

INTERACTIONS OF NITROGEN AND HYDROGEN ON IRON SURFACES

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Interactions between nitrogen and hydrogen on single and polycrystalline Fe surfaces were studied by thermal desorption and Auger spectroscopy under UHV conditions and by applying total pressures up to about 1 atm. Molecularly adsorbed nitrogen, $N_{2,ad}$, is displaced from the surface by admission of hydrogen. Adsorbed hydrogen in turn inhibits adsorption of molecular nitrogen and as a consequence lowers the rate of dissociative nitrogen adsorption (which proceeds through $N_{2,ad}$). Ammonia synthesis is therefore most favourably run under conditions where the stationary H_{ad} -concentration is not too high, which will usually be fulfilled at the rather high reaction temperatures (≥ 700 K), even if the H_2 pressure is high. Adsorbed atomic nitrogen, N_s , on the other hand, blocks the sites for hydrogen adsorption, so that also the stationary N_s -concentration should not be too high. That this latter condition will be fulfilled with a stoichiometric $N_2 + H_2$ mixture at $T \approx 580$ K (as long as NH_3 decomposition plays no important role) was demonstrated by means of high pressure studies in which the stationary N_s -concentration was determined after evacuation. These measurements showed unequivocally that under the stated conditions dissociative nitrogen adsorption is the rate-limiting step of ammonia synthesis. Complications arise from bulk dissolution and surface segregation of atomic nitrogen which processes are affected by the presence of hydrogen.

1. Introduction

The synthesis of ammonia from hydrogen and nitrogen over iron catalysts is one of the most important catalytic processes [1]. Application of surface spectroscopic techniques to real catalysts as well as model systems (in particular clean single crystal surfaces) [2] yielded rather detailed insight into the surface properties of the individual components from which a consistent picture on the overall reaction mechanism could be developed [3]. The kinetics of the synthesis reaction itself is, however, in principle not directly accessible to low-pressure studies (i.e. $\lesssim 10^{-4}$ Torr)

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for thermodynamic reasons: In the temperature range applied in practice (~ 700 K) the equilibrium is completely shifted towards the side of the reactants and noticeable NH_3 yields can only be obtained if the total pressure is of the order of at least 1 atm. If, on the other hand, the temperature is considerably lowered (which would thermodynamically favour the product formation) the rate of ammonia production becomes too small.

The present work intends to contribute to this problem in two different and more indirect ways: First the mutual influence of hydrogen and nitrogen on their adsorption properties are studied under low-pressure conditions. Thereby it turned out that preadsorbed hydrogen inhibits adsorption of nitrogen and vice versa from which it is concluded that the steady-state reaction is most favourably run under conditions where the coverage of both reactants is not too high. Secondly a series of experiments was performed with total pressures up to nearly 1 atm (where NH_3 is actually formed in measurable quantities) and the surface was analysed subsequently after evacuation. Knowledge of the thermal properties of the surface species enables in this case information on the surface concentration of atomic nitrogen *under reaction conditions*. These data confirm unequivocally that dissociative nitrogen adsorption is the rate-limiting step in a stoichiometric $N_2:H_2$ mixture at $T \gtrsim 580$ K and demonstrate furthermore that the steady-state surface concentration of atomic nitrogen is indeed rather low under these conditions.

Complications may arise from the dissolution and surface segregation of atomic nitrogen which latter process may be accelerated by the presence of hydrogen as became evident in the present context.

2. Experimental

Two different UHV systems with base pressures around 2×10^{-10} Torr were employed: The first one was a conventional apparatus for low pressure studies ($p \lesssim 10^{-4}$ Torr) equipped with facilities for LEED, AES, thermal desorption mass spectrometry (TDS), and contact potential measurements ($\Delta\phi$) by means of the vibrating condenser technique. The second system allowed the application of pressures up to about 1 atm and is shown schematically in fig. 1. The stainless steel recipient is equipped with a manipulator to which the sample was attached, an argon ion gun, an electron gun for AES, a retarding field electron analyser for AES developed in our laboratory [5], a quadrupole mass spectrometer (Balzers QMG 111A) which could be differentially pumped through a variable leak valve, a UHV compatible membrane manometer (Kontron P 20X + UM80) for the pressure range between 0.1 and 1500 Torr, and two ionisation gauges covering the pressure range between 10^{-11} and 1 Torr. A copper tube to which a Cu foil was welded could be filled with liquid nitrogen and served as a cryopump for NH_3 and H_2O (which could be present in traces during the high pressure measurements). The recipient was separated from the pumps by a gold wire sealed 6" gate-swing valve. Pumping

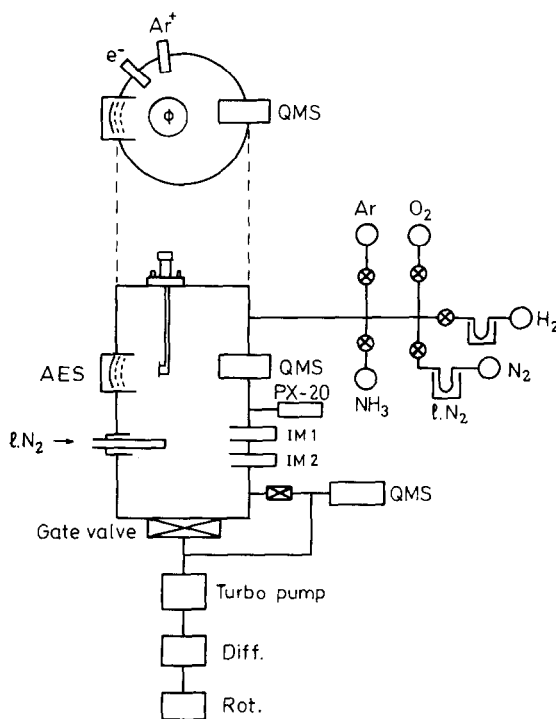


Fig. 1. UHV apparatus for studies at pressures up to 1 atm.

was achieved by a combination of a turbomolecular pump (TUP 200), an oil diffusion pump with water-cooled baffle, and a two-stage rotary pump (Balzers). The effective pumping speed at the recipient was determined to be about 130 ℓ/s which allowed evacuation from 10^3 to 10^{-9} Torr within a few minutes. The gases could be admitted to the recipient through high pressure valves connected with standard UHV valves through bakeable stainless-steel tubes. H_2 and N_2 were purified from condensable gases (H_2O , CO_2 , etc.) by flow through liquid N_2 cooled traps.

Either single crystalline or polycrystalline (wire, or disc) Fe surfaces were studied. The former were cleaned by standard argon ion bombardment/annealing cycles [5]. The wire was first degassed by keeping it for 10 h at 1000 K, and subsequently the surface was cleaned by repetitive oxidation/reduction cycles with $O_2 + H_2$ at temperatures up to 950 K. In all cases the Auger spectrum exhibited less than a few percent of carbon as the only remaining surface contamination.

3. Results and discussion

3.1. Influence of hydrogen on adsorption of molecular nitrogen

Dissociative nitrogen adsorption was found to proceed through $N_2 \rightleftharpoons N_{2,ad} \rightarrow 2N$. [6,7]. The properties of the molecularly held species on both clean and K-doped Fe surfaces have been investigated separately in detail [6,8]. Fig. 2, curve a, shows the thermal desorption spectrum for N_2 from a Fe(111) surface which was precovered with 1.1×10^{14} K-atoms/cm² and subsequently saturated with $N_{2,ad}$ by exposure at 140 K. The spectrum consists of two peaks (α_1 and α_2) arising from adsorption of N_2 at bare Fe sites and at sites in the vicinity of adsorbed K, respectively [8]. The same experiment was repeated except that prior to thermal desorption the surface was in addition exposed to 22 L H_2 . (The adsorption of hydrogen alone on clean Fe single crystal surfaces has been studied in detail previously [9]). Curve b is the resulting thermal desorption trace for N_2 : Since NH_3 formation at these low temperatures can clearly be ruled out, these data show that hydrogen is able to displace preadsorbed molecular nitrogen from the surface.

This result suggests that preadsorbed hydrogen atoms are also inhibiting the adsorption of molecular nitrogen. Qualitative confirmation for this conclusion was obtained by the following experiment: A Fe(100) surface precovered with 1.6×10^{14} K-atoms/cm² was nearly saturated with adsorbed (atomic) hydrogen and then exposed to N_2 at 155 K and $p_{N_2} = 2 \times 10^{-4}$ Torr. The uptake of $N_{2,ad}$ was followed

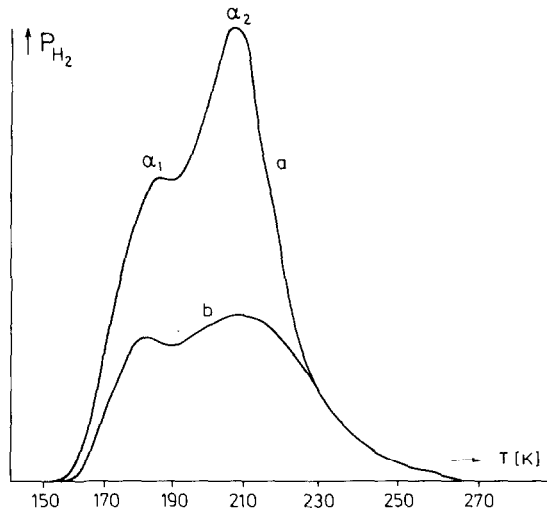


Fig. 2. Thermal desorption spectra for N_2 (at saturation coverage) from Fe(111) covered with 1×10^{14} K-atoms/cm²: (a) without hydrogen, (b) after preexposure to 22 L H_2 prior to N_2 admission.

by continuously recording the work function change $\Delta\phi$. It turned out that the maximum $\Delta\phi$ variation which could be reached in this way was only about 20% of the value obtained without the presence of preadsorbed hydrogen. Upon evacuation the small amount of $N_{2,ad}$ desorbed completely (at 155 K) which would not have been the case without the presence of H_{ad} .

While with K-promoted Fe surfaces even at 155 K a slow conversion of $N_{2,ad}$ into the atomic nitrogen species takes place, no such effect was observed to occur if the surface was covered by hydrogen prior to N_2 admission.

These results lead to the following conclusion: Hydrogen may be adsorbed on a surface already precovered with molecular nitrogen and lowers the adsorption energy of $N_{2,ad}$. As a consequence the latter species desorbs at lower temperature (= displacement of $N_{2,ad}$ by hydrogen) and has a higher activation energy for dissociation (according to the model presented in ref. [6]). At a given temperature and N_2 pressure the equilibrium $N_{2,ad}$ -coverage will be smaller than in the absence of hydrogen.

3.2. Influence of hydrogen on dissociative nitrogen adsorption

According to the preceding conclusions dissociative nitrogen adsorption at elevated temperatures is expected to be retarded by the presence of hydrogen rather than to be accelerated. Above 400 K the rate of hydrogen adsorption as well as desorption is much faster than any other surface process which might come into play (i.e. nitrogen adsorption or ammonia formation) [9] so that the stationary H-coverage will be determined by the adsorption-desorption equilibrium for hydrogen which might eventually be slightly influenced by the presence of other adsorbed species (see below).

In a first experiment on a Fe(100) surface the increase of the N_s -concentration as a function of N_2 exposure at 430 K was recorded by monitoring the AES peak height of the N-signal (as in previous work [5]) without the presence of H_2 in the gas phase. Then the same measurements were repeated with the presence of 2×10^{-6} Torr H_2 : The results were completely identical. Under these conditions the steady-state coverage of H_{ad} is estimated to be of the order of less than 5% of a monolayer (based on the separately determined adsorption properties of hydrogen [9]). Obviously at such a small hydrogen coverage the adsorption of nitrogen is not influenced to a measurable extent. It may further be concluded that at this low temperature and H_2 pressure the hydrogenation of N_s is still much slower than the dissociative adsorption of nitrogen, otherwise the N_s -concentration should also be smaller in the presence of hydrogen since eventually formed NH_3 would immediately desorb at 430 K.

Next similar experiments at 430 K were performed with Fe(111). Fig. 3, curve a, shows the variation of the surface concentration of N_s as a function of N_2 -exposure by applying an N_2 -pressure of 5×10^{-5} Torr. Curve b was obtained by using a mixture of 5×10^{-5} Torr N_2 + 1×10^{-5} Torr H_2 . Obviously the rate of N_s -forma-

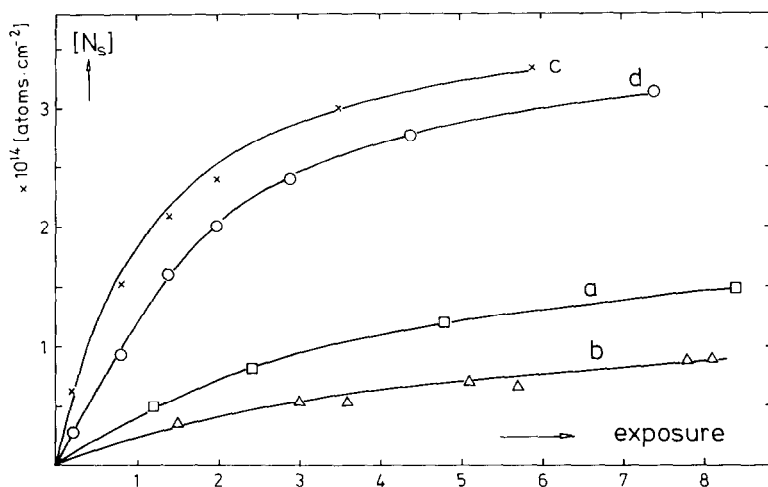


Fig. 3. Variation of the surface concentration of atomic nitrogen, $[N_s]$, on Fe(111) with N_2 exposure at 430 K: (a) clean surface, pure N_2 (5×10^{-5} Torr); (b) clean surface, $N_2 + H_2$ mixture ($p_{N_2} = 5 \times 10^{-5}$ Torr, $p_{H_2} = 5 \times 10^{-5}$ Torr); (c) surface precovered with 1.8×10^{14} K-atoms/cm², pure N_2 (5×10^{-5} Torr); (d) surface as for (c), $N_2 + H_2$ mixture ($p_{N_2} = 5 \times 10^{-5}$ Torr, $p_{H_2} = 1 \times 10^{-5}$ Torr).

tion has now become considerably smaller. The data of corresponding measurements with a K-promoted surface ($n_K = 1.8 \times 10^{14}$ K-atoms/cm²) are reproduced by curves c and d: Although the rate of N_s -formation is enhanced by the presence of K, the addition of H_2 has a quite similar effect. The latter data show that the maximum concentration of N_s is practically the same with and without H_2 , which again indicates that under these (relatively low temperature) conditions hydrogenation of N_2 is still slower than its formation.

On Fe(111) at $p_{H_2} = 1 \times 10^{-5}$ Torr and 430 K an appreciable fraction of the surface will be covered by H_{ad} [9] which accordingly inhibits the adsorption of molecular nitrogen and thereby lowers the rate of the step $N_{2,ad} \rightarrow 2N_s$. On the other hand, N_s once formed will obviously not be influenced by hydrogen (displacement or hydrogenation) under the present conditions.

3.3. Influence of preadsorbed atomic nitrogen on hydrogen adsorption

Now we ask the reverse question, namely in which way the presence of N_s influences the (dissociative) adsorption of hydrogen. Fig. 4, curves a and b, show thermal desorption spectra for $H_2/Fe(110)$ after exposure of 6 and 200 L H_2 at 140 K, respectively. The latter exposure leads to a coverage near saturation [9]. Curves c and d were recorded after identical H_2 exposures of a Fe(110) surface which was

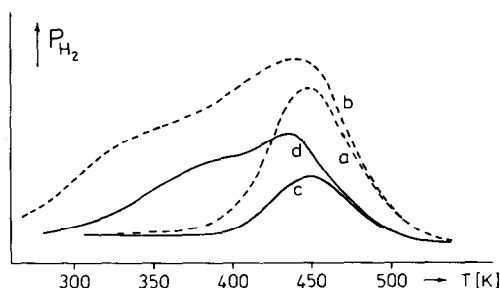


Fig. 4. Thermal desorption spectra for $H_2/Fe(110)$: (a) clean surface, 6 L H_2 exposure; (b) clean surface, 200 L H_2 exposure (= saturation); (c) surface precovered with 2.6×10^{14} N-atoms/cm², 6 L H_2 exposure; (d) surface as with (c), 200 L H_2 exposure.

precovered with 2.6×10^{14} N-atoms/cm². Obviously the desorption temperatures for H_2 are not altered, but the adsorbed amount is considerably lowered. It has to be concluded that hydrogen adsorption takes only place at sites which are free of adsorbed atomic nitrogen, i.e. N_s inhibits the adsorption of hydrogen. Since steady-state ammonia synthesis will usually take place at surfaces containing only fairly low N_s -concentrations (see below) this effect will, however, be of no marked importance for the kinetics of this reaction.

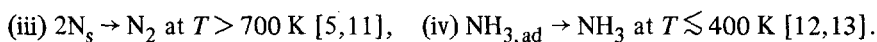
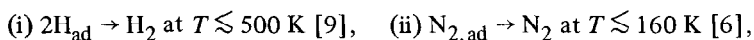
3.4. "High pressure" studies

The thermodynamic properties of the N_2 , H_2 system clearly rule out transformation into NH_3 to a measurable extent under the pressure conditions ($\lesssim 10^{-4}$ Torr) usually applied in UHV experiments. In order to approach this problem a series of measurements was performed at pressures up to nearly 1 atm.

First a Fe wire (8 cm² surface area) was exposed to a 3:1 $H_2 + N_2$ mixture with 600 Torr total pressure. With the sample kept at 570 K after 22 h an NH_3 pressure of 1.2 Torr was recorded, while the equilibrium partial pressure under these conditions was calculated to be 6.2 Torr [10]. At $T = 720$ K the equilibrium NH_3 pressure would be 1.2 Torr, whereas after 72 h $p_{NH_3} = 0.8$ Torr was recorded. These data indicate that the surface used was indeed catalytically active, but that the rate of NH_3 formation is far too low in order to enable kinetic measurements under these conditions. This conclusion becomes quite plausible if one assumes that dissociative nitrogen chemisorption is the rate-limiting step: The reaction vessel had a volume of 15 ℓ and therefore contained at $p_{N_2} = 150$ Torr about 10^{23} N_2 -molecules. This pressure corresponds on the other hand to an exposure of about 10^8 L/s, so that with a sticking coefficient of the order of 10^{-7} [5,11] about 10^{17} N_2 -molecules will be dissociatively adsorbed per second. That means that at least 10^6 s (= 300 h) are necessary in order to enable each N_2 molecule in the gas phase to become dissociatively adsorbed *once*. The experiments to be described in the follow-

ing were therefore always performed far from the equilibrium in the *gas phase*. That means also that NH_3 decomposition (= the backward reaction) can be neglected. This estimate demonstrates on the other hand that the steady-state *surface concentration* of N_s will be rapidly established if N_2 pressures of the order of 100 Torr are applied (provided that not too severe interference with bulk effects occurs which will be discussed later). The same holds of course also for the hydrogen coverage since the rate of H_2 adsorption is faster by at least 5 orders of magnitude.

Qualitative confirmation of these conclusions was obtained by the following experiments in which the surface was analysed by AES after a steady-state had been reached under high pressure conditions and the recipient had been subsequently evacuated. Before describing these data it is important to recall the thermal stability of the various surface species as determined in previous studies:



So it becomes evident that with experiments performed between 400 and 600 K atomic nitrogen, N_s , will not be affected by subsequent evacuation whereas all other species are desorbing. If bulk segregation/dissolution effects are minimized (which will indeed be the case as discussed below) AES will in fact provide the actual surface concentration of N_s which had been established under high pressure conditions.

At first a Fe(111) surface was exposed at 580 K for 1 h to a mixture of 450 Torr H_2 , 150 Torr N_2 , and 6 Torr NH_3 which corresponds to the equilibrium composition of the gas phase under these conditions. After evacuation the surface composition was analysed by AES yielding $\theta_N = 0.27$ ($[N_s] = 1.7 \times 10^{14}$ atoms/cm²). The same experiment performed *without* H_2 leads to the formation of a rather thick layer of (bulk) Fe_4N as described in detail elsewhere [14]. If instead the NH_3 is omitted (i.e. only a $N_2 + H_2$ mixture is used) a nitrogen coverage of $[N_s] = 7 \times 10^{13}$ atoms/cm² resulted. The explanation is straightforward: In a $N_2 + H_2$ mixture the stationary N_s -concentration is rather low since formation of this species is slow compared to its hydrogenation. (In contrast to the experiments described in section 3.2 the temperature is now higher, causing the nitrogen dissociation step to be rate-determining as will be discussed below. The concentration of NH_3 formed under these conditions is much too low to affect $[N_s]$ by ammonia decomposition.) If NH_3 is added to the gas phase, decomposition of this molecule causes a higher N_s -concentration which however, is still suppressed by reaction with hydrogen – otherwise bulk nitride formation occurs [14].

The following measurements were performed in order to obtain some information on the steady-state surface concentration of atomic nitrogen, $[N_s]$, *under reaction conditions*. For this purpose a clean Fe(111) surface was exposed at 580 K for about 30 min to 150 Torr N_2 at varying H_2 pressures. After subsequent evacuation $[N_s]$ was determined by means of AES.

The rate of dissociative nitrogen adsorption at 580 K and $p_{N_2} = 150$ Torr is given by $dN_s/dt = r_N = s \cdot 5.8 \times 10^{22}$ atoms/cm² s. The sticking coefficient at zero coverage is $s_0 = 4 \times 10^{-6}$ [4] and therefore the initial rate of N_s formation is about 2×10^{17} atoms/cm² s. The rate of hydrogen adsorption is much faster [9] so that the steady-state surface concentration of the reactants will be reached very rapidly.

The resulting data for $[N_s]_{\text{stat}}$ as a function of p_{H_2} (at $T = 580$ K and $p_{N_2} = 150$ Torr) are reproduced in fig. 5. $[N_s]$ has a fairly constant high value up to about 50 Torr (i.e. $p_{H_2} : p_{N_2} \approx 1:3$), but then rapidly drops and attains a rather small value at 450 Torr, i.e. with a stoichiometric mixture. Two very important conclusions can be drawn from these data as will be explained below:

- (i) Ammonia synthesis proceeds indeed via atomic rather than molecular nitrogen.
- (ii) In a stoichiometric $H_2 + N_2$ mixture and at $T \gtrsim 580$ K dissociative nitrogen chemisorption is the rate-limiting step of the synthesis reaction.

These conclusions are reached on the basis of the following arguments: Adsorption of nitrogen proceeds via $N_2 \rightleftharpoons N_{2,\text{ad}} \rightarrow 2N_s$ (1) so that two surface species, $N_{2,\text{ad}}$ and N_s may exist. If ammonia synthesis would proceed through the molecular species, viz. $N_{2,\text{ad}} + 6H_{\text{ad}} \rightarrow NH_3$, the parallel formation of N_s through $N_{2,\text{ad}} \rightarrow 2N_s$ would lead to a continuous increase of $[N_s]$ (which in this case would not be consumed) so that under steady-state conditions the surface would always be saturated by atomic nitrogen – which is obviously not the case.

If, on the other hand, NH_3 is formed from atomic nitrogen, i.e. via $N_s + 3H_{\text{ad}} \xrightarrow{k} NH_3$ (2), the steady-state concentration of this species will be determined by a combination of the (consecutive) reactions (1) and (2):

$$\begin{aligned} d[N_s]/dt &= s\sqrt{2\pi MRT} p_{N_2} (\hat{=} \text{rate of dissociative adsorption}), \\ -k[N_s]f([H_{\text{ad}}]) &(\hat{=} \text{rate of hydrogenation}), \end{aligned} \quad (3)$$

$$= 0.$$

$f([H_{\text{ad}}])$ contains the reaction order with respect to the surface concentration of atomic hydrogen, which in turn is a unique function of the hydrogen pressure, p_{H_2} (as determined by the adsorption isotherm).

$f([H_{\text{ad}}])$ will increase with increasing $[H_{\text{ad}}]$, and $[H_{\text{ad}}]$ will increase with increasing p_{H_2} (as long as saturation of the adlayer is not reached). The most simplified description is therefore obtained in terms of a power law: $f([H_{\text{ad}}]) = cp_{H_2}^x$ where the exponent x is positive and variable. At constant temperature (as underlying the measurements under discussion) eq. (3) can be reformulated as

$$d[N_s]/dt = c' p_{N_2} - c'' [N_s] p_{H_2}^x = 0,$$

yielding $[N_s]_{\text{steady-state}} = c''' p_{N_2} / p_{H_2}^x$. As a consequence at constant p_{N_2} , $[N_s]$ should decrease with increasing H_2 pressure which agrees with the experimental findings. A consequence of the formulation of the mechanism of NH_3 in terms of the consecutive reactions (1) and (2) is that the first reaction (dissociative nitrogen adsorption) is rate-limiting as soon as $[N_s]_{\text{steady-state}}$ attains a rather low value. Inspection of fig. 5 shows that this is indeed the case for a stoichiometric mixture.

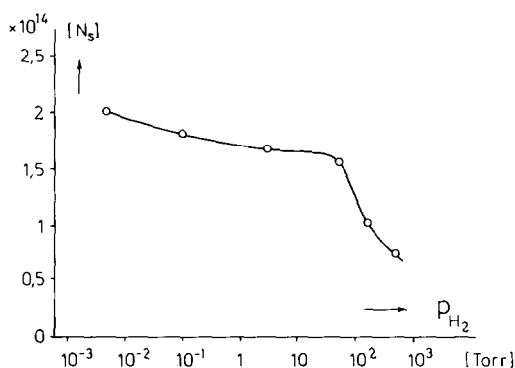


Fig. 5. Steady-state surface concentration of atomic nitrogen on a Fe(111) surface at 580 K kept at a constant N_2 pressure of 150 Torr and at variable H_2 pressures.

These conclusions can easily be qualitatively generalized:

(i) Since $[N_s]$ is determined by $p_{N_2}/p_{H_2}^x$ it is the ratio of the partial pressures of the reactants which determines this quantity rather than the *absolute* pressure. Therefore even at total pressures of several hundreds of atmospheres the situation will be quite similar.

(ii) Dissociative nitrogen adsorption proceeds fastest on the Fe(111) surface [5] and will therefore also be rate-limiting with other Fe single crystal planes as well as with polycrystalline surfaces. Since this step is accelerated by the presence of adsorbed K [8] as well as by a K + O adlayer [15] it becomes plausible why K_2O acts as a promoter for this reaction.

(iii) Dissociative nitrogen adsorption is associated with a rather low activation energy [5,11], in contrast to the subsequent hydrogenation steps [3]. As a consequence at temperatures above 580 K reaction (2) will become faster than nitrogen adsorption. The situation might, however, change at lower temperatures. That means it is expected that then eventually the step $N_s + H_{ad} \rightarrow NH_{ad}$ becomes rate-limiting, as e.g., suggested by the results of section 3.2.

3.5. Bulk diffusion and segregation of nitrogen

Several attempts to reduce the surface concentration of atomic nitrogen by exposure of nitrogen-covered Fe single crystal planes to low H_2 pressures ($\lesssim 10^{-4}$ Torr) over extended periods of time at $T \gtrsim 600$ K failed. Such attempts were only successful if higher H_2 pressures were applied. A Fe(111) surface covered by about 4×10^{14} N-atoms/cm² was exposed to 45 Torr H_2 at 580 K and the resulting variation of $[N_s]$ was recorded as a function of time by AES. The resulting data are shown in fig. 6. $[N_s]$ drops at first very rapidly due to hydrogenation and NH_3 for-

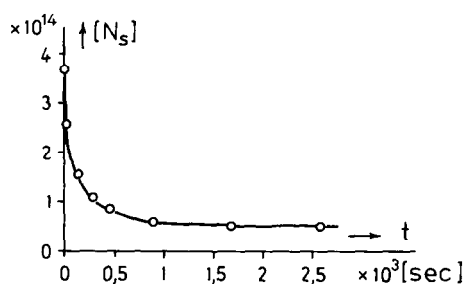


Fig. 6. Denitrogenation of a Fe(111) surface by 45 Torr H_2 at 580 K. Variation of the N_s -concentration with time.

mation, but then this process slows down and zero concentration is not reached even after long H_2 exposures. Obviously the bulk of the sample may act as a source of nitrogen atoms which are segregating to the surface. Although the nitrogen solubility in bulk Fe is very low [16] a massive sample may nevertheless provide an appreciable amount of N atoms for which segregation to the surface is exothermic with an enthalpy of 26 kcal/mole [17]. Evolution of N_2 from Fe(111) by bulk segregation and surface recombination was observed to take place rapidly above 900 K [5], but of course will also slowly occur at much lower temperatures. Obviously competition between the two processes $N_b \rightarrow N_s$ (4) (eventually promoted by hydrogen) and $N_s \xrightarrow{H_2} NH_3$ (2) will determine the concentration of N_s . If the H_2 pressure is low reaction (2) will be slow and therefore a high $[N_s]$ will always be established as long as a sufficient concentration of N atoms is present in the dissolved state. At 580 K bulk diffusion is obviously slow enough to enable measurements of the variation of $[N_s]$ as a function of H_2 pressure (fig. 5) or exposure (fig. 6) by rapid evacuation and AES recording. We have, nevertheless, to conclude that the actual $[N_s]$ -values in the high p_{H_2} -range under reaction conditions are even lower than those shown in fig. 5. In the low p_{H_2} -range (i.e. high N_s -concentrations), on the other hand, there will be a tendency for a reversal of step (4) that means for bulk dissolution so that the measured $[N_s]$ -values are somewhat too low. The choice of a Fe(111) surface (which is most active for NH_3 synthesis) and of a temperature of 580 K offered a suitable compromise to minimize these segregation processes.

Additional insight into these complex effects was obtained by measurements with a polycrystalline Fe surface covered with a composite K + O adlayer modelling the situation of a "real" ammonia synthesis catalyst [15]. Two samples, differing in their sequence of K + O doping as well as in their initial surface oxygen and nitrogen content were exposed for 8 h to 6×10^{-4} Torr H_2 at 633 K. The variations of the relative O and N surface concentrations (as monitored by the respective AES peak height ratio, $y_i = AES_i/AES(\text{fFe}, 646 \text{ eV})$ [5, 15] are listed in table 1. Whereas the oxygen concentrations decreased somewhat with the second sample due to partial reduction, in both cases the N_s -concentration *increased*, even without N_2 in

Table 1

The variations of the relative O and N surface concentrations. Conditions of treatment: K-doping at 373 K, O_2 admission at 423 K, as described in ref. [15]. Hydrogen treatment: 6×10^{-4} Torr, at 633 K

System	Treatment	Relative surface concentration	
		Y_O	Y_N
Fe + O + K	After doping	0.53	—
	8 h H_2	0.53	0.15
Fe + K + O	After doping	0.79	0.12
	8 h H_2	0.43	0.25

the gas phase! This observation suggests that hydrogen may “pull” nitrogen atoms from the bulk to the surface: high H_2 exposures may cause partial dissolution of hydrogen atoms in Fe [18] which then obviously enhance the tendency and/or rate for surface segregation of nitrogen. This conclusion is in agreement with general experience in metallurgy, whereafter the presence of an hydrogen atmosphere accelerates thermal denitrogenation of iron (although in this case certainly also reduction processes of oxides in the surface region may play an important role) [19]. Quite analogous observations were made with respect to surface segregation of carbon in nickel under the influence of hydrogen [20].

The competing character of the various processes establishing the stationary N_s -concentration can be seen from fig. 7. Here the same Fe/O + K-surfaces were exposed to a 3:1 $H_2 + N_2$ mixture with total pressure 8×10^{-4} Torr at 423 K. The N_s -concentration was monitored by AES at certain intervals. With sample A (sequence of doping: K + O, producing a more reactive surface) at first a small but dis-

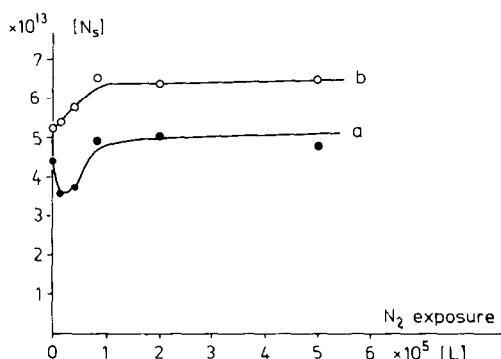


Fig. 7. Variation of the N_s -concentration on a polycrystalline Fe surface covered by a K + O adlayer upon exposure to a 3:1 $H_2 + N_2$ atmosphere ($p_{tot} = 8 \times 10^{-4}$ Torr) at 423 K.

tinct decrease of $[N_s]$ occurs, followed by a continuous increase to a steady-state value. With sample B (sequence of doping O + K) $[N_s]$ only increased continuously from the beginning. It can be concluded that in case A the removal of N_s occurred by chemical reaction, i.e. NH_3 formation. It should be mentioned that with these measurements also the surface concentration of oxygen varied and passed through a maximum. This reflects the rather complex nature of the various process which may occur at the surface of a "real" catalyst until steady-state conditions are reached. It should be pointed out that the presence of oxygen (from which at least a fraction is in close interaction with K) does not prevent ammonia formation [15]. Hence no complete reduction of the surface is needed in order to ensure catalytic activity.

In previous investigations with a Fe(111) single crystal surface [12] we had observed that addition of H_2 to N_2 (10^{-4} Torr range) increased the rate of build-up of N_s . Based on the present results it is now believed that this effect is indeed not due to an increase of the rate of dissociative nitrogen adsorption but rather caused by the hydrogen-assisted surface segregation of bulk nitrogen. Tamaru [21] had reported, on the other hand, on a real enhancement of the nitrogen uptake by a promoted iron catalyst at 520 K (followed by volumetric measurements of the gas consumption) if H_2 was added to the N_2 atmosphere. Since in these experiments the base pressure was only of the order of 10^{-5} Torr it appears plausible, however, that this effect was caused by partial reduction of iron whose parallel oxidation could certainly not be completely suppressed under these conditions.

4. Conclusions

From the described results the following conclusions can be drawn which are of relevance for the mechanism of ammonia synthesis over iron catalysts:

(i) Adsorption of hydrogen proceeds much faster than adsorption of nitrogen so that the equilibrium $H_2 \rightleftharpoons 2H_{ad}$ will always be established. Hydrogen adsorption also takes place on a surface precovered with $N_{2,ad}$ whereby this weakly held species is displaced. H_{ad} , on the other hand, inhibits the adsorption of molecular nitrogen.

(ii) Since dissociative nitrogen adsorption proceeds via $N_2 \rightleftharpoons N_{2,ad} \rightarrow 2N_s$ also this reaction will be inhibited rather than accelerated by the presence of adsorbed hydrogen. This step is, on the other hand, rate-limiting for ammonia synthesis (see below). The H_2 pressure and temperature should therefore be chosen in way that the stationary H_{ad} -concentration under reaction conditions is not too high. Although not studied in detail in the present context, it is estimated from the properties of the H_2/Fe system [9] that at the rather high reaction temperatures ($\gtrsim 700$ K) only a fraction of the surface will be covered by H_{ad} even if the H_2 -pressure is of the order of 100 atm. Experiments with Ru catalysts at somewhat lower temperatures demonstrated indeed the inhibiting effect of hydrogen on the rate of ammonia synthesis [22].

(iii) Atomic nitrogen, N_s , inhibits the adsorption of hydrogen. Therefore the surface concentration of this species should in turn also not be too high under reaction conditions.

(iv) That this latter condition will indeed be fulfilled by using a stoichiometric $N_2 + H_2$ mixture (as usually applied in industrial ammonia synthesis) at $T \gtrsim 580$ K becomes evident from the results of the high pressure studies. From these data the following unequivocal conclusions could be drawn: (a) NH_3 synthesis proceeds through hydrogenation of atomic rather than molecular nitrogen. (b) In a stoichiometric $N_2 + H_2$ mixture at $T \gtrsim 580$ K dissociative nitrogen adsorption is the rate-limiting step.

(v) A complete description of the surface processes has to include the possibility of bulk dissolution and surface segregation of atomic nitrogen (and hydrogen) which effects complicate analysis of surface concentration data. The presence of hydrogen obviously accelerates the surface segregation of dissolved nitrogen atoms.

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