

The effect of iron nanocrystallites' size in catalysts for ammonia synthesis on nitriding reaction and catalytic ammonia decomposition

Research Article

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Abstract: Iron catalyst for ammonia synthesis of various mean sizes of iron nanocrystallites were nitrided with ammonia in a differential reactor equipped with systems that made it possible to conduct both thermogravimetric measurements and hydrogen concentration analyses in the reacting gas mixture. The nitriding process was investigated under atmospheric pressure at the temperature of 475°C. It was found that along with an increase of mean size of iron nanocrystallites, with a decrease of specific surface area of the samples, nitriding degree of solid samples increased. At the same time the rate of surface reaction of catalytic ammonia decomposition decreased. Along with an increase of the samples' specific surface area an increase of the catalyst's activity was observed. However, it was also observed that the concentration of active sites on the catalysts' surface decreased along with an increase of specific surface area.

Keywords: Nitriding reaction • Catalytic ammonia decomposition • Nanocrystalline iron • Nanocrystallites' size • Active surface area

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1. Introduction

The nitriding process can be considered as a system of two parallel reactions in which, apart from the nitriding reaction, catalytic ammonia decomposition also occurs. In industrial practice, materials with small values of specific surface area are nitrided. Thus a surface catalytic ammonia decomposition reaction is of lesser importance contrary to a situation when nanocrystalline iron of relatively high specific surface area is nitrided. Therefore, iron catalysts with nanocrystalline structure, wherein iron crystallites are the active phase, are used to study two parallel reactions where one of them is a surface reaction.

Iron catalyst structure was the subject of many studies and currently many reports in this field can be found in monographs about ammonia synthesis [1-4]. Nanocrystalline structure of the catalyst is stable in high temperatures in regard to the presence of structural promoters [5-11] that form bridges to separate iron crystallites from one another. Catalyst structure depends on temperature but after stabilization in a given

temperature the surface is maintained [12]. The active surface area is ca. 50% of the specific surface area [2,13]. Potassium oxide is an activating promoter that is added to the catalyst to improve its activity in the ammonia synthesis process. Models [13-18] of the catalyst's surface wherein promoters' atoms are connected by oxygen with surface atoms of iron were proposed. Promoters' atoms do not occur inside iron crystallites [19]. Surface energy is compensated by energy of bonds between surface iron atoms and atoms of oxygen.

During the nitriding process, with specified values of nitriding potential ($P = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2}$), stationary states were observed. In stationary states, nitriding reaction rate is zero (stable mass of a solid sample), but catalytic ammonia decomposition reaction proceeds at a constant rate. Hysteresis phenomenon for the dependence of iron nitriding degree on nitriding potential in iron nitriding reaction and reduction of the obtained nitrides was observed while studying the stationary states. It was shown it is possible to create mixtures of phases, containing $\alpha\text{-Fe(N)}$, $\gamma'\text{-Fe}_4\text{N}$ and $\epsilon\text{-Fe}_x\text{N}$, of the desired composition [20,21].

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Catalytic ammonia decomposition over iron depends on many factors such as the chemical composition of the gas phase or the surface of the catalyst on which the reaction proceeds. The influence of sulfur [22,23] or water vapor [24] in gas phase on the catalytic ammonia decomposition reaction rate over iron was analyzed. Catalytic ammonia decomposition reaction occurs at a varying rate depending on the solid-state phase present in the nitriding process (Fe or Fe_xN) [21,25,26]. That is the reason why nanocrystalline iron nitriding reaction should be interpreted as a parallel reaction to ammonia decomposition.

A model for nanocrystalline materials, the gas phase reaction for the nitriding process, was developed [27]. In this model, the rate of surface reaction is the limiting step. It was observed that, apart from surface area, a distribution of the nanocrystallites' sizes also influences the rate of the reaction [28,29].

Therefore, herein two parallel reactions – nitriding and catalytic ammonia decomposition on iron catalyst for ammonia synthesis of different nanocrystallites' sizes – were described. The dependence of iron nitriding degree and the rate of surface reaction of catalytic ammonia decomposition on iron nanocrystallites' sizes (specific surface area) were studied.

2. Experimental Procedure

An industrial pre-reduced iron catalyst for ammonia synthesis was studied. The chemical composition of the catalyst was determined using inductively coupled plasma method (ICP-OES, spectrometer Perkin Elmer, type Optima 5300DV). Apart from metallic iron, the catalyst contained the promoter's oxides (3.3% wt. Al₂O₃, 2.8% wt. CaO, 0.65% wt. K₂O).

The kinetics of two parallel reactions – catalytic ammonia decomposition and nitriding of catalyst samples – was investigated making use of a tubular differential reactor equipped with a gas phase

composition analyzer and a system that made it possible to conduct thermogravimetric measurements (Fig. 1). In a platinum basket hanging on a thermobalance's arm approximately 1 g of the analyzed catalyst was placed in a form of a single layer of grains with sizes in the range of 1.0 – 1.2 mm. Samples of the gas phase were collected from sampling points which were located in direct neighborhood of the catalyst. Flow-rates of the gas reactants were regulated making use of electronic mass flow controllers.

Nitriding of the sample catalyst was performed with ammonia (gas load was constant and equaled 12 dm³ h⁻¹ g⁻¹, 100% of ammonia at the reactor inlet) at 475°C under atmospheric pressure. On the basis of previous studies conducted with various gas loads and grain sizes, it was found that the processes were carried out in the kinetic region of chemical reactions. The values of partial pressure of ammonia, p_{NH_3} , were determined making use of the material balance of the reactor. On the basis of concentrations of the gas components, the values of the nitriding potential were calculated:

$$P = \frac{p_{\text{NH}_3}^{3/2}}{p_{\text{H}_2}} \quad (1)$$

where: p_{H_2} – hydrogen partial pressure in gas phase.

The rate of the surface catalytic ammonia decomposition reaction, r_{dec} , was calculated making use of the following equation:

$$r_{\text{dec}} = \frac{X_{\text{H}_2} F_{\text{NH}_3}^0}{1.5 - X_{\text{H}_2}} \quad (2)$$

where: $F_{\text{NH}_3}^0$ – ammonia molar flow rate in the inlet stream, mol s⁻¹, X_{H_2} – molar concentration of hydrogen in the reactor, mol mol⁻¹.

In order to obtain samples of different average iron crystallite size (different values of specific surface area), the nitriding process was preceded by a reduction (to remove a passive layer) with hydrogen (9 dm³ h⁻¹ g⁻¹) and heating at various temperatures in the range between 500°C and 700°C under a hydrogen atmosphere. After every nitriding process the samples were reduced with hydrogen at 475°C and chemical composition (ICP) and values of specific surface area were determined (Thermal Desorption – single point BET method on PEAK-4 apparatus). The average size of iron nanocrystallites was determined by Scherrer's method (X-Ray Diffraction apparatus with copper lamp). XRD studies were carried out on the Philips X'Pert PRO diffractometer. The following parameters of XRD measurement were applied: high voltage 35000 V and current 0.03 A. 0.02 degree step, 10 seconds counting time per step and $2\theta = 96\text{--}102^\circ$ to analyze the mean size of nanocrystallites were applied. 0.05 degree step and

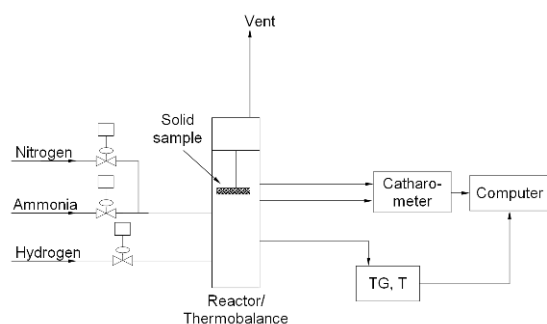


Figure 1. Reactor with thermogravimetric measurement and concentration analysis of hydrogen in gas phase.

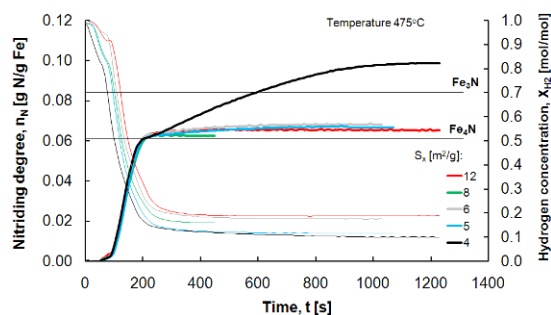


Figure 2. Nitriding degree and hydrogen concentration changes versus time (100% ammonia at the reactor inlet, $T = 475^{\circ}\text{C}$).

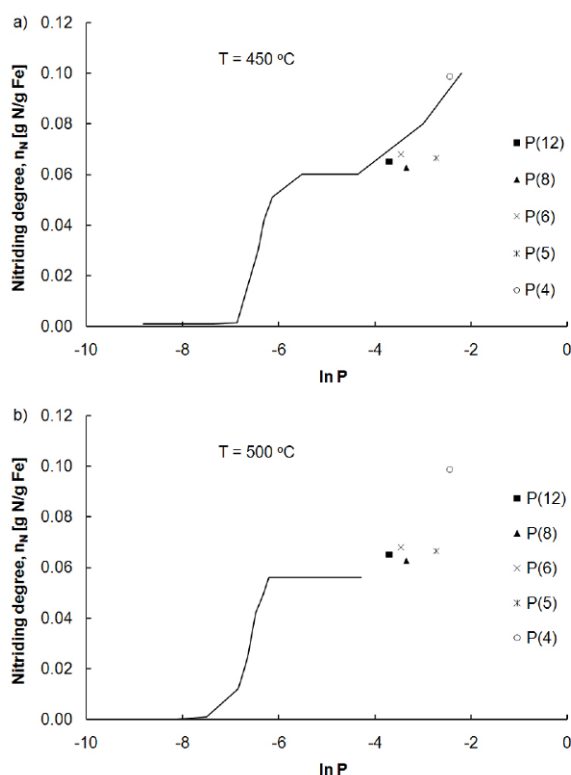


Figure 3. Nitriding degree as a function of the natural logarithm of nitriding potential.

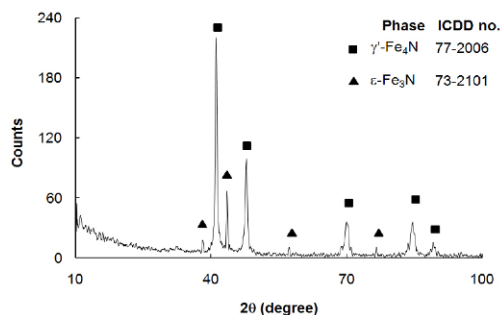


Figure 4. XRD pattern for sample P(12) nitrided with ammonia at 400°C .

3 second counting time per step for the purposes of phase analysis were applied. The X'Pert High Score program with the ICDD base to the phase analysis was used. The mean size of nanocrystallites in samples reduced at 500°C was 20 nm, whereas those of samples reduced at 550°C , 600°C , 650°C and 700°C were 28 nm, 33 nm, 36 nm and 40 nm, respectively. On the basis of previous studies [18] the dependence of specific surface area on the heating temperature of the catalyst was determined. The values of specific surface area were: $12\text{ m}^2\text{ g}^{-1}$, $8\text{ m}^2\text{ g}^{-1}$, $6\text{ m}^2\text{ g}^{-1}$, $5\text{ m}^2\text{ g}^{-1}$ and $4\text{ m}^2\text{ g}^{-1}$ for temperatures: 500°C , 550°C , 600°C , 650°C and 700°C , respectively. No changes of the samples' composition were noticed.

3. Results and Discussion

The results of thermogravimetric measurements and changes of hydrogen concentrations in the gas phase as functions of time are shown in Fig. 2.

In this paper, the nitriding degree of solid samples, n_N [g N/g Fe] is defined as a ratio of nitrogen mass to mass of iron in solid samples.

Initially, the mixing process in gas phase between hydrogen, which was left in the reactor after the reduction process, and ammonia, let into the reactor, was observed. The mixing process occurred simultaneously with two parallel reactions – nitriding and catalytic ammonia decomposition. Consequently, changes of gas phase composition occurred. The concentration of hydrogen was decreasing until a constant value was reached. When a stable mass of a solid sample is observed (stationary state; the nitriding reaction rate is zero) only catalytic ammonia decomposition with a constant rate on a given nitrided phase occurs. On the basis of previous work [20] the dependence of the nitriding degree of solid sample on the nitriding potential and temperature was shown by graphs. Some examples of results of these dependences for processes performed at 450°C and 500°C [20] are plotted with solid lines in Figs. 3a and b. In the aforementioned figure, points for samples with different values of specific surface area nitrided at 475°C are presented as well. The samples P(12), P(8), P(6) and P(5) were nitrided until a composition approximately corresponding to the stoichiometric composition of γ' - Fe_4N phase was obtained. A sample with specific surface area of $4\text{ m}^2\text{ g}^{-1}$ was nitrided in a stationary state to a composition which exceeds the stoichiometric composition of Fe_3N phase. However, the phase composition given by XRD shows that two phases exist simultaneously: γ' and ϵ (Fig. 4).

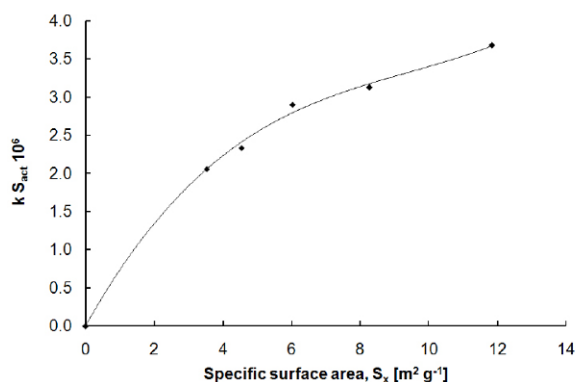


Figure 5. Active surface area as a function of specific surface area.

The rate of the ammonia decomposition reaction over γ' and ϵ phases, as a function of the logarithm of nitriding potential, for a sample with a given specific surface area ($12 \text{ m}^2 \text{ g}^{-1}$) was described by means of the following empiric equation [21]:

$$r_{\text{dec}} = 6.2 \cdot 10^{-6} - 2.3 \cdot 10^{-6} \ln P \quad (3)$$

On the assumption that catalytic ammonia decomposition occurs on catalysts of constant chemical composition of the surface, Eq. 3 can be modified as follows:

$$r_{\text{dec}} = k S_{\text{act}} (A - \ln P) = k S_x f(C_a) (A - \ln P) \quad (4)$$

where: S_{act} – active surface area, S_x – specific surface area of sample X, k – catalytic ammonia decomposition reaction rate constant, C_a – concentration of active sites on the surface of catalyst, A – constant value at a given experimental temperature.

After transformations of Eq. 4 and making use of Eqs. 1, 2 and 3, the graphical dependence of relative activity of surface on specific surface area ($k S_{\text{act}} = f(S_x)$; Fig. 5) when $k = \text{const}$ (samples were nitrided at the same temperature) was elaborated. When values of the specific surface area were increasing, the activity of the catalyst was increasing too – the rate of surface reaction of catalytic ammonia decomposition was increasing.

This dependence describes relative changes of active surface area as a function of specific surface area. This dependence is non-linear which suggests that concentration of active sites in samples with different values of specific surface area is changing.

When $k S_{\text{act}} = f(S_x)$ expression (from Eq. 4) is divided by the corresponding specific surface area of sample X then changes of concentration of active sites as a function of specific surface can be observed (Fig. 6).

This dependence indicates that the concentration of active sites in catalytic ammonia decomposition was decreasing along with an increase of the specific

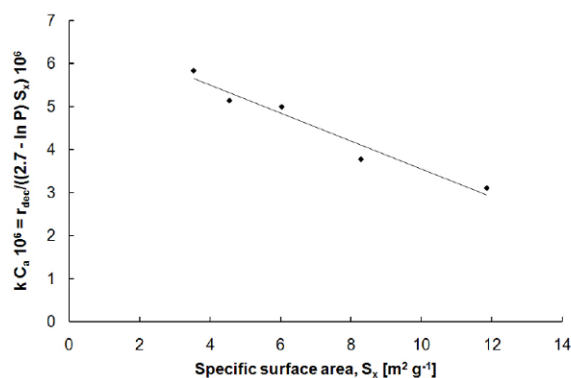


Figure 6. Concentration of active sites on the surface of catalyst as a function of specific surface area.

surface area. Previously, it was found [2] that the activity of catalyst in ammonia synthesis depends on active surface area, but not on specific surface area. In [23] changes of relative values of the amount of active sites in ammonia synthesis, ammonia decomposition, and in iron carburization were determined. Relative values of the amount of active sites were changing similarly for those processes and were increasing when temperature was increasing as well [18,23]. The rate of catalytic ammonia decomposition depends on the summary content of potassium oxide in a catalyst [16,30-32]. Potassium oxide does not create a solid solution in iron but occurs in spaces between iron crystallites and wets the surface of crystallites. According to the double-layer model of the surface of the fused iron catalyst for ammonia synthesis [13-18], content of potassium oxide influences the activity of a catalyst – the activity increases because the amount of active sites increases due to geometrical reasons (in the neighborhood of potassium ions, iron atoms are uncovered – active sites). The surface of iron is also wetted with oxides of other promoters. However, only potassium influences an increase of the number of active sites. The total content of potassium was constant in the studied samples. Because the crystallites' surface is wetted by potassium, the surface content of potassium is changing along with changes of specific surface area of the samples. When specific surface area is greater, potassium concentration is lower. That is why the rate of catalytic ammonia decomposition is increasing slowly when specific surface area is greater and specific surface area increases because the amount of active sites is decreasing.

4. Conclusions

It was observed that along with an increase of the mean size of iron nanocrystallites, the nitriding degree of solid samples was increasing as well. Simultaneously, the rate

of surface reaction of catalytic ammonia decomposition was decreasing. The greater the specific surface area, the higher activity of catalysts was observed, but this kind of increasing dependence was not of a linear type.

This suggests that the concentration of active sites is decreasing along with an increase of specific surface area.

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