Dependence of the preparation method on the phase composition and particle size of the binary NiO–ZrO_2 system oxides

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Abstract. Was studied how preparation method influences phase composition, oxide particle size and catalytic activity of the binary NiO–ZrO_2 systems. The processes taking place under the thermal influence while NiO–ZrO_2 catalysts are formed from precursors, obtained using a variety of methods, were determinated using the methods of simultaneous TGA-DTG/DSC analysis and XFA. Was studied the influence of the precursor preparation method upon the catalysts' phase composition, sizes of the nickel oxide and zirconium dioxide particles. The research revealed that preparation of precursor using coprecipitation method makes it possible to obtain a binary system, where nickel oxide has minimal size, determined by CSR, and monoclinic phase prevails in ZrO_2, after heating it to 800 °C. The research unearthed that the catalyst exhibiting maximal catalytic activity by deep oxidation of methane is nickel oxide-zirconium dioxide, containing equal amounts of monoclinic and tetragonal phases of ZrO_2.

1. Introduction

Zirconium dioxide has a number of valuable characteristics, which make is suitable for use in manufacture of ceramic materials [1], microelectronics [2], fuel elements [3], also as a catalyst by partial oxidation of methane to syngas [4, 5] high-temperature shift catalyst for methane [6, 7]. Most of the studies is devoted to the investigation of the influence of the amount of the active component (metal) [8] or the second oxide introduced on the phase composition, metal dispersion, stability and catalytic activity of the systems obtained in the methane oxidizing conversion reaction [9, 10], yet they do not focus on the influence the catalyst precursor preparation method has on physical, chemical and catalytic properties of the zirconium dioxide-based systems. The research works [6, 7] show that changing synthesis methods for ZrO_2 can change characteristics of the catalyst and the carrier it is based on, but to the date, the influence of preparation methods on ultimate characteristics of zirconium dioxide-based binary oxide systems hasn't been studied yet.

The goal of this research work is to unearth the influence of the oxidic nickel-zirconium system precursor preparation stages and methods of nickel compound doping on the phase compounds, porous structure and catalytic activity of the synthesized binary oxides.

2. Experimental Part

The Acros reagents were used to obtain binary oxide nickel-zirconium systems with a mole ratio of NiO : ZrO_2 = 1 : 4.3 : $ZrO(NO_3)_2 \cdot 2H_2O$, Na_2CO_3, $Ni(NO_3)_2 \cdot 6H_2O$.

The catalyst precursors were prepared in the following way:

1) Sample No. 1 (hereafter referred to as $ZrO_2 \cdot nH_2O$).

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Twofold excess of Na_2CO_3 (c = 0.5 mol/L) was poured into boiling $ZrO(NO_3)_2$ (c = 0.25 mol/L) solution; the suspension obtained was boiled for 0.5 hours until gas release stopped. The suspension was centrifuged, rinsed with double-distilled water till pH=7. The precipitation obtained was dried at T = 60 °C for 2 hours and at T = 110 °C for 4 hours. By fractionation of $ZrO_2 \cdot nH_2O$ two fractions were obtained: 0.20–0.25 mm and 0.020-0.025 mm.

2) Sample No. 2 (hereafter referred to as Ni-Zr(o)) was prepared by solvent distilling.

The 0.20–0.25-mm fraction of $ZrO_2 \cdot nH_2O$ sample was added to the measured amount of solution $Ni(NO_3)_2$ (c = 0,1 mol/L). Water was distilled off until the sample was dried in a rotary evaporator at T = 45 °C and at negative pressure of $48 \cdot 10^{-3}$ Bar. The precursor was dried the same way with 1.

3) Sample No. 3 (hereafter referred to as Ni-Zr(o)-950) was prepared by solvent distilling.

The sample was prepared the same way as Ni-Zr(o) sample following the method (2). The precursor was dried the same way with 1.

4) Sample No.4 (hereafter referred to as Ni-Zr (d-p)) was prepared by deposition-precipitation method.

The 0.020-0.025-mm fraction of $ZrO_2 \cdot nH_2O$ was added to a measured amount of $Ni(NO_3)_2$ (c = 0.0058 mol/L) solution and boiled up and added twofold excess of Na_2CO_3 (c = 0.5 mol/L) solution while stirring vigorously; the rest of the procedure was the same with Sample 1.

5) Sample No. 5 (hereafter referred to as Ni-Zr(co)), was prepared by coprecipitation.

Twofold excess of Na_2CO_3 (c = 0.5 mol/L) solution was poured into boiling solution of $ZrO(NO_3)_2$ (c = 0.25 mol/L) and $Ni(NO_3)_2$ (c = 0.058 mol/L) salts; the rest of the procedure was the same with Sample 1.

Baking of precursors for samples No. 1, 2, 4, 5 was carried out with increase in temperature from 20 to 800 °C with heat rise rate of 10 °/min in an air stream, with exposition time of 4 hours at 800 °C. Baking of Sample No.3 was carried out with increase in temperature from 20 to 950 °C with heat rise rate of 10 °/min in an airstream with exposition time of 4 hours at 950 °C.

Quantitative determination of nickel oxide in the baked samples was carried out using Oxford ED-2000 (Great Britain, Oxford Instruments) energy-dispersing X-ray-fluorescent spectrometer. Phase composition of the samples was determined using Rigaku Miniflex 600 X-ray diffractometer CuK_α-emission (l=1.5418 Å). Radiography specifications: scan velocity 2 degrees/min, scanning angular range 2q: from 10° to 100°. Average size (*D*) of the coherent scattering region (CSR) was determined by X-ray imaging based on Fourier analysis of diffraction peaks' profile. The average CSR size was evaluated according to Scherrer-Selyakov equation [8]. Thermal analysis of the samples was carried out using Netzsch STA-449 (Germany) simultaneous TGA-DTG/DSC analysis device, with heat rise rate of 10 °C/min. The samples' BET surface area (S_{sp}) was determined using TriStar II (3020) (Micromeritics, USA) device. Catalytic activity in the methane deep oxidation reaction was studied using a flow-through catalytic device in the temperature range of 400–700 °C, with contact time of 0.5 sec, the reaction mixture contained the following: CH_4 – 0.5 %, O_2 – 12.7 %, N_2 – 86.2 % vol.

3. Results and Discussion

Simultaneous TGA-DTG/DSC analysis of hydrated zirconium dioxide is marked by a wide endothermic peak (Figure 1. *a*) in the temperature range of 50–400 °C, which corresponds with removal of the hydration water, the weight reduction calculation makes it possible to calculate the formula of the obtained and dried zirconium oxide as $ZrO_2 \cdot 2H_2O$, which agrees with the data provided in the research work [11].

Peak exotherm at (T_{max}) 491.1 °C, can be assigned to crystallization process of the noncrystalline ZrO_2 into the tetragonal variety (t-ZrO_2), which corresponds with the data provided in the research work [11]; exo-effect at T_{max} = 701.4 °C indicates partial transition of metastable tetragonal phase into the monoclinic one (m-ZrO_2). Slight reduction of the sample weight in the temperature range

500−1000 °C may mark removal of hyperstoichiometric oxygen and residual water of crystallization [11].

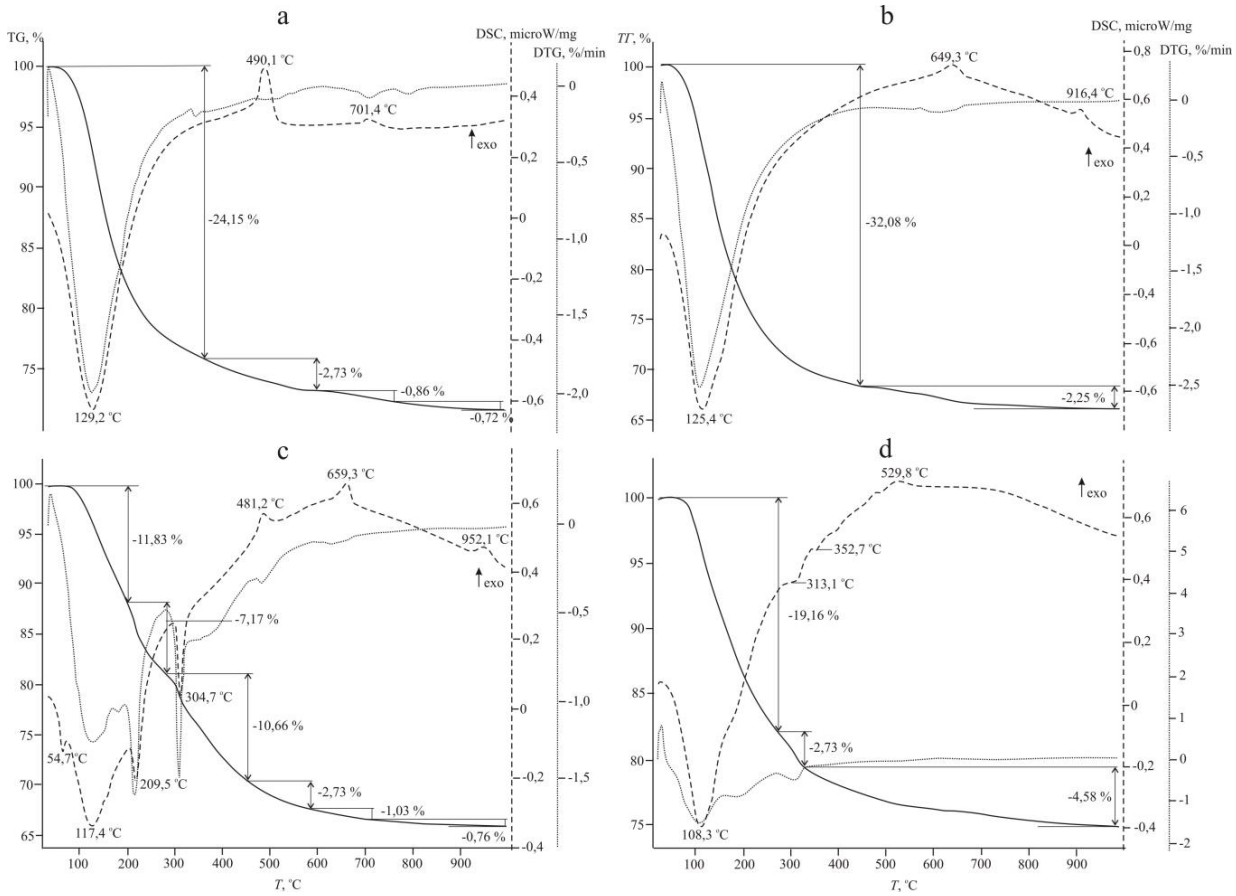


Figure 1. Synchronous TGA-DTG/DSC analysis of precursors of catalysts: (a) – $ZrO_2 \cdot nH_2O$, (b)– Ni-Zr(o), (c) – Ni-Zr(d-p), (d) – Ni-Zr(co).

According to the data obtained by RFA (Figure 2.*a*), two phases are present in the ZrO_2 sample heated up to 800 °C: the tetragonal one, t-ZrO_2 (2Θ = 30.14; 35.13; 50.56; 60.02; 62.75; 74.35) and the monoclinic one, m-ZrO_2 (2Θ = 17.39; 23.90; 28.12; 31.31; 40.62), containing 32% of m-ZrO_2. As we obtain zirconium dioxide in the annealing temperature range of 700–1000 °C, regardless of the initial precursor production method, by a) solution deposition [9, 10]; b) pyrogenic decomposition of zirconyl chloride, two phases of zirconium dioxide are produced: the monoclinic and the tetragonal ones.

According to TGA-DTG/DSC analysis statistics, Ni-Zr(o) sample (Figure 1.*b*), is marked by endothermic peak at T_{max} = 54.7 °C, which corresponds with melting of nickel nitrate hydrate on the surface of $ZrO_2 \cdot 2H_2O$ granules, the endothermic peak at T_{max} = 117 °C with weight reduction corresponds with removal of hydrated water from $ZrO_2 \cdot 2H_2O$. The overlapping weight reduction endothermic peaks of T_{max} = 209.5 °C and T_{max} = 304.7 °C correspond with removal of water from nickel nitrate hydrate (according to TGA, the design equation is $Ni(NO_3)_2 \cdot 4.5H_2O$) and decomposition of nickel nitrate with production of nickel oxide. The exothermic peak at T_{max} = 481.2 °C (Figure 1.*b*) marks crystallization of the X-ray amorphous ZrO_2 into t-ZrO_2, and at T_{max} = 659.3 °C it marks partial transition of ZrO_2 tetragonal phase into the monoclinic one [11]. According to XFA (Figure 2.*b*), Ni-Zr(o) binary oxide system heated up to 800 °C contains two phases of zirconium dioxide (tetragonal

and monoclinic ones), as well as the cubic phase NiO (2Θ = 37.16; 43.18; 62.75). At that, the content of ZrO_2 monoclinic phase is lower than that for pure ZrO_2 (Table 1).

Table 1. Influence of a way of preparation of a precursor on phase structure, size of particles of oxides, catalytic activity of NiO-ZrO_2 systems.

Parameter	**$ZrO_2 \cdot nH_2O$**	**Ni-Zr (o)**	**Ni-Zr (d-p)**	**Ni-Zr (co)**	**Ni-Zr (o)-950 °C**
S_{sp}, m^2/g	1.9	6.3	4.6	4.1	1.3
NiO:ZrO_2, mol	-	1 : 4.32	1 : 4.33	1 : 4.30	1 : 4.32
quantity m-ZrO_2, %	32.1	13.3	49.4	99.5	99.3
D_{NiO}, nm	-	29	25	20	38
$D_{m\text{-}ZrO2}$, nm	20	20	29	31	41
$D_{t\text{-}ZrO2}$, nm	28	29	24	-	-
T_{80}, °C*	600	520	460	490	550

* T_{80},°C – temperature is 80% of conversion of methane

According to Figure 1.*b*, Ni-Zr(o) sample is marked by exothermic peak at T_{max} = 952 °C, which attests further phase transition of the remaining t-ZrO_2 to m-ZrO_2. The Ni-Zr(o)-950 sample heated up to 950 °C consists of m-ZrO_2 and NiO (Figure 2.*e*); however high-heat treatment leads to the following phenomena: increase in the CSR average size of nickel oxide and zirconium dioxide crystallites (Table 1). According to TGA/DSC analysis (Figure 1. *c*), Ni-Zr(d-p) system is marked by wide endothermic peak at T_{max} = 125.4 °C and sample weight reduction in the temperature range 50–490 °C which is representative of the process of water removal from the hydrated zirconium oxide and decomposition of nickel hydroxocarbonates.

The exothermic peak at T_{max} = 679.3 °C can be related to simultaneous processes of amorphous zirconium dioxide crystallization and phase transitions; further transition of t-ZrO_2 phase into the monoclinic one takes place at the temperature of 916.4 °C (Figure 1.*c*). According to XFA (Figure 2.*c*), this is a multiple-phase system and contains t-ZrO_2, m-ZrO_2 and NiO phase, but specific gravity of the monoclinic phase compared to the samples of Ni-Zr(o) and ZrO_2 obtained from $ZrO_2 \cdot 2H_2O$, increased (Table 1), which probably is due to the initial ten-fold reduction of the hydrated zirconium oxide particles and possibly, with the mineralizing effect of nickel oxide. Average sizes of the nickel oxide crystallites for Ni-Zr(o) and Ni-Zr(d-p) samples are similar (Table 1). NiO particles of the same size (27–29 nm) were obtained by deposition of nickel onto heat-treated ZrO_2 [7].

TGA-DTG/DSC analysis of Ni-Zr(co) sample also revealed analogous to the previous samples wide endothermic peak accompanied with sample weight reduction in the temperature range of 50−460 °C (Figure 1.*d*) with faint endothermic peaks at T_{max} = 313.1 and 352.7 °C, which are concerned with decomposition of nickel hydroxocarbonates in the bulk of catalyst granule (the same effect was observed in the research work [6]) and faint exothermic peaks at temperatures of 490 and 529.8 °C, concerned with crystallization and phase transitions of ZrO_2. According to Figure 2.*d*, in the Ni-Zr(co) sample heat-treated at the temperature of 800 °C, monoclinic phase of zirconium dioxide and cubic NiO prevail, the sizes of nickel oxide crystallites are smaller than those in the samples obtained from the precursors prepared using methods 2–4 (Figure 2.*d*, Table 1).

By adding nickel oxide and heat-treating it at T = 800 °C BET surface area of the samples grows larger compared to that of pure ZrO_2; Ni-Zr(co) sample has the smallest BET surface area among binary systems. Increase of the heat-treatment temperature up to 950 °C also promotes further shrinkage of the Ni-Zr(o)-950 catalyst BET surface area (Table 1). The size of m-ZrO_2 crystallites increases as the proportion of monoclinic phase in zirconium dioxide grows. Size of t-ZrO_2 crystallites is approximately the same in all systems: 26−29 nm (Table 1). Catalytic properties of a system depend not only on the range of particle dimensions of the NiO active component, as [7] shows, but also on the proportion of tetragonal and monoclinic phases in ZrO_2.

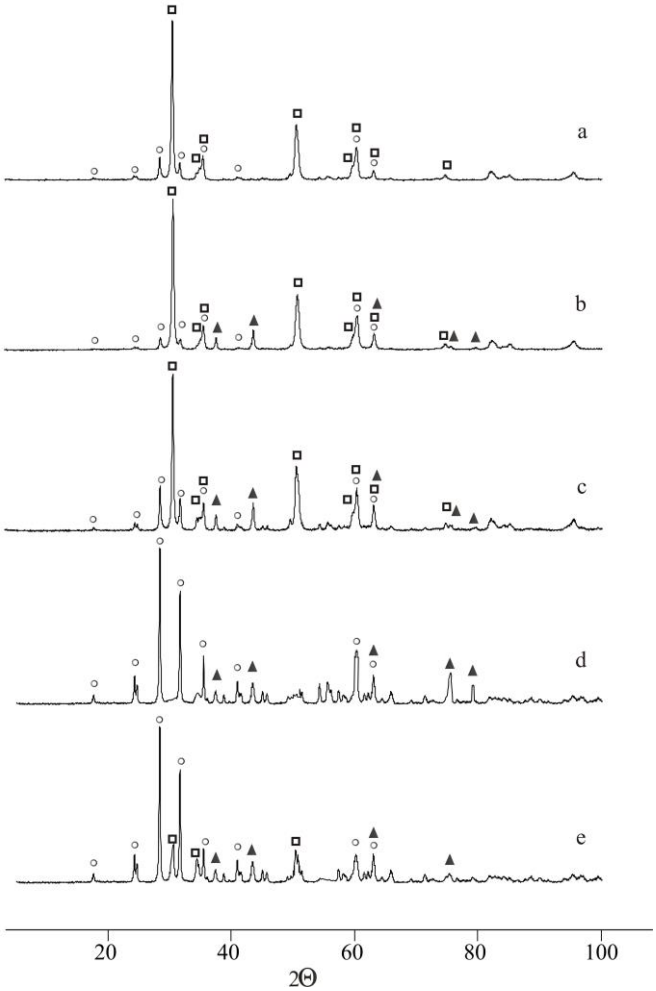


Figure 2. XRA ranges of binary NiO-ZrO_2 of systems: (a) – $ZrO_2 \cdot nH_2O$, (b) – Ni-Zr(o), (c) – Ni-Zr(d-p), (d) – Ni-Zr(co), (e) – Ni-Zr(o)-950. The reflexes relating to: □ – ZrO_2 is tetragonal, ○ – ZrO_2 monoclinic, ▲ – NiO cubic

According to [7], in the methane deep oxidation reactions, the temperatures at which methane conversion reaches a specific level, which is 80% in our case, is the catalytic activity criterion for the catalyst. Therefore, a catalyst's activity is the higher, the lower 80% methane conversion temperature is. According to the Table 1, Ni-Zr (d-p) catalyst with NiO particle size of 25 nm showed the highest catalytic activity compared to other systems, while equal amounts of t-ZrO_2 and m-ZrO_2 were present in zirconium dioxide (Table 1). We believe this leads to increase in oxygen exchange ability of zirconium dioxide, which is one of the key factors in its oxidation-reduction reactions proceeding involving gas-phase oxygen.

4. Conclusion

Thus, the studies have shown that the variation of the preparation method of the precursor and the temperature of heat treatment can produce NiO–ZrO_2 oxide binary systems with a variety of tetragonal and monoclinic phase proportions in zirconium dioxide. The nickel oxide particle size for binary systems can also be adjusted in the process of NiO–ZrO_2–system precursor formation. Activity of NiO–ZrO_2 catalysts in the oxidation-reduction reaction of methane deep oxidation involving gas-phase oxygen depends both on the active component's - nickel oxide's - range of particle dimensions and the proportion of monoclinic and tetragonal phases in the zirconium dioxide supporter, which provides for

the binary oxide system's high oxygen exchange ability in general. The catalyst containing equal amounts of monoclinic and tetragonal phases of zirconium dioxide with NiO particle size of 25 nm exhibits maximal catalytic activity in oxidation-reduction reaction of hydrocarbon oxidation.

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