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Mechanism and Kinetics of Reactions
of C₁ Molecules on Cu-Based Catalysts

A. Ya. Rozovskii

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 117912 Russia

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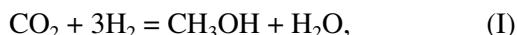
Abstract—The mechanism and kinetics of reactions occurring in the course of natural gas processing into motor fuels and other chemical products are considered with emphasis on copper-based catalysts. The following reactions are considered: methanol and methyl formate syntheses, dimethyl ether synthesis from syngas and by methanol dehydration, water-gas shift reaction, steam reforming of methanol and its decomposition to produce syngas, and others. It is shown that a key role in the mechanisms of the above reactions belong to transformations of stable, strongly (“irreversibly”) chemisorbed species, and this fact determines the specific features of the schemes of their mechanisms and kinetic models. The use of the specific features of reaction mechanisms makes it possible to increase the process efficiency (methanol and dimethyl ether syntheses) and provide a high selectivity (methyl formate synthesis).

Copper-containing systems are catalytically active in various reactions of C₁ molecules. These include such important processes as methanol and methyl formate synthesis, dimethyl ether synthesis, and CO oxidation. In this work, we mainly consider reactions involved in the known scheme of natural gas conversion into motor fuel and other valuable chemical products (Scheme 1).

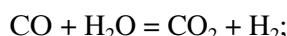
A methane molecule, which is the main component of natural gas, is rather inert. Therefore, to convert methane into valuable chemicals, it is usually oxidized by oxygen (autothermal reforming), H₂O (steam reforming) or CO₂ (dry reforming), or their combinations. The product of these processes is syngas, which is a mixture of carbon oxides and hydrogen. Syngas is further used in chemical syntheses.

The main reactions considered in this paper are listed below:

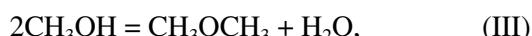
Methanol synthesis is a molecular chain reaction in which an excessive oxygen atom is inserted into water and CO₂ molecules in turn:



Water-gas shift reaction (WGSR) plays an important role in numerous processes of C₁ chemistry, from numerous methane reforming processes to various syngas conversions:



Dimethyl ether (DME) synthesis by methanol dehydration,



as well as in the complex process of direct DME synthesis from syngas by coupling reactions (I)–(III) in a single reactor;

Methyl formate (MF) synthesis by methanol dehydration,



and, finally, the nowadays “fashionable” conversions of methanol into hydrogen-rich gaseous mixtures:

Steam Reforming of Methanol



and methanol decomposition



The two reactions mentioned last are rather easy and provide a means to use methanol for the storage and transport of hydrogen and syngas.

The above scheme shows the place of the cited processes and the role they play or can play in natural gas conversion.

Although these reactions are different, they have a common property: the reaction system contains species that are strongly (“irreversibly”) adsorbed on the active sites of the catalyst. These are H₂O, CH₃OH, CO₂, and CO for the first two reactions and reaction (V); methanol and DME in reaction (III); and methanol and methyl formate in reaction (IV). The term “irreversibly” is used here in the sense that the characteristic times of desorption of a given species are much longer than the characteristic time of a catalytic reaction, and the active site of a catalyst is freed from the adsorbed species via any reaction of this species rather than via desorption. In connection with this, let us dwell on some specific features of reactions of this sort.

Reactions with the Participation of Strongly Adsorbed Species

First of all, the question arises as to how adsorbed products are replaced by the reactants from the gas phase in the absence of adsorption.

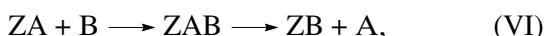
As early as a quarter of a century ago, Sadovnikov [1] first suggested an answer to this question when interpreting data on the dehydrogenation of cyclohexane to benzene [2]. In that experiment, a flow reactor was fed with cyclohexane pulses and benzene pulses were observed at the outlet. Unexpectedly, a regularly scheduled pulse with ¹⁴C-labeled cyclohexane led to a pulse of nonlabeled benzene. Sadovnikov proposed that active sites are occupied by strongly adsorbed benzene, and the supply of cyclohexane leads to the formation of an intermediate complex containing both species and to the substitution of benzene. More recently, in an experimental study of alcohol dehydration, Sadovnikov showed that an isotopically labeled water T₂O molecule or an alcohol molecule from the gas phase substitutes for the strongly adsorbed nonlabeled water molecule [3].

Minachev *et al.* [4] observed a series of irreversible substitution reactions in a system containing ethylene, propylene, acetylene, and the La₂O₃ catalyst for low-temperature hydrogenation of unsaturated compounds. Strongly adsorbed ethylene was completely displaced by propylene and/or by acetylene from the gas phase, propylene was displaced by acetylene, but not by ethylene, and acetylene was not displaced by any of the above reactants. It is clear that acetylene substitution for propylene and the absence of ethylene substitution for propylene cannot be explained within the framework of classical mechanisms of substitution via adsorption–desorption processes. Such a “selectivity” is only typical of chemical reactions.

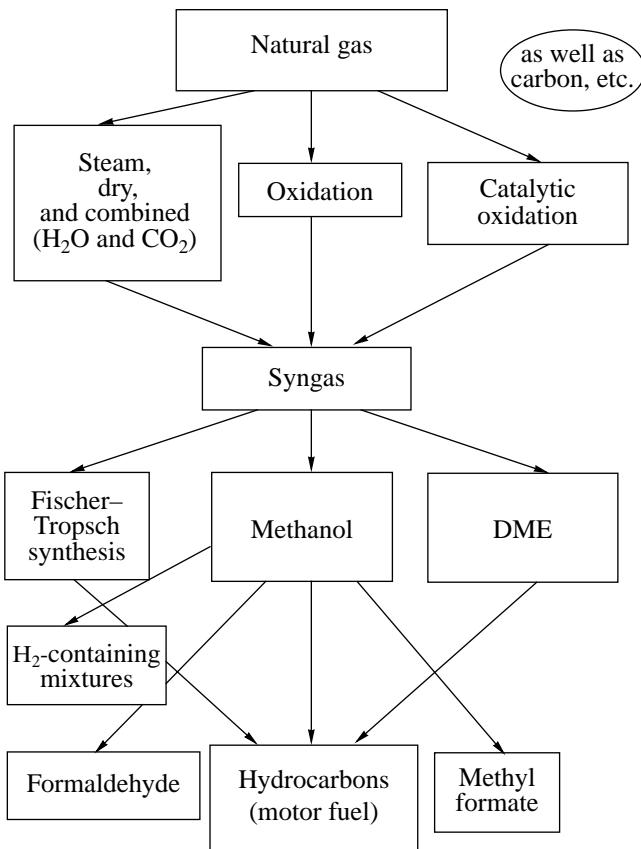
Kolbanovskii and Gagarin [5] gave a quantum-chemical explanation for the possibility of such reactions using the ethanol–Al₂O₃ system as an example.

Finally, several publications of our laboratory surveyed in [6] showed the key role of substitution reactions in carbon oxide transformations over Cu-based catalysts.

In principle, the substitution of gas-phase molecules for the surface species could be explained within the framework of classical approaches, taking into account the dynamic nature of adsorption–desorption equilibrium. However, for instance, the irreversible nature of substitution in the experiments reported by Minachev and colleagues makes such an explanation impossible. It is clear that we are talking about an independent chemical reaction, which was called adsorption substitution in [7]. In the cases studied, this reaction occurs via the formation of an intermediate complex containing both species (a two-species complex) on the active site of the surface, which can schematically be described as follows:



The main pathways of natural gas processing into motor fuel and valuable chemical products



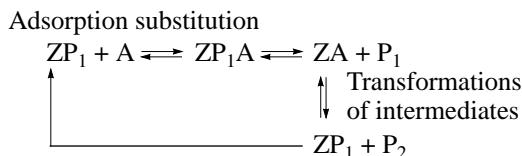
Scheme 1.

where Z is the active site and A and B are the interacting species (molecules). This reaction is in contrast to the reactions proved by Azatyan [8]: atomic substitution of atoms in polyatomic molecules on solid surfaces occurring with the participation of atoms from the gas phase probably without the formation of an intermediate complex.

The participation of adsorption substitution in a catalytic process has long-standing consequences. First of all they are stipulated by the appearance of a two-species complex, ZAB, on the active site. Therefore, the description of equilibrium between the adsorbed layer and the gas phase changes. Specifically, if the adsorption sites are at equilibrium and if Langmuir's other assumptions are correct, the equation for the adsorption isotherm contains nonlinear terms in the denominator, and this further leads to a more complex kinetic description of reactions [7].

On the other hand, the inclusion of the adsorption substitution reaction in a catalytic process leads to constraints on the nature of allowable steps and schemes of the reaction, which makes the mechanistic study easier. A typical mechanistic scheme is shown below in simplified form, where P₁ and P₂ are the reaction products

and P_1 strongly binds with the active site, whereas P_2 evolves into the gas phase.



Scheme 2. Typical scheme of a reaction mechanism with the formation of a strongly adsorbed species

The macrostep called here *transformation of intermediates* actually involves the main part of the reaction mechanism. However, it does not contain adsorption and desorption steps. The steps of surface migration have a minor contribution to this reaction because their rates in the presence of strongly adsorbed species are low.

Let us now consider specific reactions.

METHANOL SYNTHESIS

Methanol synthesis is one of the most studied heterogeneous catalytic reactions. A detailed description of mechanistic and kinetic studies of methanol synthesis can be found in [9]; therefore, here we will only dwell briefly on the most important points.

In modern industry, methanol is produced from syngas. This process corresponds to the following stoichiometry of the overall equation:



which is composed of Eqs. (I) and (II). Because copper-based catalysts show very high activity in the water-gas shift reaction, provided mutual transformation of carbon oxides, this reaction is close to equilibrium under conditions of methanol synthesis. This was the reason for the difficulty in deciding which of the carbon oxides is the immediate precursor of methanol. For solving this problem, kinetic experiments were needed with very short contact times (10^{-3} s) and/or with the use of carbon-labeled compounds. In both variants, the experiment gave an unequivocal answer: the immediate precursor of methanol is only CO_2 on copper-based catalysts.

Study with the Use of Isotopically Labeled Molecules

Below we provide the results of two experiments using ^{14}C -labeled oxides CO and CO_2 carried out using a commercial SNM catalyst in a closed circulation setup where methanol and water formed in the reaction were continuously frozen out from the circulating gaseous flow. In the first experiment, a mixture containing the ^{14}CO additive (~1%) where CO_2 dominated was used ($\text{CO} \sim 1$; $\text{CO}_2 \sim 20$; $\text{H}_2 \sim 73$; $\text{N}_2 \sim 6$ vol %; the reaction temperature was 180°C ; the total pressure was 5 MPa; the initial ^{14}CO label was 406 arbitrary units;

and the specific radioactivity of other components was 0). The analysis of the gaseous mixture at the end of the experiment showed the specific radioactivity of the components: 189 arbitrary units for CO and 9 arbitrary units for CO_2 , whereas the label for methanol corresponding to the integral average value for the whole run was 5 arbitrary units.

In the second experiment, CO dominated in the reaction mixture ($\text{CO} \sim 30$; $\text{CO}_2 \sim 4$; $\text{H}_2 \sim 59$; $\text{N}_2 \sim 7$ vol %; 240°C ; ~5 MPa), and the initial label of $^{14}\text{CO}_2$ was 5900 arbitrary units (and zero for the rest of the components). For quantitative characterization, a medium sample of the gas was withdrawn during the run. This sample corresponded to the average methanol sample analyzed. The results of analysis of average samples were as follows: $\text{CO} \sim 430$; $\text{CO}_2 \sim 1480$; methanol, 1500 arbitrary units.

Thus, in both experiments, including the second one, which provided the most favorable conditions for methanol formation from CO , only CO_2 was the precursor of methanol.

Liu *et al.* [10] and Vedage *et al.* [11] used labeled oxygen ^{18}O in their mechanistic studies of methanol synthesis. In the first of these studies, experiments were carried out in a nonstationary system and the initial gaseous mixture contained the C^{18}O_2 label. Before introducing the mixture containing labeled CO_2 , the catalyst was stabilized in stationary methanol synthesis from the gaseous mixture containing no labeled compounds, and then the rates of labeled and nonlabeled compounds were measured for 15 min. The formation of $\text{CH}_3^{16}\text{OH}$ and $\text{CH}_3^{18}\text{OH}$ were observed in the experiments. The initial rates of formation of these compounds were used by the authors to characterize the contributions of CO_2 and CO as potential methanol precursors, and they came to the conclusion that both oxides participate in methanol formation.

However, our analysis of data presented in [10] showed that this conclusion was premature. In that work, data for the dynamics of formation of $\text{CH}_3^{16}\text{OH}$ and $\text{CH}_3^{18}\text{OH}$ and for the distribution of the label in other components during the whole run (15 min) were given for one of the experiments. This made it possible to calculate the dynamics of changes of ^{18}O fractions in CO_2 and methanol. Figure 1 shows the dynamics of label ^{18}O accumulation in methanol (curve 2) and its decrease in CO_2 (curve 1), which is the only source of ^{18}O in the system. These plots were constructed by us [9] using data from [10]. It is seen from this figure that there is a “buffer” in the system, which decelerates label transfer from CO_2 to methanol: the fraction of ^{18}O in methanol increases and approaches the fraction of this label in CO_2 , although the latter decreases with time. As this takes place, the fraction of ^{18}O in other components of the gas phase (CO and H_2O) remains much lower than in CO_2 and methanol. It follows from these data that the buffer accumulating the oxygen label

from CO₂ and then transferring it to methanol is bound to the catalyst.

Catalyst treatment with water or the addition of water to the reaction mixture retards the formation of CH₃¹⁸OH and does not affect the rate of CH₃¹⁶OH synthesis [10]. Proceeding from this data, the buffer, or at least the source of oxygen in the buffer, is water.

It is clear that the initial rates of CH₃¹⁸OH formation in this system do not reflect the real role of CO₂ in methanol synthesis. This is also clear from the figure, in which the fraction of ¹⁸O in CO₂ and methanol differ drastically at the beginning of the experiment and become close after 15 min of the run, while the fractions of ¹⁸O in other components (mostly CO) remained the same.

It is seen from data shown in the figure that the estimate of CO₂ contribution as a precursor of methanol made on the basis of the initial rates of CH₃¹⁸OH formation is incorrect and that CO₂ is the main precursor of methanol, to say the least.

The study reported in [11], which will be discussed below in more detail, was carried out in a stationary flow-type setup, which eliminated the above distorting effects, but the contact time was so long that the fraction of oxygen ¹⁸O, introduced in the form of H₂¹⁸O, in the components of the reaction mixture at the reactor outlet, was practically the same in water (3.3%), methanol (3.4%), and CO₂ (3.6%) and differed only in CO (0.6%), according to our calculations [6, p. 44]. Correspondingly, these data cannot point to the source of oxygen in methanol, although only two of the three molecules remain as candidates: CO can be excluded from the list of potential methanol precursors. In this case, this is not very important since data based on experiments with ¹⁴C unequivocally lead to this conclusion.

It is more important to determine the source of hydrogen in the CH₃ group of methanol, and there are two candidates: hydrogen and water. Vedage *et al.* [11] also studied the transitions of deuterium in the D₂O–CO–H₂ system (the initial mixture). It was found that approximately one deuterium atom is involved in the CH₃ group of methanol. Based on this evidence, Vedage *et al.* concluded that methanol is produced by the reaction between CO and H₂O [11].

This conclusion contradicted the above data obtained in the experiments with ¹⁴C, and we checked it experimentally under analogous conditions [12]. At long contact times under comparable conditions [11] (the contact time in [11] was 0.36 s), the results were reproduced. Then, the contact time in our experiments was shortened by two orders of magnitude (reduced to 0.003 s), so that the reactor became close to the differential reactor from the standpoint of label transfer. Figure 2 illustrates the results obtained. As can be seen from this figure, the isotopic fraction of deuterium in the CH₃ group of methanol at a short contact time strictly corresponds to the isotopic fraction in hydrogen

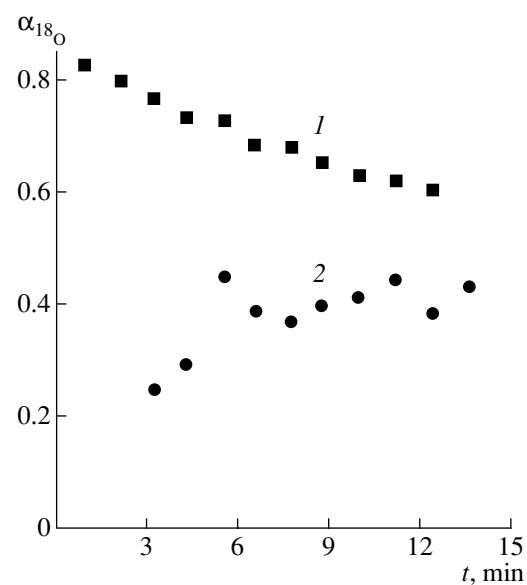


Fig. 1. Dynamics of evolution of the isotopic fraction of ¹⁸O in (1) CO₂ and (2) methanol calculated in [9] using experimental data from [10] (the fraction $^{18}\text{O}\alpha_{^{18}\text{O}} = ^{18}\text{O}/(^{18}\text{O} + ^{16}\text{O})$).

for both the initial mixture where CO₂ dominates (curve 2) and the initial mixture where CO dominates (curve 1). For both mixtures, the concentration of deuterium in the CH₃ group of methanol (1–4%) is much lower than its concentration in water (the average fraction of deuterium in water in the reaction zone was 70–85%).

These results undoubtedly point to the fact that only hydrogen, but not water, participates in the formation of the CH₃ group in the methanol molecule and that the conclusion drawn in [11] that methanol is formed from CO and H₂O is incorrect and based on poorly planned experiments. Obviously, the appearance of deuterium in the CH₃ group of methanol at long contact times are stipulated by secondary reactions. These reactions are most likely due to exchange between intermediate structures formed via the reversible reactions of methanol dehydrogenation or dehydration and surface hydroxyl groups.

Transformations of Surface Compounds

A radically new method for the study of transformations of surface compounds was as follows: to obtain the initial surface compound, the reduced catalyst was treated by a certain reactant supplied in a flow of helium, the weakly bound reactant was removed by purging with helium, and then the flow was switched to a mixture of helium with another reactant, the reaction with which was the subject of study. After a certain time, the flow composition was measured at the reactor outlet. By combining the data measured in a series of such experiments, the kinetic curves of reaction product formation were obtained.

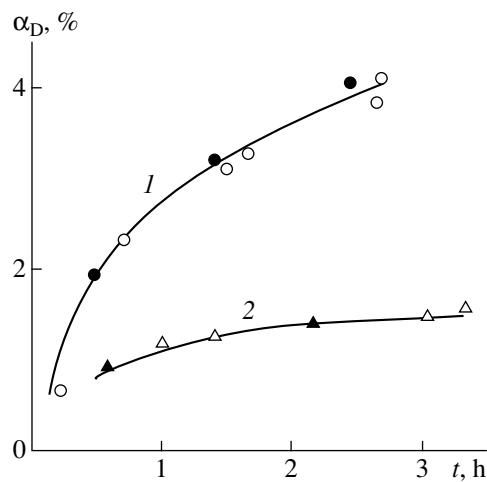


Fig. 2. Dynamics of accumulation of the isotopic fraction of deuterium in hydrogen (open circles) and in the CH_3 group of methanol (solid circles) in a closed (with respect to gas) circulation setup in methanol synthesis (240°C , 10^6 h^{-1} , 5 MPa) from the mixtures with different compositions containing D_2O : (1) CO , 0.85; CO_2 , 0.034; H_2 , 3.6; D_2O , 0.024 MPa and (2) CO , 0.037; CO_2 , 0.99; H_2 , 4.1; D_2O , 0.029 MPa.

Two difficulties can prevent obtaining reliable information in such experiments. The first of these is associated with the fact that switching the flow does not provide a stepwise change in the flow composition in a real system. Figure 3 shows the dynamics of the change in the gas flow composition at the reactor outlet in a typical kinetic setup. As can be seen, the jump in fact lasts ~ 20 s, largely due to longitudinal mixing. Correspondingly, for the first 20 s of a run, the reaction occurs at a variable concentration of the reactant in the gas phase.

The second difficulty is due to the fact that kinetic curves are constructed on the basis of several runs. This stipulated severe requirements for the reproducibility of results. As data presented above and below (Fig. 4) borrowed from [9] show, such reproducibility was achieved (points obtained in different experiments fell on a single kinetic curve). Moreover, these data were obtained in a series of consecutive experiments in which the catalyst surface was oxidized with water and reduced with CO in turn. So both the rates of surface species transformation and the states of the surface after each treatment were reproduced.

Figure 5 shows the dynamics of oxidation by water vapor (2.4 kPa and 250°C) of the commercial Cu-Zn-Al oxide catalyst SNM-1 reduced by carbon monoxide. The moment when the middle of the front passes is taken to be zero (see Fig. 3). The points are based on the averaged data from several runs. It is seen that at short times the rates of formation of all reaction products increase in agreement with an increase in the concentration of water in the gas phase. Carbon monoxide molecules are formed noticeably earlier than other

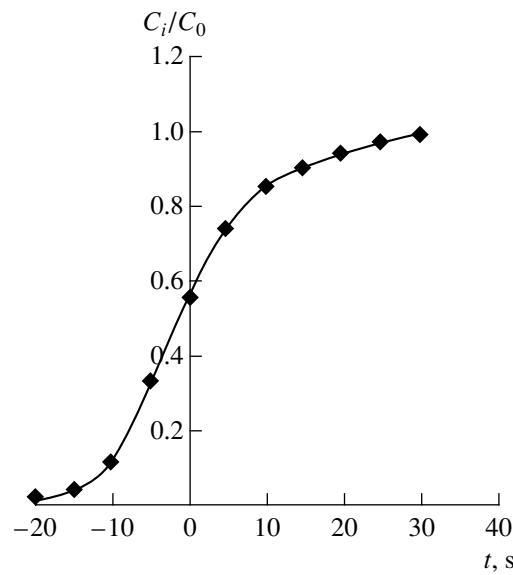
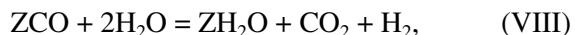


Fig. 3. Dithering of the front in a typical kinetic setup with a stepwise change in the composition of the gaseous flow (C_i and C_0 are the current and supplied concentration of the i th component).

products, and it is clear that the reaction of adsorption substitution of water for CO is faster than other transformations of surface species. The curves of CO_2 and H_2 evolution have maximums. In the case of CO_2 , the maximum approximately corresponds to the achievement of the constant concentration of water in a flow of helium. In the case of H_2 , the maximum is shifted toward longer times.

The peak of CO_2 may involve “reaction-formed” CO_2 obtained via the overall reaction



where one water molecule is consumed for the conversion of adsorbed CO, the second is consumed for the substitution of CO_2 formed on the active site, and “residual” CO_2 “remained” on the site after reduction. The evolution of hydrogen in a large amount and with a small shift in time shows that, in addition to CO conversion, a reaction with hydrogen evolution occurs. In the given system, such a reaction can only be the oxidation of surface Cu (or Cu^+) by water with hydrogen evolution. Comparison of curves of CO_2 and H_2 evolution shows that the rate of this reaction is lower than the rate of adsorbed CO conversion. The delay of the H_2 peak means that this reaction occurs after the removal of CO and CO_2 from the oxidation site, which is “protected” from oxidation before the removal of these species. Correspondingly, the stoichiometric equation of this reaction can be conditionally written in the following form:



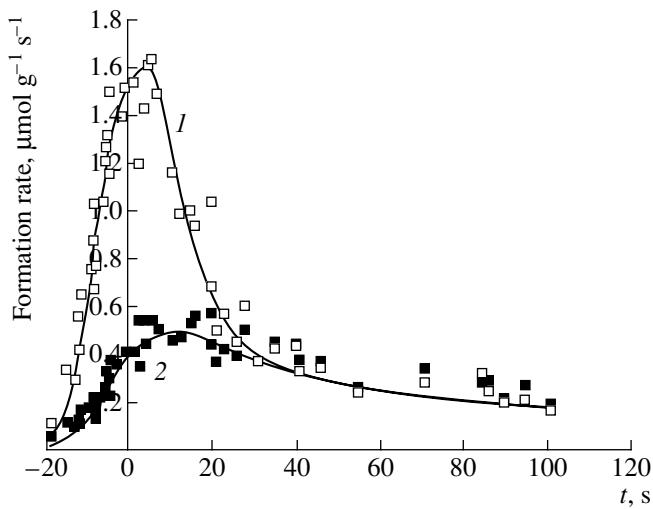


Fig. 4. Dynamics of product formation (1) CO₂ and (2) H₂ in the interaction of gas-phase CO ($P_{\text{CO}} = 19$ kPa) with the surface of commercial Cu-Zn-Al oxide catalyst SNM-1 reduced by carbon monoxide and then oxidized by water at 250°C.

Sites oxidized by water can be reduced in the reaction with CO via the overall stoichiometric equation

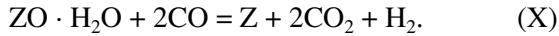
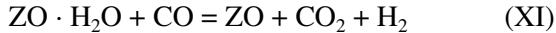
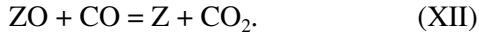


Figure 5 shows the dynamics of evolution of the products of this interaction (data were not averaged) stipulated by the reactions



and



Correspondingly, the dynamics of proper reduction (reaction (XII)) can be determined as the difference between the rate of CO₂ evolution (in both reactions) and the rate of H₂ evolution in reaction (XI) only. The reaction kinetics of reduction thus determined is shown in Fig. 6a.

Figure 6b shows a characteristic curve of this reaction (the dependence of the reaction rate on the amount of converted surface oxygen constructed using averaged points). It is seen that the dropping branch of the curve is a linear dependence after establishing the stationary concentration of CO in a flow; that is, the reaction rate is proportional to the amount of unreduced sites remaining on the surface. Therefore, these sites have the same chemical properties, at least in the case of oxidative-reductive transformations.

Finally, additional information can be obtained from the “tails” of curves in Fig. 4. Starting from ~30 s, both CO₂ and H₂ evolve in the stoichiometric amount 1 : 1.

Analysis of the dynamics of their evolution showed that it corresponds to the diffusion law (\sqrt{t}). This means that when the site reduction is completed and

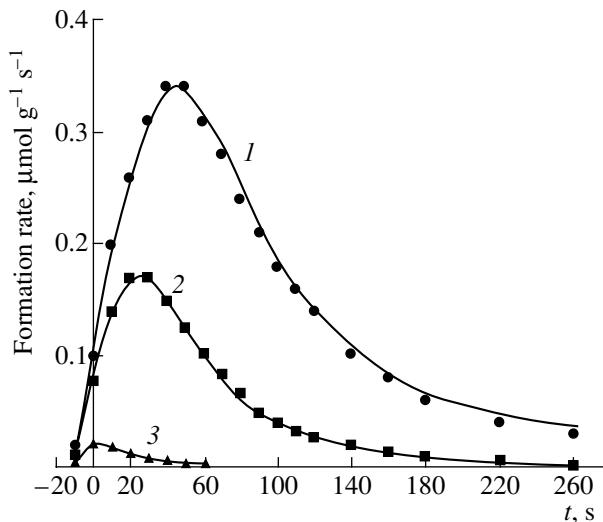


Fig. 5. Dynamics of product formation (1) H₂, (2) CO₂, and (3) CO in the reaction between water vapor ($P_{\text{H}_2\text{O}} = 2.4$ kPa) with the surface of commercial Cu-Zn-Al oxide catalyst SNM-1 reduced by carbon monoxide at 250°C.

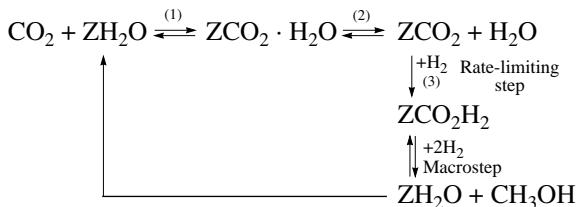
rapidly reacting water species bound to the active sites are exhausted, further reaction (of CO conversion by adsorbed water) occurs due to water species migrating from other sites via the diffusion law. However, this means that water is unreactive on other sites. That is, sites whose transformations were discussed above together with the transformations of species adsorbed on them are the only active sites on the surface.

Their concentration can easily be determined by, for instance, an intercept in Fig. 6b. If we know the concentration of active sites, the specific surface areas of catalysts, and data on the rates of methanol synthesis, we can estimate the activity of a single site, which is often referred to as the turnover number. These calculations have been carried out for four samples, two of which were commercial catalysts of methanol synthesis and the other two were samples whose activity decreased substantially after a long time-on-stream. Table 1 shows the results obtained. As can be seen from this table, the values of the activity are virtually the same for different samples: 0.47 ± 0.05 s⁻¹, although the rate of methanol synthesis on the samples differs by five times.

Figure 7 shows the kinetic and characteristic curves of the reaction of adsorption substitution of gas-phase water for CO strongly adsorbed on the active sites for freshly reduced and deactivated commercial catalysts for methanol synthesis. An analogous trend is observed: the right branches of the characteristic curves are linear and their slope is the same for all samples. That is, the number of sites on the surface decreases, but their properties (the reactivity of surface compounds) remains the same.

Mechanistic Schemes and the Kinetics of Methanol Synthesis

Based on the above data, we construct a simplified scheme of the reaction mechanism of methanol synthesis (Scheme 3). It completely corresponds to the standard Scheme 2. The steps of transformations of intermediate compounds on active sites are in the right vertical column. Taking into account that the order in H_2 of the stationary reaction of methanol synthesis is equal to unity, the first step of hydrogenation is highlighted in the scheme as a rate-limiting step. The horizontal row reflects the adsorption substitution of gas-phase CO_2 for a strongly bound H_2O molecule.



Scheme 3. Simplified mechanistic scheme of methanol synthesis.

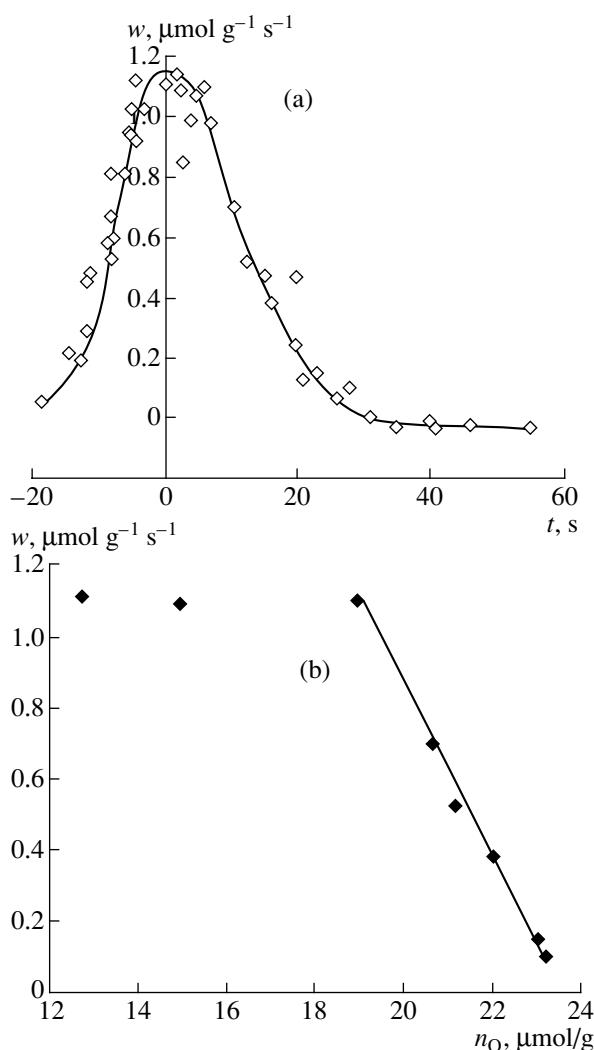


Fig. 6. (a) Kinetic and (b) characteristics curves of reduction of active sites on the SNM catalyst preliminarily oxidized by water (conditions are the same as for Fig. 4; n_O is the amount of reacted oxygen).

Thus, the kinetic study of transformations of surface species made it possible to trace the transformations of strongly adsorbed species, to determine the concentration of active sites on the catalyst, and to obtain information on the specific features of its deactivation.

Table 1. The specific activity per one active site (turnover number) of Cu–Zn–Al oxide catalysts in methanol synthesis

| Sample* | I | II | III | IV |
|---------------------------------------------------------------------------------|------|------|------|------|
| Rate of methanol synthesis (productivity), $\mu\text{mol g}^{-1} \text{s}^{-1}$ | 26.0 | 11.6 | 6.3 | 4.6 |
| Concentration of active sites, $\mu\text{mol/g}$ | 49.6 | 25.0 | 14.6 | 9.6 |
| Specific activity (per one site), s^{-1} | 0.52 | 0.46 | 0.43 | 0.48 |

* Samples I and II are commercial catalysts with different activities; samples III and IV are the same samples deactivated in the course of operation in methanol synthesis.

pounds on the catalysts for methanol synthesis, various structures were observed: methoxy, surface carbonate and hydrocarbonate, as well as formaldehyde and formate complexes, whose role in methanol synthesis remains debatable. Conclusions on the role of the corresponding structure in the reaction mechanism drawn by various authors usually disagree or, more often, contradict each other. Let us provide several examples.

Fujita *et al.* [13] used Fourier-transform diffuse-reflectance infrared (DRIFT) spectroscopy and TPD under conditions of methanol synthesis from CO₂ and H₂ on Cu/ZnO catalysts to observe the formation of two forms of formate HCOO–Cu and one form of formate HCOO–Zn. In hydrogenation, all formates transformed into methoxy groups.

Nomura *et al.* [14] studied the hydrogenation of CO₂ using the catalytic system Cu–TiO₂ with various additives (ZnO, ZrO₂, etc.) by *in situ* FTIR spectroscopy. The additives affected the concentrations of surface formates and the activity of the catalytic system in a similar manner.

Based on the DRIFT study of the Cu–Zn–Al and Cu–Zn–Al–Mn systems, Li *et al.* [15] also concluded that formate can be an intermediate in methanol synthesis.

The route carbonate–formate–methoxide–methanol was proposed by Chen *et al.* [16] for the Cu–ZnO and Cu–ZnO–Al₂O₃ catalysts with low concentrations of copper.

The method of vibrational spectroscopy [17] was used to study methanol synthesis at 3–25 bar on Cu/ZrO₂ and on an analogous catalyst promoted with silver. Surface intermediates were identified *in situ*. Weigel *et al.* [17] concluded that surface formaldehyde and methylate are the main intermediates on the pathway to methanol, and formate is not the direct precursor of methanol. The presence of silver leads to an increase in the activity mostly due to an increase in the concentration of surface formaldehyde. The development of these studies by Ortelli *et al.* [18] using *in situ* FTIR and ¹³C-labeled compounds led them to conclude that methanol is formed exclusively from the formaldehyde intermediate on the Cu–ZnO₂ catalyst, but not from the surface formate. The principle disagreement between the results reported in these two papers and other papers mentioned above are obvious.

As a result of the study of a series of catalytic systems based on Cu–ZrO₂ (with CrO_x and MnO_x additives) using a wide spectrum of physicochemical methods (*in situ* DRIFT, XPS, XRD, TPR, DTA, DTG, and others), Kilo *et al.* [19] concluded that, in the hydrogenation of CO₂, methanol is mostly formed from bidentate surface carbonate via adsorbed CO, π -bonded formaldehyde, and surface methylate.

The participation of such intermediates as CO and formaldehyde in methanol synthesis probably needs to be further justified since they are unstable under conditions of methanol synthesis. Specifically, as shown above, water readily replaces CO on the active sites,

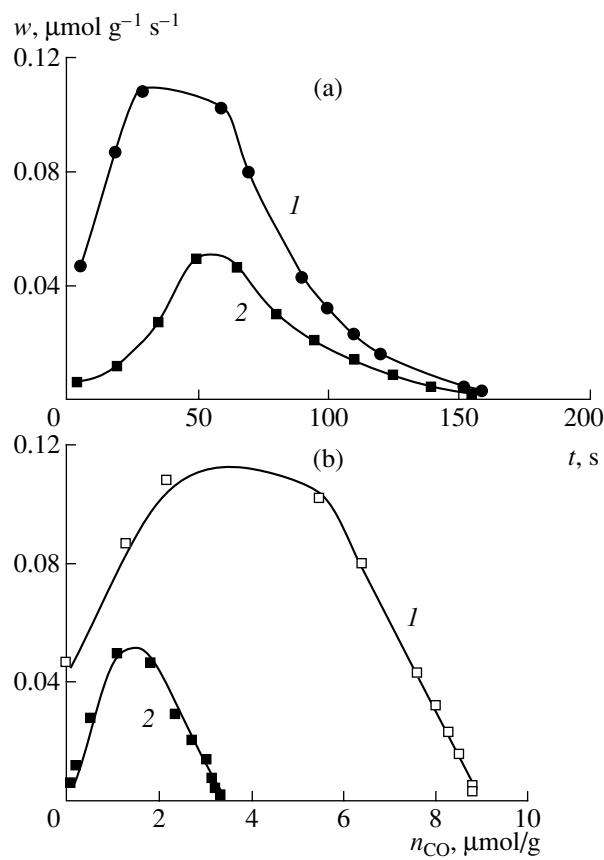


Fig. 7. (a) Kinetic and (b) characteristics curves of the reaction of adsorption substitution of gas-phase water for CO strongly bound to the active sites (250°C, 2.4 kPa): (1) freshly reduced commercial catalyst; (2) the same sample deactivated in the process of methanol synthesis (n_{CO} is the amount of substituted CO).

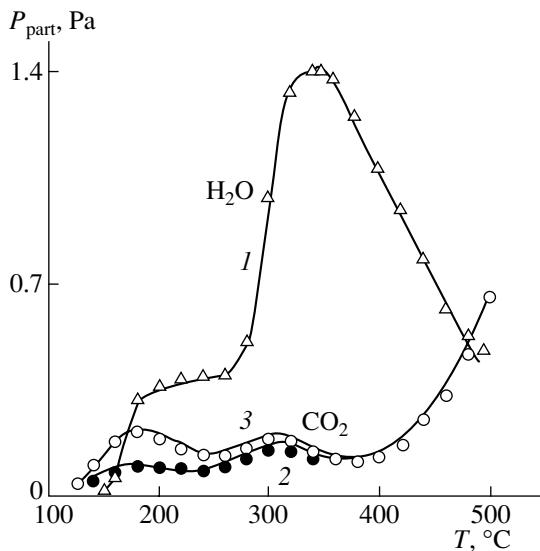


Fig. 8. TPD spectra of the commercial Cu–Zn–Al₂O₃ catalyst SNM-1 reduced by carbon oxide after exposure to H₂O (0.67 kPa, 100°C, 10 min): (1) H₂O, (2) CO₂, (3) after additional exposure to CO₂ (0.67 kPa, 100°C, 10 min).

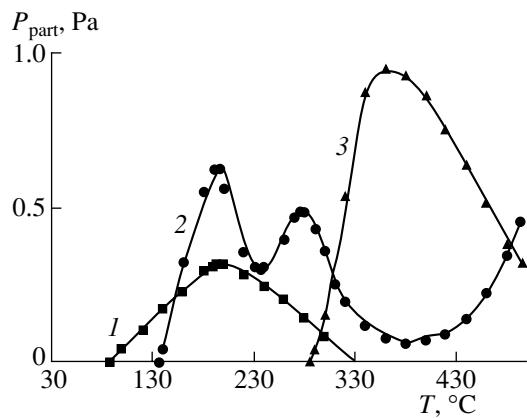


Fig. 9. TPD spectra of the commercial Cu–ZnO–Al₂O₃ catalyst SNM-1 reduced by carbon oxide after exposure to H₂O (0.67 kPa, 100°C, 10 min) and then to CH₃OH (0.67 kPa, 30°C, 10 min): (1) H₂, (2) CO₂, and (3) H₂O.

and this reaction is almost irreversible under conditions of methanol synthesis.

The mechanism of methanol synthesis on an ultradispersed Cu–ZnO–Al₂O₃ catalyst in the hydrogenation of CO₂ and CO/CO₂ was studied by *in situ* FTIR spectroscopy by Q. Sun *et al.* [20]. The authors concluded that methanol is formed directly by the hydrogenation of CO₂ in the mixtures CO₂ + H₂ and CO + CO₂ + H₂ and that the key intermediate is a bidentate formate.

The same method supplemented with kinetic studies was used by F. Lepeltier *et al.* to investigate the hydrogenation of CO₂ on the catalysts ZnAl₂O₄ and Cu–ZnAl₂O₄ at 250°C and a pressure of 0.3 MPa [21]. The authors identified various surface species (carbonates, various formates, methoxy groups, etc.) and determined that the limiting step on the Cu–ZnAl₂O₄ catalyst is carbonate hydrogenation to formate on copper, whereas on the ZnAl₂O₄ support the active intermediate is one of the formates on zinc. The authors assumed that CO is formed on the Cu–ZnAl₂O₄ catalyst via the same surface intermediates as methanol, whereas on ZnAl₂O₄ carbon monoxide is formed from a formate of the second type. It was shown that this formate is inactive in the presence of copper on the catalyst, whereas methoxide are inactive on the support in the presence and absence of copper. The nature and role of the surface compounds determined strongly depend on the composition of the mixture and on the presence of copper in the catalyst. A combination of *in situ* IR spectroscopy and kinetic methods adds reliability to the results obtained.

Similar conclusions were drawn by Amenomiya and Tagawa and reported at the 8th Congress on Catalysis [22], one of the first reports on the process of methanol synthesis studied by *in situ* IR spectroscopy. The sequence of transformations of surface compounds on copper proposed in that work is hydrocarbonate–formate–methoxide.

Overall, we can state that researchers disagree even about formate complexes, which are rather easy to identify. The spectrum of opinions ranges from their acceptance “as key intermediates” to the complete denial of their role in methanol synthesis. We cannot exclude that this diversity of opinions is due to the effect of conditions of measurements and sample biography. Specifically, the concentrations of water and other surface compounds on both active sites and on the surfaces of various phases involved in the catalyst composition are hard to control and can vary over a broad range. The possibility of interphase spillover of surface complexes and an unusual medium for the catalyst components may stipulate their nonstandard behavior under process conditions. Even a relatively simple component of the γ-Al₂O₃ catalyst in the complex system (methanol–DME–methyl formate) may have the properties of an oxidation catalyst and transform methanol into formaldehyde in the presence of oxygen traces [23].

The sequences of transformations of intermediate species reported in [16, 21, 22] are the closest to Scheme 3, which can be considered proven and which largely agrees with these sequences. These are consecutive transformations of the surface species: carbonate (or hydrocarbonate), formate, and methoxy species. If we accept this sequence as a basis, then the assignment of the intermediate in Scheme 3 will be as follows: ZCO₂ is carbonate, ZCO₂H₂ is formate in combination with hydroxyl, and ZCO₂ · H₂O is the hydrocarbonate in combination with hydroxyl.

Although Scheme 3 is simplified, it is sufficient for constructing a theoretical kinetic model of methanol synthesis based on its mechanism. The simplified variant of the rate law is as follows:

$$w = \frac{k_3 K_1 p_{CO_2} p_{H_2}}{K_1 p_{CO_2} + K_{-2} p_{H_2O} + K_1 K_{-2} p_{CO_2} p_{H_2O}}, \quad (1)$$

where the numbers in subscripts correspond to the order of steps in Scheme 3, and k and K are the rate and equilibrium constants, respectively. It follows from this equation that methanol synthesis should be strongly retarded by water, and the reaction order with respect to hydrogen should be close to unity (this was supported experimentally in [6, 9]).

The simplest analysis of Eq. (1) reveals its interesting features [7] (see also [24, 25]). After simple rearrangements it can be described in the following form:

$$w = \frac{k_3 K_1 p_{CO_2} p_{H_2}}{(1 + K_1 p_{CO_2})(1 + K_{-2} p_{H_2O}) - 1}. \quad (2)$$

At high concentrations and/or in the case of the strong retardation by the product, we can neglect “–1” in the denominator. Thus, the kinetics of the reaction imitate the kinetics for the “two-site model,” a reaction occurring with the participation of two different sites.

It can also be easily seen that, under the same but more severe conditions, the equation can be simplified:

$$w = kp_{\text{H}_2}/(1 + bp_{\text{H}_2\text{O}}), \quad (3)$$

where k and b are the parameters and the unity in the denominator can be neglected.

The denominator of this form is usually assumed to mean strong retardation by the reaction product in the framework of classical understanding. This retardation usually leads to the almost complete occupation of active sites by a product that retards the reaction. However, in this case the nominator should contain a term that involves p_{CO_2} . Its absence makes the kinetics impossible from the standpoint of the classical theory. Nevertheless, such kinetics has been observed many times in experimental studies (see [25]). In the framework of the description illustrated above, this kinetics is one of the most probable explanations of the system behavior.

Equation (1) can be considered as a theoretically justified rate law, because it is based on a mechanistic scheme obtained independently. Comparison of the rate law with experimental data showed that it correctly reflects the process kinetics and provides a description of the available and published experimental data [6, 9]. However, in the kinetic study of methanol synthesis in a flow-type reactor under experimental conditions (high CO : CO₂ ratios in the initial mixture), kinetic anomalies were detected that cannot be predicted based on Scheme 3.

Figure 10 shows the kinetic curves of methanol synthesis on the Cu-Zn-Al oxide catalyst 51-2 (ICI) in a flow reactor from the CO₂ + H₂ mixture (curve 1) and from syngas enriched in CO (curve 2). Curve 1 corresponds to the "normal" kinetics of the reaction retarded by the products. Curve 2 is anomalous: the average rate of the reaction in a flow reactor increases with an increase in the contact time after a "normal" initial period (i.e., the productivity of the unit volume of the catalyst increases with an increase in the loading). Such an increase in the rate (autocatalysis) could be observed if methanol synthesis were accelerated by the products. However, experimental verification showed that none of the products (methanol or water) catalyzes the process.

Another possible explanation is the activation of surface sites by the products: site oxidation by water. However, water additives to the initial mixture lead to a retardation of methanol synthesis. Figure 10 shows also kinetic curve 3 obtained in a less arguable experiment in which 0.3 vol % O₂ was added to syngas enriched in CO. It is seen that no activation effect was observed. On the contrary, the rate of synthesis decreased (due to retardation by water formed), and the anomalous form of the kinetic curve is reproduced.

Further analysis showed that the beginning of rate increase, the minimum on curves 2 and 3 (Fig. 10),

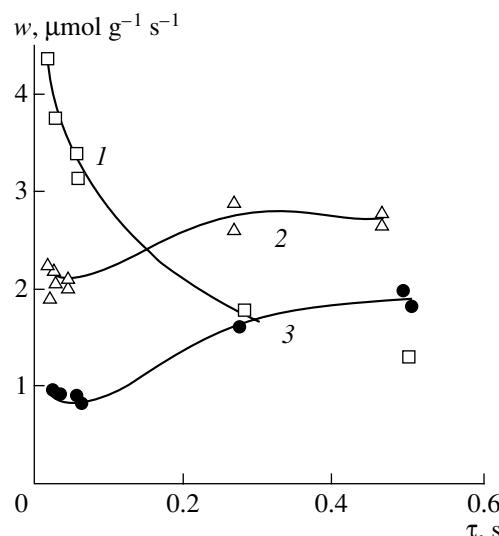


Fig. 10. Kinetics of methanol synthesis on the Cu-Zn-Al oxide catalyst 51-2 in a flow reactor: (1) from the mixture CO₂ + H₂; (2) from syngas enriched in CO; (3) from mixture 2 with the 0.3% oxygen additive.

approximately corresponds to the equilibrium in WGSR (at shorter contact times, the reverse WGSR dominates). With an increase in the contact time after the minimum, this reaction begins to occur in the direction of the conversion of CO by water and shifts the ratio of the stationary concentrations of ZH₂O and ZCO₂ (see Scheme 3) toward ZCO₂. In this situation, methanol synthesis and WGSR should be coupled and their mutual effect on each other is a natural result of this coupling.

In the section devoted to the transformations of surface species, we showed that water strongly adsorbed on the active site readily converts in the reaction with gas-phase CO. Indirect data suggest that this reaction also occurs via the formation of an intermediate two-species complex. The further construction of the scheme of its transformations is complicated due to the fact that the carbon label in CO does not transfer to methanol and, therefore, to ZCO₂, which is a methanol precursor.

Only two variants probably satisfy such a requirement: (1) in the formation of CO₂ and H₂, both species evolve into the gas phase and free a site on which CO₂ or H₂O preferentially adsorbs and (2) the CO₂ formed in the reaction remains on the site but rapidly exchanges with the gas-phase CO₂. If we adopt variant 1, we meet difficulties in constructing the scheme of the reverse WGSR or violate the principle of microscopic reversibility. Therefore, variant 2 is more plausible. It has experimental analogs in the form of accelerated desorption of adsorbed CO or NO in the presence of the same gas-phase molecules, as has been observed many times.

Such observations mean, in the framework of the approach developed here, that the reaction of adsorp-

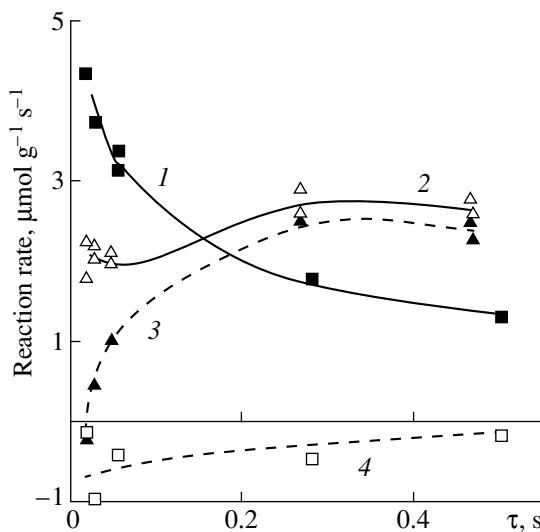
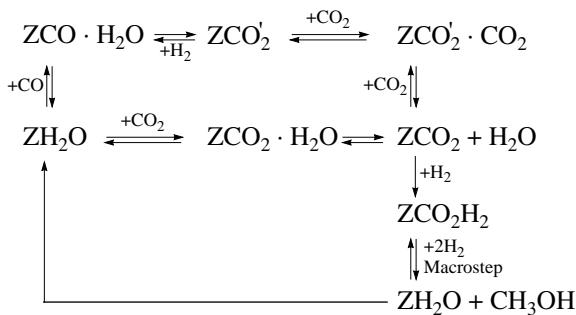


Fig. 11. Kinetics of methanol synthesis (1, 2) and WGSR (3, 4) on the catalyst 51-2 (250°C, 5 MPa, curves correspond to the calculation, points correspond to the experiment): (1, 4) CO₂, 21.8; CO, 3.6; H₂, 74 vol %; (2, 3) CO₂, 3.2; CO, 18.2; H₂, 78 vol %.

tion substitution for similar species occurs rapidly (if it occurs).

Taking into account the above consideration, we may construct a complete scheme of the transformations (up to the rate-limiting step) in methanol synthesis coupled with WGSR (Scheme 4). As can be seen, this scheme is similar to Scheme 3 and differs only in that it has an additional upper row. Note that WGSR on copper-based catalysts can occur via several routes. However, in connection with the specific features of the situation (the active sites are almost completely filled with CO₂ and H₂O) under conditions of methanol synthesis, the only realizable route is the one shown in the scheme.



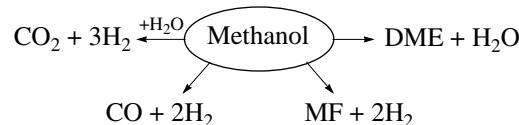
Scheme 4. Complete scheme of methanol synthesis coupled with WGSR.

The theoretical kinetic model based on Scheme 4 describes both normal and anomalous kinetics of methanol synthesis [26]. Figure 11 shows the results of computer simulation of the process for both cases that take place in the transformations of initial mixtures with

various compositions. As can be seen, the kinetic model correctly describes the specific features of reactions and very different kinetic curves in the framework of the same model with the same parameters.

Thus, for methanol synthesis, which has been relatively well studied, we can determine the scheme of the reaction mechanism, develop a theoretical kinetic model of the process, and carry out computer simulation of the process.

Copper-based catalysts are usually associated with methanol synthesis and the oxidative transformations of CO and other molecules. However, they show a high activity in numerous reactions of C₁ molecules, including those listed at the beginning of this article. The mechanisms of these reactions have been less studied than methanol synthesis, but the above information helps us to understand them since they all belong to methanol conversions complicated with other reactions. This area of research may be described in simplified form by Scheme 5. Let us begin with steam reforming of methanol, because information on methanol synthesis proved to be most applicable to this reaction as well.



Scheme 5. Scheme of reactions studied.

STEAM REFORMING OF METHANOL

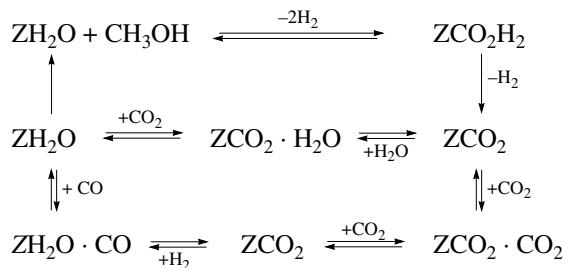
Steam reforming of methanol has recently attracted considerable recent attention as a pathway to pure hydrogen. Taking into account the simplicity of methanol storage and transport, this interest is undoubtedly justified. It is important that in steam reforming one methanol molecule gives three hydrogen molecules:



Because methanol synthesis occurs as hydrogenation of carbon dioxide (see above), the steam reforming of methanol is essentially the reverse of synthesis. At the same time, it is unclear whether the kinetic and mechanistic schemes are applicable to the reverse reaction, which occurs with a very different composition of the mixture that contacts the catalyst. In connection with this, the kinetics of this process was studied by Lin *et al.* in our laboratory. Because the results of this work will be published in [27], we only briefly consider the conclusions drawn in that work.

The sequence of transformations of intermediates is shown in Scheme 6. The upper horizontal row of this scheme corresponds to the occurrence of the macrostep, which in principle can involve the reaction of adsorption substitution of gas-phase methanol for strongly bound water. We will discuss it in more detail when considering the mechanisms of DME synthesis. In other respects, Scheme 6 is an “upside down” ver-

sion of Scheme 4 for the methanol synthesis mechanism.



Scheme 6. The sequence of intermediate transformations in steam reforming of methanol on copper-based catalysts.

A theoretical kinetic model based on Scheme 6 was checked against experimental data obtained by us and taken from the literature. In all cases, it was found that the calculation and experiment reasonably agree with each other. This was the case even if we described both methanol synthesis and its steam reforming using the same parameters of the equation. Perhaps, this can be considered to be the most strict verification of the model.

To illustrate this, Fig. 12 shows the kinetic curves of steam reforming of methanol on the Cu–Zn–Al oxide catalyst 51-2 at 245°C and a pressure of 6 and 21 atm. The initial gaseous mixture consisted of methanol and water in the ratio H₂O : CH₃OH ≈ 1.3 : 1. Calculations were performed independently for each experimental point. The results of calculations and experimental data are compared in Fig. 12. It is seen that the kinetic model correctly describes the dependence of conversion on the contact time and pressure in the system. We can conclude that the mechanistic scheme proposed for methanol synthesis is also applicable to the reverse reaction, steam reforming of methanol.

DIMETHYL ETHER SYNTHESIS

The role of dimethyl ether was reconsidered recently after 1995, when a number of well-known companies, such as Amoco, Haldor Topsoe, and others, showed the possibility of using it as environmentally friendly diesel fuel at the International Congress/Exhibition in Detroit [28]. Moreover, according to estimates by Kikkawa and Aoki [29], the use of DME as fuel for gas-turbine units is more economical than the use of liquefied gas.

Currently DME is commercially produced by methanol dehydration on γ -Al₂O₃ or another dehydration catalyst (reaction (III)).

Some projects have proposed the process of direct DME synthesis from syngas using a combination of a copper-based catalyst and a dehydration catalyst (e.g., γ -Al₂O₃). This process involves reactions (I) and (II) in addition to (III) and was developed at pilot and/or experimental–industrial unit scale. Most projects pro-

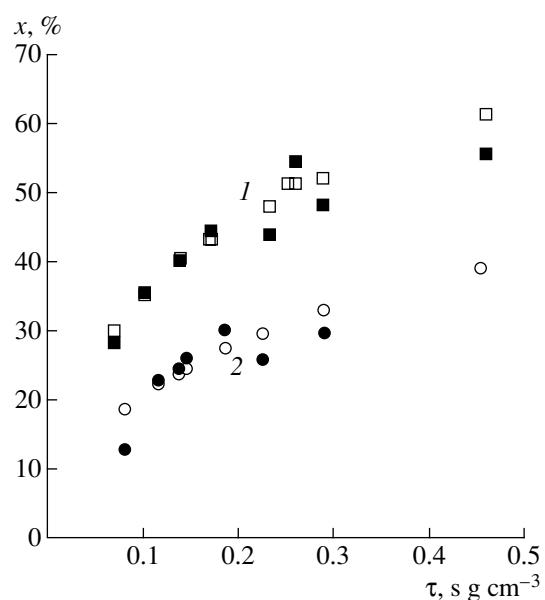


Fig. 12. Kinetics in the steam reforming of methanol on the Cu–Zn–Al oxide catalyst 51-2 in a flow reactor at 245°C; the initial mixture composition is H₂O : CH₃OH = 1.3 : 1 (open circles refer to the calculation and solid circles refer to the experiment) at a pressure in the system equal to (1) 6 and (2) 21 atm.

posed the use of gas-phase synthesis, although NKK (Japan) proposed a liquid-phase process [30]. All projects involve methanol synthesis and its further dehydration (reactions (I)–(III)). Because temperature intervals for these three reactions are rather close, they can all be carried out in the same reactor.

Note that such united one-step process is rather productive (see below). The synthesis of methanol is thermodynamically unfavorable, which necessitated the use of flow schemes with circulated gaseous mixture. In the one-step process, methanol and water produced by reactions (I) and (III) transform further: methanol is consumed by reaction (III), and water is consumed by WGSR (II). Thermodynamic limitations can be overcome in this way. As a result, it is possible to achieve one-pass conversions of CO as high as 90%, and DME produced directly from syngas is cheaper than the equivalent amount of methanol.

As shown above, there are theoretical kinetic models for reactions (I) and (II) based on the reaction mechanism. For the complete description of direct DME synthesis from syngas, it is also desirable to have a mechanistic scheme of dehydration (and a kinetic model based on it).

Although the dehydration of alcohols (especially, ethanol) became a classical task for beginners in chemistry, reliable data on the mechanism of this reaction are rather scarce. It is clear that at least one of the reaction products (water) strongly adsorbs on active sites. Taking into account the data reported in [3, 5], we expect

Table 2. Methanol transformation on $\gamma\text{-Al}_2\text{O}_3$ at 250°C in the pulse regime [31]

| Methanol concentration in a pulse, μmol | Amounts of products at the reactor outlet, μmol | | |
|----------------------------------------------------|------------------------------------------------------------|----------|----------------------|
| | DME | methanol | H_2O |
| 52 | — | — | 98 |
| 62 | — | 1 | 42 |
| 50 | 13 | 3 | 26 |
| 55 | 17 | 3 | 13 |
| 53 | 10 | 4 | 13 |
| 162 | 179 | 17 | 38 |

that, in the system methanol–water–alumina, a reaction of adsorption substitution may occur in both directions and provide water replacement by methanol on the active site.

A very informative experiment that clarifies a number of properties of the reaction system has been carried out by Ivanov and Makhlin [31]. Methanol in the form of pulses in helium was supplied to a flow-type reactor with the catalyst $\gamma\text{-Al}_2\text{O}_3$. The resulting data are summarized in Table 2. As can be seen, methanol is completely consumed in the first pulse; DME is not formed and two water molecules are formed for each methanol molecule consumed. It is clear that for reaction of adsorption substitution of methanol for strongly bound water occurs. The stoichiometry of water formation unexpectedly confirms the composition of the complex on the active site (H_4O_3), the existence of which was based on the kinetic data of the nonstationary reaction of strongly adsorbed water with gas-phase CO (see [6, p. 127]).

In further pulses, the amount of water drastically decreases, and the gas flow at the outlet starts to contain a small amount of residual methanol, which increases from one pulse to another. In the second pulse, methanol is present in an extremely small amount, whereas DME is completely absent. In the second to fifth pulses, the amount of water formed is stabilized and approximately corresponds to the amount of DME formed; the concentration of methanol at the outlet of the reactor is still insignificant. Finally, in the sixth pulse, the amount of supplied methanol is tripled, and the amount of water formed is increased proportionally. The concentration of methanol at the reactor outlet increased by a factor of greater than 4. In fact, we can state that methanol was present in the gas phase along the whole length of the catalyst bed for this pulse only. The change in the yield of DME is the most dramatic: its concentration increased by more than an order of magnitude.

First of all, it is clear from the above data that, in the case of methanol supply, strongly adsorbed water is

substituted (this was already commented on above) and virtually all the methanol remains on the catalyst surface. DME is formed, but its yield is insignificant. After five pulses, only ~ 80 of $\sim 260 \mu\text{mol}$ of methanol transforms into DME, and $\sim 170 \mu\text{mol}$ remains on the surface ($\sim 10 \mu\text{mol}$ comes out from the reactor). With a further increase in the concentration of methanol in the gas phase, a “light-off” takes place: all of the methanol on the catalyst together with that supplied to the reactor in the pulse transforms into DME and comes out from the reactor. The yield of DME is even higher than the overall amount of methanol, which is probably due to experimental error.

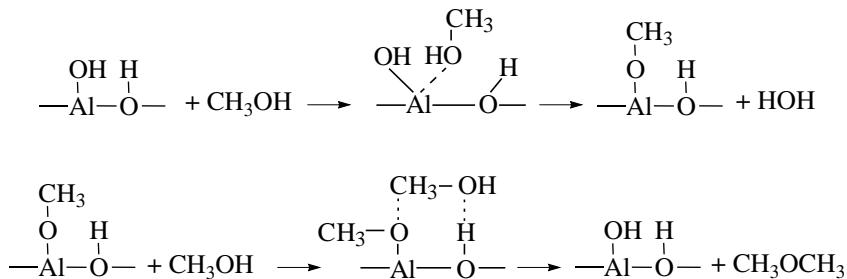
Such a drastic reaction to an increase in the amount of methanol in a pulse can be due to only one of two situations: (1) DME is formed in the reaction of strongly adsorbed methanol (or a methoxy group) with a gas-phase methanol molecule and (2) DME is formed but remains on the active site and is then replaced by methanol from the gas phase (the formation of phase-like structures in the adsorption layer appears to be incredible in this case).

In both cases, the appearance of DME at the outlet of the reactor requires the presence of methanol in the gas phase, which is observed in the sixth pulse. However, there is an argument against situation (2): the methanol that replaced DME on the active site should remain there, whereas the amount of DME formed together with methanol remaining on the active sites would be much higher than the amount of methanol supplied, and this cannot be explained by experimental error.

Thus, we come to the conclusion that the formation of DME occurs by the interaction of strongly adsorbed methanol with a methanol molecule from the gas phase. Note also that the amount of water formed in the sixth pulse is almost tripled, along with the amount of methanol. This does not correspond to the formation of water due to the formation of DME. Therefore, water

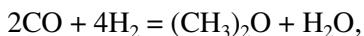
formed in the reaction remains on the active site (and is then removed by adsorption substitution with methanol assistance, in which case a new cycle of transformations begins).

The detailed mechanism of this reaction is shown in Scheme 7 [31], from which it is seen that it corresponds to the above schemes of reaction mechanisms with strongly adsorbed species in all the principal positions.



Scheme 7. Scheme of methanol dehydration to DME on γ -Al₂O₃ [31].

The direct synthesis of DME from syngas is of great interest. The stoichiometry of this process depends on reaction conditions and the composition of the syngas, first and foremost, on the concentration of hydrogen and the nature of the molecule that serves as the carry-out agent for excess oxygen atoms from the system. The extreme situations correspond to two stoichiometric equations of the overall reactions:



With theoretical kinetic models of all the three reactions comprising the process of direct DME synthesis from syngas (reactions (I)–(III)), one may attempt to construct a kinetic description of the overall process. This attempt will not necessarily be successful, because the mutual effect of the reactions on each other and on the state of the catalyst surface can considerably affect the kinetic regularities of the overall process. Nevertheless, comparison of the results of calculations with experimental data showed that the kinetic model thus obtained describes the observed patterns of direct DME synthesis from syngas.

Figure 14 shows the kinetic curve of direct DME synthesis from syngas at a pressure of 5 MPa. It is seen that experimental points fall on the curves calculated on the basis of the theoretical kinetic model. Moreover, the model correctly describes the specific effect of temperature on the process rate due to the superposition of regularities of various reactions occurring in the system. It is likely that the application of the described approach

Therefore, the structure of the kinetic model of this reaction is analogous to those considered above. Calculations show that the theoretical model agrees with experimental data. Figure 13 illustrates the kinetics of methanol dehydration to form DME in a flow reactor at 260°C and atmospheric pressure for various initial concentrations of methanol in a nitrogen flow. It is seen that the calculated and experimental data are very close.

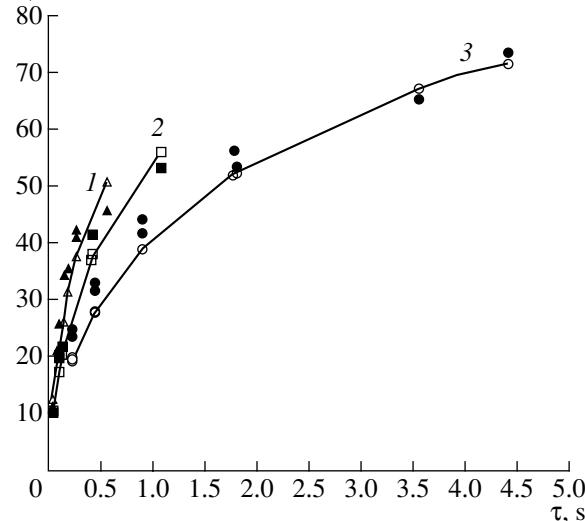


Fig. 13. Kinetics in methanol dehydration to DME on γ -Al₂O₃ at 1 atm and 260°C (open circles refer to the calculation and solid circles refer to the experiment) with a methanol concentration in a flow (vol %) of (1) 30, (2) 50, and (3) 100.

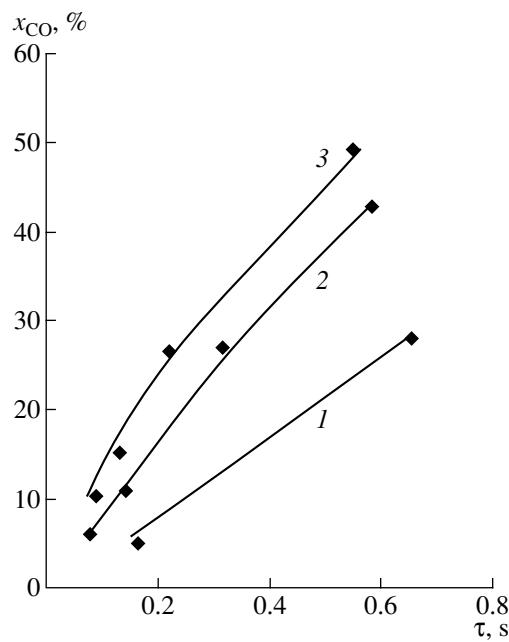


Fig. 14. Kinetics of CO conversion in direct DME synthesis from syngas at 5 MPa and a temperature of (1) 240, (2) 260, and (3) 280°C. The curves show calculations according to the theoretical kinetic model, and points refer to the experiment.

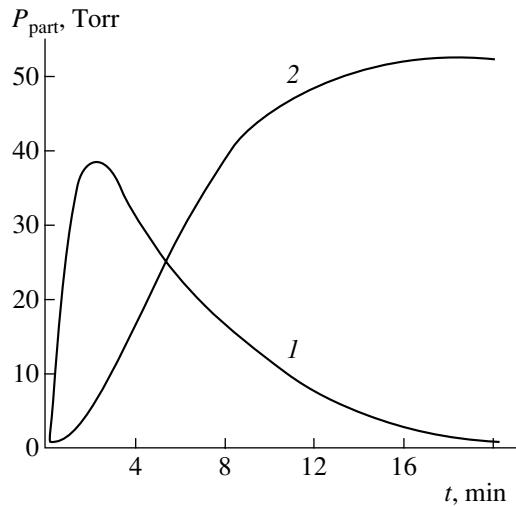


Fig. 15. Kinetics of synthesis and decomposition of methyl formate (MF) in methanol dehydrogenation in a closed system on a Cu-Zn-Al oxide catalyst at 300°C [32]: (1) MF and (2) CO.

hydrogen. MF is readily formed in methanol dehydrogenation on copper-based catalysts.

The specific features of the reactions were studied by Shlegel' *et al.* [32] using an original method. In a closed circulation setup, a pulse of methanol was supplied and changes in the composition of the circulating gaseous mixture were traced. For methanol dehydro-

genation, a Cu-Zn-Al oxide catalyst was used. Figure 15 shows the kinetics of product (MF and CO) accumulation at 300°C. As can be seen, the figure is a classical illustration of the kinetics of a consecutive reaction, which is suitable for a handbook. There is no doubt that the reaction occurs via the scheme



As can be seen from data reported in [32], at low temperatures where the resolution is higher, all the reactions are suppressed and the interaction of methanol with residual adsorbed water (to form CO₂ and H₂) only occurs at the initial stages of interaction.

It is noteworthy that, according to Fig. 15, the formation of CO only occurs due to the decomposition of MF but not methanol. Thus, this direction of transformation can be used for obtaining methyl formate and for methanol transformation into syngas (via the intermediate formation of MF).

Although methyl formate synthesis by methanol dehydrogenation can be carried out at a temperature lower than 200°C and is attractive due to its simplicity, its practical application meets certain difficulties due to the unfavorable thermodynamics of the process. However, the equilibrium yield of MF increases with temperature (Fig. 16) and reaches values that are acceptable for practical purposes, for instance, at 240°C, although its decomposition into CO and H₂ becomes noticeable even at much lower temperatures. With an increase in temperature, the decomposition of MF dominates (see Fig. 16), and it is impossible to approach equilibrium while preserving a high selectivity.

The study carried out in our laboratory [33–35] was an attempt to overcome these difficulties using information on the kinetics and mechanism of the reaction. Knowledge of the regularities of MF hydrogenation to methanol, which is the reverse reaction of MF synthesis, and the regularities of MF decomposition played a key role in this study. Let us briefly dwell on the arguments and conclusions of these studies.

Figure 17 shows the dependence of MF conversion with the formation of CO and H₂ on the contact time on a copper-containing catalyst in a flow reactor at 167°C. As can be seen, even at a relatively low temperature, MF intensively decomposes. Points corresponding to the initial concentrations of MF, 0.317 and 1.00 vol %, which differ more than three times, fall on the same kinetic curve up to 90% conversion.

This means that the decomposition of MF occurs as a first-order reaction (the conversion is independent of the initial concentration). However, with an increase in the concentration of MF to 5.45 vol %, the values of conversion decrease by a factor of 2–3 compared to the expected values, and methanol appears in the reaction products (due to decarbonylation and/or hydrogenation by the hydrogen formed) [33, 35]. Therefore, MF decomposition is retarded by either MF or by the by-product methanol.

The choice of the retardation agent can be made based on the data on MF decomposition in a hydrogen atmosphere. Table 3 shows data [35] on the kinetics of this reaction at the same temperature (167°C). At low concentration, MF transforms via two pathways: hydrogenation to methanol and decomposition into CO and H₂. An increase in the concentration of MF to 5.4 vol % leads to a catastrophic decrease in the rate of CO formation, even when MF hydrogenation to methanol almost reaches equilibrium. It becomes clear that methanol, which can strongly adsorb on the active sites, is the main retardation agent.

The fact that MF decomposition can completely be suppressed at noticeable methanol concentrations unequivocally suggests that methanol decomposition to CO + H₂ on copper-based catalysts only occurs via the intermediate formation of MF.

The conversion of MF in the reaction of its hydrogenation to methanol changes rather insignificantly with a change in the concentration of MF; that is, the rate of reaction of MF decomposition is approximately proportional to its initial concentration in the gas phase. Therefore, the dependence of MF concentration on the active sites on its initial concentration in the gas phase is close to proportional, which can be observed only at low coverages of active sites with methyl formate. The main component of the adsorbed "layer" in this case is the strongly adsorbed methanol.

Because the decomposition of MF and its hydrogenation occur with the participation of adsorbed MF and no other reactants are required for decomposition, we may conclude that a free site that is adjacent to the adsorbed species is necessary for the decomposition of MF to CO and H₂. Filling these sites when methanol appears in the system causes the effects observed. The reaction order of MF hydrogenation with respect to MF is also close to unity. Obviously, this reaction may occur only after the gas-phase MF substitution for methanol (a methanol molecule is formed as a result of each act of hydrogenation). Because it is not retarded when methanol occupies adjacent sites, we may assume that hydrogen reacts directly from the gas phase. Such a reaction should occur via steps, at least because the probability of triple collisions is low. According to the principle of microscopic reversibility, the reverse reaction, methanol dehydrogenation to MF, should also occur in steps.

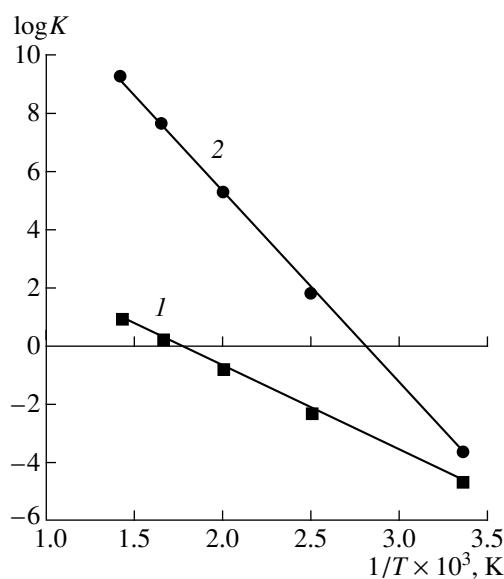


Fig. 16. Temperature dependence of the equilibrium constants in the reactions of (1) synthesis and (2) decomposition of MF.

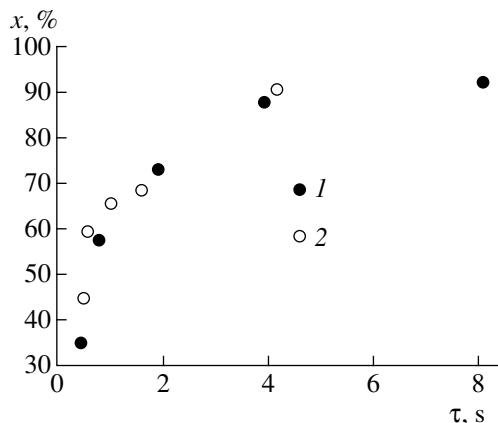
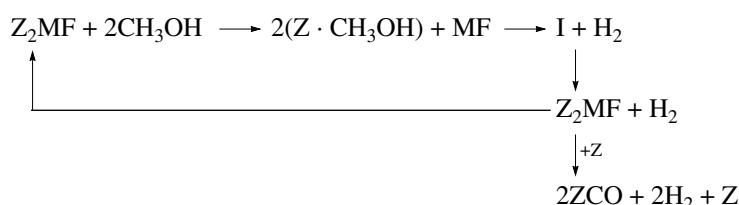


Fig. 17. Kinetics of MF decomposition on the copper-based catalyst at 167°C and initial concentration of MF: (1) 1.00 and (2) 0.317 vol %.

In view of the above reasoning, we may write down a very rough scheme of the sequence of transformations in the dehydrogenation of methanol to methyl formate (Scheme 8).



Scheme 8. Simplified scheme of the mechanism of methanol dehydrogenation to methyl formate with further decomposition into CO + H₂.

Table 3. Kinetics of MF decomposition in a hydrogen atmosphere at 167°C [35]

| Contact time, s | Concentration at the reactor outlet, vol % | | MF conversion, % | | | Selectivity to methanol, % |
|--------------------------------------------------|--------------------------------------------|------|------------------|-------|-------------|----------------------------|
| | methanol | MF | total | to CO | to methanol | |
| Initial mixture: 1.16 vol % MF in H ₂ | | | | | | |
| 0.6 | 0.99 | 0.08 | 94 | 51 | 43 | 46 |
| 1.3 | 0.88 | < | 100 | 62 | 38 | 38 |
| Initial mixture: 2.55 vol % MF in H ₂ | | | | | | |
| 0.3 | 2.10 | 0.92 | 64 | 23 | 41 | 64 |
| 0.6 | 2.92 | 0.38 | 85 | 28 | 57 | 67 |
| 1.7 | 2.68 | 0.05 | 98 | 46 | 52 | 53 |
| Initial mixture: 5.40 vol % MF in H ₂ | | | | | | |
| 0.3 | 5.00 | 2.80 | 48 | 2 | 46 | 96 |
| 0.5 | 6.77 | 1.65 | 69 | 7 | 62 | 90 |
| 1.3 | 10.50 | 0.28 | 97 | 0 | 97 | 100 |

Table 4. Highly selective synthesis of MF by methanol dehydrogenation

| T, °C | v ₀ , 1 g ⁻¹ h ⁻¹ | P, MPa | P _M , MPa | x, % | x _{MF} , % | x _{MF} /x _∞ | S, % |
|-------|----------------------------------------------------|--------|----------------------|------|---------------------|---------------------------------|------|
| 190 | 21.7 | 0.85 | 0.14 | 21.5 | 20.7 | 73 | 96 |
| 240 | 20.3 | 0.85 | 0.13 | 44.1 | 42.0 | 99 | 95 |

Note: v_0 is the space velocity, P_M is the initial partial pressure of methanol, x is conversion, x_{MF} and x_∞ are the current and equilibrium conversion of MF into methanol, and S is the selectivity to MF.

The first step (conditionally) reflects the adsorption substitution of methanol for MF. It is not excluded that intermediate I may immediately be formed due to this step. The structure of this intermediate was classified as semiacetal in [33].

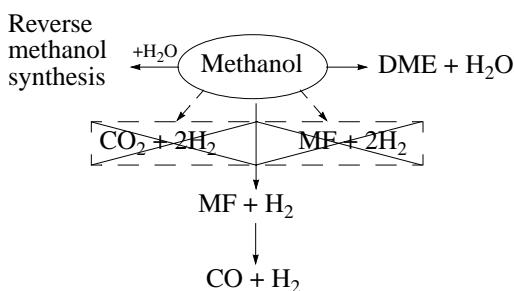
The above reasoning leads us to simple methods for process selectivity control. At high concentrations of methanol in the system, a high selectivity to MF is expected. At low concentrations of methanol and high temperatures, methanol is expected to transform selectively to syngas via the intermediate formation of MF and its decomposition.

Table 4 shows data on the highly selective synthesis of MF by methanol dehydrogenation. It is seen that, at a high partial pressure of methanol, the selectivity is high (95%) with a near equilibrium conversion (99%). The highly productive methanol decomposition into syngas via the formation and decomposition of MF was also made practical.

In conclusion, let us return to the scheme of methanol transformation presented above (Scheme 5). Taking into account the information obtained, it should be corrected in view of Scheme 9. That is, the information obtained affected the whole view of the nature of the occurring steps. At the same time, we realize that this

information only provides a superficial understanding of the essence of the occurring processes and may be insufficient to develop kinetic models.

For the purposes of illustration, let us return to methanol dehydration on $\gamma\text{-Al}_2\text{O}_3$, which is one of the simplest among the reactions studied and which is an important component of the process of DME synthesis from syngas. Recently [36], Ukharskii and Matyshak carried out an IR spectroscopic study of methanol adsorption on $\gamma\text{-Al}_2\text{O}_3$ and found three types of stable methoxy compounds with intensity maxima at 1160 and 1190 cm^{-1} (linear methoxy groups) and 1090 cm^{-1}

**Scheme 9.** Corrected scheme of methanol transformations.

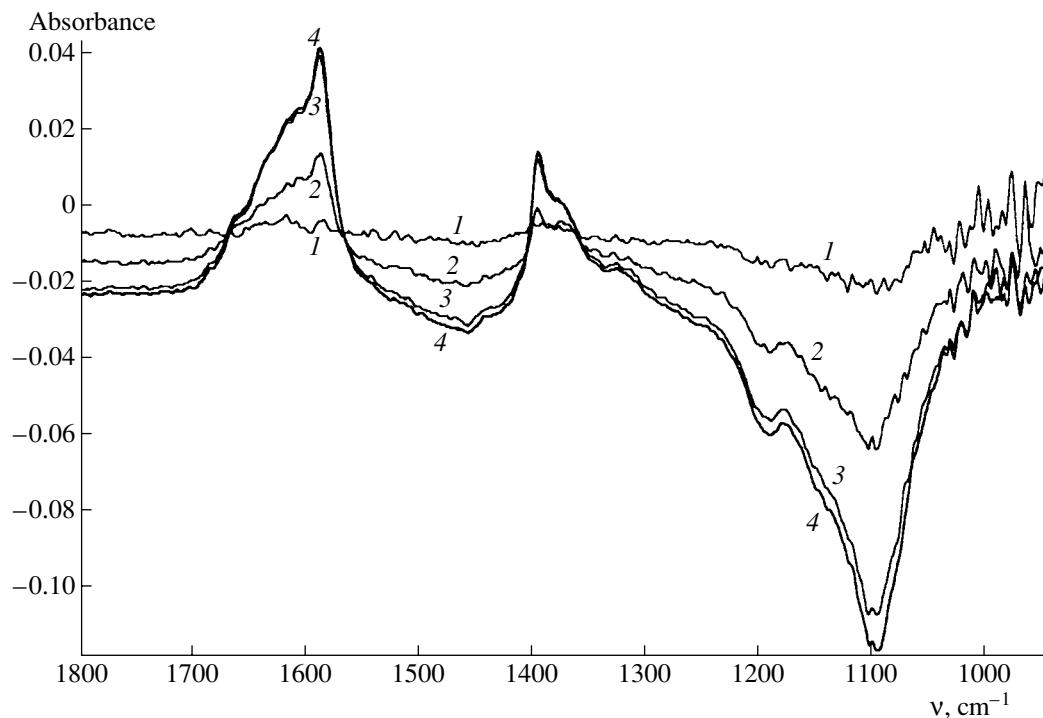


Fig. 18. Differential IR spectra of methoxy group oxidation on γ -Al₂O₃ by oxygen to adsorbed formaldehyde [36] after (1) 20, (2) 130, (3) 540, and (4) 720 s.

(a bridging methoxy group). Transformations of these surface compounds, which were studied *in situ* in the reaction with gas-phase oxygen, led to the formation of a surface complex close to adsorbed formaldehyde (absorption bands at 1630 cm⁻¹). However, an important feature was uncovered: the reactivities of various methoxy groups were substantially different.

Figure 18 shows the differential spectra of oxidation of surface methoxy groups at the initial period of the reaction (20–720 s). As can be seen, the growth of the concentration of adsorbed formaldehyde (see the absorption band at 1630 cm⁻¹) is almost entirely determined by the consumption of the methoxy group of only one type (the absorption band at 1090 cm⁻¹); another methoxy group (the absorption band at 1190 cm⁻¹) reacts with a much lower rate; the third methoxy group (the absorption band at 1160 cm⁻¹) is a spectator. Thus, information on the sequence of intermediate transformations is insufficient because it is necessary to take into account the different reactivities of intermediates of one type.

We expect that the scale of studies yet to be performed to gain a complete understanding of the mechanisms of the processes under consideration is not smaller than the scale of the studies that have already been performed. Nevertheless, the fact that most of the surface species are stable in these processes (i.e., readily available for study) makes the situation easier and allows one to be optimistic about prospects for research in this area.

CONCLUSION

Using examples of various reactions of C₁ molecules, the possibilities of developing theoretical kinetic models of heterogeneous catalytic reactions based on mechanistic information reveal themselves most vividly. This is not surprising taking into account the relative simplicity of these reactions. Of course, if the systems under study become more complex, additional difficulties appear. However, taking into account the fruitfulness of such models, a transition to describing chemical systems of this sort seems to be inevitable. At the same time, the data presented in this paper illustrate the fruitfulness of using different variants of the kinetic methods for mechanistic studies of reactions.

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[†] Deceased.

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