Interaction of Nitrogen and Oxygen on Iron Surfaces

By

G. Ertl and M. Huber

Institut für Physikalische Chemie, Universität München,
München, W.-Germany

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Oxygen is a strong poison for the catalytic synthesis of ammonia from \( \text{N}_2 + \text{H}_2 \) over iron catalysts. On the other hand the formation of nitride in the surface region of iron samples provides protection against corrosion by oxygen. Surface analysis by means of Auger spectroscopy reveals that preadsorption of oxygen blocks the surface sites for dissociative nitrogen chemisorption. If on the other hand a nitried surface is exposed to oxygen, an oxide layer will be formed and the nitrogen atoms are displaced into the bulk where they cause retardation of further oxide growth. These effects are made plausible on the basis of the energetics of the various steps involved.

1. Introduction

Oxygen is one of most effective elements in poisoning the synthesis of ammonia over iron catalysts [1]. From thermodynamic data it can easily be estimated that even at 820 K a vanishingly small oxygen partial pressure over iron would give rise to the formation of oxides (\( \lesssim 10^{-26} \) atm), so that a metallic Fe surface can only be maintained under the reducing action of the
gas mixture used for the synthesis reaction. But also a very small water content in the hydrogen \( \frac{p_{H_2O}}{p_{H_2}} \geq 4 \times 10^{-4} \) Torr at 370 K) would again cause oxide formation [2], which underlines the very stringent conditions concerning gas purification.

On the other hand, nitrogenation of iron (by decomposition of ammonia) has been used for long times for hardening the surface region of steels [3], whereby also an anticorrosive effect, viz. inhibition or better retardation of the attack by oxygen or water is observed [4]. Since both processes, oxide as well as nitride formation, are preceded by the formation of chemisorbed oxygen or nitrogen layers, it is suggested that the mentioned inhibition effects are caused by blocking of the surface sites by pretreatment with the respective other element. The present paper describes the results of a series of experiments with a clean iron surface where this hypothesis was checked by surface analysis by means of Auger electron spectroscopy (AES). The conclusion will be that the just stated assumption is only partly correct.

2. Experimental

The experiments were performed within an UHV system which was equipped with an Auger electron spectrometer and a quadrupole mass spectrometer [5]. A polycrystalline Fe foil (0.8 cm² surface area, 0.3 mm thickness, 99.998 % purity) was used as sample which could be resistively heated. The sample temperature was recorded by a thermocouple spot-welded at the edge. Cleaning of the surface was achieved by prolonged oxidation-reduction cycles as well as by Ar⁺ ion bombardment; the state of purity was monitored by AES.

The surface concentration of nitrogen or oxygen was derived from determining the ratio of the intensities of the N1s (380 eV) or O1s (530 eV) AES signals over the Fe peak intensity at 655 eV, \( \frac{I_{N,380}}{I_{Fe,655}} \) and \( \frac{I_{O,530}}{I_{Fe,655}} \), respectively. The absolute nitrogen coverage was estimated on the basis of single crystal data [6, 7]: on all of the most important planes [(110), (100) and (111)] the maximum nitrogen surface concentration was \( 6 \times 10^{14} \) atoms/cm² corresponding to \( \theta_N = 0.85 \pm 0.05 \). If the surface atom density of polycrystalline iron is taken as the average of the four most densely packed planes a value of about \( 1.3 \times 10^{15} \) results. \( n_N = 6 \times 10^{14} \) atoms/cm² thus corresponds to a maximum coverage \( \theta_N = 0.46 \).

In a similar way data for oxygen adsorption on Fe(100) and (110) [8] were used to estimate that \( \theta_O = 0.9 \) corresponds to an oxygen coverage of \( 6.5 \times 10^{14} \) atoms/cm².

3. Results and discussion

The first series of experiments concerned the possible inhibition of (dissociative) nitrogen adsorption by the presence of preadsorbed oxygen on
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The surface. Since the dissociative chemisorption of nitrogen is a slow and activated process [6, 7] exposure to N\textsubscript{2} was performed at 670 K (which is also within the temperature range applied for ammonia synthesis) at a partial pressure of $1 \times 10^{-4}$ Torr until the maximum surface concentration of atomic nitrogen, $n_{max}$, was reached. These conditions are very far away from the thermodynamically allowed range in which formation of bulk nitrides is possible [5]; instead only 'surface nitride' phases are formed which have been characterized in detail with single crystal studies [6, 7]. Preadsorption of oxygen was achieved by exposing the clean iron surface to $5 \times 10^{-7}$ Torr O\textsubscript{2} at 300 K for varying times prior to the treatment with N\textsubscript{2}. The resulting surface concentrations of oxygen, $n_{0}$, were determined by AES as outlined in section 2.

The results are shown in Fig. 1 which clearly demonstrates that there is a linear decrease of the nitrogen uptake with the surface content of oxygen. The conclusion is that the nitrogen atoms occupy similar types of surface sites as the oxygen atoms. This statement is however only of rather qualitative nature, since it is well known that oxygen [8] as well as nitrogen [6, 7] interaction with iron causes surface reconstruction leading to different configurations of the Fe surface atoms. In any case it is evident that a O:Fe ratio of about 0.5 in the surface region will completely suppress the dissociative chemisorption of nitrogen, whereas further oxygen uptake up to the stoichiometry of FeO is readily achieved under the applied conditions [8]. Furthermore, there is no decrease of the O-Auger signal intensity due to
subsequent adsorption of nitrogen, that means that N atoms are obviously not able to displace oxygen from the surface into deeper layers of the metal.

The present findings are in agreement with earlier qualitative observations: Schulz and Schäfer [9] observed a strong suppression of the nitrogen isotope exchange reaction by the presence of oxygen, and Grabke [10] interpreted his kinetic measurements on nitrogenation of iron in \( \text{N}_2/\text{H}_2/\text{O}_2 \) mixtures by an inhibition effect due to adsorbed oxygen. The influence of the degree of reduction of Fe catalysts on the rate of dissociative nitrogen adsorption has been studied in detail by Scholten et al. and lead to similar conclusions [11, 12]. Oxygen impurities in the reaction gas for ammonia synthesis will thus cause partial oxidation of the iron particles which may be deliberated from the poisoning oxygen only by reduction with \( \text{H}_2 \) (or NH\(_3\)). But sequential oxidation/reduction cycles will be accompanied by transport of iron atoms which may lead to sintering of the small iron particles so that the effective surface area and thereby the activity of the catalyst is decreasing.

The reverse sequence of interactions was performed by first producing a complete layer of ‘surface nitride’ by treatment of a clean iron surface with NH\(_3\) (1 \( \times \) 10\(^{-5}\) Torr for 30 min) at 670 K [5]. Subsequent admission of 5 \( \times \) 10\(^{-6}\) Torr \( \text{O}_2 \) for 30 min at room temperature caused — somewhat surprisingly — a drastic variation of the surface composition: nitrogen was no longer detectable by AES whereas the intensity of the oxygen signal indicated already the formation of a thin oxide layer. Similar effects were observed at higher temperatures or even if an about 20 Å thick layer of bulk Fe\(_4\)N was covering the metal. Since nitrogen desorption from iron has a high activation energy (< 50 kcal/mole) and takes place only above 700 K the N atoms at the surface cannot have been displaced into the gas phase but one has rather to assume that they were diffusing into deeper layers and presumably dissolved in the bulk.

If a sample treated in this way was heated up to 1 250 K no desorption of \( \text{N}_2 \) could be observed. This could only be achieved after reduction of the oxide layer which therefore forms a very efficient barrier for back-diffusion of nitrogen atoms to the surface where only they may recombine to \( \text{N}_2 \).

A plausible explanation for the observed effects can be obtained on the basis of energetic considerations: the structure of the surface layer formed by chemisorption of nitrogen (‘surface nitride’) is quite similar to that of Fe\(_4\)N [6, 7], so that its stoichiometry will be designed by \((\text{Fe}_4\text{N})_x\). (If the topmost atomic layer alone is considered for the Fe(100) surface a stoichiometry \( \text{Fe}_2\text{N} \) would result. The other planes reconstruct upon interaction with nitrogen.) The studies by Ekelund and Leygraf [8] on the other hand revealed that interaction of oxygen with Fe at low pressures leads to formation of FeO (through various intermediate structures). Also the calorimetrically determined heat of chemisorption of oxygen on iron (133 kcal/mole \( \text{O}_2 \)) agrees rather well with the heat of formation of FeO (2 \( \times \) 65 = 130 kcal/mole \( \text{O}_2 \)).
The heat of chemisorption of N\textsubscript{2} on Fe is about 52 kcal/mole \[6, 7\], that means
\[
8 \text{Fe} + \text{N}_2 \rightarrow 2 (\text{Fe}_4\text{N})_s + 52 \text{ kcal/mole}
\]
or
\[
\text{Fe} + \frac{1}{8} \text{N}_2 \rightarrow (\text{FeN}_{0.25})_s + 6.5 \text{ kcal/mole}
\]  
(1)

whereas on the other hand
\[
\text{Fe} + \frac{1}{2} \text{O}_2 \rightarrow \text{FeO} + 65 \text{ kcal/mole}.
\]  
(2)

From this it becomes plausible, that the relatively small energy gain from reaction (1) is obviously not sufficient to ‘push’ the oxygen atoms into the bulk, although this process might be limited by kinetics rather than by thermodynamics. Therefore preadsorbed oxygen acts as an inhibitor for nitrogen chemisorption. On the other hand the heat of segregation of N atoms dissolved in α-Fe to the surface was determined to be about 26 kcal/g-atom \[15\], that means
\[
(\text{FeN}_{0.25})_s \rightarrow \text{Fe} + 0.25 \text{N (dissolved)} - 7 \text{ kcal/mole}.
\]  
(3)

Combination of Eqs. (2) and (3) leads to
\[
(\text{FeN}_{0.25})_s + \frac{1}{2} \text{O}_2 \rightarrow \text{FeO} + 0.25 \text{N (dissolved)} + 58 \text{ kcal/mole},
\]  
(4)

which demonstrates that displacement of N atoms from the surface into the bulk by interaction with gaseous O\textsubscript{2} will be energetically rather favourable. The bulk diffusion coefficient of N in pure Fe has at 900 K a value of about \num{1e-7} cm\textsuperscript{2}/s and an activation energy of 18.9 kcal/mole \[16\]. Extrapolation to room temperature yields a mean displacement by diffusion of about 5 Å within 30 min. This process will, however, certainly be strongly accelerated by the rearrangement of the Fe atoms in the course of oxide formation (oxygen chemisorption on Fe(100) was found to cause an expansion of the topmost layers \[17\]), as well as by the energy release associated with the oxygen attack so that displacement of the N atoms even at room temperature becomes feasible. On the other hand the further growth of the oxide will certainly be retarded by previous formation of a nitride layer in the surface region — this is the well known anti-corrosive effect. Sputter profiles recorded by Russo and Kaplow \[4\] from iron surfaces with and without pretreatment with nitrogen and subsequently exposed to air directly demonstrated this phenomenon.

Why is such a protection not achieved by simple treatment in air (a 4:1 N\textsubscript{2}:O\textsubscript{2} mixture)? The answer is very simple: the sticking probability for
dissociative chemisorption of nitrogen is smaller by at least five orders of magnitude than that of oxygen [6—8], so that no chance for surface nitride formation exists at all.

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References