

EFFECT OF STRUCTURAL PROMOTERS ON THE REDUCTION PROCESS OF NANOCRYSTALLINE COBALT OXIDES

Z. Lendzion-Bieluń, M. Podsiadły, U. Narkiewicz and W. Arabczyk

Institute of Chemical and Environment Engineering, Szczecin University of Technology, Puiaskiego 10, 70-322 Szczecin, Poland

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Abstract. The effect of structural promoters (CaO i Al₂O₃) addition on the reduction process of cobalt oxides was studied. The mixture of hydroxides of cobalt, calcium and aluminium, obtained by precipitation from nitrates, was calcinated at 900 °C. After the reduction with hydrogen, the nanocrystalline cobalt was obtained, doted with small amount of structural promoters. The reduction kinetics was studied using thermogravimetry. The reduction process is described by the equation: $\alpha=1-(1-\alpha_0)\cdot e^{-kt}$. The apparent activation energy of the reduction process was determined.

1. INTRODUCTION

The nanocrystalline metals are very interesting because of their unique magnetic, optic, and chemical properties and they can be applied in electronics, catalysis, medicine, xerography, etc. A lot of preparation methods of nanocrystalline metals such as Au, Pd, and Fe was developed recently [1-4]. Among various chemical methods of powder preparation, the synthesis of metals from aqueous salt solutions followed by reduction with hydrogen under increased pressure and at high temperature is the most frequently used [5]. Nanocrystalline cobalt (crystallite size from 5 to 13 nm) was obtained by chemical condensation of vapours (*Chemical Vapor Condensation – CVC*) [6,7]. Jang *et al.* [8] obtained nanocrystalline cobalt powder by the re-

duction of cobalt chloride vapours with hydrogen. Yin *et al.* [9] obtained cobalt with mean crystallite size of 9 nm by the thermal decomposition of Co₂(CO)₈ in toluene. Guo *et al.* [10] applied hydrazine as a reducing agent for cobalt chloride and obtained cobalt of regular (*fcc*) and hexagonal (*hcp*) structure. It is known that water under the effect of γ radiation generates a lot of active particles, which can reduce the ions of metals to atoms. Among others, the nanocrystals of cobalt and nickel were obtained from colloidal suspension under the effect of γ rays. Using this method Kapoor [11] obtained cobalt of regular structure and crystallites of 5 – 6 nm. Wang *et al.* [12] obtained hexagonal cobalt using a similar preparation method.

Corresponding author: M. Podsiadły, e-mail: mpodsiadly@ps.pl

In the present paper the preparation method of nanocrystalline cobalt doted with structural promoters (CaO i Al_2O_3) obtained by reduction of oxides is described.

2. EXPERIMENTAL

The nanocrystalline cobalt doted with calcium and aluminium oxides was obtained by coprecipitation of corresponding hydroxides, followed by calcination and reduction.

Nitrates of cobalt (II), calcium, and aluminium were dissolved in water. The metal hydroxides were precipitated from the solution using 25% ammonia solution or KOH solution.

The obtained deposit was washed with water, filtered and next dried at 70 °C. Next preparation step was the calcination at 900 °C during 3 hours.

The chemical composition of the samples was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY 238 Ultrace equipment from Jobin Yvon). The phase composition of the samples was determined using XRD technique (CoK_α radiation).

The precursor of nanocrystalline cobalt after the calcination was reduced under pure (99.999%) hydrogen flow of 20 dm^3/h . The reduction was carried in a differential reactor with thermogravimetric mass measurement. The sample of precursor of nanocrystalline cobalt of 0.5 g was placed as a single layer of grains in a platinum basket. Taking into account this single layer packing of grains in the basket and the conditions of the reaction rate measurements (the fixed concentration on the reactor inlet and outlet, a low maximal partial pressure of the reaction product - H_2O), the experimental reactor can be considered as a differential one. The reduction process was studied under polythermal conditions. The process was carried out in the temperature range of 25 – 500 °C, with the heating rate of 2 °C/min. The reduction processes were also carried out isothermally in several temperatures. Before each isothermal reduction the sample was annealed under a flow of pure helium (99.9996%) up to the process temperature.

After each reduction experiment, the samples of nanocrystalline cobalt were passivated to avoid a dramatic oxidation in contact of the samples with air. The mean crystallite size of cobalt was determined on the basis of Scherrer's equation.

The specific surface area was determined using a thermal desorption of nitrogen.

Table 1. Content of promoters in the precursor of nanocrystalline cobalt.

Sample name	CaO [wt.%]	Al_2O_3 [wt.%]	K_2O [wt.%]
P0	0.00	0.00	0.00
P1	0.38	0.64	3.62
P2	0.29	3.78	0.00
P3	1.68	2.27	0.00

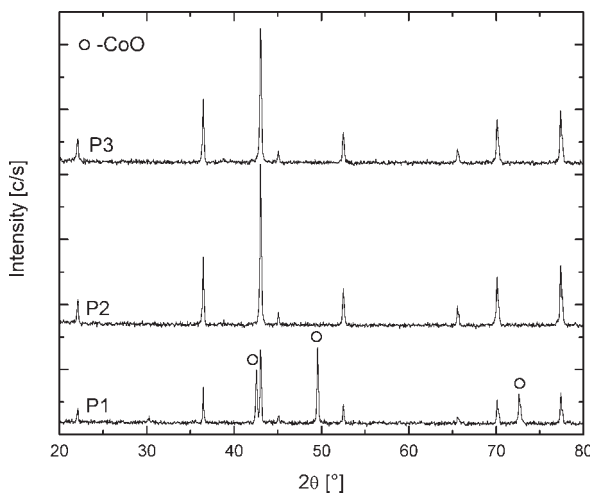


Fig. 1. XRD spectra of the samples after calcination at 900 °C (3h). The non marked peaks are attributed to Co_3O_4 .

3. RESULTS AND DISCUSSION

The coprecipitated deposits were calcinated and a series of samples of the precursor of nanocrystalline cobalt having various structural promoters concentration is obtained. The chemical composition of the samples after calcinations is presented in Table 1.

The XRD spectra of the same samples are shown in Fig. 1. Only Co_3O_4 was found in the samples P0 (not shown here), P2 and P3. According to the literature, the phase transition from Co_3O_4 to CoO occurs at the temperature above 900 °C [13]. The two cobalt oxides - Co_3O_4 and CoO - are present in the sample P1 (with K_2O addition) only. Taking into account the results presented in Fig. 1, this phase transition took place only in the sample containing potassium oxide. It can be concluded that the addition of potassium oxide causes the decrease of the temperature of transition from Co_3O_4 to CoO.

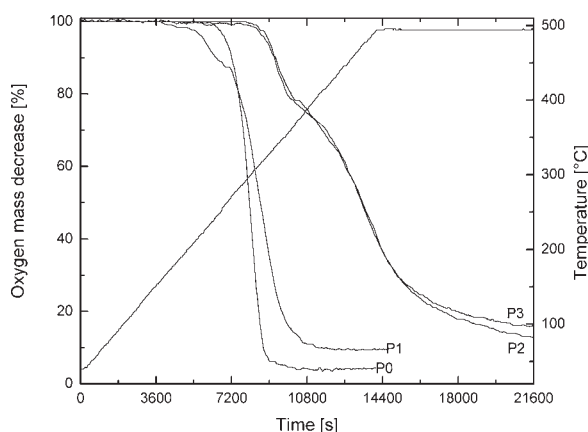


Fig. 2. Polythermal reduction of the precursor of nanocrystalline cobalt.

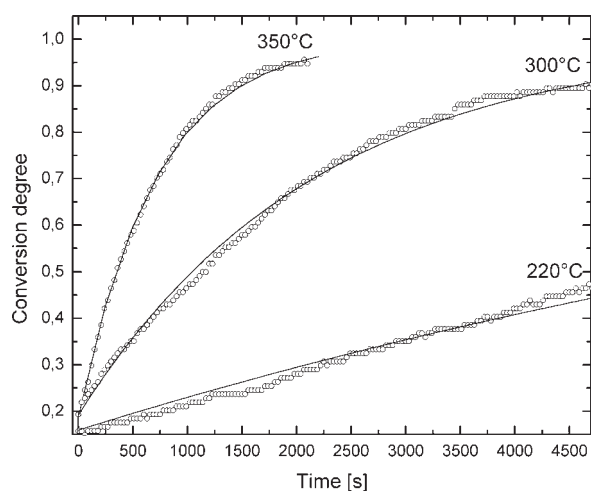


Fig. 3. Conversion degree of cobalt oxides in the sample P1 as a function of reduction time.

The oxygen mass change in the samples during the polythermal reduction is presented in Fig. 2. The reduction of sample P0 without promoters begins at the 250 °C. The reduction of the sample with potassium oxide and low calcium and aluminium oxides content starts at the temperature of about 200 °C; the reduction of others samples commences at a temperature higher than 300 °C. The addition of K₂O reduces the reduction temperature, while the addition of CaO and Al₂O₃ raises the reduction temperature of Co₃O₄. All the TG curves (except the sample P0, without promoters) have two inflexion points, which indicates a two-stage reduction process. The mass decrease of the samples P2 and P3 in the first reduction step is about 22%, which corresponds to the mass of oxygen which could be released in the case of the reduction of Co₃O₄ to CoO. The mass decrease of the sample P1 in the first reduction step is about 13%, but in this case a part of Co₃O₄ was reduced to CoO during the calcinations. In the first reduction step Co₃O₄ is reduced to CoO, and the reduction of CoO starts after a complete reduction of Co₃O₄. The similar results showing a two-steps reduction of iron–cobalt catalyst for ammonia synthesis are described in [14,15].

However, the reduction of CoO is not complete and some unreduced CoO remains in the sample after the reduction. The remaining unreduced mass fraction of samples P1 and P2 equals about 9% and 13%, respectively. The content of Al₂O₃ in these samples is different, while the content of CaO is

similar. The sample P3 contains the highest concentration of Al₂O₃ and CaO and the mass decrease in this sample is the lowest - about 16% of oxygen remain connected with Co. The mass decrease of sample P0, without promoters, is the greatest. Only 4% of oxygen remain in sample. It can be then concluded that the total mass decrease connected with reduction process depends on the concentration of structural promoters: CaO and Al₂O₃. The increase of the concentration of promoters causes the increase of the mass of CoO, which is bound in hardly reducible three-dimensional structures xAl₂O₃·yCaO·zCoO, then the mass of oxygen released by a sample diminishes.

All the precursors of nanocrystalline cobalt were also reduced with hydrogen under isothermal conditions. On the basis of the thermogravimetric data a conversion degree of CoO to Co (2nd reduction stage) as a function of time was determined. Fig. 3. shows the conversion degree of cobalt oxide in the sample P1 as a function of time. For the description of the reduction kinetics of cobalt oxides the following equation has been taken:

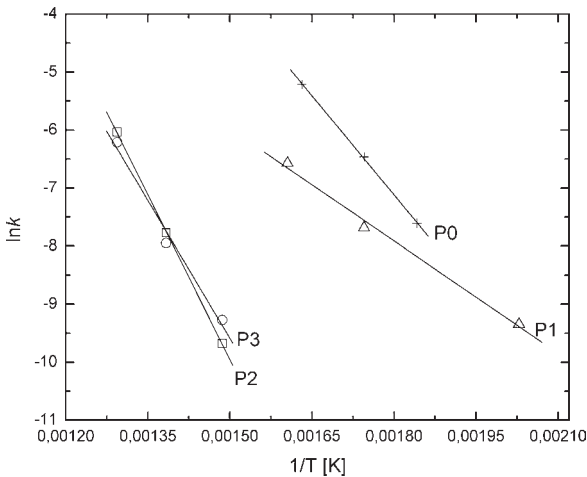
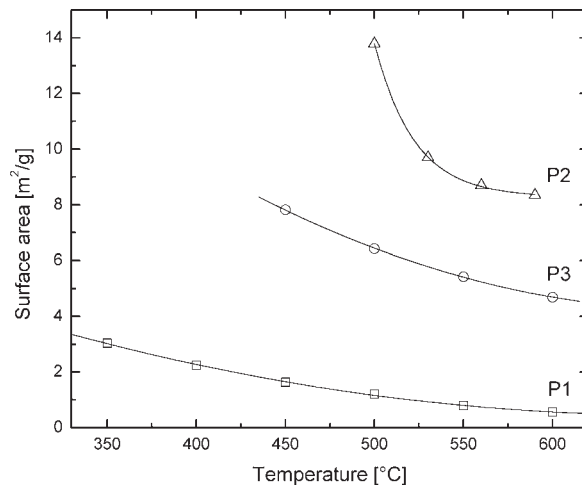
$$\alpha = 1 - (1 - \alpha_0) \cdot e^{-kt}, \quad (1)$$

where: α – conversion (reduction) degree, α_0 – initial conversion (reduction) degree, k – reaction constant rate, t – time.

The experimental points are fitted with lines corresponding to Eq. (1). The Arrhenius lines were plotted (Fig.4) on the basis of reaction constant rates k

Table 2. Apparent activation energy of the reduction of cobalt oxides.

Sample	Content of promoters [%-wt.]			Apparent activation energy [kJ/mol·K]
	Al ₂ O ₃	CaO	K ₂ O	
P0	0.00	0.00	0.00	95
P1	0.64	0.38	3.62	54
P2	3.78	0.29	0.00	158
P3	2.27	1.68	0.00	132

**Fig. 4.** Arrhenius dependence for the reduction process of cobalt precursors.**Fig. 5.** Effect of temperature on the specific surface area of the nanocrystalline cobalt.

determined from Eq. (1). The values of apparent activation energies for the samples under the study, determined from the Arrhenius equation, are shown in Table 1.

The addition of structural promoters causes an increase of apparent activation energy of reduction process of cobalt oxides. The samples P2 and P3 with higher content of Al₂O₃ and CaO have higher apparent activation energy of reduction. The addition of K₂O causes a decrease of apparent activation energy. For the sample P0 (without promoters) the value of apparent activation energy is between those of samples P1 and P2/P3.

The effect of temperature on the specific surface area of the nanocrystalline cobalt obtained after the reduction of cobalt oxide is shown in Fig. 5. With an increase of temperature the specific surface area of the nanocrystalline cobalt decreases. The highest surface area is observed for the sample P2, containing the most of aluminium oxide. When the

content of this oxide decreases, the specific surface area decreases, too.

Fig. 6 presents the dependence of the mean crystallite size of cobalt on the temperature of reduction of cobalt oxide. The average crystal size was calculated from diffraction peak half-widths using the Scherrer formula. The smallest crystallites of cobalt were obtained after the reduction of Co₃O₄ at lower temperatures. With an increase of temperature, the crystallites undergo sintering, forming greatest grains. Assuming the ideal spherical form of the grains the surface of nanocrystalline cobalt has been calculated and compared with a measured one determined using thermal decomposition of nitrogen (Fig. 7). The measured surface area is five times smaller than the calculated one. This difference can be due to the fact that small cobalt crystallites can be attached one to another, having common walls which are inaccessible to an adsorbate.

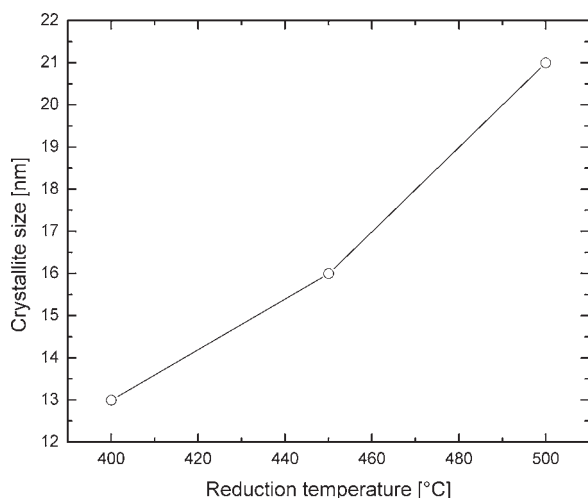


Fig. 6. Effect of the reduction temperature of precursor P3 on the mean crystallite size of cobalt.

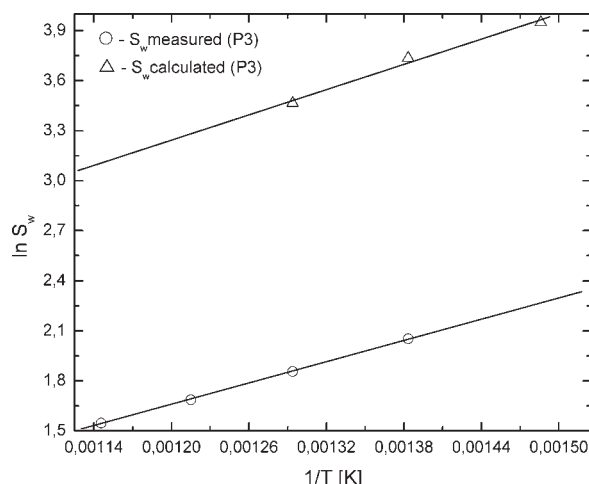


Fig. 7. Dependence of the specific surface area (calculated and measured) of nanocrystalline cobalt on the temperature.

4. CONCLUSIONS

- The nanocrystalline cobalt doped with small amount of Al₂O₃ and CaO has been obtained. The mean crystallite size of cobalt has been in the range of 15 to 30 nm and the specific surface area – from 1.5 to 13.8 m²/g;
- The addition of potassium oxide to the cobalt precursor causes the decrease of the temperature of conversion of Co₃O₄ to CoO;
- The reduction of cobalt oxide occurs in two stages;
- The increase of the structural promoters content causes the increase of the apparent activation energy of the reduction of cobalt oxides;
- The increase of the structural promoters content causes the increase of the specific surface area and decrease of the mean crystallite size of cobalt nanoparticles.

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