INTERACTION OF H_2 AND N_2 ON Fe, INVESTIGATED BY PULSED LASER ATOM PROBEY. LI⁽¹⁾, W. DRACHSEL, J.H. BLOCK and F. OKUYAMA⁽²⁾*Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-1000 Berlin 33, F.R.G.*

Abstract - The interaction of hydrogen and nitrogen has been studied on iron field emitters at low temperatures ($T < 300$ K) and low pressures ($p < 10^{-4}$ Torr). It is shown from thermodynamics that chemical equilibrium permits NH_3 -formation at these temperatures. However, intermediates or products of such a reaction could not be observed on iron contrary to the literature data on Pt. The iron surface is extremely sensitive to traces of H_2O and undergoes field enhanced oxidation processes. Field enhanced nitrogen adsorption leads to a depletion of hydrogen in the adsorption layer.

I - INTRODUCTION

In the industrial synthesis of ammonia from hydrogen and nitrogen, iron catalysts have been used since the early days of Fritz Haber and Alwin Mittasch. A dissociative mechanism with the dissociation of N_2 as rate limiting step was widely accepted /1/. However, the direct observation of reaction intermediates by means of field ion mass spectrometry was a tempting task. Thus in 1968, W.A. Schmidt used a FI-source with a magnetic mass spectrometer to look at the coadsorption of H_2 and N_2 on Fe as well as at the decomposition of NH_3 at 300 K /2/. The products N^+ , NH^+ or NH_2^+ were not observed; however small amounts of N_2H^+ were obtained. In contrast to these findings, Tsong and coworkers recently gave evidence for these intermediates. In their first paper /3/, by using low resolution pulsed laser atom probe mass analysis, ion intensities of NH_2^+ or NH_3^+ (distinction was not possible) were observed for a series of metals including Fe. The field and temperature dependences were studied, showing maximum yield at 120 K. In a later experiment, with high mass resolution /4/, NH_2^+ was assigned as the predominant ion species from a Pt(001) surface and a dissociative mechanism for the ammonia synthesis was deduced.

Due to the low ammonia concentration in the chemical equilibrium $1/2 N_2 + 3/2 H_2 \rightleftharpoons NH_3$ at catalytic reaction temperatures (673 K), high pressures (≈ 200 atm.) have to be

(1) Visiting scientist from Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian, P.R. of China

(2) Visiting scientist from Nagoya Institute of Technology, Gokiso-cho Showa-ku, Nagoya 466, Japan

applied in the industrial ammonia synthesis. Extrapolation to lower temperatures (fig.1) shows that the equilibrium at 100 K is shifted in favor of NH_3 . If the activation of nitrogen could be achieved by means other than the catalyst surface, which needs 673 K, high ammonia concentrations would be expected at low temperatures for thermodynamic reasons. We pose the question whether an electrostatic field of the order of 1 V/Å at a solid surface may activate nitrogen for such a reaction with hydrogen.

Fig. 1 - $\log K$ vs temperature and reciprocal temperature (inset), extrapolated to low temperatures for the reaction $3/2 \text{H}_2 + 1/2 \text{N}_2 \rightleftharpoons \text{NH}_3$;

$$K = \frac{p_{\text{H}_2}^{3/2} \cdot p_{\text{N}_2}^{1/2}}{p_{\text{NH}_3}} ; p [\text{at}] .$$

II - EXPERIMENTAL

Inspired by the contradicting literature results and the thermodynamical estimate, we tried to investigate this reaction using our pulsed laser atom probe. An older version of this instrument was described already /5,6/. The modified apparatus (fig.2) allows observation of the emitter surface with a video-camera while field desorption experiments are performed. The channelplate (with two holes) in front of the emitter gives a field ion image of the surface while a second channelplate detector, 40 cm apart from the emitter, images only a few surface atoms. This detector is used for time-of-flight measurements. The iron specimen (99.99 %) was etched in dilute HCl and cleaned in situ by annealing in 3×10^{-4} Torr H_2 at 800 K and subsequent field evaporation in hydrogen at 110 K, until the (110) and (211) areas were developed. An atomically resolved pattern of the (111) plane could not be achieved. About 50-100 atomic sites were probed with our system. The gases $^{14}\text{N}_2$, $^{15}\text{N}_2$, H_2 and D_2 were introduced from glass bottles at dynamic vacuum conditions. Residual gas pressure after bakeout was 3×10^{-10} Torr, but was essentially higher during dynamic gas inlet.

Fig. 2 - Pulsed laser atom probe.

III - Results

In our first experiments the mass spectra displayed a strong yield of mass 16 and 17 (fig.3) similar to the findings of Liu and Tsong for the Pt(001) surface ³. We measured the field as well as the temperature dependence for the reaction products NH_2 and NH_3 . Without discussing these results further, we wish to state at this point that these first results were obtained by introducing only H_2 at 5×10^{-5} Torr at a residual gas pressure in the lower 10^{-8} Torr range, due to the throttled main valve. The additional introduction of $^{14}\text{N}_2$ decreased all surface species, especially H_2^+ , whereas $m=28$ and 29 increased.

The obvious disappearance of surface hydrogen by displacement of N_2 leads to the argument that, due to the high sticking coefficient, only very low N_2 pressure is needed. Some N_2 is expected in the residual gas, as confirmed by the $^{15}\text{N}_2$ exchange reaction with chamber-wall $^{14}\text{N}_2$ leading to $^{14}\text{N}^{15}\text{N}$.

Using D_2 instead of H_2 (fig. 4), it is obvious that deuterium dominates on the surface; so if $m=16$ is labelled as NH_2^+ , then $m=18$ as ND_2^+ in this case should be much higher. The failure of this to occur might be explained as a strong isotopic effect. However, when we used labelled $^{15}\text{N}_2$ (predominating on Fe surface) and H_2 , no shift of the main peak from $m=16$ to $m=17$ was observed.

Fig. 3 - ToF-spectrum: $p_{H_2} = 3 \times 10^{-5}$ Torr,
 $p_{\text{res. gas}} = 2 \times 10^{-8}$ Torr, $T = 110$ K, $F = 2$ V/Å.

Fig. 4 - Desorption spectrum from a (110) step on Fe at 1.8 V/Å and 110 K for $p = 1 \times 10^{-5}$ Torr D_2 with residual gas $p = 2 \times 10^{-8}$ Torr.

From these findings some doubts about the correct mass assignment arose, which we tested by using CO , CH_4 , H_2O and O_2 as candidates for the residual gases. Methane gave a strong peak at $m=16$ and also a weak and broad peak at $m=15$. The other oxygen-containing species gave rise to a more or less pronounced signal at $m=16$. Since $m=32$ was absent, O_2 could be excluded; the origin of $m=16$ could be attributed to the presence of Fe-oxides, mainly visible as $(Fe_2O)^{2+}$ at $m=64$, in the spectrum. These findings revealed a strong sensitivity of the iron specimen to oxide formation from impurities.

Therefore, we performed an experiment under better conditions with the residual gas pressure below 5×10^{-9} Torr. Starting with only D_2 (fig.5a), we added $^{15}N_2$ at 10^{-8} Torr (fig.5b). In comparison, no ND_2^+ was observed (fig.5b) whereas mass=32 appeared as N_2D^+ at the (211)-Fe surface. No extra reaction products occurred when we increased the nitrogen pressure further; only a decrease of surface deuterium was observed.

Fig. 5(a) - Desorption spectrum from Fe(211); 10^{-5} Torr D_2 admitted, 110 K, res. gas 5×10^{-9} Torr;

(b) - Same as (a), but additional 1×10^{-8} Torr $^{30}N_2$ admitted.

In all of our experiments so far, there was no evidence for N_2 dissociation; neither N^+ nor FeN^+ was obtained below 300 K. Atomic N was detected in small amounts at 2 V/Å field strength only in one experiment, where the Fe-specimen was pretreated at elevated temperature of 800 K for 1/2 h in 10^{-4} Torr N_2 .

IV - CONCLUSION

The application of pulsed laser field desorption to surface reactions such as those between N_2 and H_2 has several limitations:

1. Surface analysis can be performed for these systems only at low temperatures (i.e. $T < 300$ K). Otherwise, the coverage of the surface with reacting gas molecules is too low since temperature enhanced field desorption at the required desorption (and reaction-) field strength depletes the surface. Field pulse experiments with a low or negligible reaction field strength are preferable for investigating reaction intermediates in this case.
2. Since surface reactions are frequently altered by high electrostatic fields, laser pulse desorption may lead to products which differ from those of field-free chemical surface reactions.
3. Various ions of the mass spectrum may be formed, due to bond breaking, fragmentation, association or proton-capture, which do not represent original neutral compounds.
4. The photon pulse can - in principle - create additional field ions due to photo-reactions, thermally induced surface reactions or surface diffusion from the emitter shank.

5. We have observed extended isotope exchange reactions at the chamber walls after introducing different isotope gases. This complicated the proper mass assignment.

Taking these limitations into account, the following conclusions can be drawn for the reaction of nitrogen and hydrogen on iron surfaces:

- 1.) Our "low residual gas" experiments gave no evidence for NH_3 -synthesis on low index planes of Fe below 300 K; neither was N_2 -dissociation observed. The only evidence for the dissociated form of nitrogen came from experiments in which iron was pretreated with nitrogen at 800 K.
- 2.) Iron seems to be very sensitive to contamination from residual gas (e.g. CO, H_2O) leading to field enhanced oxidation, which yields O^+ ions, for instance.
- 3.) Adsorbed N_2 (as well as CO) blocks the adsorption of H_2 (the reverse was not observed).
- 4.) At and below best image voltage, the field ionization current consists mainly of field desorbed H_2 , recombined from pairs of H atoms which have diffused from the shank. A strong isotopic effect at $T < 150$ K is indicated by the relatively lower D_2^+ rates.

Iron surfaces behaved rather differently than platinum [3,4]. Traces of H_2O and other oxygen containing compounds probably lead to surface contamination by oxidation reactions with iron, which must be field dependent. A direct correlation of the particular properties of Fe and the reaction of nitrogen with hydrogen at higher temperatures and pressures is still lacking.

REFERENCES

- /1/ Ertl, G., CRC, Critical Rev. Solid State Mater. Sci. 10 (1982) 349.
- /2/ Schmidt, W.A., Angew. Chemie 4 (1968) 151.
- /3/ Ai, C.F., and Tsong, T.T., J. de Physique, C2-3 47 (1986) 347.
- /4/ Liu, W., and Tsong, T.T., Surf. Sci. 165 (1986) L26.
- /5/ Drachsel, W., Jentsch, Th., and Block, J.H., Int. J. Mass Spectrometry Ion Phys. 46 (1983) 293.
- /6/ Drachsel, W., Block, J.H., and Viswanathan, B., Springer Ser. in Chem. Phys. 33 (1983) 221.