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Effect of potassium on the high pressure kinetics of ammonia synthesis over fused iron catalyst

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Measurements were performed of reaction rate in the process of ammonia synthesis ($T = 370$–$470°C$) on doubly promoted (DP) (Al_2O_3, CaO) and triply promoted (TP) (K_2O, Al_2O_3, CaO) iron catalysts. The latter were obtained by impregnation of the reduced and subsequently passivated DP precursors with alcoholic solution of KOH. The studies were carried out under high total pressure (10 MPa) in a wide range of ammonia partial pressure in the gas phase: from 0.25 to about 7 bar. The results are shown to be authoritative for the so-called kinetic regime. The effect of the presence of K^+ cations in the catalyst was the stronger, as the temperature of the reaction was the lower and, in particular, the ammonia pressure in the gas phase the higher. The obtained results are in good accordance with the results of Somorjai's studies on activity of iron single crystal surfaces both clean and covered with $(K + O)$ adlayer.

Keywords: ammonia synthesis; iron catalysts; potassium promotion; kinetics

1. Introduction

Fused iron catalyst for ammonia synthesis, promoted with K_2O, Al_2O_3 and CaO, is one of the most frequently studied catalytic systems. Nevertheless, despite the efforts of many research groups, some problems still remain unresolved. First of all, the promoting mechanism of potassium, and even the mechanism of the ammonia synthesis itself is unclear. Both these problems have been widely analyzed and discussed by Spencer [1].

The source of the many doubts should be seeked, i.a. in the complex nature of the unreduced oxide precursor which has a strongly heterogeneous structure, both in the micro and macro scales [2], besides the complexity of its chemical composition. For this reason attempts are made to obtain information on the nature of the action of promoters, especially of potassium, by studies of much simpler and better defined objects – single crystals of iron.

Studies with single crystals have led to many substantial conclusions concerning e.g. the structural sensitivity of nitrogen chemisorption [3–6], as well as of the ammonia synthesis reaction [7–9]. It seems, however, that in the field of explaining the role of potassium in the catalyst more importance should be given to the discovery made by Somorjai, who has shown [8–10] that the ratio of the rate of synthesis proceeding on single crystal surfaces coated with potassium coadsorbed with oxygen to the rate of synthesis on clean surfaces depends on the NH_3 partial pressure in the gas phase. The promoting effect of potassium is the stronger, as the concentration of ammonia is the higher.

However, the extrapolation of the above results to the conditions of an industrial catalyst may be doubtful because of the "material gap" connected with studies on single crystals. The aim of this work was to "single out" the effect of the presence of potassium in multipromoted fused iron catalyst on the kinetics of ammonia synthesis under high pressure (10 MPa). The term "kinetics" is meant here as a relation between the reaction rate in the so-called "kinetic regime" (where the diffusional retardation is neglected) and temperature and ammonia concentration within a wide range of p_{NH_3} from very small up to high values. It should be pointed out that, although potassium is a component of all industrial catalysts and its role is considered in many papers, no such studies have been carried out up to now. The comparative evaluations of activity of model fused catalysts, e.g. singly (Al_2O_3) and doubly (Al_2O_3, K_2O) promoted, aiming to expose the role of potassium, have still been based on integral kinetic measurements [11–13], the importance of which for obvious reasons is rather limited.

2. Experimental

2.1. Preparation of the catalysts

Two iron catalysts were the object of the studies: a doubly promoted one (CaO, Al_2O_3), free of potassium, and a triply promoted one, containing K_2O, Al_2O_3, and CaO. The first of these catalysts (base precursor) was obtained in an industrial melting (Fertilizers Plant in Tarnów, Poland). A batch of such a raw material with a grain size 0.5–0.8 mm was reduced under atmospheric pressure in a stream of purified, stoichiometric mixture of nitrogen and hydrogen, with gradual raising of the temperature up to 520°C [14,15]. After completion of the reduction the catalyst was cooled and then passivated in nitrogen containing a small amount of oxygen. A part of the material was impregnated with alcoholic solution of KOH to obtain a product containing 0.7% potassium by weight.

Two prereduced catalysts of identical texture and similar chemical composition were obtained as an effect of these procedures, differing only by the content of potassium deposited on the surface. An introduction of K^+ ions directly onto the active surface and not (as is common practice) into the magnetite, eliminated the influence of other parameters of the catalyst preparation on its final activity. In particular, it eliminated the influence of melting and cooling conditions of the precursors, variations in the contents of CaO and Al_2O_3 and the effect of activation conditions. Table 1 presents the essential characteristics of both the reduced starting material – consequently denoted below by the symbol DP (doubly promoted) – and of the material impregnated with an alcoholic solution of KOH – denoted as TP (triply promoted). In the kinetic studies two fractions of the catalysts were used: initial – with a grain size 0.5–0.8 mm – and finer (0.1–0.12 mm) – obtained by grinding of the prepared materials DP and TP.

2.2. *Measurement of the reaction rate*

Studies of the reaction rate were carried out in a flow installation composed of a section of preparation of gas for synthesis, a preliminary reactor filled with a fused iron catalyst (KM I), and a main six-channel measuring reactor. The gas for synthesis ($H_2 : N_2 = 3 : 1$) was obtained by decomposition of ammonia on a nickel catalyst at 950°C. After preliminary purification on molecular sieves the mixture was compressed and subjected to further purification from traces of oxygen compounds by passing, in series, through active carbon, palladium catalyst, and molecular sieve beds.

Fig. 1 presents a simplified scheme of the main reactor. A steel body (1) has been provided with six parallel channels (2) disposed symmetrically with respect to the axis (only two are shown in the figure). The channels accommodate reaction tubes (3) containing catalyst samples (4) in their upper, isothermal zones. Every tube has been provided with a valve (5) enabling the reduction of the pressure down to atmospheric one. The gas for synthesis A (p = constant), pure or containing ammonia, was introduced through the central tube at the bottom of the reactor. It supplied two of the channels only (corresponding valves (5) open) whereas the other four channels did not operate at that moment (corresponding valves being closed). Each of the two outlet streams of the gas B_1 and B_2 was passed alternatively either to an ammonia analyzer or to a flow meter (after absorption of NH_3 in concentrated sulfuric acid). Such a procedure enables to measure the total flow rate of each stream B_i and, consequently, also the flow rate of the corresponding streams C_i fed to the two channels, if account has been taken of the NH_3 content in the supplying gas.

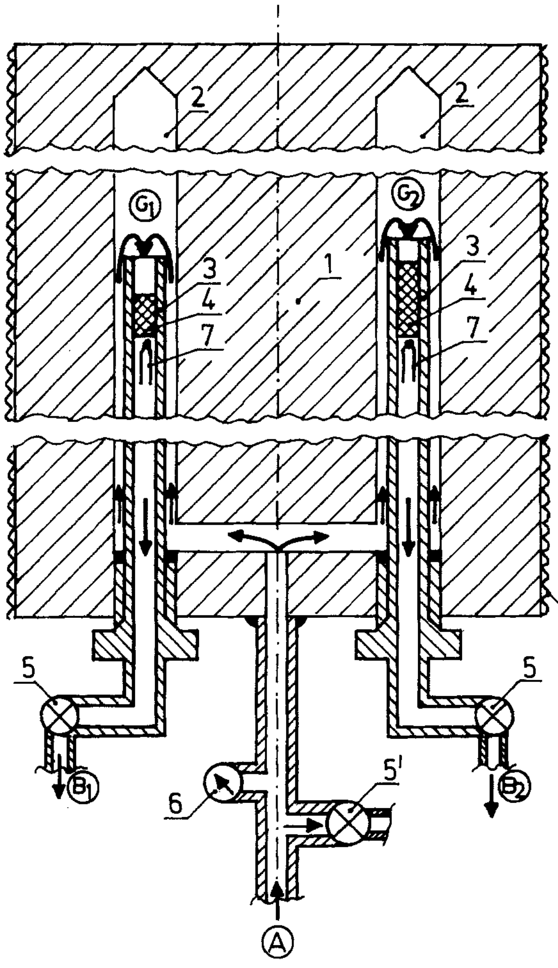

Fig. 1. Six-channel reactor for kinetic measurements. (1) Reactor body, (2) reactor channels, (3) reactor tubes, (4) samples of catalysts, (5) control valves, (6) manometer, (7) thermocouples, (8) three-section electrical heater.

After attaining the stationary state and taking the measurements (1–1.5 h), all the four remaining samples were tested successively, in pairs, at the same temperature. The temperature was then changed. The experiments were carried out under constant flow rate of the C_i stream identical in all reaction tubes, controlled by means of the valves (5).

Table 1
Chemical composition as measured by AAS, and total surface area (BET) of the catalysts

Catalyst	K [a] (wt%)	Al [a] (wt%)	Ca [a] (wt%)	S (m^2/g)
DP	0.04	1.9	2.6	19.3 (19.3) [b]
TP	0.70	1.9	2.6	19.3 (11.2) [b]

[a] wt% of element in a reduced catalyst.

[b] Total surface area after activity measurement.

The content of ammonia in the gas streams, including the stream A, was determined interferometrically. Since the method is based on differences in the refraction index, it is, in fact, not selective for ammonia. However, it is characterized by a very high precision (about 0.01% NH_3), which is especially important in the differential measurement of activity of catalysts.

Two types of experiments were performed. Experiments of the first type, without the use of the preliminary reactor, consisted in the measurement of ammonia concentration in the gas mixture at the outlet of each of the six reactor channels packed with different mass portions of one and the same catalyst. As a result, in steady state conditions of temperature and gas flow the profiles of NH_3 concentration were obtained, equivalent to the respective profiles in a single, thicker layer. Such profiles were used for the calculation of the reaction rates by means of the following equation derived basing on the mass balance for a plug flow reactor at the limit of low conversion in a differential catalyst layer:

$$r = V_0 \frac{1}{(1+x)^2} \frac{dx}{dm} \frac{17.03}{22.08}, \qquad (2.1)$$

where r is the reaction rate (kg NH_3/(kg$_{cat}$ h)), x the concentration of NH_3 (molar fraction), V_0 the flow rate of the gas (H_2, N_2) supplying the catalyst sample (dm^3(STP)/h), and m the catalyst mass.

Depending on the catalyst used, the mass of the samples varied from about 0.050 g to about 3 g, which corresponded to changes in space velocity (SV) from about 3×10^6 to 5×10^4 h^{-1}. The high space velocities ($\sim 10^6$), by two orders of magnitude higher than those applied in industrial reactors, were necessary to obtain information on the reaction rate at low partial pressures of ammonia in the gas phase.

In the other type of experiments, at higher concentrations of NH_3 a direct method of reaction rate measurement was applied with the use of the preliminary reactor. Under fixed conditions of temperature, flow rate of the gas and ammonia concentration in it (x_1) the increment of NH_3 content ($\Delta x = x_2 - x_1$) in the layer of the catalyst studied was determined, with $\Delta x \ll x_1$. The experiments were performed for different levels of x_1 controlled by changing the temperature in the preliminary reactor. The reaction rate was calculated from the equation

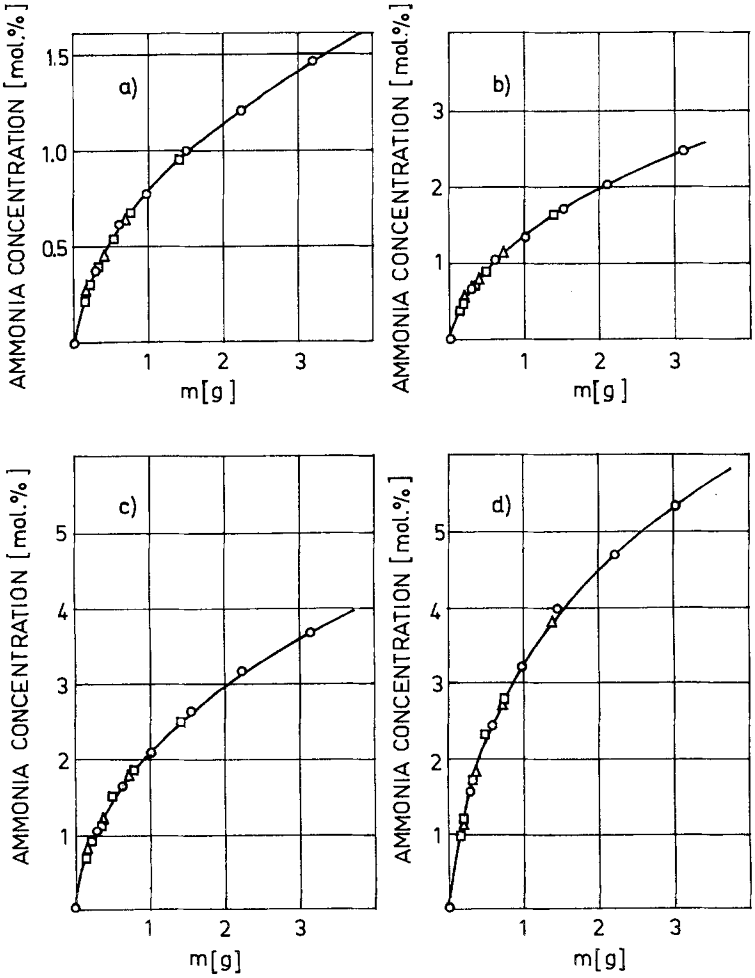

Fig. 2. Ammonia concentration profile in the bed of doubly promoted catalyst DP; V_0 = 60 dm^3(STP)/h; (a) 370°C, (b) 400°C, (c) 430°C, (d) 470°C. (○) ϕ_r = 7.6 mm, grain size 0.5–0.8 mm, (□) ϕ_r = 4.7 mm, grain size 0.5–0.8 mm, (△) ϕ_r = 4.7 mm, grain size 0.10–0.12 mm.

$$r = V_0 \frac{x_2 - x_1}{(1+x_1)(1+x_2)m} \frac{17.03}{22.08} . \qquad (2.2)$$

In either type of the experiments, depending on the kind of catalyst and the volume of the sample used, the reactor tubes differed in internal diameter ϕ_r, which was 7.6 mm, 4.7 mm or 2.3 mm. The thickness of the catalyst bed varied from several millimeters (TP catalyst, $\phi_r = 2.3$ mm) to about 3.5 cm (DP catalyst, $\phi_r = 7.6$ mm). The experiments were performed under constant total pressure (10 MPa) over a wide range of temperature (from 370 to 470°C). The temperature was measured by means of Ni/CrNi thermocouples mounted directly under each bed of a catalyst investigated.

3. Results

The profiles of ammonia concentration along the layer of doubly promoted catalyst (DP) are shown in fig. 2. The experiments were carried out with both fractions of the catalyst (0.5–0.8 and 0.1–0.12 mm) and reaction tubes of inner diameter $\phi_r = 4.7$ mm and $\phi_r = 7.6$ mm.

As may be seen in fig. 2, the experimental points relating to each temperature (T = const) are disposed on a common curve. The ammonia concentration profile (for T = const) is independent of both the grain size and the linear velocity of the gas (change of the reactor tube diameter from $\phi_r = 7.6$ mm to $\phi_r = 4.7$ mm results in a three-fold increase of linear velocity), and so neither an intraparticle diffusion nor the diffusion at the outer particle surface is significant for the rate of the process within the whole range of temperature – the process proceeds in the kinetic regime.

Fig. 3 presents, in a doubly logarithmic scale (ln–ln), the effect of ammonia partial pressure in the gas phase on the rate of reaction on the DP catalyst. Individual curves (T = const) reflect the results of measurements of the concentration profiles and the results of experiments with the preliminary reactor.

Fig. 4 shows the distribution of ammonia concentration along the bed of triply promoted catalyst (TP). The difference in activity of the two fractions of the catalyst remains invisible at 370°C. It becomes noticeable at 400°C and rises with increasing temperature, which may be accounted for the increasing effect of intraparticle diffusion in the coarser grains (0.5–0.8 mm). For this reason the diagram of the reaction rate as a function of ammonia partial pressure (fig. 5 in the ln–ln scale) has been constructed on the basis of kinetic data obtained for the fine fraction (0.1–0.12 mm) except for that at 370°C.

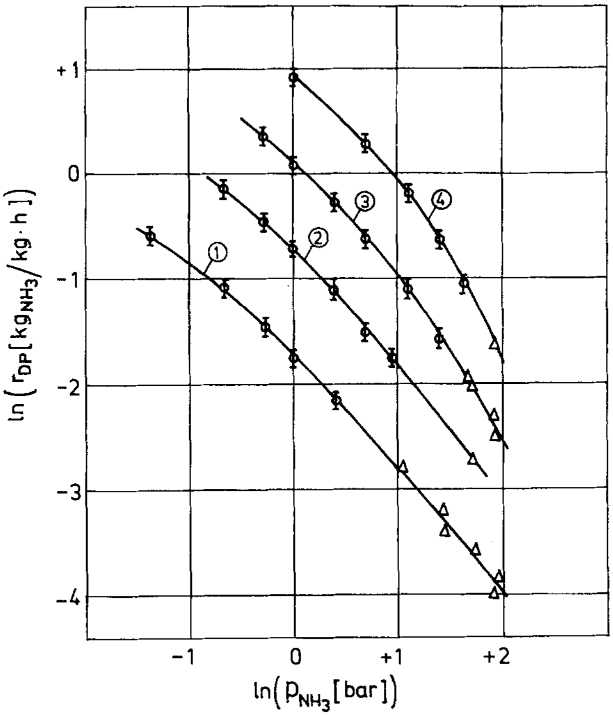

Fig. 3. Reaction rate versus p_{NH_3} in the gas phase (ln–ln) for doubly promoted catalyst (DP); (1) 370°C, (2) 400°C, (3) 430°C, (4) 470°C; (△) differential measurement.

In view of the lack of experimental evidence that might be accounted for the kinetic nature of the process effected in the presence of the fine grained catalyst but at temperatures higher than 370°C, the evaluation of possible diffusion effects inside the catalyst grain has been based on the Weisz criterion [16,17] with approximation of the reaction kinetics by a simple equation of the type $r = kc^{-1}$ [18]. The intraparticle effectiveness factor (η) is then described in terms of the following equation, which is valid only for high values of η [17],

$$\eta = 1 - \frac{1}{15} \frac{ra^2}{D_{\text{eff}} C} , \qquad (3.1)$$

where η denotes the intraparticle effectiveness factor, a the radius of the catalyst grains (m), D_{eff} effective diffusion coefficient of ammonia through the pores (m^2/s), and c the ammonia concentration (mol/m^3)

The values of D_{eff} for the industrial iron catalyst, necessary for the calculations, have been taken from the work of Kazarnovska [19]. The results of the calculations (not included in this work) have shown that the effectiveness factor η exceeds 95% and is generally close to 100% within the whole range of temperature and ammonia content in the gas. Only at 470°C for NH_3 concentrations below 0.5%, hence outside the region of the measurements, a slightly higher intraparticle diffusion effect may be expected. It should be remembered, however, that at small partial pressures of ammonia the apparent order of reaction with respect to NH_3 is greater than (−1), as may be seen in corresponding curves in fig. 5, and the criterion accepted in the calculations becomes too rigorous. Thus one may admit, that the results included in fig. 5 describe the kinetic region of the process.

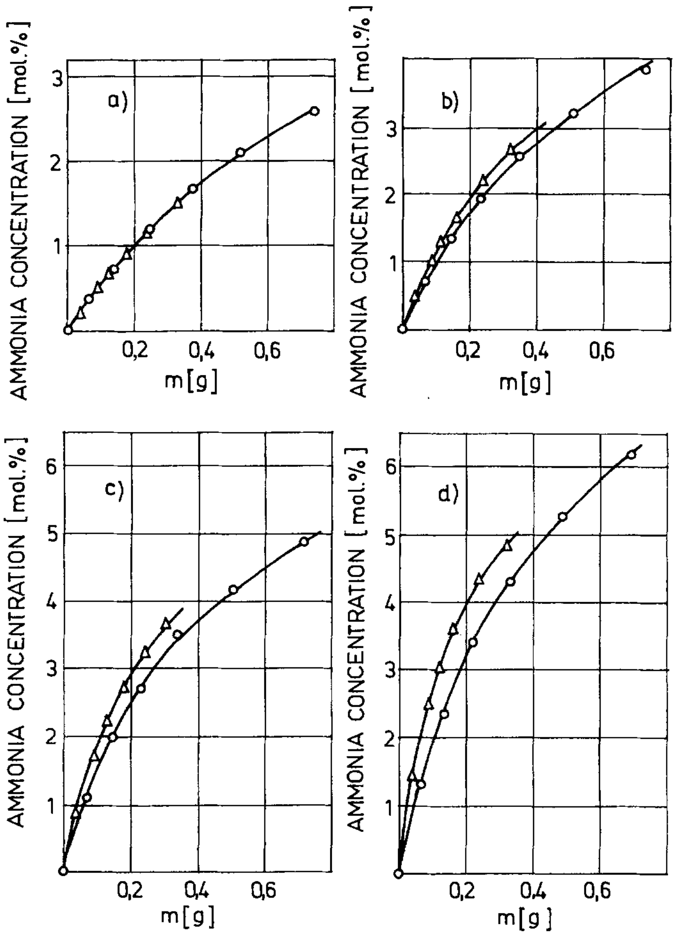

Fig. 4. Ammonia concentration profile in the bed of triply promoted catalyst TP; $V_0 = 60$ dm^3(STP)/h; (a) 370°C, (b) 400°C, (c) 430°C, (d) 470°C; (○) $\phi_r = 4.5$ mm, grain size 0.5–0.8 mm, (△) $\phi_r = 2.3$ mm, grain size 0.10–0.12 mm.

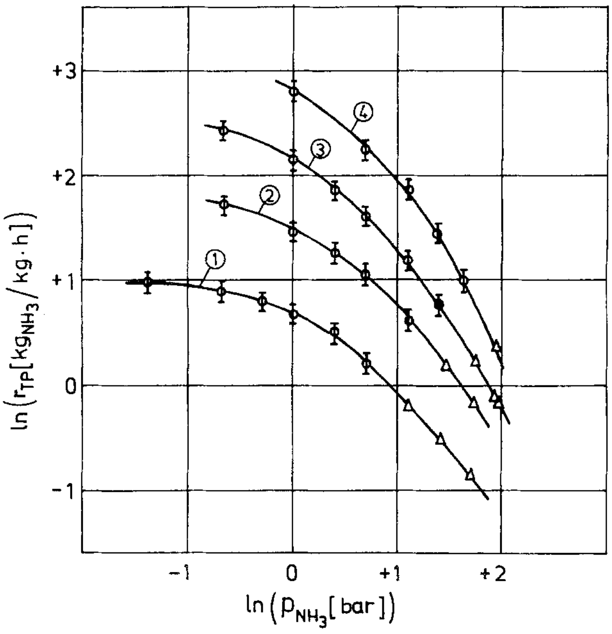

Fig. 5. Reaction rate versus p_{NH_3} in the gas phase (ln–ln) for triply promoted catalyst (TP); (1) 370°C, (2) 400°C, (3) 430°C, (4) 470°C; (◇) differential measurements.

Some doubts may be connected with the measurement of the temperature (under the catalyst beds). At low pressure (1 bar) each one of the reactor tubes has been shown to operate as an isothermal reactor (an axial profile of temperature was taken). At high pressure, however, when high conversions are typically obtained in laboratory reactors, an exothermic effect of the NH_3 synthesis can deform considerably the temperature profile, as shown by Nielsen [20]. Therefore, only the experiments performed with low conversion degrees ($x < 1\%$) and those with high conversion, which involved the preliminary reactor ($\Delta x < 1\%$), were undoubtedly isothermal. It should be noticed, however, that all the profiles of ammonia concentration were taken at relatively low conversions, by several times lower than those in ref. [20], particularly at low temperatures. Thus, all the measurements are considered to be isothermal. This is witnessed by full concordance of kinetic data, obtained by either method of measurement for the TP catalyst at 430°C, x_{NH_3} about 3% (not presented in this paper).

4. Discussion

As may be seen in figs. 3 and 5 for both catalytic systems, the decrease of ammonia concentration in the gas phase is accompanied by a decrease of the apparent order of reaction with respect to NH_3 (in absolute values) which is, however, more distinguishable for the TP catalyst, particularly at low temperatures. At 370°C the apparent order in ammonia for this catalyst varies from about -1.1 at $p_{NH_3} = 6$ bar to a value close to zero, although still negative, at $p_{NH_3} = 0.25$ bar. For the DP catalyst, not containing potassium, at the same temperature and identical range of variations in ammonia concentration the apparent order of reaction changed only by a factor of two, from the value of -1.1, the same as in the case of DP catalyst, to about -0.6. One can state, therefore, that the presence of potassium in the catalyst influences the apparent order of reaction with respect to NH_3 and that this effect increases with lowering p_{NH_3} and with lowering temperature of the process.

The differences in the kinetics of ammonia synthesis on the two catalysts are clearly seen in fig. 6 which shows the ratio of reaction rates measured with their use ($n = r_{TP}/r_{DP}$) as a function of both NH_3 partial pressure in the gas phase and temperature.

In the region of high partial pressures of ammonia, of the order of 4–7 bar, the value of the ratio n depends only on temperature: the lower the temperature of the reaction, the more pronounced is the effect of the presence of potassium. In this region the value of the ratio r_{TP}/r_{DP} varies from about 15 (for $T = 370°C$) to 8 (for $T = 470°C$).

At low concentrations of ammonia the value of n decreases with decreasing concentration, and this relationship is particularly strong at low temperatures. Extrapolation of the curve $T = 370°C$ up to the point of intersection with the axis of ordinates shows that the activity of the catalyst impregnated with potassium hydroxide is, in the limiting case ($p_{NH_3} = 0$), not more than twice as high as the activity of the DP catalyst, whereas the total effect, attainable at that temperature, is much higher ($n = 15$ for $p_{NH_3} > 4$ bar).

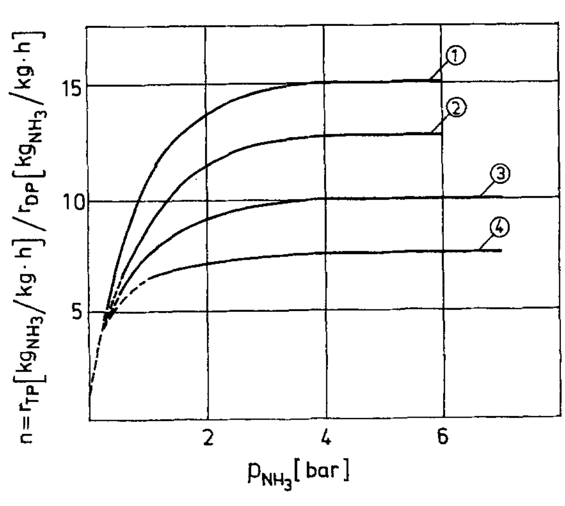

Fig. 6. Ratio of the reaction rates over TP catalyst and DP catalyst versus ammonia partial pressure in the gas phase: (1) 370°C, (2) 400°C, (3) 430°C, (4) 470°C.

With increasing temperature the value of ratio n becomes less sensitive to variations in partial pressure of NH_3, and at 470°C, in the p_{NH_3} range covering the region of measurements, it remains almost unchanged. For this reason extrapolation of the isotherm $T = 470°C$ toward small ammonia pressures, rather arbitrarily drawn in fig. 6 (broken line), should be regarded as uncertain.

The above presented results of studies on the influence of potassium ions on activity of fused iron catalyst in the reaction of ammonia synthesis correspond to those obtained by Somorjai et al. [8–10] for model surfaces of iron single crystals: clean and covered with potassium coadsorbed with oxygen. This correspondence accounts for great "kinetic" similarity of the model surfaces of iron partially coated with (K + O) adsorbed layer and the surface of an industrial catalyst. It might be possible, therefore, to settle with Somorjai's interpretation [8–10] and to accept the view that the mechanism of the promoting action of potassium in the commercial catalyst consists mainly, although not exclusively, in the shift in equilibrium from adsorbed to gas phase ammonia. It should be clearly stated, however, that the sole results of kinetic studies do not justify such unequivocal declarations. Results of high temperature TPD of nitrogen, presented recently by Fastrup [21] show, that the presence of potassium on the surface of an industrial catalyst leads to destabilization of chemisorbed nitrogen or even of NH species. The destabilization of NH_3 is not, therefore, the only consequence of introduction of potassium. A more detailed discussion of the promoting effect of potassium, taking into account, besides the views of Somorjai also the views of other authors, such as Ertl [5,6] and Fastrup [21], will be presented in a separate paper, after completion of studies on the kinetics of synthesis and decomposition of ammonia on the same TP and DP catalysts, but under atmospheric pressure.

5. Conclusions

To sum up one may state, that the results obtained in this work point to the existence of large "kinetic" similarities of the triply promoted fused iron catalyst and of iron single crystal covered with a (K + O) adlayer. Under high pressures (10 MPa) the promoting effect of potassium in fused iron catalyst depends, like in the case of Fe single crystal, on partial pressure of ammonia in the gas phase, although some effect of temperature is also observed. At high pressures of NH_3 (4–7 bar) the triply promoted catalyst is at 370°C about 25 times as active (per unit inner surface area determined by the BET method) as the doubly promoted DP catalyst. With increasing temperature the effect of potassium decreases. At 470°C it is twice lower than at 370°C.

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