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Mechanisms of methanol synthesis from hydrogen and carbon oxides at Cu–Zn-containing catalysts in the context of some fundamental problems of heterogeneous catalysis

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Abstract

It is stated that, for deduction of the kinetic equation of a heterogeneous catalytic process proceeding with a rate-determining step (RDS), it is necessary and sufficient to reveal the chemical nature of the RDS, composition of the surface intermediates, and stoichiometric number (SN) of the RDS. On the basis of calorimetric and adsorption methods applied to the Cu–Zn-containing catalysts reduced to a state identical to that occurring during the steady-state methanol synthesis from hydrogen and carbon oxides, three catalytic surfaces (S_1, S_2, and S_3) are specified and the individual steps of the steady-state process are studied. It is stated that CH_3OH is produced at S_2 (the ZnO-component) from H_2 and CO_2 by two routes N_1 and N_2 with RDSs of interaction between gaseous H_2 or CO_2 and adsorbed CO_2 or H_2, respectively, SN $=$ 2 for each RDS, and the adsorbed intermediates are H_2, CO_2, HCOH, HCOOH, and O_2; CO_2 is produced at S_1 (the Cu-component approximated by $Cu_4{\cdot}OH_2$) through the shift-reaction; S_1 and S_2 are homogeneous in their adsorption properties. The causes of the absence of manifestation of the structural heterogeneity of catalysts in their adsorption and catalytic properties are considered.

Keywords: Methanol catalytic synthesis mechanisms; Methanol catalytic synthesis kinetics; Cu–Zn-containing catalysts; Catalysis heterogeneous description

1. Introduction

Several monographs and reviews (e.g. [1–6]) are dedicated to the process of methanol production from carbon oxides and hydrogen in the presence of Cu–Zn-containing catalysts. This process is most efficient at 470–530 K and pressures of 5–19 MPa. In spite of some optimistic opinions, such as in [5,7], a number of questions on the surface-layer state and on the mechanisms and kinetics of the process is still open. The discussions are being continued (e.g. [8–20]). The discussions are concentrated around a wide circle of principal questions, from which we could set off the questions on the principal source of methanol production and on the functions of the components in the Zn–Cu–Al(Cr)-containing catalysts. In recent years, most of the authors (e.g. [6,8,12,19,20]) consider carbon dioxide to be the direct source of methanol production and the shift-reaction to be the source of carbon dioxide. The opinions on the second question differ principally. Some of authors (e.g. [12,18]) believe that methanol is formed predominantly at the ZnO-component of the catalyst, while some others (e.g. [17,20]) consider the metallic copper to be the active face in the methanol synthesis and the role of ZnO consists in spreading of the copper particles. The kinetic models for the methanol synthesis are also vastly different (see, e.g. [17,20]).

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In this paper, we concentrate our attention not only on the process of methanol formation as such, but also on some fundamental problems of the heterogeneous catalysis, namely, on the CO_2 reactivity, practical abundance of the mechanisms including a limiting step, body of the information necessary and sufficient to deduce the kinetic equation theoretically justified, and potentialities of calorimetric and kinetic data on adsorption–desorption steps to clarify the catalytic mechanisms.

We assume that the process of methanol formation at the Cu–Zn-containing catalysts proceeds under a wide range of conditions according to the following gross-mechanism:

$$CO + H_2O = CO_2 + H_2 \qquad \text{(I)}$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad \text{(II)}$$

(Apparently, at ZnO-catalysts containing no copper, the process proceeds according to other mechanism, considered below.) Such a gross-mechanism was proposed in [21–27]. In [21] (and [6]), such a conclusion was made mainly on the basis of studies of C^{14} transfer from CO to CO_2 and methanol. In [22,24], it was stated that methanol is produced not at all when the reacting gas mixture contains no carbon dioxide. This gross-mechanism is one of the problems discussed in the literature. For example, in the opinion presented in [2], it is doubtful that such a gross-mechanism is the predominant one, since reaction (II) is thermodynamically unfavorable in the vicinity of 500 K. However, the corrections introduced by the authors of [28] to the thermodynamic functions of the process under consideration and the computations performed by them denuded of the grounds for such a doubt. A number of authors (e.g. [3,29]) counts that CO, along with CO_2, contributes to the rate of the methanol synthesis. Some objections made in [2,3,29] against the above-presented gross-mechanism were rejected in [6,7,11].

According to the available data [30], in the vicinity of 500 K, reaction (I) proceeds actively at copper catalysts containing no zinc. When the operation factor (ratio of the volume of the catalyst to the volume of the reacting mixture flowing for 1 s through the catalyst layer) is less than 1 s by a factor of several units only, reaction (I) is in equilibrium [1]. In the Cu–Zn-containing catalysts, the Cu-component surface is much larger than the ZnO-component surface catalyzing the methanol synthesis (see below). Therefore, we believe that, in the process of the methanol synthesis, the relation between gaseous CO, H_2O, CO_2, and H_2 usually corresponds or almost corresponds to the equilibrium of reaction (I).

2. Principal instrumentation and experimental procedures

The principal scheme of the glass adsorption vacuum instrument is shown in Fig. 1. The instrument is supplied with grease-free bellow metal taps 4–14 and greased glass taps 15–20. The welded metal–glass connections were performed through kovar insertions. The sample and reference calorimetric ampoules (2 and 3, respectively) were housed in a FOSKA calorimeter 1 described in detail in [31,32].

The sample ampoule 2 contained an accurate weight of a sample under study (about 1 g) pretreated within another instrument to achieve a standard state (S-state). After this pretreatment, the ampoule was

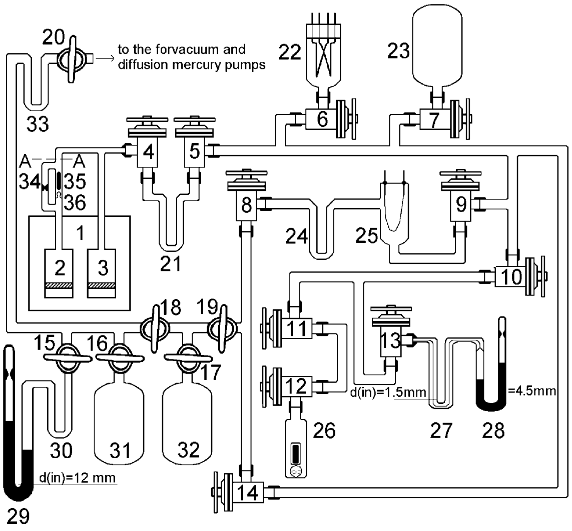

Fig. 1. Principal scheme of the apparatus: (1) microcalorimeter; (2) sample ampoule; (3) reference ampoule; (4)–(14) metal taps; (15)–(20) glass taps; (21), (24), (30), (33) U-shape traps; (22) thermocouple manometer; (23), (31), (32) bulbs for gases; (25) bulb for combustion, supplied with a Pt-wire; (26) bulb supplied with methanol in a sealed glass sphere and with a magnetic breaker; (27) and (28) device for analyses; (29) big mercury manometer; (34) sealed neck; (35) magnetic breaker; (36) neck.

sealed under vacuum across the neck 34, housed in the calorimeter 1, and sealed to the A–A section of the apparatus. Then, by using an outer magnet, the thin glass diaphragm 36 was broken by the magnetic cylinder 35 covered with glass. By the beginning of reduction, the S-state contained no hydrogen and no carbon (in either elementary or chemically bonded form) and was completely oxidized by dry oxygen at 623 K. In the apparatus shown in Fig. 1, the catalyst was reduced and the steps of methanol synthesis were studied. In line with the requirements of accurate calorimetric measurements, the reference ampoule contained a weight of inert glass spheres of the heat capacity equal to that of the catalyst.

The procedures applied have made impossible any influence of grease and mercury vapors on the measurements. Before experiments, the portion of the instrument supplied with the metal taps, up to the taps 8 and 14, was degassed down to 10^{-7} hPa. For this aim, under vacuum, all glass tubes and details were multiply processed by an outer marginal discharge from a spark coil detector of 10–20 kV power and the metal taps were heated at about 423 K for about 25 h by using an outer wire electric heater. From time to time, such processing was repeated. It was stated that, in the apparatus thus treated, the vapors under study (including water and methanol) can be adsorbed at the walls only slightly and can be frozen completely for 30–40 min from the volume of the instrument into a cold trap. It was found that, after a prolonged contact with hydrogen, some details of the metal taps, such as copper or silver-covered inserts gain the capacity to decompose water with adsorption of hydroxyls and desorption of hydrogen. Such an effect was taken into account.

We considered that the apparatus was prepared for adsorption and calorimetric experiments if the following conditions were fulfilled. First, after degassing of the apparatus segment containing the metal taps down to 1×10^{-4} Pa, the leakage into this segment should be less than 0.1 Pa for 15 h. Second, the total amount of H_2O and CO_2 frozen for 1 h within the trap 27 cooled to 77 K and connected to any segment of the apparatus should be less than 0.05 μmol.

Each of the volumes of the apparatus was calibrated. The bulbs 23, 31, and 32 were calibrated with an accuracy of 0.1% through weighing them being empty and filled up with water. All other volumes were calibrated with an accuracy of 1%. It was taken into account that the volumes with mercury manometers included depend on the pressure of the gas occurring in them. Volumes containing a trap were calibrated with the trap at the room temperature and with the trap dipped into a cooler down to a fixed level. Rather small volumes between the taps 10, 11, and 13, between the taps 4 and 5, and the volume 29–30 bounded by the tap 15 were calibrated through computation by using their geometric sizes. The other volumes, with the exception of the volume 27–28 bounded by the tap 13, were calibrated by using dry helium, Boyle's law, the bulbs calibrated, and the big manometer 29.

The pressures were measured with the mercury manometers by using a cathetometer of an accuracy of 0.01 mm, with the thermocouple-gage tube 22 calibrated to an accuracy of 2–4% by using individual gases, and with an ionization-gage tube not presented in the scheme.

The volume 27–28 (below, the device for analyses) bounded by the tap 13 was intended to analyze quantitatively very small completely vaporizable amounts of H_2O, CO_2, and their mixtures and to analyze the CH_3OH, HCOH, and HCOOH vapors desorbed from the catalyst. For example, the procedure of (H_2O+CO_2) analysis was as follows: at first, the total $(H_2O + CO_2)$ pressure was measured with the small mercury manometer 28, then the trap 27 was cooled down to 198 K by the (alcohol + dry ice) mixture and the CO_2 pressure was measured as before. Using the data on the volume value and introducing the corrections on the trap temperature and the change in the mercury level at each pressure measurement, we computed the individual amounts of CO_2 and H_2O. To preclude water condensation at the walls, the analyzed water amount should be so small that its pressure would not exceed $(0.5–0.6)p_0$ (p_0 is the pressure of the saturated water vapor). The volume of the device for analyses was limited by the sensitivity specified and was 3.163 cm^3. To minimize the volume of the device and to achieve a rather high accuracy of the pressure measurements, the trap 27 was made from a capillary of diameter 1.5 mm and the manometer 28 had a diameter of about 4.5 mm. The calibration of the elements of this device was performed before their sealing all together and was based on weighing of the mercury amounts filling up the glass tubes and the tap connection. The volume between the taps 10, 11, and 13 was equal to about 20 cm^3. To analyze the amounts that were not so small, it was summed with the volume of 3.163 cm^3. The procedures applied to analyze the mixtures containing the CH_3OH, HCOH, and HCOOH vapors are described in detail in [33].

The device 25 with the Pt wire sealed was used for H_2, CO, CH_3OH, HCOH, and HCOOH combustion in an excess of oxygen. Heating of the Pt wire was performed with an electrical potential source. The combustion was a step of analyses of the products desorbed under vacuum from the catalyst and of H_2 and CO analyses in $(H_2 + CO_2)$ and $(H_2 + CO)$ mixtures.

The treatment of the sample up to the S-state is illustrated in Fig. 2 and is described in details in [2]. In short, the procedure was as follows. Under vacuum, the source sample was heated for a long time in a glass instrument with a trap cooled to 77 K, at stepwise increase of temperatures up to 723 K. Upon completion of H_2O and CO_2 desorption, the catalyst was oxidized with O_2 at 623 K and 13 hPa. Then, the catalyst was reduced very slowly at no more than 473 K and at a H_2 or CH_3OH low pressure of about 100 Pa. The reduction was continued up to a state, at which introduction of a $(CO_2 + H_2)$ mixture and H_2 into the degassed volume over the catalyst led to methanol formation and no H_2O formation, respectively. In the course of reduction, we controlled carefully the CO_2 and H_2O amounts desorbed. The state of the catalyst thus reduced is termed the R-state.

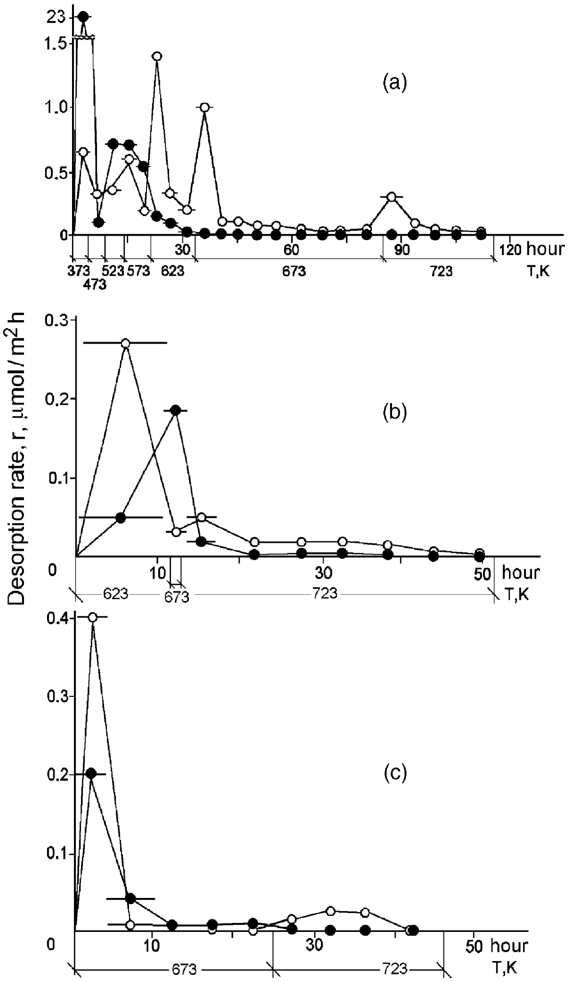

Fig. 2. Results of the thermal vacuum treatment of a source SNM-1 catalyst (a) and the same catalyst after transformation in the S-state and thermal treatment by hydrogen (b) or carbon monoxide (c). Light circles indicate the rate of CO_2 desorption; black circles indicate the rate of H_2O desorption.

The samples of gaseous mixtures and individual gases were prepared at desired pressures within the volume between the taps 5, 6, 7, 9, 10, and 14. Then, we connected this volume with the volume between the taps 4 and 5, turned off the tap 5 and turned on the tap 4 to the volume with the catalyst. The termination of the process in the ampoule 2 was fixed by the thermokinetic curve. Then, we degassed the volume between the taps 5, 6, 7, 9, 10, and 14, turned off the tap 4, turned on the tap 5 to the volume between the taps 5, 6, 7, 9, 10, and 14, and analyzed the gas in this volume. Thus, the volume between the taps 4 and 5 was used as a measuring volume to introduce gases into the volume with the catalyst and to sample the gas from this volume for an analysis. For the analyses, we used, as needed, the manometer 22, the bulb for combustion 25, and the device 27–28. The volume between the taps 11 and 12 was used as a measuring volume for the methanol vapor samples; it was suggested that, at the room temperature, the methanol pressure over liquid methanol saturated the volume of the tube 26. The volume between the taps 4 and 5 with the trap 21 cooled can be used for collection of vapors from the volume over the catalyst or for desorption from the catalyst surface. Besides, it can be used for collection of vapors from the volume between the taps 5, 6, 7, 9, 10, and 14 with subsequent isolation of the volume between the taps 4 and 5, heating of the trap 21 to the room temperature, and introduction of the vapor into the volume with the catalyst. The procedures are detailed in [12,26,31,33–35]. Below, our data of the greatest utility for understanding the mechanisms of the CH_3OH synthesis are collected together. They are used as an experimental basis for an attempt to clarify the mechanism of this process.

3. Experimental grounds

The steps of the process proceeding at the Cu–Zn–Al_2O_3 catalyst (CHM-1 [36]) reduced were studied by using calorimetric and adsorption–desorption techniques. One gram of the source catalyst before reduction contained CuO (7.2 mmol), ZnO (3.6 mmol), Al_2O_3 (0.5 mmol) (similarly to the ICI catalyst [37]) and some amount of graphite, water, and carbon dioxide. All experiments without exception were performed with no contact with the atmosphere to avoid any unregulated effect of oxygen and water vapor. The R-state was characterized by the following molar ratio of the elements: Cu:O_2:H_2:ZnO:Al_2O_3 = 1:0.125:0.25:0.5:0.07. The R-state had a surface area of 48 m^2/g and contained three principal components. The Cu-component with a surface area of about 30 m^2/g of the catalyst (surface S_1) had a composition approximated by the formula $Cu_4\cdot(OH_2)$ (termed copper hydrate [35]) and the adsorption properties inherent in copper (conceivable zinc in copper hydrate was not analyzed). The ZnO component with a surface area of about 5.2 m^2/g of the catalyst (surface S_2) had the composition ZnO unchanged principally during reduction and the adsorption properties inherent in zinc oxide (conceivable copper in zinc oxide was not analyzed). The surface area of about 13 m^2/g of the catalyst belongs to Al_2O_3 (surface S_3).

Notice that, when the catalyst was reduced only partially, i.e., the R-state was not achieved, H_2 or CH_3OH introduced into the volume over the catalyst gave only H_2O or CO_2 and H_2O, respectively, and neither gaseous H_2 or CO nor adsorbed HCOH, HCOOH, or CH_3OH were detectable. As was said above, during the previous treatment of the catalyst, the Cu-component was loosing oxygen (in the form of H_2O and (or) CO_2) and absorbing hydrogen into its body, whereas the ZnO- and Al_2O_3-components changed almost not at all. Our experiments allow us to believe that the R-state coincides or nearly coincides to the state of the catalyst under conditions of stationary methanol formation. These experiments are as follows.

At 293 K, methanol vapor was introduced up to 1.4 hPa into the volume over the catalyst; methanol was sorbed, terminal pressure was less than 0.01 Pa, heat of adsorption was equal to 79 kJ/mol [25] (measurements performed at the catalyst partially oxidized at 293 K give a value of 79 ± 10 kJ/mol [34]). Then we heated the calorimeter containing the ampoule with the catalyst up to 473 K. Over the catalyst, H_2, along with CO_2 and a small amount of water, was detected.

At 473 K, the catalyst was brought to equilibrium with H_2 and CO_2, the pressures of H_2 and CO_2 over the catalyst were equal to 0.26 and 0.1 hPa, respectively; then a gas mixture of CO (26.4 hPa) and H_2O (26.4 hPa) was introduced into the volume over the catalyst. From time to time, we analyzed the gas over the catalyst as described above. For the moments of each sampling of the gas mixture over the catalyst, we computed the partial pressures of CO, H_2O, CO_2, and H_2 and also the amount of each element (O, H, and C) in the gas phase. We took into account some decreases in the amounts of the gases over the catalyst as a result of each analysis. Reaction (I) proceeded steadily for several days with neither adsorption nor desorption of O, C, or H.

At 473 K, introduction of a $(CO_2 + H_2)$ mixture into the volume over the catalyst led to H_2O and CO formation. At 473 K, introduction of vapor of H_2O into the volume over the catalyst led to H_2 formation.

After introduction of CO_2 and H_2 into the volume with the catalyst, CH_3OH, HCOOH, and HCHO can be desorbed from the catalyst surface by heating to 473 K under vacuum. Under such conditions, CH_3OH is desorbed completely, while HCOOH and HCHO are desorbed only partially. Catalyst treatment with O_2 at 473 K leads to complete removal of HCOOH and HCHO in the form of CO_2 and H_2O. These experiments and the procedures of CH_3OH, HCOOH, and HCHO identification are considered in [33], where the full procedure of analyzing, including analysis of the gaseous and adsorbed products is detailed. Paper [33] is available in English in the British Library Board. The procedure consisted of a long series of operations and cannot be described here in detail. It includes fractionation of the desorbed products by using the differences in their vapor pressures at some temperatures and a subsequent analysis of the fractions. For the analyses, the bulb 25 with the Pt wire for combustion in an excess of oxygen, the device 27–28 for analyses of CO_2 and H_2O, the thermocouple manometer 22, and the Pd powder for absorption analyses of H_2 were used (see Fig. 1). Methanol was determined quantitatively by fractionation with the subsequent combustion at the Pt wire and analyzing of CO_2 and H_2O. As an indicator of the presence of formaldehyde, the effect of reddening of the H_2SO_4-solution of chromotropic acid (1,8-dioxynaphthalene-3,6-disulfoacid) was applied. The last reaction allows detection of 10 μg of CH_2O. Quantitative analyses of CH_2O were performed by its collection in trap 21 at 77 K, heating of the trap to 195 K, collection of the evaporated gas, and its combustion at the Pt wire in an excess of O_2 with a subsequent analysis of CO_2 and H_2O. Formic acid was detected qualitatively on the basis of the methyl-red indicator with sensitivity of 2–3 μmol or on the basis of the vapor pressure measurements. All analyses were performed in the vacuum apparatus under pressures so low that diffusion of gases within the apparatus tubes could not influence the results of the analyses. The adsorbed and desorbed elements were balanced rather well.

Some available results confirm indirectly that the state of the Cu–Zn-containing catalysts in the course of industrial production of methanol is close to the R-state realized in our experiments. According to [4,38], the water mass liberated during low-temperature reduction of the SNM-1 catalyst by a gaseous mixture of N_2 (99%) and H_2 (1%) in an industrial apparatus is equal to 17.4% of the mass of source catalysts. In our experiments, in the course of pretreatment of the source catalyst up to the R-state, the water amount collected was equal to 18.1% of the mass of the catalyst source sample. It is seen that the water production in these two cases is nearly the same.

As was mentioned, the R-state of the catalyst contains three surface areas of different chemical nature. Reactions (II) and (I) proceed at S_2 and S_1, respectively (possibly, reaction (I) proceeds partially at S_3).

To illustrate these conclusions, we will describe several most principal experiments (we express the amounts of reactants in μmol/g of the catalyst; the sensitivity of our analyses is about 0.11 μmol/g). All experiments were performed when the ampoule with the catalyst was within the calorimeter functioning at a chosen constant temperature and was connected with the vacuum instrument (Fig. 1). In these experiments, we performed adsorption at low temperatures to increase adsorption and performed desorption of the surface products not only at low temperatures but also at 473 K to shift the equilibrium to desorption. The returning of the thermokinetic curve of the calorimeter recorder to the baseline identified the moment of termination of the processes under study.

(i) This set of experiments shows that CO_2 adsorption at the surface saturated with H_2 initiates additional H_2 adsorption with no H_2 addition into the space over the catalyst and with no desorption of H-containing products. As an example, the experiments 1.1–1.9 are given in Table 1. The catalyst surface was saturated with H_2 up to equilibrium indicated by the thermokinetic curve; at a pressure of 2.0 hPa, 12 μmol of H_2/g of the catalyst were adsorbed. The CO_2 intake into the volume over the catalyst and subsequent CO_2 adsorption led to an additional H_2 adsorption up to 18 μmol/g at a H_2 pressure of 1.0 hPa. Table 1 contains the full protocol of this experiment. Notice that the trap for cooling of the products is shown in Fig. 1 (position 21).

Analogous experiments were performed at initial temperatures of 323, 303, and 298 K. They showed that H_2 and CO_2 can be adsorbed at all temperatures, CO_2 adsorption and surface CH_3OH formation being decreased with decreasing temperature. The quantities of methanol observed at 353, 323, 303, and 298 K are related as 7.6:3.1:1.2:1. Apparently, at low temperatures, the rate of the H_2 and CO_2 interaction in the adsorbed state is depressed.

For the subsequent discussion, we note that, during the experiments, neither CO nor H_2O were identified in gaseous and desorbed products.

(ii) This set of experiments shows that H_2 adsorption at the surface saturated with CO_2 at a residual CO_2 pressure initiates an additional CO_2 adsorption with no CO_2 addition into the volume over the catalyst and with no desorption of C-containing products. As an example, the experiments 2.1–2.13 are given in Table 1. At 353 K, the catalyst surface was saturated with CO_2 up to the equilibrium state indicated by the thermokinetic curve; at a pressure of 5.2 hPa,

Table 1

Interaction of the catalyst (R-state, 0.73 g) with H_2 in the experiments following CO_2 or CO preadsorption and with CO_2 in the experiments following H_2 preadsorption (the lines corresponding to the moments of beginning of preadsorption and H_2 or CO_2 intake into the adsorption ampoule after preadsorption are in italics)

Experiment and line numbers	Operation	Time interval after intake of the gas preadsorbed (h)	Temperature (K)	Pressure and adsorbed amounts				Gases desorbed[a]		
				H_2		CO_2 (or CO)		In gas phase, H_2 (μmol/g)	In trap cooled	
				Pressure at the moment indicated in column 2 (hPa)	Amount of the gas adsorbed at the catalyst (μmol/g)	Pressure at the moment indicated in column 2 (hPa)	Amount of the gas adsorbed at the catalyst (μmol/g)		CO_2 (μmol/g)	CH_3OH (μmol/g)
1.1	*H_2 intake*	*0*	*353*	*4.5*	*0.0*	*0.0*	*0.0*			
1.2		0.6	353	2.8	12	0.0	0.0			
1.3	*CO_2 intake*	*48.0*	*353*	*Not measured*		*7.9*	*0.0*			
1.4		52.5	353	1.0	18	4.4	23			
1.5		53.5	353	The trap cooled to 77 K is connected to the volume with the catalyst						
1.6		55.0	353	0.02	13	0.0	22	2.9	0.5	1.0
1.7		59.0		Beginning of heating without trap						
1.8		80.5	473	The trap cooled to 77 K is connected to the volume with the catalyst						
1.9		82.8	473	0.03	0.0	0.0	−0.6[b]	0.2	16	6.6
2.1	*CO_2 intake*	*0*	*353*	*0.0*	*0.0*	*7.9*	*0.0*			
2.2		0.8	353	0.0	0.0	5.2	14			
2.3	*H_2 intake*	*1.8*	*353*	*3.3*	*0.0*	*Not measured*				
2.4		5.3	353	0.8	16	3.6	20			
2.5		6.0	353	The trap cooled to 77 K is connected to the volume with the catalyst						
2.6		6.4	353	0.1	14	0.0	17	1.2	2.3	0.6
2.7		24.8	353	The trap cooled to 77 K is connected to the volume with the catalyst						
2.8		26.0	353	0.02	12	0.0	13	0.6	2.7	0.8
2.9		26.0		Beginning of heating without trap						
2.10		46.5	473	0.7	8.0	1.2	7.0	3.8[c]	6.0[c]	
2.11		49.5	473	The trap cooled to 77 K is connected to the volume with the catalyst						
2.12		52.2	473	0.5	−0.8	0.0	2.6	0.0	0.0	4.4
2.13[d]		78.4	473	0.0	−3.3	0.0	0.1			
3.1	*CO intake*	*0*	*353*	*0.0*	*0.0*	*11.0*	*0.0*			
3.2		1.0	353	0.0	0.0	9.3	33			
3.3	*H_2 intake*	*24*	*353*	*3.7*	*0.0*	*Not measured*				
3.4		28.7	353	2.3	9.2	9.3	33			
3.5		29.5	353	The trap cooled to 77 K is connected to the volume with the catalyst						
3.6		30.0	353	Not measured		0.0	3.0		0.5	0.0
3.7		30.2	353	Beginning of heating without trap						
3.8		49.0	473	The trap cooled to 77 K is connected to the volume with the catalyst						
3.9		50.0	473	Not measured		0.0	−1.3		3.1	1.2
4.1	*CO_2 intake*	*0*	*353*	*0.0*	*0.0*	*6.6*	*0.0*			
4.2		1.0	353	0.0	0.0	4.8	12			
4.3	*H_2 intake*	*3.0*	*353*	*2.4*	*0.0*	*Not measured*				
4.4		3.2	353	1.6	6.0	4.8	12			
4.5		3.2	353	The trap cooled to 77 K is connected to the volume with the catalyst						
4.6		3.4	353	Not measured		0.0	12		0.0	0.0
4.7		4.0	353	Beginning of heating without trap						
4.8		25.0	473	The trap cooled to 77 K is connected to the volume with the catalyst						
4.9		26.7	473	Not measured		0.0	0.8		9.7	2.0
4.10[e]		29.0	473	Not measured		0.0	−0.5			

[a] In experiments 1, 3, and 4, H_2CO in the CO_2 fraction was not controlled; in experiment 4, H_2CO was detected qualitatively.

[b] Negative values hereafter mean unbalance between adsorbed and desorbed carbon in the experiment; it can be caused by errors in analyses and by occurrence of carbon at the surface before the experiment.

[c] This gas was desorbed during heating without the trap cooled.

[d] The changes in columns 6 and 8 are caused by oxidation of the catalyst surface after step 2.12 by O_2 (6 μmol/g) at 473 K and desorption of 2.5 μmol/g of CO_2 and 2.5 μmol/g of H_2O in the cooled trap; the ratio $CO_2/H_2O = 1/1$ could be caused by oxidation of surface H_2CO or H_2COO.

[e] The changes in column 8 is caused by oxidation of the catalyst surface after step 4.9 by O_2 (6 μmol/g) at 473 K and desorption of 1.3 μmol/g of CO_2 in the cooled trap (H_2O was not controlled).

14 μmol of CO_2/g of the catalyst were adsorbed. The H_2 intake into the volume over the catalyst and subsequent H_2 adsorption led to an additional CO_2 adsorption up to 20 μmol/g at a H_2 pressure of 3.6 hPa. Table 1 contains the full protocol of this experiment.

During this experiment, likely to the above-described one, neither CO nor H_2O were identified in gaseous and desorbed products. To oxidize the surface products not capable to be desorbed at 473 K, we treated the catalyst with a portion of O_2, 6 μmol/g. During this treatment, the trap cooled to 77 K was connected to the catalyst. It was found that H_2O and CO_2 only were resulted from such a treatment and each of them comprised 2.5 μmol/g. Notice that in another similar experiment, such a finishing treatment of the catalyst by O_2 at 473 K resulted in formation of 2.0 μmol/g of H_2O and 2.0 μmol/g of CO_2. Thus, in two experiments, the H/C ratio was equal to 2.0 for a surface substance not desorbed but oxidized by oxygen and desorbed in the form of H_2O and CO_2 at 473 K. These two results gave us grounds to assume that the surface contained HCOH and (or) HCOOH adsorbed.

Analogous experiments were performed at initial temperatures of 323, 303, and 298 K. They confirmed that CO_2 and H_2 are adsorbed at all temperatures, H_2 adsorption increased CO_2 adsorption; the lower temperature, the slower additional adsorption of CO_2 after introduction of H_2 into the volume over the catalyst. Analogously to the experiments described in (i), at low temperatures, the rate of the H_2 and CO_2 interaction in the adsorbed state is depressed.

(iii) Experiments 3.1–3.9 (Table 1) show that CO_2 is the principal immediate source for the CH_3OH formation. The experiment was similar to the preceding one, but CO was used instead of CO_2. Hydrogen adsorption did not initiate additional adsorption of CO. No CH_3OH and only 0.5 μmol/g of CO_2 was desorbed at 353 K. After heating of the catalyst up to 473 K and its connection to the trap cooled to 77 K, only 1.2 μmol of CH_3OH and 3.1 μmol of CO_2/g of the catalyst were obtained. Computations show that, after this refreshment of the catalyst, the surface contains no carbon. Thus, the methanol amount formed in this experiment was less than that formed in the experiments 1.1–1.9 and 2.1–2.13 (Table 1) by factors of 6.3 and 4.8, respectively. Apparently, the small CH_3OH quantity observed in the experiments 3.1–3.9 could be produced from CO_2 obtained through oxidation of CO.

(iv) This experiment was performed at 353 K to clarify the question on the rate-determining step (RDS) of the process. In this experiment, unlike experiments 2.1–2.13 (Table 1), the period of contacting of the $(CO_2 + H_2)$ mixture with the catalyst was very short, 12 min only. Carbon dioxide was introduced into the empty volume over the catalyst. Once the equilibrium was achieved, H_2 was added into the volume over the catalyst. For 12 min, i.e., by the moment of degassing, the CO_2 content at the catalyst surface and the CO_2 pressure did not change. At 353 K, no methanol was desorbed from the catalyst. The amount of CH_3OH desorbed at 473 K was as small as 2.0 μmol/g (in the experiments 2.1–2.13 (Table 1), the CH_3OH amount desorbed was 11 μmol/g, including 5 μmol/g at 353 K and 6 μmol/g at 473 K). The precedent experiments showed that the H_2-catalyst equilibrium was established for 1–2 min; thus, a period of 12 min, in the course of which H_2 was in the gas phase, is quite sufficient for its adsorption. Nevertheless, the amount of CH_3OH produced in this experiment was considerably less than that produced in experiments 2.1–2.13. This result allows us to suggest that the methanol formation is controlled by a step of surface interaction of adsorbed molecules with gaseous molecules.

(v) This set of experiments shows (along with other experiments) that CO_2 is adsorbed at a small portion of the total surface area measured through low-temperature adsorption of Kr and that CO and CO_2 are adsorbed at different surfaces of the catalyst. At 323 K, the adsorption saturation of the surface was observed at a CO_2 pressure of 108 hPa, when 37 μmol/g were adsorbed. This amount is lower than the V_m value measured through Kr adsorption at 77 K by a factor of more than 10. Furthermore, we compared the results of two experiments performed at 303 K at the same catalyst. In one of the experiments, adsorption of CO terminated when the surface contained

> 13 μmol/g and the residual CO pressure was equal to 0.3 hPa. In the other, CO_2 (17 μmol/g) was preadsorbed and then CO (12 μmol/g) was adsorbed at a residual CO pressure of 0.12 hPa. In the case of CO and CO_2 adsorption at the same surface, one would expect a significant decrease in CO adsorption after CO_2 preadsorption. However, CO_2 preadsorption did not decrease adsorption of CO. The following results also count in favor of the conclusion that CO, on the one hand, and CO_2 and H_2, on the other hand, are adsorbed at different surfaces of the catalyst. According to our measurements performed at the R-state of the catalyst, CO_2 and H_2 preadsorbed have little or no effect on the differential heat of CO adsorption. The heat of CO adsorption at the pure surface (303 and 353 K), at the surface containing CO_2 (17 μmol/g) (303 K) or H_2 (303 K) is equal to 66 ± 4 kJ/mol. Moreover, the presence of gaseous H_2 (in different experiments, from 0.1 to 2.7 hPa) over the surface saturated with H_2 changes only slightly this value of the heat of CO adsorption.

To formulate the mechanism of the process under consideration and to estimate tentatively the constants in its kinetic equation, the following information on adsorption of individual components of the reacting gas mixture at the R-state of the catalyst is also of great importance.

At the R-state of the catalyst, the differential heats of hydrogen, carbon dioxide, methanol, carbon monoxide, and oxygen adsorption are equal to 43.8 ± 3.3 kJ/mol (298 and 303 K), 59 ± 2 kJ/mol (298–323 K), 79 kJ/mol (293 K), 65.8 ± 4.3 kJ/mol (303 and 353 K), and 485 ± 9.8 kJ/mol (293, 353, and 473 K), respectively. Catalyst treatment by small O_2 pulses at 473 K and subsequent degassing at the same temperature increased the heat of H_2 adsorption up to 49.8 ± 0.6 kJ/mol (293, 323, and 353 K). The heat of CO_2 adsorption given above was measured without preliminary degassing of the catalyst. The heat of CO_2 adsorption thus measured increased with increasing temperature up to 79 ± 1 kJ/mol (353 and 473 K). The preliminary degassing of the catalyst at 473 K led to a decrease in the heat of CO_2 adsorption down to 68–69 kJ/mol (353 K). Preadsorption of H_2 or CO_2 does not influence the heat of CO adsorption. Adsorbed H_2, CO_2, and CH_3OH are desorbed under vacuum at 298–323 K only partially and at 473 K completely.

The following experimental results taken together give grounds to think that water adsorption does not occur at the ZnO-surface catalyzing the methanol synthesis. First, at 473 K, the catalyst does not adsorb water but decomposes it to gaseous H_2 and oxygen adsorbed. Second, at 473 K, the catalyst adsorbs water neither from the $(H_2O + CO)$ mixture nor from the mixture produced as a result of contacting of the catalyst with the $(H_2 + CO_2)$ mixture. Third, the products desorbed under vacuum at 473 K from the catalyst after its contacting at 353 K with the $(H_2 + CO_2)$ or $(H_2O + CO)$ mixtures contained no water.

4. Theoretical grounds

In 1930s, Hinshelwood [39] and Schwab [40] had proposed that, during reactions proceeding in the presence of solid catalysts under conditions when diffusion does not influences the process, equilibrium is achieved in all but one of the elementary reaction steps. The non-equilibrium step was termed the rate-determining or limiting step. The limiting-step rate is described on the basis of the law of mass action. At first, these authors had believed that the adsorption–desorption steps are equilibrium and a step of surface interaction is nonequilibrium. At present, the opinion on the occurrence of RDSs in heterogeneous catalytic processes is widely distributed [41]. In [42], we showed that the notion on an adsorption step as the limiting one could be successfully used to describe the kinetics of a rather extended series of reactions proceeding under conditions of a near-complete surface coverage with one of source substances.

In this work, we use the notion of RDSs in its earlier form, namely, we suggest, based on the above-described experiments, that the rate of the process is limited by a step of surface interaction rather than by adsorption of one of the source substances at free surface centers. As is evident from the further consideration, a modification of this notion lies in our suggestion that the reaction proceeds by two routes, each of them being characterized by its own limiting step.

Notice an important peculiarity of the catalytic reactions proceeding with a limiting step. In the light of the notion of limiting steps, the difference between the product of the limiting-step equation by its stoichiometric number (SN) and the total stoichiometric equation of the corresponding reaction is the equation of equilibrium. It is not necessary for this equation to contain the entire set of the intermediates occupying centers at the surface and thus influencing the reaction rate. Suppose that several simple stoichiometric equations containing the source substances, products of the reaction, and the entire set of the actual surface intermediates are written in such a form that their sum is adequate to the above-mentioned difference equation of equilibrium. The product of the equilibrium constants of these simple equations should be equal to the equilibrium constant of the difference equation regardless of the form of each individual equation. In other words, the mode of expression of the chemical connections between the reactants, i.e., the form of the simple stoichiometric equations, is of no importance. The form of the difference equation only is of fundamental importance. This statement leads us to the conclusion that identification of the chemical nature of the limiting step and of the entire set of the surface intermediates is a necessary and sufficient condition for clarification of the mechanisms and kinetic equation for the catalytic reaction. Below, we use the methanol synthesis to illustrate this conclusion.

It goes without saying that reacting mixtures may include some substances (such as catalytic poisons, etc.) not participating in the chemical reaction but being in equilibrium with the catalyst surface. Such substances occupy a portion of the surface and thus influence the rate of the process. They do not influence the mechanisms of the process as such, but influence the form of its kinetic equation.

5. Reaction mechanism and discussion

Based on the adsorption properties of the Cu–Zn-containing catalysts, the conclusion relative to the limiting step, and the intermediates specified at the catalyst surface, we suggest that methanol is produced essentially at the ZnO-component according to the following mechanisms:

$$\mathrm{CO_2 + Z \equiv ZCO_2}, \quad \begin{cases} \mathrm{N(1)} = 0 \\ \mathrm{N(2)} = 2 \end{cases} \tag{1}$$

$$\mathrm{H_2 + Z \equiv ZH_2}, \quad \begin{cases} \mathrm{N(1)} = 2 \\ \mathrm{N(2)} = 0 \end{cases} \tag{2}$$

$$\mathrm{ZCO_2 + H_2 \leftrightarrow ZCO_2H_2}, \quad \begin{cases} \mathrm{N(1)} = 0 \\ \mathrm{N(2)} = 2 \end{cases} \tag{3}$$

$$\mathrm{ZH_2 + CO_2 \leftrightarrow ZCO_2H_2}, \quad \begin{cases} \mathrm{N(1)} = 2 \\ \mathrm{N(2)} = 0 \end{cases} \tag{4}$$

$$\mathrm{ZCO_2H_2 + Z \equiv ZO + ZCOH_2}, \quad \begin{cases} \mathrm{N(1)} = 2 \\ \mathrm{N(2)} = 2 \end{cases} \tag{5}$$

$$\mathrm{ZCOH_2 + H_2 \equiv CH_3OH + Z}, \quad \begin{cases} \mathrm{N(1)} = 2 \\ \mathrm{N(2)} = 2 \end{cases} \tag{6}$$

$$\begin{aligned}&\mathrm{CH_3OH + 2ZO}\\ &\quad \mathrm{\equiv H_2 + H_2O + CO_2 + 2Z}, \quad \begin{cases} \mathrm{N(1)} = 1 \\ \mathrm{N(2)} = 1 \end{cases}\end{aligned} \tag{7}$$

Here, Z is the adsorption center at the surface S_2, the symbol (≡) means that the step is equilibrium; the symbol (↔) means that the step is reversible only partially, i.e., it is not equilibrium, the steps marked with such a symbol are the rate-determining ones for each of the routes N(1) and N(2). The right columns contain the values of the SNs *n* for each of the steps of the methanol synthesis proceeding by these routes. To receive the total stoichiometric equation for the process of the methanol synthesis proceeding according to each of the routes, it is necessary to multiply the equation of each of the steps by its SN and to summarize the equations thus obtained. Possibly, under some conditions when the methanol vapor pressure is rather high and the temperature is low, CH_3OH occupies a significant portion of the surface. Under such conditions, the mechanisms (1)–(7) should be supplemented with the following step:

$$\mathrm{CH_3OH + Z \equiv ZCH_3OH} \tag{8}$$

with the SN equal to zero for each of the routes.

The experiments (i) and (ii) show that the process proceeds by two routes (N(1) and N(2)): through surface interaction of H_2 or CO_2 adsorbed with H_2 or CO_2 gas, respectively. We said that formation of the surface intermediates proceeds slowly as compared with the adsorption–desorption of H_2, CO_2, and CH_3OH and with the step of CH_3OH oxidation by surface oxygen.

A correlation between the results of the experiments (i)–(iii) gives grounds to suggest that the limiting steps in the routes N(1) or N(2) are the surface interactions of H_2 or CO_2, respectively. This means that the steps (3) and (4), resulting in ZCO_2H_2 or the step (5) resulting in $ZCOH_2$ limit the rate of the reaction. Thus, the oxidative number of the carbon atoms occurring at the surface S_2 changes from 4 (in ZCO_2) and 2 (in ZHCOOH) to 0 (in ZCH_2O); in CH_3OH molecules, the oxidative number of the C atoms is equal to -2. Taking into account that the C atoms with the oxidative number equal to $+4$ are usually characterized by a very low reactivity, we suppose that the limiting step is the transformation of molecules of gaseous CO_2 or adsorbed ZCO_2 containing C (+4) into C (+2). Thus, we take that the rate of this process is limited by formation of ZCO_2H_2. This important conclusion was previously presented in [25].[1] According to [25], at low temperatures, CH_3OH is produced almost not at all as a result of the reaction of adsorbed carbon dioxide with adsorbed hydrogen in the absence of gaseous H_2; however, the surface intermediates ZCO_2H_2 and $ZCOH_2$ are produced. When the temperature exceeds the room one only slightly, CH_3OH and H_2O adsorption is observed; however, at 473 K, water vapor decomposes with desorption of H_2, while CH_3OH vapor decomposes with desorption of H_2O, CO_2, and CO. As was said above, the analyses of the intermediates adsorbed at the surface of the ZnO-component after its contact with CO_2 and H_2 showed the occurrence of H_2, CO_2, HCOH, HCOOH, and CH_3OH; therewith, H_2, CO_2, and CH_3OH can be desorbed completely at 473 K. Possibly, CH_3OH occupies a significant portion of the surface under some conditions when the methanol vapor pressure is rather high and the temperature is low. Additionally, it is obvious that the ZnO surface is capable to contain oxygen adsorbed. All these conclusions are realized in the scheme of the mechanism.

The equilibrium (7) does not mean that CH_3OH is the only reducer cleaning the surface of the excessive oxygen. Indeed, the equilibrium (7) is the sum of the following equilibriums:

$$ZO + H_2 \equiv H_2O + Z \qquad (7)'$$

$$ZO + CH_3OH \equiv 2H_2 + CO_2 + Z \qquad (7)''$$

We do not use the sum $(7)' + (7)''$, since it is redundant for deduction of the kinetic equation. It is possible to abandon the equilibrium (7) and to substitute one of the following two equations:

$$ZCO_2H_2 + ZO \equiv 2Z + CO_2 + H_2O \qquad (7)'''$$

$$ZCOH_2 + 2ZO \equiv 3Z + CO_2 + H_2O \qquad (7)''''$$

Each of them should have an SN 1 for each of the routes. With $(7)'''$ instead of (7), the SNs should be as follows: for the route N(1), $n = 2$ for the steps (1) and (3), $n = 0$ for the steps (2) and (4), and $n = 1$ for the steps (5) and (6) and for the route N(2), $n = 2$ for the steps (2) and (4), $n = 0$ for the steps (1) and (3), and $n = 1$ for the steps (5) and (6). With $(7)''''$ instead of (7), the SNs should be as follows: for the route N(1), $n = 2$ for the steps (1), (3) and (5), $n = 0$ for the steps (2) and (4), and $n = 1$ for the step (6) and for the route N(2), $n = 2$ for the steps (2), (4), and (5), $n = 0$ for the steps (1) and (3), and $n = 1$ for the step (6).

The above-presented alternative forms of the mechanism (1)–(7) change neither the fundamental content of the mechanism nor the appearance of the kinetic equation capable to be deduced from them. Therefore, all these alternative forms reveal the same mechanism.

The SN of the limiting step is taken to be 2. The SN is a kinetic characteristic of catalytic processes, and it escapes determination through an analysis of steps of the process. The SN equal to 2 results from a correlation between the kinetic equation deduced from the proposed mechanism and the available kinetic data obtained under steady state conditions.

Notice that methanol, of course, could not be produced stationary by the step (7) in the direction from right to left. Indeed, this step produces ZO. Thus, the synthesis should terminate as soon as the surface is oxidized.

Terminating the presentation of the mechanism, we list its fundamental features. The methanol as such is produced predominantly from carbon dioxide and hydrogen at the ZnO-component of the catalyst. In the course of this process, carbon dioxide is produced predominantly at the Cu-component maintained in a form close in chemical composition to copper hydrate $Cu_4{\cdot}OH_2$; the relation between the gaseous components involved in the shift-reaction (I) is close to the equilibrium. The methanol synthesis proceeds

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[1] In [25], there are misprints: the steps (5)–(7) should be written as follows: (5) $ZH_2CO_2 + Z \equiv ZO + ZH_2CO$; (6) $ZH_2CO + H_2 \equiv CH_3OH + Z$; and (7) $ZCH_3OH \equiv Z + CH_3OH$ [27].

by two routes characterized by the limiting steps $ZCO_2+H_2 \leftrightarrow ZCO_2H_2$ and $ZH_2+CO_2 \leftrightarrow ZCO_2H_2$; the SNs of the limiting steps are equal to 2. The surface intermediates are as follows: Z, ZH_2, ZCO_2, ZCO_2H_2, $ZCOH_2$, ZO, and, possibly, under unusual conditions, ZCH_3OH (the chemical composition of Z is discussed below).

Notice that our notions on the capacity of reduced ZnO to adsorb CO_2 and H_2 and on its incapacity to adsorb CO correspond to the results of [43,44], respectively.

According to our mechanism, the S_2 surface adsorbs no water in the course of the steady-state methanol synthesis. The following results led us to such a conclusion. First, the catalyst reduced to the R-state at 473 K decomposes water vapor with desorption of H_2 but not adsorbs water. Second, no water can be detected at the catalyst surface after its contact with either $(H_2O + CO)$ or $(H_2 + CO_2)$ mixtures. Third, after introduction of $(H_2O + CO)$ and $(H_2 + CO_2)$ mixtures, together or apart, into the volume over the catalyst at 353 K, subsequent heating of the catalyst to 473 K, and desorption of the products into the trap cooled to 77 K, the products desorbed never contained water. It is important that the composition of the surface layer in the course of these experiments did not change. Namely, the H, O, and C amounts in the composition of the H_2O, CO, H_2, and CO_2 introduced into the volume over the catalyst were equal to the amounts of these elements in the resulted composition of these substances. Notice that works [23,29] contain no mention on significant water adsorption at the ZnO-component. The decomposition of water with desorption of hydrogen and oxidation of the catalyst by oxygen of water was observed in [3,25,45]. However, according to our conclusion, the surface S_1, at which the methanol synthesis does not proceed, is subject to oxidation. On our opinion, this process removes the catalyst from its stationary state and decreases the rate of the CO_2 synthesis from CO at the surface S_1. According to [46], water impulses decrease the rate of oxygen transport from CO to CH_3OH. The rate regression proceeds very slowly (likely to reduction of the catalyst to the R-state in our experiments). Thus, an impression may be formed that water retards the CH_3OH synthesis. Nevertheless, this effect does not mean that water is the key component for the mechanism of the methanol synthesis at the S_2 surface.

On the basis of the mechanism (1)–(7), the data [47,48] relating to the H–D exchange between H_2O molecules and CH_3-groups in the course of the methanol synthesis can be easily understood. In [47], the period of contacting of the reacting gas mixture with the catalyst was very short, about 0.03 s only, and no H–D exchange was observed, since the CH_3OH decomposition and H_2 production from H_2O were insignificant. In [48], the period of contacting was about 1 s, the shift-reaction (I) proceeded up to the equilibrium and therefore the H–D exchange was observed.

We noted above that our mechanism shares some of traits with the mechanism [6,7]:

$$ZH_2O + CO_2 = ZH_2OCO_2 \tag{9}$$

$$ZH_2OCO_2 = ZCO_2 + H_2O \tag{10}$$

$$ZCO_2 + H_2 \leftrightarrow ZH_2CO_2 \tag{11}$$

$$ZH_2CO_2 + 2H_2 = ZH_2O + CH_3OH \tag{12}$$

Namely, the mechanisms (1)–(7) and (9)–(12) include CO_2 as a source of methanol and the interaction of adsorbed carbon dioxide with gaseous hydrogen as a slow step of the synthesis. Nevertheless, these two mechanisms diverge principally. In contrast to the mechanism (1)–(7), the mechanism (9)–(11) does not fall in the category of the Schwab–Hinshelwood mechanisms with a limiting step: the step (11) is slow and the steps (9)–(12) are fast but not equilibrium. In contrast to our views, authors of the mechanism (9)–(12) consider water as a key surface intermediate, ignore surface coverage with H_2 and HCOH, and also ignore the reversibility of CO_2 adsorption.

In [6,7], conclusions on adsorption of H_2O and other proposed intermediates are based on [49,50] performed with the SNM-1 catalyst. In these works, for clearing the catalyst of CO_2 and H_2O sorbed in the course of preparation, the sample of the catalyst was heated for 2 h in an air flow of 7.2 l/h at 623 K, cooled to 523 K, and degassed for 1 h to 0.01 Pa. After clearing, the catalyst was reduced for 20 min at 523 K in a flow of He–CO or He–H_2 mixtures containing 20% of the reducing gas. The sample thus reduced was cooled to the room temperature and degassed for 15 min. Then, the authors of [49,50] carried out adsorption of CO, CO_2, H_2O, or CH_3ON at this sample, performed experiments on thermal desorption, and, based on these experiments, made their conclusions relative to “strong” and “weak” adsorption and amounts of adsorbed substances.

To test the degree of correctness of the conclusions from [49,50] and [6,7], we correlated these results with the results of Fig. 2 and of [38]. Fig. 2 contains the results of a thermal vacuum treatment of three samples (“a” is a sample of the source SNM-1 catalyst, “b” and “c” are samples of the same catalyst taken after their processing up to the S-state and after experiments on their interaction with H_2 and CO. This vacuum treatment of the samples was performed to remove entirely water and carbon from the catalyst bodies. For this aim, a sample in a thermostatically controlled degassed ampoule was connected for a time to a trap cooled to 77 K; then the trap was isolated from the catalyst and heated to the room temperature. The amounts of water and carbon dioxide desorbed from the sample were analyzed. After decreasing the rate of desorption at the initial temperature, the ampoule with the sample was heated and the experiment was continued.

The procedure of the processing was as follows. The source sample was originally degassed at 298 K for about 1 h down to a pressure of around 0.1 Pa. To minimize the evolution of oxygen, the subsequent thermal treatment was performed with no degassing. The thermal treatment was performed in the following regime: 4 h at 373 K, 4.5 h at 473 K, 5 h at 523 K, 7 h at 573 K, 12 h at 623 K, 45 h at 673 K, and 30 h at 723 K. In Fig. 2, along the horizontal axis, the duration (h) of the vacuum treatment is plotted and the temperatures (K) of the vacuum heating of the catalyst is indicated; along the vertical axis, the rates of the CO_2 and H_2O vacuum desorption averaged over the period of each measurement are plotted. The rates are expressed in $\mu mol/m^2$ h; they are related to the surface area of the sample and averaged over each period of the isothermal heating. The time intervals of averaging of the rates of desorption are indicated by the horizontal bars passing through the experimental points. In the curves of Fig. 1a, each of the points, except for the left-most ones, results from heating of the catalyst at a constant temperature. The left-most points in the curves show the average rates of desorption during an exposure interval of 4 h at 373 K and at 473 K. In Fig. 1a, for the points obtained after the 30 h treatment of the catalyst, the intervals of averaging are not identified, since they were nearly the same, namely, 5–6 h. The procedures used for Figs. 1b and c were similar to the above-described ones, but each point results from isothermal desorption; other peculiarities of the procedure are seen from the figures.

The results of Fig. 2 show that the catalyst treatment performed in [49,50] (2 h at 623 K) is completely inadequate for total freeing the catalyst from water and carbon dioxide. Indeed, even long-term heating at 673 K cleans the catalyst of carbon only partially. For total freeing the catalyst from carbon (in the form of CO_2), it is necessary to heat it for several hours at 723 K. For freeing the catalyst from water, it is necessary to heat it for many hours at 673 K (samples “b” and “c”) or for many tens of hours at a lower temperature, including 6 h at 623 K (sample “a”).

It is well known that in the course of reduction of the Cu–Zn-containing catalysts, it is necessary to follow carefully the technological procedure and to take special steps against sintering of the catalyst [4]. In industrial apparatuses, this catalyst is reduced by a H_2–He mixture containing 0.2–1% of H_2 for no less than 120 h at a temperature rising by 1°/h [4,38]. According to our results [35,45], to obtain $Cu_4{\cdot}OH_2$ with a high specific surface area, the reduction should proceed very slowly, for several hundreds of hours; the reduction rate is limited by the rate of diffusion in the solid body.

Apparently, under conditions of reduction in [49,50] (in a H_2(20%)–He reducing mixture, 20 min at 523 K), the catalyst was reduced and freed from water not completely. Moreover, as was noted above, the catalyst most likely was not cleaned from the carbon introduced in the course of production. Therefore, during the experiments on thermal desorption, freeing the samples of the surface water and carbon dioxide was accompanied by side processes of residual carbonate destruction, copper oxide reduction, and H_2O and CO_2 diffusion from the catalyst body to the surface with their unregulated desorption. Moreover, the catalyst reduced in [49,50] by a gas containing 20% of H_2 might be sintered significantly (see the preceding paragraph).

The above-presented consideration shows that it is unlikely that the properties of the samples in [49,50] were close to the properties of the actual catalysts functioning in the course of the steady-state process of methanol production. Therefore, the mechanism (9)–(12) proposed in [6,7] on the basis of [49,50] is open to question. As was indicated earlier, our data, in contrast to this mechanism, do not confirm the key role of water adsorption in the mechanism of methanol production.

Now, we consider briefly one more question relating to the mechanism of this reaction and to the general understanding of the heterogeneous catalysis as a natural phenomenon. It is well known that any surface is structurally heterogeneous. Also, it is reasonable to believe that, at not very small coverages, adsorbed particles influence the chemical reactivity of each other. It would seem that, as the surface coverage changes, these effects should influence the differential heats of adsorption of gaseous molecules and their reactivity in the adsorbed state. The question as to whether this influence is actually significant has been discussed since the famous work by Langmuir [51]. The resolution of this question is of principal importance for specification of the procedure for deduction of kinetic equations of catalytic processes. According to Langmuir, if a crystal surface contains centers of different sorts, these sorts are few in number; only for amorphous glasses, he left room for a wide distribution of the surface centers in their adsorption properties [51, p. 1371]. Different opinions on this question are available, and their extended discussion is a special theme. Notice that Boudart fixed in [52] that the surface heterogeneity was ignored, for almost 50 years, by engineers-chemists in the kinetics of catalytic processes and, in recent years, by investigators of the surfaces. Indeed, when the kinetic equation for a process is being deduced, more often than not the catalyst surface is considered to be homogeneous. Numerous results are in contradiction with the notion on a significant influence of the “induced heterogeneity” on the kinetics of catalytic processes and heats of adsorption of gases.

Constant or almost constant differential molar heats of adsorption in a wide range of the coverage were obtained under usual vacuum and under ultra-vacuum conditions for a number of adsorbent–adsorbate systems including powder and film adsorbents. The following systems can be given as examples: H_2–Fe [53,54], H_2–Ni [55], H_2–Pt (black) [56], H_2–Pt deposited at SiO_2 [57], H_2–catalyst containing Pt and W deposited at SiO_2 [57], O_2–Nb [58], O_2–W [58], O_2–Mn [58], O_2–Ni [58], O_2–Co [58,59], O_2–Fe [58], O_2–Mo [58], O_2–Ta [58], O_2–Ti [58], O_2–catalyst containing Pt and W deposited at SiO_2 [57], O_2–W deposited at SiO_2 [57], O_2–Cu [35,60], O_2–Ag [61], N_2–Ni [62], N_2–Fe promoted with Al_2O_3 and K_2O [63], CO–Ni [55], CO–Dy [64], acrylic acid–catalyst containing V and Mo, acrylic acid–catalyst containing V, Mo, and Cu, acrylic acid–catalyst containing V, Mo, and P, acrylic acid–catalyst containing V, Mo, and Cs [65], HC≡CH–platinum, H_3C–C≡CH–platinum, H_2C=C=CH_2–platinum [66], H_2–Pt [67], H_2–Ce, H_2–Dy, H_2–Lu, H_2–Er, H_2–Tm, H_2–Yb [68], etc.

A series of reliable kinetic equations deduced earlier on the assumption that the surfaces are heterogeneous were deduced somewhat later [42,69] without such an assumption and nothing proves that the surfaces reveal themselves in catalysis as the heterogeneous ones.

With these results in mind, we specially studied the properties of the ZnO- and Cu-components of the catalyst reduced to the R-state. For the ZnO-component, the following was found: the differential heat of H_2 adsorption (43.8 ± 3.3 kJ/mol in the isothermal experiments performed from 298 to 353 K) does not depend on the adsorbed quantity; the isotherm of the heats of H_2 adsorption at 293 K in the pressure range from 0 to 300 hPa is described well by the Langmuir isotherm deduced for dissociative adsorption at homogeneous surfaces; the differential heat of CO_2 adsorption (59 kJ/mol in the isothermal experiments performed at 298 and 323 K) does not depend on the adsorbed quantity; and the isotherm of CO_2 adsorption at 323 K in the pressure range from 5 to 110 hPa is described well by the isotherm deduced for adsorption of each molecule at two adsorption centers of homogeneous surface. For the Cu-component, the following was found: the heat of CO adsorption (66 ± 4 kJ/mol at 303 and 353 K) does not depend on the adsorbed quantity and the rate of O_2 adsorption is described well by the equation deduced for adsorption of each molecule at two centers of homogeneous surfaces. Thus, there is not a grain of evidence to suggest that the surface heterogeneity reveals itself in any manner in the heats of adsorption, adsorption isotherms, or rates of adsorption.

Thus, numerous results obtained for the system under consideration and for a number of other systems are in contradiction with the notion on a significant influence of the surface heterogeneity (just as the so-called “biographical” heterogeneity so the “induced” one) on the kinetics of catalytic processes and on the adsorption properties including the differential heats of chemisorption of gases. Evidently, the surface heterogeneity does not reveal itself in catalytic and chemisorption processes as a general phenomenon that could influence principally the catalytic and chemisorption processes proceeding at surfaces of any specified chemical composition.

Forecasting that not everybody will be line up with the last conclusion, notice additionally several fundamental opinions and facts counting in favor of it. In actuality, Boreskov's fundamental rule [70] on the approximate identity of the specific catalytic activity characteristic for a unit surface area of different forms (powder, wire, film, foil, etc.) of solids of any one chemical composition sets one to stumble at a fundamental influence of the surface heterogeneity on the catalytic properties of solids. From different standpoints, the notions on fundamental effects of the surface heterogeneity on the catalytic and adsorption properties of solids were called under question, for example, in [42,69,71–76].

Apparently, two possible causes could be proposed, any one of them or two together being applicable to explain the occurrence of no manifestation of the surface heterogeneity in adsorption characteristics. Firstly, in adsorption properties of surfaces, the collective characteristics of a crystal as a whole might prevail over the characteristics of the individual surface atoms. Indeed, the structural surface heterogeneity may introduce only an insignificant term into the total electron properties of the crystal as a whole with no effective change in the electron properties of the surface as such, since the surface electron gas of crystals forms a continuous equilibrium distribution with the three-dimensional electron gas acting as an effective infinite reservoir [77]. Secondly, evidently, nothing proves that, under conditions of adsorption–desorption equilibrium, surfaces are covered with unit adparticles randomly distributed. It seems likely that under adsorption–desorption equilibrium, surfaces are covered with a majority of two-dimensional crystal-like chemadphase islands permanently varying in their form and size, appearing and disappearing in such a way that their total surface area remains unchangeable in time; at surfaces of catalysts functioning under stationary conditions, such intermediate island chemadphases of different chemical compositions might exist. The occurrence of such island chemadphases is supported by a gain in the energy resulted from the two-dimensional crystallization of the unit adparticles; the steady state of the surface is provided by the adsorption–desorption processes and surface migration. Available electron micrographs of opaque adsorbed layers, for example, of oxide and amide ones (for example [78,79]), demonstrating two-dimensional chemadphases against the background of the metal surface count in favor of such a notion of surfaces under adsorption–desorption equilibrium. Under stationary conditions, the relationship between the chemadphase concentrations does not vary, since each of the chemadphases is in equilibrium with the gaseous medium. The chemadphases characterized by disparate values of decrease in the free energy at their formation from the gas components have no way to coexist at the surface. An important point is that the mechanism of establishment of equilibrium in reaction steps of catalytic processes does not influence the form of the corresponding kinetic equations.

Fig. 3 presents a schematic illustration of the last concept of catalytic reactions as applied to any instant of the stationary methanol synthesis proceeding at the S_2 surface of the catalyst through the mechanisms (1)–(7). According to this pattern, the vast majority of the two-dimensional crystals of each of the chemadphases consists of a great number of admolecules. Therefore, adsorption or desorption leading to some decrease or increase in the size of such crystals does not change significantly their molar energy, similarly to sublimation or evaporation not influencing the molar energy of rather large-sized three-dimensional crystals. In other words, if the mechanism of a catalytic reaction is similar to the mechanisms (1)–(7) and if the pattern of the surface in the course of this reaction proceeding under steady-state conditions is similar to the pattern shown in Fig. 3, no significant effect of mutual influence of admolecules on their capability to react with molecules of another chemical nature should occur. The notion similar to the one illustrated by Fig. 3 can be applied to explain the absence of any revealing of the effect of mutual influence of admolecules in the differential heats and rates of adsorption measured in a number of works.

To deduce the kinetic equation, it is not necessary to identify the chemical composition of Z. Nevertheless, this question is of interest for comparison studies of different catalysts and of different processes proceeding at similar catalysts. There-

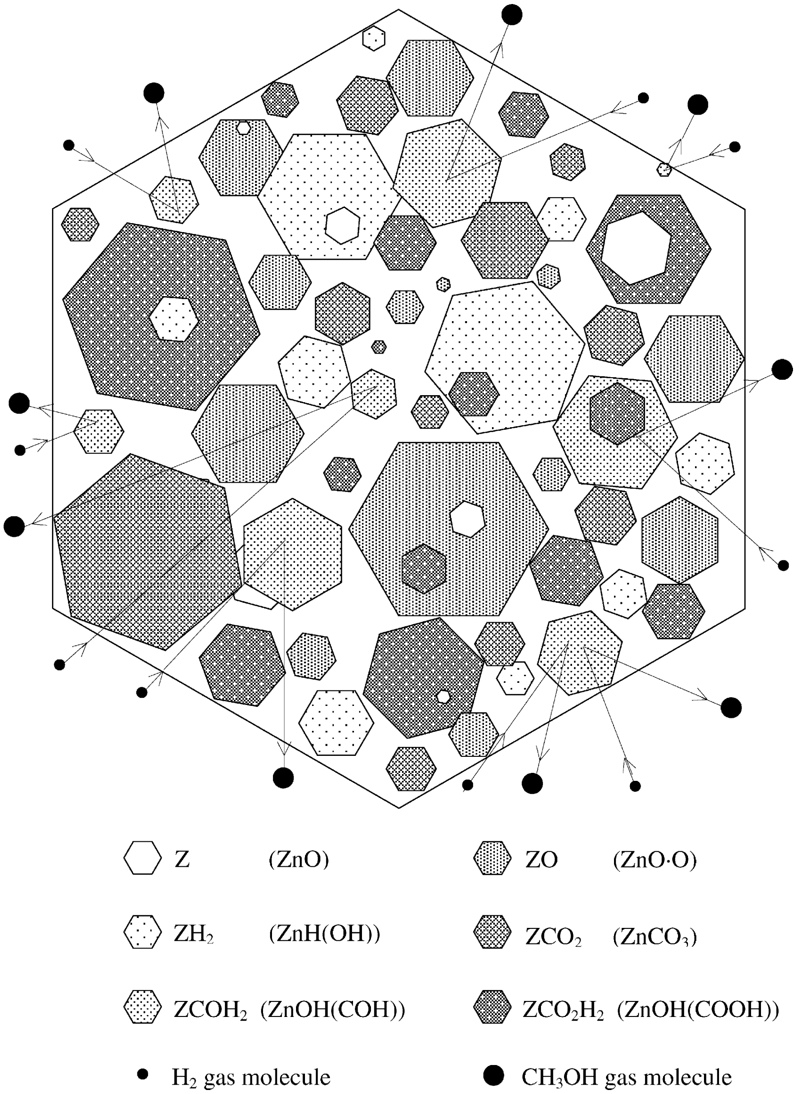

Fig. 3. Illustration to the concept of a heterogeneous catalytic process as applied to the methanol synthesis at the ZnO-component of the ZnO–$Cu_4(OH_2)$–Al_2O_3-catalyst. Under conditions of the steady-state methanol synthesis, all chemadphases are in equilibrium with the reacting gaseous mixture; the rate of the process is determined by the rates of interactions of H_2 with ZCO_2 and CO_2 with ZH_2. The hexagons represent the clusters of the chemadphases coexisting at the surface of the ZnO component of the catalyst in equilibrium with the gaseous components under conditions of the steady-state methanol synthesis.

fore, we will risk to make some suggestions on the chemical form of Z. Evidently, Z = ZnO modified possibly by copper ions dissolved in the ZnO body. In this case, the mechanisms (1)–(7) includes the following surface intermediates: $ZCO_2 = ZnCO_3$, $ZH_2 = ZnH(OH)$, $ZCO_2H_2 = ZnOH(COOH)$, $ZO = ZnO \cdot O$, and $ZCOH_2 = ZnOH(COH)$. The corresponding three-dimensional analogs are known only for $ZnCO_3$, ZnO, and ZnO·O [80]. As was noted above, the energy of O_2 adsorption at ZnO·O at the R-state is equal to 485 kJ/mol (the energy of decomposition of two moles of ZnO to oxygen and metal is equal to −701.6 kJ). It may appear that, in the schemes (1)–(7), ZnH(OH) can be considered as water adsorbed at Zn. However, this is not the case. Desorption of water from ZnH(OH) is impossible. Indeed, the enthalpy of ZnH(OH) is summed from the enthalpy of ZnO and the heat of H_2 adsorption. Therefore, water desorption from ZnH(OH) would imply that ZnO is reduced by H_2. However, this process is thermodynamically impossible at the temperatures of the methanol synthesis at the Cu–Zn-containing catalysts. In contrast to H_2O desorption, desorption of H_2 from ZnH(OH) proceeds, such a process being reversible under conditions of the methanol synthesis.

To illustrate the applicability of the proposed mechanisms (1)–(7) to description of actual kinetic data for steady-state industrial conditions, we give below the kinetic equation and two examples of its application. The deduction of this equation, the procedure for the determination of its constants, description of the procedure of application of the equation, and application of the equation to description of the process of methanol synthesis under different conditions (0.1–25 MPa and 470–570 K) will be detailed in another paper.

The mechanisms (1)–(7) lead to the following equation for the rate of the methanol synthesis:

$$r = A/B,$$

where

$$A = (k_4K_2 + k_3K_1)P_{H_2}P_{CO_2}(1 - x)$$

Table 2
Equilibrium constants for Eq. (III)

Constant	Value	Dimension
K_1	$4.91 \times 10^{-4} \times 10^{3085/T}$	MPa^{-1}
K_2	$2.1 \times 10^{-4} \times 10^{2348/T}$	MPa^{-1}
K_6	$0.00288 \times 10^{-501/T}$	MPa^{-1}
$K_7^{0.5}$	$4.3 \times 10^{6} \times 10^{-4940/T}$	MPa
$K_5K_6K_7^{0.5}$	$2.33 \times 10^{4} \times 10^{4290/T}$	MPa

and

$$B = 1 + K_1P_{CO_2} + K_2P_{H_2} + (P_{CH_3OH}/K_6P_{H_2}) + (P_{CH_3OH}P_{H_2O}P_{CO_2}/K_5^2K_6^2K_7P_{H_2})^{0.5} + (P_{H_2}P_{H_2O}P_{CO_2}/K_7P_{CH_3OH})^{0.5}. \qquad \text{(III)}$$

where K_i is the equilibrium constant for the equilibrium i in the scheme of the mechanisms (1)–(7); k_3 and k_4 are the rate constants for the steps (3) and (4), respectively, in the same mechanisms; $x = P_{CH_3OH}^{0.5}P_{H_2O}^{0.5}/K^{0.5}P_{H_2}^{1.5}P_{CO_2}^{0.5}$, where K is the equilibrium constant for the reaction (II); P_{H_2}, P_{CO_2}, etc. are the pressures of H_2, CO_2, etc. (strictly speaking, it is correct to use the activities instead of pressure). The values of the constants are given in Table 2.

Fig. 4 illustrates the applicability of Eq. (III) at 25 MPa and 558 K to description of the behavior of the actual reactor productivity as a function of the input gaseous composition. Curve 1 presents the experimental data of [4]. Curve 2 passes through the points computed with Eq. (III) relative to the maximum

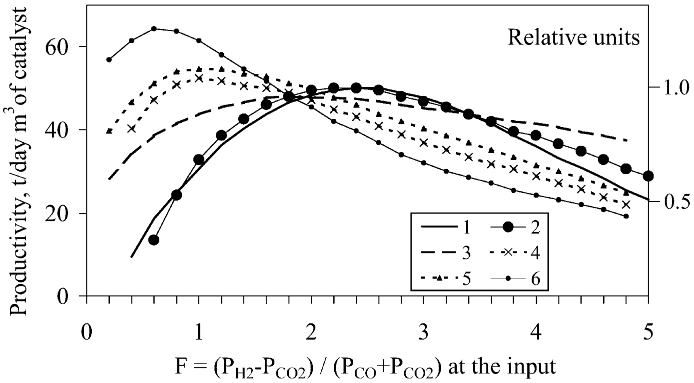

Fig. 4. Application of the kinetic equation to description of the methanol synthesis productivity at 25 MPa and 558 K: curve 1 presents the experimental data from [4]; curve 2 passes through the points computed with Eq. (III) relative to the maximum productivity; and curves 3, 4, 5, and 6 are computed in [4] with the kinetic equations from [81–84], respectively.

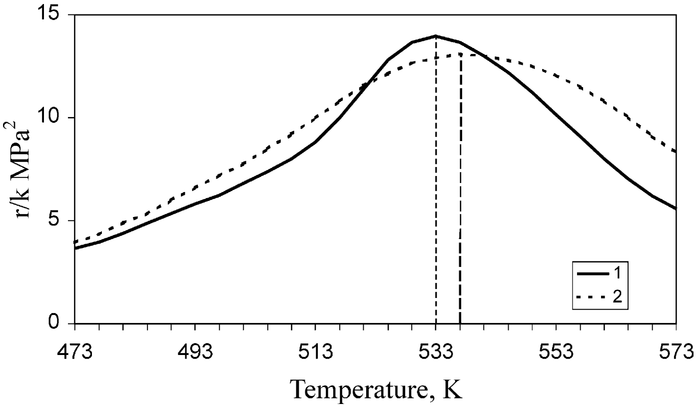

Fig. 5. Application of Eq. (III) to computation of the rate-temperature dependence at a total pressure of 5 MPa and a partial methanol pressure of 1.5 MPa for two gas compositions: $CO_2/CO/H_2$/inerts = 3.3/24.6/59.9/12.2 (curve 1) and 4.1/25.0/62.7/8.2 (curve 2).

productivity taken to be unity. For comparison, curves 3–6 from [4] are presented; they represent the results of computations performed with the kinetic equations proposed in [81] (see below) [82–84], respectively. It is seen that Eq. (III) describes the behavior of the productivity rather well.

Fig. 5 gives the results of computation performed with Eq. (III) for the rate-temperature dependence at a total pressure of 5 MPa and a partial methanol pressure of 1.5 MPa at the output of the isothermal reactor for two real compositions of the output gas mixture: $CO_2/CO/H_2$/inerts = 3.3/24.6/59.9/12.2 (curve 1) and 4.1/25.0/62.7/8.2 (curve 2) under condition of equilibrium relative to reaction (I). The computed temperatures corresponding to the maximum rates of the methanol synthesis correlate well with the temperatures of maximum rates observed in the industry according to [4]. It is seen that the kinetic equation (III) deduced from the mechanisms (1)–(7) correctly reflects the rate-temperature dependence observed under industrial conditions of the methanol synthesis.

The data presented in Figs. 4 and 5 count in favor of the mechanisms proposed. It should be emphasized that the mechanisms (1)–(7) would be, evidently, incorrect for the methanol synthesis at the ZnO–Cr_2O_3 catalysts. At such catalysts, the process proceeds at rather high temperatures (570–670 K) and pressures of 20–40 MPa. The mechanism of this process could be a theme of a special consideration. We notice only that, apparently, it may be described as follows [42]:

$$Z + H_2 \leftrightarrow ZH_2 \tag{13}$$

$$4ZH + CO \equiv CH_3OH + 4Z \tag{14}$$

$$ZH_2 + Z \equiv\!\!\rightarrow 2ZH \tag{15}$$

The arrow means that the equilibrium (15) is shifted to the right, i.e., the surface is covered with the H atoms almost entirely. The step (13) is the rate-determining one; it is not equilibrium, but is reversible only partially. If $\theta_{ZH}^4 \approx 1$ (θ_{ZH} is the surface coverage by the H atoms), we can write $K_{14} = \theta_Z^4 P_{CH_3OH}/P_{CO}$ and $K_{15} = 1/\theta_{ZH_2}\theta_Z$ (P is the pressure, K_{14} and K_{15} are the equilibrium constants for (14) and (15), respectively. The rate of the reaction is equal to the difference between the rates of step (13) from left to right and from right to left. By using the law of mass action, we can write

$$r = k_{+13}P_{H_2}\theta_Z - k_{-13}\theta_{ZH_2} = \frac{k_{+13}K_{14}^{1/4}P_{H_2}P_{CO}^{1/4}}{P_{CH_3OH}^{1/4}} - \frac{k_{-13}P_{CH_3OH}^{1/4}}{K_{15}K_{14}^{1/4}P_{CO}^{1/4}}$$

This equation was first proposed in [81] on the basis of another mechanism and was profitably applied in [4] to describe the methanol formation at the ZnO–Cr_2O_3 catalysts.

6. Conclusion

Our consideration of the mechanisms of the methanol synthesis is based on definite principal views on the mechanisms of the heterogeneous catalysis as a natural phenomenon. We believe that surfaces reveal themselves in catalytic and adsorption processes as homogeneous relative to their reactivity, in spite of the fact that their morphologies are heterogeneous. We see the cause of this fact in the energy exchange between surface atoms and between surfaces and bodies of solids and also in leveling the individual peculiarities of different atoms as a result of this energy exchange. Possibly, adsorbed surface particles join together, forming island chemadphases at the surfaces [42]. In this case, it is clear why the so-called "induced heterogeneity" (sometimes termed the mutual influence of adsorbed particles) assumed in some works does not reveal itself in the differential heats of adsorption and in the kinetics of catalytic processes. The model of catalyzing surfaces proposed by us (Fig. 3), possibly, could be an initial point for further discussions on the nature of catalysis. For the catalytic system considered in this paper, the homogeneity of the surfaces of its components is multiply proved by our data on the differential heats and rates of adsorption. Based on the experimental data, we state that the methanol synthesis proceeds predominantly at the ZnO-component and the equilibrium relative to the shift-reaction is established predominantly at the Cu-component of the catalyst. However, we in no way disclaim the possibility of methanol synthesis at copper catalysts with no zinc oxide. It is well known (e.g. [18]) that, at copper catalysts, the methanol synthesis proceeds, but its rate is significantly lower than that in the presence of zinc oxide is. On the basis of the experimental data, we consider the methanol synthesis as a process proceeding with a rate-determining (limiting) step. We show that information on the nature and bonding energy of adsorbed intermediates, but not on the form of equations of chemical interactions of these intermediates with gaseous components, is of principal importance for the kinetics of reactions of such a type. This conclusion confirms the importance of adsorption, spectral, and calorimetric studies of individual adsorption–desorption steps of catalytic processes for clarification of their mechanisms and deduction of theoretically justified kinetic equations. Mechanisms of reactions with an RDS allow description of the experimental kinetic data for many catalytic reactions proceeding not very far from the equilibrium (e.g. [39,40,85,86]). We stated that the notions on the proceeding of reactions at homogeneous surfaces and with a limiting step are applicable for description of such processes as the ammonia synthesis (at $Fe/Al_2O_3/K_2O$) [42,69,75], SO_2 oxidation (at Pt), shift-reaction (at Fe_2O_3), methanol synthesis (at ZnO/Cr_2O_3), and oxygen exchange between CO_2 and CO^{18} (at Fe_2O_3) [42]. Apparently, mechanisms of such a type are universal at least for the reactions proceeding under conditions not far from equilibrium. We are inclined to believe that some of other mechanisms proposed earlier resulted from insufficiently comprehensive studies of the nature of the adsorbed particles and their strength of bonding with the surfaces.

The methanol synthesis mechanisms proposed in this paper relate to the process proceeding at catalysts containing both ZnO- and Cu-components. We consider that these mechanisms are inapplicable neither to ZnO-catalyst nor to Cu-catalysts. Moreover, we do not exclude the occurrence of some conditions when the RDS differs from that proposed in this work and the existence of chemadphases other than those proposed in this paper.

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