Studies on the recrystalization of nanocrystalline metals

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The influence of the promoters such as CaO, Al_2O_3 and K_2O on the specific surface area of the nanocrystalline cobalt was determined. The recrystalization process of the nanocrystalline cobalt was determined and compared with the examinations conducted on the iron catalyst for ammonia synthesis. The triply promoted nanocrystalline obtained cobalt after the annealing process, has got greater specific surface area than the triply promoted iron.

Keywords: nanocrystalline cobalt, recrystalization.

INTRODUCTION

Nanocrystalline transition metals, and among them cobalt, show interesting magnetic, optical and chemical properties which forebode a wide application in different fields i.e. in the catalytic processes. It is well known that the recrystalization process, relevant to the average crystallite size growth and decrease of the specific surface area, causes a decrease in the active surface that consequently leads to a deactivation of the catalyst[1].

Based on the examinations performed with the iron catalyst for ammonia synthesis, the main phase is nanocrystalline iron, it was claimed that the one-component system aimed to decrease the specific surface area and minimize the surface energy by the surface reconstruction. In the multicomponent systems, due to the wetting process, a two-dimensional structure is created on the surface and its bond energy compensates the surface energy[2, 3, 4]. Additionally it was claimed that the sintering process of the iron catalyst proceeded at temperatures above 500°C.

The objective of this research was to determine the influence of temperature and structural promoters on the recrystalization process of nanocrystalline cobalt and compare with the examinations conducted on the iron catalyst for ammonia synthesis.

EXPERIMENTAL

Nanocrystalline cobalt was obtained by the precipitation of cobalt hydroxide, followed by calcination and reduction. The cobalt hydroxide was precipitated from the cobalt nitrate solution using the 25% ammonia solution. The obtained deposit was washed with water, filtered and next dried at 70°C. The next preparation step was the calcinations at 200°C for 2 hours. The precursor of nanocrystalline cobalt after the calcinations was reduced under the pure (99,999%) hydrogen flow of 20 Ndm^3/h. The reduction was carried out in a differential reactor with the thermogravimetric mass measurement. The sample of the precursor of nanocrystalline cobalt of 0,5 g was placed as a single layer of grains on a platinum basket. Taking into account the single layer of grains in the basket and the conditions of the reaction rate measurements (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 first reduction step (Co_3O_4 is reduced to CoO) was carried out isothermaly at 240°C. Before each isothermal reduction the sample was annealed in the flow of pure helium (99,999%) up to the process temperature.

Then, using the impregnation process, structural promoters aluminum, calcium and potassium oxide were introduced. The nitrate solutions of these elements were used for the impregnation. Drying at the temperature of 150°C over 2 hours and the polythermal reduction were the next steps of the process. The reduction process was carried out in the temperature range 25 – 500°C, with the heating rate of 2°C/min.

To evaluate the recrystallisation process of nanocrystalline cobalt the specific surface area has been determined during the overheating of cobalt under reduction conditions at the temperature of 500 to 700°C, with a step of 50°C. The surface area measurement were performed with the nitrogen adsorption/desorption method. Nitrogen adsorption on nanocrystalline cobalt was determined at -195°C and gas desorption at the room temperature. A detailed description of the iron catalyst recrystallization process was reported earlier in the[2, 3].

RESULTS AND DISCUTION

The specific surface area of Co_3O_4 obtained by precipitation, and followed by calcinations at 200°C over 2 hours, amounts to 44 m^2/g. The first step of the reduction leads to obtaining the CoO phase with the specific surface area of 33 m^2/g and the mean size of crystallites of ca 9 nm.

The chemical composition of the samples after impregnation is presented in Table 1.
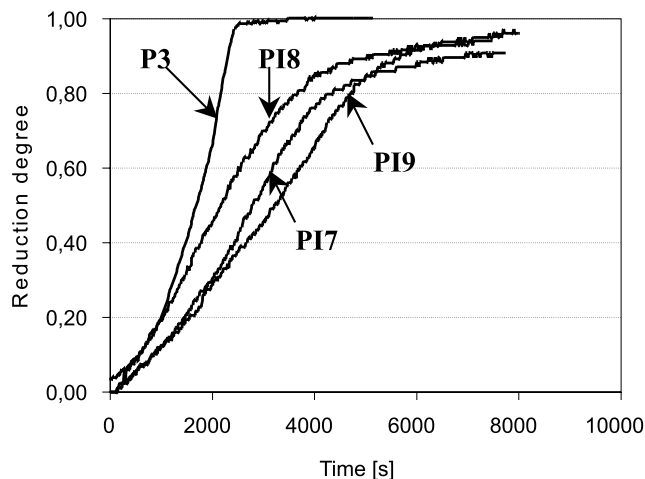
Figure 1 shows the reduction degree of the cobalt oxide as a function of polythermal reduction time at the temperature up to 500°C. The total reduction degree was reached by the sample of pure cobalt oxide (P3).

Addition of the promoters slows down the reduction process and the samples do not reach the total reduction degree.

According to the earlier studies[5] the increase of the concentration of promoters causes the increase of the CoO

Table 1. The content of promoters in the precursor of the nanocrystalline cobalt

| Sample name	Al_2O_3 [wt. %]	CaO [wt. %]	K_2O [wt. %]
P3	0.00	0.00	0.00
PI7	3.00	0.00	0.00
PI8	3.00	1,60	0.00
PI9	3.00	1,60	0.60

Figure 1. The reduction degree of the cobalt oxide after impregnation as a function of polythermal reduction time *(at the temperature range 25 – 500 ºC, with the heating rate of 2ºC/min)*

mass, which is bound in hardly reducible structures $xCoO \cdot yMe_n O_m$.

Cobalt, obtained by of the oxide phase reduction without structural promoters (P3) at 500°C, has got a relatively small specific surface area ca 2,0 m²/g. The addition of a small amount of a structural promoter, aluminium oxide (Al_2O_3 – 3.00 wt %), results in cobalt, obtained in the same way (PI7), demonstrating the specific surface area amounting to 26 m²/g. The addition of the second promoter, calcium oxide (PI8, Al_2O_3 – 3.00 wt %, CaO – 1,6 wt %), causes an increase of the specific surface area to ca 30 m²/g. After an addition of the third promoter, potassium oxide (PI9, Al_2O_3 – 3.00 wt %, CaO – 1,6 wt %, K_2O – 0,6 wt %), a decrease of the specific surface area to ca 25 m²/g is observed. A similar effect was observed in the catalyst for the ammonia synthesis where the specific surface area of the two-promoted catalyst, after reduction at the temperature of 500°C, amounts to 24 m²/g, whereas of the three-promoted catalyst amounts to ca 12 m²/g.

The specific surface area S as a function of the annealing time in a reducing atmosphere (H_2) of the nanocrystalline cobalt with structural promoters (P19) was shown in Figure 2. At the temperatures 500 – 700 ºC the specific surface area of the cobalt catalyst decreases with the increase of the reduction temperature. According to the shape of the lines representing the changes of the specific surface area during the reduction, the equilibrium state is reached at each temperature.

The obtained results were interpreted on the basis of the double layer model of the iron catalyst[6]. The basic assumption of this model concerns the equilibrium between the catalyst bulk, surface and the three-dimensional promoter oxides, bonding cobalt crystallites between them. The excess of the surface energy of the system is compensated by the energy of the Co-O bonds on the surface, the
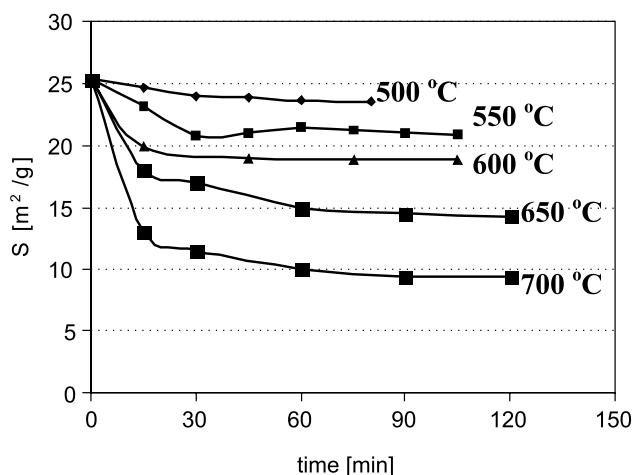
Figure 2. The specific surface area S as a function of the annealing time in a reducing atmosphere of the nanocrystalline cobalt with structural promoters PI9 (Al_2O_3 – 3,0 wt %, CaO 1,6 wt % and K_2O 0,6 wt %)

amount of oxygen atoms on the iron surface determines the specific surface area of the catalyst. The specific surface area of the catalyst can be expressed as a ratio of the number of surface cobalt atoms to the number of cobalt atoms in the bulk. The decrease of the catalyst specific surface area, according to the assumptions of the active surface model, takes place after the surface Co-O- bonds cleavage, Fig. 3. This goes with the transition of promoters from the crystallites surface to the three-dimensional structure interior which bonds crystallites.
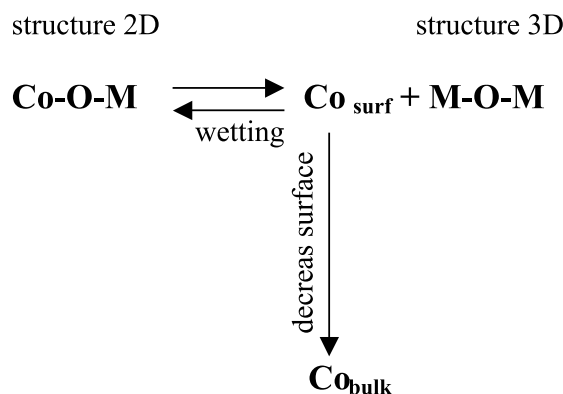
Figure 3. A diagram of the recrystallization and wetting process of the cobalt surface[7]

An equilibrium of the recrystalization process can be described by the following equation : $Co_{surf} = Co_{bulk}$. The form of the equilibrium constant k is as follows:
$$K = \frac{[Co_{bulk}]}{[Co_{surf}]} .$$

The final equilibrium states, characterized by the specific surface area depending on the annealing temperature, for triply (PI9) and for double (PI8) nanocrystalline cobalt promoted were compared with the results for the triply and double promoted iron catalyst, Fig. 4.

On the basis of the data presented in Fig. 4. the free Gibbs enthalpy of the recrystalization process has been determined. The results are presented in Table 2.

The enthalpy of the recrystalization process the triply promoted nanocrystalline cobalt amounts to $\Delta H_{Co} = 22$ kJ/mol, whereas for iron amounts to $\Delta H_{Fe} = 32$ kJ/mol.
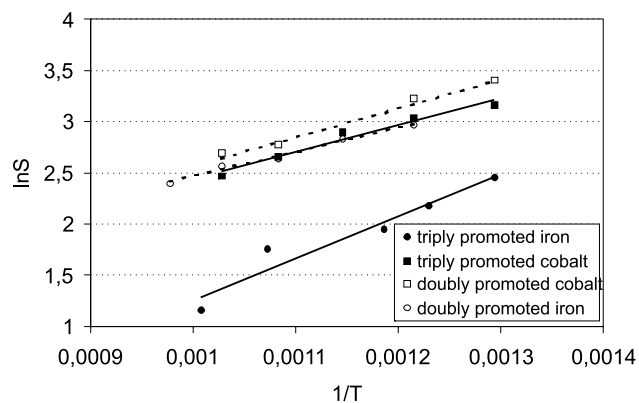
Figure 4. The specific surface area as a function of the annealing time under reducing conditions

Table 2. The values of the recrystalization process enthalpy

Sample name	ΔH [kJ/mol]
(PI9) triply promoted cobalt	22
(PI8) doubly promoted cobalt	24
triply promoted iron	32
doubly promoted iron	20

CONCLUSIONS

It was claimed that the specific surface area of nanocrystalline cobalt during the overheating process, in a short time, reaches the constant value at the defined temperature which says that it reaches the thermodynamic equilibrium state. The obtained triply promoted nanocrystalline cobalt, even after the overheating process, has got the greater specific surface area in comparison with the triply promoted iron.

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