

The effect of aluminium oxide on the reduction of cobalt oxide and thermostability of cobalt and cobalt oxide

Research Article

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Abstract: During precipitation and calcination at 200°C nanocrystalline Co_3O_4 was obtained with average size crystallites of 13 nm and a well developed specific surface area of 44 $\text{m}^2 \text{g}^{-1}$. A small addition of a structural promoter, *e.g.* Al_2O_3 , increases the specific surface area of the cobalt oxide (54 $\text{m}^2 \text{g}^{-1}$) and decreases the average size of crystallites (7 nm). Al_2O_3 inhibits the reduction process of Co_3O_4 by hydrogen. Reduction of cobalt oxide with aluminium oxide addition runs by equilibrium state at all the respective temperatures. The apparent activation energy of the recrystallization process of the nanocrystalline cobalt promoted by the aluminium oxide is 85 kJ mol^{-1} . Aluminium oxide improves the thermostability of both cobalt oxide and the cobalt obtained as a result of oxide phase reduction.

Keywords: Nanocrystalline cobalt oxides • Cobalt • Reduction • Recrystallization

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1. Introduction

Nanocrystalline cobalt oxides and cobalt have been important subjects for recent studies. These materials are applied in various fields of modern technology, which include various types of sensors, catalysts, pigments, data storage, and electrical items [1-5]. Properties of these materials depend on their preparation methods. Many routes such as sol-gel [6,7], spray pyrolysis [8], chemical vapour deposition [9], electro-chemical and sonochemical synthesis [10,11], nanocasting route [12], and precipitation [13] have been developed to synthesize cobalt oxide nanocrystals.

Cobalt oxides, which are stable in the air, exist in two forms: Co_3O_4 and CoO . The former decomposes, in air atmosphere, into the latter at 900 to 950°C. CoO obtained in this way has a relatively low specific surface area and the average size of crystallites exceeding 100 nm.

It is known that cobalt catalysts are important in industrial processes *e.g.* Fischer-Tropsch synthesis [14,15] and methane stream reforming [16]. Metallic cobalt is an active form of cobalt catalyst in these reactions, generally obtained by oxide reduction. The reduction process of pure Co_3O_4 and also oxide dispersed on

different supports was investigated by many techniques [17]. These papers [18,19] present the results of thermogravimetric studies of Co_3O_4 reduction, which reveal that the reduction of Co_3O_4 phase is a two-stage process. During the first stage Co_3O_4 is reduced to CoO and then to Co . Elemental cobalt has two phases, the (α -Co) phase is stable in bulk at the temperature below 450°C and the (β -Co) phase is stable above 450°C.

Specific surface area and the average crystallite size of active phase of catalyst are parameters which influence its catalytic properties. Sintering and growth of grains and loss of free between-grain space results in decreased catalytic activity, decreased specific surface area and the surface area of the crystalline phase [20]. Many parameters influence the rate of the recrystallization process, apart from temperature, beginning with the kind of metal of which the catalyst is built, the content of promoters, and ending with the gaseous atmosphere of reaction [21].

The recrystallization process of fine cobalt oxide Co_3O_4 and oxide promoted with aluminium oxide has been studied. The influence of the promoter on the specific surface area and average crystallite's size of cobalt oxides and cobalt was determined.

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2. Experimental procedure

Nanocrystalline cobalt oxide (Co_3O_4) was obtained by precipitation of hydroxide, followed by calcinations. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in water. Cobalt hydroxide was precipitated from the solution using 25% ammonia water solution. The obtained precipitate was washed with water, filtered and dried at 70°C . Then it was calcinated at 200°C for 2 hours. In the same way nanocrystalline cobalt with aluminium oxide was obtained. Nitrates of cobalt (II) and aluminium were dissolved in water. Metal hydroxides were coprecipitated from the solution using 25% ammonia solution.

The chemical composition of the samples was determined using ICP-AES (Ultrace JY238).

Temperature programmed reduction (TPR) processes of the cobalt oxides were carried out in a thermobalance. The processes in the thermobalance were conducted under polythermal conditions in the temperature range of $25 - 500^\circ\text{C}$ with heating rate 2°C min^{-1} and under isothermal conditions 210°C and 240°C under the flow of pure (99.999%) hydrogen ($40 \text{ dm}^3 \text{ g}^{-1} \text{ h}^{-1}$).

The phase composition and the mean crystallite size of cobalt and cobalt oxides were determined using XRD technique (Cu K_α radiation) (X'pert Pro Philips) with high-temperature cell (HTK 16) and reaction chamber (XRK900). The mean crystallites' size of cobalt oxides and cobalt was determined on the basis of the Scherrer Equation.

The specific surface area (S_{BET}) was determined using a thermal desorption of nitrogen. The nitrogen adsorption on the catalyst was determined at -195°C and the gas desorption at room temperature.

3. Results and discussion

As a result of precipitation and calcination at 200°C for 2 hours in inert atmosphere, both a pure phase of Co_3O_4 and Co_3O_4 containing 2.4% of Al_2O_3 were obtained. Table 1 presents the characteristics of these materials.

An addition of a small amount of aluminium, in the precipitation stage, leads to a growth of cobalt oxide's surface area and it also leads to a decrease in the size of crystallites compared with those of cobalt oxide without aluminium. The measurements of the lattice constant for the cobalt oxide of the sample (Co) without Al_2O_3 and of the sample (CoAl) with aluminium oxide did not show any differences.

The experiments, which were conducted in a high-temperature chamber connected to a XRD diffractometer

Table 1. Characteristics of obtained materials.

Name of sample	Al_2O_3 [wt.%]	Surface area (S_{BET}) [$\text{m}^2 \text{ g}^{-1}$]	Average size of crystallites ($\bar{d}_{\text{Co}_3\text{O}_4}$) [nm]
(Co)	-	44	13
(CoAl)	2.4	54	7

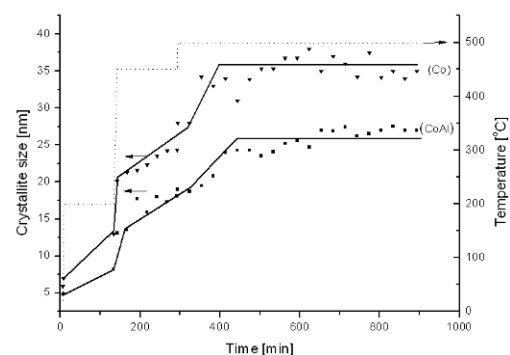


Figure 1. An average size of Co_3O_4 crystallites and change of temperature as a function of annealing time in inert atmosphere, where (Co) – Co_3O_4 and (CoAl) – Co_3O_4 with Al_2O_3 .

present changes of average size of Co_3O_4 crystallites during the process of annealing in inert atmosphere – Fig. 1.

During the long-lasting (about 500 min.) annealing process of the samples (Co) and (CoAl) at the temperature 500°C , the specific surface area didn't change significantly. It was this basis that samples reached equilibrium states.

On the basis of the average size of crystallites, from the final state after annealing process had come to an end, specific area was calculated. In the calculations, the density of Co_3O_4 was assumed to be 6.07 g cm^{-3} . It was also assumed that the crystallites had a spherical shape. The specific surface of cobalt oxide (Co) is $28 \text{ m}^2 \text{ g}^{-1}$ and that of cobalt oxide with aluminium (CoAl) is $39 \text{ m}^2 \text{ g}^{-1}$.

The TPR reduction is presented in Fig. 2. The reduction of these samples begins at 210°C . The TG curves have an inflexion point, which indicates a two-stage reduction, which agrees with the results presented above and described in [19]. The mass decrease of the samples in the first step is about 6.2%, which corresponds to the reduction of Co_3O_4 to CoO .

Pure cobalt oxide (Co) reached a complete degree of reduction at $(\Delta m/m_o) \times 100 = 26.8\%$. A small amount of Al_2O_3 in sample (CoAl) inhibits the reduction of CoO . This might be due to the fact that Al_2O_3 gets built-in into the structure of cobalt oxide (II), thus creating a solid solution of $x\text{CoO} \cdot y\text{Al}_2\text{O}_3$ which is difficult to reduce.

Cobalt obtained as a result of oxide reduction under air flow undergoes passivation. In order to determine the

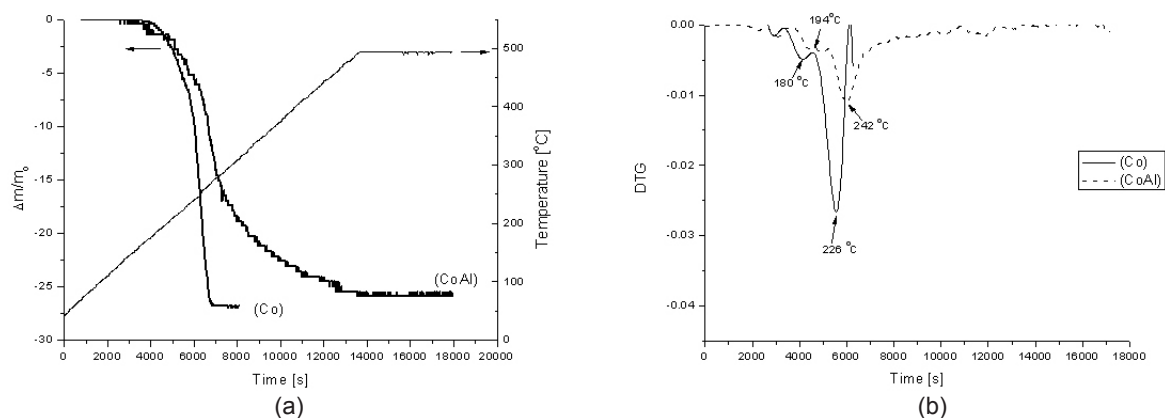


Figure 2. Polythermal reduction of cobalt oxides (Δm – mass change, m_0 – mass of Co_3O_4). (Co)- Co_3O_4 , (CoAl)- Co_3O_4 with Al_2O_3 (2.4%).

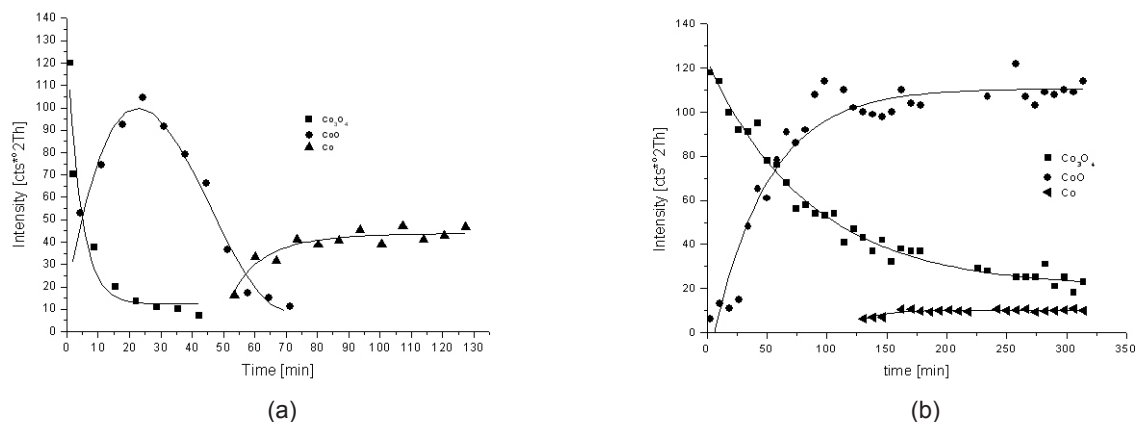


Figure 3. Dependence of changes in the area of reflexes of Co_3O_4 , CoO and Co phases as the function of the time of isothermal reduction (210 °C). A – corresponds to Co_3O_4 (Co), B – corresponds to Co_3O_4 with Al_2O_3 (CoAl).

phases of cobalt oxide's reduction (II and III) a reaction chamber connected to a XRD diffractometer was used. Fig. 3 presents the kinetics of Co_3O_4 and Co_3O_4 with Al_2O_3 reduction.

The reduction process was observed for a duration of time on the basis of the area of reflexes (220) Co_3O_4 , (220) CoO and (110) Co . The reduction is a two-stage process. During the first stage Co_3O_4 is reduced to CoO and subsequently a reduction to Co follows. Al_2O_3 significantly inhibits the reaction process. At 210 °C cobalt oxide Co_3O_4 is reduced to CoO and further reduction undergoes only in the sample without aluminium.

Fig. 4 presents diffraction patterns of samples (Co) and (CoAl) obtained after isothermal reduction processes conducted in a reaction chamber at the temperatures of 210, 240 and 500 °C. The diffraction patterns were made after cooling the reaction chamber to 25 °C in the atmosphere of H_2 . The reflexes in the diffraction patterns correspond to phases of Co and CoO respectively. The reflexes which can be seen in XRD pattern of the sample (Co) after its reduction at 210 °C correspond to nanocrystalline α - Co .

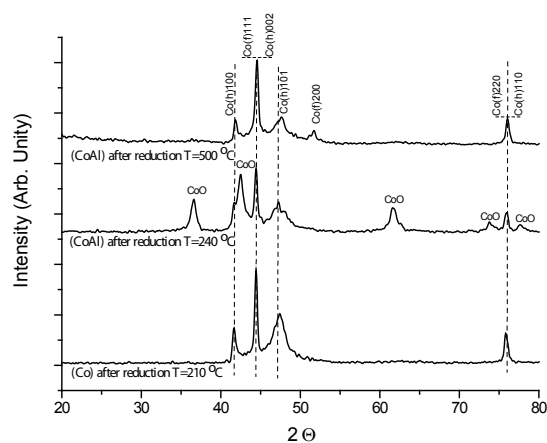


Figure 4. XRD spectra of samples after reduction.

The diffraction patterns of sample (CoAl), obtained after a reduction at 240 °C, i.e., at a temperature higher than that used for the reduction of sample (Co), apart from reflexes corresponding to α - Co also contain reflexes

corresponding to CoO phase. When the reduction temperature increased to 500°C, the diffraction patterns of sample (CoAl) showed reflexes corresponding to a mixture of α -Co and β -Co. The stability of β -Co phase at 25°C can be accounted for by the small size of cobalt crystallites [22].

The thermogravimetric studies of isothermal reduction in the temperature of 240°C were carried out. During the reduction, the specific surface area (S) of these samples has been determined, results are presented in Fig. 5. On the basis of the obtained results it can be stated that Co_3O_4 with Al_2O_3 (CoAl) is not completely reduced at this temperature. $\text{CoO-Al}_2\text{O}_3$ composite oxide may be formed, which is more difficult to reduce [23] than pure cobalt oxide. The reduction of the (CoAl) was slower than the reduction of the pure Co_3O_4 (Co). The specific surface area of (Co) and (CoAl) at the first stage (I) increased and next decreased. After the reduction process of the sample (Co), specific surface area of pure cobalt was rapidly decreasing during annealing in reduction atmosphere. It confirmed the recrystallization process. Finally, for (CoAl) the specific surface area reached value $45 \text{ m}^2 \text{ g}^{-1}$ and only $2 \text{ m}^2 \text{ g}^{-1}$ for (Co).

To evaluate the recrystallization process of the sample (CoAl) the specific surface area was determined during the heating of the sample (CoAl) under reduction conditions at the temperature of 300 to 600°C, with a step of 100°C (Fig. 6a). According to the shape of the lines representing changes of the specific surface area during the reduction, the equilibrium state was reached at all the respective temperatures.

The obtained results were interpreted on the basis of the double layer model [24] and on studies on recrystallisation of the iron catalyst for ammonia synthesis [25,26]. According to this model, the number of oxygen atoms on metal (metal = Fe, Co) surface determines the total surface area of the catalyst. A clean metal surface tends to minimise an excess of the surface energy by reduction of the surface area. When the surface is covered with an oxygen layer the surface energy is compensated by formation energy of M-O- bonds. The number of oxygen atoms is the consequence of the promotor nature. Aluminium atoms are bonded to the metal surface through three oxygen atoms. The specific surface area of cobalt oxide can be expressed as a ratio of the number of surface cobalt atoms to the number of cobalt atoms in the bulk. Recrystallization process, during the annealing process in reduction atmosphere, is connected with increasing crystallites of cobalt and decrease in their number. From the thermodynamic point of view, it is a process in which cobalt atoms migrate from the surface into the bulk.

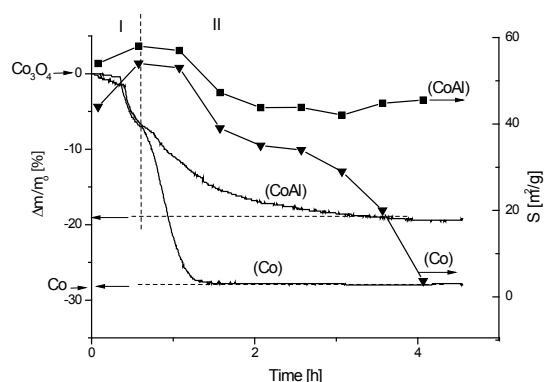


Figure 5. Changes of the specific surface area during the isothermal reduction at 240°C and TG thermoprogams of the samples (Co) - Co_3O_4 , (CoAl) - Co_3O_4 with Al_2O_3 .

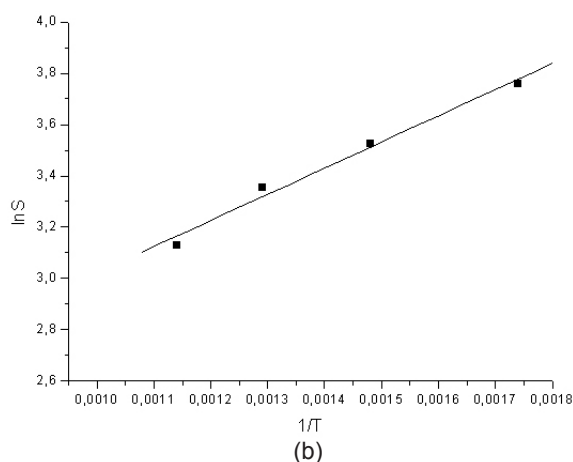
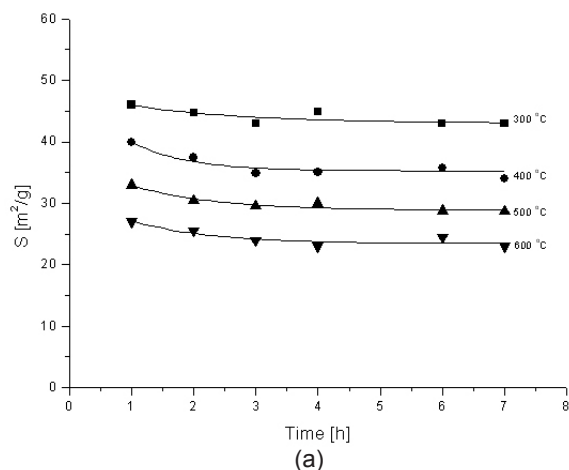


Figure 6. A - Changes of the specific surface area of Co_3O_4 with Al_2O_3 (CoAl) versus time in annealing process in reduction atmosphere, B - logarithm S in relation to reciprocal temperature.

An equilibrium of the recrystallization process can be described by the following equation:



Specific surface area can be given by:

$$S = A \frac{[Co_{surf}]}{[Co_{surf}] + [Co_{bulk}]} \quad (2)$$

$$S = \frac{[Co_{surf}]}{[Co_{bulk}]} A \quad (3)$$

where:

S - specific surface area,

A- constant,

$[Co_{surf}]$ - number of the surface cobalt atoms,

$[Co_{bulk}]$ - number of the bulk cobalt atoms

The form of the equilibrium constant K for process described by Eq.1 is as follows:

$$K = \frac{[Co_{bulk}]}{[Co_{surf}]} = \frac{A}{S} \quad (4)$$

$$\ln \frac{A}{S} = - \frac{\Delta E}{RT} \quad (5)$$

$$\ln S = \frac{\Delta E}{RT} + \ln A \quad (6)$$

The apparent activation energy of the recrystallization process has been determined on the basis of the data presented in Fig. 6b. The value of this energy has been calculated as 85 kJ mol⁻¹. In our previous investigations

[26,27] of the recrystallization of metallic catalysts for ammonia synthesis was stated that the sintering activation energy is equal to 40-50 kJ mol⁻¹. Presence of such promoters as calcium and potassium oxides, in tested metallic catalysts for ammonia synthesis, significantly decreases apparent activation energy of recrystallization process. The obtained values of the activation energy of the metallic ammonia synthesis catalysts are comparable to the values for the support catalysts [28,29].

4. Conclusions

A small addition of a structural promoter, in the form of Al₂O₃, increases the specific area of the oxide (54 m² g⁻¹) and decreases the average size of crystallites (7 nm). Al₂O₃ slows down the reduction process of Co₃O₄ by hydrogen. The apparent activation energy of the recrystallization process calculated on this basis is equal to 85 kJ mol⁻¹. Aluminium oxide improves the thermostability of both cobalt oxide and the cobalt obtained as a result of oxide phase reduction.

Acknowledgement

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