

TiO₂-NiO and TiO₂-Co₃O₄ spheres: synthesis and characterization

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Abstract. TiO₂-based composites doped with d-metal oxides are prospective catalysts. In this paper we obtained spherical particles of TiO₂-NiO and TiO₂-Co₃O₄ composites by a template method accompanied with sol-gel one. Ion exchange resin of TOKEM-100 and TOKEM-250 was used as an organic polymer matrix. Complex studies were carried out to identify the formation process, compositions and morphology of obtained particles by thermal analysis, X-ray diffractometry, scanning electron microscopy and micro-X-ray spectral analyses. The formation of TiO₂-Co₃O₄ and TiO₂-NiO composite particles ends at 600 and 500°C, respectively at using TOKEM-100 and TOKEM-250 resins. The size of final spherical particles found to be in a range from 300 to 700 μm, and their morphology depends on its composition.

1. Introduction

TiO₂ in the anatase phase is widely employed owing unique properties as chemical stability, biological safety and catalytic activity [1, 2]. Nickel oxide and cobalt oxide have also shown high catalytic activity in CO and hydrocarbons oxidation of [3–6]. Nickel oxide promotes the formation of anatase phase of TiO₂ in the TiO₂-NiO oxide system [7]. Nowadays, oxide systems based on titanium dioxide with d-metal oxides are promising candidates for application as catalysts [7]. The systems of TiO₂-NiO and TiO₂-Co₃O₄ can be used as catalysts for steam reforming of methanol [7], oxidation of hydrocarbons, and carbonmonoxide [1]. Moreover, metal oxide catalysts are studied mostly as low cost alternative to some precious metals such as Pt, Pd and Au, which are well known as oxidation catalyst [1, 3].

At present, catalytically active spherical composites have received significant attention of researchers, since they reduce pressure in a tubular furnace and increase its productivity without reconstruction during hydrocarbons conversion [8]. One of the main method for obtaining composites TiO₂-based with spherical form is a template synthesis with using porous organic and inorganic materials as the structure directing template, for example cetyltrimethyl ammonium bromide (CTAB) [9], SiO₂ [10]. Recently, structurally homogeneous reaction products in the form of spherical nanoparticles were obtained by a low-temperature sol-gel synthesis [11].

In previous studies [8, 12] it was shown, that the ion exchange resins also can be used as the structure template for obtaining spherical catalysts. Spherical TiO₂-SiO₂/M_xO_y, (M = Co, Cr) catalysts were successfully obtained.

The aim of this study was to prepare spherical TiO₂-NiO and TiO₂-Co₃O₄ particles by the template method accompanied with sol-gel method using ion exchange resins as the structure template and to investigate the morphology and composition of obtained materials.



2. Experimental part

2.1. Materials and experimental procedure

Composite particles were prepared by the technique based on template and sol-gel methods, that was proposed in the earlier work [13]. Ion exchange resins of spherical form TOKEM-100 (sulfonic cation exchange resin with styrene-divinylbenzene matrix, grain size from 0.4 to 1.2 mm, PO "Tokem" LLC, Kemerovo, Russia) and TOKEM-250 (carboxyl cation exchange resin with acryl-divinylbenzene matrix, grain size from 0.3 to 1.6 mm, PO "Tokem" LLC, Kemerovo, Russia) were used as an organic polymer matrix.

At the first stage, cation exchangers were placed into saturated aqueous solution of cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, pure 99%, Yugreaktiv, Russia) or nickel(II) nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, pure 99%, Yugreaktiv, Russia) at room temperature under continuous magnetic stirring. After stirring for 6 hours, the polymer was filtered and dried at 60 °C for 2 hours. In the second stage, the polymer was immersed into the sol of tetrabutoxytitanium for 12 hours. Sol was prepared by the method reported in previous study [14]. To prepare the aggregatively stable sol, three components were mixed: butanol-1 (99.9%, Ekos-1, Russia) as a solvent, bidistilled water as an initiator of alkoxide hydrolysis reaction (concentration of 0.5 mol/L), and HNO_3 (UralPromDelivery, Russia) in concentration of $2.5 \cdot 10^{-3}$ mol/L [15]. After 60 minutes, the tetrabutoxytitanium (TBT, concentration of 0.1 mol/L, extrapurity, Acros, USA) was added to the $\text{C}_4\text{H}_9\text{OH}-\text{H}_2\text{O}-\text{HNO}_3$ mixture. Freshly prepared solutions were kept at room temperature for three days. The obtained samples were denoted as TBT- Co^{2+} (100), TBT- Ni^{2+} (100) (TOKEM-100 was used as organic polymer matrix) and TBT- Co^{2+} (250), TBT- Ni^{2+} (250) (TOKEM-250 was used as organic polymer matrix) further in text.

Further thermal treatment of TBT- Co^{2+} (100), TBT- Ni^{2+} (100) samples was performed in several stages: calcination at 100, 200, 450, 500, 550 °C for 30 minutes at each temperature and calcination at 600 °C for 1 h. The obtained samples were denoted as $\text{TiO}_2-\text{Co}_3\text{O}_4$ (100), TiO_2-NiO (100) further in text. Thermal treatment of TBT- Co^{2+} (250), TBT- Ni^{2+} (250) samples was performed in several stages: calcination at 100, 250, 350, 400, 450 °C for 30 minutes at each temperature and calcination at 500 °C for 1 h. The obtained samples were denoted as $\text{TiO}_2-\text{Co}_3\text{O}_4$ (250), TiO_2-NiO (250) further in text. According to the data of [16], the formation of spherical particles upon destruction of the polymer matrix is possible at a heating rate less than 10 °C/min, that is why the heating rate of the muffle furnace was 5 °C/min.

2.2. Research methods

The calcination temperatures of TBT- Co^{2+} (100), TBT- Ni^{2+} (100) and TBT- Co^{2+} (250), TBT- Ni^{2+} (250) samples were chosen using synchronous thermal analysis (STA) data. Thermal analysis was carried out on a STA 449 C Jupiter instrument (Netzsch-Gerätebau GmbH, Germany) in a temperature range from 40 to 900 °C with heating rate 5 °C/min in oxygen atmosphere.

The phase composition of the prepared particles $\text{TiO}_2-\text{Co}_3\text{O}_4$ (100), TiO_2-NiO (100), $\text{TiO}_2-\text{Co}_3\text{O}_4$ (250), TiO_2-NiO (250) composites was determined by X-ray diffraction (XRD) on a Mini Flex 600 diffractometer with $\text{CuK}\alpha$ radiation (Rigaku, Japan) in the reflection angle 2θ in a range from 10 to 80°. XRD analysis of the samples was performed using the PDF-2 diffraction database.

The surface morphology of the samples was investigated by scanning electron microscopy (SEM) on a microscope TM-3000 (Hitachi, Japan) at accelerating voltage of 15 kV. The X-ray microanalyzer (Shift ED 3000) was also used for energy-dispersive X-ray (EDX) spectroscopic analysis.

3. Results and discussion

The thermal treatment of initial (TBT- Co^{2+} (100), TBT- Ni^{2+} (100) and TBT- Co^{2+} (250), TBT- Ni^{2+} (250)) samples is one of the most important stage of preparation composite particles. It allows us to destroy the template (ion exchange resins) and to obtain TiO_2 -based composites with spherical form.

Figure 1 presents thermal analysis data for the TBT-Co²⁺(100), TBT-Ni²⁺(100) and TBT-Co²⁺(250), TBT-Ni²⁺(250) samples.

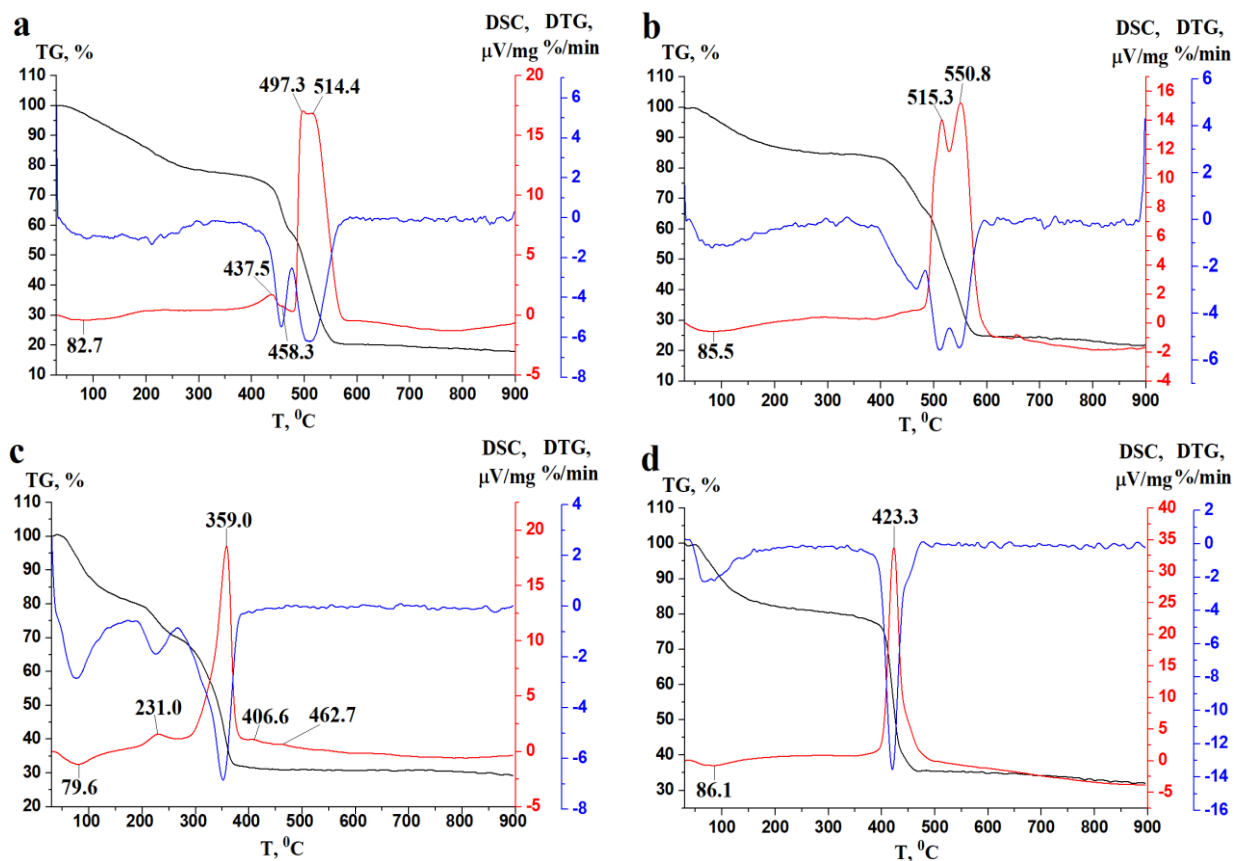


Figure 1. Thermal analysis data for initial samples:
a – TBT-Ni²⁺(100); b – TBT-Co²⁺(100); c – TBT-Ni²⁺(250); d – TBT-Co²⁺(250).

Analysis of STA data (curves of thermogravimetry (TG), differential scanning calorimetry (DSC) and differential thermogravimetry (DTG) analysis) (figure 1) allowed us to see the main stages of formation of composite particles in the temperature range from 25 to 900 °C. It is seen that the thermogravimetry (TG) curves of all samples have two weight change regions (figure 1).

The first region in the temperature range from 75 to 100 °C contains one endothermic effect. It is connected with the removal of adsorbed water molecules for all samples. Used ion exchange resins are porous materials with different polar functional groups and with high specific surface area, which makes it difficult to completely dehydrate of them, especially when impurities of metal ions presence in the samples [17, 18]. In the temperature range from 200 to 250 °C on the thermogram of the TBT-Ni²⁺(250) sample (figure 1c) there is one exothermic effect. This effect is associated with the removal of the water of crystallization.

At higher temperature, there is decomposition of an organic polymer matrix, decomposition of sol based on TBT and oxidation of organic matters for all samples. It is accompanied by several exothermic effects in the temperature range from 250 to 900 °C. Exothermic effects are observed at temperatures of 437.5; 497.3; 514.4 °C and 515.3; 550.8 °C, respectively for TBT-Ni²⁺(100), TBT-Co²⁺(100) samples (figure 1a, 1b). Exothermic peaks of the DSC profiles of TBT-Ni²⁺(250), TBT-Co²⁺(250) samples are observed at more low temperatures. We can see it at the temperature of 359.0 °C (figure 1c) and 423.3 °C (figure 1d), respectively.

Figure 1 shows that the decomposition process of TBT-Ni²⁺(100) and TBT-Co²⁺(100) samples reaches completion at a temperature of 600 °C. The decomposition process of samples prepared using TOKEM-250 ends at 500 °C (figure 1c, 1d).

The results of XRD and EDX spectroscopic analysis of prepared samples are presents in figures 2, 3 and 4 respectively.

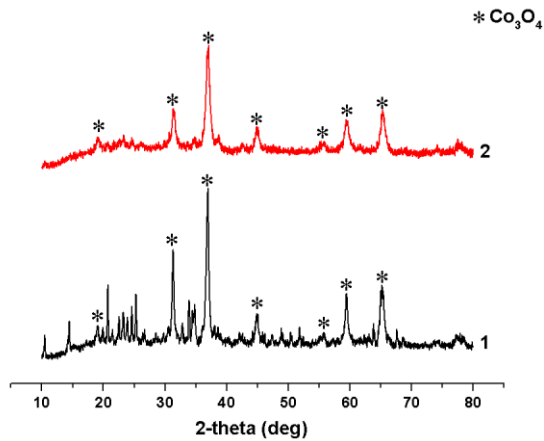


Figure 2. XRD patterns of composite particles: 1 -TiO₂-Co₃O₄(100); 2 -TiO₂-Co₃O₄(250).

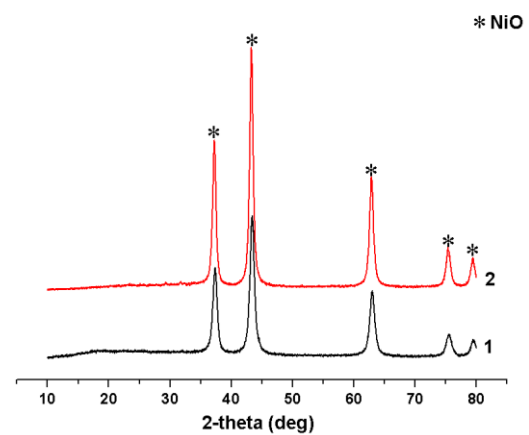


Figure 3. XRD patterns of composite particles: 1 -TiO₂-NiO(100); 2 -TiO₂-NiO(250).

According to X-ray powder diffraction data (figure 2), annealing of TBT-Co²⁺(100) and TBT-Co²⁺(250) samples at 600 and 500°C, respectively results in formation of a Co₃O₄. The only pure cobalt oxide phase identified was Co₃O₄ according to the PDF-2 cards 01-074-1656 and 00-043-1003 for obtained TiO₂-Co₃O₄(100), TiO₂-Co₃O₄(250) composite particles, respectively.

In XRD pattern of TiO₂-NiO(100) and TiO₂-NiO(250) composites prepared by annealing of TBT-Ni²⁺(100) and TBT-Ni²⁺(250) samples, the only pure nickel phase identified was NiO according to the PDF-2 card 00-044-1159 (figure 3).

The XRD patterns of all samples (figure 2 and 3) do not display any TiO₂ peak. We suggest that TiO₂ is either highly dispersed in bulk phases of Co₃O₄ and NiO or TiO₂ content is below the instrument detection limit (less 5 wt. %).

The results of a qualitative (figure 4) X-ray spectral microanalysis confirm the presence of the titanium in the composition of final TiO₂-Co₃O₄(100), TiO₂-Co₃O₄(250) and TiO₂-NiO(100), and TiO₂-NiO(250) particles. According to previous studies [8, 12] and obtained results of EDX analysis, we assume the formation of TiO₂. The results of the quantitative EDX analysis show that the content of titanium compound in the obtained samples is less than 1 wt. %. This result agrees with the XRD data.

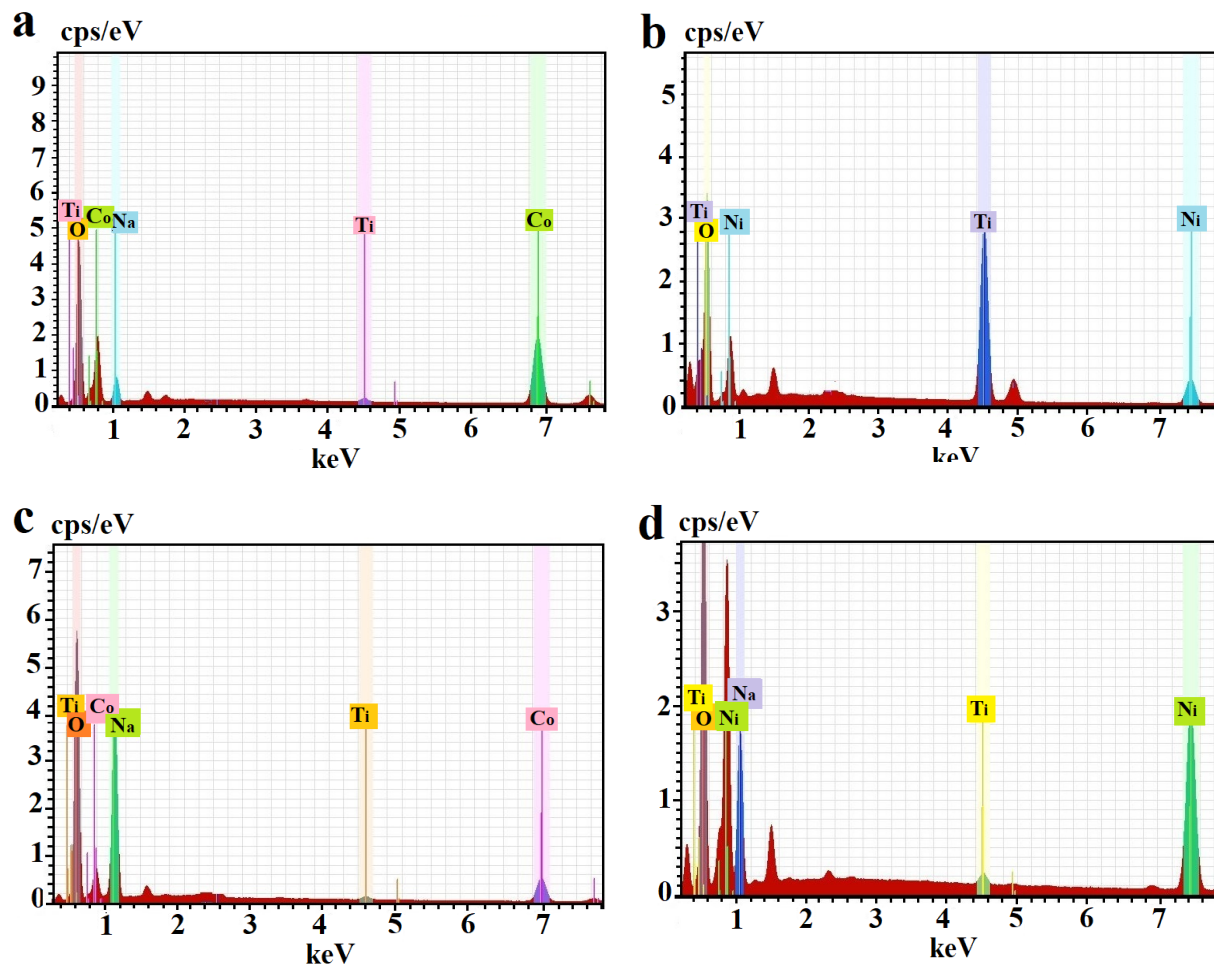


Figure 4. EDX images of samples:
 a –TiO₂–Co₃O₄(100); b –TiO₂–NiO(100); c –TiO₂–Co₃O₄(250); d –TiO₂–NiO(250).

According to SEM data, prepared TiO₂–Co₃O₄(100), TiO₂–NiO(100), TiO₂–Co₃O₄(250), TiO₂–NiO(250) particles have spherical form. The size distribution for TiO₂–Co₃O₄(100) and TiO₂–NiO(100) is 300...590 μm (figure 5a, 5b) compared to TiO₂–Co₃O₄(250) and TiO₂–NiO(250) particles side in the range of 400...710 μm (figures 5c, 5d). Particle size obviously depends on the resin type: particles prepared using TOKEM-250 resin having bigger granules are characterized by larger size.

The micrograph images (figures 5e–5h) show the formation of spherical composites with different surface morphology. Spherical TiO₂–Co₃O₄(100), TiO₂–Co₃O₄(250) composites are characterized by a more uniform morphology of the surface than other samples (figures 5e, 5g). The TiO₂–NiO(100) composite is characterized by more rougher morphology of the surface (figure 5f). The most non-uniform morphology of the surface is observed for TiO₂–NiO(250) composite (figure 5h): densely packed large agglomerates are observed on the surface of the sphere.

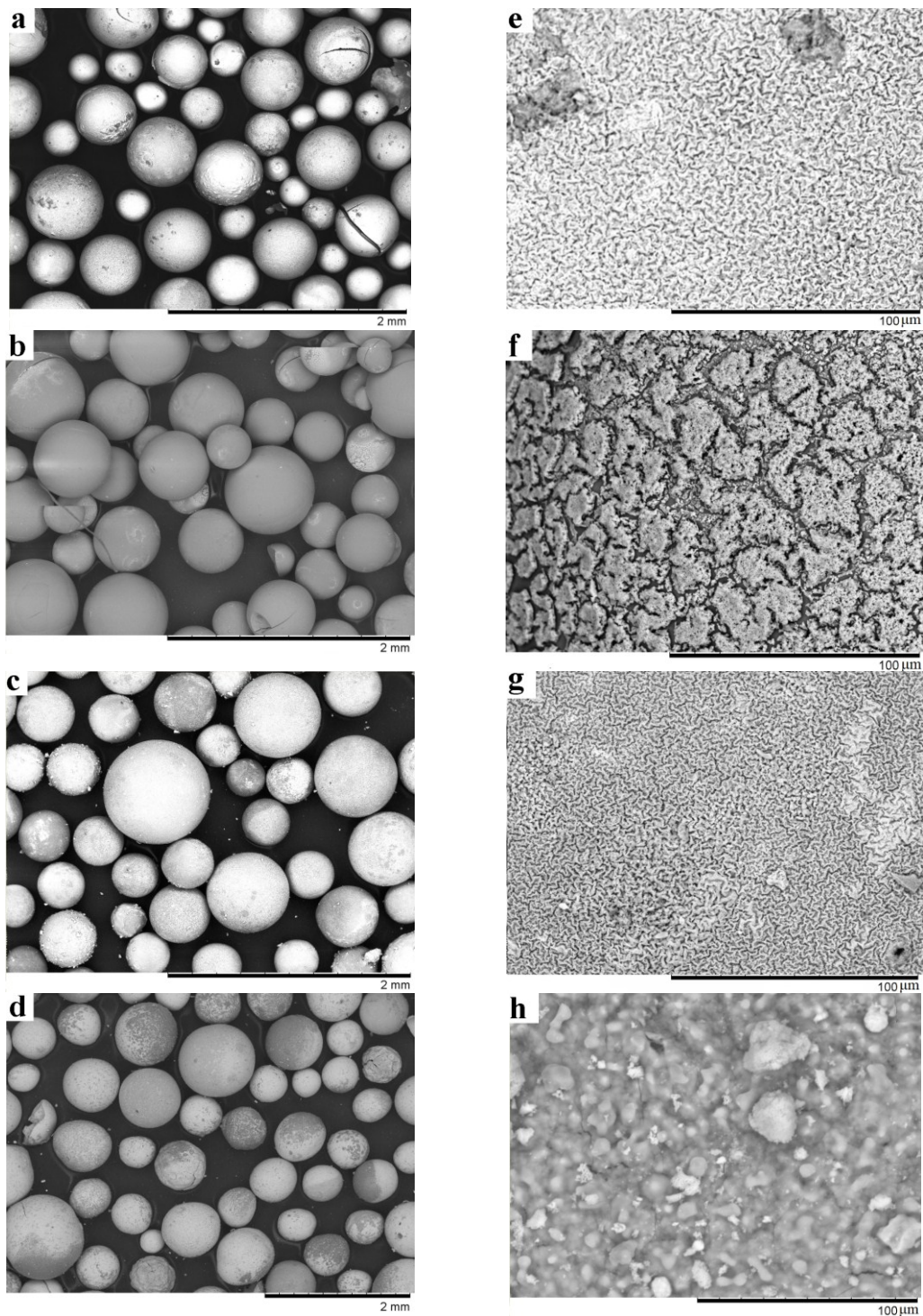


Figure 5. SEM images of composite particles: a,e – $\text{TiO}_2\text{-Co}_3\text{O}_4(100)$; b,f – $\text{TiO}_2\text{-NiO}(100)$; c,g – $\text{TiO}_2\text{-Co}_3\text{O}_4(250)$; d,h – $\text{TiO}_2\text{-NiO}(250)$.

4. Conclusion

In summary, in this paper we obtained spherical particles of $\text{TiO}_2\text{-NiO}$ and $\text{TiO}_2\text{-Co}_3\text{O}_4$ composites by a template method accompanied with sol-gel one. The main stages of formation of composite particles in the temperature range from 25 to 900 °C are removal of adsorbed water molecules and decomposition of an organic polymer matrix, decomposition of sol based on TBT and oxidation of

organic matters for all samples. The formation of $\text{TiO}_2\text{-Co}_3\text{O}_4$ and $\text{TiO}_2\text{-NiO}$ composite particles ends at 600 and 500°C, respectively at using TOKEM-100 and TOKEM-250 resins. The formation of Co_3O_4 and NiO phases and presence of the TiO_2 phase confirm by X-ray powder diffraction data and qualitative X-ray spectral microanalysis. Particle size obviously depends on the resin type: particles prepared using TOKEM-250 resin having bigger granules are characterized by larger size (400...710 μm) and particles prepared using TOKEM-100 resin having smaller granules are characterized by size in the range of 300...590 μm . Morphology of spherical composites depends on its composition: spherical $\text{TiO}_2\text{-Co}_3\text{O}_4$ composites are characterized by a more uniform morphology of the surface than $\text{TiO}_2\text{-NiO}$ composites. Prepared spherical particles of $\text{TiO}_2\text{-NiO}$ and $\text{TiO}_2\text{-Co}_3\text{O}_4$ composites are prospective catalysts.

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