



EFFECT OF THE CHEMICAL COMPOSITION OF A COPPER-ZINC-ALUMINUM CATALYST OBTAINED BY MECHANOCHEMICAL SYNTHESIS ON ITS TEXTURAL PROPERTIES

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Abstract. The research studies the influence of the ratio of initial components on the physicochemical and textural properties in the mechanochemical synthesis of catalysts for carbon monoxide conversion. The catalysts were synthesized using copper, zinc, and aluminum oxides in various percentage ratios as precursors. The specific surface area values were determined. Based on the results of X-ray phase analysis, crystallite sizes were calculated. Correlations between the specific surface area and catalyst composition were identified. Mechanochemical activation and subsequent thermal treatment do not change the phase and elemental composition of the catalysts.

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Introduction

Catalysts based on the CuO/ZnO/Al₂O₃ oxide system are an integral part of the chemical industry. They have wide application in large-scale industrial processes such as methanol synthesis [1], water-gas shift conversion of carbon monoxide in ammonia and hydrogen production [2], dimethyl ether synthesis [3, 4], etc. [5–9]. Due to the import substitution, recent efforts have been directed toward the development of technologies for the preparation of new and the improvement of existing catalysts. It ensures the relevance of the research.

The main characteristics of catalysts are their physicochemical and catalytic properties. Catalysts based on the three-component CuO/ZnO/Al₂O₃ oxide system should exhibit high activity and selectivity, mechanical strength, resistance to deactivation by catalytic poisons, and stability during operation [10].

The textural and physicochemical properties of catalysts largely depend on the methods of their preparation [11, 12]. One of the modern methods for the synthesis of catalysts is mechanochemical activation (MCA) [13]. This method is more promising, relevant,



environmentally friendly, and cost-effective compared to other ones. The technology eliminates the disadvantages of traditional synthesis routes by reducing the number of process steps and large volumes of wastewater. In addition, MCA is used to form a defective structure in catalysts and accelerate their chemical interaction processes [14]. Moreover, it also modifies the catalytic properties [15] and enhances the effect of thermal treatment [16].

During catalyst synthesis by MCA, changes occur in the crystal structure of the catalyst, including in the coherent scattering region (CSR). Catalyst activity depends on many factors, such as specific and active surface area, porosity, dispersion of the active metal, and its particle size [17].

The purpose of this study is to demonstrate the effect of the composition of the initial metal oxide mixture used in the synthesis on the change in the CSR of the finished catalyst.

Main body

During the study, a series of CuO/ZnO/Al₂O₃ catalysts for carbon monoxide conversion and methanol synthesis were synthesized. Powdered copper oxide (CuO, chemically pure), zinc oxide (ZnO, chemically pure), and aluminum oxide (γ -Al₂O₃, chemically pure) with densities of 1.9 cm³/g, 0.745 cm³/g, and 1.2 cm³/g, respectively, were selected as initial materials.

The samples were prepared by joint mechanical activation of a mixture of copper, zinc, and aluminum oxides for 15 min, followed by thermal treatment of the resulting mixture at 350 °C for 6 h. Table 1 presents the compositions and ratios of the samples.

Table 1. Chemical composition of the studied samples

No.	ZnO, wt. %	CuO, wt. %	Al ₂ O ₃ , wt. %
I	30	60	10
II	35	55	10
III	40	50	10
IV	45	45	10
V	50	40	10
VI	55	35	10
VII	60	30	10
VIII*	25	57	18

* – the composition of the sample was selected based on literature analysis.

Mechanochemical synthesis was conducted in a vibratory roller-ring mill VM-4 (Czech Republic). It is designed for grinding (dry or wet) of bulk materials in continuous mode. Characteristics are as follows: impact-shear action on the ground material, oscillation frequency is 930 min⁻¹; vibration amplitude in the radial direction is 10 mm, in the axial direction is 1 mm; mass of grinding bodies is 1194 g, mass of loaded material is 20.0–40.0 g; energy intensity of the mill under these parameters is 0.878–1.754 kW/kg.

Qualitative X-ray analysis was conducted on a POWDIX 600 X-ray diffractometer using CuK α radiation ($\lambda = 0.15406$ nm, Ni filter). The power supply parameters were 30 kV and 5 mA. A high-speed silicon linear detector was used. Scanning was performed in continuous mode, i.e., there were no delays at specific points. The method consists in comparing the interplanar spacings, lines, and their intensities obtained from the analysis of the diffractograms of the substances under study with tabulated data. The interpretation of the X-ray analysis results was performed using the Minkrist database.



The specific surface area and porosity were determined by low-temperature nitrogen adsorption using the BET method on a Sorbi-MS instrument. It is used for measuring textural characteristics of disperse and porous materials by low-temperature adsorption of inert gases.

Energy-dispersive analysis and surface morphology studies were performed on a VEGA 3 SBH TESCAN electron microscope. The elemental composition was determined using an X-ray energy-dispersive spectrometer (Oxford Instruments Nano Analysis, UK) with an X-ACT detector.

The calculation of coherent scattering regions for copper was performed according to the following formula:

$$D_{\text{circCu}} = \frac{K\lambda}{L\cos\theta};$$

where K is the Scherrer constant; λ is the X-ray wavelength; L is the peak width at half height; θ is the peak position.

Fig. 1 shows the X-ray diffraction patterns of a series of catalyst samples mechanically activated for 15 min without subsequent thermal treatment. All phases in the diffractograms were identified using the Minkrist database. The copper oxide phase corresponds to CuO (card No. 10200), zinc oxide – ZnO (card No. 5368), and aluminum oxide – Al_2O_3 (card No. 1029), respectively.

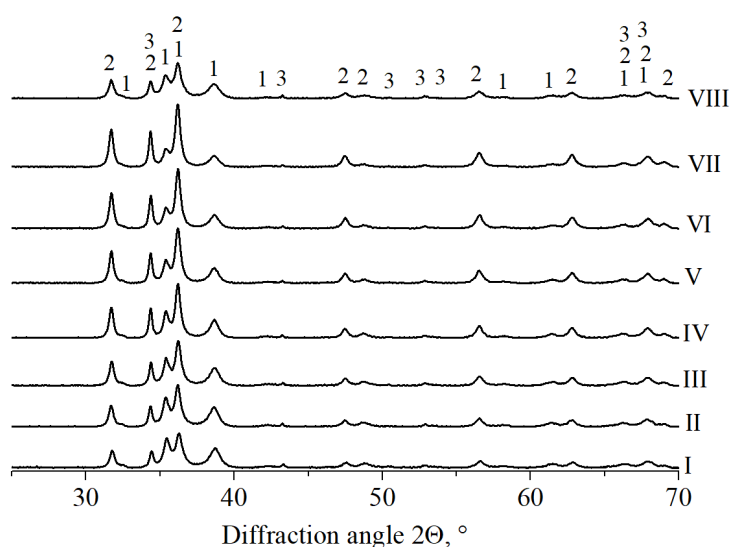


Fig. 1. X-ray diffraction patterns of samples synthesized by MCA for 15 min without calcination. The designation of the diffractograms corresponds to the sample numbers presented in Table 1. 1 – CuO; 2 – ZnO; 3 – Al_2O_3 .

With an increase in the zinc oxide content (Table 1), a noticeable increase in the intensity of the corresponding phase reflections is observed; changes are especially evident in the regions of 30–32° and 33–34°. In addition, in the region of 32–33° a gradual disappearance of the peak characteristic of the copper oxide phase occurs due to a gradual change in its amount in the samples (Table 1). The reflections of the phases characteristic of aluminum oxide change to a minor extent. However, despite all changes in the composition, peak broadening is observed in the region of 30–40°. It shows the formation of solid solutions and interaction between copper and zinc oxides, confirmed by an increase in crystallite size. X-ray diffraction patterns of the calcined samples were also obtained (Fig. 2).

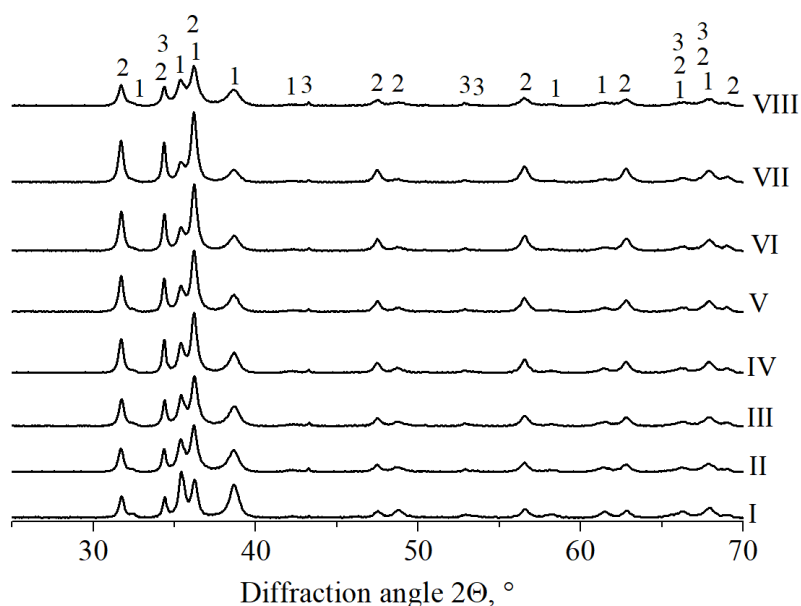


Fig. 2. X-ray diffraction patterns of samples synthesized by MCA for 15 minutes and calcined at 350 °C for 6 hours. The designation of the diffractograms corresponds to the sample numbers presented in Table 1. 1 – CuO; 2 – ZnO; 3 – Al₂O₃.

As a result of calcination of the samples at 350 °C, no significant changes in the phase composition occur. An increase in the intensity of the main reflections of the oxide phases is observed. As a result, the samples become more crystalline during calcination.

A study of the specific surface area (S_{sp}) of the synthesized samples was conducted. The results are presented in Table 2. After MCA without calcination, an increase in the specific surface area was observed with increasing zinc oxide content. Calcination makes the change in this parameter less linear, while maintaining the general trend toward an increase.

Based on the results of X-ray phase analysis, crystallite sizes (D_{CSR}) were calculated. They are approximately equal to the size of the coherent scattering region. Table 2 presents the average CSR values for the copper oxide phase. Similarly, to the specific surface area, with an increase in the zinc oxide content in the sample, a wave-like increase in the crystallite size of copper oxide occurs.

Table 2 – Textural properties of the studied samples

Sample No.	S_{sp} , m ² /g		D_{circCu} , nm	
	Samples after MCA	Samples after MCA and heat treatment at 350 °C	Samples after MCA	Samples after MCA and heat treatment at 350 °C
I	15.8±0.2	18.7±0.3	15±0.5	18±0.7
II	19.1±0.1	26.3±0.3	20±0.9	19±0.7
III	17.9±0.1	19.3±0.1	19±0.9	28±1.3
IV	19.7±0.1	22.6±0.1	18±0.8	20±1.1
V	21.0±0.0	17.2±0.1	17±0.8	22±1.2
VI	23.8±0.0	27.2±0.1	19±1.0	32±2.1
VII	24.1±0.1	24.1±0.1	23±1.1	18±0.9
VIII	19.6±0.1	22.3±0.1	19±0.7	24±2.0



Table 3 presents the change in elemental composition during the synthesis and thermal treatment of the samples.

Table 3 – Elemental composition of the samples

Sample No.	Element, %			
	O	Al	Cu	Zn
Samples after MCA				
I	22.8	5.3	47.6	24.3
II	22.9	5.6	42.6	28.9
III	22.8	5.5	38.1	33.6
IV	22.7	5.4	31.6	40.3
V	22.8	5.7	30.5	41.0
VI	22.5	5.2	26.6	45.7
VII	22.7	5.6	22.8	48.9
VIII	23.7	7.3	40.2	28.8
Samples after MCA and heat treatment at 350 °C				
I	22.7	5.3	46.5	25.5
II	22.9	5.7	42.2	29.2
III	22.7	5.4	40.3	31.6
IV	22.8	5.8	33.0	38.4
V	23.0	6.1	30.4	40.5
VI	22.7	5.6	27.0	44.7
VII	23.0	6.1	23.4	47.5
VIII	24.1	8.2	39.6	28.1

The percentage content of each component varies proportionally to the corresponding ratio of the starting raw materials. The elemental composition indicates the absence of iron in the samples. However, it could be a result of a mill wear. Calcination of the synthesized samples also showed no change in chemical composition.

The surface morphology shown in Figure 3 demonstrates the effect of copper content on the particle size of the resulting catalyst. The particle size of sample VII, containing the least amount of copper, is much larger than that of the other samples. At the same time, this sample has the highest specific surface area.

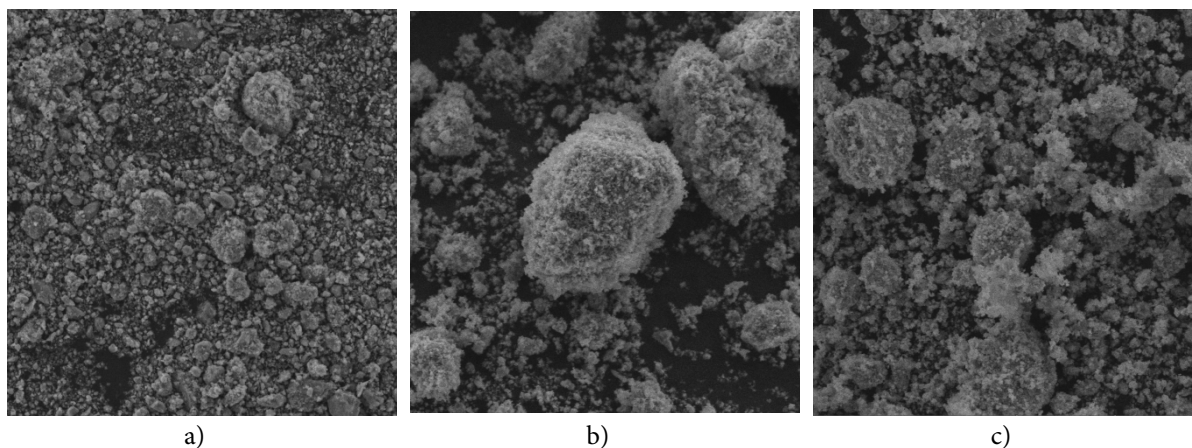


Fig. 3. Micrographs of the synthesized samples. Samples: a) – I; b) – VII; c) – VIII



Conclusions

As a result, the effect of the ratio of the initial components in the mechanochemical synthesis of carbon monoxide conversion catalysts on their textural characteristics were studied. The mechanochemical synthesis forms a solid solution from the initial copper, zinc, and aluminum oxides, which was confirmed by X-ray diffractometry.

A decrease in the copper content leads, in some samples, to an increase in the CSR size. Upon calcination of the samples, an increase in crystallite size is observed. Calcination of the samples after mechanochemical synthesis does not change the phase and elemental composition of the catalysts.

The energy-dispersive analysis performed showed that optimal conditions for the synthesis of the catalysts were selected during mechanochemical activation. It resulted in the absence of iron in the elemental composition of all obtained samples, which could have been introduced from the grinding media.

According to the total data obtained, the obtained samples of copper-zinc-aluminum composites can be used as catalysts for carbon monoxide conversion or methanol synthesis.

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Conflict of interest

The authors declare that there are no conflicts of interest to report in this paper.

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