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Catalytic Ammonia Decomposition Over Fe/Fe_4N

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Abstract The catalytic ammonia decomposition over iron and iron nitride, Fe_4N, under the atmosphere of ammonia–hydrogen mixtures of different amounts of ammonia in the temperature range of 400–550 °C by means of thermogravimetry has been studied. A differential tubular reactor with mixing has been used. The ammonia concentration in the gas phase during all the process was analysed. The balance between the inlet and outlet ammonia quantity has been used to determine a degree of ammonia conversion and the values of decomposition reaction rate. The activation energy of ammonia decomposition reaction over Fe and Fe_4N was found to be 68 and 143 kJ/mol, respectively.

Keywords Ammonia decomposition · Nitriding process · Iron catalyst · Nitrides

1 Introduction

In ammonia synthesis process, apart from a synthesis reaction, catalytic ammonia decomposition reaction over iron also occurs [1, 2]. Ammonia decomposition reaction also takes place in the first stage of iron nitriding process under ammonia atmosphere [3, 4], while the formation of nitrides is favoured from the thermodynamical point of view. Grabke [5, 6] showed, that in the initial stage of the nitriding process, the surface catalytic ammonia decomposition reaction over iron is a rate determining step. Nitriding process was studied over bulk iron [7], iron catalyst for ammonia synthesis [8] and iron thin films [9]. The decomposition of ammonia on nitrided iron can be studied when the equilibrium between the formation and decomposition of iron nitrides is achieved during the nitriding process [10]. The experimentally measured catalytic ammonia decomposition on nanocrystalline iron surface occurs at temperatures higher than 400 °C [11, 12]. Nitrogen content in the obtained nitrides depends on the temperature and ammonia concentration in a gas phase [11, 12].

Catalytic ammonia decomposition over iron depends on many factors such as, for example, chemical composition of a gas phase or a surface, on which the reaction proceeds. The influence of sulphur [13, 14] or water vapour [15] present in the gas phase on the rate of ammonia decomposition process over iron was investigated. Catalytic ammonia decomposition reaction at a stable temperature occurs with various rates depending on the solid state phase (Fe or Fe_xN) present in the reaction system [16]. Therefore, during the analysis of ammonia decomposition reaction over iron catalyst one is to take into account the fact, that in parallel to this reaction a nitriding reaction of iron, resulting in iron nitrides formation, also occurs.

It was previously found [11, 12, 17, 18], that the rates of reactions taking place in the adsorption range are limited by the rate of dissotiative adsorption of a gas phase on the solid state, and that crystallites react in the order of their sizes from the smallest to the biggest. Assuming that hydrogen which is adsorbed on a solid surface does not affect the rate of the studied surface chemical reaction and that the total specific surface area of the solid state does not change, the rate of adsorption on the surface of a single crystallite can be described as follows:

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$$r = pk_{\mathrm{ads}}S(1-\theta)^n - k_{\mathrm{des}}S\theta^n \ [\mathrm{mol/s}] \tag{1}$$

where k—rate constant, n—number of adsorption sites occupied by one adsorbed molecule, p—partial pressure of adsorbate, r—adsorption rate, S—surface area, ads—refers to adsorption, des—refers to desorption, θ—surface coverage.

After adsorption, products of the reaction can be either dissolved in a solid state or desorbed to a gas phase. Between the substance on the crystallites' surface and the one which is dissolved in the crystallites' bulk the state of the thermodynamic equilibrium is held. This equilibrium was expressed by the McLean–Langmuir equation [19]:

$$\frac{\theta}{1-\theta} = \frac{X_{\mathrm{b}}}{1-X_{\mathrm{b}}} e^{\frac{-\Delta G}{RT}} \tag{2}$$

where ΔG—Gibbs free energy of segregation of the reactant, R—gas constant, T—temperature, X—concentration, b—refers to a bulk.

In the bulk there is no concentration gradient of the reactant, and when the critical bulk concentration, X_{bCri}, of the reactant is exceeded, the phase transition of the whole crystallite occurs. The Gibbs free energy of segregation can be described by means of a linear function of the crystallite bulk concentration, X_{b}, [20]:

$$\Delta G(X_{\mathrm{b}}) = \Delta G_0 + \alpha X_{\mathrm{b}} \tag{3}$$

where α—factor considering the change of the Gibbs free energy of segregation with a change in bulk concentration.

The subject of the present considerations is the analysis of the kinetics of a catalytic ammonia decomposition reaction on α-iron or iron nitride γ'-Fe$_4$N phase. An example of such a reaction system is the nitriding process which is conducted in a tubular reactor with mixing at low and high ammonia concentrations, respectively.

2 Experimental

The kinetics of a catalytic ammonia decomposition reaction as well as nanocrystalline iron nitriding process with ammonia was investigated making use of an analytical installation equipped with a flow tubular differential reactor that made it possible to conduct thermogravimetric measurements (Fig. 1). Gas phase composition changes in the reaction volume of the reactor were analysed. The samples of gas phase were collected from two sampling points which were placed over and under a platinum basket carrying the solid sample. The gas phase composition was the same at both sampling points. There was no ammonia decomposition reaction observed on the platinum basket at the applied range of process temperatures. Hydrogen concentration in the reacting gas mixture was determined directly. The flow rate of gas reactants was determined by means of electronic mass flow controllers. The mass and temperature of the analysed solid sample as well as the data concerning hydrogen concentrations in the gas mixture were recorded digitally. In the platinum basket hanging on a thermobalance arm approximately 1 g of the analysed substance was placed in a form of a single layer of grains. The resolution of mass changes measurements was 0.1 mg.

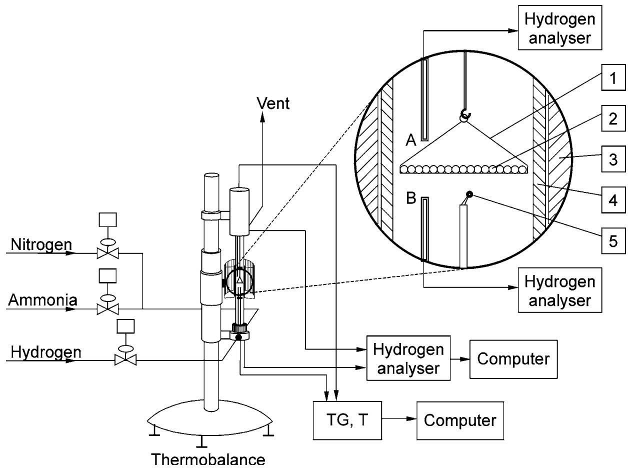

Fig. 1 Experimental equipment: 1—sample holder, 2—single layer of grains, 3—reactor furnace, 4—reactor wall, 5—thermocouple

A prereduced iron industrial catalyst for ammonia synthesis, KMIR, was analysed. The grains of size in the range of 1.0–1.2 mm were chosen for measurements.

A reduction process of a passive layer of the prereduced iron catalyst, followed by the nitriding process, was performed at the temperature of 550 °C and at pure hydrogen (99.999%) load 150 cm^3 min^{-1} g^{-1} under atmospheric pressure.

Nitriding process was conducted under atmospheric pressure, isothermally, at various temperatures in the range of 400–550 °C. Ammonia–hydrogen mixtures of various nitrogen activities, $R = p_{\mathrm{NH3}}/p_{\mathrm{H2}}^{3/2} = \mathrm{var}$ [21], were let in the reactor at a total gas load of 150 cm^3/(min g$_{\mathrm{cat.}}$). The process was stopped when the stationary state was achieved and the catalyst samples mass was stable.

The phase compositions of the nitrided solid samples were examined by means of X-Ray Diffraction analysis (XRD).

3 Results and Discussion

The mass changes of the solid samples were observed as thermogravimetric TG curves. On Fig. 2 some exemplary TG curves and changes of hydrogen concentrations in the gas phase as functions of time, for catalyst samples which were nitrided in isothermal conditions at temperatures of

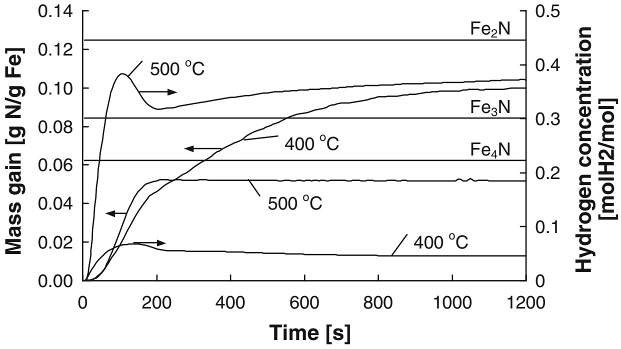

Fig. 2 Mass gain, temperature and hydrogen concentration changes versus time

400 and 500 °C, are presented. The reactor was fed only with ammonia. It was found, that at high values of nitrogen activity, *R*, iron nitrides were formed till ε phase was observed. The stoichiometric composition of iron nitrides γ'-Fe$_4$N and ε-Fe$_{3\text{-}2}$N has been marked (horizontal lines).

On the basis of thermogravimetric measurements and XRD analysis it was found, that the phase composition of the nitrided catalyst is a function of nitrogen activity (Fig. 3). In the present work a two-phase system (Fe + γ'-Fe$_4$N) was studied at *R* from the range 0.0003–0.0137. If the process meets the assumptions of the adsorption range model, crystallites react in the order of their sizes and, in stationary states, apart from nitride phase metallic iron also occurs.

Nanocrystalline substances represent a set of crystallites of various sizes, which can be described by means of grain size distribution (GSD). Hereby it was assumed, that this distribution can be of a normal type and described by the following equation:

$$\mathrm{GSD}(d,\sigma) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(\frac{-(d_N - d)^2}{2\sigma^2}\right) \tag{4}$$

where *d*—crystallite diameter, σ—standard deviation, *N*—refers to mean value.

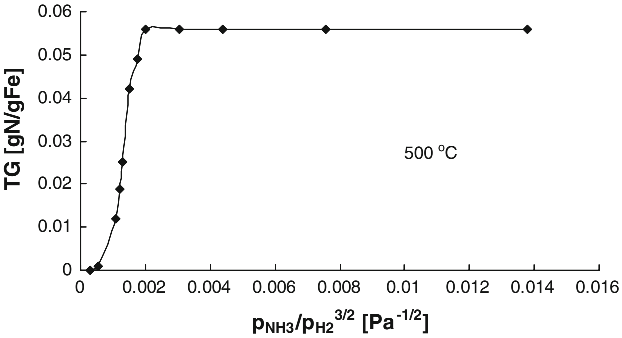

Fig. 3 Mass gain versus nitrogen activity; 500 °C

The modelling was performed making use of the assumptions of the adsorption range model. A set of spherical crystallites of diameters in the range of $1 < d < 100$ nm and the Gaussian-type size distribution of parameters such as mean diameter $d_N = 17$ nm, standard deviation $\sigma = 4$ (Fig. 4a) was taken under consideration.

The surface distribution corresponding to the crystallites of diameters from the considered range was also determined (Fig. 4b).

In a general approach, surface reaction rate can be expressed by the following equation:

$$r = R(k_1 S_1 + k_2 S_2) \tag{5}$$

where *k*—reaction rate constant, *r*—reaction rate, *R*—nitrogen activity, *S*—surface area, 1—refers to substrate, 2—refers to product.

On the basis of crystallographic data for a certain substrate and product, density changes of solid nanocrystallites during the chemical reaction were determine. It made it possible, in turn, to determine surface changes of the analysed crystallites resulting from a phase transition during product formation. In the present work it was assumed, that the density of substrates was the same as the one of products, and thus the volume of crystallites did not change during the reaction. Thus the total specific surface area of substrate and product, $S_1 + S_2$, did not change, either. The changes of the surface area of the formed product, $S = S_2/(S_1 + S_2)$, as a function of the product volume, $V = V_2/(V_1 + V_2)$, during the reaction, were determined (Fig. 5).

Ammonia decomposition is a surface reaction, thus all the changes of a surface of iron and iron nitride phases during the nitriding process were determined (Fig. 6).

On the basis of modelling results it was found, that the maximum value of the specific surface area for the assumed set of crystallites of iron and iron nitride Fe$_4$N was about 40 m^2/g. The experimentally determined specific surface area is 11 m^2/g according to the BET method, because crystallites can agglomerate in real systems. Therefore, in order to perform further calculations, factor 0.25 was used to limit the surface area values from Fig. 6.

On the basis of the results of gas phase composition measurements and using the mass balance of the reactor a conversion degree of ammonia in the ammonia decomposition reaction was calculated:

$$\alpha_{\mathrm{NH3}} = \frac{F^0_{\mathrm{NH3}} - X_{\mathrm{NH3}}F^0}{F^0_{\mathrm{NH3}}X_{\mathrm{NH3}} + F^0_{\mathrm{NH3}}} \tag{6}$$

where: α—conversion degree, *F*—molar flow rate, NH$_3$—refers to ammonia, 0—refers to the inlet stream.

The ammonia decomposition rates were determined in particular stationary states which were obtained at the applied values of nitrogen activity, *R* (Fig. 7).

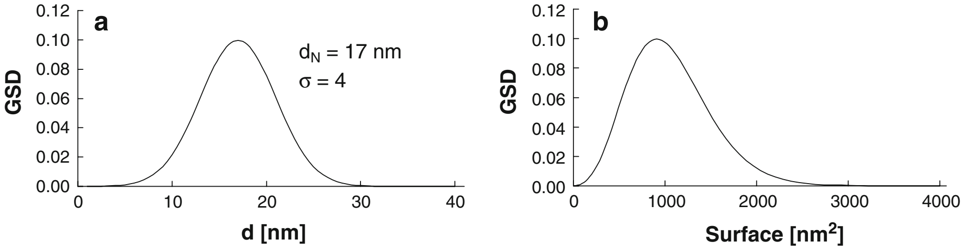

Fig. 4 a Assumed grain size distribution of crystallites; b Distribution of crystallites' surface

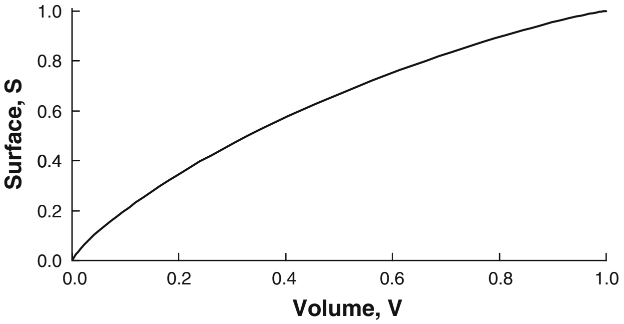

Fig. 5 Surface of crystallites versus crystallites' volume

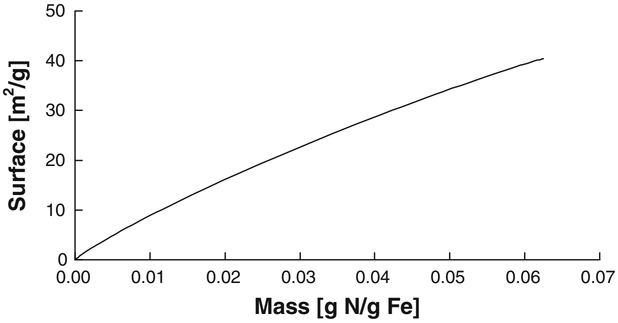

Fig. 6 Specific surface area as a function of mass gain

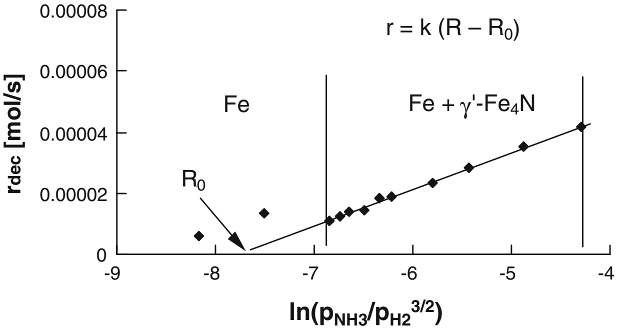

Fig. 7 Ammonia decomposition rate versus the nitrogen activity; 500 °C

The rate of ammonia decomposition reaction over two phases can be described as follows:

$$r = R(k_{\mathrm{Fe}} S_{\mathrm{Fe}} + k_{\mathrm{Fe4N}} S_{\mathrm{Fe4N}}) \qquad (7)$$

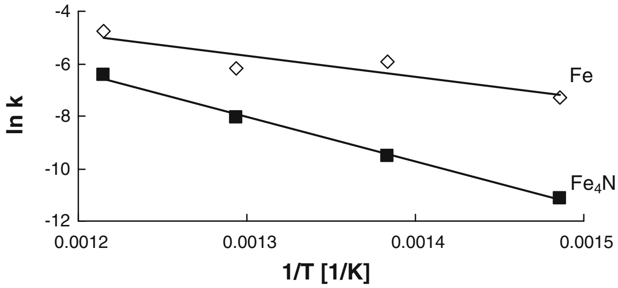

Fig. 8 Arrhenius plot for the ammonia decomposition over iron and iron nitride, Fe_4N

where k—reaction rate constant, R—nitrogen activity, S—specific surface area, Fe—refers to iron phase, Fe_4N—refers to iron nitride phase.

The values of catalytic ammonia decomposition rate constants, k_{Fe} and k_{Fe4N}, were calculated on the basis of Eq. 7 (Fig. 8). The values of the rate constant k_{Fe} were extrapolated to the case of pure metallic iron. The activation energies of catalytic ammonia decomposition reaction over iron and iron nitride, Fe_4N, were found to be 68 and 143 kJ/mol, respectively, as well as values of preexponential coefficients $k_{0\mathrm{Fe}} = 141$ and $k_{0\mathrm{Fe4N}} = 16 \cdot 10^5$.

4 Conclusions

Ammonia decomposition reaction over both iron and iron nitride is an activated process. The apparent activation energies of ammonia decomposition over iron and iron nitride were determined to be 68 and 143 kJ/mol, respectively. The rate of ammonia catalytic decomposition reaction is higher in case of nanocrystalline iron than in case of nanocrystalline iron nitride γ'-Fe_4N.

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References

1. Aika K, Tamaru K (1995) In: Nielsen A (ed) Ammonia, catalysis and manufacture, Springer, Berlin
2. Jennings JR (ed) (1991) Catalytic ammonia synthesis fundamentals and practice.Plenum Press, New York

3. Cahn RW, Haasen P (1983) Physical metallurgy. North-Holland Physics Publishing, Amsterdam
4. VDI (1990) VDI—lexikon werkstofftechnik. VDI-Verlag, Düsseldorf
5. Grabke HJ (1968) Ber Bunsen Phys Chem 4:533
6. Grabke HJ (1973) Archiv Eisenhut 44:603
7. Inokuti Y, Nishida N, Ohashi N (1975) Metal Trans A 6A:773
8. Love KS, Emmett PH (1941) J Am Chem Soc 63:3297
9. Logan SR, Moss RL, Kemball C (1958) Trans Farad Soc 54:922
10. Arabczyk W, Narkiewicz U, Moszyński D (1999) Langmuir 15:5785
11. Arabczyk W, Zamłynny J (1999) Catal Lett 60:167–171
12. Wróbel R, Arabczyk W (2006) J Phys Chem A 110(29):9219–9224
13. Arabczyk W, Zamłynny J, Moszyński D (2006) Polish J Chem 80:345–350
14. Arabczyk W, Moszyński D, Narkiewicz U, Pelka R, Podsiadły M (2007) Catal Today 124:43–48
15. Arabczyk W, Zamłynny J, Moszyński D, Kałucki K (2005) Polish J Chem 79:1495
16. Arabczyk W, Pelka R (2006) Ogólnopolskie kolokwium katalityczne, Kraków, Poland, p 106
17. Arabczyk W, Wróbel R (2003) Solid State Phenomena 94:185–188
18. Arabczyk W, Wróbel R (2003) Solid State Phenomena 94:235–238
19. Benard J (1983) Adsorption on metal surfaces: an integrated approach: studies in surface science and catalysis. Elsevier, Amsterdam, p 261
20. Fowler RH, Guggenheim EA (1939) Statistical thermodynamics. Cambridge University Press, Cambridge, p 429
21. Grabke HJ (1976) Zeitschrift für Physikalische Chemie Neue Folge 100:185–200