maximum permissible concentration for methanol. The samples of FeO/Al₂O₃, despite a high activity at the beginning of the experiments stopped operation after 20–30 h of testing and were not able of regeneration.

The gas chromatographic analysis of the reaction products revealed a feature of metha-

nol behaviour in the gas phase: in the course of cooling the gas phase after the catalytic reaction the non-oxidized methanol is reabsorbed by water to be concentrated in the condensate formed. In the course of analyzing the liquid phase, methanol can be registered within the entire temperature range under investigation, whereas the gas-phase methanol can be registered only at the temperature values lower than 300 °C. Thus, the absence of methanol in the liquid phase could be considered an important indicator of deep catalytic methanol oxidation. The optimum contact time required for achieving a substantially complete oxidation level for methanol at the temperature values higher than 300 °C is equal to 0.9 s (the methanol concentration being below the detection limits of the instrument, *i. e.* ≤3 mg/dm³).

The catalysts under consideration represent oxide systems with the presence of different nature active centres. To all appearance, the complete oxidation of methanol to yield carbon dioxide and water on the surface occurs sufficiently rapidly through the formation of methoxy groups CH₃O– [3, 8], those can spontaneously decompose at high temperature values to release carbon dioxide and water [4].

The investigation of water, methanol and oxygen behaviour at the surface of the most active catalyst CuO/Cr₂O₃/Al₂O₃ was performed using the method of thermal programmed desorption (TPD). We used a new and operating (after 100 h of continuous operation) catalyst samples.

Figure 1 demonstrates O₂-TPD spectra for initial and operating samples those represent the output signal intensity in the course of oxygen desorption depending on temperature. It can be seen that the TPD spectra for both samples exhibit several temperature maxima. For the

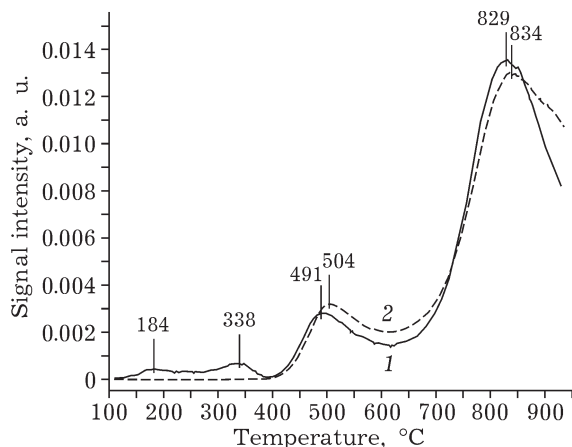


Fig. 1. O_2 -TPD spectrum with $CuO/Cr_2O_3/Al_2O_3$ (heating rate $10\text{ }^\circ\text{C}/\text{min}$): 1 – initial sample, 2 – sample after operation.

initial sample, the peaks with a maximum temperature of 184 and 338 $^\circ\text{C}$ could be attributed to adsorbed oxygen species on the catalyst surface. The peaks at temperature values amounting to 491 and 829 $^\circ\text{C}$ correspond to the lattice oxygen of the oxide phase of active components.

At the same time, we revealed some differences between the spectra. So, for the sample after operation we did not detect two low-temperature species of adsorbed oxygen with the maximum temperature at 184 and 338 $^\circ\text{C}$. The absence of oxygen peaks within the temperature range of 100–400 $^\circ\text{C}$ for the catalyst after operation, to all appearance, could be caused by the rearrangement of the surface of the active component under the influence of high-temperature reaction environment. The thermal desorption peaks with the maximum temperature values at 504 and 834 $^\circ\text{C}$, most likely could be attributed to the oxygen released from the bulk of the crystal lattice.

Thus, the catalysts (both an active component and a carrier) provide a high velocity of primary oxygen activation and the incorporation of oxygen into the crystal lattice [9]. Taking into account the temperature of methanol oxidation (450 $^\circ\text{C}$), the active form of oxygen that enters in direct contact with methanol, could be, to all appearance, presented by lattice oxygen that is formed resulting from the reoxidation of active sites.

The source of oxygen which is incorporated into the crystal lattice of the catalyst is presented by water and oxygen. On the surface of

the catalyst $CuO/Cr_2O_3/Al_2O_3$ there decomposes water, thereafter the resulting oxygen radical is incorporated into the lattice of the catalyst, and then, after releasing, takes part in the oxidation reaction [9].

According to data reported in [10], methanol can be readily desorbed and chemisorbed in different forms depending on the nature of the active sites of the catalyst and on the process conditions. It is evident that desorption of methanol at the temperature higher than 300 $^\circ\text{C}$ occurs resulting from the oxidation on the active sites of the catalyst.

Figure 2, *a* demonstrates the spectrum of methanol desorption from the surface of the catalyst. It can be seen that methanol is decomposed in an oxygen-free environment at the surface to yield formaldehyde and carbon dioxide those are desorbed at 310 $^\circ\text{C}$, as well as at 360 and 415 $^\circ\text{C}$, respectively. To all appearance, this process occurs both on copper and chromium the active centres.

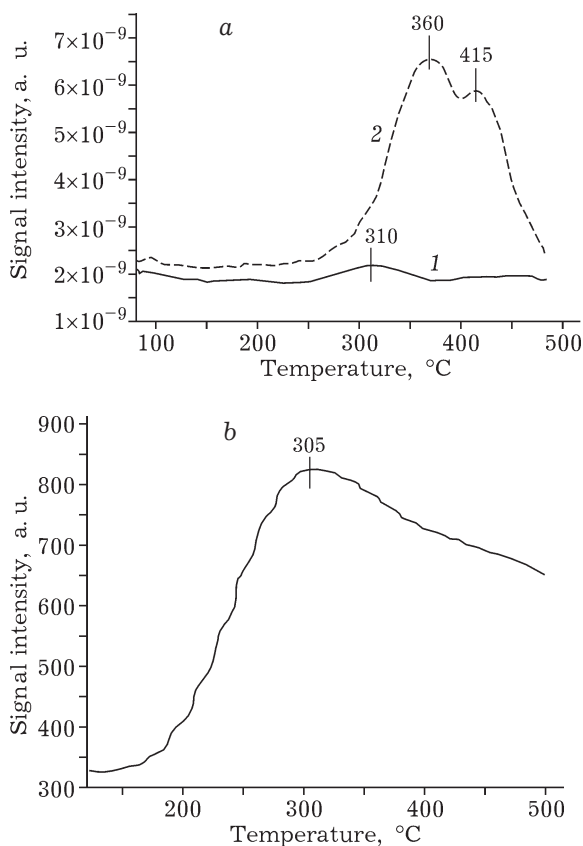


Fig. 2. Desorption spectrum for methanol (*a*) and water (*b*) in the case of $CuO/Cr_2O_3/Al_2O_3$ (heating rate $10\text{ }^\circ\text{C}/\text{min}$): 1 – initial sample, 2 – sample after operation.

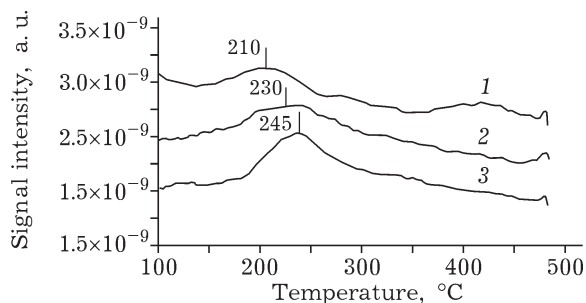


Fig. 3. Desorption spectrum for water (1), methanol (2) and carbon dioxide (3).

Basing on the data obtained, one could consider that the deep oxidation of methanol on the samples under investigation at high temperature values (≥ 400 °C) takes place with the participation of lattice oxygen, passing by the intermediate stages of formaldehyde and formic acid formation.

The TPD spectrum of water exhibits a maximum at 305 °C (see Fig. 2, b), which indicates a small amount of surface desorption energy corresponding to physical adsorption. One could consider that at the temperature values above 200 °C water is readily desorbed from the surface, and does not prevent the diffusion of methanol to the active centres of the catalyst. The TPD method was also used for analyzing desorption process for the solution of methanol and water at a molar ratio of 1 : 1 (Fig. 3). It is seen that the combined presence of water and methanol causes changing the character of desorption for methanol oxidation products. Decreasing the temperature of desorption is observed down to 230 °C for formaldehyde, and that down to 245 °C for carbon dioxide. To all appearance, this could be connected with the fact that water promotes reducing the desorption energy for the mentioned products.

CONCLUSION

1. For the process of deep methanol oxidation in water at the methanol concentrations of 1.5 mass % down to the MPC level we recommend to use catalysts based on $\text{Al}_2\text{O}_3\text{-CuO/Cr}_2\text{O}_3\text{/MgO/Al}_2\text{O}_3$, $\text{Cr}_2\text{O}_3\text{/MgO/Al}_2\text{O}_3$, $\text{CuO/Cr}_2\text{O}_3\text{/Al}_2\text{O}_3$, $\text{FeO/Al}_2\text{O}_3$. The optimum process parameters are the following: temperature 450 °C, contact time 0.9 s. The highest activity suitable for industrial application is exhibited by $\text{CuO/Cr}_2\text{O}_3\text{/Al}_2\text{O}_3$ catalyst.

2. The TPD spectrum of oxygen within the temperature range of 100–950 °C for initial and operating $\text{CuO/Cr}_2\text{O}_3\text{/Al}_2\text{O}_3$ samples demonstrated that the deep oxidation of methanol down to MPC at the temperature of 450 °C occurs due to the lattice oxygen.

3. Determining the content of methanol and its oxidation by-products should be carried out in the condensate, since the methanol is absorbed by moisture. This feature should be taken into account in monitoring atmospheric emissions.

4. For the $\text{CuO/Cr}_2\text{O}_3\text{/Al}_2\text{O}_3$ system we obtained TPD spectra obtained for methanol, water as well as for methanol and water in simultaneous presence within the temperature range of 100–500 °C. It was demonstrated that starting from 200 °C water is readily desorbed from the surface of the catalyst thereby hindering the process of deep methanol oxidation. In the presence of water, there is decreasing the surface desorption energy observed for the products of methanol oxidation.

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