

## XPS STUDIES WITH AMMONIA SYNTHESIS CATALYSTS

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Received 29 August 1978

Revised manuscript received 16 October 1978

The chemical nature and compositions of the surfaces of industrial Fe ammonia catalysts were investigated by means of X-ray photoelectron spectroscopy (XPS). Unreduced catalysts exhibit a strong enrichment of K and Al and only rather small Fe concentrations in the surface region. Treatment in  $N_2 + H_2$  mixtures (1 atm) at 350–400°C causes complete reduction of iron and a substantial increase of the surface concentration of this element whereas the other cations remain in their oxidized state. The establishment of the synthesis equilibrium was followed by means of a mass spectrometer. Under reaction conditions only relatively small stationary concentrations of atomic nitrogen are present on the surface which supports the conclusion that dissociative chemisorption of nitrogen is the rate-limiting step. After cooling the catalyst to room temperature in the reaction gas mixture in addition  $NH_2$  adsorbed to the oxidic components as well as NH and/or  $NH_2$  attached to iron were discovered.

### 1. Introduction

The Haber–Bosch process for the direct synthesis of ammonia from the elements,  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ , over promoted iron catalysts was developed during the beginning of this century and has since then developed into a huge industry [1]. Despite numerous studies in the past seven decades the detailed mechanism of this important catalytic reaction has not yet been fully explored [2]. It is hoped that further progress in this field may be achieved by the use of modern surface spectroscopic techniques along two lines. Firstly individual reaction steps and their influencing parameters may be studied with well-defined (preferentially single crystal) surfaces under gas pressures which are very far away from the real conditions. A series of papers dealing with this aspect have been published recently from our group [3–10] as well as from other laboratories [11–15]. Secondly a characterization of the surface properties of practical catalysts as well as studies under more realistic pressures conditions (say 1 atm instead of  $< 10^{-4}$  Torr) are needed. The ultimate goal is to combine the conclusions from both approaches in order to obtain a microscopic picture of this important chemical process.

The present work follows along this second way and is mainly concerned with the chemical characterization of the surface region of industrial catalysts and their

eventual modification under reaction conditions as well as with the identification of the nitrogen-containing species which may be formed during the interaction with the reactants. This information was obtained by the use of X-ray photoelectron spectroscopy (XPS). In situ analysis of the composition of the gas atmosphere by means of a mass spectrometer demonstrated the activity of the used catalysts through their ability to establish the thermodynamic equilibrium between the reactants and the product.

## 2. Experimental

The experiments were performed with a modified commercial XPS apparatus (Vacuum Generators, ESCA 3). The experimental setup is illustrated schematically by fig. 1. The spectrometer chamber is equipped with a X-ray source (Al K $\alpha$  and Mg K $\alpha$ ) and a hemispherical energy analyser and can be isolated from the preparation chamber by a Viton-sealed valve. Chemical treatments of the samples are per-

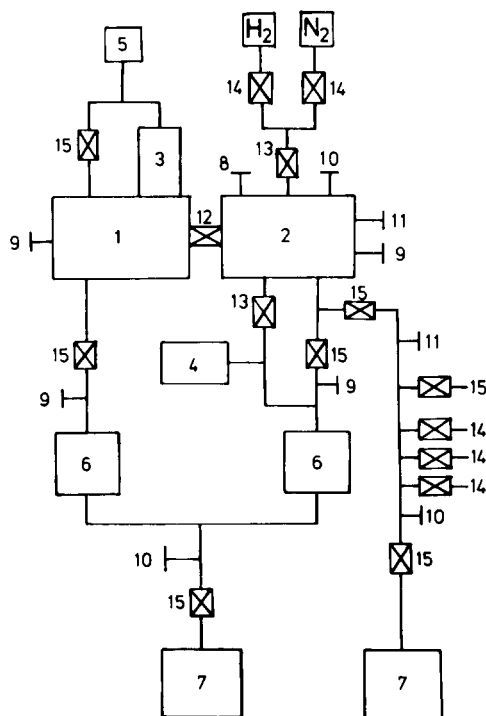


Fig. 1. Experimental apparatus (schematic): 1 spectrometer chamber, 2 preparation and reaction chamber, 3 X-ray source, 4 quadrupole mass spectrometer, 5 ion pump, 6 oil diffusion pumps with baffles, 7 rotary pumps, 8 argon ion gun, 9 ionization gauge, 10 Pirani gauge, 11 high pressure manometer, 12 Viton sealed gate valve, 13 leak valves, 14 gas inlet valves, 15 shut-off valves.

formed within the preparation chamber at pressures up to 1 atm while the spectrometer chamber is held under UHV conditions. The sample is mounted on a manipulator which allows transfer from the preparation into the spectrometer section and heating up to about 400°C. The temperature is measured by means of a chromel–alumel thermocouple. The X-ray source was operated with a stabilized electron current of 20 mA at an acceleration voltage of 12 kV. All spectra were recorded with the Al source ( $h\nu = 1486.6$  eV).

High purity gases were introduced through leak valves. The pressure was measured with a membrane manometer which was compatible with UHV conditions (Kontron P20X + UM80, 0.5 to 1000 Torr), a Pirani gauge (0.05 to 1 Torr) as well as with an ionisation manometer ( $10^{-10}$ – $10^{-2}$  Torr). Partial pressures could be recorded with a quadrupole mass spectrometer (Vacuum Generators Q7) which was attached through a variable leak valve and was pumped through a bypass line.

The samples were industrial ammonia catalysts from BASF and Haldor Topsøe. Suitable pieces were mounted on the manipulator by means of thin tungsten wires.

### 3. Results and discussion

#### 3.1. Characterization of the catalyst surfaces

XPS may be used for qualitative as well as quantitative analysis of the elemental composition of the surface region. The depth probed by this technique depends on the kinetic energies of the photoemitted electrons and is roughly about 10–20 Å, whereby of course the topmost atomic layers contribute more strongly to the observed intensity [16]. Quantitative analysis was achieved by the use of tabulated (experimental and theoretical) ionisation cross sections for the corresponding levels of the various elements [17]. The data concern the weighted average of the composition in the surface region across the probing depth of the technique and have to be considered at best as semi-quantitative values reflecting the trends of surface segregation if compared with the bulk composition. No attempt was made to extract more precisely the actual composition of the topmost atomic layer from these data since it is well known that the various constituents are in a non-uniform lateral distribution over the surface over which the large diameter of the X-ray excitation source averages. More detailed and qualitative information would be obtained by the use of scanning Auger electron spectroscopy in connection with depth profiling by means of noble gas ion sputtering.

Fig. 2 shows a typical spectrum over a limited energy range from a non-reduced catalyst (BASF S 6–10) exhibiting the presence of various elements. Not shown are the peaks originating from O and C which are the constituents with the highest concentrations. Table 1 compares the approximate compositions of the surface regions of various unreduced catalysts with the nominal bulk composition of one of the samples. Carbon is considered as a surface impurity partly arising from contact of

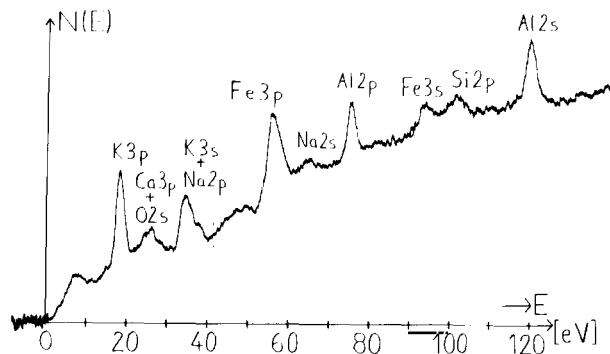


Fig. 2. Section of a typical spectrum from an unreduced catalyst (BASF S 6-10).

the sample with air and oil vapours from the pumping system and is not taken into account for the evaluation of the "true" composition. The concentration of Fe as the catalytically active component is surprisingly low, whereas potassium and aluminium (which act as promoters) appear to be strongly enriched at the surface. The composition varied sometimes appreciably between different catalysts and even between different pieces from the same charge indicating the existence of strong inhomogeneities even over macroscopic dimensions. The qualitative features, however, were in all cases rather similar.

Commercial ammonia catalysts are usually supplied in the unreduced form but also as samples where the oxide constituents have been partly reduced. The latter need only rather short reduction treatment within the synthesis plant in order to become catalytically active. The partly pre-reduced catalysts were found to exhibit usually a qualitatively rather similar surface composition as the non-reduced samples. Typically they exhibited a higher Fe and a lower C-content. Sometimes the outmost oxide layer was rather thin which became evident from the identification of small amounts of metallic iron. (The possible distinction between Fe in its oxidized and metallic form will be outlined below.)

Table 1  
Compositions (in at. %) of the surface regions of various unreduced doubly-promoted Fe catalysts and the bulk of the BASF S 6-10 catalyst

| Element                                     | Al   | Na | K    | Fe   | O     | Ca  | Si   | Cl      |
|---|------|----|------|------|-------|-----|------|---------|
| Concentration in the surface region (%)     | 6-10 | <1 | 6-20 | 1-6  | 50-70 | 1-5 | ≈2   | 0.5-3.5 |
| Concentration in the bulk (%) (BASF S 6-10) | 2    |    | 0.35 | 40.5 | 53.2  | 1.7 | 0.25 |         |

Three different samples were reduced with  $N_2/H_2$ -mixtures within the vacuum system. The  $N_2:H_2$  ratio varied between 1:2 and 1:3. The total pressure was about 600 to 700 Torr, and the reduction was performed at temperatures between 350 and 400°C. At different stages the reducing gas was pumped off and the sample analyzed by XPS. Since during the reduction  $H_2O$  is formed which in turn may re-oxidize the surface [18], the composition of the gas atmosphere was carefully analyzed by the mass spectrometer which was attached to the reaction chamber through a leak. As soon as  $H_2O$  became detectable the gas atmosphere was replaced by a fresh  $N_2 + H_2$  mixture. These reduction conditions are quite similar to those applied in practice [19,20], although the total pressure is then usually higher which is, however, without importance (see ref. [1], p. 97). A higher temperature would yield faster reduction, but would also lower the activity since the crystallites could increase in size more easily [21].

During the reduction procedure appreciable variations of the surface composition take place which are indicated qualitatively in table 2. A typical example for the composition of the surface region of a reduced sample (catalyst II of sect. 3.2) is as follows: Fe 15%, K 8%, Ca 7%, Al 11%, Si 2%, Na 2%, O 46%, N 0.5%, Cl 0%, C 9%. It is remarkable that the concentration of the catalytically active element Fe increases considerably by the reduction process. In turn the concentration of C is lowered, and it was observed that the carbon content is the smaller the higher the Fe concentration. From this observation it is concluded that carbon covers those parts of the surface which do not contain iron. It is believed that C atoms on metallic iron are reacted off either by hydrogen to  $CH_4$  or by oxygen to CO.

Variations of the chemical state of the elements during reduction may be followed by observing changes of the corresponding core-level ionization ("chemical shifts"). Fig. 3 shows the Fe  $2p_{3/2}$  peak at various stages of reduction where a very pronounced effect is observed: With the unreduced sample a broad maximum centered at 711.3 eV is observed which is identified with the starting material  $FeAl_2O_4 +$

Table 2  
Qualitative changes of the surface compositions by reduction of the catalysts

| Elements | Variation of surface concentration  |
|----------|-------------------------------------|
| Fe       | Increases by up to a factor 3       |
| K        | Essentially unchanged               |
| Ca       | Increases by up to a factor 2-3     |
| Al       | Increases typically by 25%          |
| Si       | Essentially unchanged               |
| Na       | Increases markedly                  |
| O        | Decreases appreciably (as expected) |
| N        | Build-up of small concentration     |
| Cl       | Disappears nearly completely        |
| C        | Strongly suppressed                 |

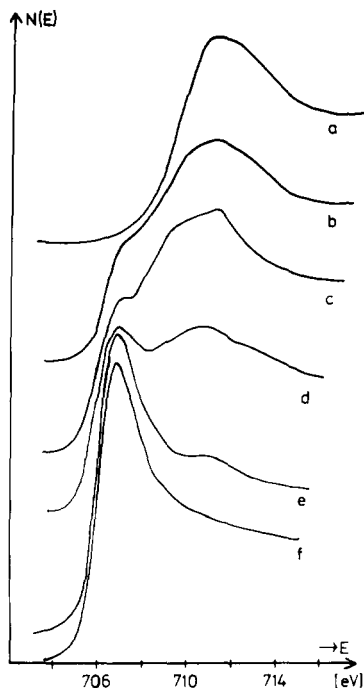


Fig. 3. XPS data of the Fe  $2p_{3/2}$  level at various stages of reduction: a unreduced sample, b–e continuous increase of the content of metallic iron, f completely reduced sample.

$\text{Fe}_2\text{O}_3$  [22]. With increasing degree of reduction this peak is decreasing whereas simultaneously a new one at 706.8 eV is growing up. The latter is identified with metallic  $\alpha$ -Fe which is the only iron species left after complete reduction. Its relatively narrow width, the ionization potentials as well as the chemical shift of about 4 eV agree qualitatively well with the results of earlier studies on the oxidation of pure Fe into  $\text{Fe}_2\text{O}_3$  ( $\Delta E = 4.2$  eV [23]) and into  $\text{Fe}_3\text{O}_4$  ( $\Delta E = 3.5$  eV [24]). Slight differences in the absolute values of the binding energies may be attributed to the general problem of the reference level, as well as to the “paracrystalline” structure of Fe in the reduced catalysts [25].

Another variation is observed with the O 1s peak whose maximum is shifted from 532.9 eV to 531.4 eV upon reduction. The unreduced sample exhibits only a weak shoulder at the latter energy. This effect is not solely interpreted as being caused by the removal of part of the oxygen, since a large portion of the oxygen remains in the sample. This obvious chemical shift might be connected with the structural transformation, e.g. the disappearance of an ordered spinel structure by reduction of one of the components. With partly pre-reduced samples the O 1s peak was found at the beginning at 531.5 eV (sometimes a shoulder at higher binding energies is observed) and is only decreasing its intensity during further reduction which may support this

conclusion.  $\text{Fe}_3\text{O}_4$  has a spinel structure, consisting of compact  $\text{O}^{2-}$  ions, which form octahedral and tetrahedral interstices.  $\text{Fe}^{3+}$  ions can be replaced by  $\text{Al}^{3+}$  ions to form  $\text{FeAl}_2\text{O}_4$  without altering the lattice. Upon reduction of the iron ions aluminium is structurally transformed into  $\text{Al}_2\text{O}_3$ . This hypothesis is supported by the observation that addition of alumina lowers appreciable the reduction rate of  $\text{Fe}_3\text{O}_4$  [26] which would be difficult to explain if separate particles of  $\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$  would exist.

None of the other cations was observed to exhibit a chemical shift of its core-level binding energies which indicates that iron is the only element which is transformed into its metallic state by the applied reduction procedure. Another qualitative observation appears to be worth mentioning: If pure iron oxides are reduced into the metallic state it was found that considerably more rigorous treatments had to be applied than in the case of the Fe catalysts. This was also the case if a once reduced catalyst became accidentally reoxidized. This effect is probably due to the much higher degree of dispersion, but might also be influenced by the presence of the other components although no explanation for such an effect could be offered at present.

### 3.2. Formation of ammonia

The establishment of the equilibrium  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  through the formation of  $\text{NH}_3$  from  $\text{N}_2 + \text{H}_2$ -mixtures was studied with two reduced catalyst samples, mainly in order to check that the samples were indeed catalytically active and did not further change their surface composition even by prolonged operation under reaction conditions. The second purpose was to demonstrate that reliable data for the gas composition in a UHV system may be continuously obtained by mass spectrometry even if it is operated under atmospheric pressure conditions.

The vacuum system was operated as a batch reactor. The sample was moved behind the closed valve separating the spectrometer chamber from the rest of the apparatus. A  $\text{H}_2 + \text{N}_2$  mixture with varying composition and a total pressure of 700 Torr was introduced and the sample kept at temperatures between 320 and 370°C. Gas analysis was performed by means of a continuously pumped quadrupole mass spectrometer which was attached to the reaction chamber through a variable leak valve. The partial pressures of  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{NH}_3$  were continuously recorded until over a longer period of time (several hours) no further variation took place. The data were then considered to represent the equilibrium composition of the gas phase within the reaction chamber at the given sample temperature. Identical experiments without the catalysts revealed no detectable formation of  $\text{NH}_3$  even over very long periods of time which demonstrated that in fact only the activity of the catalyst was responsible for the establishment of the equilibrium. On the other hand it was observed that the sample holder (which was always at a higher temperature than the catalyst) showed some tendency for decomposition of  $\text{NH}_3$ . As a consequence the equilibrium composition corresponding to the temperature of the catalyst could not

be reached if the rate of formation was too small. It turned out that this disturbing effect dominated at sample temperatures below 320°C. Since the equilibrium concentration of NH<sub>3</sub> drops rapidly with temperature no attempts were made to perform measurements above 370°C.

The theoretical equilibrium yields of NH<sub>3</sub> at give temperatures and N<sub>2</sub> and H<sub>2</sub> pressures were evaluated through the tabulated equilibrium constant  $K_p = p_{\text{NH}_3} / p_{\text{N}_2}^{1/2} p_{\text{H}_2}^{3/2}$  (see ref. [1], p. 21).

The experimentally derived ammonia yields for different conditions are reproduced in table 3 together with the corresponding theoretical values. As can be seen the agreement is (with one exception) fairly good. The experimental values are generally somewhat lower than the theoretical ones which is due to the above-mentioned effect that the hot sample holder tends to dissociate the formed NH<sub>3</sub>. Catalyst I contained less Fe in the surface region than catalyst II and was therefore less active. As a consequence the NH<sub>3</sub> yield determined with this sample at the lowest temperature (325°C) is too low by 50%. The results demonstrate in general that reliable measurements of the gas composition can be performed by the applied technique and that the samples are in fact catalytically active.

After finishing these experiments again XPS data were recorded which demonstrated that no noticeable changes of the chemical state and composition of the surface region of the catalysts had occurred. A special situation is found, however, with the N 1s peak which yields information on the surface species formed as will be outlined in the next section.

### 3.3. Nitrogen containing surface species

Several characteristic peak shapes and binding energies of the N 1s level were observed during this work which may be used for an identification of various nitrogen containing species on the surfaces of the catalysts. In a previous study [10] the formation of surface and bulk nitrides on pure iron was followed by the XPS technique.

Table 3

Experimental and theoretical NH<sub>3</sub> yields from N<sub>2</sub> + H<sub>2</sub> mixtures at various ratios with a total pressure of 700 Torr and at different temperatures

| Catalyst | T(°C) | $p_{\text{N}_2} : p_{\text{H}_2}$ | Experimental<br>NH <sub>3</sub> yield (°/00) | Theoretical<br>NH <sub>3</sub> yield (°/00) |
|----------|-------|-----------------------------------|--|---|
| I        | 370   | 0.38                              | 4.4  | 5.2   |
| I        | 340   | 0.73                              | 6.7  | 7.8   |
| I        | 325   | 0.46                              | 5.0  | 10.8  |
| II       | 350   | 0.71                              | 6.7  | 7.1   |
| II       | 335   | 0.58                              | 9.4  | 9.3   |
| II       | 345   | 0.57                              | 6.7  | 7.8   |
| II       | 320   | 0.55                              | 9.8  | 11.5  |

It revealed that atomic nitrogen exhibits a relatively narrow (2 eV wide) peak at an ionization energy of 397.8 eV, which is in agreement with other data reported in the literature [11,13,14,27]. The shapes and ionization energies of the Fe 2p core levels remained practically unaffected by the nitride formation which indicates a negligible ionic character of the Fe–N bond.

(i) A quite similar N 1s peak with a binding energy of 397.5 eV was observed if a well reduced catalyst was operated in a  $N_2 + H_2$  mixture at 350°C for a longer period of time and if the gas was completely pumped off while the catalyst was still hot (fig. 4). This species is accordingly identified with atomic nitrogen. An estimate of its actual surface concentration will be given below. The binding energies of all the other elements were unaffected by the presence of this species which is rather strongly held at the surface and disappears only above 400°C. There is strong evidence that the nitrogen atoms are in fact only attached to the metallic iron: The high bond strength indicates a strong chemical interaction. A loosely bound nitrogen species on the surface of one of the oxides can therefore be ruled out. If however one of the other cations would change its chemical state from an oxide into a nitride one would expect pronounced marked chemical shifts of their core level ionization energies which is not observed. (By transforming iron oxide into nitride this shift is in fact of the order of 4 eV!)

(ii) If instead the reduced catalyst is cooled down to room temperature in the reaction mixture which is only subsequently pumped off N 1s spectra as reproduced in fig. 5 are recorded. These features are rather broad (about 5 eV) and exhibit at least three distinct peaks. One of them is still at 397.5 eV and is again identified with atomic nitrogen on Fe. The origin of the other two peaks will be discussed later. Upon heating in vacuo at first the species characterized by a N 1s binding energy around 400.5 eV disappears at about 100°C (fig. 6). At even higher temperatures ( $\approx 200^\circ\text{C}$ ) also the species in the 399 eV range is removed and the situation characterized by fig. 4 (only atomic nitrogen) is established.

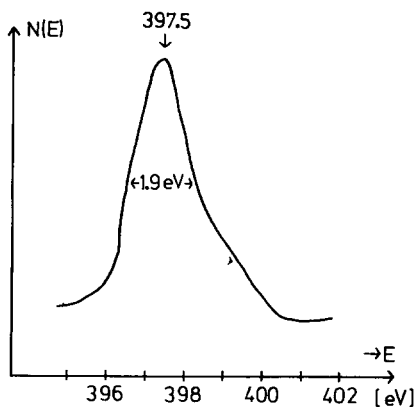


Fig. 4. N 1s peak from atomic nitrogen surface species.

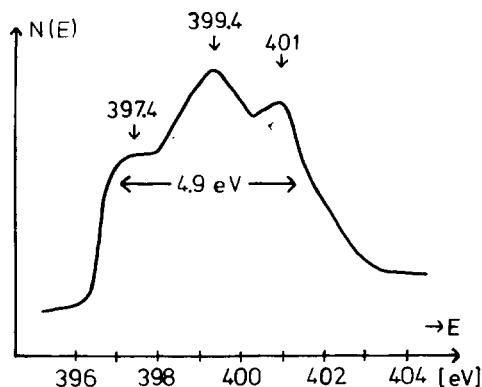


Fig. 5. N 1s spectrum from a catalyst cooled down to room temperature in the reaction mixture, exhibiting the presence of at least three different nitrogen containing surface species.

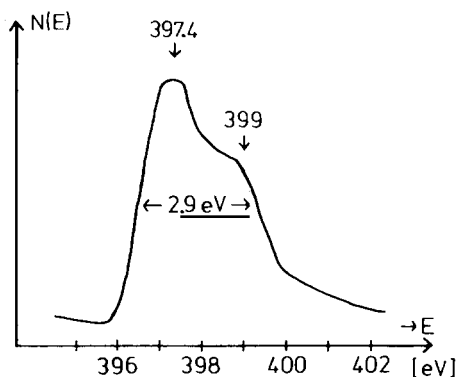


Fig. 6. N 1s spectrum from a sample characterized by fig. 5 after subsequent heating to 100°C in vacuo.

(iii) If the N 1s level of the pre-reduced catalysts without any further treatment is recorded one observes only a weak maximum at about 400.5 eV. When the reduction had been started spectra of the type as reproduced in fig. 7 are obtained which are similar in shape to fig. 5. According to the Fe 2p peaks these samples contain most of the iron in the oxidized form. The shoulder at 397.5 eV in fig. 7 is only observed if the catalysts contain already small amounts of metallic iron. This observation supports again the above conclusion that atomic nitrogen is only attached to reduced Fe. These pre-reduced catalysts were clearly smelling of ammonia when removed from the container. This simple test demonstrates that  $\text{NH}_3$  is present on the surface of these samples. The N 1s peak in the energy range around 400.5 eV is identified with adsorbed  $\text{NH}_3$  for the following reason: Grunze [14] reported on a N 1s binding energy of about 400 eV if a clean Fe(111) surface was exposed to am-

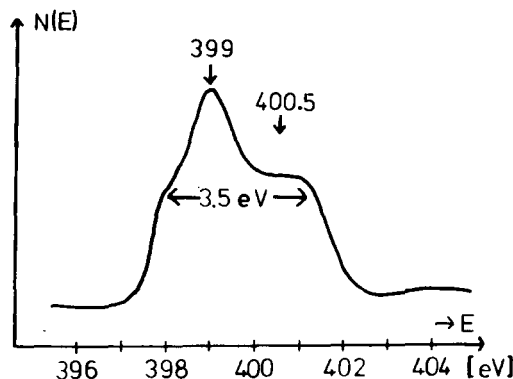


Fig. 7. N 1s spectrum from a "pre-reduced" catalyst (most of the iron is still in the oxidized form) without any further treatment.

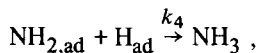
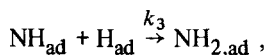
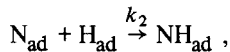
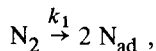
monia at 126 K. The non-dissociative character of adsorption could in this case clearly be demonstrated on the basis of the UPS data from the valence electron region [7,8]. On the other hand ammonia adsorbed on clean iron either desorbs or dissociates at room temperature [8,9], whereas in the present case it is still stable above room temperature. This effect together with the observation that this species is even observed if the catalyst contains no reduced iron at all leads to the conclusion that the adsorbed ammonia detected in the present study is attached to the surfaces of the oxide particles rather than to metallic iron.

The remaining species characterized by an ionization energy in the range of 399 eV has to be identified with adsorbed NH and/or NH<sub>2</sub>. The maximum of this peak scatters by about 0.5 eV which indicates that in fact a mixture of both species may be present. Matloob and Roberts [13] suggested that particles with binding energies around 398 and 399 eV, which were observed as transients during the decomposition of N<sub>2</sub>H<sub>4</sub> on polycrystalline iron, are to be identified with NH<sub>ad</sub> and NH<sub>2,ad</sub>, respectively. Similar conclusions were reached by Grunze with the system N<sub>2</sub>H<sub>4</sub>/Fe(111) [14]. In a recent study with the system NH<sub>3</sub>/Fe(110) adsorbed NH was identified as predominant intermediate which is stable up to about 150°C where it dissociates completely [9,28]. Since the 399 eV peak was also observed with samples which contained almost no metallic iron it is concluded that the NH/NH<sub>2</sub> species may also be formed on oxide surface, in contrast to N<sub>ad</sub>.

The discussed results suggest that under reaction conditions ( $T \gtrsim 350^\circ\text{C}$ ) obviously atomic nitrogen is the only surface species which is present in appreciable concentrations. However, one has to be careful with quantitative conclusions since spectroscopic measurements may never be performed under pressure conditions as applied for the reaction. Since adsorbed NH<sub>3</sub> and NH/NH<sub>2</sub> either desorb or dissociate in vacuo at higher temperatures it cannot be excluded that these species are also present on the surface under the actual pressure conditions during the reaction.

Qualitative information may, however, be obtained on the nature of the rate-

limiting step under reaction conditions from the following considerations: If the reaction mechanism is formulated as a sequence of consecutive steps



the stationary concentration of  $\text{N}_{\text{ad}}$  should be rather small if the first step (i.e. the dissociative chemisorption of nitrogen) is rate-limiting, but should be close to the saturation value if this step is faster than the subsequent hydrogenation of the nitrogen atoms. Since no nitrogen atoms are lost during pumping-off the gas mixture at 350°C the afterwards recorded N concentration should reflect the actual situation under reaction conditions. (By contrast it can even be expected that this amount still increases due to decomposition of  $\text{NH}_3$  which is not so quickly pumped off as  $\text{N}_2$  and  $\text{H}_2$ .)

Analysis of the intensities of the N 1s and Fe 2p peaks revealed an atomic ratio in the surface region of about N : Fe  $\approx$  1 : 15 which is much smaller than that which is observed if the same catalyst is saturated with atomic nitrogen (N : Fe  $\approx$  1 : 4). From this result it is concluded that in fact chemisorption of nitrogen is the rate-limiting step for ammonia synthesis from a stoichiometric mixture of  $\text{N}_2 + \text{H}_2$  at a pressure of about 1 atm and in the temperature range around 350°C. This conclusion is in agreement with the assumed reaction mechanism which is commonly accepted in the literature [2]. It is also supported by the results of a recent more detailed kinetic study with clean iron surfaces [29]. In this work it was found for example that under steady-state conditions at  $p_{\text{N}_2} = 150$  Torr and  $T = 580$  K the surface concentration of atomic nitrogen (as determined by Auger electron spectroscopy) dropped by a factor of 3 when the  $\text{H}_2$  pressure was increased from 10 Torr to 450 Torr.

#### 4. Conclusions

The main conclusions of the present work are:

(i) Unreduced industrial ammonia catalysts contain rather little Fe in the surface region (if compared with the bulk composition), whereas Al and K are strongly enriched at the surface. Such an effect was already suggested in the earlier literature by Emmett et al. [30,31] on the basis of indirect information. The XPS data indicate the existence of an iron-aluminium spinel which would agree with the  $\text{FeAl}_2\text{O}_4$  species reported in the literature [22–34].

(ii) Operation of the catalyst in a  $\text{H}_2 + \text{H}_2$  mixture at reaction conditions leads

to the reduction of iron in its metallic state, together with an substantial increase of the surface concentration of this element. All the other cations remain in their oxidized state. Complete reduction into  $\alpha$ -Fe is also reported in the literature [35]. According to other papers [25,36] this process takes completely place only if the  $\text{Al}_2\text{O}_3$ -content (referred to the concentration of  $\alpha$ -Fe) is smaller than 2%. Although the studied BASF catalyst contained nominally more than 2%  $\text{Al}_2\text{O}_3$  there was no evidence for the presence of Fe in the surface region other than in the metallic state. The situation might however be different in the bulk which is not probed by the XPS technique.

(iii) The surface concentration of atomic nitrogen under reaction conditions at 1 atm is rather small which supports the conclusion [1,37] that metallic iron rather than iron nitride is the catalytically active species. These findings are also supporting the widely accepted reaction mechanism whereafter dissociative chemisorption of nitrogen is the rate-limiting step.

(iv) Besides atomic nitrogen adsorbed  $\text{NH}_3$  as well as  $\text{NH}$  and/or  $\text{NH}_2$  species were identified. Ammonia is attached to oxidic parts of the surface whereas the latter species are reaction intermediates on metallic iron. This result is in agreement with previous model studies with clean Fe single crystal surfaces [8,9,28] and is of importance for understanding the mechanism of ammonia synthesis.

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