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Production of CeO_2/NiO and CeO_2/NiO-Pt Nanocomposites by EPM

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***Abstract*—Nanocomposites CeO_2/5wt.% NiO, CeO_2/Pt and CeO_2/5wt.% NiO-Pt with different Pt loading were produced by the extractive-pyrolytic method (EPM) and characterized by XRD and SEM. NiO and Pt were deposited on a carrier (CeO_2 nanopowder) by thermal decomposition of nickel hexanoate and n-trioctylammonium hexachloroplatinate, respectively. XRD analysis showed that in CeO_2/5wt.% NiO nanocomposites the mean size of nickel oxide crystallites increases (from amorphous to 18 nm) when the pyrolysis temperature increases from 300 °C to 700 °C. In CeO_2/ Pt nanocomposites with the Pt content from 0.3 wt.% to 2.4 wt.%, both with NiO and without it, the Pt particles are X-ray amorphous. With a higher metal content (4.8 wt.%) in CeO_2/NiO-Pt composites, the mean size of Pt crystallites was 4 nm that is twice less if compared with the CeO_2/Pt composite. The produced nanocomposites were tested in glycerol oxidation processes by molecular oxygen. It has been found that CeO_2/Pt and CeO_2/5 wt.% NiO-Pt composites are catalytically active in alkaline glycerol water solutions. It was shown that the Pt weight loading (0.3 – 1.2 %) in the composites significantly affected the glycerol conversion (12 – 68 %). The main product of oxidation was glyceric acid.**

***Index Terms*—extractive-pyrolytic method, nanocomposites, platinum, nickel oxide, ceria.**

I. Introduction

Due to its redox properties and high oxygen storage capacity, cerium oxide is widely used as a catalyst support in oxidation and hydrogenation reactions [1-3]. The ceria-supported nickel oxide catalysts exhibit high catalytic activity in the reactions of isopropanol conversion [2], benzene hydrogenation [3] and others. Platinum supported on ceria is the most promising catalyst for application in the water-gas-shift (WGS) reaction [4, 5]. It was found [6, 7] that the modification of ceria-supported platinum catalysts by oxides of transition or rare-earth metals could contribute to the enhancement of the WGS reaction rate. Moreover, as the authors note, the efficiency of such catalytic systems is determined as by the nature of the introduced metal as by the way of carrier modification (surface or bulk). In some cases, the bulk modification of ceria by oxides of rare-earth metals can negatively affect the catalyst activity. For example, in the reaction of n-butane oxidation, such materials are much less active than pure ceria [8]. For the bulk modification of ceria, the sol-gel method is usually used as in [6, 8] or the urea-nitrates combustion method as in [7]. The impregnation method involving the use of aqueous solutions of metal salts is widely used for the surface modification of ceria by metal oxides [2, 3, 6] and platinum metals [6, 7].

The extractive-pyrolytic method (EPM) is a new method of "soft chemistry" which involves the use of extraction systems for the preparation of noble metal nanoparticles on carriers [5, 9-11] and functional powder- or film-like oxide materials on substrates [12, 13]. The use of platinum-containing organic solutions (extracts) at the stage of impregnation of powder carriers followed by pyrolysis allows to produce materials which exhibit high catalytic activity in the WGS reaction [5] and in the reaction of glycerol oxidation by molecular oxygen in aqueous solutions [9]. The main advantages of the EPM for the production of catalysts are its simplicity, high productivity and low cost.

The aim of this work is to study possibilities of the EPM for the surface modification of the support by nickel oxide at the preparation of CeO_2/NiO and CeO_2/NiO-Pt composites, to investigate the phase composition and morphology of the produced materials, and to examine the influence of the modifier on the catalytic activity of the platinum-containing composites in the reaction of glycerol oxidation by molecular oxygen.

II. Experimental

To produce a nickel-containing organic extract (precursor)- nickel hexanoate in hexanoic acid – the method of exchange extraction by fat acids with addition of alkali was applied [14]. Hexanoic acid $C_5H_{11}COOH$ with no diluent was used as an extractant. To define the concentration of nickel in the organic solution, the metal was reextracted in a diluted HCl solution (1:5) and the concentration of nickel in the aqueous solution was defined photometrically [15].

The thermal stability of nickel hexanoate, obtained after removing a hexanoic acid excess from the extract in vacuum, was studied by the method of thermogravimetric analysis using a derivatograph Q-1500D (F.Paulik, J.Paulik, L.Erdey system). The sample was heated in the air at 5 °C/min until 400 °C.

To produce a CeO_2/5 wt.% NiO composite, the Ni-containing extract (C_{Ni} = 0.78 M) was diluted by ethanol

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until the concentration C_{Ni} = 0.23 M, and a carrier (commercial CeO_2 nanopowder) was impregnated with the produced solution. Then the sample was dried at room temperature and thermally treated in the air: it was heated from room temperature to a pyrolysis end temperature (T_{pyr}) at the 10 °C/min rate and then annealed.

The CeO_2/5 wt.% NiO composites produced at T_{pyr}=300 °C and 700 °C were used as a carrier for the deposition of platinum. The production of a platinum-containing precursor – a solution of n-trioctylammonium hexachloroplatinate in toluene – and Pt-containing composites is described in detail in [5]. Platinum content in the produced composites was 0.3 wt.% - 4.8 wt.%.

The phase composition of the produced composites was characterized by the X-ray diffraction method using a diffractometer D8 Advance (Bruker Corporation) with CuK_α radiation (λ = 1.5418 Å). The XRD patterns were referenced to the PDF ICDD 04-0802 for Pt identification, to PDF ICCD 47-1049 and PDF ICCD 04-0850 for NiO and Ni identification, respectively. The mean size of platinum, nickel oxide and nickel crystallites (d) was defined from the (111), (200) and (111) peak widths, respectively, by the Scherrer method.

SEM measurements were made using the Zeiss EVO50XVP (3 nm resolution at 30 kV) which was equipped with the Energy Dispersive Spectrometer (EDX) for composition analysis.

The specific surface area (SSA) of the samples was measured by the BET method at the temperature of liquid nitrogen using the HROM-3 chromatograph. Magnetic measurements were made at room temperature by a vibrating sample magnetometer (Lake Shore Cryotronics, Inc., model 7404), with a maximum magnetic field of 1 T.

Glycerol was oxidized by molecular oxygen in the presence of the produced composites in alkaline aqueous solutions in a thermo-stated slurry bubble column reactor operated in a batch mode. In order to determine the concentration of the reaction products, liquid samples were collected periodically from the reaction mixture. The filtered samples were analyzed by a high performance liquid chromatograph (WATERS 2487).

III. Results and Discussion

It is known [16] that the thermal decomposition of metal-organic compounds has a complex mechanism, with subsequent stages of dehydration and decomposition of hydrocarbon chains and is accompanied by the emission of gaseous products CO_2, CO, CH_4, C_2H_6. In this study thermogravimetric analysis was applied to determine the minimum temperature for the decomposition and removal of the organic component of the Ni-containing precursor. The DTA and TG results are summarized in Table 1.

The performed investigations have revealed two stages of the decomposition process. At the first stage, the mass losses between 90 - 220 °C are determined both by the removal of molecules of water and carbonic acid and by the release of terminal ethylene molecules [17]. At the second stage, the exothermal maxima at 290 °C and 300 °C correspond to the decomposition of the organic moiety of the sample and to the combustion of the gaseous products of decomposition. Upon achieving 300 °C, the mass losses practically diminished and comprised 80.7%. The further temperature increase to 345 °C was accompanied by small mass losses (1.5%).

Table 1: Results of thermogravimetric analysis of nickel hexanoate.

DTA		TG
Peak, °C	Temperature range, °C	Mass losses, %
195 (endothermic)	90 - 220	18.2
290, 300 (exothermic)	220 - 345	64.0
Total mass loss, %		
Experiment		82.2
Calculation for NiO		74.2
Calculation for Ni		79.7

The difference between the experimentally found value of the total mass loss in the sample and the calculated value (see Table 1) can be caused as by the presence of chemically bounded water and small amounts of carbon acid in the initial sample as by the presence of Ni along with NiO in the final product of decomposition that is confirmed by the investigation results described below.

The XRD analysis of the pyrolysis products (T_{pyr} = 400 °C, t_{anneal} = 5 min) of the nickel-containing precursor showed (see Fig. 1) the presence of a crystalline phase of nickel (d_{Ni} = 40 nm) in the sample along with the basic phase of NiO (d_{NiO}=20 nm).

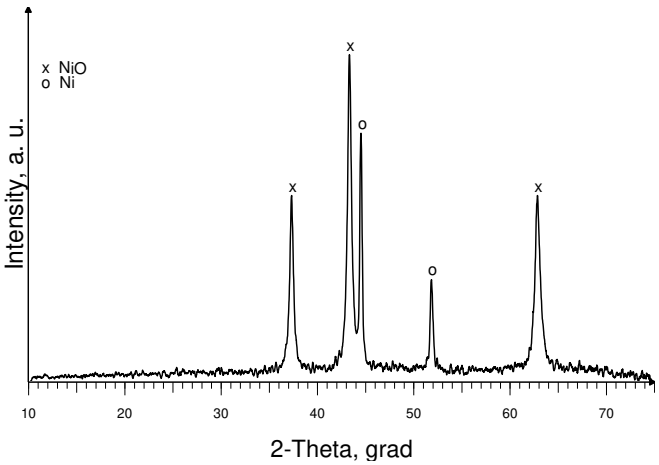

Fig. 1: XRD pattern of the Ni-containing precursor pyrolysis products.

Metallic nickel exhibits spontaneous magnetization (σ), i.e. it is ferromagnetic. The σ value allows to evaluate the concentration of ferromagnetic even at its low content in the investigated material. That is why the pyrolysis products of the nickel-containing precursor were characterized by magnetic measurements. The investigations have shown ferromagnetic properties of the sample: the coercivity H_c = 15 kA/m and the magnetization σ = 10.6 $A \cdot m^2/kg$, which, with reference to the magnetization value 54.39 $A \cdot m^2/kg$ of pure nickel [18], corresponds to the metal content 19 wt.% in the produced material.

It was found (Fig. 2) that after thermal treatment of the nickel-containing extract on the carrier at 300 °C the products

of decomposition were x-ray amorphous (Fig. 2, curve 1) and the specific surface area (SSA = 29 m^2/g) of the produced CeO_2/NiO composite was a bit larger than the SSA of the carrier (26 m^2/g). With the temperature increase from 500 to 700 °C, the x-ray patterns of the produced samples showed the increase in intensity of the NiO diffraction peak (200) (Fig. 2, curve 2, 3) and hence the increase of d_{Ni} from 10 nm to 18 nm.

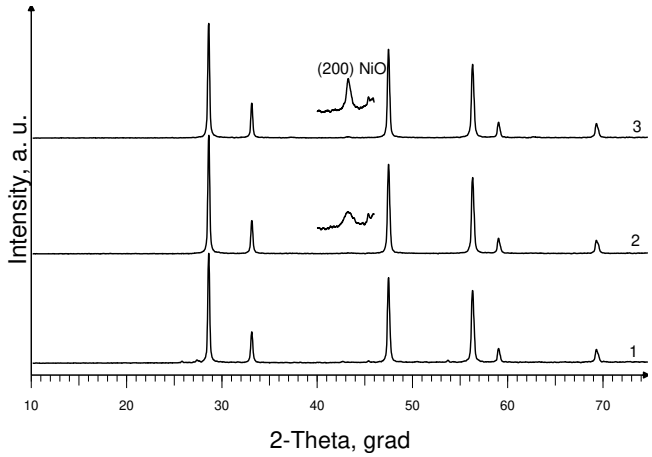

Fig. 2: XRD patterns of the CeO_2/5 wt.% NiO composites produced under different conditions: 1 - T_{pyr} = 300 °C, t_{anneal} = 30 min; 2 - T_{pyr} = 500 °C, t_{anneal} = 5 min; 3 - T_{pyr} = 700 °C, t_{anneal} = 5 min.

The magnetic measurements revealed the presence of only small amounts of nickel in the composite produced: 0.002 % at 300 °C (H_c = 2 kA/m, σ = 1.2 10^{-3} emu/g) and < 0.0002 % at 700 °C (σ < 7 10^{-5} emu/g).

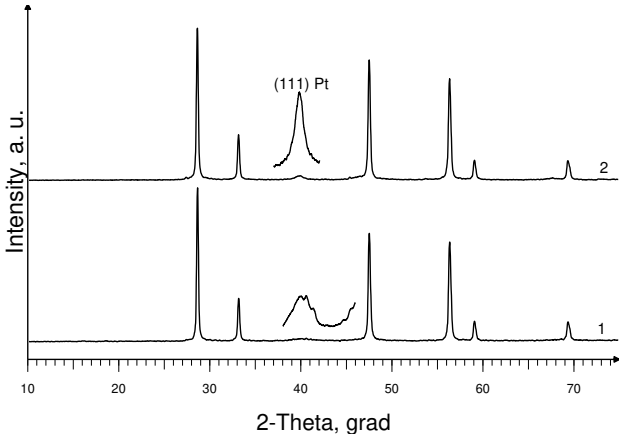

Fig. 3: XRD patterns of samples: 1 - CeO_2/5 wt.% NiO-4.8wt.% Pt; 2 - CeO_2/4.8 wt.% Pt. (Production conditions: CeO_2/5 wt.% NiO - T_{pyr} = 300 °C, t_{anneal} = 30 min; CeO_2/5 wt.% NiO-Pt 4.8 wt.% and CeO_2/Pt 4.8 wt.% - T_{pyr} = 300 °C, t_{anneal} = 5min).

In order to study the influence of the modifier (NiO) on d_{Pt} and on the catalytic properties of new materials, a series of CeO_2/Pt and CeO_2/5wt.% NiO-Pt composites with different Pt-content was produced. With reference to the XRD data, in CeO_2/Pt nanocomposites with the Pt content from 0.3 wt.% to 2.4 wt.% the platinum particles are amorphous both with the presence of nickel oxide and without it. With the higher metal content (4.8 wt.%), the observed widening of the Pt diffraction peak (111) (Fig. 3) evidences of d_{Pt} decrease in the presence of NiO in the Pt-containing composite. In this case, d_{Pt} = 4 nm, which is twice less if compared with d_{Pt} in a non-modified composite. Note that independent on the conditions of thermal treatment (300 °C or 700 °C) at the stage of carrier modification, the nickel oxide is amorphous in all produced Pt-containing composites.

Figure 4 displays a typical SEM image of the CeO_2/5 wt.% NiO-Pt 4.8 wt.% sample. The data testify that the composite particles form agglomerates with irregular shapes and sizes from 2 to 50 μm. The EDS spectrum shows the presence of platinum and nickel in the produced composite.

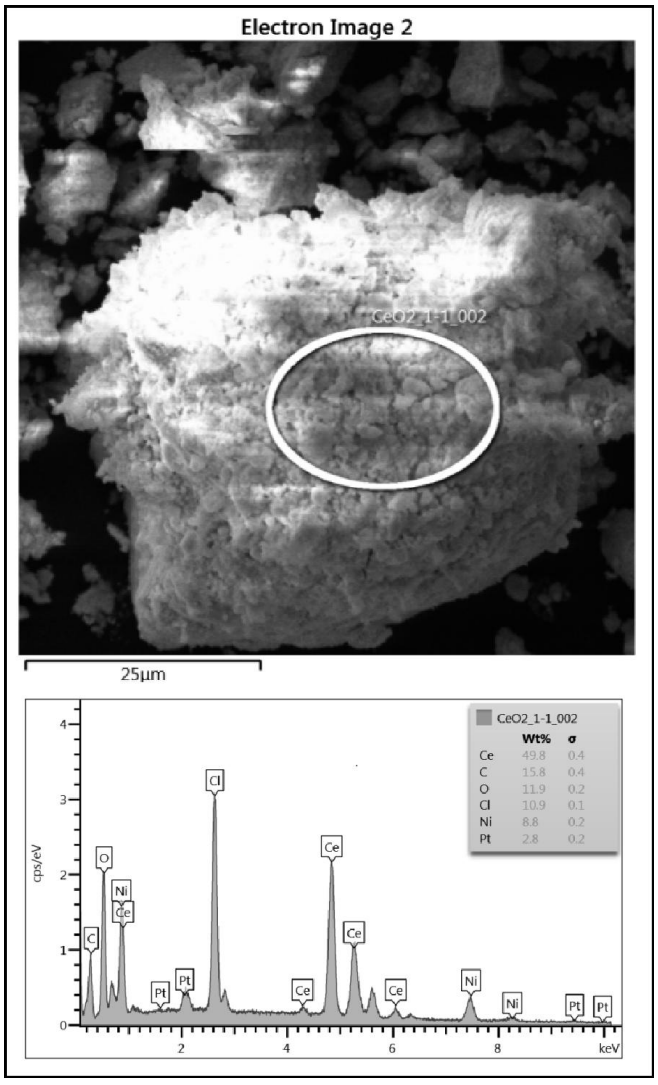

Fig. 4: SEM micrograph and EDS spectrum of the CeO_2/5 wt.% NiO-Pt 4.8 wt.% composite. (Production conditions: CeO_2/5 wt.% NiO - T_{pyr} = 700 °C, t_{anneal} = 5min; CeO_2/5 wt.% NiO-Pt 4.8 wt.% - T_{pyr} = 300 °C, t_{anneal} = 5min).

The catalytic activity of the composites produced by EPM was tested in the reaction of glycerol oxidation by molecular oxygen. To produce the catalysts NiO was deposited on CeO_2 by the pyrolysis of Ni-containing extract at 300 °C and annealing for 30 min, then Pt was deposited on NiO-CeO_2 composites by the pyrolysis of Pt-containing extract at 300 °C and annealing for 5 min. The composite activity was characterized by the degree of glycerol conversion. The results of the oxidation reaction versus the composite

composition are summarized in Table 2. The data presented in the Table testify that in the presence of CeO_2/5 wt.% NiO the reaction of glycerol oxidation does not take place, whereas all Pt-containing composites are catalytically active. The main product of oxidation in all cases is glyceric acid, but lactic, tartronic, glycolic, acetic, oxalic and formic acids are by-products.

The composites with the 0.6 wt.% platinum content are the most catalytically active. The conversion of glycerol in the presence of CeO_2/0.6 wt.%Pt and CeO_2/5 wt.% NiO-0.6 wt.% Pt was 63-68%. Yet, the selectivity of the process for glyceric acid did not exceed 42-47%.

The largest selectivity for glyceric acid was found at the glycerol oxidation in the presence of CeO_2/1.2 wt.% Pt (the 74% selectivity at the 44% conversion). With reference to the obtained results, the modification of the Pt-containing composites leads to enhancing of their catalytic activity, i.e. the modifier has a promoting effect. The conversion of glycerol increases by 10-50% depending on the platinum content in the composite, yet, in this case, a decrease of the selectivity of the glycerol oxidation process was observed. A similar promoting effect was found in [19] when investigating the oxidation of glycerol in the presence of the Pt/TiO_2 and $Pt_mNi_nO_x$/TiO_2 catalysts. It was shown that reducing the size of the platinum particles when introducing NiO into the catalyst composition could result not only in its enhanced activity, but in decrease of the oxidation process selectivity.

Table 2: Glycerol oxidation over different composites.

Composite	Conversion, mol%	Selectivity, mol%			
		Lactic acid	Glyceric acid	Glycolic acid	Others
CeO_2/5 wt.% NiO	0.4	0	19	0	81
CeO_2/0.3 wt.% Pt	12	22	57	4	17
CeO_2/5 wt.% NiO-0.3 wt.% Pt	24	11	39	39	11
CeO_2/0.6 wt.% Pt	63	4	42	9	45
CeO_2/5 wt.% NiO-0.6 wt.% Pt	68	28	47	15	10
CeO_2/1.2 wt.% Pt	44	15	74	4	7
CeO_2 /5 wt.% NiO-1.2 wt.% Pt	53	32	49	12	7

Reaction conditions: $c_{0(glycerol)}$=0.3 mol/L, Po_2= 1 atm, $c_{0(NaOH)}$=1.5 mol/L, n(glycerol)/n(Pt) =300 mol/mol, 60 °C, t = 300 min.

IV. Conclusions

The performed investigations have demonstrated that the EPM allows to produce fine dispersed particles of NiO on the powder carrier (from X-ray amorphous to d=18 nm). The modification of the CeO_2/4.8 wt.% Pt composite by nickel oxide results in the twice decrease of the mean size of the platinum crystallites.

The investigation of the catalytic properties of the produced composites at liquid phase oxidation of glycerol has revealed that the modification of the Pt-containing composites by NiO enhances their catalytic activity by 10-50% depending on the platinum content in the composite.

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