Kinetic Studies of the Recrystallization Process of Iron Catalyst for Ammonia Synthesis*

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Kinetics of the recrystallization process of iron catalyst for ammonia synthesis was studied. A sample of pre-reduced triply promoted iron catalyst was investigated. The specific surface area of the catalyst was determined at different degrees of reduction at 500 ℃. In order to evaluate the process of the recrystallization of the catalyst surface area the annealing conditions in the temperature range from 540 ℃ to 720 ℃ were investigated. After reduction the catalysts were passivated and their mean crystallite size was measured using the XRD method.

Surface area of annealed iron catalyst decreases with the increase of temperature. The higher annealing temperature was used, the larger mean size of iron crystallite was measured. The constant ratio of the surface area calculated from the average crystallite sizes (S_r) and the surface area measured using the BET method (S_{BET}) indicates that the sintering of iron crystallites takes place during reduction of the catalyst at high temperatures. Activation energy of sintering, E, was calculated to be 40 kJ mol^{-1}.

It is well known that the sintering processes cause catalyst deactivation due to the crystallite growth and simultaneously a loss of catalytic surface area. With the decrease of surface area, which is catalytically active, the reduction of excessive surface energy takes place. Generally, sintering takes place at temperatures above 500 ℃. Three principal mechanisms of metal crystallite growth have been described: crystallite migration, atomic migration, and vapour transport [1].

Nevertheless, there are durable materials, which maintain the surface properties over a long time irrespectively to the working conditions, including those promoting the sintering process. The iron catalyst for ammonia synthesis with developed specific surface area could be mentioned as an example. Long operation of this catalyst at temperatures higher than 500 ℃ and under pressures up to 20 MPa results in only a slight loss of the catalyst activity. On the basis of the observed catalyst durability a hypothesis was formulated that, under the process conditions, catalyst was present in the chemical equilibrium state. A model of the catalyst active surface based on this hypothesis was developed [2, 3]. This model assumes chemical equilibrium between the iron crystallites and the surface wetted by the promoter oxides, and bridges composed of the promoters that bond the particular iron crystallites.

Surface of the iron crystallites (S_{Fe}) is formed by free metal atoms (Fe) and iron atoms bonded with promoters (M) through oxygen bond (Fe—O—M). The greater the radius of promoter atom (M), the smaller number of Fe—O— bonds is formed. The equilibrium is a result of compensation between the energy of Fe—O— bonds formation and the surface energy. The catalyst specific surface area depends on the concentration of surface oxygen atoms. The larger the number of surface Fe—O— bonds, the larger is the catalyst specific surface area.

Electrospectroscopic studies demonstrated that the potassium atoms on the iron surface are bonded through oxygen atoms [4]. The assumption of *Ertl* [5] that, under the ammonia synthesis conditions, the ratio of the atoms of potassium and oxygen on the iron surface was 1 : 1 was confirmed by this information. Moreover, it was proved that the oxygen atoms are located under the layer of potassium atoms [4].

In order to explain durability of the iron catalyst, the influence of reduction temperature and the catalyst chemical composition on its surface properties was investigated [6]. Faceting of the iron surface in this catalyst was also reported. Experimental observations confirmed the above-mentioned hypothesis [7].

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The present study is focusing on the understanding of kinetics of the iron catalyst recrystallization under the conditions of catalyst annealing.

EXPERIMENTAL

Pre-reduced, triply promoted iron catalyst for ammonia synthesis was used in this work. The chemical composition of catalyst was determined using an inductively coupled plasma atomic emission spectroscopy (ICP-AES). The samples contained iron as well as 0.65 mass % K_2O, 3.3 mass % Al_2O_3, 2.8 mass % CaO, 0.31 mass % SiO_2, and 1 mass % of oxides of other metals (Mg, Ni, Cr, Ti, and V). Samples of 0.5 g of the catalyst with a grains fraction of 1.0—1.2 mm were used.

Detailed conditions of the catalyst reduction and annealing were described previously [7, 8]. In brief, measurements of the surface area of the catalyst were obtained using nitrogen adsorption/desorption analysis. The experiments were carried out in a Peak-2 instrument (manufactured by the Technical University of Łódź) equipped with U-tube quartz reactor of 4 mm internal diameter and a thermal conductivity detector. The catalyst was reduced at a temperature of 500 ℃ in the gas mixture (5 vol. % of N_2 in H_2, flow rate 50 cm^3 min^{-1}, purity 99.999 %). The nitrogen adsorption on the catalyst was determined at −195 ℃ and the gas desorption at room temperature. The evolution of the specific surface area of catalyst was investigated during the reduction. Reduced catalyst was annealed under the reduction conditions in the temperature range from 540 ℃ to 720 ℃ and the specific surface area of catalyst was measured at established time intervals.

The crystallite size of iron in the sintered catalyst was determined using the XRD method with an HZG-4X-ray diffractometer with CoK_α radiation wavelength $\lambda = 0.1788$ nm. The average size of iron crystallites, d, was calculated on the basis of the Scherrer equation.

RESULTS AND DISCUSSION

Changes of the specific surface area of iron catalyst during heating under the reduction conditions are shown in Fig. 1. The measurements were performed both during the reduction at 500 ℃ as well as annealing of catalyst above the temperature of 500 ℃.

The specific surface area of pre-reduced, triply promoted iron catalyst was 9 m^2 g^{-1}. By heating it in the hydrogen atmosphere at 500 ℃, reduction of the passive layer takes place. The specific surface area of completely reduced catalyst amounted to 12 m^2 g^{-1} and was consistent with the previous results [8]. Subsequent heating did not cause any changes of the surface area. An increase of temperature causes a decrease of the catalyst specific surface area to 8.9 m^2 g^{-1} at 540 ℃ and to 3.2 m^2 g^{-1} at 720 ℃. Despite of a long annealing time no further changes of the catalyst specific surface area have been observed. Observed course of the surface area changes during both reduction and annealing allows to conclude that the equilibrium state is achieved.

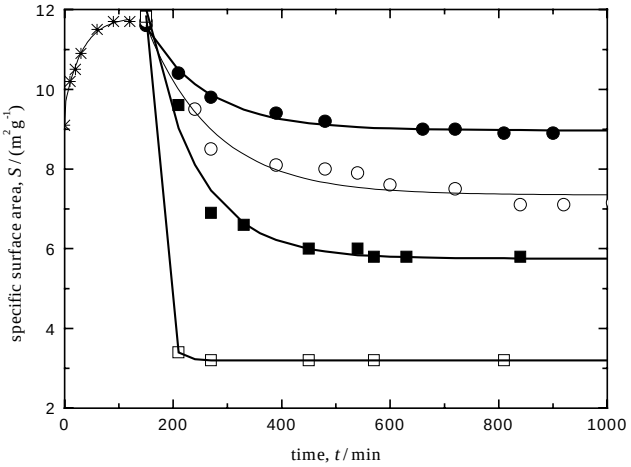

Fig. 1. Specific surface area of pre-reduced triply promoted iron catalyst *vs.* time data during reduction at 500 ℃ (∗) and annealing at 540 ℃ (●), 570 ℃ (○), 660 ℃ (■), and 720 ℃ (□).

After the reduction process was completed the samples were passivated. An average crystallite size of 17 nm was obtained for the catalyst reduced at a temperature of 500 ℃. An enhancement of temperature causes an increase of average crystallite size of iron (43 nm after annealing at 720 ℃).

A spherical shape of the iron crystallites was assumed in further consideration. The catalyst specific surface area was estimated from the average crystallite radius, r, using the relation

$$S_r = \frac{6}{\rho_{Fe} r} \qquad (1)$$

where ρ_{Fe} is the iron density and S_r represents the catalyst specific surface area.

Surface area of iron catalyst can be estimated in two ways: measuring by the BET method, which indicates the total surface of pores or calculating from the crystallite size of iron. These two methods do not give identical results. Variation of the surface area calculated from mean crystallite sizes (S_r) and those measured using the BET method (S_{BET}) with temperature is shown in Fig. 2. The surface area calculated from crystallite size is much larger than the measured surface area using gas physisorption, but the S_r/S_{BET} ratio is constant and equals 3.7. It is justified because single crystallites are not separated. Instead, rather large particles (agglomerates) are formed as shown in Fig. 3. Prior to sintering, large pores are filled with small crystallites. These crystallites and voids between

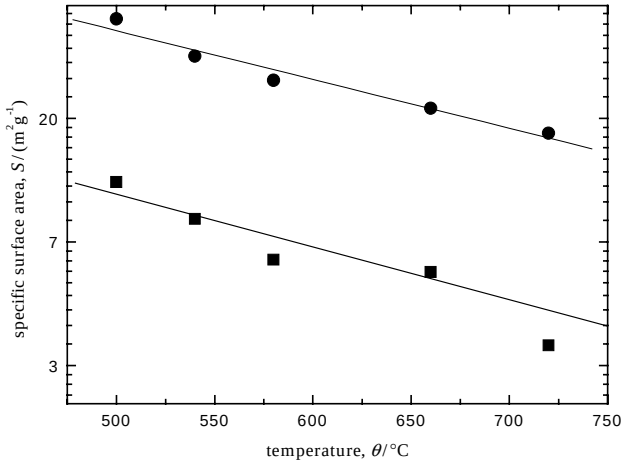

Fig. 2. Surface area of iron catalyst calculated from average crystallite sizes (S_r) (●) and the BET surface area (S_{BET}) (■) as a function of temperature.

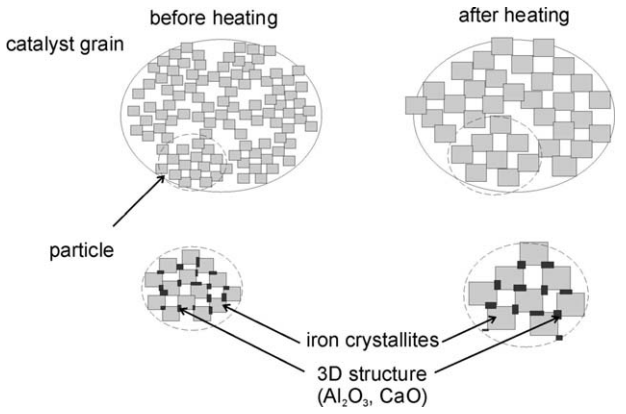

Fig. 3. Scheme of changes in iron catalyst grain during reduction at high temperatures.

them are responsible for a large surface area of the catalyst. While sintering advances, small crystallites become bigger, however, also pores among these crystallites grow. Subsequently, overall decrease of the catalyst surface area is observed.

The growth of grains has been the subject of several reviews [9—11]. Through motion of grain boundary at high temperatures occur the shrinkage and elimination of small grains. Result of this phenomenon is an increase in the average size of the remaining grains. Grain growth in materials is driven by the reduction of the total grain boundary energy that accompanies the surface area decrease [9].

For the pure materials the rate of the average grain radius $\bar{r}$ increase is directly proportional to the average grain boundary energy, $\bar{\gamma}_{gb}$, and the average grain boundary mobility, $\bar{m}$, and inversely proportional to the average grain radius

$$\frac{d\bar{r}}{dt} = \alpha \frac{\bar{m}\bar{\gamma}_{gb}}{\bar{r}} \qquad (2)$$

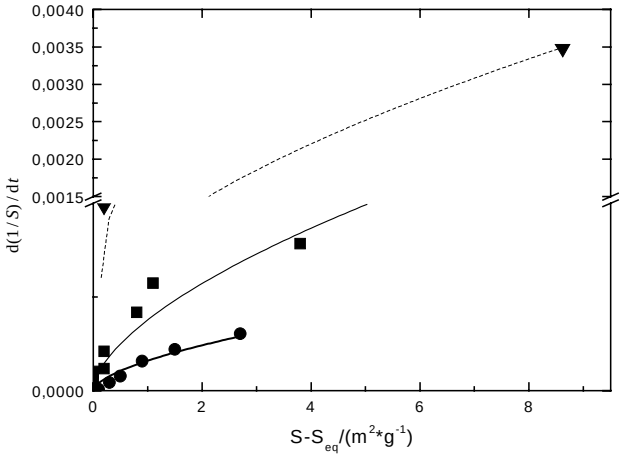

Fig. 4. Variation of $d(1/S)/dt$ *vs.* the difference $(S - S_{eq})$ (at 540 °C (●), 660 °C (■), and 720 °C (▼)).

The grain boundary mobility depends on the temperature

$$\bar{m} = \bar{m}_0 \exp(-Q_{gb}/(kT)) \qquad (3)$$

where $\bar{m}_0$ is a temperature-independent constant, Q_{gb} is the activation energy for the rate-limiting atomic process involved in boundary motion. Basing on eqns (*2*) and (*3*) the rate of grain growth is described by

$$\frac{d\bar{r}}{dt} = \bar{m}_0 \gamma_{gb} \left(\frac{1}{\bar{r}}\right) \exp(-Q_{gb}/(kT)) \qquad (4)$$

The surface area of iron catalyst ultimately does not reach zero given sufficient time, but for a given temperature it approaches a limiting, equilibrium surface area. The results for the annealed iron catalyst indicate that the equilibrium state is reached at each temperature after 15 h. Thus, the term S_{eq} should be taken into account in eqn (*3*). It accounts for the observed asymptotic approach of the surface area to a limiting, equilibrium surface area S_{eq} at infinite time. Regarding eqn (*1*) the final form of sintering rate of iron catalyst is given by

$$\frac{d(1/S)}{dt} = \frac{6}{\rho_{Fe}} \bar{m}_0 \gamma_{gb} (S - S_{eq}) \exp(-Q_{gb}/(kT)) \qquad (5)$$

The relation $d(1/S)/dt$ *vs.* the difference $(S - S_{eq})$ obtained for each temperature is shown in Fig. 4.

Assuming that the average grain boundary energy, $\bar{\gamma}_{gb}$, is temperature-independent, the product $\frac{6}{\rho_{Fe}} \bar{m}_0 \gamma_{gb} \exp(-Q_{gb}/(kT))$ can be determined as the sintering rate constant, k_s. It was earlier reported [1] that the simple power law expression

$$-\frac{d(1/S)}{dt} = k_s (S - S_{eq})^m \qquad (6)$$

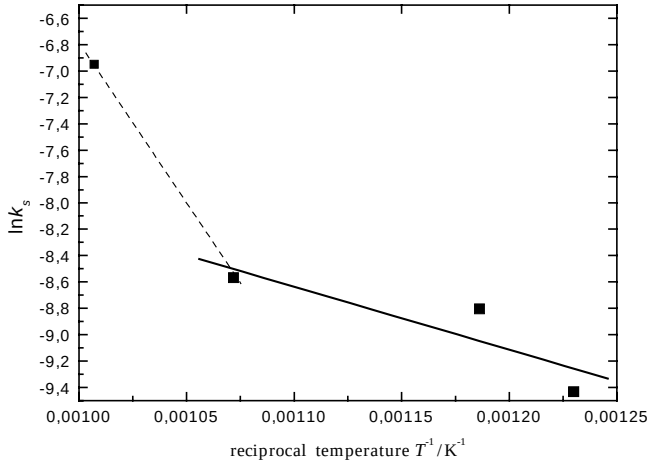

Fig. 5. Sintering rate constant, k_s, *vs.* reciprocal absolute temperature.

describes the presented relationship. In the present study the value of index m equals 0.6.

The logarithm of the sintering rate constant *vs.* the reciprocal temperature is shown in Fig. 5. The result obtained for sintering at 720 ℃ significantly diverges from those obtained for 540 ℃, 570 ℃, and 660 ℃ and this was disregarded in further considerations. Considering the sintering rate constants, k_s, at temperature between 540 ℃ and 660 ℃, the sintering activation energy E was calculated to be 40 kJ mol^{-1}. This value is consistent with the sintering activation energies for Pt, Ni, and Ag catalyst [12].

The presented model [1] was successfully used to describe the sintering of pure materials. During the sintering of iron catalyst the increase of promoter oxide on the grain boundary of iron is expected and the grain boundary energy change can take place. At 720 ℃ this phenomenon would be the most prominent leading to the divergence from the model used herein.

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