

# RECYCLING OF CARBONE OXIDES (CO, CO<sub>2</sub>) CONVERSION INTO METHANOL AT ATMOSPHERIC PRESSURE OVER MECHANOCHEMICAL ACTIVATED CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> CATALYST

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## Abstract

The catalytic process for methanol production by synthesis gas conversion under the conditions of mechanochemical activation (MCA) of copper-zinc-aluminum oxide catalyst in the temperature range 160–280 °C at a pressure of 0.1 MPa are investigated. The use of mechanical action force is one of the promising ways to improve the activity of heterogeneous catalysts designed to simplify the manufacturing process lines, improving the efficiency of catalytic processes and reduce the cost of the target product. Given the importance of technology for methanol production on copper-zinc-aluminum oxide catalysts and high demand for methanol in the world [1–3], clarification of the peculiarities of the process of methanol production by synthesis gas conversion in terms of mechanical load on the catalyst is important in scientific and applied ways.

It is established that specific catalytic activity, performance of methanol synthesis catalyst and the conversion of initial reagents are increased in the conditions of mechanochemical activation, because of the increasing concentration of defects and formation of additional active centers. It is revealed that mechanochemical treatment of copper-zinc-aluminum oxide catalyst can reduce reaction initiation temperature and optimum temperature synthesis by 20–30 °C, and increase the maximum performance of the catalytic system.

Increase of the catalyst activity under mechanical stress is explored by increase of defect concentration of crystal lattice of the catalyst, as confirmed by the tests of catalyst surface structure by scanning electron microscopy, Raman spectroscopy and X-ray analysis.

A new effective method for synthesis gas conversion into the methanol under conditions of mechanochemical activation of the catalyst can be used in industry as an alternative to methanol production at high pressures.

**Keywords:** heterogeneous catalysis, copper-zinc-aluminum oxide catalyst mechanochemical activation, synthesis gas, methanol.

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## 1. Introduction

Among the technologies of large-scale production of synthetic liquid fuels one of the most promising technologies is methanol production from synthesis gas [4–6]. Methanol is an environmentally friendly liquid fuel, good solvent and multi-purpose semi-finished product. Important chemicals, including oxygenate additives for fuels, can be obtained from it.

Most industrial processes is based on catalytic reactions [6–8], and their improvement is associated with the development of more active catalysts, simplification of production process lines, the ability to conduct processes in less stringent conditions. Much attention is paid to different ways of activating catalysts. One of the alternative ways to increase the activity of catalysts, according to the literature, may be the use of mechanical action force [9, 10].

The article outlines the main research results of influence of mechanochemical activation of industrial copper-zinc-aluminum oxide catalyst on its physicochemical properties and the course of synthesis gas conversion into methanol at atmospheric pressure.

In general, methanol synthesis from carbon monoxide and hydrogen on copper-zinc-aluminum oxide catalysts can be written as follows:



Except these reactions, the inverse endothermic reaction of carbon dioxide and hydrogen is occurred:



From a thermodynamic point of view, methanol production from synthesis gas is exothermic reaction and, consequently, high pressures and low temperatures are favorable for the synthesis.

The basis of modern industrial technology is low temperature manufacturing process of methanol from synthesis gas in the presence of copper-zinc-aluminum oxide catalysts at a temperature of 260 °C and a pressure of 5–10 MPa, which was first implemented by ICI in the early 60th of XX century. Nevertheless, interest in technologies for methanol production has been simmering: design of reactors is improving, production technology of low-temperature catalysts with different ratios of oxides is continuously improving, new ways of activation of catalysts are developed. Mechanochemical activation is attracting attention among them [11–13]. Mechanochemical phenomena are the basis of a wide range of fundamental processes [14–16], however, the lack of systematic research in the field of catalysis does not allow to predict the influence of mechanical stress on the activity of heterogeneous catalysts.

## 2. Materials and Methods

The laboratory unit with gradientless vibrational reactor was established to make catalytic research. Schematic diagram of this unit is given in [17].

Research of synthesis gas conversion into methanol was carried out in the presence of industrial methanol synthesis catalyst SLTM-U (Severodonetsk Low-temperature Methanol, Ukraine). Its initial physicochemical characteristics are given in [18].

The method of scanning electron microscopy (SEM) was used for determination of the surface morphology, particle size and thickness of investigated catalyst [19]. Tests were conducted on the scanning electron microscope JSM-6490 (Jeol, Japan), equipped with energy dispersive and wave spectrometers to study the chemical composition of the surface.

X-ray analysis (XRD) [20] of industrial and mechanically activated catalyst was performed on diffractometer “MiniFlex-600” (Rigaku, Japan) using monochromatic radiation source  $\text{CuK}\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ).

Raman spectra [21] were recorded on a triple spectrometer Horiba Jobin-Yvon T64000 (Horiba Scientific, France), equipped with confocal microscope UV-Visible-NIR Olympus BX41 (Japan) and multichannel CCD-detector.

Analysis of initial and output products of the reaction was carried out by gas chromatography, the organic components – the chromatograph “Agilent Technologies 7890” (USA) with flame ionization detector; inorganic components – chromatograph “Chrome-5” with thermal conductivity detector (Czech Republic).

### 3. Experimental procedures

The principle of catalytic unit is shown in [17]. Vibration reactor with the catalytic system has reciprocates in a vertical plane under the influence of generator of frequency vibration generator. Catalytic system for vibration reactor was prepared by the method described in [18]: pre-dispersed catalyst was deposited on the glass-ceramic balls with different surface morphology (homogeneous and heterogeneous relief). Continuous vibration reactor movement provided the catalyst system in vibration excited state, in conditions close to ideal mixing conditions.

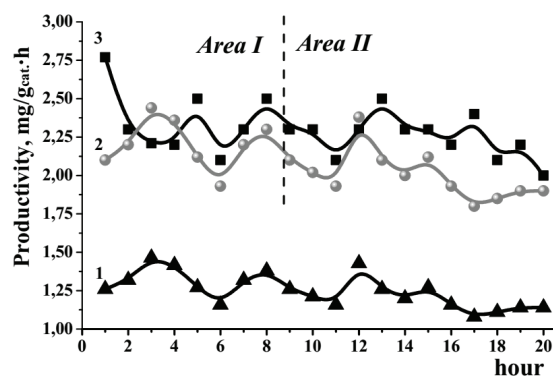
For comparison, corresponding experiments were made with granulated industrial catalyst (grain size 0.4–0.6 mm) placed in a stationary bed of tubular reactor in the absence of its vibration.

Experiments were performed in static and circulation mode under the pressure of 0.1 MPa in the range of operating temperatures for industrial catalyst SLTM-U 160–280 °C. Gas mixture of hydrogen and carbon monoxide with the addition of carbon dioxide (4 % vol.) or without it delivered into reactor from top to bottom. The gas circulation was carried out using a peristaltic pump LDIPLS-301. The volume rate of circulation was 6,000–16,000 h<sup>-1</sup>, covering a circulation range of gaseous mixture in industrial processes of methanol synthesis [6, 7]. Circulation rate was 30–80, which is known, to ensure the reactions in gradientless conditions [7].

Mechanically activated catalyst activity compared with the industry was evaluated according to the results of its performance in reaction of methanol production from synthesis gas, process efficiency – the conversion values of feedstock conversion for carbon and selectivity depending on the temperature.

### 4. Results and Discussion

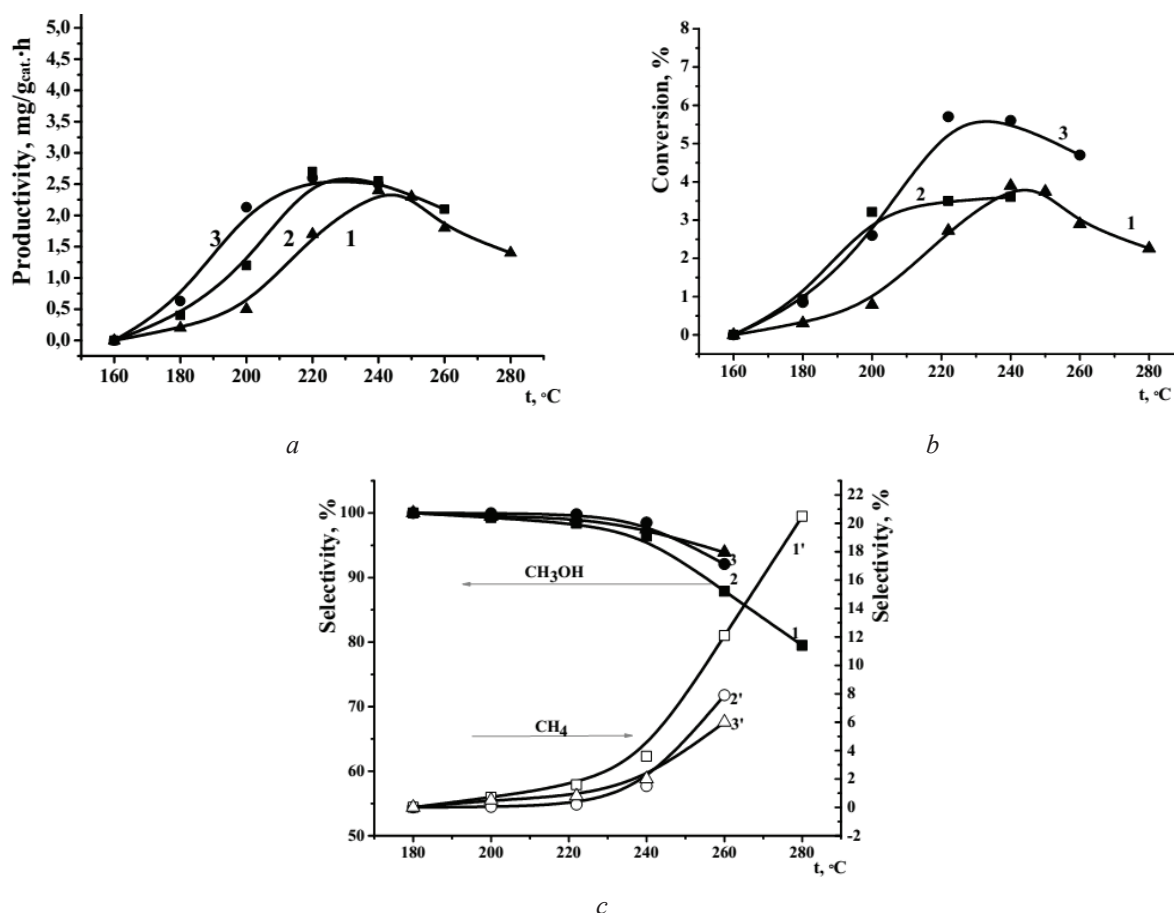
The results of comparative studies of methanol synthesis at a temperature of 220 °C and pressure of 0.1 MPa in different conditions of catalytic reactions – in stationary and vibration excited state shows that patterns of catalytic activity change in time are indistinguishable for granulated and pre-mechanically processed catalyst, although the absolute values of performance for the last are approximately 50 % higher (Fig. 1).



**Fig. 1.** Change of the catalyst productivity for methanol in time: granular catalyst in a tubular reactor (1); fine-dispersed catalyst deposited on the balls with a smooth (2) and relief (3) surface (vibration reactor). Zone I – stationary conditions; Zone II – vibration conditions. P=0.1 MPa; t=220 °C, the reactor vibration frequency is 5 Hz, mole ratio of H<sub>2</sub>: CO=4.0, CO<sub>2</sub> content – 4 %

The transition of catalytic system from a fixed (Fig. 1, Zone I) in vibration excited (Fig. 1, Zone II) state performed in a stable catalyst performance values in zone I. It is established that this transition is not affected the activity of the catalyst. The obtained result does not depend on the size and morphology of the surface of the glass-ceramic balls used as carriers of the catalyst. In particular, the catalyst deposited on unmodified smooth balls and the balls with a relief surface showed the same character of the process (curves 2 and 3).

The temperature dependence of the catalytic activity performance of the catalyst under optimum conditions of reactor vibration (5 Hz) [18] compared with granular catalyst investigated in a stationary bed of the tubular reactor is shown in Fig. 2.

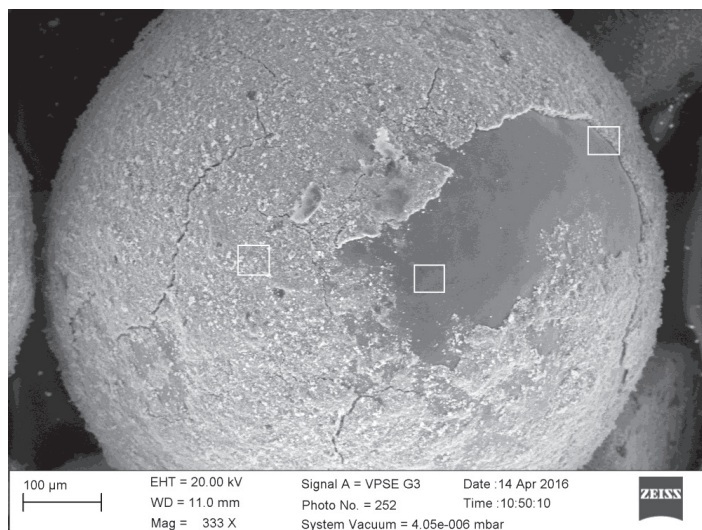


**Fig. 2.** Temperature dependence of the catalyst performance for methanol (a) synthesis gas conversion for carbon (b) and selectivity for the reaction products (c): 1 – industrial catalyst in a stationary bed; 2–3 – mechanically activated catalyst in the vibration reactor ( $f=5$  Hz), deposited on the balls with a smooth uniform (2) and heterogeneous (3) surface; ( $P=0.1$  MPa,  $U=1,1 \cdot 10^3$  h<sup>-1</sup>, molar ratio  $H_2:CO=4.0$ ,  $CO_2$  content – 4 %.)

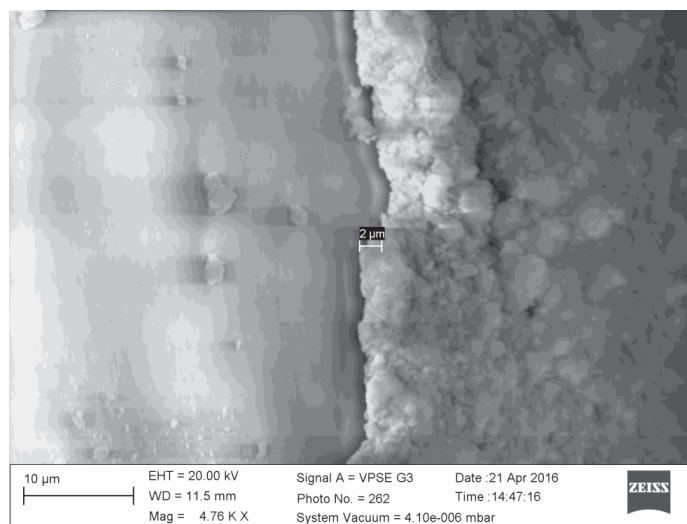
According to shown in Fig. 2 data, maximum values of performance, feedstock conversion and selectivity for methanol for granular catalyst are achieved at a temperature of 240 °C and reaction initiation – at a temperature of 180 °C. Mechanochemical catalyst activation during the preparation of the catalyst system reduces the thermal behavior by 20 °C (to 220 °C). Stable active catalyst in vibration reactor stored in the temperature range 210–240 °C. Decrease of the optimum temperature for conservation of active catalyst condition reduces the chance of overheating active copper component of the catalyst and its deactivation. The implementation of synthesis gas conversion at temperatures above optimal causes increase in the rate of adverse reactions, including methane formation and, therefore, reduce of process selectivity for the desired product and conversion degree into methanol for carbon.

SEM method defined layer thickness of the deposited catalyst which was  $\approx 2$  m (Fig. 3).

The size of the particles in the surface layer of the catalyst, according to electron microscopy research, decreases from 200–2000 nm (before the catalytic reaction) to 30–200 nm (after the reaction in vibration dilution conditions). Change of surface morphology and structuration of mechanically activated catalyst is observed after catalyst research (Fig. 4).

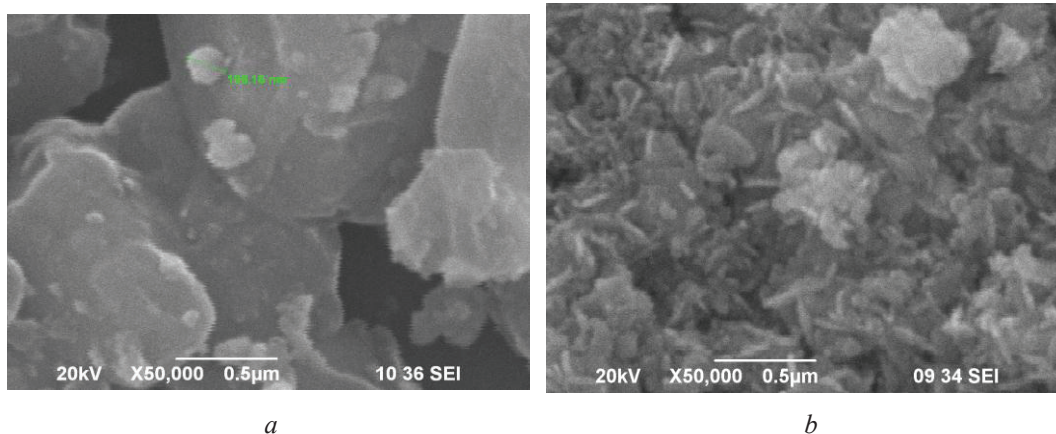


*a*



*b*

**Fig. 3.** Crack SEM images of adhesive surface layer of the catalyst on glass-ceramic balls to determine its thickness: *a* – a general view, *b* – an enlarged area



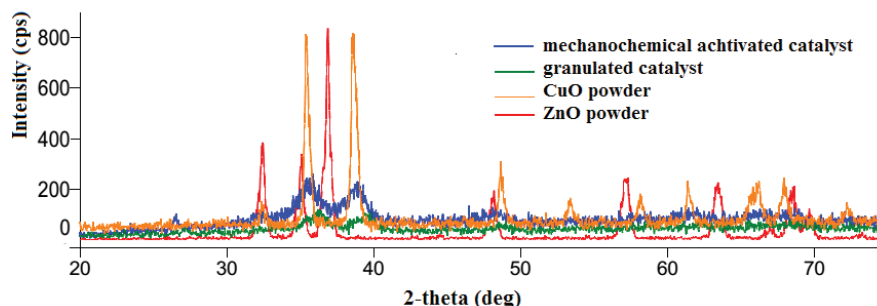
*a*

*b*

**Fig. 4.** SEM image of the catalyst deposited on the surface of the glass-ceramic balls, *a* – before catalytic reaction; *b* – after catalytic reaction

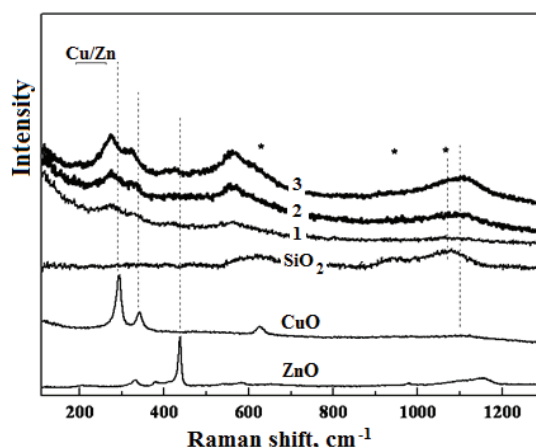


X-ray diffractogram indicates the changes in the crystal lattice of the industrial catalyst after its mechanical activation (**Fig. 5**). The displacement of the first two most intense peaks for the mechanically activated catalyst compared to industry may be due to a change in interplanar distance in the crystal.



**Fig. 5.** Diffractograms of industrial granular, mechanically activated catalyst SLTM-U and initial oxides CuO, ZnO

Raman spectra are also indicates changes in the structure of mechanically activated catalyst compared to granulated (**Fig. 6**, curves 1–3).

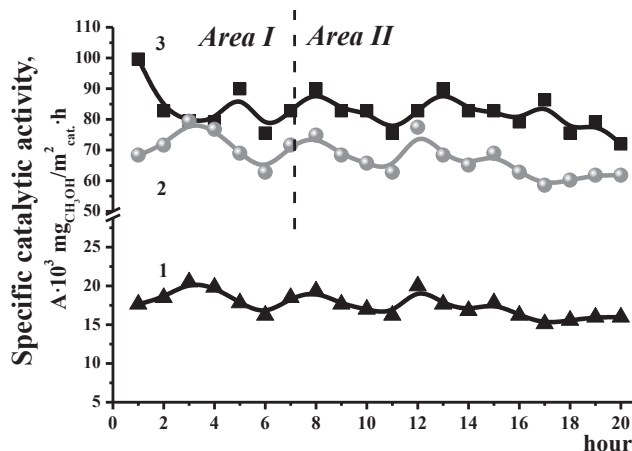


**Fig. 6.** Raman spectra of the catalyst samples (1 – industrial granular 2 – mechanically treated, before reaction, 3 – mechanically treated, after reaction) compared with the spectra of initial oxide ZnO, CuO and inert basis of crushing material – SiO<sub>2</sub>

Phonon bands of initial oxides and SiO<sub>2</sub> at 274, 320, 410, 552 and 1100 cm<sup>-1</sup> are presented in the spectra of all catalyst samples. Position and shape of these bands in relation to the initial components have low-energy shift and a significant increase in half-width. This is due to the increasing number of structural defects and disordering of the catalyst lattice, and the change in intensity indicates the change in size of nanocrystals (structural perfection). The lowest intensity and half-width of these bands is observed for industrial granular catalyst (curve 1) and increase for the mechanically activated catalyst samples (curves 2 and 3). The broad weak bands in the frequency range 100–250 cm<sup>-1</sup> can be induced by vibrations of replacement systems Cu/Zn, arising as a result of mechanical activation of the catalyst, especially for curves 2 and 3 (**Fig. 6**).

Mechanochemical catalyst treatment, as shown by XRD and Raman methods (**Fig. 5, 6**), is accompanied by the defects with corresponding increase in the concentration of Cu<sup>+</sup> active centers on the surface. Productivity increase of mechanically activated copper-zinc aluminum oxide catalyst is explained by structural and morphological changes that occur in the MCA of the object [22–24].

Decrease in the specific surface area of 71.4 to 27.8–30.7  $\text{m}^2/\text{h}_{\text{cat}}$  and the corresponding increase of specific catalytic activity of 2–3 times (Fig. 7) are observed in mechanochemical activation of industrial copper-zinc aluminum oxide SLTM-U catalyst.



**Fig. 7.** Change of the specific catalytic activity of the catalyst in time: 1 – granular catalyst; 2 – catalyst deposited on unmodified balls (vibration reactor); 3 – catalyst deposited on modified beads (vibration reactor). ( $P=0.1$  MPa,  $U=1 \cdot 10^3$   $\text{h}^{-1}$ , molar ratio  $\text{H}_2$ :  $\text{CO}=4.0$ ,  $\text{CO}_2$  content – 4 %). Zone I – stationary conditions, Zone II – vibration conditions (5 Hz)

This change of specific catalytic activity with decrease of the value of specific surface area can be explained by the destruction of the porous structure and the increase of concentration of defects in the crystal lattice and active centers on the catalyst surface unit. Similar results were obtained by Polish scientists using mechanochemical methods of material preparation [25].

## 5. Conclusions

The regularity of hydrogenation reaction of carbon oxides is investigated in the temperature range of 160–280 °C under pressure of 0.1 MPa for mechanically activated copper-zinc-aluminum oxide catalyst. It is established that mechanochemical activation of the catalyst lowers the temperature of reaction initiation and maximum catalyst activity by 20–30 °C and increases its productivity by 50 % and the specific catalytic activity – in 2–3 times – compared to granulated industrial catalyst of the same chemical composition. Decrease of the optimum process temperature helps prevent sintering of the catalyst and, thus, prolonging the use of catalytic contact without regeneration. Methods of electron spectroscopy, Raman spectroscopy, X-ray analysis and thermal desorption of argon help to investigate the surface condition of mechanically activated catalyst compared to granular. It is shown that increased activity of the catalyst system is due to structural and morphological transformations during mechanical treatment, accompanied by the growth defects of the crystal structure of the catalyst and the corresponding increase in the concentration of active centers.

Mechanochemical catalyst activation in the conversion of carbon oxides is an alternative to the use of high pressure and, therefore, will contribute to efficiency of the process as a whole. This research points to the prospects of studying the impact of various low-cost ways of machine treatment of solid catalysts on their activity in heterogeneous processes.

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