

The Role of Hydrogen in the Reactions of Synthesis of Ammonia and Methanol

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Abstract—Publications on the mechanisms of ammonia synthesis on an iron catalyst and methanol synthesis on a copper zinc aluminum catalyst were analyzed. Based on the analysis of the energy balance of individual reaction steps, a hypothesis was put forward that hydrogen is a source of energy required for the chemisorption of other reagents. In the ammonia synthesis, this occurs through the formation of surface iron hydrides; and in the methanol synthesis, surface zinc hydrides. An energy diagram was constructed, which shows that, at the dissociation step, fragments of the adsorbed nitrogen molecule receive additional energy through the formation of iron hydride, and this energy ensures the breakdown of the bond in the nitrogen molecule. A scheme of the methanol synthesis was proposed, according to which the copper surface and the zinc oxide surfaces of the catalyst are independent phases: the synthesis occurs on the copper surface, whereas the intermediate step of CO oxidation to CO₂ proceeds on the zinc oxide surface and the copper surface simultaneously. The mechanism of the CO₂ conversion to methanol was considered, which comprises the steps of binding of CO₂ to hydrogen chemisorbed on the copper surface, formation of formate, hydrogenation of formate to formic acid, and decomposition of formic acid into hydroxyl and formyl with further hydrogenation to methanol. In this case, CO₂ molecules move from the zinc oxide surface to the copper one, and H₂O molecules migrate in the opposite direction. The heterogeneous catalysis was considered from the standpoint of the potential theory of adsorption, within which kinetic equations for the ammonia synthesis and the methanol synthesis were proposed. The purpose of this work was to refine the mechanism of the considered processes.

Keywords: surface free energy, catalyst, formate mechanism, intermediates, dissociation energy

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INTRODUCTION

Previously [1], we presented the energy balance of the dissociative chemisorption of the nitrogen molecule on the surface of an iron catalyst, which supplements the mechanism of the reaction of ammonia synthesis and gives a new insight into the role of hydrogen in this reaction.

This energy balance is schematized as an energy diagram of the dissociative chemisorption of nitrogen and hydrogen molecules on an iron catalyst (Fig. 1).

The energy diagram (Fig. 1) shows that the free energy of the α -Fe active site (460 kJ/mol) is insufficient for the dissociation of the nitrogen molecule. Borso et al. [2] derived the values of the strength (550 kJ/mol) of the chemical bond between the metal and the nitrogen on the Fe(100) and Fe(111) surfaces, which confirmed the order of the surface free energy that we calculated. At the dissociation step, reactive fragments of the adsorbed nitrogen molecule receive additional energy from the adsorbed system through the formation of iron hydride (about 460 kJ/mol) by overcoming the activation barrier of the breakdown of

the bond in the nitrogen molecule. Ertl et al. [3] described the dissociative chemisorption of nitrogen as a sequence of steps $N_2 \rightleftharpoons N_{2ad} \rightarrow 2N_{ad}$, i.e., the “direct” mechanism $N_2 \rightarrow 2N_{ad}$ is unlikely, which is confirmed by the energy diagram.

EXPERIMENTAL DATA ON AMMONIA SYNTHESIS

The heterogeneous catalysis on a nonuniform surface is considered from the standpoint of the potential theory of adsorption, within which the following kinetic equation is proposed [4, 5]:

$$\frac{dy}{dt} = k(A + 1)\exp(-bY). \quad (1)$$

Here, k is the process rate constant; b is a temperature-dependent constant; t is the contact time; $Y = \frac{X}{X_e - X}$; and X and X_e are the current and equilibrium ammonia (or methanol) concentrations in the reacted gas, respectively, vol %.

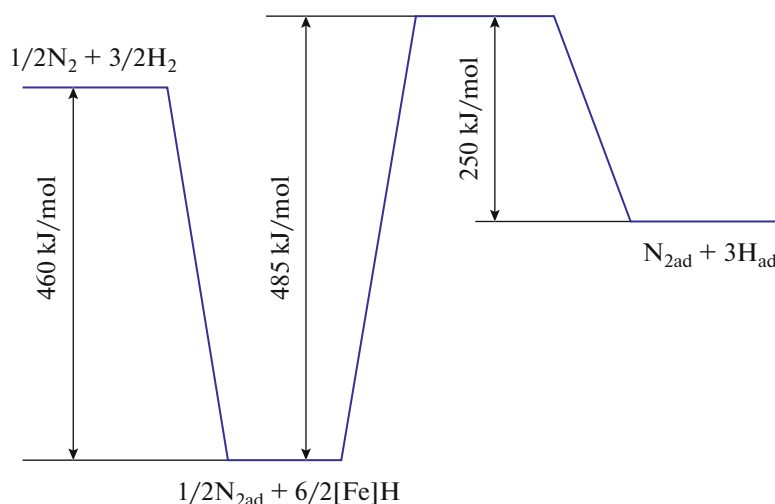


Fig. 1. Energy diagram of the dissociation of the nitrogen molecule.

For ammonia synthesis, the parameter $A = 0$, and the integral form of Eq. (1) has the form

$$X = X_e \frac{1}{b} \frac{\ln(bkt + \exp(bY_0))}{1 + \frac{1}{b} \ln(bkt + \exp(bY_0))}, \quad (2)$$

where $Y_0 = \frac{X_0}{X_e - X_0}$; X_0 and X_e are the current and equilibrium ammonia concentrations in the initial gas, respectively, vol %, and b and k are approximated by temperature-dependent expressions

$$b = \frac{3850}{T} - 4.06, \quad (3)$$

$$k = 10^8 \exp\left(-\frac{114860}{RT}\right). \quad (4)$$

The contact time calculated under the operating conditions in the reactor, s:

$$t = E_0 \frac{3600 P T_0}{V_{\text{vol}} P_0 T}, \quad (5)$$

where E_0 is the porosity of the fixed catalyst bed; P and P_0 are the gas pressures under the operating and normal conditions, respectively; T and T_0 are absolute temperatures under the operating and normal conditions, respectively; V_{vol} is the volume flow rate of the reaction mixture under normal conditions; and 114 860 kJ in Eq. (4) is the apparent activation energy of ammonia synthesis.

Figures 2 and 3 present the curves calculated from Eq. (1) and the points representing the experimental data over a wide range of ammonia synthesis conditions.

As Figs. 2 and 3 show, the experimental and calculated ammonia contents in the reacted gas agree well. Consequently, Eq. (1) is applicable over a wide range

of operating conditions. The process temperature is taken into account by constants k and b ; and the pressure, by the equilibrium ammonia concentration. The ammonia synthesis was studied in a flow-through reactor packed with an SA-1 granulated iron catalyst with an average sieve diameter of 0.75 mm.

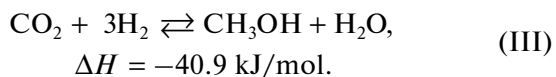
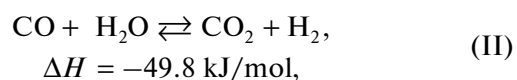
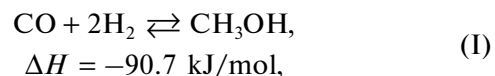
Kinetic equation (1) was used to calculate the temperature conditions in the packing of an industrial ammonia synthesis column. The temperatures in the catalyst boxes that were calculated from both Eq. (1), and the Temkin–Pyzhov equation agree satisfactorily with the temperatures measured with a thermocouple under industrial conditions.

It is reasonable to continue the refinement of the effect of hydrogen in the methanol synthesis on a Cu/ZnO/Al₂O₃ catalyst.

SOME EXPERIMENTAL FEATURES OF METHANOL SYNTHESIS

In industry, methanol is synthesized from a non-stoichiometric mixture of hydrogen, carbon dioxide, and carbon monoxide at a pressure of 50–100 bar and a temperature of 500–550 K on a KATALKO 51-8 Cu/ZnO/Al₂O₃ catalyst (Klariant) [6, 7].

Hydrogen and carbon oxides in syngas enter the following main reversible chemical reactions:



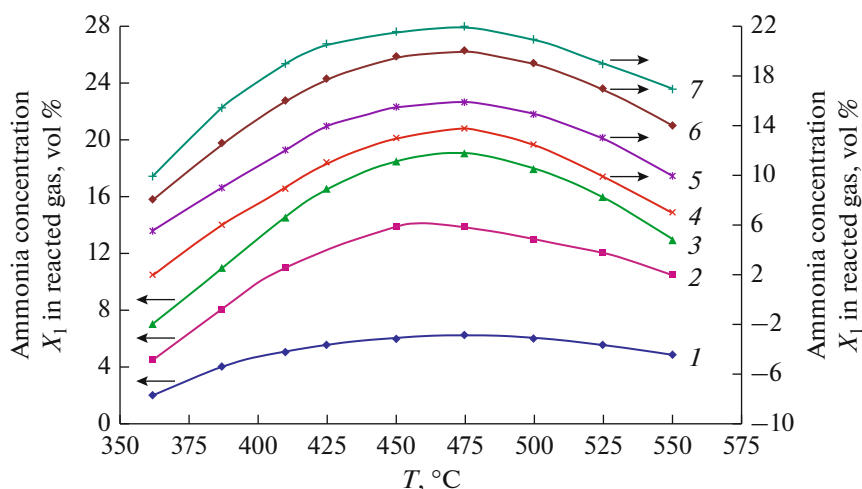


Fig. 2. Temperature dependence of the ammonia concentration X_1 in the reacted gas at a volume flow rate of the nitrogen–hydrogen mixture of $3 \cdot 10^4 \text{ h}^{-1}$, pressure of 30 MPa, and various compositions of the mixture at $\text{H}_2 : \text{N}_2$ molar ratios of (1) 1 : 3, (2) 1 : 1, (3) 2 : 1, (4) 10 : 1, (5) 7 : 1, (6) 5 : 1, and (7) 3 : 1.

The thermodynamic equilibrium dictates that the process should be performed at low conversion per run and high circulation rate of the reaction mixture. The reaction is highly exothermic; therefore, the conversion is maximum at low temperatures and high pressures. The optimal stoichiometric ratio between the components of syngas for methanol synthesis is $([\text{H}_2] - [\text{CO}_2])/([\text{CO}] + [\text{CO}_2]) = 2$. Note that this ratio is independent of the equilibrium of the water gas shift reaction (Eq. (II)) and, therefore, should not be used to describe the reactivity of syngas. For this purpose, the $[\text{CO}]/[\text{CO}_2]$ ratio can be used.

Isotope exchange experiments and other studies showed that the main source of carbon for the formation of methanol obtained from syngas on a $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst is CO_2 , and a consensus on this issue has been reached [6, 8–10]. However, although numerous studies of catalytic hydrogenation of CO_2 to methanol have been made, the mechanism of the reaction at a molecular level still remains debatable.

Let us analyze the effect of hydrogen on the methanol synthesis from CO_2 , CO , and H_2 on a $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst. The catalyst is manufactured as a homogeneous mixture of oxides of copper, zinc, and aluminum and is reduced before use to obtain phases of metallic Cu, ZnO, and Al_2O_3 . It is universally accepted that metallic copper is an active phase in the hydrogenation of CO_2 [6, 8, 9]. The deformation of crystals at the steps of preparation and reduction of the catalyst forms its surface system. The surface free energy YS is related to the cohesive energy of solid, H_{coh} , and to the number of bonds between the atom and its nearest neighbors that should be broken to form the surface [7]:

$$YS = H_{\text{coh}} \frac{Z_s}{Z} N_s, \quad (6)$$

where Z_s is the number of missing nearest neighbors of the surface atom, Z is the coordination number of the bulk atom, and N_s is the density of atoms on the surface.

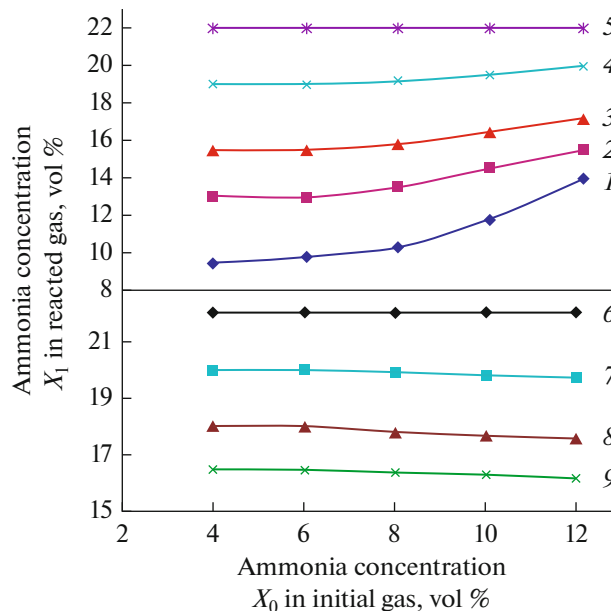


Fig. 3. Dependence of the ammonia concentration X_1 in the reacted gas on the ammonia concentration X_0 in the initial gas at a volume flow rate of the nitrogen–hydrogen mixture of $3 \cdot 10^4 \text{ h}^{-1}$, pressure of 30 MPa, and various temperatures of (1) 350, (2) 385, (3) 400, (4) 425, (5) 450, (6) 475, (7) 500, (8) 525, and (9) 550°C.

From the available data on the cohesive energy of crystalline copper (387 kJ/mol) and the Z_s/Z and N_s values typical of face-centered cubic (fcc) lattice, one can find that the surface free energy of copper in the catalyst is about 422 kJ/mol.

Let us consider the dissociation of H_2 on the Cu surface of the catalyst. Norskov [11] asserted that the molecularly adsorbed state does not exist for the H_2 molecule on pure copper and nickel surfaces. The dissociation energy of the hydrogen molecule is about 435–460 kJ/mol. The surface free energy of the copper component of the catalyst (422 kJ/mol) is close to the dissociation energy of the hydrogen molecule. Analysis of the possible additional energy sources on the catalyst surface suggests that one of such sources can be zinc oxide, which can be a promoter of copper. The surface free energy of the zinc oxide crystal at a cohesive energy on the order of 400 kJ/mol reaches more than 360 kJ/mol, which quite compensate for the energy deficiency for the dissociation of the hydrogen molecule on the surface of the copper phase of the catalyst:



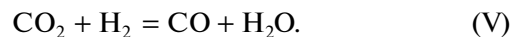
A CO molecule adsorbed on an active site of the surface of the copper component of the catalyst can be hydrogenated by reaction (I) to formyl HCO (the bond energy exceeds 75 kJ/mol) and then through formaldehyde to methanol.

However, in parallel to the methanol synthesis, the water gas shift reaction occurs on the catalyst surface. Isotope exchange experiments [6] demonstrated that methanol is synthesized mainly from CO_2 produced by the water gas shift reaction, and, correspondingly, the role of CO in the process changes.

The surface free energies of the zinc oxide and copper components of the catalyst are similar, and they can act as independent phases. Therefore, reactant molecules can be adsorbed on different phases of the catalyst surface. An additional energy source on the zinc oxide surface can be the bond energy of zinc hydride, and also the copper component of the catalyst surface as a promoter of zinc oxide.

The understanding of how an active site on Cu/ZnO/ Al_2O_3 forms is a key to the development of active and selective of catalytic systems. The ability of hydrogen to be adsorbed on different components of the catalyst enables CO and CO_2 molecules to interact with it and other adsorbed species both on the copper, and the zinc surface. The base planes of a zinc oxide crystal (with the wurtzite structure) are polar. The (0001) plane corresponds to the surface bounded by zinc cations (Zn–ZnO); and the (0001*) plane, to the surface bounded by oxygen anions (O–ZnO). The adsorption and dissociation of the hydrogen molecule on the zinc oxide surface (Zn–ZnO) lead to the formation of zinc hydride, the average bond energy in it is 263 kJ/mol. The adsorption of CO_2 on the ZnO sur-

face creates the condition for the interaction with hydrogen and a shift of the equilibrium of the water gas shift reaction in the opposite direction:



Investigation of the water adsorption on a ZnO surface by various methods showed that some of the water molecules are dissociated, whereas the others are not [12, 13]. After the adsorption of a CO molecule on the ZnO surface on which there are adsorbed H_2O molecules, the water gas shift reaction can occur. Thus, the ZnO surface of the catalyst has an excess of the free energy for the water gas shift reaction simultaneously with the water gas shift reaction and the methanol synthesis on the Cu surface. The simultaneous occurrence of the three processes results in the formation of an excess of water in the system, which shifts the chemical equilibrium toward the formation of CO_2 . The CO_2 molecule that is newly formed by reaction (II) is desorbed from the ZnO surface (the desorption energy is 15 kJ/mol) and then adsorbed on the Cu surface, where it reacts with a surface hydrogen atom and transforms into methanol by reaction (III). The source of oxygen in methanol is CO_2 formed from CO [14]. It is known that the mechanism of the water adsorption on the atomically smooth Cu(111) and Cu(100) surfaces is nondissociative. The adsorption energy of nondissociated H_2O on the Cu surface does not exceed 34 kJ/mol, which enables its desorption with subsequent adsorption on the ZnO surface with the preservation of its molecular form [15]. Moreover, the surface diffusion of water to form associates of several water molecules is not improbable. Experimental estimates of the energy barrier to the surface diffusion of water for metals range from 5 to 20 kJ/mol. Note a specific feature of the water gas shift reaction. This reaction is typically performed in a nonstoichiometric mixture, and side reactions in an excess of water vapor virtually do not occur. This is probably why process (II) occurs on the ZnO surface, which is relatively “free of other reactions.” A CO_2 molecule that is desorbed from ZnO and are adsorbed on active sites of the Cu surface that became free creates a closed cycle of exchange with the water molecule in the water gas shift reaction. This also allows one to conclude that most of the CO molecules transform into CO_2 on the ZnO surface and is likely to confirm the cause of the nonparticipation of carbon-containing intermediate compounds in the water gas shift reaction. It is suggested that the methanol synthesis from CO, CO_2 , and H_2 on a Cu/ZnO/ Al_2O_3 catalyst by Eq. (I) should be considered in two consecutive steps of transformation of CO_2 : reaction (II) on the ZnO and Cu surfaces and reaction (III) on the Cu surface.

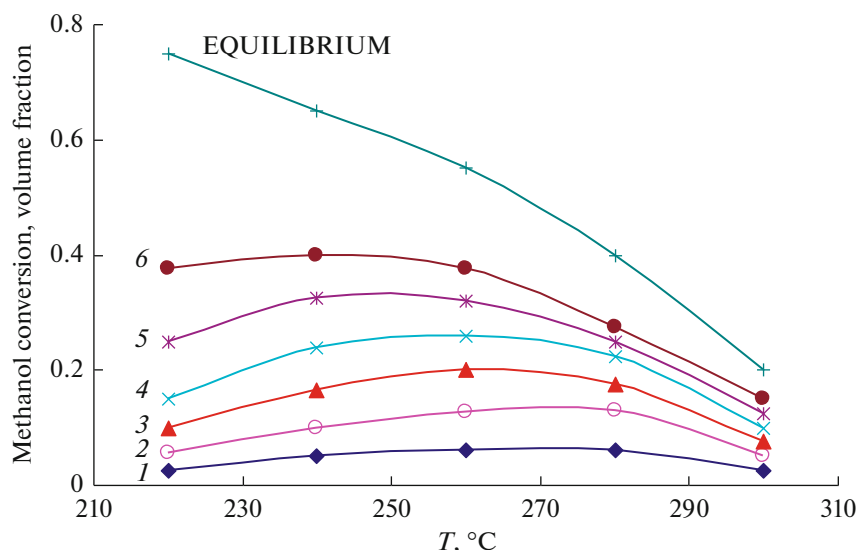
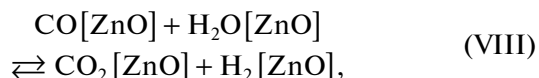
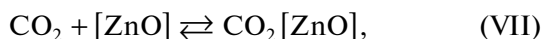
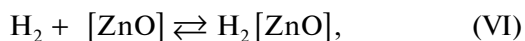


Fig. 4. Dependence of the methanol conversion (volume fraction) on the temperature of the methanol synthesis on a Cu–Zn-catalyst at contact times of the key reactant of (1) 1.2, (2) 1.75, (3) 5.0, (4) 7.0, (5) 14.0, and (6) 28.0 s.

DISCUSSION OF CONSIDERED VARIANTS

In view of the above, it seems necessary to supplement the scheme of the mechanism of methanol synthesis on a Cu/ZnO/Al₂O₃ catalyst with water gas shift reaction on zinc oxide:

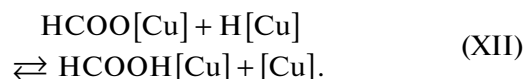


The literature review [10] showed that, for copper-containing catalysts, the formate mechanism of methanol synthesis from CO₂ is most convincing. The mechanism comprises the dissociative adsorption of hydrogen on the copper part of the surface and the direct interaction of CO₂ with the surface H* to form formate HCOO* by the Eley–Rideal mechanism. Note that formate and methoxy group are the only intermediates that are experimentally observed under the conditions of the methanol synthesis on a commercial catalyst:



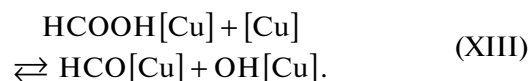
The mechanism of methanol synthesis through the sequential hydrogenation of formate to formic acid was considered previously [16, 17]. The obtained data confirmed that the reaction route through formic acid is favorable. Monodentate formate easily transforms into bidentate formate. A hydrogen molecule adds to the Cu–O bond of formate, which results in the fact

that a hydrogen atom adds to the oxygen atom to convert formate to formic acid, and the remaining hydride ion regenerates the active site to form H* [10]:

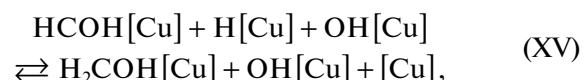
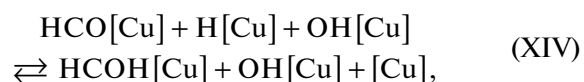


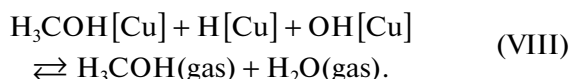
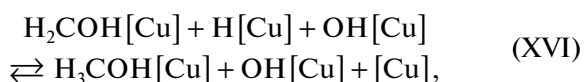
It appears that the hydrogenation of adsorbed formates is a step that determines the rate of the methanol synthesis on Cu because methanol is desorbed at the same temperature at which the adsorbed formate decomposes into CO₂ and H₂ [8].

Formic acid differs from other carboxylic acids by the fact that the carboxylic group in it is bound to not a hydrocarbon radical, but a hydrogen atom. Formic acid shares properties of both carboxylic acids, and aldehydes, i.e., is an aldehydoacid. Therefore, formic acid *HCOOH decomposes as an aldehyde to form formyl *HCO and hydroxyl *OH at an active site of the catalyst. The energy of the bond between the carbon atom and the hydroxyl in formic acid is about 360 kJ/mol and is the lowest of the energies of the bonds between its atoms.



The further transformation of the surface formyl *HCO into methanol occurs through the hydrogenation to formaldehyde *H₂CO and methoxyl *H₃CO:





The kinetics of the methanol synthesis was evaluated using Eq. (1) under the following conditions: pressure, 5–30 MPa; temperature, 220–300°C; contact time of the key reactant, 0.4–10 s; composition of the initial gas, 69–79 vol % H₂, 9–29 vol % CO, and 0–12 vol % CO₂; parameter *A*, 0.45–1.97. A part of the data was taken from the literature [18].

The constants *b* and *k* in Eq. (1) for a copper-containing catalyst are expressed as

$$b = 2.6 \times 10^{-2} \exp\left(\frac{15000}{RT}\right), \quad (7)$$

$$k = 0.54 \times 10^7 \exp\left(-\frac{75000}{RT}\right). \quad (8)$$

The parameter *A*, which takes into account the ratios between the reactants in the initial gas, was calculated as $A = 0.5 (N_{\text{H}_2} - N_{\text{CO}_2}) / (N_{\text{CO}} + 2N_{\text{CO}_2})$.

Figure 4 presents the curves calculated from Eq. (1) and the points representing the experimental data on the methanol content in the reacted gas. The calculated and experimental data agree well.

CONCLUSIONS

The presented data gave a new insight into the role of hydrogen in the processes of ammonia and methanol synthesis.

(1) The energy diagram (Fig. 1) illustrates the dissociative adsorption of the nitrogen molecule in which the necessary additional energy is provided by the formation of iron hydride. Kinetic equation (1) based on the potential theory of adsorption describes well the experimental data over a wide range of operating conditions.

(2) It seems reasonable to supplement the scheme of the mechanism of the methanol synthesis from CO, CO₂, and H₂ on a Cu/ZnO/Al₂O₃ catalyst with water gas shift reaction (II) on the ZnO surface, which becomes the main in the production of the CO₂ molecule—the immediate precursor of methanol. A closed cycle forms, in which the CO₂ molecules formed by reaction (II) are desorbed from the ZnO surface, bound to active sites of the Cu surface that became free, and hydrogenated to form methanol, whereas the H₂O molecules desorbed from the Cu surface are

adsorbed on the ZnO surface and shift water gas shift reaction (II) to the right.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Menshov, V.N. and Tubin, L.A., *Russ. Chem. Bull.*, 2018, vol. 67, no. 6, p. 1104.
2. Borso, F., Ertl, G., Grunze, M., and Weiss, M., *J. Catal.*, 1977, vol. 49, p. 18.
3. Ertl, G., Li, S.B., and Vais, M., Kinetics of nitrogen adsorption on Fe(111) surface, *Nauka o Poverkhnosti*, vol. 114, 1982, p. 515.
4. Anokhin, V.N., Men'shov, V.N., and Zuev, A.A., *Zh. Prikl. Khim.*, 1975, vol. 18, no. 3, p. 16.
5. Anokhin, V.N., Men'shov, V.N., Tarasov, L.A., Sharikov, A.V., and Babankov, V.P., *Theoretical Foundations of Catalysis in Technology of Bonded Nitrogen*, Moscow: NIITEKhIM, 1978, vol. 1, p. 33.
6. Rozovskii, A.Ya. and Lin, G.I., *Teoreticheskie osnovy protsessy sinteza metanola* (Theoretical Foundations of Synthesis of Methanol), Moscow: Khimiya, 1992, p. 272.
7. Chorkendorf, I. and Naimantsvedrait, Kh., *Sovremennyye kataliz i khimicheskaya kinetika* (Modern Catalysis and Chemical Kinetics), Dolgoprudnyi: ID Intellekt, 2013, p. 504.
8. Waugh, K.C., *Catal. Lett.*, 2012, vol. 142, p. 1153.
9. Chinchin, G.C., Mansfield, K., and Spencer, M.S., *Chemtech.*, 1990, vol. 20, p. 692.
10. Volnina, E.A. and Kipnis, M.A., *Kinet. Catal.*, 2020, vol. 61, no. 1, p. 119.
11. Norskov, J.K., *Rep. Prog. Phys.*, 1990, vol. 53, no. 10, p. 1253.
12. Woll, C., *Prog. Surf. Sci.*, 2007, vol. 82, p. 55.
13. Wang, Y., Meyer, B., Yin, X., Kunat, M., Langenberg, D., Traeger, F., Birkner, A., and Woll, Ch., *Phys. Rev. Lett.*, 2005, vol. 95, p. 266104.
14. Rozovskii, A.Ya. and Lin, G.I., *Top. Catal.*, 2003, vol. 22, p. 137.
15. Kuznetsov, A.M., *Sorovskii Obrazovatel'nyi Zh.*, 2000, vol. 6, no. 5, p. 45.
16. Kattel, S., Ramirez, P.J., Chen, J.G., Rodriguez, J.A., and Liu, P., *Science*, 2017, vol. 355, p. 1296.
17. Grabow, L.C. and Mavrikakis, V., *ACS Catal.*, 2011, vol. 1, p. 365.
18. Barkovskii, A.I., Pomerantsev, V.M., and Anokhin, V.N., *Physicochemical Fundamentals of Synthesis of Methanol. "Metanol-3."* Proc. 3rd All-Union Workshop, Nauka, 1986, p. 16.

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