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<th>ADSORPTION OF NH₃ ON IRON SINGLE CRYSTAL SURFACES: (110), (111) AND STEPPED (111) SURFACES</th>
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<td>YOSHIDA, Kiyohide</td>
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ADSORPTION OF NH\textsubscript{3} ON IRON SINGLE CRYSTAL SURFACES; (110), (111) AND STEPPED (111) SURFACES

By

Kiyohide YOSHIDA*\textsuperscript{a)}

(Received May 16, 1980)

Abstract

The adsorption and decomposition of ammonia on the Fe (110), (111) and stepped (111) surfaces were studied by means of LEED, Auger electron spectroscopy and thermal desorption spectroscopy. A well ordered (2×2) surface structure is produced on the (110) surface on ammonia adsorption followed by flashing to 310 K. It was attributed to adsorbed NH\textsubscript{2} and NH by considering the amount of hydrogen desorbed. This surface structure is to some extent destroyed by the LEED beam exposure and then recovers again on mild heating. After the desorption of hydrogen the surface structures \( \begin{bmatrix} 4 & 0 \\ -1 & 3 \end{bmatrix} \), \( (3 \times 3) \), \( \begin{bmatrix} 2 & -1 \\ 2 & 4 \end{bmatrix} \) and \( \begin{bmatrix} 2 & 0 \\ 1 & 6 \end{bmatrix} \) due to nitrogen adatoms are produced on the (110), (111), 3(111)×(110) and 4(111)×(110) surfaces, respectively. On the oxygen-covered (110) surface, another surface structure \( \begin{bmatrix} 1 & -1 \\ 1 & 2 \end{bmatrix} \) besides the (2×2) is formed of adsorbed NH\textsubscript{2} and NH under the LEED beams. The surface structure \( \begin{bmatrix} 7 & 0 \\ -3 & 4 \end{bmatrix} \) produced after complete decomposition of ammonia differs from the structure \( \begin{bmatrix} 4 & 0 \\ -1 & 3 \end{bmatrix} \) on the oxygen-free (110) surface formed after a similar treatment.

1. Introduction

The interaction between ammonia and iron surface has been extensively studied in relation to the synthesis of ammonia. Wahba and Kembal\textsuperscript{b)} have measured calorimetrically the heats of adsorption of ammonia and hydrogen on evaporated iron films at 249 K. They have concluded the dissociative adsorption of ammonia as NH\textsubscript{3}→NH\textsubscript{2}(a)+H(a). The dissociation has also been deduced from measurement of changes in the work function due to ammonia adsorption on the films evaporated.\textsuperscript{b)} The rate of the decomposition of ammonia has been suggested to be controlled by the desorption of nitrogen from the dependences on NH\textsubscript{3} and H\textsubscript{2} pressures.\textsuperscript{b)} Through X-ray diffraction analysis the formation of \( \gamma' \)-nitride Fe\textsubscript{4}N has been

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concluded when the proportion of ammonia is high. Similar results have been reported by Löffler and Schmidt using scanning electron microscope and Auger electron spectroscopy (AES). Infrared spectroscopic observation of the surface species produced after the decomposition or synthesis of ammonia has been accomplished by Nakata and Matsushita. The species newly formed has been identified as NH$_2$(a) by comparing its spectrum with that of the species deuterated.

Kishi and Roberts have reported ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) studies on the adsorption of ammonia over polycrystalline iron surface at 80-290 K under very low pressures. Ammonia is adsorbed molecularly at 80 K, while dissociatively at 290 K. At high coverages molecular ammonia coexists with dissociated species even at 290 K. On the Fe (111) surface around 300 K Gay et al. have obtained similar results to those at 290 K mentioned above. Recently, Grunze et al. have studied the ammonia adsorption and decomposition on the clean and nitrogen-covered Fe (111) and Fe (100) surfaces using UPS, LEED (low-energy electron diffraction), thermal desorption spectroscopy (TDS) and work function measurements. Their results have shown that the last species containing N-H bonds is lost from the surface at 320 K, either through desorption as NH$_3$ or dissociation into N(a) and H(a), and that the presence of preadsorbed atomic nitrogen suppresses the complete dissociation.

In the previous paper we reported the adsorption and decomposition of ammonia on the Fe (110) and Fe (111) surfaces, and pointed out the difference between them. On the Fe (111) surface the desorption spectra of hydrogen and nitrogen were similar to those reported by Grunze et al., while on the Fe (110) surface a well ordered surface structure was observed after the adsorption, and further two desorption peaks of hydrogen appeared contrary to a single desorption peak over the Fe (111). In this paper we will report the ammonia adsorption and decomposition on the stepped Fe (111) surfaces besides on the Fe (110) and Fe (111) surfaces. The mechanism of the evolution of hydrogen from the surface covered with ammonia is discussed. We also studied the effects of the LEED beams and oxygen impurity on the surface structures produced by the adsorption of ammonia on the Fe (110) surface. Details of the experimental equipment and sample cleaning procedure were reported previously.

2. Results

2.1 NH$_3$ adsorption on the (110) surface
2.1.1. **Surface structures**

The adsorption of ammonia around 273 K produces a \((2 \times 2)\) pattern with very weak and diffuse half-order spots above 1 L \((1 \text{ L} = 10^{-6}\text{torr}\cdot\text{sec})\). The integral-order spots remain unchanged in their intensity and sharpness. The half-order spots become very sharp and bright on mild heating \((\sim 310 \text{ K})\) (Fig. 1). The overlayer structure due to the ammonia adsorbed is very sensitive to the LEED beam exposure \((\geq 30 \text{ eV})\). The half-order spots are altered to be more diffuse by a short irradiation. They, however, recover again very sharp and bright on mild heating. This \((2 \times 2)\) pattern is stable on flashing up to \(\sim 470 \text{ K}\). Above this temperature the half-order spots become weak in intensity. On flashing to \(\sim 520 \text{ K}\), the \((2 \times 2)\) pattern changes into a sharp \(\begin{vmatrix} 4 & 0 \\ -1 & 3 \end{vmatrix}\) pattern and further into a \((1 \times 1)\) pattern on flashing to \(\sim 900 \text{ K}\)\(^*\). The \(\begin{vmatrix} 4 & 0 \\ -1 & 3 \end{vmatrix}\) LEED pattern, and schematic diagrams of the LEED pattern and the \(\begin{vmatrix} 4 & 0 \\ -1 & 3 \end{vmatrix}\) surface structure are shown in Fig. 2. Table 1 shows the LEED patterns obtained after flashing the surface covered with

![Fig. 1. LEED pattern of the \((2\times2)\) surface structure obtained after chemisorption of \(\text{NH}_3\) on the \(\text{Fe}\) (110) at \(\sim 273 \text{ K}\) and then flashing to \(\sim 310 \text{ K}\) \((82 \text{ eV})\).](image)

\(^*\) After long exposure of ammonia and stepwise flashing to higher temperature, oxygen was detected with nitrogen on the surface by AES and then a \((2\times2)\) surface structure due to oxygen adatoms was formed on flashing to \(\sim 900 \text{ K}\).
Fig. 2 a. LEED pattern of the $\begin{pmatrix} 4 & 0 \\ -1 & 3 \end{pmatrix}$ and $\begin{pmatrix} 3 & -1 \\ 4 & 0 \end{pmatrix}$ surface structures obtained after heating the NH$_3$ covered surface to ~520 K (87 eV).

Fig. 2 b. Schematic diagram of the LEED pattern of the $\begin{pmatrix} 4 & 0 \\ -1 & 3 \end{pmatrix}$ and $\begin{pmatrix} 3 & -1 \\ 4 & 0 \end{pmatrix}$ surface structures.

TABLE 1. LEED patterns due to NH$_3$ adsorption on the clean surface

<table>
<thead>
<tr>
<th>LEED pattern</th>
<th>Flashing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>weak (2×2)</td>
<td>(as adsorbed around 273 K) 310~470 K</td>
</tr>
<tr>
<td>bright (2×2)</td>
<td>~520 K</td>
</tr>
<tr>
<td>$\begin{pmatrix} 4 &amp; 0 \ -1 &amp; 3 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 3 &amp; -1 \ 4 &amp; 0 \end{pmatrix}$ (1×1) $\sim$900 K</td>
</tr>
</tbody>
</table>
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Fig. 2 c. Schematic diagram of the $\| \frac{3}{4} \frac{-1}{0} \|$ and $\| \frac{4}{0} \frac{-1}{3} \|$ surface structures.

ammonia to various temperatures.

A weak (2 × 2) pattern due to residual oxygen adatoms was occasionally observed during the surface cleaning procedures. The adsorption of ammonia on the oxygen-contaminated surface produces the (2 × 2) pattern with very weak and diffuse half-order spots, which is quite similar to that observed on the clean surface. The overlayer structure due to adsorbed ammonia is also sensitive to LEED beam exposure, i.e. the half-order spots become further diffuse and a new $\| \frac{1}{1} \frac{-1}{2} \|$ pattern is superposed contrary to the clean

Fig. 3 a. LEED pattern of the (2×2)+$\| \frac{1}{1} \frac{-1}{2} \|$ surface structure obtained after mild heating the NH₃ covered Fe(110) −(2×2) which undergoes LEED beam effect (80 ev).
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Fe(110)-(2x2)/NH₃

Fig. 3 b. Schematic diagram of the LEED pattern of the (2x2)+ surface structure.

Fig. 4 a. LEED pattern of the \[ \begin{array}{c} 7 \\ -3 \\ 4 \end{array} \] surface structure obtained after heating the NH₃ covered Fe(110)-(2x2) to \( \sim 600 \text{ K} \) (97 eV).
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Fe(llO)-(2x2)/NH₃

Fig. 4b. Schematic diagram of the LEED pattern of the \( \begin{vmatrix} 7 \\ 4 \\ -3 \\ 4 \end{vmatrix} \) surface structure.

surface. On mild heating up to 310 K the mixed pattern becomes sharp and bright. The LEED pattern and the schematic diagram are shown in Fig. 3. The \( \begin{vmatrix} 1 \\ 1 \\ 1 \\ 2 \end{vmatrix} \) pattern disappears on flashing to \( \sim 390 \) K and a weak \( (2 \times 2) \) pattern which is probably due to oxygen still remains. On flashing to \( \sim 500 \) K, a \( \begin{vmatrix} 7 \\ 4 \\ -3 \\ 4 \end{vmatrix} \) pattern newly appears as shown in Fig. 4, while the weak \( (2 \times 2) \) pattern is still observed on parts of the surface. The \( (2 \times 2) \) pattern also changes into a \( \begin{vmatrix} 7 \\ 4 \\ -3 \\ 4 \end{vmatrix} \) pattern after repeated ammonia adsorption and flashing to high temperatures. Table 2 shows the LEED patterns obtained after flashing the oxygen-contaminated surface covered with ammonia to various temperatures, and also the LEED beam exposure effect.

Table 2. LEED patterns due to NH₃ adsorption on the oxygen contaminated \( (2 \times 2) \) surface

<table>
<thead>
<tr>
<th>LEED pattern</th>
<th>Flashing temperature</th>
<th>LEED pattern (LEED beam effect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>weak ( (2 \times 2) ) (as adsorbed around 273 K)</td>
<td>{diffuse ( (2 \times 2) ), diffuse ( \begin{vmatrix} 1 \ 1 \ 1 \ 2 \end{vmatrix} )|</td>
<td></td>
</tr>
<tr>
<td>bright ( (2 \times 2) ) ( 310 \sim 390 ) K</td>
<td>{bright ( (2 \times 2) ), bright ( \begin{vmatrix} 1 \ 1 \ 1 \ 2 \end{vmatrix} )|</td>
<td></td>
</tr>
<tr>
<td>( \begin{vmatrix} 7 \ 4 \ -3 \ 4 \end{vmatrix} ) ( \sim 500 ) K</td>
<td>( \begin{vmatrix} 7 \ 4 \ -3 \ 4 \end{vmatrix} ) ( \begin{vmatrix} 1 \ 1 \ 1 \ 2 \end{vmatrix} ) ( (1 \times 1) ) |</td>
<td></td>
</tr>
</tbody>
</table>
2.1.2. *Thermal desorption*

Hydrogen and nitrogen are main products desorbed on flashing the ammonia adsorbed surface. Nitrogen starts to be desorbed around 750 K. The desorption spectra of hydrogen are shown in Fig. 5. The spectra show two desorption peaks, the first peaks around 380 K (termed as \( \beta_1 \)) and the second around 435 K (\( \beta_2 \)). The desorption peaks are similar to those for hydrogen adsorption (Fig. 6). The ratio of population of \( \beta_1 \) and \( \beta_2 \) hydrogen is estimated to be 2 to 1 for the adsorption around 273 K. Assuming that all the desorbed hydrogen arise from the decomposition of ammonia adsorbed and that the coverage* of hydrogen (\( \theta \)) is 0.5 when the C(2 \( \times \) 2)

\[ 
\begin{align*}
\text{Fe(110)/NH}_3 & \\
\beta_1 & \text{380} \\
\beta_2 & \text{435} \\
\end{align*}
\]

*Fig. 5. Thermal desorption spectra of hydrogen from the Fe(110) following NH\(_3\) adsorption at \( \sim 273 \) K.*

\[ 
\begin{align*}
\text{Fe(110)/H}_2 & \\
\alpha & \text{1L (1x1)} \\
\beta & \text{1BL C(2 \times 2)} \\
\gamma & \text{60L, streak pattern} \\
\end{align*}
\]

*Fig. 6. Thermal desorption spectra of hydrogen from the Fe(110) following H\(_2\) adsorption at \( \sim 273 \) K.*

* The coverage means the mount of adspecies per a surface Fe atom in the outermost layer.
Adsorption of NH₃ on Iron Single Crystal Surfaces

The adsorption of ammonia around 273 K produces a (1×1) pattern with high background intensity around 0.5 L. On flashing the surface to ~420 K the pattern begins to vary and changes to a weak (5×5) pattern* with streaks around 750 K. After repeated ammonia adsorption and flashing to ~750 K, a (\sqrt{2} \times \sqrt{2} \Gamma) R 10.9° pattern appears instead of the (5×5) pattern. On flashing the surface to higher temperatures the (\sqrt{2} \times \sqrt{2} \Gamma) R 10.9° pattern disappears and then a (3×3) pattern develops. The latter becomes finally sharp on flashing up to ~900 K. Above this temperature a (1×1) pattern with high background intensity recovers.

On flashing the ammonia adsorbed Fe (111) surface, hydrogen and nitrogen are mainly desorbed. Nitrogen starts to be desorbed around 750 K as on the (110) surface. The desorption spectra of hydrogen show only a single but broad peak around 390 K. The peak temperature is independent of ammonia exposure as shown in Fig. 8. The desorption of hydrogen is observed over the temperature range where the \( \beta_1 \) and \( \beta_2 \) hydrogen are

*) The (5×5) pattern is observed after long exposure of NH₃ and stepwise flashing. The pattern may be ascribed to oxygen impurity from AES observation.
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desorbed in the case of the adsorption of hydrogen as shown in Fig. 10.

2.3. \textit{NH}_3 \textit{adsorption on the stepped Fe(111) surface}

The adsorption of ammonia on the \textit{3(111)\times(110)} surface (see Fig. 10) around 273 K produces a \textit{(1\times1)} pattern with high background intensity above 0.5 L. On stepwise flashing the surface up to \textasciitilde700 K the pattern

![Graph](image-url)

\textbf{Fig. 8.} Thermal desorption spectra of hydrogen from the Fe(111) following \textit{NH}_3 adsorption at \textasciitilde273 K.

![Graph](image-url)

\textbf{Fig. 9.} Thermal desorption spectra of hydrogen from the Fe (111) following \textit{H}_2 adsorption at \textasciitilde273 K and at various exposures.
Adsorption of NH₃ on Iron Single Crystal Surfaces

3(111)x(110) or (554)

Fig. 10. Schematic diagram of the Fe-3(111)x(110) surface structure.

Fig. 11 a. LEED pattern of the $\frac{2}{2} - \frac{1}{4}$ surface structure obtained after heating the NH₃ covered Fe-3(111)x(110) to ~700 K (72 eV).

Stepped Fe(111)/NH₃

Fig. 11 b. Schematic diagram of the LEED pattern of the $\frac{2}{2} - \frac{1}{4}$ surface structure.
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shows sharp streaks in both the directions normal and parallel to the steps. A \( \begin{pmatrix} 2 & -1 \\ 2 & 4 \end{pmatrix} \) pattern appears after such flashing procedures are repeated. The LEED pattern and the schematic diagram are shown in Fig. 11. On the

\[ 4 \{111\} \times \{110\} \]

**Fig. 12.** Schematic diagram of the Fe-4 \( \{111\} \times \{110\} \) surface structure.

**Fig. 13 a.** LEED pattern of the \( \begin{pmatrix} 0 & 2 \\ 1 & 6 \end{pmatrix} \) surface structure obtained after heating the NH\(_3\) covered Fe-4 \( \{111\} \times \{110\} \) to \( \sim 800 \) K (34 eV).

**Fig. 13 b.** Schematic diagram of the LEED pattern of the \( \begin{pmatrix} 2 & 0 \\ 1 & 6 \end{pmatrix} \) surface structure.
4(111)×(110) surface (see Fig. 12), on the other hand, a \(|2\ 0\ 0|\) pattern is observed on ammonia adsorption followed by flashing to \(\sim 700\) K as shown in Fig. 13. These “coincidence” patterns disappear after the desorption of nitrogen above \(\sim 850\) K and then their respective (1×1) patterns recover. The desorption spectra of hydrogen and nitrogen from ammonia adsorbed on the stepped surfaces are similar to those for the flat (111) surface.

![Nitrogen (1s) spectra from the Fe (110) following NH3 adsorption at \(\sim 273\) K and heating the surface at several temperatures.](image)

3. Discussion

On the adsorption of ammonia around 273 K, a new surface structure is formed on the (110) surface. The new structure is very sensitive to both mild heating and LEED beam exposure as described in the foregoing section. Such behaviours of the overlayer structure show that the adspecies are more mobile than adsorbed \(\text{C}_2\text{H}_2\), which forms a (2×2) surface structure on the Fe (110) surface but is not either affected by the mild heating nor the LEED beams.\(^9\) The (2×2) surface structure has been concluded to be composed mainly of \(\text{NH}_2(a)\).\(^1,\ 2,\ 8\) Our recent XPS studies on ammonia adsorption showed the existence of both \(\text{NH}_3(a)\) and \(\text{NH}_x(a)\) (\(x=1\) or 2) on the (110) surface at 273 K. The former is little observed after flashing to \(\sim 310\) K.\(^10\) Thus, the poorly ordered (2×2) surface structure at 273 K is suggested to be composed of \(\text{NH}_3(a)\), \(\text{NH}_x(a)\) and \(\text{H}(a)\). On the other hand, the well ordered (2×2) surface structure obtained after flashing to \(\sim 310\) K consists of \(\text{NH}_x(a)\) and \(\text{H}(a)\).

The adsorption of hydrogen on the clean Fe (110) surface shows the two desorption peaks, \(\beta_1\) and \(\beta_2\) as shown in Fig. 6. Before the completion
of the C(2×2) surface structure due to the adsorption of hydrogen, only
the \( \beta_2 \) -peak was observed. The \( \beta_1 \) -peak appeared at coverages higher than
0.5. These two peaks have been explained as follows.\textsuperscript{10} A hydrogen mole-
cule desorbed in the \( \beta_2 \) -state is produced from the combination of hydrogen
adatoms located on the second nearest or farther sites. Above the coverage
of 0.5, a hydrogen atom is adsorbed on the first nearest site and then the
strong repulsive interaction between such hydrogen adatoms produces a new
desorption peak at lower temperature. Similar hydrogen desorption peaks
\( \beta_1 \) and \( \beta_2 \) were also obtained from the ammonia adsorbed on the Fe(110)
surface as shown in Fig. 5. Hydrogen is desorbed mainly as the \( \beta_1 \) -state. The
coverage of the \( \beta_1 \) hydrogen is estimated to be 0.5. The activation
energy for the desorption is almost the same as that for the \( \beta_1 \) -state in the
case of hydrogen adsorption. The amount of the \( \beta_2 \) -state hydrogen is roughly
half of the \( \beta_1 \) -state hydrogen. These phenomena may be explained as
follows. The surface is covered with molecular ammonia and the partially
dissociated species, when the \((2\times2)\) pattern with weak and diffuse half-
order spots is observed after the adsorption of ammonia around 273 K.
Since the species containing nitrogen has already produced a \((2\times2)\) surface
structure, hydrogen atoms released from the adsorbed ammonia can not
produce the C\((2\times2)\) surface structure. They also make the \((2\times2)\) surface
structure. When the surface is heated, \( \text{NH}_3(a) \), \( \text{NH}_2(a) \) and \( \text{NH}(a) \) further
release hydrogen atoms. These hydrogen atoms can be adsorbed on the
sites closest to those occupied by the hydrogen atoms adsorbed first. There-
fore, hydrogen in the \( \beta_1 \) -state is produced when the surface is heated. The
remnant hydrogen adatoms are desorbed as the \( \beta_2 \) -state. The appearance
of the \( \beta_1 \) -state above 273 K indicates that the \( \text{NH}_x(a) \) is further decomposed
and releases hydrogen. Around the peak temperature of the \( \beta_2 \) -state (435 K)
the ordered \((2\times2)\) surface structure is formed only of \( \text{N}(a) \) and \( \text{H}(a) \). The
ordered surface structure begins to be destroyed with desorption of the \( \beta_2 \)
hydrogen.

On the oxygen-contaminated \((110)\) surface, adsorbed ammonia forms
the poorly ordered \((2\times2)\) surface structure as on the clean surface. The
\((2\times2)\) surface structure is altered with mild heating or LEED beam exposure
as on the clean surface. In addition, the new surface structure, poorly
ordered \( \begin{bmatrix} 1 & -1 \\ 2 \end{bmatrix} \), is induced by the LEED beams. This surface structure
develops into more ordered one on mild heating as the poorly ordered \((2\times2)\)
surface structure on the clean surface. The \((2\times2)\) and \( \begin{bmatrix} 1 & -1 \\ 2 \end{bmatrix} \) surface struc-

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tases seem to consist of NH₄(a). The same \[ \begin{array}{c}
7 \\
-3
\end{array}  \begin{array}{c}
4 \\
4
\end{array} \] surface structure as that produced after complete desorption of hydrogen is also observed on adsorption of the N₂O at high temperature. It is not produced only on the oxygen adsorption. The fact suggests that the \[ \begin{array}{c}
7 \\
-3
\end{array}  \begin{array}{c}
4 \\
4
\end{array} \] surface structure is ascribed to both nitrogen and oxygen adatoms.

From the ammonia adsorbed Fe(111) surface a single broad hydrogen desorption peak is observed, in contrast to the two peaks on the Fe(110) surface. The peak temperature is independent of ammonia exposure above 1 L. Grunze et al. have obtained almost the same result above 0.6 L. Ammonia undergoes extensive dehydrogenation on the Fe(111) surface at low coverages and around 300 K. The fact indicates that the rate of the desorption of hydrogen is determined by the combination step of the hydrogen adatoms. The dissociation of ammonia is rapid. At high coverage ammonia is adsorbed molecularly, however, the combination of hydrogen adatoms may be considered to be slow as compared to that of the dissociation of ammonia, since the deuterium exchange between hydrogen adatoms and ammonia admolecule is fast and further the desorption of hydrogen occurs at temperatures higher than that of ammonia. Although there are several different kinds of hydrogen atoms on the surface, H(a), NH(a), NH₂(a), and NH₃(a) the rate of hydrogen desorption is controlled only by the step \[ 2H(a) \rightarrow H_2. \] The desorption of hydrogen is observed over a wide range of the temperature where the β₁ and β₂ hydrogen are desorbed in the case of the adsorption of hydrogen. This broad peak may be attributed to the disordered surface structure due to the adsorption of ammonia. On the disordered surface the site available for hydrogen adsorption should be distributed randomly. Even at low coverages of ammonia a part of hydrogen atoms released is adsorbed on the sites of which the nearest adsorption places are already occupied. The others can be adsorbed on the sites of which the nearests are not occupied. The former is desorbed as the β₁-state, while the latter produces the β₂-state hydrogen, as dicussed above. In this model the β₁ hydrogen is desorbed at low temperatures, and further continued to be created through the decomposition of ammonia even at high temperatures where in the case of the Fe(110) the surface is ordered as the (2×2) structure, consisting of N(a) and H(a), and only the β₂-state hydrogen is evolved.

The oxygen impurity observed after long exposure of ammonia and stepwise flashing seems to arise from residual CO in the vacuum chamber.
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It means that CO is well adsorbed on the iron surfaces covered with ammonia and liable to decompose.

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