An In Situ IR Spectroscopic Study of Methanol Conversion on an SNM-1 Catalyst

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Abstract—According to data obtained by spectrokinetic measurements under the reaction conditions of methanol conversion, formate and carbonate complexes were detected on the surface of an SNM-1 catalyst. The reaction products were H_2, CO_2, methyl formate, and CO. The surface of the SNM-1 catalyst was a copper oxide surface modified with aluminum and zinc oxides. Methoxy groups were formed on this surface upon interaction with methanol. With consideration for the high oxidizing ability of copper, the methoxy groups were rapidly converted into formate and carbonate. An analysis of the experimental data suggested that carbonate was the main source of CO_2, whereas hydrogen resulted from the decomposition of formate and the formation and consumption of methyl formate as a reaction intermediate.

INTRODUCTION

The generation of hydrogen from methanol for fuel cells is a problem of considerable current interest. Catalytic systems based on Cu–Zn–Al, which are commercial catalysts for methanol synthesis from CO and H_2, can be used in the reverse reaction of methanol decomposition and in the steam or oxidative reforming of methanol.

The studies of methanol synthesis resulted in a great number of publications concerning the interaction of methanol with systems based on Cu–Zn–Al. These systems are currently under study in the processes of methanol conversion into hydrogen-containing gas mixtures.

Data on the adsorption of methanol on the surfaces of copper and zinc oxide single crystals were reported [1, 2]. It was found that methanol was adsorbed as methoxy groups on the surfaces of these samples. At 330–400 K in the presence of copper, methoxy groups were decomposed with the formation of formaldehyde and adsorbed hydrogen atoms, whereas the formation of a formate complex occurred in the presence of oxygen. On the surface of zinc, a formate complex was the main conversion product of methoxy groups in the course of temperature-programmed desorption (TPD).

Manzoli et al. [3] used Fourier transform IR spectroscopy to study methanol decomposition on a Cu/ZnO catalyst. They found that, at 150°C, methoxy groups (absorption bands at 1058 cm^{-1} on ZnO and

978 cm^{-1} on Cu) were present on the surface. In addition, a formate complex on zinc oxide (absorption bands at 1575, 1381, 1369, and 2866–2868 cm^{-1}), molecularly adsorbed formaldehyde (absorption band at 1751 cm^{-1}), and a carbon-containing compound (hypothetically, a carbonate complex), which was characterized by a broad absorption band at 1490–1190 cm^{-1}, were detected. On a CuO/Zn–aluminosolicate sample [4], methoxy groups (absorption bands at 2930 cm^{-1} on Cu and 2920 and 2830 cm^{-1} on Zn) and a formate complex (absorption bands at 2967 and 2880 cm^{-1} on Zn and 2775 cm^{-1} on Cu), which are reaction intermediates in this process, were detected by IR spectroscopy under the above reaction conditions.

Based on a study of methanol decomposition on the Cu/ZnO/Al_2O_3 system performed by X-ray photoelectron spectroscopy (XPS) and TPD, Raimondi et al. [5] proposed a mechanism according to which methanol was adsorbed with the formation of methoxy groups on zinc oxide (287.2 eV). The methoxy group can undergo desorption with the formation of methanol, conversion into a formate complex, or oxidative transformation to CO and H_2. The formate complex decomposes to form CO, CO_2, and H_2. At temperatures lower than 180°C, desorption is the main reaction path of the conversion of methoxy groups. The other reactions become noticeable at temperatures higher than 230°C. Chauvin et al. [6] used IR spectroscopy and TPD to demonstrate that, in the decomposition of methanol on Cu/$ZnAl_2O_4$, the formation of CO, CO_2, and H_2 resulted from the degradation of

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a formate complex (HCOO$_{ads}$). This complex was formed from methoxy groups via an intermediate dioxymethylene complex (CH$_3$O$_{ads}$ + O$_{ads}$ = H$_2$CO$_{2, ads}$). Turco et al. [7] proposed an analogous reaction mechanism for methanol decomposition on a Cu/ZnO/Al$_2$O$_3$ catalyst (hydrotalcite derivative). Choi and Stenger [8] considered formaldehyde (CH$_3$O$_{ads}$ = CH$_2$O$_{ads}$ + H$_{ads}$) and methyl formate (2H$_2$CO$_{ads}$ = HCOOCH$_{3ads}$) as the main reaction intermediates of methanol decomposition. Methyl formate further decomposed to form CO and H$_2$ in the gas phase.

An analysis of published data indicates that, in the interaction of methanol with Cu–Zn–Al catalytic systems, methoxy groups (–OCH$_3$) and formate (HCOO–) and aldehyde (H$_2$CO–) complexes are the main surface complexes. Dioxymethylene and carbonate complexes were also mentioned. At the same time, the reaction paths of formation of these surface compounds and the role of these complexes in the formation of products in the gas phase during methanol conversion were not determined.

To study methanol conversion by the spectrokinetic method (the simultaneous measurement of the rates of conversion of surface compounds and the rates of formation of reaction products), we decided on the following series of catalysts: γ-Al$_2$O$_3$ ⟶ Cu/γ-Al$_2$O$_3$ ⟶ CuO/ZnO/Al$_2$O$_3$. The results of a study of methanol conversion on γ-Al$_2$O$_3$ and 10 wt % Cu/γ-Al$_2$O$_3$ systems were published previously [9, 10]. It was found that formate and aldehyde-like complexes and bridging and linear methoxy groups occurred on the surface of γ-Al$_2$O$_3$, as well as on the surface of 10 wt % Cu/γ-Al$_2$O$_3$, under conditions of this reaction. The composition of products on these catalysts was different: in the presence of the copper-containing catalyst, a considerable amount of hydrogen and an amount of CO were formed in addition to dimethyl ether and CO$_2$. The formation of hydrogen was explained by the fact that the recombination of hydrogen atoms can occur on the surface in the presence of copper. The conversions of formate and aldehyde-like surface complexes are the sources of CO$_2$ in the gas phase.

In this work, we performed a similar study of methanol conversion reactions on a commercial SNM-1 catalyst (CuO/ZnO/Al$_2$O$_3$).

EXPERIMENTAL

The commercial SNM-1 catalyst (CuO/ZnO/Al$_2$O$_3$: 52–54 wt % CuO, 24–28 wt % ZnO, and 5–6 wt % Al$_2$O$_3$), which was prepared by coprecipitation, was used in this study. The specific surface area was 80 m^2/g.

As reactants, 4 and 2% methanol mixtures with helium and 4% methyl formate or dimethyl ether mixtures with helium were used. Up to 3% oxygen or water was added to a mixture of methanol with helium.

Spectrokinetic measurements under methanol conversion conditions were performed in accordance with a procedure analogous to that described in [11]. The experimental setup included a Bruker IFS-43 Fourier transform IR spectrometer, a heated flow reactor cell (V = 1 cm^3) [11], a gas preparation unit, and a system for the analysis of products and reactants. The intensity of absorption bands in transmission spectra was measured in absorbance units (A). Usually, the number of scans was 360 or 120, and the resolution was 4 cm^{-1}.

The concentrations of reactants and reaction products were measured using a 3700 chromatograph with heated lines; helium was a carrier gas. Methyl formate, methanol, and methane were determined on a column with Porapak Q using a flame-ionization detector. Analysis for O$_2$, CO, H$_2$, and CO$_2$ was performed on columns with molecular sieve 5A and Porapak Q using a thermal-conductivity detector.

The sample as a 20- to 30-g pellet with a surface area of 2 cm^2 was placed in a cell, which simultaneously served as a catalytic flow reactor. Before measurements, the sample was treated in a flow of 5% O$_2$/He or H$_2$ at 400°C for 1 h, cooled to the required temperature, and exposed to a reaction mixture (30 ml/min). The experiments were performed in the temperature range of 30–400°C.

The procedure of steady-state and non-steady-state spectrokinetic studies consisted in the simultaneous measurements of the concentrations of surface compounds by in situ IR spectroscopy and the rate of formation of reaction products by chromatography in the course of reaching a steady state in the reactions of methanol conversion or on the removal of methanol from a flow of the reaction mixture.

The experiments on CO adsorption were performed with a sample treated in a flow of H$_2$ at 400°C for 1 h or after the decomposition reaction of 2% CH$_3$OH in He on the oxidized sample. Next, the sample was cooled to 100°C, and a mixture of 18 vol % CO/He was supplied to it. In a flow of CO/He, the sample was cooled to room temperature; thereafter, the CO/He mixture was replaced by He, which was blown for 10 min. The IR spectra were recorded in the course of the entire experiment.

RESULTS

Catalyst Characterization

The IR spectrum of the initial sample exhibited a broad absorption band in the region of 1220–1650 cm^{-1} and low-intensity absorption bands at 2490, 1776, 1120, and 1062 cm^{-1}. According to published data [12], this spectrum is characteristic of a bulk carbonate. The conditioning of the sample in a He flow at 400°C resulted only in an insignificant decrease in the intensities of the above absorption bands. A dramatic decrease in the absorption band of

a carbonate phase was observed in the spectrum recorded after the training of the sample in a flow of H_2. The concentration of a carbonate complex was subsequently evaluated from the intensity of an absorption band at $1220-1650$ cm^{-1} at a frequency of 1440 cm^{-1}.

To characterize the surface states of a sample after the reaction of methanol decomposition and a sample reduced in H_2, we performed the adsorption of CO molecules in a range from room temperature to $100°C$. In this case, absorption bands due to carbonyl or carbonate complexes were absent from the spectra.

Steady-State Experiments

Methanol conversion. Methanol decomposition on both reduced and oxidized samples came into play above $200°C$; the products were H_2, CO_2, methyl formate, and CO (Fig. 1a). The reduced sample exhibited a lower activity (conversion was no higher than 60% at $375°C$ on this catalyst) as compared to the oxidized catalyst (80% at $325°C$). Note that, at temperatures higher than $325°C$, the conversion of methanol on the oxidized sample decreased, whereas the conversion on the reduced sample continued to insignificantly increase.

From spectroscopic data (Fig. 1b), it follows that the concentration of carbonate complexes on the oxidized sample increased as the temperature was increased from room temperature to $200°C$. The intensity of absorption bands due to methanol in the gas phase (1056 cm^{-1}) decreased. At $100°C$, an absorption band at 1600 cm^{-1} appeared in the spectra; the intensity of this band passed through a sharp maximum at $200°C$. The absorption band intensity of the carbonate complex also changed. Above $200°C$, an absorption band at 1750 cm^{-1} appeared; the intensity change of this band with temperature correlated with change in the concentration of methyl formate in the gas phase (Figs. 1a, 1b). At $250°C$, an absorption band at 2180 cm^{-1} was observed in the spectra; its intensity passed through a maximum at $300°C$ as the temperature was increased.

According to published data [13, 14], an absorption band at 1600 cm^{-1} is due to vibrations in the surface formate complex, an absorption band at 2180 cm^{-1} is due to vibrations in the $Cu^{1+}-CO$ carbonyl complex, and an absorption band at 1750 cm^{-1} is due to vibrations in methyl formate in the gas phase. This was supported by the measurement of the spectrum of methyl formate in a gas cell.

The spectra recorded under reaction conditions for the reduced sample exhibited only absorption bands due to methanol in the gas phase. The intensity of these bands decreased with temperature. Above $225°C$, an absorption band at 2180 cm^{-1} appeared in the spectra. As the temperature was increased, its intensity passed through a maximum at $350°C$. For both the oxidized and reduced samples, the intensities
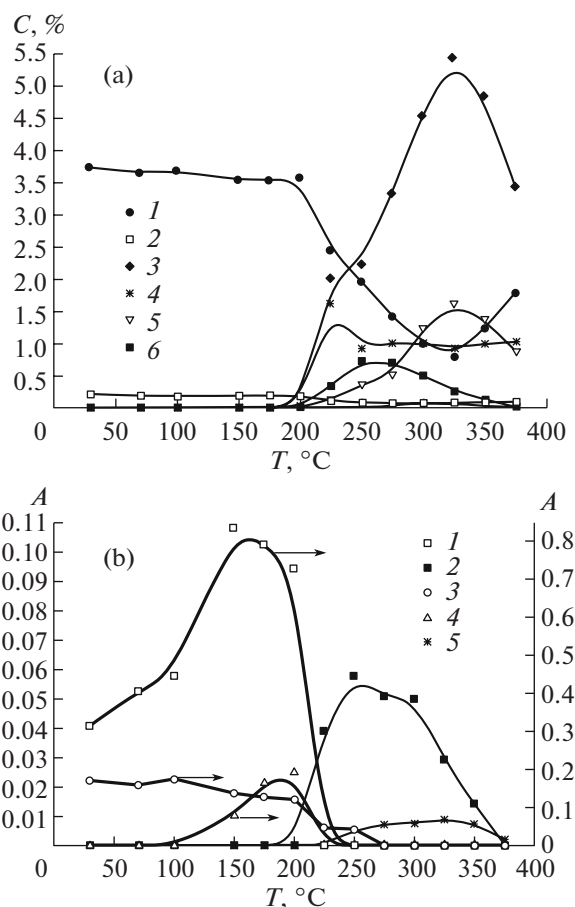

Fig. 1. The temperature dependence of (a) the concentrations of products and reactants [(1) CH_3OH, (2) O_2, (3) H_2, (4) CO_2, (5) CO, and (6) $HCOOCH_3$] and (b) absorption band intensities at (1) 1440, (2) 1750, (3) 1056, (4) 1600, and (5) 2180 cm^{-1} under the methanol conversion conditions (4%) on the oxidized sample.

of absorption bands at 2180 cm^{-1} changed symbatically with the concentration of CO in reaction products.

The observed dramatic change in the concentrations of CO_2 and H_2 in the gas phase at $200-225°C$ and the decrease in the intensities of absorption bands at 1440 and 1600 cm^{-1} at $200-225°C$ (Fig. 1) allowed us to assume that the formate and carbonate complexes are the sources of CO_2 and H_2 in the gas phase.

Figure 2 shows the results of an experiment (oxidized sample; 2% methanol in helium) on heating and subsequent cooling of the sample in a flow of the reaction mixture. It can be seen that, in the course of cooling, the sample exhibited a much lower activity (Fig. 2a).

Absorption bands due to carbonate and formate complexes were present in the spectra recorded in the course of heating. As the temperature was increased from 200 to $225°C$, their concentration dramatically decreased (Fig. 2b). In the course of cooling, the
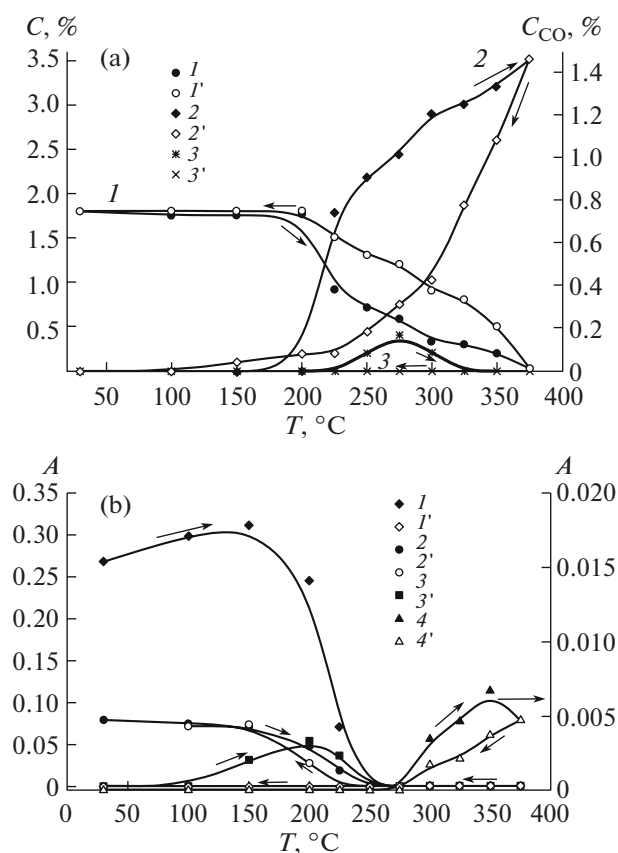
Fig. 2. The temperature dependence of (a) the concentrations of products and reactants [(*1*, *1'*) methanol, (*2*, *2'*) H_2, and (*3*, *3'*) methyl formate] and (b) absorption band intensities at (*1*, *1'*) 1440, (*2*, *2'*) 1056, (*3*, *3'*) 1600, and (*4*, *4'*) 2180 cm^{-1} on an oxidized sample (*1–4*) on heating and (*1'–4'*) on cooling in a flow of methanol (2%).

Fig. 3. The temperature dependence of (a) the concentrations of products and reactants [(*1*) $HCOOCH_3$, (*2*) H_2, (*3*) CO, (*4*) CO_2, (*5*) CH_4, and (*6*) CH_3OH] and (b) absorption band intensities at (*1*) 1600, (*2*) 1440, (*3*) 1750, and (*4*) 2180 cm^{-1} on an oxidized sample (*1–4*) on heating and (*1'–4'*) under the conditions of methyl formate conversion (4%) on the oxidized sample.

absorption bands of carbonate and formate complexes were not detected. Below 225°C, absorption bands due to methanol in the gas phase (1056 cm^{-1}) appeared.

On heating and cooling in the region of 375–275°C, the spectra exhibited an absorption band at 2180 cm^{-1} (Fig. 2b). Note that the intensity of this absorption band on cooling was lower than that on heating. As in the previous experiments, changes in the concentration of CO in the gas phase correlated with changes in the concentration of a carbonyl complex on the catalyst surface (Figs. 2a, 2b).

Because methyl formate was detected among the products of methanol conversion, we performed a special experiment to study the interaction of methyl formate with the catalyst surface.

Methyl formate conversion. The reaction of methyl formate conversion began above 150°C (Fig. 3a). The conversion products were H_2, methanol, CO, and CO_2. At temperatures higher than 250°C, a small amount of CH_4 was formed. From spectroscopic data (Fig. 3b), it follows that the concentrations of carbon-
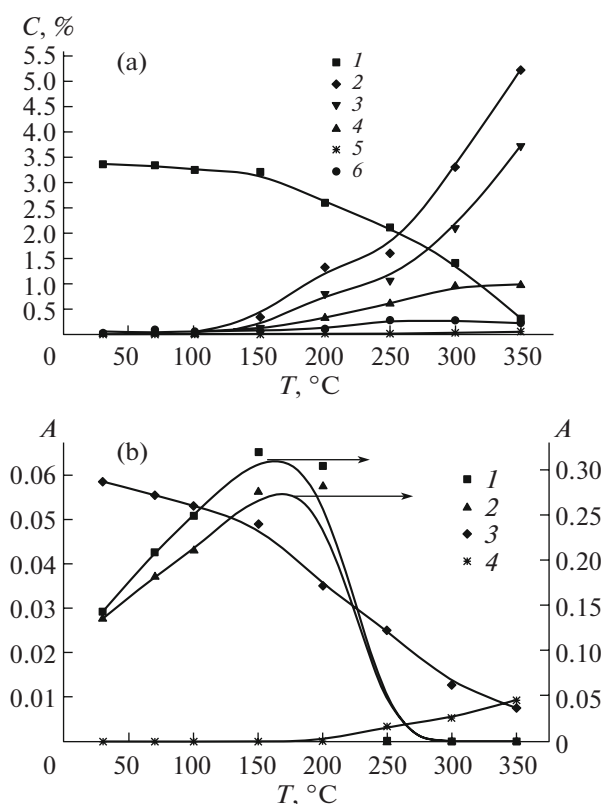
ate (absorption band at 1440 cm^{-1}), formate (absorption band at 1600 cm^{-1}), and methyl formate (absorption band at 1750 cm^{-1}) dramatically decreased as the temperature was increased from 200 to 250°C. At temperatures higher than 200°C, an absorption band at 2180 cm^{-1} appeared in the spectra. A decrease in absorption band intensities at 1600 and 1440 cm^{-1} corresponds to the appearance of reaction products (CO_2 and H_2) in the gas phase (Figs. 3a, 3b). The change in the concentration of CO correlates with the change in the concentration of the absorption band at 2180 cm^{-1}.

To determine the effect of the oxygen and water concentrations on the activity of the catalyst and the properties of surface compounds, we performed a series of experiments on the oxidized sample at various O_2 and H_2O contents of a mixture with methanol in helium.

Effect of the oxygen concentration. The effects of oxygen (Fig. 4) were different at various temperatures. At a relatively low temperature (250°C), the addition of oxygen (Fig. 4) resulted in a considerable decrease
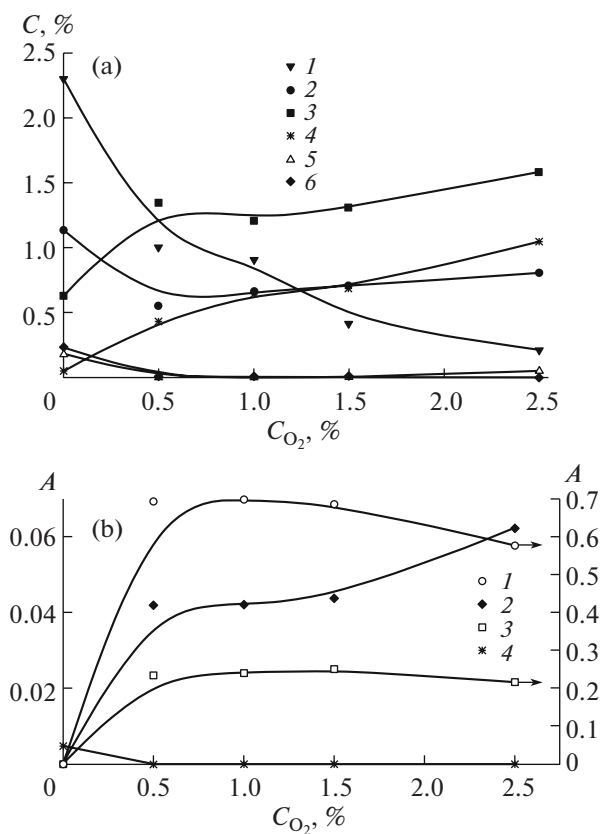
Fig. 4. Dependence of (a) the concentrations of products and reactants [(1) H_2, (2) CO_2, (3) CH_3OH, (4) O_2, (5) CO, and (6) $HCOOCH_3$] and (b) absorption band intensities at (1) 1440, (2) 1056, (3) 1600, and (4) 2180 cm^{-1} on the oxygen content of the reaction mixture on the oxidized sample. $T = 250°C$.
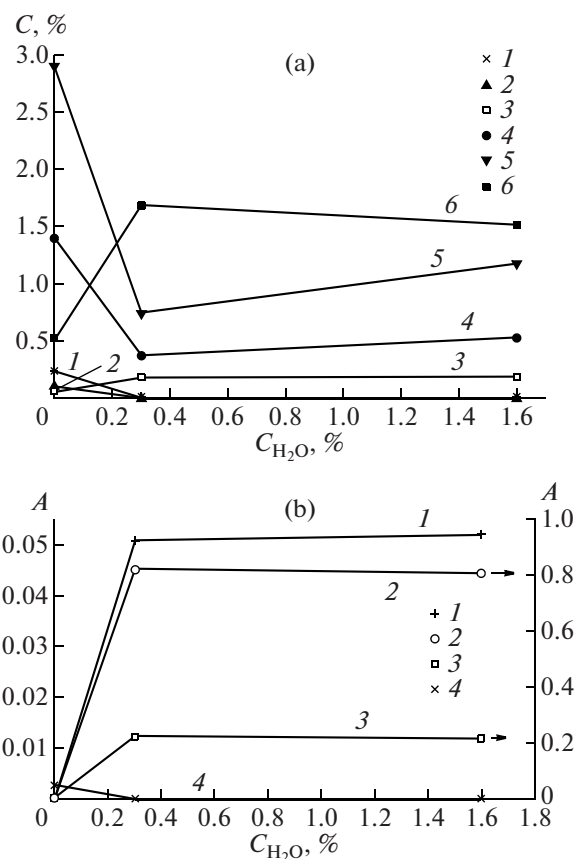
Fig. 5. Dependence of (a) the concentrations of products and reactants [(1) $HCOOCH_3$, (2) CO, (3) O_2, (4) CO_2, (5) H_2, and (6) CH_3OH] and (b) absorption band intensities at (1) 1056, (2) 1440, (3) 1600, and (4) 2180 cm^{-1} on the water vapor content of the reaction mixture on the oxidized sample. $T = 250°C$.

in activity and a corresponding increase in the concentration of formate and carbonate complexes on the catalyst surface (Fig. 4b). In the presence of oxygen in the reaction mixture, methyl formate was not detected among the products (Fig. 4a).

At an elevated temperature, the addition of oxygen (up to 1%) to the reaction mixture did not cause a decrease in activity. An increase in the concentration of oxygen to 2.5% was accompanied by a decrease in methanol conversion. Absorption bands due to carbonate and formate complexes were absent from the spectra measured under these conditions. The absorption band intensity at 2180 cm^{-1} decreased as the oxygen content of the reaction mixture was increased.

Effect of the water concentration. The effects of water on the conversion of methanol (Fig. 5) were also different at various temperatures. The addition of water vapor at 250°C resulted in a considerable decrease in methanol conversion (Fig. 5a). Absorption bands due to surface carbonate (1440 cm^{-1}) and formate (1600 cm^{-1}) and methanol in the gas phase (1056 cm^{-1}) appeared. Under these conditions, the

absorption band at 2180 cm^{-1} was absent (Fig. 5b). Note that only an absorption band at 2180 cm^{-1} was detected on the surface in the absence of water vapor.

At 300°C, the addition of water to methanol had almost no effect on the conversion but decreased the concentration of CO and increased the concentration of hydrogen. The absorption band intensity at 2180 cm^{-1} decreased in the presence of water vapor.

A comparison between spectroscopic data and chromatographic analysis data allowed us to state that the change in the absorption band intensity at 2180 cm^{-1} in the spectra is consistent with the change in CO concentration in the gas phase (Figs. 2, 4, 5).

Figure 6 shows the results of a comparison of the absorption band intensity at 1600 cm^{-1} (formate) and the concentration of H_2 in the gas phase, as well as the absorption band intensity at 1440 cm^{-1} (carbonate) and the concentration of CO_2 in the gas phase. The results of this comparison suggest that formate and carbonate are the sources of H_2 and CO_2, respectively, in the gas phase.
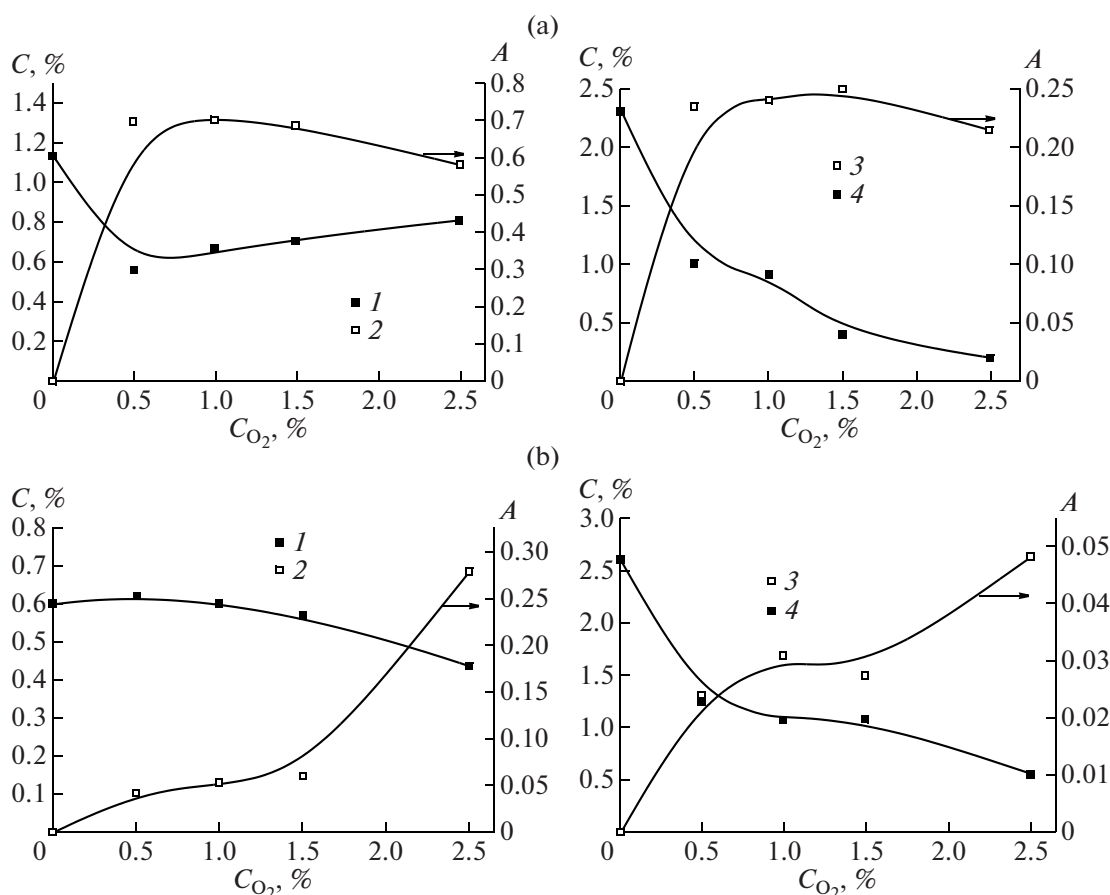
Fig. 6. Dependence of absorption band intensities and product concentrations on the oxygen content of the mixture (2% methanol) for the oxidized sample: (*1*) CO_2, (*2*) 1440 cm^{-1}, (*3*) 1600 cm^{-1}, and (*4*) H_2; T = (a) 250 or (b) 275°C.

Because the temperature dependence of methyl formate concentration passed through a maximum and the concentration of CO began to increase with a decreasing methyl formate concentration (Fig. 1a), we can conclude that CO was formed as a result of methyl formate decomposition (Fig. 3).

Unsteady-State Experiments

On the oxidized sample, we performed experiments on the isothermal desorption (T = 225°C) of surface compounds in a flow of helium with the simultaneous analysis of desorption products and the recording of IR spectra. The desorption temperature was chosen based on the fact that surface compounds were absent from the surface of the oxidized sample at a higher temperature, whereas methanol conversion did not occur on the given catalyst at a lower temperature.

Methanol, CO_2, H_2, and CO were present in the products formed upon the desorption of surface compounds. The concentration of these products decreased in the course of desorption. CO and hydrogen were detected in the products for 10−12 min, and

CO_2 was detected over 30 min after the onset of desorption (Fig. 7a). In this case, the following changes occurred on the surface: carbonyl complexes were not detected 10−15 min after the onset of desorption (Fig. 7b); the concentration of formate (absorption band at 1600 cm^{-1}) decreased in the course of desorption; and the concentration of carbonate (absorption band at 1440 cm^{-1}) changed only slightly in time (Fig. 7b).

DISCUSSION

Mechanism of Methanol Conversion

Under the conditions of methanol conversion, formate complexes and a carbonate phase occurred on the catalyst surface. Note that a carbonyl complex with a vibration frequency of 2180 cm^{-1} also occurred. According to published data [13−15], this frequency can be due to vibrations in the Cu^{2+}−CO complex. On the other hand, the occurrence of these complexes at a high temperature is improbable because the bond strength of these complexes to the surface is low [13−15]. It is more likely that this frequency can be assigned to vibrations in the CO molecule bound to

the copper ion in a state close to +1 ($Cu^{1+}-CO$). This state of copper occurred only under reaction conditions because a decrease in the reaction temperature resulted in a decrease in the concentration of a carbonyl complex to zero (Fig. 2). Moreover, we did not detect the formation of carbonyl complexes as a result of the adsorption of CO test molecules on the sample before and after the reaction.

In the presence of methanol in the gas phase, the concentration of formate and carbonate complexes increased (Fig. 1b). This fact suggests the participation of methanol in the formation of these complexes. The coincidence of the temperatures of the onset of reaction product formation and the onset of carbonate and formate complex consumption (Figs. 1a, 1b) evidences for the participation of these complexes in the formation of reaction products. A maximum in the temperature dependence of the concentration of CO_2 (Fig. 1a) can be explained by the decomposition of the carbonate phase, which is a reservoir of CO_2 in this case. Another source of CO_2 is the formate complex.

Another explanation of the experimental data can be based on the hypothesis that carbonates and formates freed the surface at which the conversion of methanol occurred at a high rate as the temperature was increased. In our opinion, the former explanation is most likely for the following reasons:

• the carbonate complex was not removed from the surface even on heating at 400°C in a flow of an inert gas;

• the carbonate complex was removed from the surface at 225°C on heating in a flow of the reaction mixture with the formation of CO_2 as the reaction product (Figs. 1, 2);

• a correlation occurred between changes in the concentration of the surface carbonate complex (1440 cm^{-1}) and the concentration of CO_2 in the gas phase (Fig. 7);

• the higher the rates of formation of CO_2 and hydrogen, the lower the concentrations of formate and carbonate complexes on the surface (Fig. 6);

• the conversion of the formate complex (1600 cm^{-1}) into hydrogen was quantitatively consistent (Fig. 7); in the course of a desorption experiment after 10 to 13 min, 0.04×10^{19} hydrogen molecules in the gas phase were formed from 0.07×10^{19} formate complexes.

Note that the proposed explanation is consistent with concepts of the mechanism of a process reverse to methanol synthesis [16, 17], according to which hydrogen is formed through a formate complex, whereas CO_2 is formed through a carbonate complex.

A correlation between the temperature dependences of methanol, methyl formate, and CO concentrations in the gas phase (Fig. 1a) and surface carbonyl concentration (Fig. 1b) unambiguously suggests that the main source of CO in the gas phase is the decom-
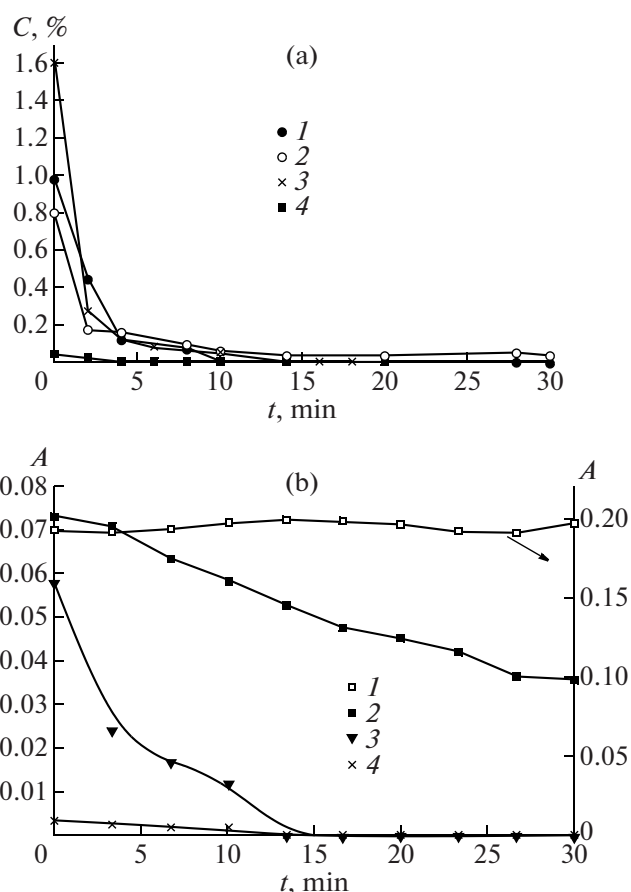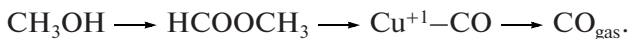

Fig. 7. Dependence of (a) the concentrations of products and reactants [(*1*) CH_3OH, (*2*) CO_2, (*3*) H_2, and (*4*) CO] and (b) absorption band intensities at (*1*) 1440, (*2*) 1600, (*3*) 1056, and (*4*) 2180 cm^{-1} on time during desorption in a flow of helium on the oxidized sample. $T = 225$°C.

position of methyl formate and a surface carbonyl complex is an intermediate in this process:

$$CH_3OH \longrightarrow HCOOCH_3 \longrightarrow Cu^{+1}-CO \longrightarrow CO_{gas}.$$

The proposed reaction scheme is also supported by the fact that CO was not detected in reaction products in the absence of methyl formate from the gas phase. Data obtained in the reaction of methyl formate conversion on the same catalyst are indicative of this sequence of reactions steps in the formation of CO (Fig. 3). CO is the main product of methyl formate decomposition. In the same way, a correlation was observed between changes in the concentrations of CO in the gas phase and the carbonyl complex on the surface.

Note that the conversion of methanol dramatically increased (Fig. 1a) and the concentration of surface complexes simultaneously decreased (Fig. 1b) in a narrow temperature range. This fact can be explained by a transfer to the outer-diffusion reaction mode or a change in the surface state, which can be due to surface reduction.

The reaction performed on a sample prereduced in hydrogen showed that, in this case, activity was much higher than on an oxidized sample. In this case, absorption bands due to formate and carbonate complexes were absent from the spectra. It is likely that reduction in hydrogen resulted in a considerable decrease in the number of active centers. This was also supported by the fact that the concentration of the carbonyl complex ($Cu^{1+}-CO$) on the reduced sample was lower than that on the oxidized one.

The same effects were observed on heating the sample in a reaction atmosphere (Figs. 2a, 2b). The occurrence of these effects suggests that the heating of the sample in the reaction atmosphere resulted in sample reduction accompanied by a decrease in the number of active centers.

The addition of oxygen or water to methanol at 250°C (Figs. 4, 5) resulted in a decrease in activity and the appearance of surface formate and carbonate complexes. In other words, an increase in the rate of methanol conversion resulted in a decrease in the concentrations of these components on the surface; the inhibition of the process by the addition of water or oxygen resulted in an increase in the concentration of surface complexes.

Taking into account these circumstances, we believe that a dramatic increase in methanol conversion and a simultaneous decrease in the concentration of surface complexes over a narrow temperature range were due to a change to the outer-diffusion reaction mode. This change in the reaction mode can be due to high activation energies of corresponding reaction steps.

At elevated temperatures, the catalyst was reduced and the activity decreased. The temperature of the onset of reduction can be evaluated from data given in Fig. 1a. Indeed, at a temperature higher than 325°C, the conversion of methanol decreased, evidently, because of surface reduction.

Effects of Oxygen and Water on the Conversion of Methanol

The effects of oxygen and water were different at various temperatures. At a relatively low temperature (250°C), the addition of oxygen (Fig. 4) or water (Fig. 5) resulted in a considerable decrease in activity and a corresponding increase in the concentrations of formate and carbonate complexes on the catalyst surface. In this case, the formation of CO stopped. The set of the above facts can be explained by an additional oxidation of the surface in the presence of either oxygen or water. This explanation was supported by a dramatic decrease in the concentration of the $Cu^{1+}-CO$ complex upon the introduction of oxygen or water into the reaction mixture composition (Figs. 4b, 5b). Moreover, the occurrence of the oxidation of surface copper (in the Cu^0 or Cu^{1+} state) with water was demonstrated in [8, 16, 17].

In other words, the surface of an efficiently operating catalyst should not be in an oxidized state. Experiments on a reduced sample showed that the surface of an efficiently operating catalyst should not be in a reduced state. Because oxidation or reduction affected the state of copper, it is believed that Cu^{1+} is an optimum state of copper as a catalyst constituent.

At an elevated temperature, the addition of oxygen up to 1% or water to the reaction mixture did not cause a decrease in activity. It is likely that, at 300°C, the oxidation of the catalyst by oxygen or water was compensated by reduction under the action of methanol (Fig. 1). An increase in the concentration of oxygen from 1 to 2.5% resulted in a decrease in methanol conversion: at these oxygen concentrations, the oxidation of the surface was the predominant process. A decrease in the concentration of carbonyl complexes suggests that this is true. Thus, the main role of oxygen and water in the conversion of methanol consists in changing the state of the catalyst surface, namely, in oxidizing this surface.

Comparison between the Mechanisms of Methanol Conversion on the 10 wt % Cu/γ-Al₂O₃ and SNM-1 Catalysts

Under the reaction conditions of methanol conversion on the surface of 10 wt % Cu/γ-Al_2O_3, formate and aldehyde-like complexes and bridging and linear methoxy groups were formed. Dimethyl ether, CO_2, H_2, and CO were detected in the reaction products.

In the absence of methanol in the gas phase, the interaction between two bridging methoxy groups resulted in the formation of dimethyl ether in the gas phase. In the presence of methanol in the gas phase, the interaction of gas-phase methanol with the bridging methoxy group on the surface was observed. This reaction mainly contributed to the formation of dimethyl ether.

The linear methoxy group underwent desorption to form methanol in the gas phase and surface formate and aldehyde. In accordance with the proposed mechanistic scheme, the formate complex is the source of formation of CO_2 in the gas phase, and the surface aldehyde complex is the source of CO formation. The main reaction of hydrogen formation is the recombination of hydrogen atoms at copper clusters.

Under the same conditions, only formate and carbonate complexes were detected on the surface of the SNM-1 catalyst. The compositions of products were also different; CO_2, H_2, CO, and methyl formate were found by analysis. The above data indicate that carbonate and formate are the main sources of CO_2 and hydrogen, respectively. Carbon monoxide resulted from the intermediate formation and consumption of methyl formate.

It is clear that the difference between the properties of 10 wt % Cu/γ-Al_2O_3 and SNM-1 catalysts is due to differences in their surface properties.

The formation of methoxy groups on 10 wt % Cu/γ-Al$_2$O$_3$ occurred with the participation of surface hydroxyl groups of γ-Al$_2$O$_3$ modified with copper ions. Copper particles, which participated in the formation of hydrogen and in the activation of oxygen, occurred on the same surface.

The surface of the SNM-1 catalyst is a copper oxide surface modified with aluminum and zinc oxides. According to published data [18], methoxy groups were formed on this surface by the interaction of methanol with coordinatively unsaturated cations. The resulting methoxy groups [18−20] were characterized by a high reactivity. Depending on the state of copper, the temperatures of formation and conversion of methoxy groups into formate and/or formaldehyde fall in the range of 100−150°C.

As a result, the methoxy groups were rapidly converted into formate, carbonate, and an aldehyde-like surface complex ($CH_3O_{ads} = CH_2O_{ads} + H_{ads}$) [8] (because of this, they cannot be detected using in situ IR spectra). The conversions of formate and carbonate resulted in the formation of hydrogen and CO. This reaction scheme is reverse to the scheme of methanol synthesis on this catalyst developed by Rozovskii [16]. The surface aldehyde complex converted into methyl formate ($2H_2CO_{ads} = HCOOCH_{3ads}$), which further decomposed to form CO and H$_2$ in the gas phase.

In conclusion, note that the difference in the properties of 10 wt % Cu/γ-Al$_2$O$_3$ and SNM-1 catalysts is due to differences in their surface properties, which manifests itself in the formation of methoxy groups of different nature by the interaction with methanol. In turn, the difference in the nature of methoxy groups is responsible for different reaction paths in the subsequent transformations.

We failed to detect surface compounds under reaction conditions on the reduced SNM-1 catalyst. Therefore, it contained a relatively small number of very active centers. Based on the sensitivity of Fourier transform IR spectroscopy, we can estimate their concentration at $<10^{15}$ center/m^2 [21]. It is an important problem to determine the nature of these centers for the subsequent reproduction of them in large amounts in other catalysts.

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