JOURNAL OF CATALYSIS **169,** 407–414 (1997)
ARTICLE NO. CA971664

Effect of Potassium on the Kinetics of Ammonia Synthesis and Decomposition over Fused Iron Catalyst at Atmospheric Pressure

Z. Kowalczyk,*[,1] J. Sentek,* S. Jodzis,* M. Muhler,† and O. Hinrichsen†

*Warsaw University of Technology, Department of Chemistry, Koszykowa 75, 00-664 Warsaw, Poland; and †Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin (Dahlem), Germany

Received July 31, 1996; revised November 25, 1996; accepted February 3, 1997

Ammonia synthesis and decomposition have been performed over a doubly promoted (Al_2O_3, CaO) and a triply promoted (Al_2O_3, CaO, K_2O) fused iron catalyst at atmospheric pressure. Additionally, the temperature-programmed surface reaction (TPSR) of N_{ads} with H_2 has been studied over both catalysts. No effect of potassium on the turnover frequency of NH_3 synthesis was found. On the contrary, a significant fivefold increase in the rate of NH_3 decomposition in the presence of potassium was observed. The effect was found to be strongly dependent on the concentration of NH_3 in the gas phase. The promoting mechanism of potassium is discussed in relation to the surface structure of the catalyst under varying operating conditions. © 1997 Academic Press

1. INTRODUCTION

Fused iron catalysts promoted with K_2O, Al_2O_3, and CaO have been applied for about 80 years in the industrial production of ammonia. However, despite extensive studies of the catalysts, the role of the promoters has not yet been univocally explained. The mechanism of potassium promotion seems to be particularly unclear and controversial (1–6). There are also still some doubts concerning the mechanism of ammonia synthesis on iron and, therefore, also the kinetics of the reaction (7).

Much progress in the understanding of the mechanism of NH_3 synthesis was achieved by means of the kinetic simulation of the process based on the results of detailed studies carried out with single crystals of iron (8–15). Such a simulation has shown that “kinetic and spectroscopic data collected on iron single crystals in UHV conditions can be used to predict the rate of ammonia synthesis over a commercial iron catalyst in a plug-flow reactor operating under industrial conditions” (16). The microkinetic modelling can also be used to test hypotheses on possible potassium promotion mechanisms as shown by Fastrup (3) and Stoltze and Nørskov (17) (repulsions between adsorbed K and adsorbed N or all NH_x species on the surface).

However, it should be clearly stated that the experimental kinetic data, indispensable for verifying all microkinetic calculations (including those which illustrate the effect of potassium) are not satisfactory, being limited to measurements of total conversion, as determined in integral reactors (e.g., (18, 19)).

It was not until recently that detailed kinetic data have been published pointing clearly to the effect of the presence of potassium in fused iron catalyst on the rate of high pressure ammonia synthesis at 100 bar (20). The aim of the present work was to determine the effect of potassium on the rate of ammonia synthesis at low pressure (1 bar) and, which seems to be very important, also on the rate of decomposition of NH_3 at the same pressure. Two fused iron catalysts were used in the present study. One of them was free of potassium. For a better characterization of the two catalytic systems, the temperature-programmed surface reaction (TPSR) of chemisorbed atomic nitrogen (N_{ads}) with H_2 has been studied.

2. EXPERIMENTAL

2.1. *Catalysts*

A detailed description of the two catalysts has been given elsewhere (20). The doubly promoted (CaO, Al_2O_3) potassium-free precursor was manufactured in an industrial melting furnace in the Plant of Nitrogen Fertilizers at Tarnów, Poland. A batch of the material with a grain size of 0.5–0.8 mm was preliminarily reduced in a 3 : 1 mixture of H_2 and N_2, then cooled to room temperature, and passivated in nitrogen containing small amounts of oxygen (21). Such a prereduced catalyst, denoted as DP (doubly promoted) in the following, was then used for the TPSR and kinetic studies. The triply promoted catalyst (CaO, Al_2O_3, K_2O), denoted as TP, was obtained by impregnation of the DP material with an alcoholic solution of potassium hydroxide.

---

[1] Correspondence author.

0021-9517/97 $25.00

The content of potassium in the TP catalyst was about 0.7% by weight.

2.2. *TPSR Studies*

The experimental setup consisted of three gas lines (He, H_2, N_2), a purification unit, a U-tube reactor, and a nondispersive infrared detector for NH_3 (22). The temperature was measured by means of a thermocouple inserted in the catalyst bed. The mass of the sample was about 0.5 g. The experimental TPSR procedure was as follows (22): the sample was first treated in a flowing $H_2 : N_2 = 3 : 1$ mixture (40 Nml/min) at 673 K for several days until a high and stable ammonia concentration in the outlet gas was attained. Then the temperature was lowered to 573 K and the hydrogen flow was stopped. The sample temperature was kept constant at 573 K for 2 h in pure N_2 (50 Nml/min), followed by cooling in nitrogen to room temperature. The flowing gas was then changed to H_2 (50 Nml/min) and, after about 1 h, the temperature was raised linearly with a rate of 2 K/min up to 783 K. The Fe metal area was calculated, assuming the Fe(111) surface atom density of 0.7×10^{19} Fe atoms/m^2.

2.3. *Measurement of NH_3 Synthesis and Decomposition Reaction Rates*

The activity of the catalysts in ammonia synthesis at atmospheric pressure was measured in a multichannel flow reactor fed with a synthesis gas obtained by decomposition of NH_3 and purified from traces of residual ammonia and oxygen compounds. The content of water vapor, which was the major impurity in the gas, was below the limit of detection which amounted to about 2 ppm. A detailed description of the apparatus and of the experimental procedure is given in Ref. (20). The outlines are as follows: the channels of the reactor (optionally 4.7 or 7.6 mm in diameter) were packed with different mass portions of one and the same catalyst (DP or TP). After preliminary rereduction (depassivation) of the samples at 743 K the reactor was cooled to 673 K and measurements were started. The concentration of NH_3 was determined by means of an interferometer in the outlet gas of each channel of the reactor, the flow intensity being kept constant and identical for each catalyst sample. The temperature was then reduced to 643 K and the measurements were repeated. As a result, the profiles of ammonia concentration were obtained, equivalent to those for a single but thicker layer of the catalyst. From such profiles the reaction rate versus ammonia concentration was calculated by means of the Eq. [1] (20, 23),

$$r = V_0 \frac{1}{(1 + x_{NH_3})^2} \frac{dx_{NH_3}}{dm} \frac{17.03}{22.08}, \qquad [1]$$

where r is the reaction rate (kg NH_3/kgcat h), x is the ammonia concentration (molar fraction), V_0 is the flow rate of the gas (H_2, N_2) (dm^3(STP)/h), m is the mass of the catalyst (g).

Measurements of the rate of ammonia decomposition over the catalysts were carried out in a differential flow reactor fed with a gas obtained by mixing two separately purified gas streams: NH_3 and $H_2 : N_2 = 3 : 1$. Final purification of the mixture was carried out in a guard reactor. Prior to the measurements, the catalyst samples were stabilized for several days in a stream of $H_2 + N_2$ mixture at 743 K. The stream was then supplemented with ammonia, and the experiments were performed under steady-state conditions with gas mixtures containing 5–80% NH_3.

The temperature of the catalyst bed was measured by means of a thin thermocouple ($\varnothing = 0.5$ mm) positioned axially in a steel sheath ($\varnothing = 1.0$ mm). In all measurements the axial temperature profiles of the catalyst bed were determined and the mean temperature was derived. It has to be pointed out that the temperature gradient inside the catalyst bed owing to the heat of reaction did not exceed 3–5 K, being in most cases less than 2 K. Optionally two quartz reaction tubes were used, with inner diameters 8 mm and 4 mm, respectively. The flow rate of the gas mixture in the reaction tube was maintained constant (35 Nl/h), and the sample mass varied from 0.3 to 2.5 g.

The variations in ammonia concentration in the catalyst bed were determined interferometrically. The reference gas for the interferometric measurement was a stream of the gas mixture fed into the reactor. Thus the two gas streams being passed through the interferometer corresponded to those at the outlet and the inlet of the reactor, respectively. In this way, any decrement of ammonia concentration due to reaction in the catalyst bed ($\Delta x_{NH_3} = x_{2,NH_3} - x_{1,NH_3} \ll x_{1,NH_3}$) was measured directly, and even very small differences of the order of 0.2% could be measured with a satisfactory precision of the order of ±0.01%, independently of the absolute concentration of NH_3 in the gas mixture. The reaction rate was calculated by means of Eq. [2] derived from a simple mass balance for a plug-flow differential reactor,

$$r = V_1 \frac{x_{1,NH_3} - x_{2,NH_3}}{(1 + x_{2,NH_3})m} \frac{17.03}{22.08}, \qquad [2]$$

where V_1 is the flow rate of the inlet gas and x_{1,NH_3}, x_{2,NH_3} are the molar fractions of ammonia in the inlet and outlet streams, respectively.

3. RESULTS

Figure 1 presents the results of TPSR studies with the two catalysts used. The TP spectrum with a characteristic broad peak centered at about 473 K corresponds very well to the published data (22). Quite a different spectrum was obtained, however, with the DP sample. Hydrogenation of N_{ads} starts at a temperature about 50 K higher than that observed for the TP sample in agreement with Ref. (22).

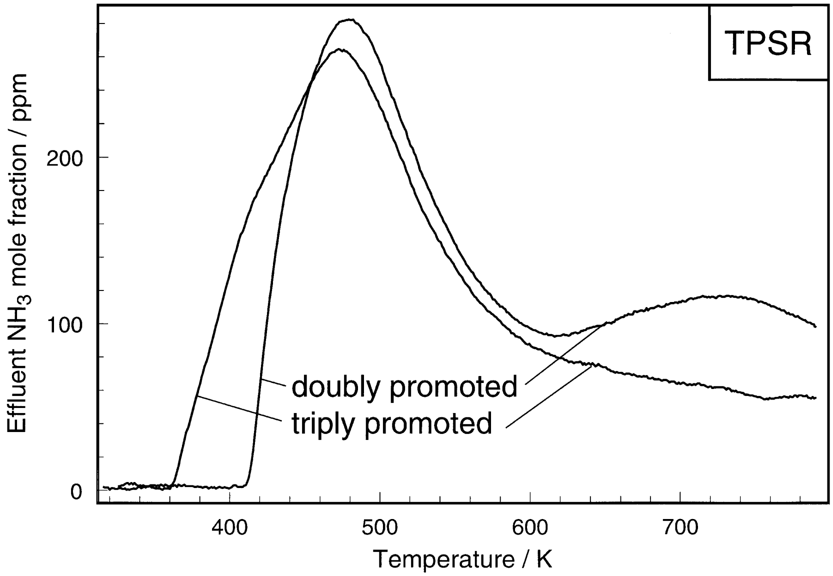

FIG. 1. TPSR data of N_{ads} in H_2 observed for the DP and the TP catalyst.

Furthermore, an additional small and diffuse peak appears with a maximum at about 723 K. The origin of the small peak in the DP spectrum is unclear. Either some of the active sites are significantly different from those responsible for the main peak, or, more probably, ammonia readsorbs on Al_2O_3, which partly covers the iron surface (in the TP sample Al_2O_3 is neutralized by the introduced potassium hydroxide (21)).

The total concentration of N_{ads} atoms per unit mass of catalyst and, consequently, the specific surface area of Fe metal is similar for the two materials and amounts to 118 μmol/g or 10.2 m^2/g for TP and 123 μmol/g or 10.6 m^2/g for DP. The obtained data agree well with those obtained by Fastrup *et al.* (22) for the multiply promoted fused iron catalyst (115 μmol/g) and for the catalyst free of potassium (124 μmol/g).

Table 1 presents the rates of ammonia synthesis in kg NH_3/(kg · h) and the corresponding TOF values for the two catalysts as a function of the NH_3 concentration in the gas phase. Within the range of the experimental error (±10–15%), there is no difference in activity between the two materials tested, neither if referred to unit mass, nor if referred to the number of active sites. Thus, the results confirm the widely accepted observation that potassium does not activate the surface of iron under low-pressure NH_3 synthesis conditions.

The promoting effect of potassium has been observed, however, for the decomposition of ammonia. This is clearly shown in Fig. 2, in which the rate of the process over both catalysts at 673 K is plotted as a function of the NH_3 concentration in the gas phase. Within the whole range of ammonia content (5–80%), the triply promoted catalyst (TP) exhibits a much higher activity than the doubly promoted one (DP). The influence of the NH_3 content on the rate of reaction is different for each of the two samples. When x_{NH_3} is less than about 25% and, hence, within the range of thermodynamic stability of α-Fe (24), the DP catalyst is almost insensitive to changes in ammonia concentration ($r \cong$ const). At above 25–30% NH_3, a systematic increase of the reaction rate is observed, presumably due to the formation of successive phases of iron nitrides with catalytic properties different from pure Fe. The change of x_{NH_3} from 70% to 80% results in a drastic, almost twofold increase in activity of the DP catalyst. Contrary to this observation, the activity of the potassium-containing catalyst (TP) is found to increase with increasing concentration of ammonia over the whole range of x_{NH_3} (5–80%). At lower ammonia concentrations (5–30%), the dependence is roughly linear.

TABLE 1

Rates of Ammonia Synthesis (kg_{NH_3}/kg · h) and TOF of DP and TP Catalysts at 1 bar

	PD sample				TP sample			
	643 K		673 K		643 K		673 K	
x_{NH_3} (mol %)	*r*	TOF	*r*	TOF	*r*	TOF	*r*	TOF
0.05	0.04	0.0053	0.08	0.0105	0.04	0.0055	0.08	0.011
0.10	0.020	0.0027	0.04	0.0053	0.022	0.0030	0.04	0.0055
0.15	0.015	0.0020	0.020	0.0027	0.014	0.0019	0.022	0.0030
0.20			0.015	0.0020			0.015	0.0021

Note. Results of TPSR studies have been used for the calculation of TOF.

The differences in activity of the two catalysts towards ammonia decomposition are clearly seen in Fig. 3, in which the ratio of decomposition rates ($n = r_{TP}/r_{DP}$) is shown as a function of the NH_3 concentration in the gas phase. The range of ammonia concentration has been limited here to 30%, which is only slightly higher than the limit of stability of α-Fe (in NH_3 synthesis, for obvious thermodynamic reasons, only α-Fe is stable and, therefore, the range of x_{NH_3} was limited). The results presented were obtained at 673 K, but it should be added that at higher temperatures (703 K—not shown in this work) the relationship was similar. It is evident that the effect of potassium is stronger, the higher the ammonia concentration is. It should be noted that a very similar relationship was obtained when comparing the rate of ammonia synthesis obtained with the same catalysts at high pressure (100 bar) (20).

Figure 4 shows the effect of temperature on the rate of ammonia decomposition for each of the two catalysts as ln r vs $1/T$ measured at 20% and 30% NH_3 in the gas phase. The relationships are almost linear for both samples. Within the whole range of temperature, the TP sample is about 5 times more active than the DP sample (for constant x_{NH_3} equal to 20 or 30%, respectively).

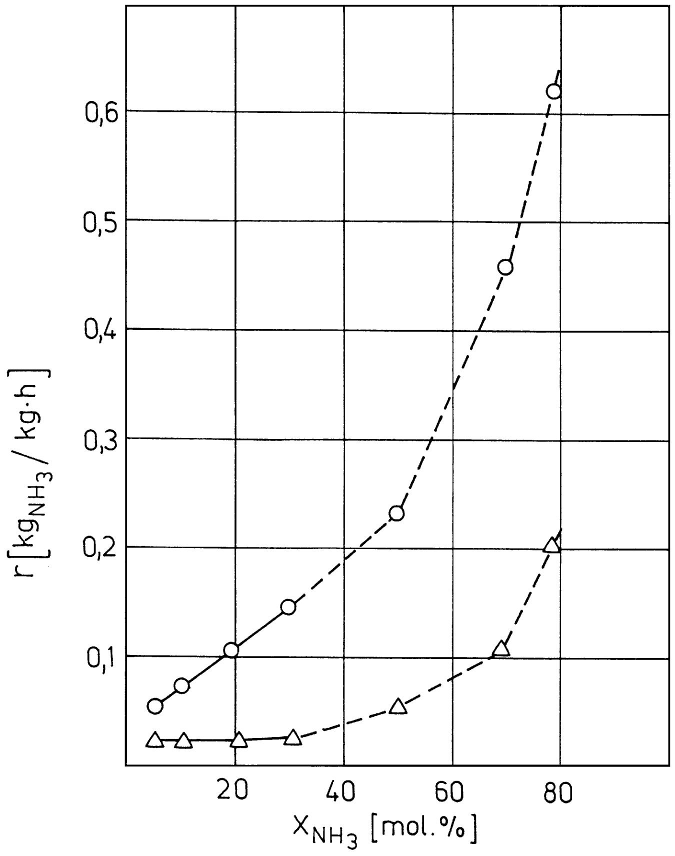

FIG. 2. Rate of ammonia decomposition vs NH_3 content in the gas phase; $T = 673$ K; △, DP; ○, TP.

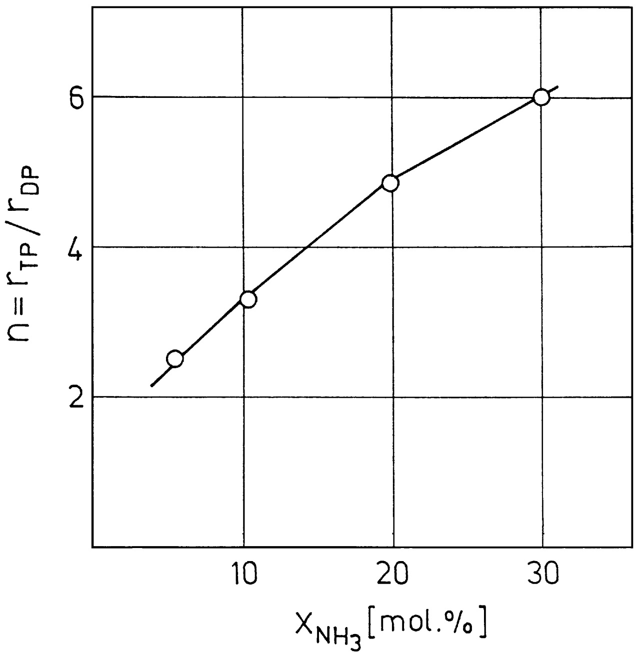

FIG. 3. The ratio of the rates of NH_3 decomposition over TP and DP catalysts vs NH_3 content in the gas phase; $T = 673$ K.

4. CALCULATION OF THE SURFACE COVERAGE OF N_{ads}

The dissociative chemisorption of nitrogen is generally accepted to be the rate-determining step in ammonia synthesis over iron. Consequently, the limiting step in NH_3 decomposition is the desorption of chemisorbed nitrogen or, more precisely, the recombination of N_{ads}. All the other steps involved proceed in a pseudo-stationary equilibrium. In the microkinetic analysis, it is furthermore assumed that there is only one type of active sites on the surface of the catalyst. Under such assumptions, according to Langmuir–Hinshelwood kinetics, the overall reaction rate can be expressed as

$$r = \pm k_{-2}\Theta_N^2\left(K_p\frac{p_{N_2}p_{H_2}^3}{p_{NH_3}^2} - 1\right), \qquad [3]$$

where k_{-2} is rate constant of N_{ads} recombination, Θ_N is surface coverage of nitrogen atoms, K_p is equilibrium constant for the reaction $3H_2 + N_2 = 2NH_3$, and p_i are the partial pressures of the reagents.

Equation [3] stands for both the synthesis (+) and the decomposition (−) of ammonia. With the simplifying assumptions made, it is valid over the whole range of Θ_N, as shown by our derivation, and not only for high coverages by chemisorbed nitrogen, as suggested by Aparicio and Dumesic (25). For stoichiometric $H_2:N_2 = 3:1$ mixtures containing ammonia, Eq. [3] assumes a simpler

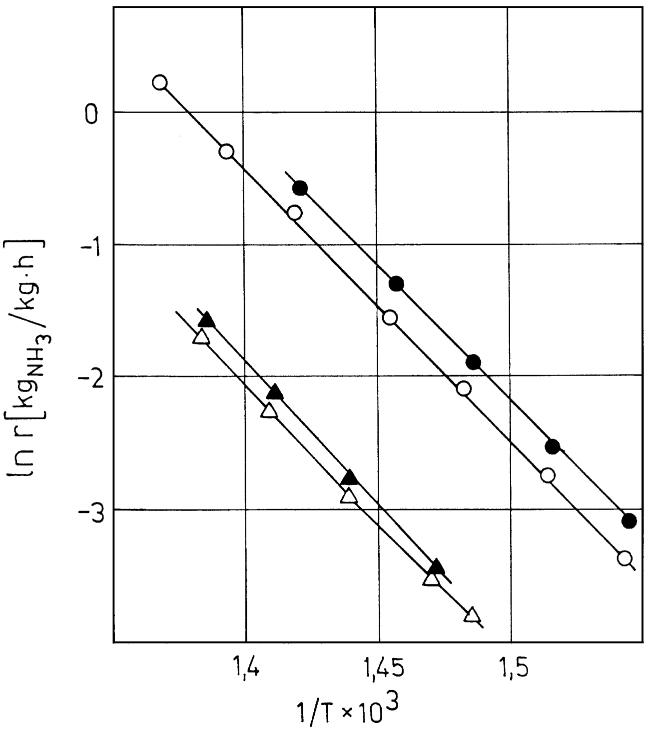

FIG. 4. Rate of ammonia decomposition (ln scale) vs $1/T$; △, DP (20% NH_3); ▲, DP (30% NH_3); ○, TP (20% NH_3); ●, TP (30% NH_3).

form [4]:

$$r(x_{NH_3}, \Theta_N) = \pm k_{-2}\Theta_N^2\left[\frac{27}{256}K_p\frac{(1-x_{NH_3})^4}{x_{NH_3}^2}p^2 - 1\right] \quad [4]$$

from which it results that, under fixed conditions of temperature and pressure (k_{-2} and K_p become constant), the rate of the reaction (ammonia synthesis or decomposition) depends on two parameters only: Θ_N and x_{NH_3}. Alternatively, Eq. [4] can be written as

$$\Theta_N = (r(x_{NH_3}))^{0.5}k_{-2}^{-0.5}\left[\frac{27}{256}K_p\frac{(1-x_{NH_3})^4}{x_{NH_3}^2}p^2 - 1\right]^{-0.5}. \quad [5]$$

Equation [5] may be used for the calculation of the surface coverage of chemisorbed atomic nitrogen (Θ_N) as a function of NH_3 concentration (x_{NH_3}) in the range of ammonia synthesis from experimentally obtained relationships $r_{synt} = r(x_{NH_3})$ for T, $p = \text{const}$. For such calculations, it is necessary to know the recombination constants (k_{-2}) for both DP and TP samples (K_p is known). The values of k_{-2} may be calculated, or at least estimated, from the kinetic data obtained for ammonia decomposition at atmospheric pressure. At relatively high NH_3 partial pressures, the value of Θ_N is close to unity and, correspondingly, the term in square brackets (Eq. [4]) reaches the value −1. Hence Eq. [4] simplifies to $r(x_{NH_3}) = k_{-2}$. It is not easy, however, to derive the value of x_{NH_3} for which the surface coverage becomes close to 1 ($\Theta_N \cong 1$) due to the formation of iron nitrides at NH_3 concentrations above 25–30% depending on the temperature. It has, therefore, been arbitrarily assumed that the surface is saturated with nitrogen atoms at NH_3 concentration equal to 20%, the value being slightly lower than that corresponding to the phase transition Fe–$Fe_4N(\gamma')$. The above simplification raises no doubts in the case of the DP catalyst, for which the decomposition of ammonia proceeds with a constant rate at NH_3 concentrations within 5–20% NH_3 (Fig. 2), thus suggesting that saturation close to $\Theta_N = 1$ is reached. In the case of the TP catalyst the simplification may lead, however, to a slight underestimation of the k_{-2} value, particularly at low temperatures.

The results of all the calculations are presented in Figs. 5–7. Figure 5 shows k_{-2} (recalculated into N_2 molecules/sites on the basis of the TPSR data) versus $1/T$ for the two catalysts. The data have been supplemented, for comparison, by those determined by Muhler *et al.* (26) from the analysis of the TPD spectrum of nitrogen for the multiply promoted KMI catalyst. There is full agreement between absolute values of k_{-2} for the TP and KMI samples despite the different measuring techniques applied (decomposition of NH_3 and TPD of nitrogen). The small difference in activation energy (167 kJ/mol for TP and 146 kJ/mol for KMI) probably

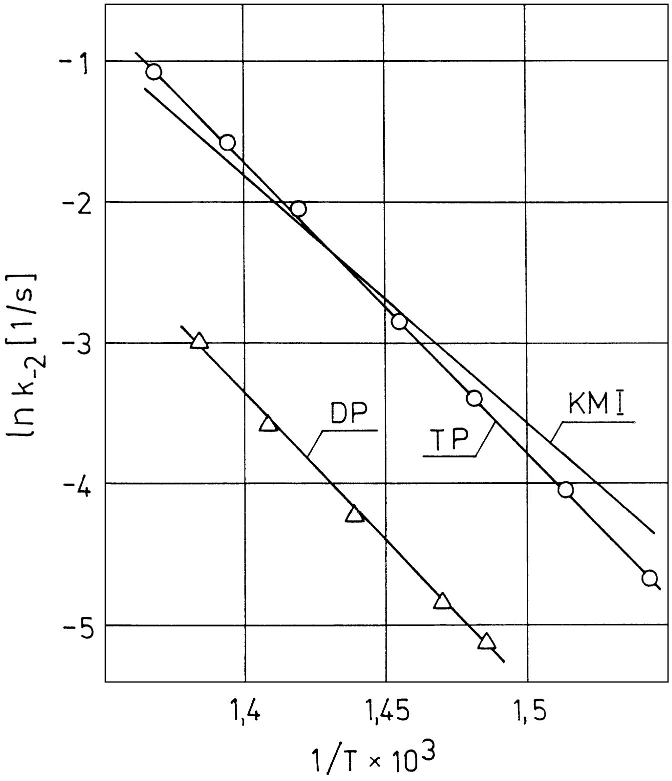

FIG. 5. Rate constants (k_{-2}) for the recombination of N_{ads} (ln scale) vs $1/T$; △, DP ($E = 173$ kJ/mol), ○, TP ($E = 167$ kJ/mol); KMI, as calculated from the results of N_2 TPD from the multiply promoted catalyst KMI (26) ($E = 146$ kJ/mol).

results from the underestimation of k_{-2} for the TP sample at lower temperatures. The recombination constant (k_{-2}) of the potassium-free DP sample is about 5 times lower than that obtained for the TP sample in agreement with Ref. (27).

Figures 6 and 7 show the coverages of the Fe surface by N_{ads} (Θ_N) at 673 K as a function of the relative conversion (y) (defined as the ratio of ammonia concentration x_{NH_3} to its equilibrium concentration $x^*_{NH_3}$) calculated from Eq. [5]. In the calculations, the reaction rates for NH_3 synthesis at atmospheric pressure were used and those found for identical catalysts at a pressure of 100 bar, published elsewhere (20). As may be seen in Figs. 6 and 7, there is a steady increase in Θ_N for both catalysts, both at high and low pressures with increasing conversion (y). At a pressure of 1 bar the values of Θ_N are much higher for the potassium-free catalyst (DP) than for that containing potassium (TP). At a pressure of 100 bar the relationship is inverse: $\Theta_{N,DP}$ is lower than $\Theta_{N,TP}$. First of all, it should be noticed that generally the values of Θ_N are much lower than those resulting from the surface science-based models using Langmuir isotherms and the initial N_2 sticking coefficient (Stoltze–Nørskov, Bowker–Waugh). The derived coverages of N_{ads} are in good agreement with values of about 0.5 calculated for ammonia synthesis at high conversion assuming strongly activated N_2 chemisorption (3, 12, 15).

The Langmuir isotherm with coverage-independent rate constants seems to be a rather poor approximation of the kinetic results (3, 25). Ertl's measurements have already shown that the sticking coefficient of nitrogen on Fe(111) and Fe(100) planes decreases with increasing coverage (28). This means that the coverages presented in Figs. 6 and 7 are underestimated, especially at low conversions, since k_{-2} values could be significantly lower than those for coverages close to unity (used in the calculations). The other isotherms analyzed by Aparicio and Dumesic (25), which are based on coverage-dependent rate constants, yield better fits, as does the Temkin–Pyzhev equation.

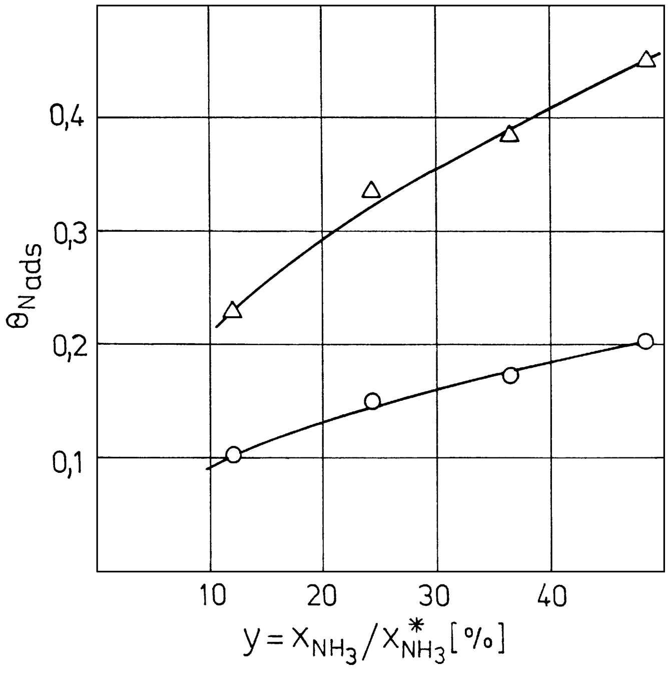

FIG. 6. Surface coverage by nitrogen atoms ($\Theta_{N,ads}$) vs relative conversion (y) in ammonia synthesis at atmospheric pressure; $T = 673$ K; △, DP; ○, TP.

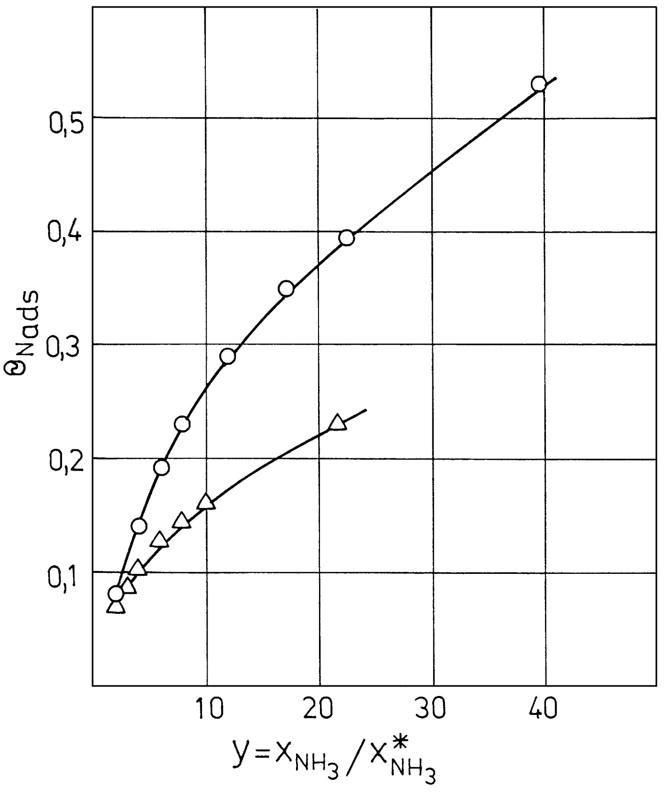

FIG. 7. Surface coverage by nitrogen atoms ($\Theta_{N,ads}$) vs relative conversion (y) in ammonia synthesis at a pressure of 100 bar; $T = 673$ K; △, DP; ○, TP.

5. DISCUSSION

The present experimental results, together with those presented earlier (20) show clearly that the effect of potassium in the catalyst depends on the process parameters, both for the synthesis and for the decomposition of ammonia. In ammonia synthesis at high pressure (100 bar) potassium enhances the reaction rate, especially at high partial pressures of NH_3. The increase in activity as measured for $x_{NH_3} = 5$–7% is even higher than tenfold (20). On the contrary, potassium does not promote the iron surface at atmospheric pressure. It is possible that a small effect has not been noticed because of experimental errors.

When decomposing ammonia, the effect of potassium is clearly observed, being the higher, the higher the ammonia concentration in the gas phase is. An about fivefold increase of the k_{-2} value (Fig. 5) can be interpreted as resulting from the destabilization of N_{ads} (decrease in the heat of N_2 chemisorption or increase in the preexponential factor for desorption), as stated by Fastrup (3, 27), on the basis of N_2 TPD and TPA experiments. The above interpretation of the role of potassium in ammonia synthesis catalyst does not explain fully, however, the pressure-dependent effect of potassium. An about 15-fold increase in the reaction rate (forward) of NH_3 synthesis at 100 bar and an about tenfold increase at 1 bar are predicted from microkinetic simulations (3), when the heat of chemisorption and, correspondingly, E_{-2} are reduced by 16.7 kJ/mol. The former result agrees very well with the experimental results, presented in (20), but the latter does not correspond to that presented in this paper, where the effect of potassium was not observed. Therefore, also other explanations should be taken into consideration, when discussing the mechanism of potassium promotion in NH_3 synthesis.

5.1. *Dominant Fe Planes in the Catalysts—Surface Reconstruction*

The rate of ammonia synthesis measured by Somorjai *et al.* (5, 6, 29) on the Fe(111) plane at 673 K, a pressure of 20 bar and NH_3 concentrations close to zero is 1.3×10^{-8} mol $NH_3/(cm^2 \cdot s)$, which corresponds to the TOF value of about 11 NH_3 molecules/(site · s) using the Fe(111) atom density of 0.7×10^{19} Fe atoms/m^2. However, the synthesis rate over the triply promoted (TP) catalyst at 673 K and a pressure of 100 bar reaches the value of about 7 kg $NH_3/(kg_{cat} \cdot h)$ (20) when the ammonia concentration is close to zero. Taking into account the results of the TPSR studies (118 μmol/g), one obtains TOF $\cong$ 1.0, which is about one order of magnitude lower than that obtained with the Fe(111) plane. Assuming that the TOF is roughly proportional to the overall pressure, one may conclude that, under comparable conditions of pressure and temperature and at p_{NH_3} close to zero, the Fe(111) surface is about 50 times more active than that of the fused iron catalyst. This seems to be strong evidence that the Fe(111) planes are not dominant in the commercial catalyst when the concentration of ammonia in the gas phase is close to zero. Contrarily, the share of Fe(111) plane is only a small portion of the iron surface accessible for the reactants.

On the other hand, it is strongly suggested by Schlögl *et al.* (19, 30) that under NH_3 synthesis conditions the multiply promoted iron catalyst exposes mainly Fe(111) planes. The N_2 TPD data obtained by Muhler *et al.* (26) with the KMI catalyst confirm such a hypothesis. It has also been suggested that the structure of the surface can depend on the conditions of NH_3 synthesis (reconstruction of the surface, which may be controlled by the concentration of atomic nitrogen dissolved in the bulk) (27, 28, 31, 32).

If one accepts the concept of reconstruction, it is possible to present the following explanation for the role of potassium. At low ammonia concentrations in the gas phase (low total pressure or low conversion at high pressure), mainly the planes of low activity (Fe(110) and Fe(100)) are exposed to the reactant gases. When the NH_3 content is high (NH_3 synthesis at high pressure, decomposition of NH_3) the new, highly active sites, characteristic for Fe(111), e.g., C-7 sites, can be formed locally on the less active Fe(110) and Fe(100) surfaces. Such new sites would be unstable and the role of potassium would consist in stabilizing the surface structure. It is obvious that new sites show their own preexponentials and energies of activation, different from those of other sites.

According to the hypothesis presented above, an increase in the activity of the TP catalyst with respect to ammonia decomposition for $5\% < x_{NH_3} < 25\%$ (Fig. 2) should rather be correlated with an increase in the number of highly active sites (C-7), than with a substantial growth of surface saturation with atomic nitrogen. A further increase in the concentration of ammonia in the gas phase (in the region where iron nitrides are formed) leads probably to restructuring of the surface of both catalysts studied (TP and DP) and, as a consequence, to an increase in the reaction rate (Fig. 2) (more new active sites). For this reason the effect of potassium becomes less evident (about threefold at 80% NH_3 in the gas phase).

The surface reconstruction may also be used to explain the differences in the TPSR spectra of the DP and TP samples at lower temperatures (Fig. 1). The TP catalyst surface is endowed with C-7 sites when saturated with N_{ads}. The nitrogen atoms adsorbed on such sites are more readily hydrogenated, which is manifested by the shift in the TPSR peak toward lower temperatures. Also the shape of the TPD curve, presented in Ref. (26) could be explained partly in this way. Readsorption of N_2 would then not be the only phenomenon responsible for the shoulder at high temperatures in the TPD spectrum.

Further investigations are necessary to confirm or to reject the concept of reconstruction. Studies of hysteresis in NH_3 synthesis, similar to those presented by Waugh *et al.* (33) may be especially informative.

5.2. *Potassium–Alumina Interaction*

In fused iron catalysts the Fe surface is partly covered by alumina, which may store, K_2O (34) as suggested by Brunauer and Emmet (35) and by Boudart (36) (islands of $K_2O{-}Al_2O_3$). In such a case, potassium would be partly present on the Fe surface as K_xO_y and partly on Al_2O_3 islands as a $K_2O{-}Al_2O_3$ complex (in the TP catalyst K_2O neutralizes Al_2O_3 and the smaller peak in the TPSR spectrum is not observed; see Fig. 1). According to this model a competitive chemisorption of the more basic K_xO_y and the less basic NH_3 takes place on acidic alumina sites (OH groups). With increasing p_{NH_3} some K_xO_y is replaced and diffuses onto the bare Fe planes (surface diffusion). Hence, the higher the partial pressure of NH_3 in the gas phase is, the higher the concentration of K_xO_y groups on the Fe surface is, and consequently the higher the effect of potassium is. It should be noticed that p_{NH_3} in ammonia synthesis at 100 bar is usually more than one order of magnitude higher than that in NH_3 decomposition at 1 bar, and 3–4 orders of magnitude higher than that in NH_3 synthesis at 1 bar. That is why the effect of potassium in NH_3 synthesis at 100 bar is higher than that observed in NH_3 decomposition at 1 bar.

6. CONCLUSIONS

The reaction rate of ammonia synthesis and decomposition at 1 bar vs NH_3 content was studied over a doubly (Al_2O_3, CaO) and a triply (Al_2O_3, CaO, K_2O) promoted fused iron catalyst. The latter was obtained by the impregnation of the former (in its prereduced state) with a KOH solution. Additionally, temperature programmed surface reaction (TPSR) spectra for both materials were measured.

- No effect of potassium on the rate of NH_3 synthesis at 1 bar was observed in agreement with literature data. On the contrary, potassium enhances the rate of ammonia decomposition. In the stability range of α-Fe, the effect is the stronger the higher the NH_3 content in the gas phase is (fivefold for 20% NH_3). The k_{-2} constant of N_{ads} recombination, as determined from the measurements of NH_3 decomposition over the triply promoted catalyst corresponds very well to that determined by Muhler *et al.* (26) from TPD spectra of the industrial KMI catalyst.
- The coverages of N_{ads} in NH_3 synthesis, as derived from kinetic measurements for the two catalysts at 1 bar and 100 bar, are much lower than those resulting from surface science-based models using the initial N_2 sticking coefficient (Stoltze–Nørskov, Bowker–Waugh). These results confirm that the Langmuir isotherm with coverage-independent rate constants is a rather poor approximation of the reaction kinetics over a broad range of experimental conditions (3, 25).
- A comparison between the TOF of NH_3 synthesis over the Fe(111) single crystal plane (Somorjai (5, 6, 29) and the TOF over a fused iron catalyst indicates that Fe(111) is not dominant in the latter, when the NH_3 concentration in the gas is close to zero. It is suggested that the reconstruction of the surface takes place when p_{NH_3} increases (coverage-dependent reconstruction). The role of potassium would consist in stabilizing the reconstructed, more active iron surface (new active sites, e.g., C-7). It is also suggested that the coverage of iron by K_xO_y groups depends on the partial pressure of ammonia due to competitive chemisorption of basic K_xO_y and less basic NH_3 on acidic OH groups from Al_2O_3, which is present on the Fe surface.

ACKNOWLEDGMENT

The authors benefitted from discussions with Professor G. Ertl.

REFERENCES

1. Ertl, G., Lee, S. B., and Weiss, M., *Surf. Sci.* **114**, 527 (1982).
2. Ertl, G., *in* "Catalytic Ammonia Synthesis: Fundamentals and Practice" (J. R. Jennings, Ed.), Chap. 3, Plenum, New York, 1991.
3. Fastrup, B., *Topics in Catal.* **1**, 273 (1994).
4. Strongin, D. R., and Somorjai, G. A., *J. Catal.* **109**, 51 (1988).
5. Somorjai, G. A., and Materer, N., *Topics in Catal.* **1**, 215 (1994).
6. Strongin, D. R., and Somorjai, G. A., *in* "Catalytic Ammonia Synthesis: Fundamentals and Practice" (J. R. Jennings, Ed.), Chap. 4, Plenum, New York, 1991.
7. Spencer, M. S., *Catal. Lett.* **13**, 45 (1992).
8. Stoltze, P., and Nørskov, J. K., *Phys. Rev. Lett.* **55**, 2502 (1985).
9. Stoltze, P., and Nørskov, J. K., *Surf. Sci.* **197**, L230 (1988).
10. Stoltze, P., *Phys. Scripta* **36**, 824 (1987).
11. Stoltze, P., and Nørskov, J. K., *J. Catal.* **110**, 1 (1988).
12. Bowker, M., Parker, T., and Waugh, K. C., *Appl. Catal.* **14**, 101 (1985).
13. Bowker, M., Parker, T., and Waugh, K. C., *Surf. Sci.* **197**, L223 (1988).
14. Parker, J., Waugh, K. C., and Bowker, M., *J. Catal.* **114**, 457 (1988).
15. Bowker, M., *Catal. Today* **12**, 153 (1992).
16. Dumesic, J. A., and Treviño, A. A., *J. Catal.* **116**, 119 (1989).
17. Stoltze, P., and Nørskov, J. K., *Topics in Catal.* **1**, 253 (1994).
18. Nielsen, A., "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," Jul. Gjellerups Forlag, Copenhagen, 1968.
19. Schütze, J., Mahdi, W., Herzog, B., and Schlögl, R., *Topic in Catal.* **1**, 195 (1994).
20. Kowalczyk, Z., *Catal. Lett.* **37**, 173 (1996).
21. Kowalczyk, Z., Jodzis, S., Diduszko, R., and Kowalczyk, E., *Appl. Catal. A: General* **87**, 1 (1992).
22. Fastrup, B., Muhler, M., Nygard Nielsen H., and Pleth Nielsen, L., *J. Catal.* **142**, 135 (1993).
23. Kowalczyk, Z., Jodzis, S., and Sentek, J., *Appl. Catal.* **138**, 83 (1996).
24. Kuntze, J. "Nitrogen and Carbon in iron and steel, Thermodynamics," Akademie Verlag, Berlin, 1990.
25. Aparicio, L. M., and Dumesic, J. A., *Topics in Catal.* **1**, 233 (1994).
26. Muhler, M., Rosowski, F., and Ertl, G., *Catal. Lett.* **24**, 317 (1994).
27. Fastrup, B., *J. Catal.* **150**, 345 (1994).
28. Bozso, F., Ertl, G., Grunze, M., and Weiss, M., *J. Catal.* **49**, 18 (1977).
29. Strongin, D. R., Carrazza, J., Bare, S. R., and Somorjai, G. A., *J. Catal.* **103**, 213 (1987).
30. Schlögl, R., Schoonmaker, R. C., Muhler, M., and Ertl, G., *Catal. Lett.* **1**, 237 (1988).
31. Dumesic, J. A., Topsøe, H., Khammmouma, S., and Boudart, M., *J. Catal.* **37**, 503 (1975).
32. Dumesic, J. A., Topsøe, H., and Boudart, M., *J. Catal.* **37**, 513 (1975).
33. Waugh, K. C., Butler, D. A., and Hayden, B. E., *Topics in Catal.* **1**, 43 (1994).
34. Andrew, S. P., *Appl. Catal. A: General* **90**, N14 (1992).
35. Brunauer, S., and Emmet, P. H., *J. Am. Chem. Soc.* **62**, 1732 (1940).
36. Borghard, W. S., and Boudart, M. S., *J. Catal.* **80**, 194 (1983).