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СОДЕРЖАНИЕ И ФОРМЫ АДСОРБИРОВАННОГО ВОДОРОДА НА КАТАЛИЗАТОРАХ СИНТЕЗА МЕТАНОЛА НА ОСНОВЕ $CuO/ZnO/Al_2O_3$

Д.В. Смирнов, Р.Н. Румянцев, Д.А. Прозоров, Т.Н. Борисова,
Ю.Е. Романенко, А.В. Афинеевский, Н.Е. Гордина

Дмитрий Владимирович Смирнов (ORCID 0000-0002-5550-3866), Руслан Николаевич Румянцев (ORCID 0000-0002-7763-2028)*, Дмитрий Алексеевич Прозоров (ORCID 0000-0002-1749-2828), Татьяна Николаевна Борисова (ORCID 0000-0003-1001-0184), Юрий Евгеньевич Романенко (ORCID 0000-0002-9551-9010)*, Андрей Владимирович Афинеевский (ORCID 0000-0001-6933-5130), Наталья Евгеньевна Гордина (ORCID 0000-0002-1067-4688)

Ивановский государственный химико-технологический университет, пр. Шереметевский, 7, Иваново, Российская Федерация, 153000
E-mail: morgandvs37@gmail.com, rnr86@ya.ru*, prozorovda@mail.ru, borisova.tat.n@gmail.com, romanenko@isuct.ru*, afineevskiy@mail.ru, gordinane@mail.ru

С помощью комплекса синхронного термического анализа и масс-спектрометрии исследованы состояния водорода, связанного активными центрами $CuO/ZnO/Al_2O_3$ катализатора синтеза метанола. Показано наличие на поверхности катализатора четырех форм водорода: молекулярной слабосвязанной и трех атомарных прочносвязанных с температурами десорбции от 200 до 900 °C. Определено наличие структурного водорода в структуре активного катализатора за счет разницы в величинах реакционно-способного и структурного водорода. По данным синхронного термического анализа и масс-спектрометрии определены температуры и теплоты десорбции молекулярных и атомарных форм водорода в исследуемых каталитических системах. Показано влияние структуры $CuO/ZnO/Al_2O_3$ катализатора, полученного различными способами, на состояние адсорбированного водорода, и активности в реакции синтеза метанола. Также проведены исследования каталитических систем состава $CuO/ZnO/Al_2O_3$ методами рентгенофазовой и энергодисперсионной спектроскопии, температурно-программированного восстановления в среде водородсодержащего газа, электронной микроскопии, низкотемпературной адсорбции азота, определена селективность катализатора по метанолу, метану и диметиловому эфиру в интервале температур 200-300 °C и давлении в системе 3 МПа. Активность и селективность каталитических систем сравнивается с промышленными аналогами. Проанализирована морфология поверхности катализатора при различных ускоряющих напряжениях катода электронного микроскопа. Экспериментально доказано отсутствие прямой зависимости величин активности и селективности исследуемых каталитических систем с величинами удельной поверхности. Эксплуатационные свойства промышленных и каталитических систем, синтезированных в работе, близки, разницу в селективности по метанолу однозначно можно объяснить адсорбционными свойствами по отношению к водороду.

Ключевые слова: масс-спектрометрия, адсорбция водорода, катализатор синтеза метанола

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CONTENT AND FORMS OF ADSORBED HYDROGEN ON METHANOL SYNTHESIS CATALYSTS $CuO/ZnO/Al_2O_3$

D.V. Smirnov, R.N. Rumyantsev, D.A. Prozorov, T.N. Borisova,
Yu.E. Romanenko, A.V. Afineevskii, N.E. Gordina

Dmitry V. Smirnov (ORCID 0000-0002-5550-3866), Ruslan N. Rumyantsev (ORCID 0000-0002-7763-2028)*, Dmitry A. Prozorov (ORCID 0000-0002-1749-2828), Tat'yana N. Borisova (ORCID 0000-0003-1001-0184), Yury E. Romanenko (ORCID 0000-0002-9551-9010)*, Andrei V. Afineevskii (ORCID 0000-0001-6933-5130), Natalya E. Gordina (ORCID 0000-0002-1067-4688)

Ivanovo State University of Chemistry and Technology, Sheremetevskiy ave., 7, Ivanovo, 153000, Russia
E-mail: morgandvs37@gmail.com, rnr86@ya.ru*, prozorovda@mail.ru, borisova.tat.n@gmail.com, romanenko@isuct.ru*, afineevskiy@mail.ru, gordinane@mail.ru

The condition of hydrogen bound by the active centers of $CuO/ZnO/Al_2O_3$ has been investigated by the complex of thermal analysis and mass spectrometry. There are four forms of surface hydrogen: molecular weakly bound and three atomic strongly bound with desorption temperatures 200-900 °C. The presence of structural hydrogen in the active catalyst have been determined due to the difference in the values of reactive and structural hydrogen. Desorption temperatures and heats have been determined for molecular and atomic forms of hydrogen in the studied catalytic systems. The effect of the catalyst structure obtained by various methods on the adsorbed hydrogen condition and reaction activity in methanol synthesis is shown. Also, studies of catalytic systems of the composition $CuO/ZnO/Al_2O_3$ were carried out using the methods of X-ray phase and energy dispersive spectroscopy, temperature-programmed reduction in a hydrogen-containing gas, electron microscopy, low-temperature nitrogen adsorption, and the selectivity of the catalyst for methanol, methane and dimethyl ether was determined in the temperature range of 200-300 °C and pressure in the system 3 MPa. The activity and selectivity of catalytic systems are compared with industrial analogues. The morphology of the catalyst surface have been analyzed at various accelerating voltages of the electron microscope cathode. The absence of a direct relationship between the activity and selectivity values of the studied catalytic systems and the specific surface area has been experimentally proven. The operational properties of industrial and catalytic systems synthesized in the work are close. The difference in selectivity for methanol can be unambiguously explained by the adsorption properties with respect to hydrogen.

Key words: mass spectrometry, hydrogen adsorption, methanol synthesis catalyst

INTRODUCTION

There are three main stages of methanol synthesis: hydrogenation reactions of carbon monoxide and carbon dioxide, as well as reverse vapor-gas reactions [1]:

$$CO + 2H_2 \leftrightarrow CH_3OH,\ \Delta H^{\circ}_{298} = -90.8\ (kJ\cdot mol^{-1})$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O,\ \Delta H^{\circ}_{298} = -49.4\ (kJ\cdot mol^{-1})$$

$$CO + 2H_2O \leftrightarrow CO_2 + 2H_2,\ \Delta H^{\circ}_{298} = -41.0\ (kJ\cdot mol^{-1})$$

According to numerous studies [2-6] adsorption of CO_2, CO, H_2 is required for methanol synthesis on supported $CuO/ZnO/Al_2O_3$ catalysts. It is experimentally proved that surface hydrogen exists in individual adsorption conditions and has different reactivity regarding various compounds [2, 7].

Since the conversion process is exothermic and proceeds with a decrease in volume (see reactions above), traditionally [8] the reaction is carried out at relatively low temperatures and high pressures.

In industry, the presented reactions are carried out from a non-stoichiometric mixture of hydrogen and carbon oxides at 5-10 MPa and 220-280 °C. The authors of [9-11] note the optimal temperatures relative to the selectivity of methanol yield are in the range of 180-270 °C.

The authors of [12-13] found that the main source of carbon in methanol synthesis on $CuO/ZnO/Al_2O_3$ is CO_2. The rates of methanol formation from CO_2 become higher than from CO at temperatures above 215 °C [14].

Methanol synthesis catalyst is a homogeneous mixture of copper, zinc, and aluminum oxides. The catalyst with reduced copper is considered activated. If copper is not reduced, CO_2 is adsorbed on the surface irreversibly [15].

It is known that the activity and selectivity of a heterogeneous catalyst are largely determined by the adsorption states of reactants on its surface [16].

There are conflicting data on the adsorption values and condition of hydrogen adsorbed on the methanol synthesis catalysts, as well as catalytic systems based on supported copper for other reactions involving hydrogen [2-6].

One of the first kinetic models of methanol synthesis by A.A. Karavaev [17] suggested that the rate-limiting step is precisely hydrogen adsorption on the catalyst surface. According to [4], the limiting step is the surface CH_3O complex reduction by adsorbed hydrogen.

On the one hand, there is a hypothesis [18] that molecular hydrogen does not exist on the surface of copper and nickel catalysts. On the other hand, there is another hypothesis [3] that hydrogen dissociates during adsorption. However, several studies [7, 16, 19-20] have shown the presence of several individual adsorption forms of hydrogen, both molecular and atomic, with heats of adsorption from 10 to 150 kJ/mol.

The direct experimental determination of amounts of various "metal-hydrogen" surface complexes in gaseous and liquid media is accompanied by several problems [21-23]. Therefore, the authors often use various mathematical models that allow calculating the values of hydrogen adsorption and the binding energy of "metal-hydrogen" with certain approximations from indirect data.

As mentioned, the maximum values of hydrogen adsorption on transition metals were obtained by a combination of various physicochemical research methods: thermal and flash desorption, secondary ion desorption, diffraction of slow electrons, mass spectroscopy, potentiometry, spectroscopy, adsorption calorimetry, kinetics. There are literature data mainly for gaseous media [4].

In addition, various mathematical models are most often used to distinguish adsorbed hydrogen by individual forms (including quantitative determination of forms ratio) [23] using hydrogen adsorption values. Direct experimental methods making it possible to classify reactive hydrogen according to individual adsorption forms are not mentioned in the literature. There are also no experimental methods for separating the total amount of adsorbed and reactive hydrogen.

Hydrogen chemical removal from the catalyst surface gives the most objective and reliable data of reactive hydrogen adsorption values [16, 21]. Nevertheless, this method is also fraught with difficulties caused by reagent adsorption [22].

The most effective experimental method for separating desorbed hydrogen into atomic and molecular forms can be considered the mass spectrometric analysis [24-25].

The goals of this work were the determination of the total value of the hydrogen content in the reduced $CuO/ZnO/Al_2O_3$ catalyst and its effect on the activity and physicochemical properties of the catalyst.

EXPERIMENTAL

Materials

The following reagents were used during the experimental part:

– copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), basic substance content 99.7%;

– zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), basic substance content 99.5%;

– aluminum nitrate ($Al(NO_3)_2{\cdot}9H_2O$), basic substance content 99.7%;

– ammonium carbonate ($(NH_4)_2CO_3$), mass fraction of ammonia (NH_3) 36.5 %;

– double-distilled water.

The following compressed gases were used during the reduction, the catalytic experiment, and the reaction products analysis on a gas chromatograph:

Hydrogen H_2, basic substance content 99.99%;

Carbon monoxide CO, basic substance content 99.80%;

Carbon dioxide CO_2, basic substance content 99.80%;

Nitrogen N_2, basic substance content 99.99%;

Helium He, basic substance content 99.99%;

Argon Ar, basic substance content 99.7%.

An industrial catalyst for the methanol synthesis (grade K, sample #1) was used as a reference sample.

Catalyst preparation

Catalyst sample 2 was obtained by mixing 2M aqueous solutions of copper, zinc, and aluminum nitrates in the ratio corresponding to the industrial catalyst and heated to 70 °C. 2M aqueous solution of ammonium carbonate was used as a precipitator. The temperature of the precipitator did not exceed 30 °C to avoid its thermal decomposition. Next, the resulting mixture was dosed into a container with 100 ml of a buffer solution and vigorously stirred at 70 °C with Mindray SK-500 II syringe pumps so the pH of the solution was 7. The resulting suspension was kept for 1 h and filtered off. The resulting precipitate was repeatedly washed with bidistilled water at 70 °C. The precipitate was dried for 4 h at 120 °C and then calcined at 350 °C in a muffle furnace for 4 h at a heating rate of 5 °C/min.

Activity test

Before starting work, the catalysts were reduced with a gas mixture of 20 vol.% H_2 and 80 vol.% N_2 with a stepwise temperature increase in from 25 °C to 300 °C at a rate of 2 °C per minute at a reactor pressure of 2 MPa and a gas space velocity of 8700 h^{-1}.

The catalytic activity of the sample was determined in the methanol synthesis reaction by a PKU-2VD flow-through reactor (Russia) at a pressure of 2.0 MPa. 0.5 g of a catalyst with a particle size of 0.3-0.6 mm was loaded into a steel reactor with a fixed catalyst bed, which was installed in a furnace. The required gas mixture was supplied to the reactor using gas flow controllers. The reaction gas medium included, vol.%: H_2 – 68.90, N_2 – 1.36, CO – 21.00, CO_2 – 8.70. The volumetric gas velocity was 8700 h^{-1}. The reactor temperature varied from 200 to 300 °C. The gas mixture after the reactor was fed through a heated line to a Kristallux 4000M chromatograph (Russia) for analyzing the reaction products. For this purpose, we used thermal conductivity detectors, and a flame ionization detector. Columns with NaX and HayeSep Q adsorbents were used to separate the gas mixture at 65 °C.

Adsorption experiment

The adsorption properties of the catalyst concerning hydrogen were studied using an apparatus complex, which included STA 449 F3 Jupiter® NETZSCH synchronous thermal analyzer and QMS 403 C Aëolos® mass spectrometer, PulseTA® reaction gas dosing systems, evacuation systems, high-temperature oven, and a sensor for STA 449 F3 Jupiter®. The ionization voltage was 70 V. The analysis of catalyst samples was carried out at temperatures from 30 °C to 950 °C in an argon atmosphere. Molecular masses of the fragments and the probabilities of their occurrence were obtained from the international base NIST (https://www.nist.gov).

A freshly prepared catalyst was reduced in a stream of hydrogen at 400 °C, and transferred under a layer of water into a cuvette of the apparatus complex in the amount of at least 15 mg. Thermally desorbed gases were analysed by the mass spectrometer. The experimental procedure is described in detail in the work [25].

Catalyst characterization

XRD was performed on a Bruker D8 Advance diffractometer using CuKα-radiation (λ = 0.15406 nm, voltage 40 kV, 20 mA, angles 2Θ = 10°÷100°, scanning speed 4°/min, resolution 0.01°). To identify XRD data, the MINCRYST crystallographic database was used.

Specific surface area and porosity were determined using the apparatus complex "Sorbi MS", applying nitrogen low-temperature adsorption according to the BET method.

Micrographs were obtained using a scanning electron microscope VEGA 3 TESCAN. The micrographs were employed to determine the morphology of catalyst particles using the SE mode, and the agglomerate size dispersion was determined using the BSE mode. 200 measurements of the particle diameter were made to identify the average size of the agglomerate.

The elemental composition was determined with an energy dispersive spectrometer (EDS) (Oxford Instruments Nano Analysis, UK) with an X-ACT detector.

TPR was carried out in a quartz reactor with a U-shaped tube on a chemisorption analyzer "Chemosorb" (Russia). Samples (50 mg) were purged with Ar for 30 min to remove physically absorbed water and then reduced with a gas mixture of vol.%: H_2 – 10%, Ar – 90% at a heating rate of 10 °C/min to 500 °C.

Characterization via powder X-ray diffraction (XRD)

The interplanar distances (d), the dimensions of the coherent scattering region (CSR) were calculated from XRD data.

The identification of crystalline phases on the XRD patterns was carried out by comparing the calculated interplanar distances with those given in the ASTM database. The interplanar distances were calculated according to the Bragg equation [26]:

$$d = \lambda/2\sin\Theta, \tag{1}$$

where λ is the wavelength (m), $\Theta = X_c/2$ is the diffraction angle, calculated as the gravity center position of reflex [27]:

$$Xc = \frac{\int_{-\infty}^{+\infty} I\,(\vartheta)d\vartheta}{I_{max}} \text{ or } Xc = \frac{\sum_{i=1}^{N-1}(I_i+I_{i+1})\Delta\vartheta}{2I_{max}}, \tag{2}$$

where I is the intensity at the diffraction angle ϑ and I_{max} is the maximum intensity.

The dimension of coherent scattering region (CSR) was estimated using the modified Scherrer equation [28], after linearization:

$$\beta ph \cos\Theta = \lambda/DSCR + 4\varepsilon \sin\Theta, \tag{3}$$

where D_{SCR} is the dimension of the coherent scattering region, e is the value of the relative mean square micro deformation (MD), β_{ph} is the integral physical broadening of the X-ray sample profile, calculated using the Gaussian function [29]:

$$\beta_s^2 = \beta_{ph}^2 + \beta_{inst}^2 \tag{4}$$

where β_s^2 is the integral broadening of the X-ray profile of the sample, β_{inst}^2 is the instrumental broadening. Broadening of the X-ray profile of the etalon was used as instrumental broadening.

Integral broadening of X-ray profile was calculated by the equation [27]:

$$\beta = \frac{\int_{-\infty}^{+\infty} I\,(\vartheta)\vartheta d\vartheta}{\int_{-\infty}^{+\infty} I\,(\vartheta)d\vartheta} \text{ or } \beta = \frac{\sum_{i=1}^{N-1} I_i\vartheta_i}{\sum_{i=1}^{N} I_i}. \tag{5}$$

RESULTS AND DISCUSSION

Composition, morphology, and structure of catalysts

The structure of the studied catalyst samples is noticeably different despite the similar nature of the activities of the catalytic systems at 260-300 °C.

According to the obtained diffraction patterns, the catalysts contain CuO and ZnO phases. Typical reflections for the Al_2O_3 phase are practically absent, which is explained by its small amount and being in an X-ray amorphous state. In addition, the close arrangement of the CuO peaks at 2θ = 35.4° and ZnO at 2θ = 36.3° indicates the formation of a CuO-ZnO solid solution. For sample #2, a much weaker diffraction peak of CuO was observed at 2θ = 38.8°, which indicates a lower crystallinity of CuO following the Scherrer equation. The average crystallite size of the CuO phase of sample #2 is 530 Å, sample #1 470 Å (Table 1). Energy dispersive analysis data indicate a close chemical composition of both the obtained catalyst and a commercial one (Table 1).

Table 1

Properties of the studied $CuO/ZnO/Al_2O_3$ catalysts

***Таблица 1*. Свойства $CuO/ZnO/Al_2O_3$ катализаторов, исследуемые в работе**

Sample	#1	#2
$S_{уд}$, m^2/g	101	106
Total pore volume, cm^3/g	0.173	0.196
Elemental composition, %	Cu 49.29; Zn 21.83; Al 5.24; O 23.64	Cu 42.93; Zn 23.67; Al 6.03; O 27.38
$D_{SCR\ (CuO)}$, Å	470	530
Active surface Cu, m^2/g	38.3	31.3
Average particle size Cu, Å	175.6	215.1

The nitrogen adsorption-desorption isotherms in Fig. 1 obtained for the studied catalysts refer to type IV according to IUPAC classification [16]. Isotherms of this kind are characteristic of objects with transition pores (mesopores), i.e., pores with diameters ranging from tens to hundreds of angstroms. The data obtained indicate that the samples do not have any significant differences. The specific surface area of samples #1 and #2 is close in their values and is 106 and 101 m^2/g (Table 1).

Temperature-programmed reduction and catalytic properties

Sample #1 TPR profile (Fig. 2) consists of a broadened peak in the temperature range 150-275 °C. The TPR curve of sample #1 exhibits a peak at 219 and 228 °C with two maxima of hydrogen absorption. This type of reduction can be due to the presence of copper particles in a different dispersed state. The maxima of hydrogen absorption for all catalysts correspond to the reduction of copper (II) oxide according to the scheme: $Cu^{2+} \rightarrow Cu^0$.

Since the active component of the catalyst is a reduced finely dispersed copper, the catalytic properties will depend not only on the specific surface area but also on the active surface of the copper and its dispersion. According to TPR data, the active surface of copper and its dispersion were calculated (Table 1). The active surface is 38.3 and 31.3 m^2/g for samples #1 and #2, respectively.

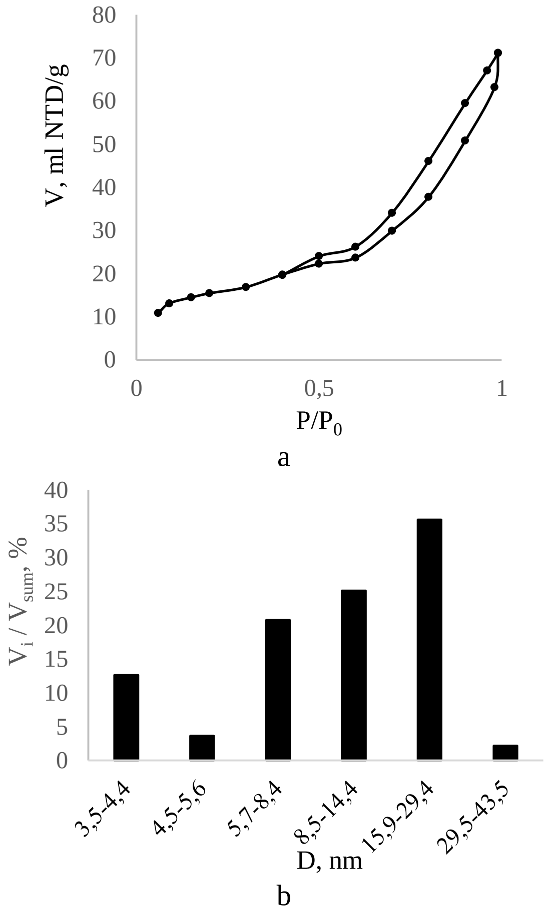

Fig. 1. Nitrogen adsorption-desorption isotherms (a) and pore distribution (b) of sample N 1

Рис. 1. Изотермы адсорбции-десорбции азота (a) и распределение пор (b) образца № 1

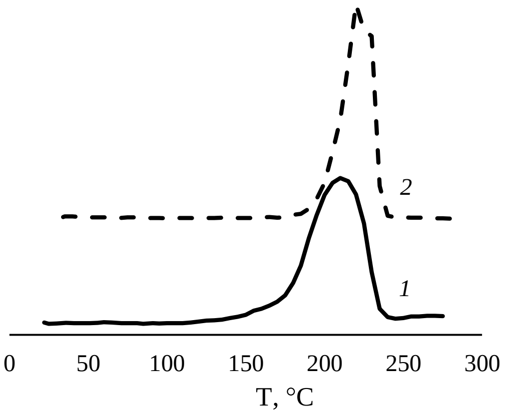

Fig. 2. TPR profiles for sample N 1 and N 2

Рис. 2. Профили TPR для образцов № 1 и № 2

The studies carried out at 2 MPa showed the process temperature has a significant effect on the activity of the catalyst. The samples had high catalytic activity. The activity was expressed in terms of specific productivity for methanol. The activity of both samples increases with temperature and passes through a maximum at 260 °C (Fig. 3). Methanol productivity of the industrial catalyst (sample #1) was 0.066 $\mu mol \cdot s^{-1} \cdot g_{cat}^{-1}$. The sample synthesized by the coprecipitation method had an activity of 0.051 $\mu mol \cdot s^{-1} \cdot g_{cat}^{-1}$. A further increase in temperature leads to a decrease in the specific productivity concerning methanol, and a more intense decrease is observed for the industrial catalyst. The drop in activity may be due to thermal deactivation of the sample, which occurs due to a decrease in the active copper surface as a result of the sintering of its particles.

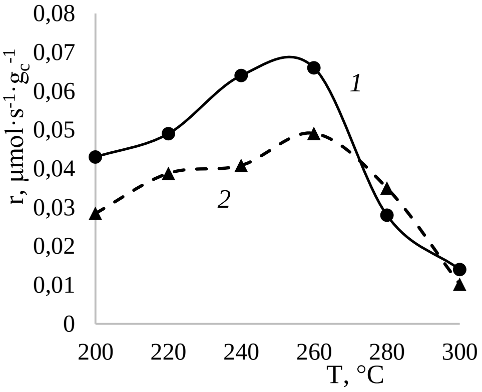

Fig. 3. Productivity for methanol on sample N 1 (1) and on sample N 2 (2)

Рис. 3. Производительность по метанолу на образце № 1 (1) и на образце № 2 (2)

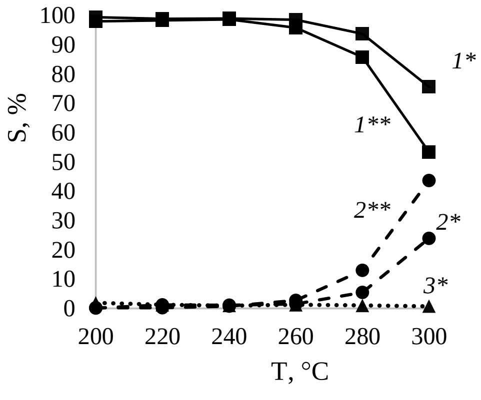

Fig. 4. Selectivity on methanol (1), methane (2), dimethyl ether (3) * is for sample N 1, ** is for sample N 2

Рис. 4. Селективность по метанолу (1), метану (2), диметиловому эфиру (3) * – образец № 1 ** – образец № 2

The methanol selectivity of the obtained sample is higher than that of the industrial one over the entire temperature range (Fig. 4). In the range of 200-240 °C, this indicator slightly increases for both catalysts, reaching a maximum at 240 °C. The maximum values are 98.6% for an industrial sample and 98.97% for a synthesized sample. A further increase in temperature up to 300 °C leads to a more intense decrease in the selectivity of the industrial catalyst and an increase in the difference between the samples. The synthesized sample has a more stable selectivity to methanol.

The selectivity to dimethyl ether in the industrial sample was kept at approximately the same level of ~1% over the entire temperature range. An insignificant amount of ethanol ~0.3%, propanol, and C_{5+} alcohols are fixed at temperatures above 280 °C.

The data obtained on the activity and selectivity of $CuO/ZnO/Al_2O_3$ are in good agreement with the literature data [30, 31].

Adsorption properties of catalysts

Experimental data on the structural properties of the methanol synthesis catalyst suggest that the catalysts have the same chemical and phase composition. They have some differences in texture characteristics (Fig. 2). Otherwise, they do not have any significant differences in the intensities of reflections in XRD patterns (Fig. 1), CSR sizes, specific surface area and porosity (Table 1 and Fig. 4). However, the activity and selectivity of catalysts in the studied temperature ranges differ significantly. This fact can be explained by the different adsorption capacity of catalysts with concerning reactants, primarily hydrogen.

We calculated the material balance of the catalytic systems using the data of the complex of synchronous thermal analysis and mass spectrometry. The method took into account the probability of the appearance of reactants fragments, as well as impurities in an inert gas, determined by the chromatographic method (Table 2).

As follows from the material balance, the main amount of hydrogen bound to the surface of the $CuO/ZnO/Al_2O_3$ catalyst is desorbed at 30 °C and below. However, most of it is molecular adsorption form, which can be explained by the experimental conditions and the actual saturation of the catalyst with hydrogen in the solvent. The remaining 15% of hydrogen is completely removed from the catalyst surface in the temperature range from 100 to 900 °C. The obtained values of the total hydrogen content on the catalyst are a combination of the values of adsorbed, occluded, and dissolved hydrogen, as well as hydrogen dissolved in water.

Table 3 shows the temperatures and heats of desorption of hydrogen individual adsorption forms, which allows us to draw conclusions about the energy of the "hydrogen-metal" bond with certain approximations.

Table 2

Material balances of the investigated samples of $CuO/ZnO/Al_2O_3$ catalyst

***Таблица 2*. Материальные балансы исследуемых восстановленных образцов $CuO/ZnO/Al_2O_3$ катализатора**

Molecular masses*, Da	The amount of a component, mg	
	Sample #1	Sample #2
1	$4.78 \cdot 10^{-9}$	$3.57 \cdot 10^{-9}$
2	$0.77 \cdot 10^{-5}$	$0.81 \cdot 10^{-5}$
8	0.0002	0.0002
16	0.0789	0.0452
17	3.8699	4.2578
18	38.445	34.235
19	0.0555	0.0235
20	0.0411	0.0632
32	0.6532	0.4569
33	0.0022	0.0030
34	0.0022	0.0030
Solid phase	22.155	18.118
Total	65.3032	57.2058

Notes: * Molecular masses of fragments of the catalytic system components according to the international database NIST

** Fragments of the studied system with molecular weights of 32, 33, and 34 correspond to oxygen, which is inevitably part of argon

Примечания: * Молекулярные массы осколков компонентов каталитической системы по данным международной базы NIST

** Фрагменты исследуемой системы с молекулярными массами 32, 33 и 34 соответствуют кислороду, который неизбежно содержится в аргоне

Table 3 shows the data of all recorded thermal effects at 200-950 °C. Thermal effects at 200 °C and below are difficult to interpret unambiguously due to the presence of side processes associated with the evaporation of water and its adsorbed molecules. At temperatures above 800 °C, an increase in the catalyst mass and an exothermic thermal effect were observed in all experiments, which is explained by the oxidation of metallic copper and zinc with oxygen contained in argon.

The results of a comprehensive study of hydrogen adsorption on methanol synthesis catalysts with the composition $CuO/ZnO/Al_2O_3$ make it possible to discuss several processes occurring during hydrogen desorption, e.g. oxidation of active sites of the catalyst surface with oxygen and water. The method also makes it possible to establish the values of the total amount of adsorbed hydrogen, as well as the amount of reactive hydrogen in the reduction of carbon monoxide and carbon dioxide subsequently.

According to the data obtained, it can be argued that the catalyst surface is energetically inhomogeneous for hydrogen. Based on the experimental data, the presence of six individual forms of adsorbed hydrogen is shown: one molecular and five atomic. Only two forms match for both catalysts, which are designated by numbers 4 and 5 in Table 3. At the same time, for sample #2, Form 1 is unlikely to be active, since its desorption temperature is lower than the main temperature of the experiment (see Fig. 1). It can be assumed that the high activity of sample #1 at low temperatures is explained by the presence of forms 2 and 3. With an increase in the temperature of the experiment, the contribution of forms 2 and 3 decreases, thus the activity of both catalysts becomes close.

Table 3

Thermodynamic effects of desorption of hydrogen atomic forms from the surface of the catalytic system "$CuO/ZnO/Al_2O_3$ - water" at 200-950 °C (reduction conditions: medium – hydrogen; pressure – atmospheric; temperature rise rate – 4°C; maximum temperature 950 °C)

Таблица 3. Термодинамические эффекты десорбции атомарных форм водорода с поверхности каталитической системы «$CuO/ZnO/Al_2O_3$ катализатор – вода» в интервале температур от 200 до 950 °C (условия восстановления: среда – водород; давление – атмосферное; скорость подъема температуры 4 °C; максимальная температура 950 °C)

Peak No.	Heat effects		Peak area, °C^2	$\Delta_d H^o(T)$ kJ/g$_{cat}$
	T_1, °C	T_2, °C		
Industrial catalyst sample (22.155 mg)				
1*	352.6	362.5	0.219	0.13
2*	422.1	432.1	0.203	0.12
3*	695.3	705.2	0.268	0.05
4**	814.5	824.4	0.075	-0.15
Coprecipitation catalyst sample (18.118 mg)				
1*	196.7	199.2	0.139	0.0207
2*	713.5	722.7	0.7	0.386
3*	802.4	831.4	0.6327	10.988
4**	905.8	913.2	0.00151	-0.067

Notes: T_1 – initial heat effect temperature; T_2 – final heat effect temperature

* – hydrogen desorption, ** – oxidation of copper

Примечания: T_1 – начальная температура теплового воздействия; T_2 – конечная температура теплового воздействия

* – десорбция водорода, ** – окисление меди

CONCLUSION

This work shows the fundamental possibility of studying the properties of the catalyst surface towards hydrogen and the thermodynamics of reactive gases desorption using a complex of synchronous thermal analysis and mass spectrometry. The data obtained can form the basis for the development of a scientifically based selection of catalytic systems for reactions involving hydrogen-containing gases subsequently.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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