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Spectroscopic Study of the Properties of Surface Compounds in Methanol Conversions on Cu/γ-Al_2O_3

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Abstract—The reactions of methanol on the (10% Cu)/γ-Al_2O_3 surface were studied by the spectrokinetic method (simultaneous measurements of the conversion rates of surface compounds and the product formation rates). Bridging and linear methoxy groups result from the interaction of methanol with surface hydroxyl groups. Formate and aldehyde-like complexes form by the oxidative conversion of the linear methoxy groups. Hydrogen forms via the recombination of hydrogen atoms on copper clusters, and the hydrogen atoms result from interconversions of surface compounds. The source of CO_2 in the gas phase is the formate complex, and the source of CO is the aldehyde complex. In the absence of methanol in the gas phase, dimethyl ether forms by the interaction between two bridging methoxy groups. When present in the gas phase, methanol reacts with methoxy groups on the surface. The roles of oxygen and water vapor in the conversions of surface compounds are discussed.

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This work continues a series of studies of methanol conversion on the commercial copper-containing catalyst SNM-1 [1–4]. Since the SNM-1 catalyst is a complicated three-component system, we chose to study the following catalysts in the order of increasing complexity of their composition:

$$\gamma\text{-}Al_2O_3 \longrightarrow Cu/\gamma\text{-}Al_2O_3 \longrightarrow \text{SNM-1}(CuO/ZnO/Al_2O_3).$$

Earlier, we carried out an in situ IR spectroscopic study of the conversion of surface compounds in the methanol/γ-Al_2O_3 system [8]. It was found that, in the absence of methanol in the gas phase, dimethyl ether (DME) results from the interaction between two bridging methoxy groups. In the presence of methanol, DME results from the interaction between methanol from the gas phase and a surface methoxy group. Linear methoxy groups turn into a formate and an aldehyde, which are sources of CO_2 in the gas phase.

The complexes resulting from the interaction between methanol and the surface of a Cu-containing oxide catalyst (methoxy groups and formate, aldehyde, and dioxymethylene complexes) have already been characterized properly (see, e.g., [5–8]). However, the role of these complexes in the formation of reaction products is still unclear.

Here, we report an in situ IR spectroscopic study of the properties of the surface compounds and their role in the formation of methanol conversion products on the catalyst (10 wt % Cu)/γ-Al_2O_3.

EXPERIMENTAL

The (10 wt % Cu)/γ-Al_2O_3 catalyst was prepared by impregnating alumina with an aqueous solution of $Cu(NO_3)_2$. The properties of γ-Al_2O_3 (Ryazan Petroleum Refinery) are described elsewhere [8].

The reactant in the methanol decomposition reaction was a mixture containing 4% methanol and helium as the balance. Helium contained up to 0.2% oxygen as an impurity.

In oxidative reforming, 3.3% oxygen was added to the mixture; in steam reforming, 3.0% water vapor was added. Experiments were performed on oxidized catalyst samples (400°C, 3.3% O_2 in He, 1 h) and on reduced samples (400°C, H_2, 1 h).

Spectrokinetic measurements under conditions of methanol reforming were carried out using a procedure similar to the procedure reported in [9]. A detailed description of these measurements is presented in our earlier paper [8]. In steady- and unsteady-state spectrokinetic studies, we simultaneously measured the reactant conversion rate by chromatographing the gas phase and the concentrations of surface compounds by in situ IR spectroscopy.

CO (18% CO/He) was adsorbed on a catalyst sample pretreated with flowing H_2 or 5% O_2/He at 400°C for 1 h. Adsorption was performed under heating at a

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† Deceased.

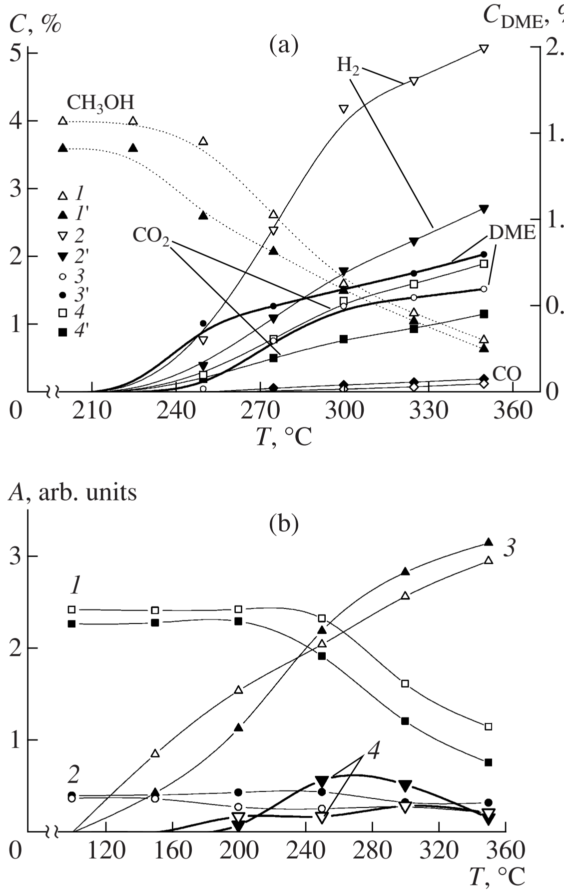


Fig. 1. Temperature dependences of (a) product concentrations and (b) IR absorption band intensities under conditions of (*1'*–*4'*) methanol decomposition and (*1*–*4*) methanol steam reforming on the reduced (10% Cu)/γ-Al_2O_3 sample. (b): (*1*) 1090 cm^{-1}, (*2*) 1190 cm^{-1}, (*3*) 1590 cm^{-1}, and (*4*) 1320 cm^{-1}.

constant rate of 7 K/min in the 20–400°C range with simultaneous recording of the IR spectrum.

RESULTS

Steady-State Measurements

Spectroscopic measurements under steady-state reaction conditions demonstrated that the surface of the catalysts contains the same surface compounds as the γ-Al_2O_3 surface [8], namely, a formate complex (1590, 1390, and 1375 cm^{-1}), aldehyde complexes (1682, 1658, 1633, and 1320 cm^{-1}), and bridging and linear methoxy groups (1090 and 1190 cm^{-1}, respectively). At the same time, there is a significant difference between the reaction products: the reaction over the (10 wt % Cu)/γ-Al_2O_3 catalyst yields considerable amounts of H_2 and CO_2 along with DME. Above 300°C, the formation of CO (~0.5%) is observed.

Table 1. Ratios of the products of methanol steam reforming and decomposition on the (10% Cu)/γ-Al_2O_3 catalyst ($T = 350$°C)

Sample	$C_{i,\text{ steam reforming}}/C_{i,\text{ decomposition}}$			
	H_2	CO_2	DME	CO
Oxidized	2.08	1.97	0.73	0.60
Reduced	1.87	1.64	0.75	0.65

Figure 1 presents product composition data and absorption band intensity data for the surface compounds on the reduced catalyst for methanol decomposition (4% MeOH in He) and methanol steam reforming (4% MeOH + 3% H_2O in He). A simultaneous analysis of the catalytic and spectroscopic data (Figs. 1a, 1b) shows that, for the above reactions, there is always a correlation between the absorption band intensities and the product concentrations: the lower the temperature at which the consumption of bridging methoxy groups begins, the lower the DMR formation temperature; the lower the temperature at which the consumption of linear methoxy groups begins, the lower the temperature at which the formation of H_2, CO, and CO_2 begins. An evident slowdown of the growth of the formate complex concentration begins near the same temperature point (curves *3*). This correlation between the surface compound and product concentrations suggests that the above complexes may be intermediates in methanol conversion.

Note that, as compared to methanol decomposition, methanol steam reforming (4% MeOH + 3% H_2O in He) yields larger amounts of H_2 and CO_2 and smaller amounts of DME and CO (Table 1).

The reduced catalyst is less active in the processes examined than the oxidized catalyst. The methanol conversion in steam reforming over the reduced and oxidized catalysts at 350°C is 81 and 94%, respectively. However, the H_2 selectivity of the reduced catalyst is higher than that of the oxidized catalyst (62 versus 38%). The reduced catalyst was also tested in oxidative methanol reforming. As compared to methanol decomposition (Fig. 1a), partial oxidation on this sample yields a lower H_2 concentration and a comparable amount of DME.

Unsteady-State Measurements

Desorption in flowing helium. After the establishment of the steady-state values of the catalytic activity and surface compound concentrations under 4% MeOH + He flow, we carried out isothermal desorption of surface complexes into flowing helium, simultaneously identifying the desorption products and monitoring the time evolution of the intensities of the absorption bands of the surface compounds. Figure 2 presents the results of a typical run at 300°C for the reduced catalyst. The desorption products are DME, CH_3OH, CO_2, H_2, and CO. The DME, CH_3OH, and CO concentrations decrease with time (Fig. 2b), just like the concentrations of bridging and linear methoxy groups and the aldehyde complex (Fig. 2a). The CO_2 and H_2 concentrations pass through a maximum (Fig. 2b, curves *3*, *4*), and so does the concentration of the formate complex (Fig. 2a, curve *3*).

Studies of the time dependences of the methoxy group absorption band intensities at different temperatures (Fig. 2) demonstrated that, as in the case of γ-Al_2O_3, the concentrations of bridging and linear methoxy groups decrease according to a second- and first-order rate law, respectively (Table 2).

Clearly, the methoxy group disappearance rate constants for the reduced sample are much larger than the same constants for γ-Al_2O_3. The rate constants observed for the oxidized (10% Cu)/γ-Al_2O_3 catalyst are similar to those observed for γ-Al_2O_3 (Table 2). From the temperature dependences of the disappearance rate constants, we derived the corresponding activation energies (Table 3).

The time dependences of the concentrations of the formate and aldehyde complexes pass through a maximum (Fig. 2). The point in time at which this maximum occurs depends on the run temperature and the state of the sample. As the temperature is raised, the maximum shifts to shorter times. For the reduced sample, the maximum is observed at longer times. The presence of a maximum in the concentration curves suggests that both the aldehyde and formate complexes form and disappear during the process.

Desorption in a helium/oxygen flow. In these experiments, we examined a prereduced (10% Cu)/γ-Al_2O_3 sample, varying the oxygen concentration in the helium/oxygen mixture (1.0, 2.0, and 3.3% O_2).

Figure 3 presents the results of the desorption run in He/2% O_2 at 300°C. The CO_2 conversion, like the concentration of the formate complex, passes through a maximum (Figs. 3a, 3b, curves *3*). The H_2, DME, CO, and methanol concentrations decrease with time (Fig. 3b, curves *1*, *2*, *4*). This decrease is accompanied by a decrease in the concentrations of bridging and linear methoxy groups (Fig. 3a, curves *1*, *2*). The concentration of the aldehyde complex passes through a maximum (Fig. 3a, curve *4*).

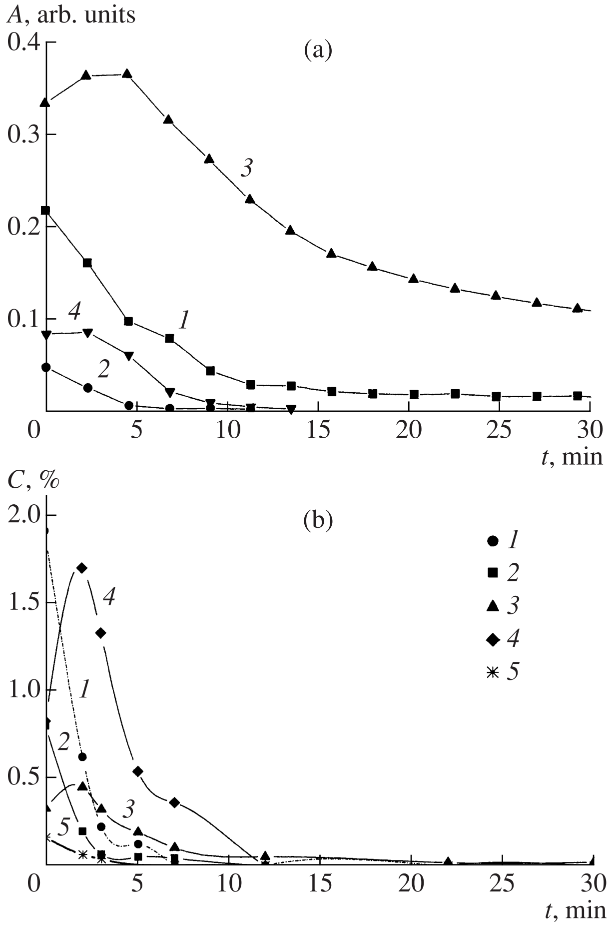


Fig. 2. Time dependences of (a) IR absorption band intensities and (b) product concentrations for the reduced (10% Cu)/γ-Al_2O_3 sample. Conditions: desorption in flowing helium, T = 300°C; (a): (*1*) 1090 cm^{-1}, (*2*) 1190 cm^{-1}, (*3*) 1590 cm^{-1}, and (*4*) 1320 cm^{-1}; (b): (*1*) CH_3OH, (*2*) DME, (*3*) CO_2, (*4*) H_2, and (*5*) CO.

Table 2. Temperature dependences of the rate constants of disappearance of bridging and linear methoxy groups on (10% Cu)/γ-Al_2O_3 and γ-Al_2O_3 (for comparison)

T, °C	$k_{(1190\ cm^{-1})}$, min^{-1} $n = 1$			$k_{(1090\ cm^{-1})}$, min^{-1}* $n = 2$		
	10% Cu/γ-Al_2O_3		γ-Al_2O_3	10% Cu/γ-Al_2O_3		γ-Al_2O_3
	oxidized	reduced		oxidized	reduced	
180	0.029	0.10	0.026	0.045	0.078	0.030
210	0.038	0.12	0.044	0.061	0.210	0.042
240	0.045	0.17	0.076	0.063	0.461	0.061
270	0.093	0.28	0.101	0.150	0.720	0.076

* The constants were determined from spectroscopic data in which the concentration was expressed in terms dimensionless absorbance (A).

Table 3. Activation energies of the conversions of the bridging and linear methoxy groups on (10% Cu)/γ-Al_2O_3 and γ-Al_2O_3

Methoxy group	Activation energy, kJ/mol		
	10%Cu/γ-Al_2O_3		γ-Al_2O_3
	oxidized	reduced	
Bridging (1090 cm^{-1})	26	50	25
Linear (1190 cm^{-1})	21	23	30

Raising the oxygen concentration in the oxygen/helium mixture from 0 to 3.3% has no significant effect on the rate constants of the disappearance of bridging and linear methoxy groups (Table 4), as in the case of γ-Al_2O_3.

The addition of oxygen to the gas stream exerts only a weak effect on the time dependence of the concentration of the formate complex and shows itself only as an increase in the concentration of this complex. Likewise, adding oxygen to helium does not change the way in which the concentration of the aldehyde complex (absorption band at 1320 cm^{-1}) varies with time (Fig. 3) and alters only the maximum concentration of the complex.

Desorption in a helium/water vapor flow. These experiments were performed using the reduced (10% Cu)/γ-Al_2O_3 sample at different concentrations of water vapor in helium (0.6 and 3% H_2O).

As in the case of desorption into the helium/oxygen flow, the H_2, CO, DME, and methanol concentrations decrease steadily with time and the CO_2 concentration passes through a maximum (Fig. 4b). The concentrations of bridging and linear methoxy groups and the aldehyde complex decrease with time, and the formate concentration passes through a maximum (Fig. 4a). The effective rate constants of the disappearance of methoxy groups in the presence of water vapor are listed in Table 5. Evidently, water vapor exerts no significant effect on the methoxy group disappearance rate. Earlier [8], the same situation was observed in similar experiments on γ-Al_2O_3.

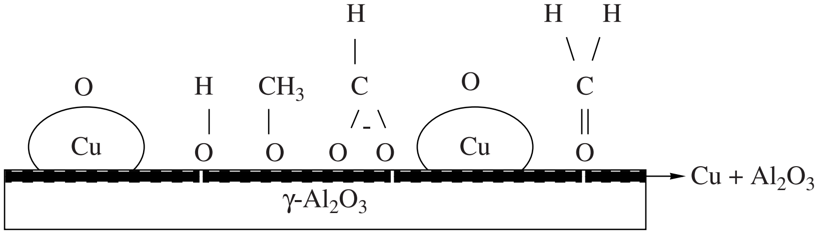
The character of the time dependences of the formate and aldehyde complex concentrations does not change on passing to the helium/water vapor flow: both of them appear as a curve with a maximum. However, in the presence of water vapor, the formate concentration is lower and the aldehyde complex concentration is somewhat higher.

The unsteady-state measurements demonstrated that the methoxy group disappearance rate depends considerably on the character of catalyst pretreatment and is almost unaffected by oxygen and water vapor admixtures. At the same time, both oxygen and water vapor change the quantitative parameters of the conversion of the surface aldehyde and formate complexes. These changes are accompanied by qualitative and quantitative changes in the formation of H_2, CO, and CO_2 (Figs. 2–4).

DISCUSSION

State of the Catalyst Surface

The surface of (10% Cu)/γ-Al_2O_3 involved in methanol conversion contains the same surface complexes as γ-Al_2O_3 [8]. This fact and the equality of the conversion rates of methoxy groups on (10% Cu)/γ-Al_2O_3 and γ-Al_2O_3 (Table 2) suggest that the formation of the observed complexes takes place on the γ-Al_2O_3 surface free of copper oxide particles.



The shift of absorption bands (±2–5 cm^{-1}) relative to the corresponding bands for γ-Al_2O_3 (Fig. 5) is due to the modification of the γ-Al_2O_3 surface by the supported copper [10]. Copper ions can occupy defect sites on the γ-alumina surface and form the aluminate $CuAl_2O_4$ [4, 11, 12]. This is confirmed by TPR data for (10% Cu)/γ-Al_2O_3 up to 650°C, according to which the extent of reduction of copper in this sample does not exceed 40% precisely because of the irreducibility of the copper ions of aluminates in this temperature range. The model of the catalyst takes into account that, according to TPR data and IR spectroscopic data for adsorbed CO molecules, the total copper atom coverage of the surface is approximately 90%.

The change in the state of the surface is due to the pretreatment of the catalyst with a flowing oxidizer or reductant. The methoxy group concentration on the surface of the oxidized sample is 1.5 times higher than that on the surface of the reduced sample. A similar effect was observed in other studies [13–15].

The totality of the above results can be explained in terms of the model in which the state of the copper particles on the γ-Al_2O_3 surface changes significantly

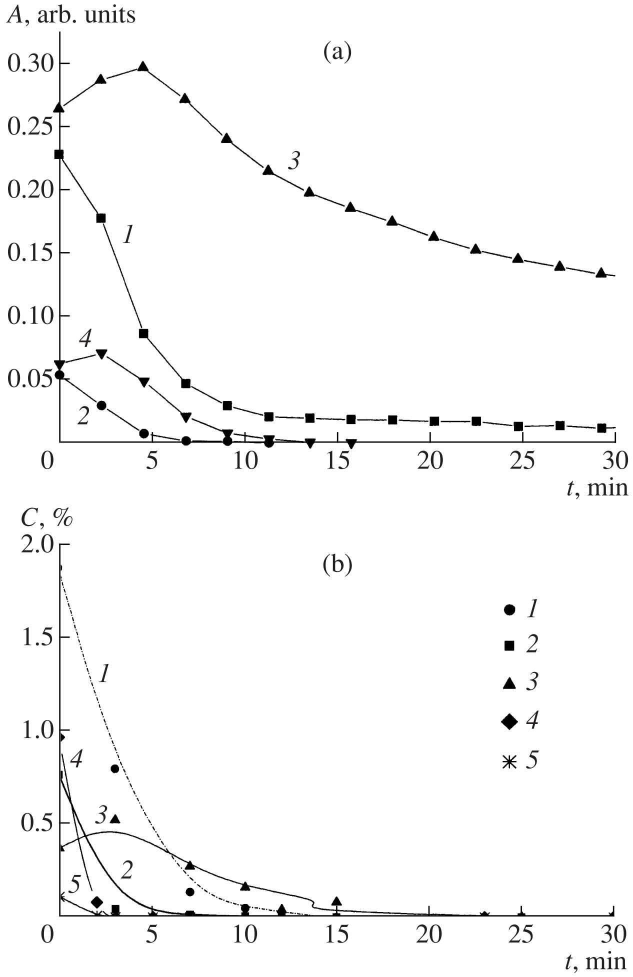


Fig. 3. Time dependences of (a) IR absorption band intensities and (b) product concentrations for the reduced (10% Cu)/γ-Al_2O_3 sample. Conditions: desorption in a He/2% O_2 flow, T = 300°C; (a): (*1*) 1090 cm^{-1}, (*2*) 1190 cm^{-1}, (*3*) 1590 cm^{-1}, and (*4*) 1320 cm^{-1}; (b): (*1*) CH_3OH, (*2*) DME, (*3*) CO_2, (*4*) H_2, and (*5*) CO.

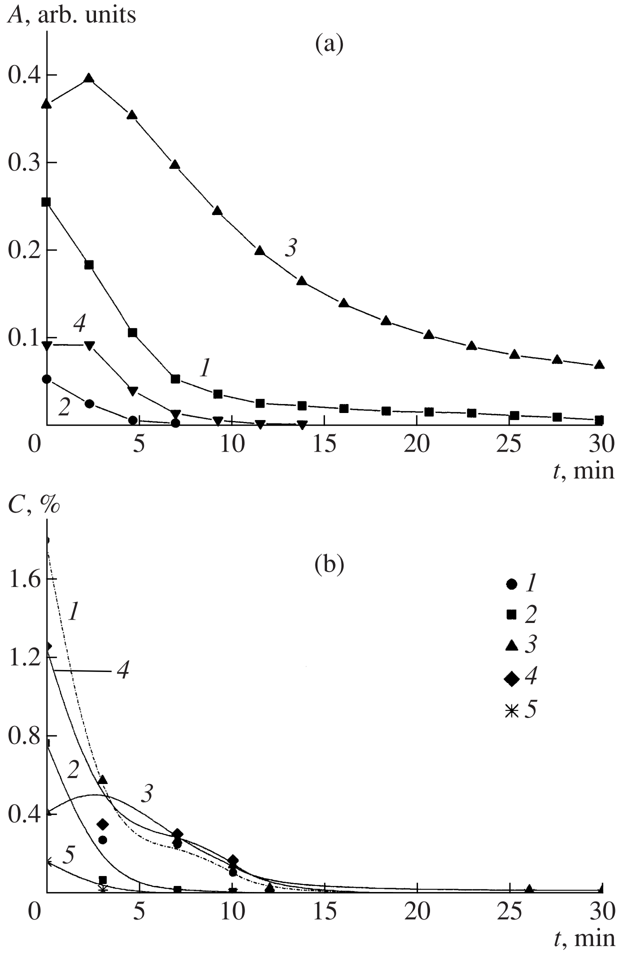
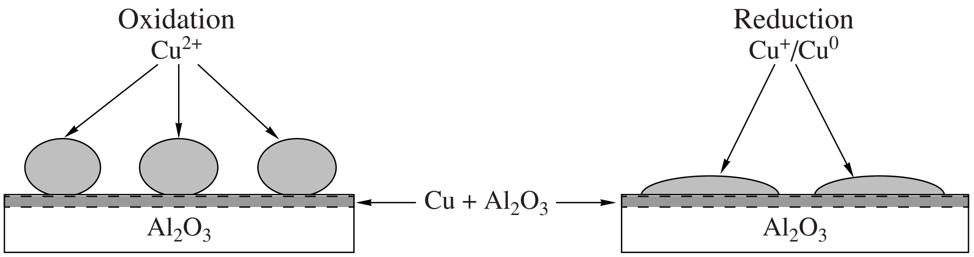


Fig. 4. Time dependences of (a) IR absorption band intensities and (b) product concentrations for the reduced (10% Cu)/γ-Al_2O_3 sample. Conditions: desorption in a He/3% H_2O flow, T = 300°C; (a): (*1*) 1090 cm^{-1}, (*2*) 1190 cm^{-1}, (*3*) 1590 cm^{-1}, and (*4*) 1320 cm^{-1}; (b): (*1*) CH_3OH, (*2*) DME, (*3*) CO_2, (*4*) H_2, and (*5*) CO.

under oxidative or reductive conditions [4, 16–18]. Oxidation may be accompanied by the aggregation of copper particles and by an increase in the free surface fraction of γ-Al_2O_3. Conversely, reduction is accompanied by the delocalization of copper particles and by a decrease in the free surface fraction of γ-Al_2O_3.



Eventually, the decrease in the free surface fraction upon reduction causes a decrease in the methoxy group concentration.

In order to determine the state of copper in the oxidized and reduced samples, we carried out CO adsorption in a linear heating regime. For the oxidized sample,

Table 4. Rate constants of disappearance of the bridging and linear methoxy groups as a function of the oxygen concentration in helium for the reduced (10% Cu)/γ-Al_2O_3 sample (T = 240°C)

O_2 concentration, %	$k_{(1190\ cm^{-1})}$, min^{-1} $n = 1$	$k_{(1090\ cm^{-1})}$, min^{-1} $n = 2$
0	0.170	0.461
1.0	0.187	0.394
2.0	0.161	0.456
3.3	0.174	0.422

Table 5. Rate constants of disappearance of methoxy groups as a function of the water vapor concentration in helium for the reduced (10% Cu)/γ-Al_2O_3 sample (T = 240°C)

H_2O concentration, %	$k_{(1190\ cm^{-1})}$, min^{-1} $n = 1$	$k_{(1090\ cm^{-1})}$, min^{-1} $n = 2$
0	0.170	0.461
0.6	0.187	0.357
3.0	0.150	0.31

an absorption band at 2120 cm^{-1} (Cu^+–CO [19–21]) appears in the IR spectrum above 120°C and its intensity passes through a maximum at 260°C (this is due to the reduction process $Cu^{2+} \longrightarrow Cu^+$ in the CO atmosphere). For the reduced sample, a strong absorption band at 2105 cm^{-1} (Cu^0–CO [19–21]) is observed even at room temperature. As the sample is heated, this band weakens so that the 2120 cm^{-1} band (Cu^+–CO) becomes noticeable on its background. Thus, at the reaction temperature in the presence of the reaction mixture, the dominant state of copper in the oxidized sample is Cu^{2+} with a Cu^+ admixture and the dominant state of copper in the reduced sample is Cu^0 with a Cu^+ admixture.

Conversion of the Surface Compounds

Methanol adsorption on the surfaces of the oxidized and reduced samples is accompanied by a decrease in the OH group concentration and by an increase in the concentrations of bridging and linear methoxy groups (Fig. 6). Thus, the formation of methoxy groups on the surface of (10% Cu)/γ-Al_2O_3 takes place via the classical scheme involving surface OH groups [19]: the formation of linear methoxy groups involves terminal hydroxyl groups, and the formation of bridging methoxy groups involves geminal hydroxyls.

In the isothermal desorption of surface complexes from (10% Cu)/γ-Al_2O_3, the following compounds were identified in the gas phase: methanol, DME, H_2, H_2O, CO_2, and CO (Figs. 2–4). Since the surface of the sample at the experimental temperatures contains only methoxy groups and the formate and aldehyde complexes, it can be deduced that all of the desorption products result from the conversion of these complexes.

Since the bridging methoxy groups disappear according to a second-order rate equation, it can be assumed that this complex is the source of DME in the gas phase. The same DME formation mechanism was described for (5 wt % Cu)/SiO_2 [14]. Another argument in favor of this mechanism is that the disappearance rate of the bridging methoxy groups is independent of the presence of oxygen and water vapor (Tables 2, 4, 5). A comparison between the conversion rate of the bridging methoxy group and the DME formation rate on

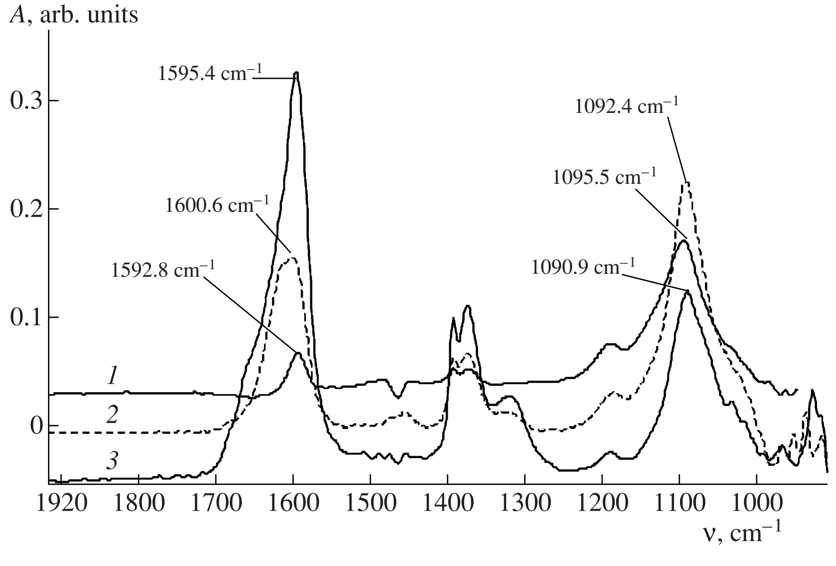


Fig. 5. IR spectra of (*1*) γ-Al_2O_3, (*2*) (10% Cu)/γ-Al_2O_{3ox}, and (*3*) (10% Cu)/γ-Al_2O_{3red} after methanol adsorption at T = 210°C.

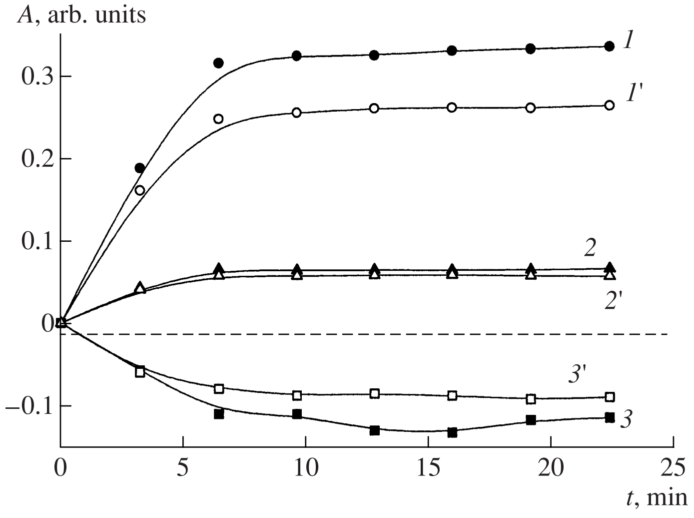


Fig. 6. Time dependences of IR absorption band intensities in methanol adsorption on the (*1–3*) oxidized and (*1'–3'*) reduced (10% Cu)/γ-Al_2O_3 samples at $T = 210°C$: (*1*, *1'*) 1090, (*2*, *2'*) 1190, and (*3*, *3'*) 3730 cm^{-1}.

reduced (10% Cu)/γ-Al_2O_3 (by analogy with γ-Al_2O_3 [8]) demonstrated that the rate of DME formation by the interaction of two methoxy groups is 9.28×10^{17} molecule/min, and the experimentally measured rate is 5.85×10^{18} molecule/min ($T = 300°C$). This estimate is evidence that DME forms via two pathways, the main pathway being the interaction between a methanol molecule from the gas phase and a surface methoxy group.

The concentrations of the formate and aldehyde complexes on the surface begin to decrease when there are almost no linear methoxy groups on the surface. Therefore, it is these groups that are involved in the formation of the formate and aldehyde complexes (Figs. 2–4). The fact that linear methoxy groups disappear according to a first-order rate equation suggests that their desorption yields methanol in the gas phase as well.

From our data concerning the pathways of the formation of the surface complexes on Cu-containing catalytic systems and from relevant data available from the literature [5, 13–15, 22–27], we derived a scheme of surface reactions leading to the formation of the observed reaction products. When composing this scheme, we took into account that, during desorption, the formate and aldehyde complex concentrations as a function of time pass through a maximum (Figs. 2–4). Therefore, it is likely these complexes that are sources of CO and CO_2 in the gas phase. The formate complex can yield CO_2 ($HCOO_{ads} \longrightarrow CO_2 + H_{ads}$) [13, 26, 28–30], and the aldehyde complex yields CO in the gas phase ($H_2CO_{ads} \longrightarrow CO + H_2$) [5].

This scheme accounts for the observed order of product concentrations in the gas phase in steady- and unsteady-state experiments: $[H_2] > [CO_2] > [CO]$ (Fig. 1).

DME results from the interaction between two methoxy groups (step (XIII); step (XIV) takes place when methanol is present in the gas phase). This is why the disappearance of methoxy groups obeys a second-order rate law and the disappearance rate constants are independent of the oxygen and water vapor concentrations (Tables 4, 5).

Scheme. Surface reactions involved in methanol conversion on the Cu/γ-Al_2O_3 catalyst.

Step	
$2Z + O_{2(g)} \longrightarrow 2ZO$	(I)
$CH_3OH_{(g)} + ZOH \longrightarrow CH_3OZ + H_2O_{(g)}$	(II)
$CH_3OZ + ZOH \longrightarrow HCOOZ + ZH + H_{2(g)}$	(III)
$CH_3OZ + ZO \longrightarrow H_2COZ + ZOH$	(IV)
$CH_3OZ + ZH \longrightarrow CH_3OH_{(g)} + 2Z$	(V)
$HCOOZ \longrightarrow CO_{2(g)} + ZH$	(VI)
$H_2COZ + Z \longrightarrow CO_{(g)} + 2ZH$	(VII)
$H_2O_{(g)} + 2Z \longrightarrow ZOH + ZH$	(VII)
$ZH + ZO \longrightarrow ZOH + Z$	(IX)
$ZH + ZH \longrightarrow H_{2(g)} + 2Z$	(X)
$2ZOH \longrightarrow H_2O_{(g)} + ZO + Z$	(XI)
$3CH_3OH + 1/2O_2 + H_2O \longrightarrow 7H_2 + 2CO_2 + CO$	
$CH_3OH_{(g)} + ZOH \longrightarrow CH_3OZ + H_2O_{(g)}$	(XII)
$2CH_3OZ \longrightarrow (CH_3)_2O_{(g)} + ZO + Z$	(XIII)
$CH_3OH_{(g)} + CH_3OZ \longrightarrow (CH_3)_2O_{(g)} + ZOH$	(XIV)
$H_2O_{(g)} + ZO + Z \longrightarrow 2ZOH$	(XV)
$2CH_3OH \longrightarrow (CH_3)_2O + H_2O$	

According to the above scheme, the concentration of linear methoxy groups on the surface changes according to the equation

$$d[CH_3OZ]/dt = -Q_{CH_3OZ}(k_3Q_{ZOH} + k_4Q_{ZO} + k_5Q_{ZH}). \quad (1)$$

Using known extinction coefficients for characteristic absorption bands [31], we estimated the concentrations of linear methoxy groups, the formate, and the aldehyde on the surface. The amounts of linear methoxy groups, aldehyde, and formate on the surface of the oxidized sample (T = 270°C) were found to be 2.4×10^{18}, 4.6×10^{16}, and 2.8×10^{17} complex/g, respectively. Thus, no more than 10% of the linear methoxy groups turn into the formate or aldehyde. Therefore, reactions (III) and (IV) make only a small contribution to the disappearance rate of the linear methoxy groups in Eq. (1) and these groups are mainly consumed via reaction (V). Accordingly, the first order of the disappearance of the linear methoxy groups is explained by the constancy of Q_{ZH} during methoxy group conversion, as in the case of γ-Al_2O_3 [8].

Using the results of the unsteady-state spectroscopic measurements (Figs. 2–4) and known extinction coefficients, it is possible to correlate the amounts of CO forming in desorption into He, He/O_2, and He/H_2O flows with the amount of the surface aldehyde complexes capable of yielding CO. According to our estimates, the surface of the sample at 300°C contains 3.1×10^{17} aldehyde complexes per gram. The amount of CO formed in the gas phase is 2.8×10^{17} molecule/g. Evidently, the amount of the resulting CO and the amount of the reacted aldehyde complex are in satisfactory agreement. Therefore, it is the decomposition of the aldehyde complex that yields CO, thus verifying step (VII).

The formation of CO_2 in the gas phase is due to the decomposition of the formate complex (scheme, step (VI)). In desorption experiments, the CO_2 concentration changes in the same way as the formate complex concentration (Figs. 2–4). Our estimates demonstrate that the surface of the sample at 300°C contains 4.5×10^{17} formate complexes per gram. The corresponding amount of CO_2 in the gas phase is 4.1×10^{17} molecule/g. The similarity of these values is evidence that it is the decomposition of the formate complexes that yields CO_2. Therefore, step (VI) is also valid.

Adding water vapor to the flowing reaction mixture cause a significant increase in the hydrogen formation rate and a decrease in the CO formation rate (Fig. 1). In terms of the above scheme, the increase in the hydrogen formation rate is explained by the increase in the surface coverages Q_{ZOH} and Q_{ZH}. The CO formation rate is $w_{CO} = k_7Q_{CH_2OZ}Q_Z$. According to this expression, the slowdown of CO formation is due to the decrease in the free surface area (step (VIII)) and in the aldehyde complex concentration on the surface (step (IV)).

These considerations suggest that the above scheme of surface reactions correctly describes the main features of methanol conversion on (10% Cu)/γ-Al_2O_3.

Role of Cu in Methanol Conversion on (10% Cu)/γ-Al_2O_3

The same set of intermediates is observed in the reactions of methanol on γ-Al_2O_3 [8] and (10% Cu)/γ-Al_2O_3. The conversions of these intermediates occur in similar ways. However, hydrogen does not form in methanol conversion on γ-Al_2O_3 [8] and does form in considerable amounts on (10% Cu)/γ-Al_2O_3. This indicates unambiguously that extra reactions between the same complexes are possible in the presence of copper. The main new reaction is the recombination of hydrogen atoms (step (X)) that have resulted from interconversions of surface compounds (scheme).

In addition, copper substantially enhances the oxidizing power of the catalyst. This is manifested as a decrease in the formation and disappearance temperatures of the formate and aldehyde complexes and as the appearance of CO and CO_2 in the gas phase. The enhancement of the oxidizing properties is due to the capacity of copper to activate oxygen. Studies of methanol oxidation on copper powder [24, 27] demonstrated that, in the oxidation of the methoxy group into the aldehyde, the active species is suboxide oxygen bound to defect sites of copper particles. This oxygen species forms only under the action of the reaction medium and only on the copper metal surface. The following processes can occur on the copper surface under methanol oxidation conditions [28]:

$$\{O\}_{\text{subsurface}} \longrightarrow \{O\}^a;$$

$$O_{2\,(g)} \longrightarrow 2\{O\}^b; \quad \{O\}^b \longrightarrow \{O\}_{\text{subsurface}}.$$

The active oxygen species in methanol oxidation is $\{O\}^a$. The adsorbed oxygen species $\{O\}^b$ is involved in the oxidation of the copper-containing catalyst ($2Cu + \{O\}^b \longrightarrow Cu_2O$) and in the formation of subsurface oxygen. In our case, the oxidizing function of the (10% Cu)/γ-Al_2O_3 catalyst is due to oxygen atoms activated by copper clusters. As a consequence, steps (I), (IV), and (IX) take place, involving copper particles.

Reduction (a decrease in the surface oxygen concentration) changes both the state of the copper particles and the state of the γ-Al_2O_3 surface modified by copper ions. This decreases the methoxy group concentration and, as a consequence, diminishes the activity of the catalyst. Another effect of reduction is a decrease in the frequency of the C–O vibrations in the methoxy groups (Fig. 5), which indicates a weakening of the methoxy group–surface bonds. This fact shows itself as an increase in the methoxy group disappearance rate constant (Table 2). The increase in this rate constant, when accompanied by a decrease in catalytic activity, is manifested as an increase in hydrogen selectivity (Table 1).

According to the above mechanism, the main reaction yielding hydrogen is the recombination of hydrogen atoms on copper clusters. The source of CO_2 in the gas phase is the surface formate complex, and the source of CO is the surface aldehyde complex.

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