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Study of the Kinetics of Ammonia Synthesis and Decomposition on Iron and Cobalt Catalysts

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Abstract Activity of cobalt and iron catalysts in ammonia synthesis was determined under a pressure of 10 MPa and at the temperature range of 673–823 K, in a six-channel integral steel reactor. The catalytic ammonia decomposition was studied in a differential reactor under the atmosphere of low concentration of ammonia (<6%) in the temperature range of 673–823 K under atmospheric pressure. The determined values of the activation energy for the ammonia synthesis reaction over cobalt and iron catalysts are 268 and 180 kJ/mol, respectively, whilst for the ammonia decomposition reaction they are equal to 111 and 138 kJ/mol. The cobalt catalyst showed lower activity than a commercial iron catalyst in ammonia synthesis reaction. The cobalt catalyst turned out to be more effective in ammonia decomposition reaction than the iron one.

Keywords Ammonia synthesis · Ammonia decomposition · Iron catalyst · Cobalt catalyst

1 Introduction

Catalysts for ammonia synthesis have been the study subject for over 100 years now. Until 1990, when Kellog Advanced Ammonia Plant introduced carbon-supported ruthenium catalyst, iron catalyst was the only catalyst used in industrial ammonia synthesis [1, 2]. However, various ruthenium-supported catalysts were shown to be very active as well [3, 4].

Large energy consumption in the process has made researches look for more effective catalysts working in lower temperatures and pressures. Studies conducted by the Haldor-Topsoe company [5, 6] place pure cobalt relatively low in terms of catalytic activity. Cobalt is located on the right-hand side of the volcano curve and so far only low catalytic activity has been reported for cobalt catalysts [7–9].

The volcano curve, which describes the relation between the activity of various catalysts of ammonia synthesis and dissociative adsorption energy for nitrogen, shows that pure cobalt-supported catalysts will not be active. However, a conclusion can also be drawn that there is a possibility of obtaining an active catalyst consisting of two metals: cobalt and molybdenum which separately do not indicate sufficient activity. Cobalt was widely studied in alloys with iron (systems active in ammonia synthesis) [10, 11] and it was studied as a modifier of iron catalyst [12].

The theoretical and experimental investigations conducted in study [13] suggest that an optimal catalyst for ammonia synthesis is not an optimal catalyst for ammonia decomposition reaction. A good catalyst of ammonia decomposition reaction more weakly bonds nitrogen in comparison to a synthesis catalyst. It should be noted that the maximum both on the synthesis and decomposition curves shifts depending on the conditions in which the reaction is conducted.

The goal of the present study was trying to find an answer to the question why a cobalt-supported catalyst seems to be less active in ammonia synthesis reaction in comparison with an industrial iron catalyst as well as checking the course of an opposite reaction during a synthesis on a cobalt catalyst.

A cobalt catalyst contains nanocrystalline cobalt and promoters—oxides of calcium, aluminium and potassium. The chemical composition of the obtained catalyst,

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regarding the prompters' content, is similar to the composition of an industrial iron ammonia synthesis catalyst.

2 Experimental

Cobalt oxide (Co_3O_4) was obtained by precipitation of hydroxide, followed by calcinations. Cobalt nitrate (II) 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 343 K. Then, it was calcinated at 473 K for 2 h.

On the basis of previous studies conducted by means of temperature-programmed reduction [14], it is known that Co_3O_4 is reduced in two steps. Firstly, CoO and then Co is obtained. It is possible to stop the reduction process at this step when one selects proper process conditions. A precursor of CoO phase catalyst was obtained by conducting the first stage of Co_3O_4 reduction at the temperature of 483 K. The reduction process of cobalt oxide was carried out in a thermobalance, under the flow of pure (99.999%) hydrogen (40 dm^3/g h).

Promoters, such as aluminium, calcium and potassium oxides, were added to the catalyst by means of the CoO phase impregnation, making use of the solutions of nitrates of these elements and then calcinating them again at temperature 773 K. The chemical composition of the sample was determined using ICP-OES.

The phase composition and the mean crystallite size of cobalt oxides were determined using XRD technique (Cu K_α radiation). The mean crystallites' size of cobalt oxides was determined on the basis of the Scherrer equation.

The specific surface area was determined using a thermal desorption of nitrogen. The surface was measured after heating the catalyst for 1 h at the temperature of 773 °C, in a gas atmosphere (H_2 95 vol % and N_2 5 vol %).

The activity of catalysts in ammonia synthesis was determined under a pressure of 10 MPa and at the temperature range of 673–823 K, in a six-channel integral steel reactor. In order to determine the catalytic activity of the catalysts, 1 g samples of the catalyst grains 1–1.2 mm were put into each channel of the reactor and reduced with hydrogen–nitrogen mixture (3:1) under the atmospheric pressure. The temperature-programmed reduction was as follows: 673 K, 5 h; 723 K, 12 h; 773 K, 24 h. A commercial iron catalyst KM1R, as basis standard, was examined in the same conditions.

The ammonia concentration measurements were performed utilising the interferometer. Based on the obtained results, the reaction rate constants for ammonia synthesis were calculated from the Temkin–Pyzhev equation (Eq. 1) [15]:

$$k = V_{\text{in}} \cdot \left[-\frac{1}{2}(1-z)^{3.5} \cdot \ln\left[1 - \frac{\frac{z^2}{(1-z)^4}}{\frac{z_e^2}{(1-z_e)^4}} \right] \right] \quad (1)$$

where V_{in} is the inlet gas velocity, z is the molar fraction of ammonia and z_e is the equilibrium molar fraction of ammonia in given conditions (pressure and temperature). The rate constant k was assumed to be a measure of the catalyst activity.

Ammonia decomposition reaction was conducted under atmospheric pressure, feeding the reactor with ammonia–hydrogen mixture containing ca. 6% of ammonia (total gas load was 150 cm^3/min), at various temperatures in the range 673–823 K.

Prior to the ammonia decomposition experiments, the catalysts were reduced in conditions identical as those before the synthesis reaction had commenced.

The kinetics of ammonia decomposition on catalysts was investigated making use of an analytical installation equipped with a flow tubular differential reactor which made it possible to conduct thermogravimetric measurements (Fig. 1). In a platinum basket hanging on balance arm, ca. 0.3 g of the analysed substances was placed in a form of a single layer of grains. The resolution of mass changes measurement was 0.1 mg. The mass and temperature of the analysed solid samples were recorded digitally. Gas phase composition changes were analysed at the reactor output. Ammonia concentration in the reacting gas mixture was determined directly (using Siemens Ultramat 6 ammonia analyser), and the results were recorded digitally. The flow rate of ammonia and hydrogen was determined by means of mass flow controllers.

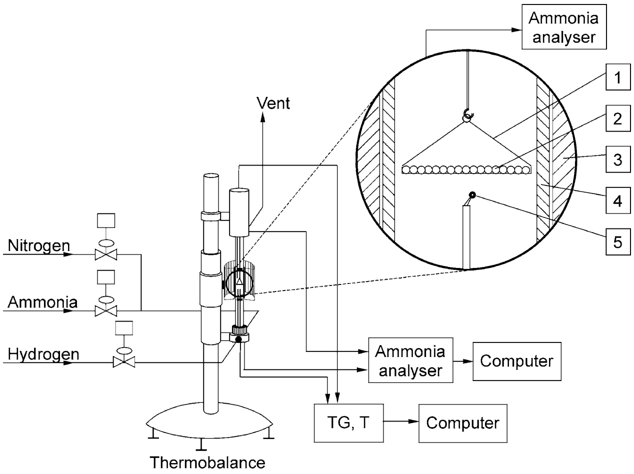


Fig. 1 Experimental equipment: 1 sample holder, 2 single layer of grains, 3 reactor furnace, 4 reactor wall and 5 thermocouple

3 Results

3.1 Characteristic of Catalysts

Cobalt oxide Co_3O_4 obtained as a result of precipitation and calcination processes was characterized with an extended specific surface area which amounted to $\sim$44 m^2/g. After conducting the first step reduction, CoC phase was obtained (Fig. 2) with a slightly smaller specific surface area of 33 m^2/g and crystallites amounting to 10 nm in size.

Promoters' oxides were introduced into the obtained CoO phase by means of impregnation followed by calcination. The promoters were placed on an extended area which guaranteed their good dispersion.

The active form of the cobalt catalyst was obtained after the reduction process. The specific surface area of the obtained catalyst amounted to 20 m^2/g. As a result of performed quantitative analysis of the oxidised form of the obtained cobalt catalyst, the contents of calcium oxide (1.33 wt %), aluminium oxide (2.36 wt %) and potassium oxide (0.52 wt %) were determined. The molar ratio of Al_2O_3/CaO was about 1.

Having compared the composition and structure of the obtained catalyst with an industrial iron catalyst [16], a conclusion can be drawn that a cobalt catalyst was obtained with a similar chemical composition and a slightly larger specific surface area. The area of the iron catalyst after reduction at the temperature of 773 K amounted to 12 m^2/g.

3.2 Activities in Ammonia Synthesis

The rate constants, k, were calculated making use of Temkin–Pyzhev Eq. (1), taking into account the results of the ammonia concentration measurements which were conducted during the synthesis reaction. In Fig. 3 the logarithmic dependence of the ammonia synthesis reaction rate constant (ln k) on reciprocal temperature for cobalt catalyst and industrial iron catalyst as basis standard catalyst is presented. From the slope of curves, the apparent energy activation for ammonia synthesis was determined. The value for the cobalt catalyst is 268 kJ/mol and for the iron catalyst it equals 180 kJ/mol.

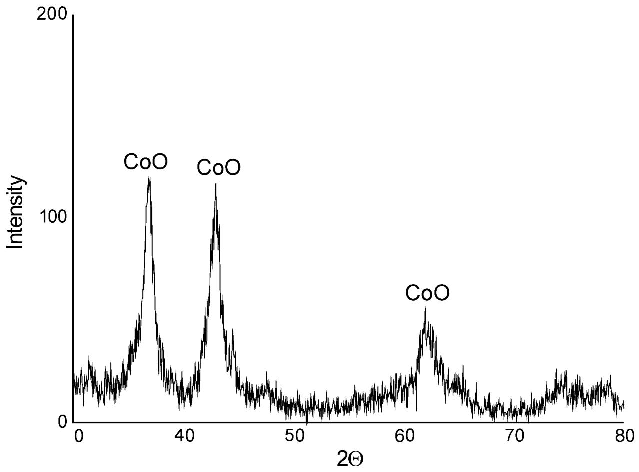


Fig. 2 XDR diffraction pattern of CoO obtained by reduction of Co_3O_4

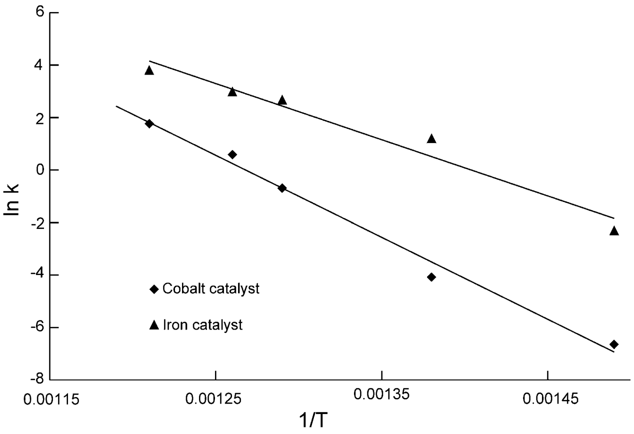


Fig. 3 The dependence of the reaction rate constant on the reaction temperature of the ammonia synthesis

3.3 Activities in Ammonia Decomposition

In Fig. 4 the change of ammonia concentration at the outlet of the reactor as well as the temperature as the functions of time in the ammonia decomposition reaction on cobalt and iron catalysts are presented.

From the obtained dependencies, it can be clearly seen that at certain temperatures stationary states were achieved, in which ammonia concentration did not change.

On the basis of balance of reaction system, in which the reaction $NH_3 = 1.5H_2 + 0.5N_2$ takes place, one obtains:

$$F_{NH_3} = F^0_{NH_3} - \alpha_{NH_3} F^0_{NH_3} \tag{2}$$

$$F_{H_2} = F^0_{H_2} + 1.5\alpha_{NH_3} F^0_{NH_3} \tag{3}$$

$$F_{N_2} = 0.5\alpha_{NH_3} F^0_{NH_3} \tag{4}$$

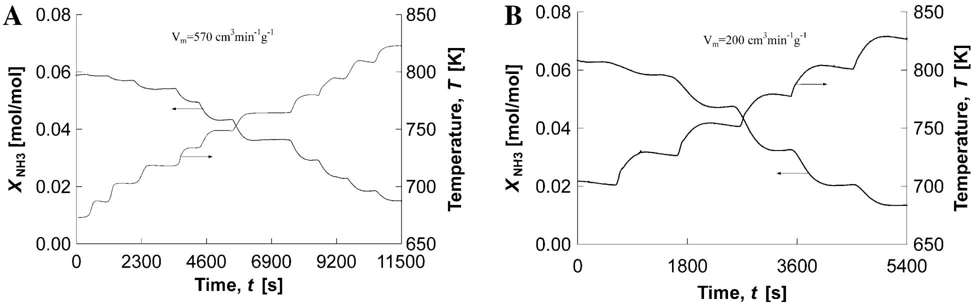
$$F^0 = F^0_{NH_3} + F^0_{H_2} \tag{5}$$

$$F_{out} = F_{NH_3} + F_{H_2} + F_{N_2}. \tag{6}$$

After transformations of Eqs. 2–6, one obtains the following expression describing both the conversion degree of ammonia:

$$\alpha_{NH_3} = \frac{F^0_{NH_3} - X_{NH_3} F^0}{F^0_{NH_3} X_{NH_3} + F^0_{NH_3}} \tag{7}$$

Fig. 4 Changes of ammonia concentration in gas phase versus the time of ammonia decomposition on cobalt (**a**) and iron (**b**) catalysts



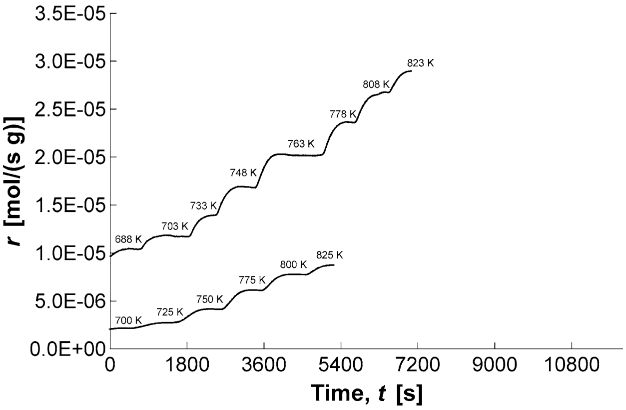


Fig. 5 Rates of ammonia decomposition on the cobalt and iron catalysts

and hydrogen concentration at the output from the reactor

$$X_{H_2} = \frac{F^0_{H_2} + 1.5\alpha_{NH_3}F^0_{NH_3}}{F^0 + \alpha_{NH_3}F^0_{NH_3}} \tag{8}$$

where F is flow rate (mol s^{-1}), X *is* concentration (mol mol^{-1}) and α is conversion degree

$$r = \alpha_{NH_3}F^0_{NH_3} \tag{9}$$

Making use of the values of ammonia conversion degree in every moment of the reaction and the flow rate of ammonia at the input of reactor (Eq. 9), one can determine the changes of the reaction rate of catalytic ammonia decomposition as a function of time (Fig. 5).

4 Discussion

The rate of catalytic ammonia synthesis reaction can be described by Temkin–Pyzhev Eq. (10)

$$r = r_1 - r_2 = k_1 p_{N_2}\left(\frac{p^{3/2}_{H_2}}{p_{NH_3}}\right) - k_2\left(\frac{p_{NH_3}}{p^{3/2}_{H_2}}\right) \tag{10}$$

Assuming that under the applied ammonia decomposition process conditions the ammonia synthesis does not occur ($r_1 = 0$), one can obtain:

$$r_2 = k_2\left(\frac{p_{NH_3}}{p^{3/2}_{H_2}}\right) \tag{11}$$

Knowing the rate of ammonia decomposition determined from Eq. (9) for several stationary states (Fig. 5) and by substituting them into Eq. (11) the values of constant rates of ammonia decomposition k_2 were determined.

The values of the reaction rate constants of catalytic ammonia decomposition, k_2 determined by means of Eq. (11), are shown in Fig. 6 as a function of the reciprocal temperature, $1/T$. From the slope of these curves the apparent activation for ammonia decomposition process was determined. The values amount for the cobalt catalyst 111 kJ/mol and for the iron catalyst 138 kJ/mol, respectively.

Making use of the ammonia synthesis reaction rate constant, k, which was calculated from Eq. (1), all the changes of the ammonia reaction rate, r, depending on ammonia concentration, were determined. The calculations were performed for the temperature of 723 K. In order to perform the calculations, a modified Temkin–Pyzhev Eq. (12), with the value of coefficient $\alpha = 0.5$, was applied.

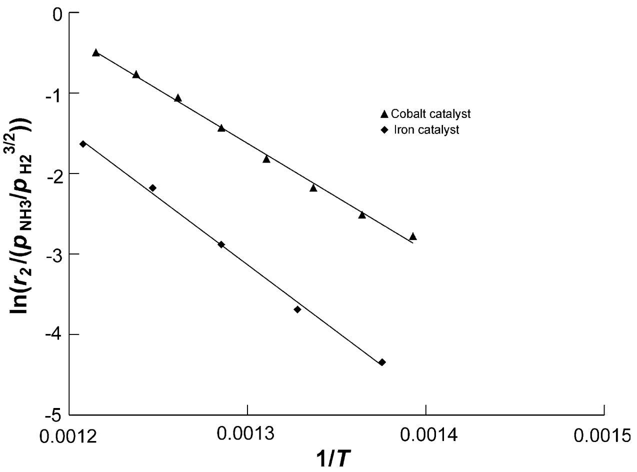


Fig. 6 The dependence of the reaction rate constant on the reaction temperature of the catalytic decomposition of ammonia

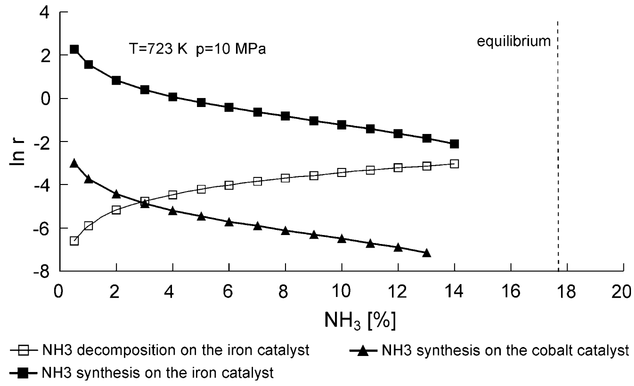


Fig. 7 Dependencies of ammonia synthesis and decomposition rates on ammonia concentration for cobalt and iron catalysts ($T = 723$ K, $P = 10$ MPa)

$$r = k \cdot \frac{(1-z)^{2.5}}{z} \cdot \left[\frac{(z^r)^{2.5}}{(1-z^r)^4} - \frac{z^2}{(1-z)^4} \right] \tag{12}$$

where z is ammonia molar fraction and z^r is ammonia molar fraction at the equilibrium state at the given synthesis conditions.

On the basis of the value of the reaction rate constant of ammonia decomposition k_2 determined under atmospheric pressure conditions and assuming that this value does not depend on the pressure one can calculate how the rate of this reaction, r_2, changes at synthesis reaction conditions.

In Fig. 7, changes of the ammonia synthesis rate, r, and the rate of ammonia decomposition, r_2, on cobalt and iron catalysts, as a function of ammonia concentration, are presented. The calculations were performed for the temperature of 723 K and the pressure of 10 MPa.

Assuming that the mechanism of synthesis and decomposition reactions on a cobalt catalyst are identical with those on an iron catalyst, it is possible to determine by using the same equations that on the iron catalyst the rate of both reactions, along with an increase of ammonia concentration, approach the state of equilibrium. On the cobalt catalyst, given the same assumptions, the calculated rate of ammonia decomposition is higher than the rate of synthesis, which is in contradiction with the empirical observations.

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