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Study of the ammonia decomposition over iron catalysts

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The decomposition of ammonia is a reaction associated with the process of the nitriding of metals. The kinetics of the ammonia decomposition on iron catalysts has been studied using a differential reactor with internal mixing. The balance between the inlet and outlet ammonia quantity has been used to determine the degree of conversion. The rate of ammonia decomposition could be described by the following expression: $r = k_0 \exp(E_a/RT) p_{NH_3}$. The activation energy of the ammonia decomposition process has been found for samples with potassium as $E_a = 96$ kJ/mol, for samples without potassium as $E_a = 87$ kJ/mol.

Keywords: ammonia decomposition, iron catalyst, kinetics

1. Introduction

Iron catalysts are commonly applied in the processes of ammonia synthesis. The composition of the catalysts comprises α-Fe as well as the promoters introduced in the form of oxygen compounds of calcium, aluminium and potassium. Preliminary works that concern the decomposition of ammonia over these catalysts have appeared in the forties. Previous experimental results concerning the kinetics of ammonia decomposition have been presented in [1].

As a result of these works many equations have been given in which the reaction rate is expressed by different functions of concentrations. At present, the Temkin–Pyzhew equation [2] is most frequently used for the description of the kinetics of the catalytic decomposition of ammonia over iron catalysts. According to the measurements performed by these authors, the apparent activation energy increases with an increase of pressure and amounts from 150 to 220 kJ/mol for the pressures from 10 to 100 MPa [3]. The values of the apparent activation energy at normal pressures revealed in the literature by other authors [1] are very divergent and they vary from 150 to 240 kJ/mol. The investigations were also carried out at pressures lower than atmospheric. The apparent activation energy determined for the pressure range from 0.01 to 0.49 of atmosphere has a value of 162 kJ/mol [4]. A large dispersion between the results can be caused by different investigated objects (different composition of the catalysts) on the one hand, or by an oversimplified measurement technique applied for the determination of the reaction rate.

During the catalytic decomposition of ammonia, the chemical composition of the catalyst can undergo a change depending on the composition of the reacting mixture. In the presence of the iron catalyst different nitrides can be formed with a summary composition FeN_x, where x can take the values from 0 to 0.5. It may be speculated that in such process the reaction mechanism changes with a change of surface composition.

In the nitriding process two reactions proceed parallel to each other, the first being the formation of nitride proceeding at the phase boundary between a metal and nitride, the second one is the ammonia decomposition on the catalyst surface. The kinetics of the nitriding process is presented in [5,6].

The presented work was undertaken to determine the rate of ammonia decomposition over a fine crystalline sample of iron nitride obtained from the catalyst for ammonia. Here, samples with the specific surface of 11 m^2/g are used in the studies, therefore, the rate of both processes, nitriding and the catalytic decomposition of ammonia, is significantly higher in comparison with the rate for the processes proceeding in the metal working technology.

2. Experimental

An examination of ammonia decomposition process was carried out over a fused iron catalyst PS3 INS with the grain sizes from 1 to 1.5 mm. The catalyst after reduction contained 3.3% Al_2O_3, 3.2% CaO and 0.8% K_2O. These catalysts are composed of the elementary α-Fe grains with an average diameter about 30 nm (determined by electron microscopy and X-ray diffraction). The specific surface area of these samples is 11 m^2/g (according to BET), and the porosity coefficient $\varepsilon \approx 0.5$. The samples of the reduced catalyst as well as the samples of the catalyst with the potassium compounds were washed out with hot water after the reduction. As a result of washing out with water, the content of potassium oxide decreased to 0.05 at the invariable content of the remaining promoters. The investigations were performed in the temperature range from 325 to 500 °C under the atmospheric pressure.

The experimental setup for the examination of the ammonia decomposition consists of a gas cylinder with ammonia of technical grade, a drier filled with solid KOH, an ammonia decomposer and a tank reactor with internal mixing. In this reactor the catalyst is fixed in baskets made from stainless steel.

The catalyst was reduced polythermally in the temperature range from 325 to 500 °C in a nitrogen–hydrogen mixture. This mixture was obtained by ammonia decomposition at temperature of 650 °C over a nickel catalyst supported on aluminium oxide. After the reduction of the catalyst, the temperature of the decomposer was reduced to 150 °C. At this temperature the process of ammonia decomposition proceeds no more, and the used catalyst Ni/Al_2O_3 performs a role of absorber of oxygen compounds from gaseous ammonia.

The process of ammonia decomposition was carried out over the iron catalyst at constant temperature and at different space velocity. By a change of space velocity, the measurement of the reaction rate of ammonia decomposition was possible at different concentrations at the reactor inlet.

The installation for the determination of the nitriding degree of the catalyst is constructed with an ammonia gas cylinder, drying washer with KOH, decomposer, deoxidizer, and thermobalance.

The nitriding was also carried out in these measurements by pure ammonia. The sample mass was about 300 mg.

A catalyst grain was placed in a single layer over a platinum wire net attached to an arm of the spring balance. Such placing ensured a constant composition of the nitriding mixture in the sample surrounding. The sample was reduced in the thermobalance by a N_2/H_2 gas mixture in the temperature range from 325 to 500 °C until a constant mass of the sample was attained. After the reduction process, a proper temperature of nitriding was adjusted and when it was reached, the hydrogen stream was changed to the nitriding mixture. The process was run isothermally until the catalyst mass was stabilised at a constant level.

The examination of the reduced catalyst as well as obtained nitrides was performed after passivation of the samples by water vapour. The catalyst composition was determined by the X-ray fluorescence method, the crystallite size by the transmission electron microscope method with the use of extraction replica. The surface area was measured by the method of low-temperature nitrogen physisorption using the ASAP 2010 apparatus.

3. Results and discussion

The change of ammonia conversion over the iron catalyst PS3 INS as a function of space velocity is shown in figure 1.

The conversion degree α was calculated on the basis of the ammonia mass balance at the inlet and outlet of the reactor. With an increase of space velocity to 7 $Ndm^3/g\,h$, the conversion degree decreases to 0.2.

The influence of ammonia concentration on the reaction rate of its decomposition is presented in figure 2, in the logarithmic system. From this diagram was determined the reaction order in relation to ammonia $n = d\ln r/d\ln p_{NH_3} = 1$.

This allows one to describe the rate of the ammonia decomposition by

$$r = k_0 \exp(-E_a/RT)p_{NH_3}^n,$$

where k_0 is the preexponential coefficient, E_a the apparent activation energy of the ammonia decomposition process, R the gas constant, T temperature, and p_{NH_3} the partial pressure of ammonia.

Examining the ammonia decomposition process at constant loading and different temperatures, the dependence

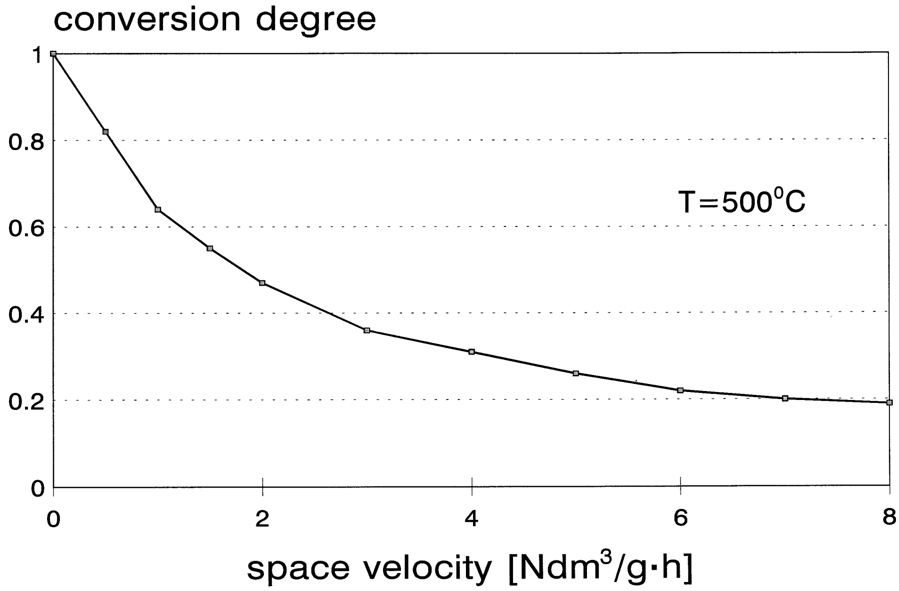

Figure 1. The dependence of decomposed ammonia amount on the reactor space velocity.

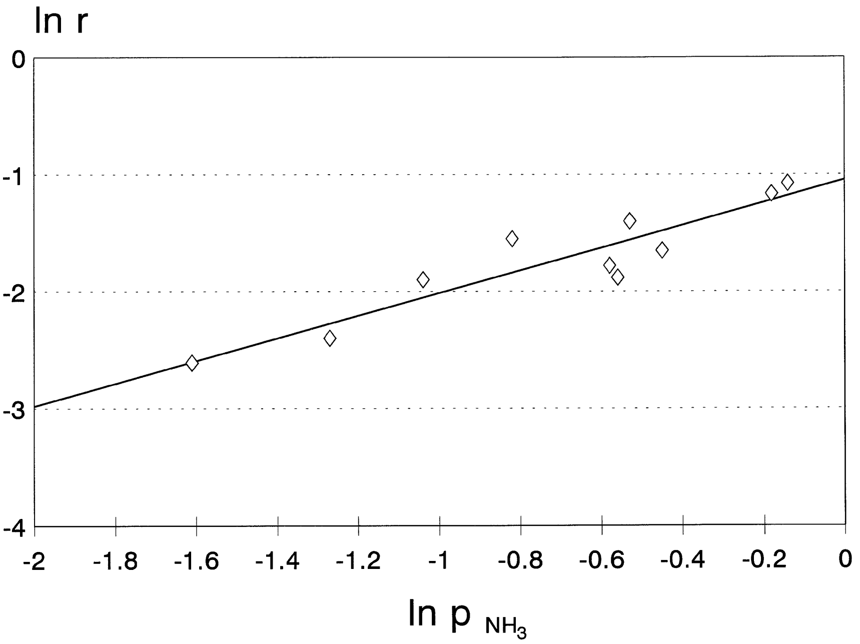

Figure 2. The dependence of ammonia decomposition rate on its molar concentration at the reactor outlet.

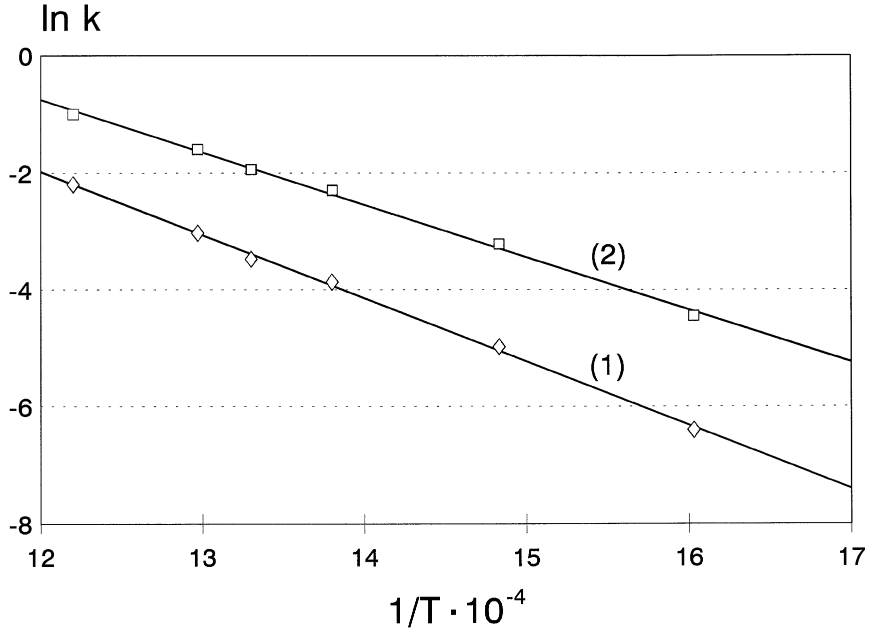

Figure 3. The dependence of ammonia decomposition rate on the temperature for the catalyst with potassium (1) and without potassium (2).

of the reaction rate logarithm on the temperature reciprocal was determined, which is graphically illustrated in figure 3.

For the catalyst containing the potassium compounds on the surface, this dependence can be presented in a linear form over the whole investigated temperature range. From the slope of this curve the apparent activation energy for the ammonia decomposition process was determined. It has a value of 96 kJ/mol.

For the catalyst being doubly promoted by aluminium oxide and calcium oxide (without potassium), the ammonia decomposition process is significantly faster in comparison with the catalyst containing potassium, whereas the apparent activation energy is lower, having a value of 87 kJ/mol. It is necessary to emphasise that the given activation energy concerns the ammonia decomposition on iron nitrides.

The degree of catalyst nitriding was also investigated. The dependence of the catalyst sample mass gain in mass measured by a thermogravimetic method (expressed in weight percents) on the reaction time for two space velocities and for the catalyst with potassium and without potassium, is shown in figure 4. The equilibrium state is established after 10 min. The gain of sample mass is depen-

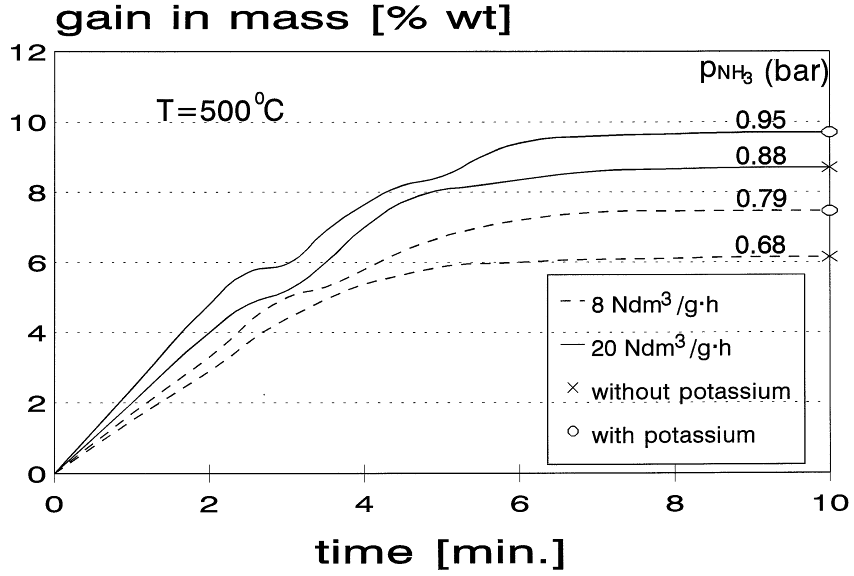

Figure 4. The gain in catalyst sample mass in dependence on the reaction time.

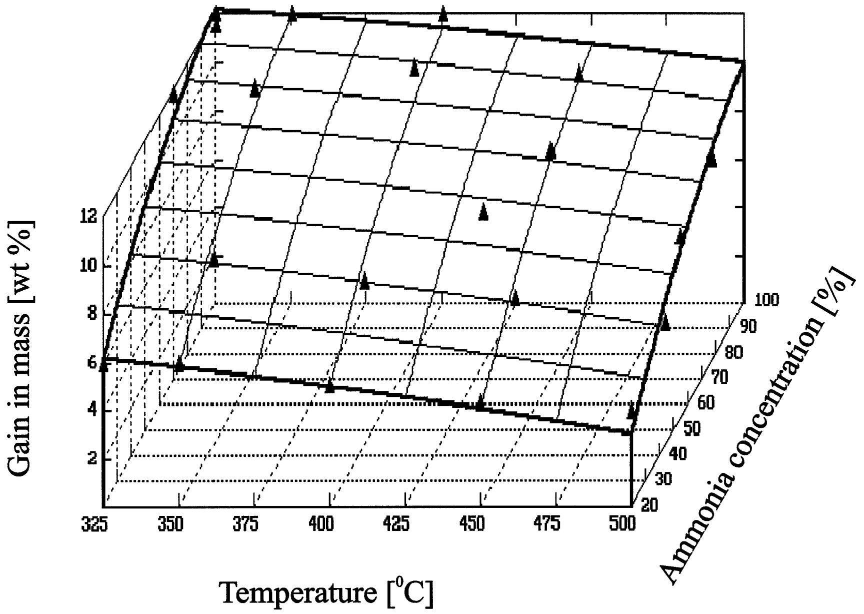

Figure 5. A 3D plot of the dependence of a catalyst nitriding degree expressed in weight percents on the temperature and the ammonia concentration at the reactor outlet.

dent on the partial pressure of ammonia and independent of catalyst composition.

On the basis of several measurements performed at different temperatures and at different ammonia concentrations, a three-dimensional plot (figure 5) was made, illustrating the dependence of the catalyst mass gain on the temperature and ammonia concentration at the stationary state.

The ammonia decomposition over the iron catalyst at ammonia concentrations where it does not undergo nitriding, proceeds with the apparent activation energy of about 160 kJ/mol [7]. The apparent activation energy over the nitriding samples is significantly lower. At the same degree of iron nitriding (Fe_4N), the presence of potassium oxide onto the catalyst surface changes the apparent activation energy from 87 to 96 kJ/mol with simultaneous four-fold decrease of the reaction rate.

These observations are in compliance with the Lowe and Emmett results, who observed that after the impregnation of iron catalyst with potassium compounds, the catalyst activity is significantly lower in the ammonia decomposition process and they are in a disagreement with the results presented in work [7].

In [8–10] a model of the catalyst active surface has been presented. According to this model, the iron surface is wetted by the oxides of promoters, whereas directly on the iron surface there are oxygen atoms (non-metal), and upon the oxygen atoms are adsorbed the promoter metal atoms.

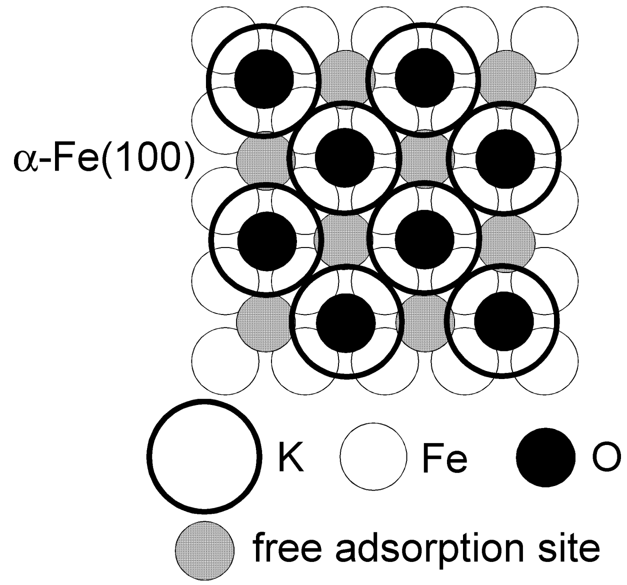

Figure 6. A ball model of α-Fe surface covered with O and K.

For stabilisation of a potassium atom on the iron surface at temperatures over 250 °C one oxygen atom is adequate.

A privileged site for chemisorbed nitrogen atoms is a gap in the monolayer formed by the oxygen atoms (figure 6). In the presence of potassium oxide about 50% of the adsorption sites in the monolayer of non-metal is occupied by the oxygen atoms, the remaining adsorption sites could be occupied by chemisorbed nitrogen atoms.

The catalyst surface covered by potassium oxide possesses a basic character, and only in the voids between the potassium atoms is placed a free iron atom on which the desorption of an ammonia molecule can proceed. The adsorbed ammonia molecules are placed under the potassium atoms. The ammonia dissociation leads to the formation of adsorbed nitrogen atoms, localised under the potassium atoms. With the statistical presentation of the surface (figure 6) it can be expected, that each adsorbed nitrogen atom is surrounded by oxygen and potassium atoms. The diffusion of nitrogen atoms under the monolayer of potassium atoms with regard to the geometrical consideration resembles the diffusion in a solid state. It can be expected, that it will be significantly slower in comparison with diffusion processes proceeding on the clean surface of iron, therefore, the number of collisions decreases between adsorbed nitrogen atoms which may lead to the formation of nitrogen molecules.

The rinsing of catalyst as well as prepared nitrides is connected with the passivation, thus with the formation of a thin layer of iron oxides. As a result of oxidation of the iron surface covered with potassium, the atoms of this element remain on the surface in oxide form [11], therefore, they are well dissolved in water. The same solubility of potassium compounds after nitriding indicates that, as a result of passivation of nitrides, potassium remains also on the surface. The ammonia adsorption may proceed on the clean surface of iron. This is a typical process for surface diffusion. There is a large likelihood of collision of nitrogen atoms and their recombination to molecules.

4. Conclusion

The reaction rate of catalytic ammonia decomposition of ammonia over iron nitrides is directly proportional to the ammonia concentration and on the surface of iron nitrides it proceeds four-fold faster in comparison with the ammonia decomposition rate over nitrides covered by potassium oxide.

The apparent activation energy of ammonia decomposition over iron nitrides is nearly two-fold smaller in comparison with clean iron.

The presence of potassium onto the catalyst surface slightly changes the apparent activation energy for the ammonia decomposition process.

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