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Kinetics studies of recrystallization process of metallic catalysts for ammonia synthesis

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ABSTRACT

The kinetics of the process of recrystallization of iron-based and cobalt-based catalysts for ammonia synthesis were investigated by measuring the specific surface area using thermal desorption method. During sintering of the catalysts in constant temperature their surface areas asymptotically approach a non-zero value, which is the residual surface area (S_r). An equation analogous to the General Power-Law Equations model (GPLE) was used to quantitatively describe this process. It was found that the recrystallization rate for both catalysts depends exclusively on their initial surface area and the sintering temperature. The apparent activation energy of the recrystallization process was calculated, which amounted to 50 kJ mol^{-1} for both catalysts.

1. Introduction

The temperature and reaction environment are the parameters that can influence the properties of the catalyst resulting in decrease of its activity in particular chemical process [1,2]. Catalyst can be exposed to elevated temperature for extended periods of time not only in operation, but also during its manufacture and activation. As a result, the catalytically active phase can be transformed into non-active phase, or the process of recrystallization may occur, because of increased activity of the crystalline network of the catalyst. 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, and sometimes in changes to morphology of crystallites [3].

Many parameters influence the rate of the recrystallization process, apart from temperature, beginning with the kind of metal of which the catalyst is built, its dispersion, the content of promoters and impurities, the structure and texture of the support material, and ending with the gaseous atmosphere of reaction [4]. The crystallite growth is thought to occur through the mechanism of migration of crystallites or atoms, or through vapour transport [5,6].

The catalyst deactivation processes resulting from high temperature and reaction conditions are usually investigated by measurements of catalytic activity, specific surface area, the crystallite size or the dispersion of the active phase. It is furthermore necessary to select a proper kinetic model in order to interpret the kinetic parameters of the process [7]. This is an essential condition of drawing correct conclusions on the mechanism of reaction. Initially, the model used to describe the deactivation assumed that the measured parameter: catalytic activity, surface area or dispersion, will reach a zero value after a sufficiently long time [8,9]. Later it was found that the catalysts always retain some level of non-zero residual activity that is dependent of the type of catalyst and the process conditions [8–14]. The data available on changes of specific surface area and dispersion during annealing in constant temperature also indicate, that these parameters never reach zero value [1,13,15–17]. Two models were suggested that describe the kinetics of deactivation of catalysts that preserve the residual activity. The General Power-Law Equations model (GPLE) allows for kinetic description of the sintering process with residual dispersion reached in a finite annealing time, and involves influence of the type of metal, temperature, atmosphere, promoters and supporting material on the process kinetics [1,17–19]. The general power law expression can be given as follows:

$$-\frac{d(D/D_0)}{dt} = k_s\left(\frac{D}{D_0} - \frac{D_{eq}}{D_0}\right)^m \tag{1}$$

where D is the metal dispersion on the support, D_0 is the initial dispersion, t is the sintering time,

k_s is the sintering rate constant, m is the sintering order and the D_{eq} is defined as the limiting value of dispersion after sintering for infinite time. Another model, the Deactivation Model with Residual Activity (DMRA) allows for interpreting the changes of catalytic activity in time [14,20].

Most of the work published to date concerning the temperature-induced growth of grains is devoted to sintering and redispersion of metallic phases (Pt, Ni, Rh) on supports (Al_2O_3, SiO_2, C)

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Table 1
Chemical composition of investigated catalysts.

	CaO [wt.%]	Al_2O_3 [wt.%]	K_2O [wt.%]	MnO [wt.%]
Iron catalyst (prereduced form)	2.8	3.3	0.65	–
Cobalt catalyst (oxidized form)	2.4	2.8	0.61	0.32

[21–26]. The stability of metal crystallites in reductive atmosphere decreases along with the decrease of melting temperature, from Ru > Ir > Rh > Pt > Pd > Ni > Cu > Ag [5]. For metals deposited on a supporting material, this property can also be linked to the strength of interaction between metal and the support. For example, for platinum the stability decreases in the following order: $Pt/Al_2O_3 > Pt/SiO_2 > Pt/C$ [5].

The aim of this work was to investigate the kinetics of sintering of metallic catalysts for ammonia synthesis, namely the fused iron catalyst and precipitated cobalt catalyst. The active phases of those catalysts were composed of iron and cobalt crystallites, respectively, doped with non-reducible oxides of aluminum, calcium and potassium in weight fraction not exceeding a total of 7 wt.%.

2. Experimental

2.1. Catalyst preparation

Two types of catalysts were investigated: a pre-reduced fused iron catalyst [27–29] and precipitated cobalt catalyst doped with manganese. The method of preparation of iron catalysts for ammonia synthesis consists of fusing of magnetite with addition of promoter oxides (Al_2O_3, CaO and K_2O). After melting, the liquid catalyst was cooled down in controlled conditions. The catalyst was then crushed and sieved to obtain the desired fraction of grain size. The prereduced catalyst was obtained by reduction of the catalyst in the stream of hydrogen in controlled conditions (the rate of increasing of temperature, flow-rate and pressure of hydrogen, water vapour concentration), called also the “activation process”. The activated catalyst was then passivated, so that it contains only the amount of oxygen necessary to form the passive layer of iron oxide covering the reduced core of α-Fe phase. This layer is usually 2–3 nm thick, and comprises about 2 wt.% of catalyst, while the oxidized form contains about 27 wt.% of oxygen.

The precursor for the cobalt catalyst: cobalt oxide Co_3O_4, was obtained by precipitation of the cobalt hydroxide followed by calcinations. Nitrate (V) of cobalt (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 70 °C. Then it was calcinated at 200 °C for 2 h. It was further promoted with oxides of calcium, aluminum and manganese by impregnation of nitrates of those elements under decreased pressure using a rotavapor. After impregnation, the catalyst was calcinated again in 200 °C for 4 h and then in 500 °C for 2 h in air.

Chemical composition of the catalysts was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) method, using Optima 5300DV (Perkin Elmer) – see Table 1.

Average crystallite size of passivated catalyst samples was determined with X-Ray Diffraction Method (XRD) using X-Pert PRO (Philips) with copper lamp.

2.2. Sintering procedure

The catalysts in U-tube quartz reactor of 4 mm internal diameter were reduced at a temperature of 500 °C in the gas mixture (5 vol.% of N_2 in H_2, flow rate 50 $cm^3\ min^{-1}$, purity 99.999%) for 12 h [30]. Then the specific surface area of the samples was determined using single point BET method. The specific surface of the iron and the cobalt catalyst equals 12 $m^2\ g^{-1}$ and 29 $m^2\ g^{-1}$, respectively. It was estimated that the measurement error of specific surface area was 0.5 $m^2\ g^{-1}$. Sintering of the reduced catalysts was carried over in temperatures ranging from 540 °C to 720 °C. At each temperature, the specific surface area was determined at predefined time intervals, until steady value was reached. Details of this procedure are described elsewhere [31].

3. Results and discussion

Fig. 1 displays the variation of the specific surface area of the iron and cobalt catalysts at time of sintering at each temperature in reductive atmosphere [31]. As seen in this figure, the surface areas of the catalysts asymptotically approach a non-zero value of residual surface (S_r). Increase of the sintering temperature leads to decrease of the residual surface, S_r. Also, the time required to achieve the steady state decreases with the increase of the temperature.

Fig. 2 displays the relationship between the residual surface area, S_r of the fused iron catalyst of the steady state in each temperature and reciprocal average crystallite size, *1/d* [31]. The data

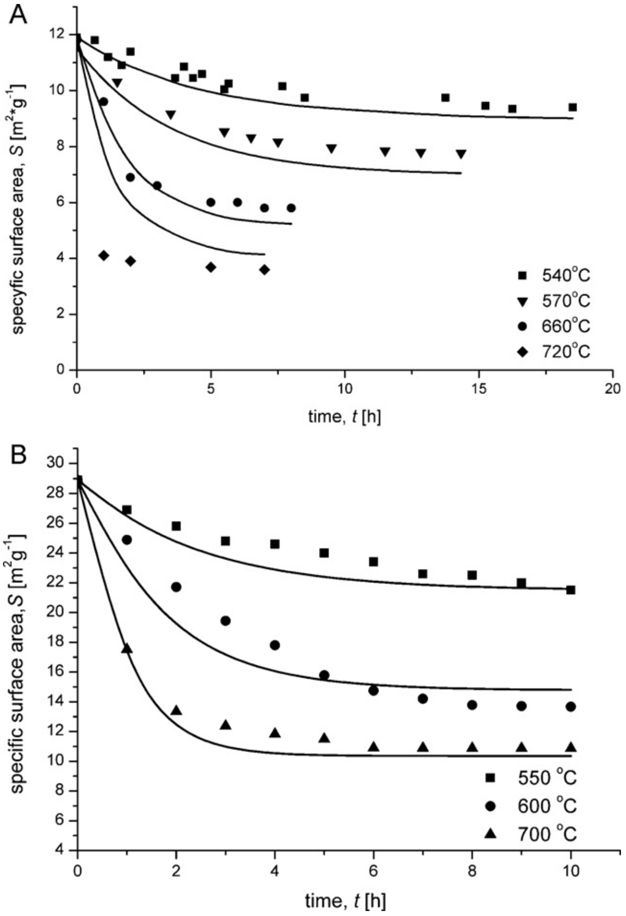

Fig. 1. The relationship between specific surface area of ammonia synthesis catalysts and the temperature and time of sintering in reductive atmosphere: (A) fused iron catalyst [31]; (B) precipitated cobalt catalyst. Points represent the measured data, lines are plots from the model equation (7).

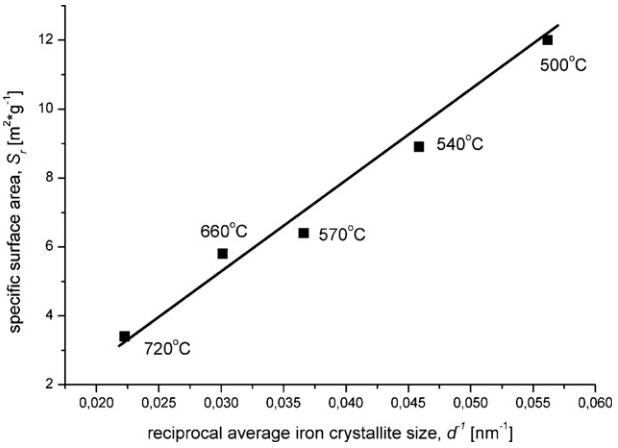

Fig. 2. Residual specific surface area and reciprocal average iron crystallite size at different temperature [31].

shown in Fig. 2 indicates that the change of specific surface area is due to the growth of iron crystallites. The rate of the recrystallization process of the metallic catalysts, as well as the rate of changes of dispersion in the supported catalysts, can be described by an equation analogous to the GPLE model:

$$-\frac{dS}{dt} = k_s(T)(S - S_r(T))^m \quad (2)$$

where S is the specific surface area of the catalyst [m^2 g^{-1}], k_s is recrystallization rate constant, S_r is residual surface area achieved in a finite period of annealing time [m^2 g^{-1}], m is kinetic order of sintering.

The kinetic order of sintering m is usually 1 or 2, according to the published literature, and the determination of the appropriate value is made empirically to obtain the best fit the predictions from the model equation to the measured data [7]. In this example we assumed $m = 1$ and obtained the following equation describing the relationship between the catalyst's surface area and the temperature and time of annealing:

$$S = S_r + (S_0 - S_r)\exp(-k_s t) \quad (3)$$

where S_0 is the initial surface area of the catalyst. Two parameters in Eq. (3), the rate constant, k_s and the residual specific surface area, S_r, depend on the temperature of the process. Figs. 3 and 4, respectively, show the effect of temperature on the residual specific surface area, S_r, and the rate constant, k_s, of the sintering process of iron and cobalt catalyst.

The equation describing the dependence of the residual specific surface area, S_r, on the temperature has a general form:

$$S_r = A\exp\left(-\frac{B}{T}\right) \quad (4)$$

where A and B are constants independent of process temperature.

However, the effect of temperature on the crystallites sintering process rate constant, k_s, can be described by Arrhenius equation:

$$k_s = k_0\exp\left(-\frac{E}{RT}\right) \quad (5)$$

where E – apparent activation energy of recrystallization process. Taking into account the dependence of S_r and k_s on temperature the integral form of Eq. (3) was received.

$$S = A\exp\left(\frac{B}{T}\right) + \left(S_0 - A\exp\left(\frac{B}{T}\right)\right)\exp\left[-k_0 t\exp\left(-\frac{E}{RT}\right)\right] \quad (6)$$

Lines in Figs. 3 and 4 are parallel to each other. Value of the pre-exponential coefficient in Eq. (4) is dependent on the type of catalyst.

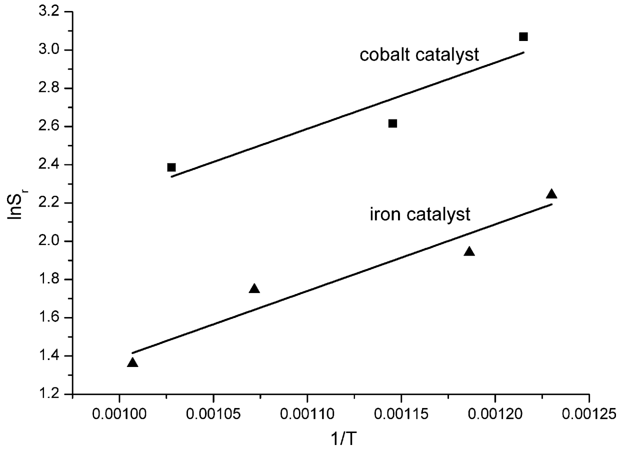

Fig. 3. Dependence of the residual specific surface area, S_r, of iron and cobalt catalyst on temperature of annealing in an atmosphere of hydrogen.

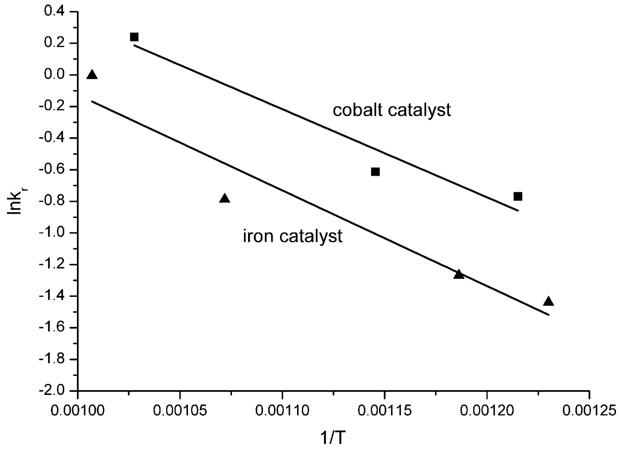

Fig. 4. Dependence of the sintering process rate constant, k_s, for the cobalt and iron catalyst on temperature of annealing in an atmosphere of hydrogen.

Presentation of the measurement data in the form of the dependences of the relative surface areas (S/S_0) allows one to write a common equation for both catalysts in the following form:

$$-\frac{d(S/S_0)}{dt} = 373.8\left(\frac{S}{S_0} - 0.011\exp\left(\frac{3473.5}{T}\right)\right) \quad (7)$$

On the basis of the obtained equation, model curves describing the changes in specific surface area with time, depending on the annealing temperature, were plotted for both catalysts (Fig. 1).

Based on the obtained Eq. (7), the activation energy of recrystallization process of cobalt and iron catalyst was calculated. The value of this energy is 50 kJ mol^{-1}. The obtained values of the activation energy of recrystallization process of metallic ammonia synthesis catalysts are comparable to the typical values for the support catalysts [23–26].

4. Conclusions

Kinetic data for the recrystallization process of metallic ammonia synthesis catalysts were described by power law equation accounting for the fact that the surface of catalysts during sintering process at a constant temperature reaches a residual value different from zero. The equation includes the effect of temperature on the residual specific surface area and the rate constant of recrystallization of catalysts. Activation energy of recrystallization process of cobalt and iron catalyst is the same and is 50 kJ mol^{-1}.

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