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# ИССЛЕДОВАНИЕ СВОЙСТВ $CuO-ZnO-Al_2O_3$ КАТАЛИЗАТОРОВ ДЛЯ СИНТЕЗА МЕТАНОЛА

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***В работе проведено комплексное исследование современных промышленных каталитических систем марки ММ-7 и К. Лучший образец – катализатор марки ММ-7 исследован до и после 5 лет промышленной эксплуатации в крупнотоннажном агрегате синтеза метанола. Для изучения физико-химических характеристик катализаторов были использованы методы рентгенофазового анализа, сканирующей электронной микроскопии, низкотемпературной адсорбции-десорбции азота, индикаторный метод Гаммета, газовой хроматографии. Проведено температурно-программируемое восстановление образцов. В работе приведены данные по фазовому составу катализаторов, их морфологии, удельной поверхности, дисперсности и размеру частиц меди. Установлено, что катализатор марки ММ-7 по своим физико-химическим характеристикам и каталитической активности превосходит катализатор марки К. Исследование отработанного катализатора после 5 лет промышленной эксплуатации показало, что потеря активности происходит по причине термической дезактивации и отравления каталитическими ядами – соединениями серы. Каталитическая активность образца оценивалась по удельной производительности по метанолу на каталитической установке высокого давления ПКУ-2. Условия эксперимента были максимально приближены к промышленным: давление в реакторе составляло 2,0 МПа, интервал исследуемых температур 200-300 °С, объемная скорость газа 8705 $ч^{-1}$. Максимальная удельная производительность по метанолу достигается при 260 °С и составляет 0,07 мкмоль/гкат·с. Также приведены данные образцов по селективности по метанолу. Максимальная селективность по метанолу достигается на катализаторе марки ММ-7 и составляет 98,7 % при 220 °С. В качестве побочных продуктов, образующихся в процессе синтеза метанола, идентифицированы метан и диметиловый эфир.***

**Ключевые слова:** $CuO-ZnO-Al_2O_3$ катализатор, синтез метанола, физико-химические свойства, активность, промышленная эксплуатация, дезактивация

# STUDY OF PROPERTIES OF $CuO-ZnO-Al_2O_3$ CATALYSTS FOR METHANOL SYNTHESIS

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***In this work, a comprehensive study of modern industrial catalytic systems of the MM-7 and K brands was carried out. The best sample, the catalyst of the MM-7 brand, was investigated before and after 5 years of commercial exploitation in a large-scale methanol synthesis unit. To study the physicochemical characteristics of the catalysts, the methods of X-ray phase analysis, scanning electron microscopy, low-temperature nitrogen adsorption-desorption, Hammett indicator method, and gas chromatography were used. Temperature-programmed recovery of the samples was carried out. The paper presents data on the phase composition of catalysts, their morphology, specific surface area, dispersion and size of copper particles. It was found that the MM-7 catalyst in terms of its physicochemical characteristics and catalytic activity is better than the K catalyst. The study of the spent catalyst after 5 years of commercial exploitation showed that the loss of activity occurs due to thermal deactivation and poisoning with catalytic poisons - sulfur compounds. The catalytic activity of the sample was evaluated by the specific productivity for methanol in the catalytic high-pressure unit PKU-2. The conditions of experiment were as close as possible to industrial ones: the pressure in the reactor was 2.0 MPa the range of the investigated temperatures was 200-300 °C, and the volume hourly space velocity of 8705 $h^{-1}$. The specific productivity for methanol is reached 0.07 μmol/gcat·s at 260 °C. The data of the samples on the selectivity to methanol are also given. The maximum selectivity for methanol is reached with a catalyst of the MM-7 brand and is 98.7% at 220 °C. Methane and dimethyl ether have been identified as by-products at the methanol synthesis.***

**Key words:** $CuO-ZnO-Al_2O_3$ catalyst, methanol synthesis, physicochemical properties, activity, commercial exploitation, decontamination

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## INTRODUCTION

Methanol is an important chemical compound with an extremely broad range of uses. In 2017, the global production of methanol reached about 110 million tons [1]. In the period from 2017 to 2021, significant growth rates of the production of this product are projected from 11.16 to 13.86% [2]. Russia is currently the world's leading methanol producer, traditionally export-oriented. Methanol production in Russia at the end of 2017 amounted to 4.07 mil. t and it is predicted that in the period 2019-2023 its production in the country will continue to grow [3]. In the chemical industry, methanol is used in the production of formaldehyde, aromatic compounds, ethylene, acetic acid, and other chemical products [4]. Also, at present, a significant share of methanol is used in the energy sector, which is a factor in the growth of its world consumption. Methanol is considered an ideal alternative fuel fast dismissing oil and gas resources [5]. Therefore, there is an increase in consumption of methanol as a raw material for the production of fuel additives methyl tertiary butyl ether, olefins, dimethylether, dimethylcarbonate, biodiesel fuel, and the direct blending into gasoline is also used [6].

Industrially, methanol is produced from syngas ($H_2/CO_2/CO$), which is mainly produced from natural gas. The process of methanol synthesis is carried out at a temperature of 200-300 °C and a pressure of 5-10 MPa over $Cu-ZnO-Al_2O_3$ catalysts [7].

Analysis of literature sources shows that a lot of publications [8-10] are devoted to the issues of methanol synthesis, including those published in recent years [11-12]. The first studies devoted to copper-containing catalysts for methanol synthesis appeared in print about a hundred years ago [13]. In most works, the main attention is paid to the optimization of the methanol synthesis process [14] and the study of the ternary catalytic system $Cu-ZnO-Al_2O_3$ [15-16].

Despite the large number of studies devoted to this catalyst, interest in them does not wane for several reasons: the great importance of these catalysts for industry and the development of new technologies and units for the synthesis of methanol, including a large unit capacity. The mechanism of this reaction is still not fully understood, although there are many discussed theories [17-19]. Currently, the search for effective promoting additives for these industrial catalysts continues [20-22].

Current low-temperature catalysts for methanol synthesis are based on the composition of oxide compounds of copper, zinc, aluminum and chromium [23-25].

In Russia, there is no competitive production of catalysts for methanol synthesis, therefore, catalysts from the following companies are used at Russian enterprises: Johnson Matthey (Great Britain), Haldor Topsoe (Denmark), Clariant (Germany), which today are the leading manufacturing companies methanol synthesis catalysts. In this regard, import substitution and the development of our own production of catalysts for methanol synthesis are of strategic importance both for the chemical industry of Russia and for its economy [13].

Since the methanol production process is large-scale, researchers working on the development of catalytic systems face a number of difficulties. The main one is the transition from laboratory samples to industrial ones, which is complicated by the lack of data on the physicochemical properties of catalysts, as well as forecasts on the duration of their operation in real industrial conditions. As noted earlier, many works have been published on the preparation and study of catalysts for the synthesis of methanol, but most of them are of fundamental orientation [2, 4, 7, 9]. An important reference point for the development of new catalytic systems is the availability of data on the patterns of formation of their structure and the physicochemical properties of existing analogues. The presence of an array of such data is the basis for improving existing technologies for obtaining new types of catalysts, as well as technologies and equipment, both for the production of the catalysts themselves, and for the implementation of technological processes in units of new generations.

The purpose of the work is to study the physicochemical and catalytic properties of CuO-ZnO-$Al_2O_3$ methanol synthesis catalysts used in methanol synthesis units of high unit capacity before and after operation in industrial conditions.

## EXPERIMENTAL PART

Materials MM-7 brand catalysts before and after industrial explotation was chosen as the object for research. The running time of the MM-7 catalyst in an industrial unit was 5 years.

Characterization X-ray diffraction (XRD) was performed on DRON-3M with Cu Kα – radiation (λ = 0.15405 nm, the Ni-filter) over the range 2θ = 25-70°. Source operating at 40 kV and 20 mA. Scanning rate is 2º $min^{-1}$. The initial slit is 2 mm, the detector slit is 0.25 mm. XRD analyzes data were identified with the help of Mincryst and PDF-4 databases. Interplanar distances are calculated using the Wolfe-Bragg equation [26]:

$$d = \lambda/2\sin\theta \quad (1)$$

where λ is the wavelength, Θ = Xc/2, the diffraction angle, which was calculated from the position of the center of gravity of the reflex. The specific surface area of the catalysts was determined by the BET method using Sorbi MS device. Before the study, the samples was dried in a stream of nitrogen at a temperature of 200 °C for 60 min. Adsorption-desorption isotherms were obtained by the dynamic method of low-temperature nitrogen adsorption-desorption. The scanning electron microscope measurement and energy dispersive analysis was carried out on Vega 3SBH (TESCAN), equipped with an attachment for energy dispersive analysis Oxford Instruments.

The study of the acid-base properties of the catalyst surface was carried out by the method of adsorption of acid-base indicators (Hammett indicator method) with pKa values in the range from 1.3 to 14.2, according to the method described in [27].

The study of the mechanical properties of the catalysts was carried out by crushing on a laboratory hydraulic press with a piston diameter of 52 mm. The mechanical strength was expressed as the ultimate compressive strength of the layer (σ), which was calculated by the formula [28]:

$$\sigma = P_c \cdot \left(\frac{D}{d}\right)^2 \quad (2)$$

where $P_c$ is the average statement of the pressure gauge, kgs/$cm^2$; D – piston diameter, cm; d – tablet diameter, cm.

The catalytic activity of the catalysts was determined in the methanol synthesis in the catalytic high-pressure unit PKU-2 at a pressure of 2.0 MPa. The catalyst with a weighed amount of 0.5 g with fraction 0.3-0.6 mm) was loaded into a fixed bed steel reactor, which was installed in the furnace. The required gas mixture was supplied to the reactor using gas flow regulators. The composition of the gas feed was $H_2/CO/CO_2/N_2$ = 68.2:21.04:8.13:1.3 (vol. %). A volume hourly space velocity of 8.705 $h^{-1}$. The temperature in the reactor varied from 200 to 300 °C. To determine the reaction products, we used a Kristalluks-4000M gas chromatograph with two types of detectors (FID and TCD). Samples were then reduced *in-situ* stepwise increase from 200 to 300 °C at 1 °C $min^{-1}$ using a 20% $H_2$/ 80% $N_2$ gas mixture.

## RESULTS AND DISCUSSIONS

The crystalline structures of industrial and after industrial samples were characterised by XRD, and the results are summarised in Fig. 1. The XRD patterns

of industrial catalysts contain pronounced peaks corresponding to the diffraction of the ZnO with a zincite structure and CuO with a tenorite structure. Broadened reflections in the range 2θ = 30-40°, corresponding the formation of copper-zinc solid solution. However, despite the similar composition, the X-ray diffraction patterns of catalysts K and MM-7 have significant structural differences. The X-ray diffraction pattern of sample K shows the presence of a large number of pronounced reflections, which indicates the crystallinity of the catalyst structure (Fig. 1a). The MM-7 catalyst is partially crystallized. The X-ray diffraction pattern shows diffraction reflections from the crystalline phase and diffuse halos from the amorphous phase (Fig. 1b). Zinc oxide is required in the composition of the catalyst to maintain high dispersion of copper and prevent sintering of its particles during the reaction [29]. No peaks related to oxide alumina, magnesium could be distinguished, indicative of good dispersion and low concentration additives. The processing of X-ray diffraction data and the study of the fine crystal structure of the catalyst show that the average crystallite size of copper oxide is 9 and 7 nm for K and MM-7 brand catalysts, respectively.

The X-ray diffraction pattern of a spent catalyst (Fig. 1c), after 5 years of industrial operation in a large-scale methanol production unit, shows clearly pronounced reflections of zinc copper oxides, which is due to an increase in crystallite size during thermal deactivation of the catalyst. For example, the size of copper oxide crystallites is 17 nm. Compounds of catalytic poisons were not detected using XRD.

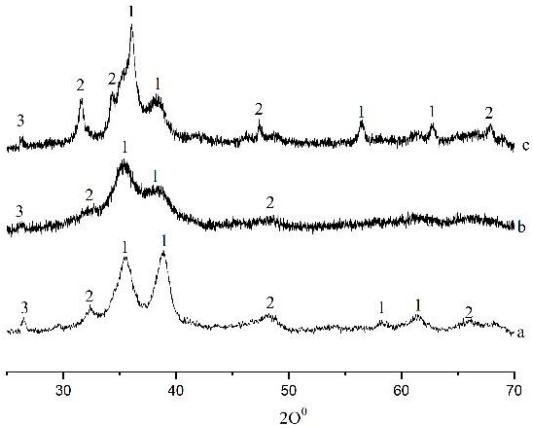


Fig. 1. The X-ray pattern of K (a), MM-7 (b), MM-7spent (c) brand catalyst 1 – CuO; 2 – ZnO; 3 – C
Рис. 1. Рентгенограмма катализатора марки К (a), ММ-7 (b) и ММ-7spent (c) 1 – CuO; 2 – ZnO; 3 – C

XRD does not give a clear picture of the composition of the catalyst. From the data of energy dispersive analysis it can be seen that in the composition of the K catalyst, in addition to the main components, there is a promoting additive (Mg). At the same time, the X-ray diffraction pattern lacks reflections characteristic of magnesium oxide, which can be explained by its small amount, which complicates its detection and/or its X-ray amorphous state. Magnesium is added to the catalyst because it promotes the formation of crystallites during the preparation of the catalyst and their distribution over the surface of the support so that a high copper surface is maintained during the entire service life of the catalyst, which leads to an increase in the dispersion of copper, as mentioned in [25]. The spent catalyst found 8.22% of the mas. sulfur, which indicates not only thermal deactivation of the contact, but also its poisoning with sulfur compounds. The X-ray diffraction patterns of all samples show a reflection at 2θ ≈ 26°, which is characteristic of graphite. Graphite was added to catalysts (up to 2 wt. %) to improve formability during tableting.

***Table 1***

**Elemental analysis data for industrial catalysts**

***Таблица 1.* Данные элементного анализа катализатора**

| Sample | Elemental composition, % wt. | | | | | |
|---|---|---|---|---|---|---|
| | Cu | Zn | Al | Mg | O | S |
| K | 54.95 | 21.96 | 2.90 | 0.44 | 19.75 | - |
| MM-7 | 49.29 | 21.83 | 5.24 | - | 23.64 | - |
| MM-7 $_{spent}$ | 45.27 | 20.28 | 3.45 | - | 22.78 | 8.22 |

SEM images of catalysts are depicted in Fig. 2. Catalyst brand K consists of particles that form aggregates of a loose sponge-like structure. The MM-7 catalyst is a “monolithic” structure consisting of aggregates of various sizes and shapes.

The data of the low-temperature nitrogen desorption method, obtained by the BET method, show that the samples have a developed specific surface area, which is 84.0 ± 0.5 $m^2/g$ and 101 ± 1 $m^2/g$ for samples of grades K and MM-7, respectively. Nitrogen adsorption-desorption isotherms can be classified as type IV (Fig. 4 a, b, c). Isotherms of this kind are characteristic of objects with transition pores (mesopores) according to Dubinin's classification, that is, pores with diameters ranging from tens to hundreds of angstroms. By processing nitrogen adsorption-desorption isotherms, it has been found that there are no micro- and macropores in the samples. The distribution of pores relative to their total volume (Table 2) shows that catalysts K and MM-7 have mesopores with sizes from 3.5 to 30 nm and 3.5 to 15, respectively. Pores with a size of 5 to 15 nm are predominant. The total pore volume is 0.085 and 0.173 $cm^3/g$ (Table 2). The specific surface area of the spent catalyst decreases to 55 $m^2/g$,

and the total pore volume to 0.092 $cm^3/g$. During operation, the catalyst is reduced before starting work; the active phase is metallic copper. Obviously, a decrease in the surface occurs due to thermal deactivation – partial sintering of the catalyst and, as a consequence, blocking of the catalyst pores and a decrease in their number and volume (Tables 2, 3).

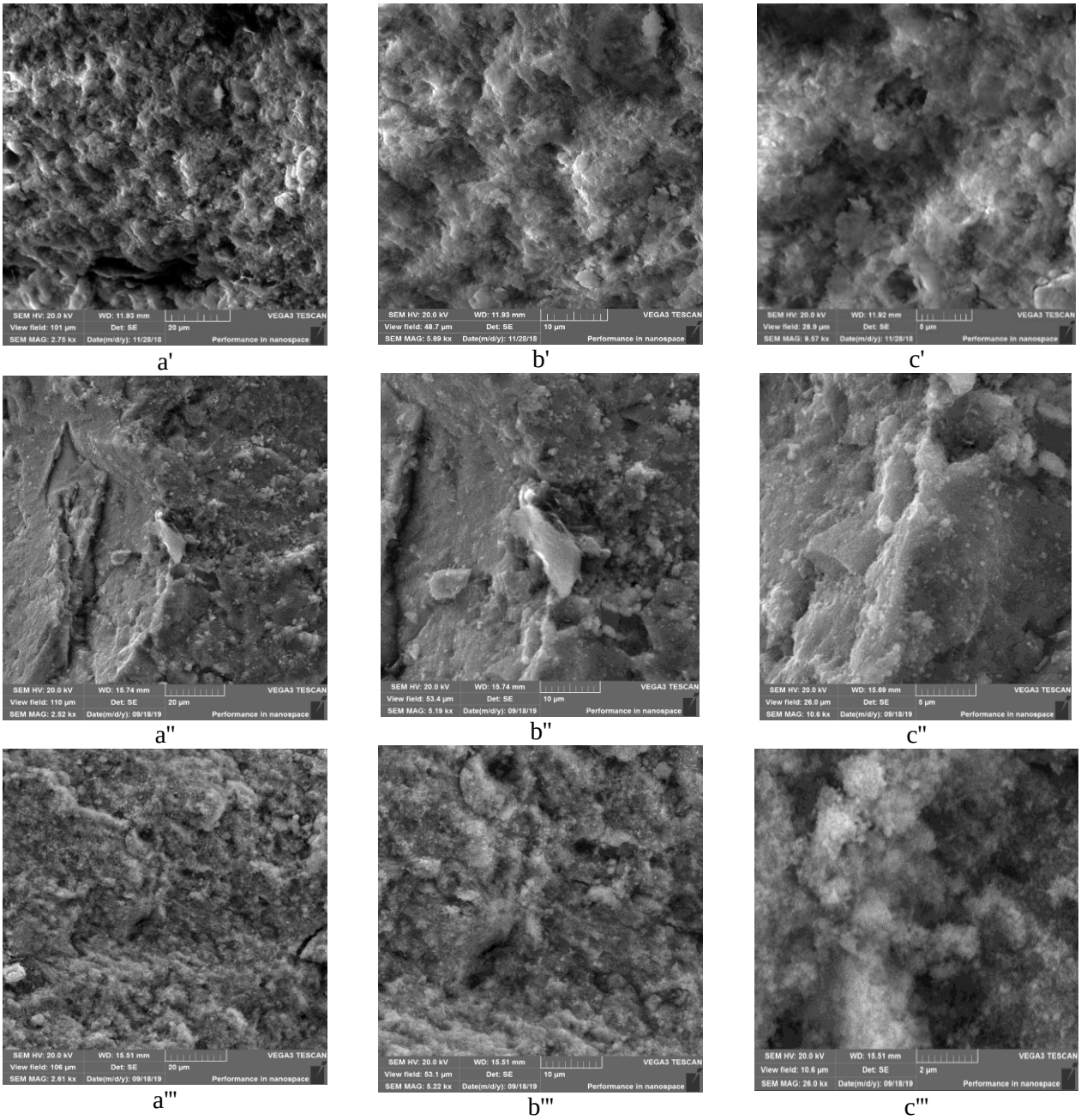


Fig. 2. SEM images of K (a), MM-7 (b), MM-7spent (c) brand catalysts with 20 μm (,) ,10 μm (,,) and 5 μm (,,,) resolution
Рис. 2. СЭМ изображения катализатора марки К (a), ММ-7 (b) и ММ-7отр (c) с разрешением 20 мкм (,), 10 мкм (,,) и 5 мкм (,,,)

The data of the low-temperature nitrogen desorption method, obtained by the BET method, show that the samples have a developed specific surface area, which is 84.0 ± 0.5 $m^2/g$ and 101 ± 1 $m^2/g$ for samples of grades K and MM-7, respectively. Nitrogen adsorption-desorption isotherms can be classified as type IV (Fig. 4 a, b, c). Isotherms of this kind are characteristic of objects with transition pores (mesopores) according to Dubinin's classification, that is, pores with diameters ranging from tens to hundreds of angstroms. By processing nitrogen adsorption-desorption isotherms, it has been found that there are no micro- and macropores in the samples. The distribution of pores

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***Table 2***

**The distribution of the pore relative to their total volume**

***Таблица 2.*** **Распределение пор относительно их общего объема**

| $D_i$, nm | Catalyst | | |
|---|---|---|---|
| | K | MM-7 | MM-$7_{spent}$ |
| | $dV_i/V_{sum}$, % | $dV_i/V_{sum}$, % | $dV_i/V_{sum}$, % |
| 3.4957 | 12.63 | 6.54 | 8.2999 |
| 4.4297 | 3.67 | 3.2256 | 1.8165 |
| 5.8631 | 20.77 | 23.045 | 12.098 |
| 8.4406 | 25.13 | 47.635 | 18.216 |
| 14.998 | 35.60 | 19.554 | 34.684 |
| 29.351 | 2.19 | - | 24.886 |

The data obtained for the specific surface area, total pore volume and mechanical strength of the catalysts are summarized in Table 3.

***Table 3***

**Physical characteristics of CuO-ZnO-$Al_2O_3$ catalyst**

***Таблица 3.*** **Физические характеристики CuO-ZnO-$Al_2O_3$ катализатора**

| Sample | Specific surface area, $S_{уд}$, $m^2/g$ | Total pore volume, $\sum V_{пор}$, $cm^3/g$ | Mechanical strength of bed, MPa | Granule sizes, mm |
|---|---|---|---|---|
| K | 84.0 ± 0,5 | 0.085 | 20.0 | 5×5 |
| MM-7 | 101 ± 1 | 0.173 | 22.1 | |
| MM-$7_{spent}$ | 55.0 ± 0.5 | 0.092 | 6.7 | |

On the surface of the K and MM-$7_{otr}$ brand catalyst, the main centers predominate to a large extent, and in the MM-7 brand catalyst the total number of acidic and basic centers is practically equal. Among the main centers, the strongest centers make the largest contribution to the total concentration, their share is 51-86%. Among the acid sites, catalyst K mainly contains sites of weak strength, their contribution to the total concentration of acid sites is 38.0%. In the catalyst MM-7 and MM-$7_{spent}$, acidic centers of medium strength predominate, their proportion is 50-76%. The predominance of the main centers on the surface of the K catalyst determines the value of its acidity function equal to 11.0. On catalyst MM-7, the total number of acidic and basic sites is practically the same, which determines the value of the acidity function of the neutral value 7. The spent catalyst is weakly alkaline.

The reducibility of the industrial catalysts was studied by H2-TPR. Temperature programmed reduction (TPR) was carried out in a Chemisorption analyzer «Chemosorb» instrument in the temperature range 20-310 °C with a heating rate of 10 °C/min using helium as the carrier gas.

TPR profiles of the K, MM-7 brand catalysts showed a sharp peak at 210 and 243 °C, respectively, due to the transformation of CuO to Cu°. The signal for the MM-7 sample modified with magnesium was found to be quite broad compared to the K sample and consists of three peaks at 221, 233 and 243 °C. This fact may indicate the presence of Cu particles in a different state.

The data obtained for the active copper surface, dispersion and average particle size of the catalysts are summarized in Table 4.

***Table 4***

**Chemisorption analysis data**

***Таблица 4.*** **Данные хемосорбционного анализа**

| Catalyst | Active copper surface, $m^2/g$ | Dispersion, % | Average particle size of copper, nm |
|---|---|---|---|
| K | 38.31 | 5.9 | 17.56 |
| MM-7 | 53.19 | 8.2 | 12.64 |

The catalytic activity of the samples in the methanol synthesis reaction was estimated from the methanol productivity in a flow-through unit.

The maximum catalytic activity of all samples is observed in the temperature range 240-280 °C. The MM-7 catalyst has the highest catalytic activity, which is explained by its developed specific surface area and porosity. The maximum is reached at a temperature of 240 °C, the productivity of methanol at which is 0.09 $\mu mol/g_{cat} \cdot s$. Catalyst K is inferior in this value, its productivity at the same temperature is 0.076 $\mu mol/g_{cat} \cdot s$. With a further increase in temperature, the specific productivity for methanol decreases, which may be due to thermal deactivation of the sample, which occurs due to sintering of copper particles. The value of the productivity of the spent catalyst over the entire range of the studied temperatures does not exceed 0.005 $\mu mol/g_{cat} \cdot s$, which is due to its poisoning with sulfur and thermal deactivation.

Analysis of the gas mixture at the outlet of the reactor showed the presence of by-products: methane and DME. It is interesting to note that methanol selectivity decreased with increasing temperature after 240 °C, while the selectivity for both methane and DME increased.

## CONCLUSION

In this study, a comprehensive study of the physicochemical characteristics of $CuO\text{-}ZnO\text{-}Al_2O_3$ methanol synthesis catalysts before and after operation in industrial conditions is carried out. It has been established that, in terms of its physicochemical characteristics and catalytic properties, the MM-7 catalyst is significantly superior to the K catalyst. It has been shown experimentally that the catalytic activity of all samples reaches its maximum at 260 °C and is 0.07, 0.055, and 0.01 $\mu mol/g_{cat} \cdot s$ for the MM-7, K, and MM-$7_{otr}$ catalysts, respectively. It was revealed that the loss of activity during industrial operation occurred due to poisoning of the catalyst with sulfur compounds, as well as thermal deactivation. The higher catalyst bed temperatures may be responsible for the increased formation of methane and DME.

The results of the work performed can be used in the development of new, more efficient catalysts for the methanol synthesis process, and also taken into account when choosing catalysts for industrial operation and identifying the causes of deactivation and prolongation of service life in industrial conditions.

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