Synthesis of the catalysts based on oxides of some d-elements

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Abstract. In this work, nanocomposite materials were synthesized on the basis of a mixture of nitrates of Ni (II), Zr (IV), Mg (II) and Al(OH)$_3$ with glycine by the solution combustion method. The synthesized nanocatalysts with the composition $x$NiO$_y$ZrO$_2$/$z$Al$_2$O$_3$ (TiO$_2$, MgO) are characterized by a high specific volume ($0.80 \pm 0.05$ cm$^3$/g), an average size ($1.85 \pm 0.05$ nm) of pores, a relative specific surface area ($180 \pm 8$ m$^2$/g) and a big monolayer capacity ($3.17 \pm 0.24$ mol/kg). A hysteresis loop is observed in isotherms during the absorption of benzene vapours, while in the case of hexane it is absent. The resulting nanocatalysts can be used as a selective catalyst for the conversion of methane in a flow reactor.

1. Introduction
There is a tendency of decrease of the reserves and production volumes of renewable energy sources, including light oils and natural gas in the world. That entails the need to deepen the processing of hydrocarbon raw materials. Therefore, it is necessary to create new or modernize existing processes of processing hydrocarbon raw materials. The most common process in oil and gas processing plants is the catalytic conversion of hydrocarbons raw materials. For a long time of its existence, the process has undergone changes both in the method of contact of the raw material and the catalyst, and in the catalysts used. These changes made it possible to obtain the maximum amount of products. The choice of the catalyst for the process plays an important role; the yield and quality of the target products depend on the chosen catalyst. The use of nanocatalysts leads to an increase in their selectivity and productivity due to the size effect [1]. In this regard, researchers are involved in the development of various nanocatalysts and their modification for processing natural gas [2].

The goal of this work is to synthesize nanocatalysts based on oxides of some d-elements and to study the phase composition, geometric and sorption characteristics.

2. Material and methods
For the preparation of the catalysts we used nickel (II) nitrate hexahydrate — Ni(NO$_3$)$_2$$\cdot$6H$_2$O (extra pure, Reachem 98%), zirconium oxynitrate — ZrO(NO$_3$)$_2$ (extra pure, Reachem 98%), magnesium nitrate dihydrate — Mg(NO$_3$)$_2$$\cdot$2H$_2$O (extra pure, Reachem 98%), aluminum oxide — Al$_2$O$_3$ (extra pure), titanium (IV) oxide — TiO$_2$ (extra pure, Reachem 98%).

Figure 1 shows schematically the process of synthesis of the nanocatalysts. In the process Al$_2$O$_3$ obtained from a local raw material, bentonite, was used [3]. To ensure the stability of the nickel catalyst, alkali [4], alkaline earth metals [5] and some oxides of d-elements are used as promoters. Rare metal oxides play an important role in catalytic processes. It has now been proven that the use of inexpensive two - and multicomponent metal oxides instead of rare metals used as additives to the...
support allows one to prepare high-quality and inexpensive catalysts. For this purpose, during the synthesis, magnesium (MgO) and titanium (TiO\textsubscript{2}) oxides were used as additional promoters. According to the technology, metal nitrates were dissolved in water and glycine was added to the solution in a molar ratio of glycine / nitrate = 5. The obtained Al\textsubscript{2}O\textsubscript{3} was calcined at 400 °C (programmed temperature up to 400 °C with a heating rate of 1-2 °C / min) for 4 hours. The obtained Al\textsubscript{2}O\textsubscript{3} was added to the solution, the mixture was stirred for 60 min. Excess water was distilled off the mixture and the mixture was heated to 80 °C to obtain a gel. After that, the gel was calcined at a temperature of 400 °C. In this case, the resulting gel must boil with the formation of a foam in order to form a self-combusting powder. The resulting powder was kept in an air stream at 400 °C for 3 hours. As a result, a nanostructured catalysts of the composition NiO/TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, NiO/ZrO\textsubscript{2}/TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} and NiO/ZrO\textsubscript{2}/MgO/Al\textsubscript{2}O\textsubscript{3} was formed [6].

![Figure 1. Technological scheme for the preparation of nanocatalysts](image-url)

The structure of the catalysts was studied by powder X-ray diffraction on a Panalytical Empyrean (XRD) instrument, the geometric characteristics by SEM EVO MA 10 (Carl Zeiss), and the sorption isotherm — on a McBain - Bakr instrument. The results were processed by graphical and analytical methods of the statistical method.
3. Results and discussion

Phase analysis by X-ray diffraction (XRD) goes beyond elemental composition to characterize the crystalline forms present. An active metallic element might be present as pure metal, oxide, mixed oxide, carbonate, carbide, etc. Catalyst support materials can undergo changes under reaction conditions. If crystal structures are available, as they are for most inorganic phases, the Rietveld method can be used based on these structures.

The phase composition established by the diffractometry method is shown in figure 2. CuK$_\alpha$-irradiation ($\beta$-filter, Cu, current mode 1.5406A°) was used to obtain the diffractogram. The voltage was 30 kV, the voltage of the current in the tube was 10-20 amps. The phase composition of the catalyst was examined by the International Center for Diffraction Data – ICDD.

Energy Dispersive X-ray analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its X-ray emission spectrum. Figure 3 and the table 1 give the results of Energy Dispersive X-ray analysis for the nanocatalysts consisting of elements O, Ni, Zr, Al, (Mg, Ti) [7,8,9]. It can be seen that Al is the dominant element in the sample, although oxygenium is also found in the sample.

![Figure 2. X-ray spectrum of the composite.](image1)

![Figure 3. Elemental analysis of the catalyst.](image2)

Geometric characteristics of synthesized nanocatalysts are presented in the table.

| Composite | Elemental composition | Pore volume V, cm$^3$/g | Average pore size, nm | Relative specific surface area (BET), S, m$^2$/g | Monolayer capacity, $\alpha_m$, mol/kg |
|-----------|-----------------------|-------------------------|-----------------------|---------------------------------|-----------------------------------|
| K1        | Ni, Ti, Al, O         | 0.81                    | 1.80                  | 182                             | 2.48 ± 0.18                       |
| K2        | Ni, Zr, Ti, Al, O     | 0.77                    | 1.87                  | 190                             | 3.34 ± 0.36                       |
| K3        | Ni, Zr, Mg, Al, O     | 0.85                    | 1.90                  | 197                             | 3.7 ± 0.42                        |

Determination of geometric characteristics and surface of the synthesized nanostructured catalysts show that the synthesized nanocatalysts are characterized by a large volume of pores (0.80 ± 0.05 cm$^3$/g), an average pore size (1.85 ± 0.05 nm), and a big monolayer capacity (3.17 ± 0.24 mol/kg) (Table 1).
It was found that a change in the composition of the catalyst has no noticeable effect on the porosity of the layer and the porosity of the particles. The specific total pore volume of the samples with added oxides of different metals is greater than that of the original one.

The sorption isotherm of hexane and benzene vapours in the nanocatalysts (see Figure 4,5) also confirms the above data.

![Figure 4. Sorption isotherm of hexane vapours in the nanocatalysts.](image1)

![Figure 5. Isotherm of sorption of benzene vapours the nanocatalysts.](image2)

To study the texture and sorption properties of the composites, adsorption isotherms were obtained using benzene and hexane vapours. To obtain adsorption isotherms, a sensitive McBain-Bakr quartz spiral device was used. Benzene, used as an adsorbate, was purified in a vacuum by repeated freezing and defrosting by removing dissolved gases from the solvent. In each adsorption system, keeping in vacuum it continued to a residual pressure of $1.33 \times 10^{-3}$ Pa. Sorption isotherms of nanocatalysts were obtained by heating the samples at 473 K for 8 h by studying the adsorption of benzene and hexane vapors.

Based on the results obtained and Balandin's multiplet theory, the synthesized nanocatalysts can be used as a catalyst for the conversion of methane in a flow reactor. The methane conversion reaction was carried out in a flow reactor. The progress of the reaction was monitored by gas chromatography.

4. Conclusions
The nanocomposites with the composition $x\text{NiO}/y\text{ZrO}_2/z\text{Al}_2\text{O}_3/(\text{TiO}_2, \text{MgO})$ have been synthesized. The synthesized nanocomposites are characterized by a high volume ($0.80 \pm 0.05$ cm$^3$/g) and an average pore size ($1.85 \pm 0.05$ nm), a relative specific surface area ($180 \pm 8$ m$^2$/g) and a big monolayer capacity ($3.17 \pm 0.24$ mol/kg). A hysteresis loop is observed in isotherms during the absorption of benzene vapors, while in the case of hexane, it is absent. The resulting nanocatalysts can be used as a selective catalyst for the conversion of methane in a flow reactor.

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