ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 5, pp. 784–792. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.A. Matyshak, O.N. Sil'chenkova, I.T. Ismailov, V.F. Tret'yakov, 2009, published in Kinetika i Kataliz, 2009, Vol. 50, No. 5, pp. 816–824.

Properties of Surface Compounds in Methanol Conversion on Copper-Containing Catalysts Based on CeO_2 According to In Situ IR-Spectroscopic Data

V. A. Matyshak[a], **O. N. Sil'chenkova**[a], **I. T. Ismailov**[b], **and V. F. Tret'yakov**[b]
[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 117912 Russia*
e-mail: matyshak@polymer.chph.ras.ru

Received May 21, 2008

Abstract—Formate and carbonate complexes and bridging and linear methoxy groups were detected on the surfaces of CeO_2 and 5.0% Cu/CeO_2 under the reaction conditions of methanol conversion using IR spectroscopy. The reaction products were H_2, methyl formate, CO, CO_2, and H_2O. The bridging and linear methoxy groups were the sources of formation of bi- and monodentate formate complexes, respectively. Methyl formate was formed as a result of the interaction of the linear methoxy group and the formate complex. The study demonstrated that the recombination of hydrogen atoms on copper clusters and the decomposition of methyl formate were the main reactions of hydrogen formation. Formate and carbonate complexes were the source of CO_2 formation in the gas phase, and the decomposition of methyl formate was the source of CO. It was found that the addition of water vapor to the reaction flow considerably decreased the rate of CO formation at a constant yield of hydrogen. The effects of water vapor and oxygen on the course of surface reactions and the formation of products are discussed. To explain the mechanism of methanol conversion, a scheme of surface reactions is proposed.

DOI: 10.1134/S002315840905022X

INTRODUCTION

In recent years, the generation of H_2-containing gas mixtures from methanol has received increasing attention because of the development of fuel cells operating on hydrogen. Hydrogen-rich mixtures can be obtained by the catalytic decomposition, steam reforming, and autothermal reforming of methanol. Evidently, information on the mechanism of surface reactions is useful for the development of efficient catalysts for these processes.

Copper-containing systems based on CeO_2 and ZrO_2 modified to improve their activity, selectivity, and operational stability [1, 2] and catalysts containing noble metals [3, 4] are considered the most active catalysts in the production of hydrogen-containing mixtures from methanol.

Methoxy groups ($–O–CH_3$) are considered as possible intermediates in studies of methanol conversion on oxide systems. In particular, it is believed that the interaction of two methoxy groups results in the formation of dimethyl ether [5], whereas the formation of formaldehyde can occur via the interaction of the methoxy group with oxygen [6, 7]. Formate complexes [8] and complicated complexes containing two methoxy groups and a surface hydroxyl groups [9] are also considered as intermediate compounds in the reactions of methanol conversion.

The surface compounds formed by the interaction of methanol with oxide catalysts have been adequately characterized; however, the role of these complexes in the formation of products, such as carbon monoxide, carbon dioxide, and hydrogen, remains unknown [5–17].

Previously, Matyshak et al. [18, 19] used a spectrokinetic method (simultaneous measurement of the rate of conversion of surface compounds and the rate of formation of reaction products using in situ IR spectroscopy [20]) to study the role of surface complexes in methanol conversion on γ-Al_2O_3 and Cu/γ-Al_2O_3. It was found that, in the absence of methanol from 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 methanol from the gas phase with the surface methoxy group was observed. This reaction made the main contribution to the formation of dimethyl ether.

The linear methoxy group is desorbed with the formation of methanol in the gas phase to form surface formate and aldehyde complexes. The surface formate and aldehyde complexes are the sources of formation of CO_2 and CO in the gas phase, respectively. The main reaction of the formation of hydrogen is the recombination of hydrogen atoms on copper clusters.

In this work, we performed an analogous study of the role of surface complexes in methanol conversion on copper-containing catalysts based on CeO_2.

EXPERIMENTAL

Cerium oxide with the specific surface area S_{sp} = 73 m^2/g was prepared by the decomposition of $Ce(NO_3)_4 \cdot 6H_2O$ in air at 500°C for 2 h. The specific surface area was determined using the BET method based on the low-temperature adsorption of argon. CuO/CeO_2 samples were prepared by the impregnation of CeO_2 with an aqueous nitrate solution (to support 5.0 wt % CuO) followed by drying at 100°C and calcination at 500°C in air for 2 h.

A 4% mixture of methanol in helium was used as reactants. Up to 3% oxygen was added to the mixture of methanol with helium. Helium used in this study contained up to 0.2% oxygen as an impurity.

Spectrokinetic measurements under the reaction conditions of methanol conversion were performed in accordance with a procedure analogous to that described elsewhere [20].

The experimental setup included a Perkin Elmer Spectrum RX 1 FT IR System or Bruker IFS-45 Fourier transform IR spectrometer, a heated flow reactor cell (V = 1 cm^3), a gas preparation unit, and a system for the analysis of products and reactants.

A sample as a 20- to 30-mg 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 an inert gas (He) flow at 450°C for 1 h and cooled to a required temperature, and the flow of a reaction mixture (30 ml/min) was turned on. Then, the concentrations of the resulting products and the spectra of surface compounds were measured at various temperatures.

The procedure of unsteady-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 reaction of methanol conversion or on the removal of methanol from a flow of the reaction mixture.

The intensity of absorption bands was measured in absorbance units (A) in difference spectra, which were obtained by subtracting the spectrum of the sample in an inert gas flow from the spectrum of the sample in a flow of the reaction mixture at the same temperature. Usually, the number of scans was 64, and the resolution was 4 cm^{-1}.

The concentrations of reactants and reaction products were measured using a 3700 chromatograph (Khromatograph plant, Moscow) with heated lines; helium was a carrier gas. Dimethyl ether, methanol, and methane were determined on a column with Porapak Q using a flame-ionization detector. Analysis for CO, H_2, and CO_2 was performed on columns with molecular sieves 5A and Porapak Q using a thermal-conductivity detector.

RESULTS

Steady-State Measurements in the Conversion of Methanol on CeO_2

The IR spectra measured in the course of methanol decomposition (4% MeOH in He) on CeO_2 exhibited absorption bands due to linear (1098 cm^{-1}) and bridging (1050 cm^{-1}) methoxy groups [11, 13, 22], monodentate (1577, 1370, and 1355 cm^{-1}) and bidentate (1555, 1370, and 1355 cm^{-1}) formate complexes [23], and a carbonate complex (1508, 1370, and 1065 cm^{-1}) in the region of C–O vibrations. In the region of 2800–3000 cm^{-1}, a number of absorption bands due to stretching C–H vibrations in methoxy groups and formate complexes [11, 13, 21, 22] were observed. The vibration frequencies of methoxy groups and formates increased with reaction temperature.

In the region of the stretching vibrations of surface OH groups, negative absorption with a maximum at 3640 cm^{-1} was observed. Negative intensity values in difference spectra indicated that hydroxyl groups were consumed in the course of methanol interaction with the surface.

Figure 1 shows the temperature dependence of the concentrations of methanol and its conversion products, as well as of the absorption band intensities measured in the same experiment. It can be seen that the formation of CO_2, CO, H_2, and CH_4 was observed only at temperatures higher than 300°C (Fig. 1b). Dimethyl ether was not detected in the reaction products.

From the data shown in Fig. 1a, it also follows that a decrease in the intensity of absorption bands due to methoxy groups (curves *1*, *2*) was accompanied by in increase in the intensity of absorption bands due to formate complexes (curves *3–5*) (the apparent increase in the absorption band intensity of the bridging methoxy group in curve *2* can be explained by the fact that the intensity of the absorption band of a carbonate complex manifests itself at the same frequency and increases with temperature). In turn, an increase in the intensity of absorption bands due to surface carbonate complexes (curves *6*, *7*) corresponds to a decrease in the intensity of absorption bands due to formate complexes.

Unsteady-State Measurements in the Conversion of Methanol on CeO_2

After reaching the steady-state concentrations of surface compounds (in a flow of 4% methanol in helium) and removing methanol from the reaction mixture, the isothermal desorption of surface compounds was performed (in a flow of helium). In this

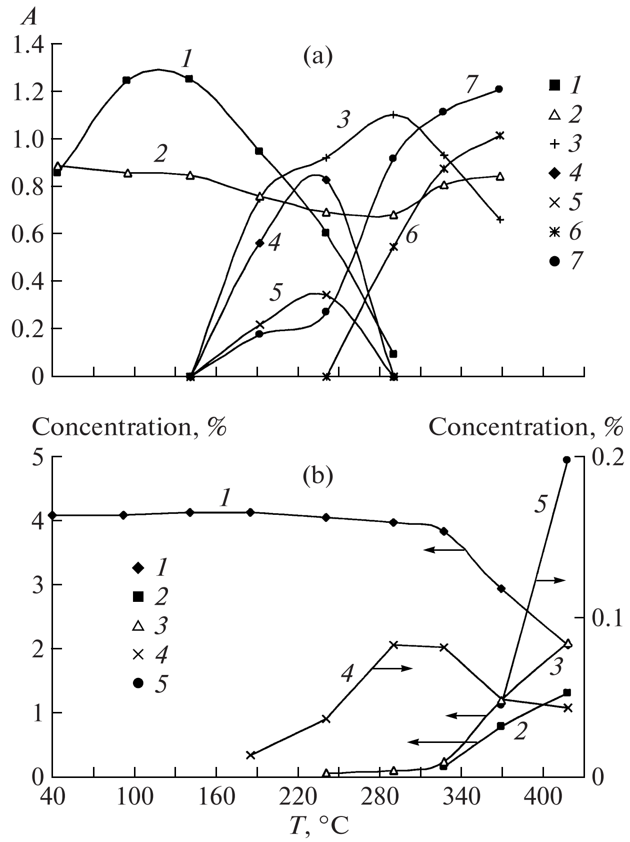


Fig. 1. The temperature dependence of (a) the absorption band intensities of surface compounds [(*1*) linear (1098 cm^{-1}) and (*2*) bridging (1050 cm^{-1}) methoxy groups, (*3*–*5*) formate complexes (1577, 1555, and 1355 cm^{-1}, respectively), and (*6*, *7*) carbonate complexes (1508 and 1370 cm^{-1}, respectively)] and (b) the concentrations of products [(*1*) CH_3OH, (*2*) H_2, (*3*) CO, (*4*) CO_2, and (*5*) CH_4] under the conditions of methanol decomposition on CeO_2.

case, the absorption band intensities of formate complexes and bridging and linear methoxy groups in the IR spectra were monitored. These experiments were performed at 150–300°C.

The resulting kinetic curves allowed us to determine apparent constants and the order of reaction of the consumption of surface complexes and to estimate the activation energy. The equation that describes changes in the concentration of methoxy groups is of first order. Table 1 summarizes the corresponding rate constants of methoxy group transformations.

The curves of the buildup of formate on the surface at low temperatures were also treated using first-order equation coordinates. Table 1 gives the rate constants of formate formation. The intensities of absorption bands due to formate complexes increased with temperature, whereas the time dependence of these intensities acquired the shape of a curve with a maximum. This character of dependences suggests that not only the formation but also the consumption of formate occurred at elevated temperatures.

The following activation energies of methoxy group transformations were determined from the temperature dependence of the constants: E_a^{1098} = 33 kJ/mol and E_a^{1050} = 21 kJ/mol.

Note that the rate constant of consumption of the linear methoxy group was almost the same as the rate constant of formation of monodentate formate (absorption band at 1577 cm^{-1}), and the rate constant of consumption of the bridging methoxy group was the same as the rate constant of formation of bidentate formate (1555 cm^{-1}).

Methanol Conversion on 5% CuO/CeO_2

Under the conditions of methanol conversion on 5% CuO/CeO_2, the intensity of absorption bands due to methoxy groups observed in the IR spectra was lower than that on CeO_2; the vibration frequencies were also slightly different. The spectrum was found much more complicated in the region of absorption due to formate complexes.

The deconvolution of the spectra obtained under the reaction conditions in the region of 1500–1600 cm^{-1} indicated that, in addition to absorption bands due to two formate complex forms localized on CeO_2 (absorption bands at 1577 and 1555 cm^{-1} (see above)), two other forms of this complex were also observed (absorption bands at 1587 and 1560 cm^{-1}). Because the latter two forms were observed only in the presence of copper oxide as a sample constituent, it is believed that they were localized on its surface.

Figure 2b shows the dependence of the concentrations of MeOH and reaction products (H_2, methyl for-

Table 1. Rate constants of consumption of methoxy groups and formation of formates under the reaction conditions of methanol conversion on CeO_2 at 190°C

Surface compound	Frequency, cm^{-1}	Consumption rate constant k, min^{-1}, $n = 1$	Formation rate constant k, min^{-1}, $n = 1$
Linear methoxy group	1098	**0.054**	–
Bridging methoxy group	1050	0.019	–
Bidentate formate	1555	–	0.023
Monodentate formate	1577	–	**0.056**

mate, CO, CO_2, and CH_4) and the intensities of absorption bands on the temperature of the experiment. It can be seen that the composition of the reaction products on the copper-containing catalyst changed (methyl formate was detected). Moreover, the formation of reaction products came into play at lower temperatures, and they concentrations were much higher than those on CeO_2 (Figs. 1b, 2b). It is of interest that, on going from 250 to 300°C, the concentration methanol at the reactor outlet increased (curve *1*) with a simultaneous decrease in the concentrations of H_2 and CO_2 (curves *2*, *4*). This fact can be explained by the occurrence of the reverse reaction of methanol synthesis from H_2 and CO_2 in this temperature range.

Figure 2a shows the temperature dependence of the intensities of absorption bands due to surface compounds measured in the same experiment. It can be seen that a decrease in the intensity of absorption bands due to methoxy groups (curves *1*, *2*) was initially accompanied by an increase and the subsequent decrease in the intensity of absorption bands due to formate complexes (curves *4*, *6*, *7*). In turn, the decrease in the intensity of absorption bands due to formate complexes corresponds to an increase in the intensity of absorption bands due to surface carbonate compounds (curves *3*, *5*). As the temperature was increased, the absorption bands due to methoxy groups and formate complexes shifted toward low frequencies.

From a comparison between spectroscopic and catalytic data (Figs. 2a, 2b), it follows that the formation of reaction products and the transformation of formate and carbonate complexes occurred over the same temperature range. Note that the formation of CO_2 and H_2 (curves *2*, *4*) began simultaneously. The temperature of these processes corresponds to the temperature at which the intensity of the absorption bands due to formate complexes decreased (Fig. 2a, curve *4*). The formation of CO (Fig. 2b, curve *3*) began at a higher temperature, which corresponded to the temperature of methyl formate formation (Fig. 2b, curve *6*).

Effects of oxygen and water on the conversion of methanol on 5% CuO/CeO_2. The addition of oxygen at relatively low temperatures (200–270°C) caused a decrease in the concentrations of H_2 and CO. Simultaneously, the concentration of CO_2 increased. An opposite effect was observed at elevated temperatures (above 270°C): the addition of oxygen caused an increase in the concentration of hydrogen. Recall that, in the absence of oxygen, a decrease in methanol conversion with temperature was observed (Fig. 2) because of the occurrence of the reverse reaction of methanol synthesis. However, this effect disappeared upon the addition of oxygen. In this case, the observed increase in the concentration of hydrogen can be due to the fact that the reverse reaction of methanol synthesis from CO_2 and H_2 was inhibited in the presence of O_2. It is of interest that the addition of oxygen also inhibited the reaction of methyl formate formation.

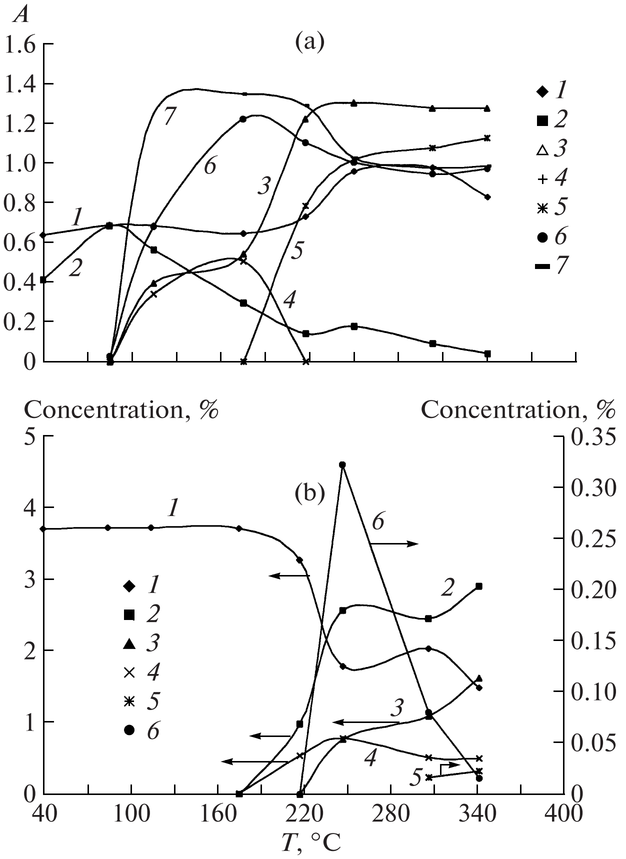


Fig. 2. The temperature dependence of (a) the absorption band intensities of surface compounds [(*1*) bridging (1050 cm^{-1}) and (*2*) linear (1098 cm^{-1}) methoxy groups, (*3*, *5*) carbonate complexes (1366 and 1508 cm^{-1}, respectively), and (*4*, *6*, *7*) formate complexes (1370, 1560, and 1587 cm^{-1}, respectively),] and (b) the concentrations of products [(*1*) CH_3OH, (*2*) H_2, (*3*) CO, (*4*) CO_2, (*5*) CH_4, and (*6*) $HCOOCH_3$] under the reaction conditions of methanol decomposition on 5% Cu/CeO_2.

The effect of O_2 on the concentration of surface compounds manifested itself as a considerable increase in the thermal stability of both formate and carbonate complexes. This circumstance may be responsible for the inhibition of the reaction of methanol synthesis. In this case, the intensity of absorption bands due to methoxy groups changed only slightly.

Figures 3a and 3b illustrate the effect of water vapor on the course of the reaction of MeOH conversion. It can be seen that the addition of water vapor to the reaction mixture considerably decreased the concentrations of CO and methyl formate (Fig. 3a, curves *4*, *6*), decreased the surface concentration of methoxy groups (Fig. 3b, curve *1*), and only slightly affected the other parameters.

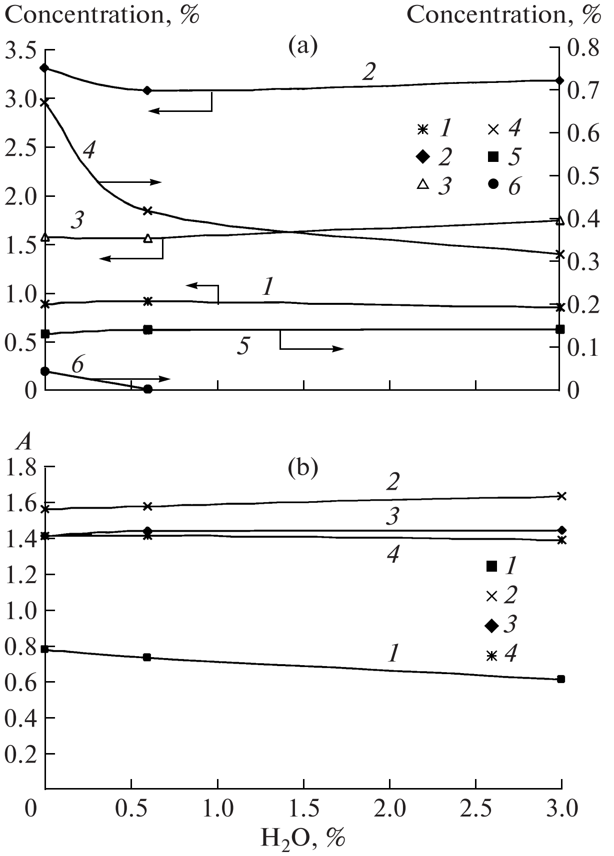


Fig. 3. Dependence of (a) the concentrations of (*1*) CH_3OH, (*2*) H_2, (*3*) CO_2, (*4*) CO, (*5*) O_2, and (*6*) $HCOOCH_3$ and (b) the concentrations of surface compounds [(*1*) bridging methoxy group (1050 cm^{-1}), (*2*, *3*) carbonate complexes (1371 and 1508 cm^{-1}, respectively), and (*4*) formate complex (1577 cm^{-1})] on the concentration of H_2O under the reaction conditions of methanol decomposition on 5% Cu/CeO_2 at 300°C.

Unsteady-State Measurements in the Conversion of Methanol on 5% CuO/CeO_2

In the conversion of methanol under unsteady-state conditions, the time dependence of absorption band intensities in the course of isothermal desorption cannot be described in the coordinates of a first- or second-order rate equation (Fig. 4). This is likely due to the fact that linear and bridging methoxy groups, as well as the formate complex, are consumed in several reaction paths. We used initial rates as a parameter that characterizes the conversion of surface compounds in this case. Table 2 summarizes the corresponding values.

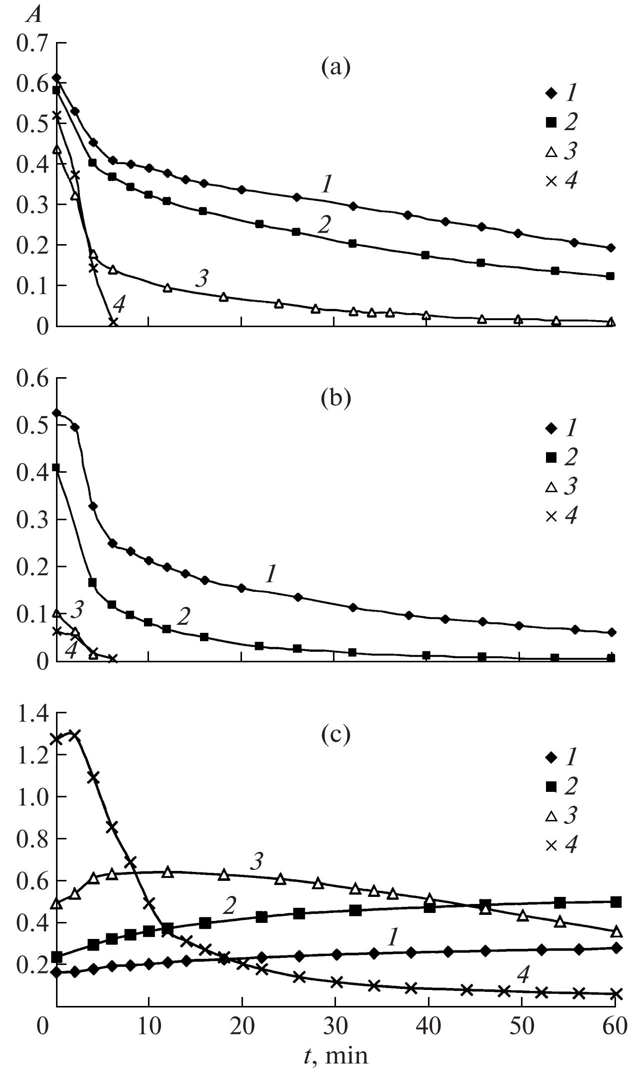


Fig. 4. The time dependence of the absorption band intensities of (a) bridging (1050 cm^{-1}) and (b) linear (1098 cm^{-1}) methoxy groups and (c) formate (1371 cm^{-1}) at various temperatures: (*1*) 120, (*2*) 150, (*3*) 210, and (*4*) 250°C (desorption in a flow of helium; 5% Cu/CeO_2).

An analysis of the data in Table 2 indicates that the rate of consumption of methoxy groups increased with temperature. An unexpectedly high reaction rate was found for the consumption of the linear methoxy group at 210°C. At 250°C, the addition of water vapor and, to an even greater extent, the addition of oxygen led to an increase in the rates of consumption of methoxy groups of both types. An analogous effect was also observed in surface carbonate complexes. The presence of water vapor and an increase in the oxygen content had only a weak effect on the rate of consumption of formates localized on both CeO_2 and CuO.

DISCUSSION

Model of the Active Surface

On the surface of a 5% Cu/CeO_2 sample, the same methoxy groups as on CeO_2 were observed under the reaction conditions of methanol conversion. However, the intensity of the corresponding absorption bands in the spectra was much lower. These facts suggest that the formation of the observed complexes occurred on the CeO_2 surface free of copper oxide particles. At the

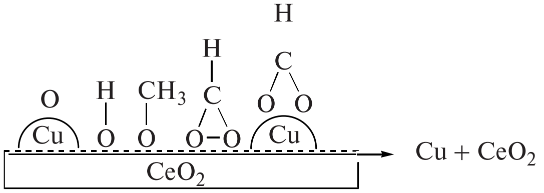
Table 2. Initial rates of conversion of surface compounds under the reaction conditions of methanol conversion on 5% Cu/CeO_2

Surface compound	Frequency, cm^{-1}	Initial rate of consumption of surface compounds, arb. units					
Temperature, °C		120	150	210	250	250*	250**
Linear methoxy group	1098	0.026	0.056	0.40	0.20	0.58	0.36
Bridging methoxy group	1050	0.011	0.018	0.059	0.28	0.50	0.40
Formate	1355(Ce)	–	–	–	0.021	0.024	0.027
	1370(Ce)	–	–	–	0.018	0.024	0.03
	1355(Cu)	–	–	–	0.058	0.046	0.045
	1370(Cu)	–	–	–	0.062	0.050	0.047
	1560(Cu)	–	–	–	0.06	0.056	0.056
	1587(Cu)	–	–	–	0.15	0.12	0.13
Carbonate	1371	–	–	–	0.13		
	1508	–	–	–	0.14	0.59	0.42
	1065	–	–	–			0.37
		Initial rate of formation of surface compounds, arb. units					
Formate	1355	0.024	0.051	–	–	–	
	1370	0.036	0.052	–	–	–	
	1555	0.038	0.039	–	–	–	
	1577	0.034	0.071	–	–	–	

* Addition of O_2 to the reaction mixture.

** Addition of H_2O to the reaction mixture.

same time, the shift in the frequencies (±2–5 cm^{-1}) of absorption bands with respect to the values observed on CeO_2 and an increase in the rate constants of methoxy group transformations (Tables 1, 2) can be explained by the surface modification of CeO_2 upon supporting copper [24]. Based on these data, we propose the following model of the catalyst:



This model was also supported by TPR data for Cu/CeO_2 [25, 26], according to which the TPR spectra exhibited two peaks of hydrogen absorption in the region of 100–200°C. The first (low-temperature) peak corresponds to the reduction of Cu^{2+} ions localized in a near-surface layer of the CeO_2 lattice, and the second corresponds to the reduction of CuO particles on the surface of CeO_2.

Transformation of Surface Compounds

Methoxy groups. The formation of methoxy groups by the interaction of methanol with the surface of CeO_2 was accompanied by a decrease in the intensity of absorption bands due to hydroxyl groups (3600 and 3640 cm^{-1}). Therefore, they were formed in accordance with a classical reaction scheme with the participation of surface hydroxyl groups [10], linear and bridging, with the participation of terminal and bridging hydroxyl groups, respectively. In this case, the formation of methoxy groups can be accompanied by the cleavage of both the O–H and the C–O bond in the alcohol molecule. Lamotte et al. [27] used the adsorption of oxygen-labeled methanol to demonstrate that the formation of methoxy groups on CeO_2 occurred with O–H bond cleavage in the alcohol molecule. Recall that the formation of these groups on γ-Al_2O_3 (upon the interaction of methanol with acidic surface hydroxyl groups) was accompanied by C–O bond cleavage in the alcohol molecule. This difference in the nature of methoxy groups may explain the fact that dimethyl ether was formed on γ-Al_2O_3 and not formed on CeO_2.

Formate complexes. The IR spectra obtained under the reaction conditions on CeO_2 exhibited absorption bands due to vibrations in surface monodentate (1577, 1370, and 1355 cm^{-1}) and bidentate (1555, 1370, and 1355 cm^{-1}) formate complexes (e.g., see [10, 28–33]).

Table 1 lists the rate constants of consumption of methoxy groups and formation of formate complexes. It can be seen that the rate constant of consumption of the linear methoxy group coincides with the rate constant of formation of monodentate formate (1577 cm^{-1}). The above ratio is also characteristic of the rate constants of consumption of the bridging methoxy group and formation of bidentate formate (1555 cm^{-1}). This fact suggests that the monodentate formate results from the oxidative conversion of the linear methoxy group, whereas the bidentate formate results from the oxidative conversion of the bridging methoxy group. The data in Fig. 1 also support the formation of formates from methoxy groups: a decrease in the intensity of absorption bands due to methoxy groups was accompanied by an increase in the intensity of absorption bands due to formates.

Two additional formate complex species (1587 and 1560 cm^{-1}) localized on the surface of copper oxide were also observed on 5% Cu/CeO_2. In this case, it is difficult to correlate the rate constants of consumption of methoxy groups to the rate constants of formation of various formate species, although corresponding estimations (Table 2) indicated that, at low temperatures, the rate constants of consumption of methoxy groups were close to the rate constants of formation of formates. In addition, a decrease in the concentration of methoxy groups with temperature was accompanied by an increase in the concentration of formate complexes (Fig. 2). These facts suggest that methoxy groups are also a source of formate formation on the copper-containing sample.

Several reaction paths can be hypothesized for the consumption of formate complexes. The first of them is related to the formation of surface carbonate complexes. The occurrence of this reaction path was demonstrated by the fact that the decrease in the intensity of absorption bands due to formates in the spectra of the sample with increasing temperature (Fig. 2) was accompanied by an increase in the intensity of absorption bands due to carbonate complexes (1065, 1370, and 1508 cm^{-1}). The formation of carbonate complexes came into play at temperatures that correspond to the almost complete absence of methoxy groups from the surface. It is obvious that carbonates underwent decomposition with the release of CO_2 as the temperature was increased.

The second reaction path in the consumption of formates is associated with their decomposition to form CO_2 and hydrogen in the gas phase. This is supported by the fact that the simultaneous appearance of CO_2 and hydrogen in the gas phase coincided with a decrease in the surface formate concentration in terms of temperature (Figs. 2a, 2b).

The formation of methyl formate implies the occurrence of an additional reaction path for the consumption of the formate complex. In accordance with published data [31–33], methyl formate is formed by the condensation reaction of a formate complex and the methoxy group. In our case, methyl formate is formed with the participation of the linear methoxy group, as supported by a dramatic increase in the rate constant of consumption of this methoxy group at 210°C (Table 2). At this temperature, methyl formate began to form at a considerable rate (Fig. 2). It is likely that the reverse reaction of methyl formate decomposition into the formate complex and the methoxy group also occurred. This was demonstrated by a decrease in the rate of consumption of the linear methoxy group on going from 210 to 250°C (Table 2). The increase in the concentrations of CO and H_2 with increasing temperature of the experiment, which was accompanied by a decrease in the concentration of methyl formate (Fig. 2), evidenced the occurrence of methyl formate decomposition with the formation of CO and H_2 in the gas phase.

In the presence of oxygen in the reaction mixture, the deep oxidation of methanol occurred. This circumstance was supported by the fact that only CO_2 was formed in reaction products at relatively low temperatures (Figs. 1, 2). Moreover, the reaction of CO oxidation can occur in the presence of oxygen.

From the above data, it follows that the formation of reaction products (Figs. 1, 2b) corresponds to the temperature range of formate and carbonate conversion. In other words, methoxy groups, formates, and carbonates can be reaction intermediates in the conversion of methanol on 5% Cu/CeO_2. The following reaction scheme is proposed to describe the process:

Number	Step	*N*
I	$2Z + O_{2(g)} \longrightarrow 2ZO$	2
II	$CH_3OH_{(g)} + ZOH \longrightarrow CH_3OZ + H_2O_{(g)}$	7
III	$CH_3OZ + ZO \longrightarrow HCOOZ + Z + H_2$	4
IV	$CH_3OZ + HCOOZ \longrightarrow HCOOCH_3Z + ZO$	2
V	$CH_3OZ + ZH \longrightarrow CH_3OH_{(g)} + 2Z$	1
VI	$HCOOCH_3Z \longrightarrow HCOOCH_{3(g)} + Z$	1
VII	$HCOOCH_3Z \longrightarrow 2CO + 2H_2 + Z$	1
VIII	$HCOOZ + ZO \longrightarrow ZCO_3 + ZH$	1
IX	$HCOOZ \longrightarrow CO_{2(g)} + ZH$	1
X	$ZCO_3 \longrightarrow CO_{2(g)} + ZO$	1
XI	$H_2O_{(g)} + 2Z \longrightarrow ZOH + ZH$	5
XII	$ZH + ZO \longrightarrow ZOH + Z$	2
XIII	$ZH + ZH \longrightarrow H_{2(g)} + 2Z$	2

$$6CH_3OH + 2O_2$$
$$= HCOOCH_3 + 8H_2 + 2CO + 2CO_2 + 2H_2O,$$

where N is the stoichiometric number of the step.

This reaction scheme explains the first order of consumption of methoxy groups on CeO_2. Indeed, the expression for the rate of transformation of the methoxy group has the following form:

$$d(CH_3OZ)/dt = -\theta_{CH3OZ}(k_3\theta_O + k_4\theta_f + k_5\theta_{ZH}). \quad (1)$$

In the presence of CeO_2, methyl formate is not formed ($k_4 = 0$), desorption with the formation of methanol is negligibly small [34] ($k_5 = 0$), and θ_O = const because impurity oxygen (to 0.2%) always occurred in the gas flow. It is clear that the first order can be observed on 5% Cu/CeO_2 only at low temperatures when methyl formate is not formed.

Role of Copper in Methanol Conversion on 5% Cu/CeO_2

In the presence of copper as a catalyst constituent, the activity considerably increased and the composition of products changed, whereas the composition of surface complexes remained almost the same (Figs. 1, 2). These facts suggest that new reactions between the same complexes can occur on the surface. The recombination of hydrogen atoms (step XIII) on copper clusters (hydrogen atoms result from mutual transformations of surface compounds) and the reaction between the linear methoxy group and the formate complex (localized on copper) to form methyl formate are the most important of the above reactions. As a result, the following two main reaction paths of hydrogen formation occur: the recombination of hydrogen atoms on copper oxide particles and the decomposition of methyl formate ($W_{H2} = k_7\theta_{mf} + k_{13}\theta_H^2$).

Similarly, there are the following two main reaction paths of CO_2 formation: the decomposition of formate and carbonate ($W_{CO_2} = k_9\theta_f + k_{10}\theta_{CO_3}$). This equation can be checked. Indeed, the constants k_9 and k_{10} and the surface coverages θ_f and θ_{CO_3} were measured at 250°C using IR spectroscopy. The rate of CO_2 formation is also known. In accordance with a procedure described elsewhere [20], we estimated the rate of formate and carbonate conversion into CO_2. This value was 5.3×10^{18} molecule/min on a sample. The rate of CO_2 formation on the same sample was 6.1×10^{18} molecule/min, as measured by chromatography. The measured value is somewhat higher than the calculated value because of the oxidation of a portion of CO and methanol by impurity oxygen.

The decrease in the temperatures of the formation and consumption of the surface formate complexes suggests that the oxidizing power of the catalyst was considerably higher in the presence of copper. The activation of oxygen on supported copper was responsible for this capacity. In studies of the reaction of methanol oxidation on copper powder [35, 36], it was found that suboxide oxygen bound to defect sites of copper particles is active in the oxidation of methoxy groups. The formation of this oxygen species occurs only under the action of the reaction atmosphere and only on the surface of copper metal. It is likely that the presence of copper metal is responsible for the occurrence of steps III, VIII, and XII in the process of methanol conversion on 5% Cu/CeO_2.

It is of interest that the addition of both water vapor and oxygen resulted in the suppression of the formation of methyl formate. It is likely that surface oxidation occurred in the presence of both water vapor and oxygen. Upon oxidation (as the concentration of surface oxygen increased), both the state of copper particles and the state of the CeO_2 surface modified with copper ions changed (the occurrence of the oxidation of surface copper in the state Cu^0 or Cu^{+1} with water was demonstrated [37–39]). On the oxidized surface, the oxidative conversion of the methoxy group was predominant over the condensation reaction of the methoxy group and formate.

Surface oxidation (by impurity oxygen) also occurred in the course of unsteady-state experiments after the removal of methanol from the flow of the reaction mixture. This is evidenced by the considerable decrease in the frequencies of absorption bands due to methoxy groups and formates at the initial points in time. It is clear that this change in the surface state affected the reactivity of methoxy groups. This reactivity was sufficiently high at the initial points in time. As a result, the kinetic curve can be adequately described in terms of a first-order equation after a 6-min experiment, when surface properties remain almost unchanged. These facts suggest that the rate of transformation of methoxy groups on a sample in the reduced state is higher than that on the oxidized sample.

The above consideration indicates that the main reaction of hydrogen formation is the recombination of hydrogen atoms on copper clusters, as well as the decomposition of methyl formate. Formate and carbonate complexes are the sources of CO_2 formation in the gas phase. The decomposition of methyl formate is the source of CO. The addition of water vapor to the reaction flow is useful: the rate of CO formation decreases considerably at an invariable yield of hydrogen.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 07-03-00373.

REFERENCES

1. Lindström, B., Pettersson, L., and Menon, P.G., *Appl. Catal., A*, 2002, vol. 234, p. 111.
2. Zhang, X. and Shi, P., *J. Mol. Catal. A: Chem.*, 2003, vol. 194, p. 99.
3. Iwasa, N., Mayanagi, T., and Ogawa, N., *Catal. Lett.*, 1998, vol. 54, p. 119.

4. Kapoor, M.P., Raj, A., and Matsumura, Y., *Microporous Mesoporous Mater.*, 2001, vols. 44–45, p. 565.
5. Schiffino, R.S. and Merril, R.P., *J. Phys. Chem.*, 1993, vol. 97, p. 6425.
6. Krylov, O.V. and Matyshak, V.A., *Promezhutochnye soedineniya v geterogennom katalize* (Intermediates in Heterogeneous Catalysis), Moscow: Nauka, 1996.
7. Matyshak, V.A., Khomenko, T.I., Lin, G.I., Zavalishin, I.N., and Rozovskii, A.Ya., *Kinet. Katal.*, 1999, vol. 40, no. 2, p. 295 [*Kinet. Catal.* (Engl. Transl.), vol. 40, no. 2, p. 269].
8. Neophytides, S.G., Marchi, A.J., and Froment, G.F., *Appl. Catal., A*, 1992, vol. 86, p. 45.
9. Martin, K.A. and Zabransky, R.F., *Appl. Spectrosc.*, 1991, vol. 45, p. 68.
10. Davydov, A.A., *IK-Spektroskopiya v khimii poverkhnosti okislov* (IR Spectroscopy Applied to the Chemistry of Oxide Surfaces), Novosibirsk: Nauka, 1984.
11. Daturi, M., Binet, C., Lavalley, J-C., Galtayries, A., and Spoken, R., *Phys. Chem. Chem. Phys.*, 1999, vol. 1, p. 5717.
12. Sidkon, A. and Nix, R.M., *J. Phys. Chem. B*, 1999, vol. 103, p. 6984.
13. Novakova, J., Kubelkova, L., and Dolysek, Z., *J. Catal.*, 1987, vol. 108, p. 208.
14. Lamotte, J., Moravek, V., Bensitel, M., and Lavalley, J.C., *React. Kinet. Catal. Lett.*, 1988, vol. 36, p. 113.
15. Knop-Gericke, A., Havecker, M., Schedel-Niedrig, Th., and Schlogl, R., *Top. Catal.,* 2000, vol. 10, p. 187.
16. Carley, A.P., Owens, A.W., Rajumon, M.K., Roberts, M.W., and Jackson, S.D., *Catal. Lett.*, 1996, vol. 37, p. 79.
17. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.*, 1971, vol. 67, p. 3585.
18. Matyshak, V.A., Berezina, L.A, Sil'chenkova, O.N., Tret'yakov, V.F., Lin, G.I., and Rozovskii, A.Ya., *Kinet. Katal.*, 2009, vol. 50, no. 1, p. 120 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 1, p. 111].
19. Matyshak, V.A., Berezina, L.A, Sil'chenkova, O.N., Tret'yakov, V.F., Lin, G.I., and Rozovskii, A.Ya., *Kinet. Katal.*, 2009, vol. 50, no. 2, p. 270 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 2, p. 255].
20. Matyshak, V.A. and Krylov, O.V., *Catal. Today*, 1996, vol. 25, p. 1.
21. Chuah, G.K., *Catal. Today*, 1999, vol. 49, p. 131.
22. Binet, C. and Daturi, M., *Catal. Today*, 2001, vol. 70, p. 155.
23. Li, C., Sakata, Y., Arai, T., Domen, K., Maruya, K., and Onishi, T., *J. Chem. Soc., Faraday Trans. 1*, 1989, vol. 85, no. 4, p. 920.
24. Manzoli, M., Chiorino, A., and Boccuzzi, F., *Appl. Catal., B*, 2005, vol. 57, p. 201.
25. Liu, Y., Hayakawa, T., Suzuki, K., Hamakawa, S., Tsunoda, T., Ishii, T., and Kumagai, M., *Appl. Catal., A*, 2002, vol. 223, p. 137.
26. Firsova, A.A., Il'ichev, A.N., Khomenko, T.I., Gorobinskii, L.V., Maksimov, Yu.V., Suzdalev, I.P., and Korchak, V.N., *Kinet. Katal.*, 2007, vol. 48, no. 2, p. 298 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 2, p. 282].
27. Lamotte, J., Moravek, V., Bensitel, M., and Lavalley, J.C., *React. Kinet. Catal. Lett.*, 1988, vol. 36, no. 1, p. 113.
28. Millar, G.J., Rochester, C.H., and Waugh, K.C., *J. Chem. Soc., Faraday Trans.*, 1991, vol. 87, no. 17, p. 2795.
29. Millar, G.J., Rochester, C.H., and Waugh, K.C., *J. Chem. Soc., Faraday Trans.*, 1991, vol. 87, no. 17, p. 2785.
30. Burcham, L.J. and Wachs, I.E., *Catal. Today*, 1999, vol. 49, p. 467.
31. Sambeth, J.E., Centeno, M.A., Paul, A., et al., *J. Mol. Catal. A: Chem.*, 2000, vol. 161, p. 89.
32. Busca, G., *Catal. Today*, 1996, vol. 27, p. 457.
33. Fisher, I.A. and Bell, A.T., *J. Catal.*, 1998, vol. 178, p. 153.
34. Siokou, A. and Nix, R.M., *J. Phys.Chem. B*, 1999, vol. 103, p. 6984.
35. Knop-Gericke, A., Havecker, M., Schedel-Niedrig, Th., and Schlögl, R., *Top. Catal.*, 2000, vol. 10, p. 187.
36. Prosvirin, A.P., Tikhomirov, E.P., Sorokin, A.M., Kaichev, V.V., and Bukhtiyarov, V.I., *Kinet. Katal.*, 2003, vol. 44, no. 5, p. 724 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 5, p. 662].
37. Choi, Y. and Stenger, H.G., *Appl. Catal., B*, 2002, vol. 38, p. 259.
38. Rozovskii, A.Ya., *Kinet. Katal.*, 2003, vol. 44, no. 3, p. 391 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 3, p. 360].
39. Rozovskii, A.Ya. and Lin, G.I., *Teoreticheskie osnovy sinteza metanola* (Theoretical Principles of Methanol Synthesis), Moscow: Khimiya, 1990.