Kinetics and Mechanism of NH₃ Formation by the Hydrogenation of Atomic Nitrogen on Rh(111)

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The reaction between atomic nitrogen and H₂ has been studied in order to elucidate the mechanism of NH₃ formation on Rh(111). Atomic nitrogen layers of 0.10 monolayer (ML) coverage were obtained by adsorbing NO at 120 K and selectively removing the atomic oxygen from dissociated NO by reaction with H₂ at 375 K. The rate of NH₃ formation is first order in the atomic nitrogen coverage and linearly proportional to the H₂ pressure below 5 × 10⁻⁷ mbar. Static secondary ion mass spectrometry (SSIMS) indicates that N and NH₂ are the predominant reaction intermediates, while small amounts of NH₃ are also detected. The NH₂ surface coverage increases with increasing H₂ pressure. The presence of NH₂ is also indicated by the appearance of a reaction-limited H₂ desorption state in temperature-programmed desorption (TPD) spectra. The hydrogenation of NH₂ to NH₃ is expected to be the rate-determining step in the NH₃ formation. From the temperature dependence of the NH₃ formation rate an effective activation energy of 40 kJ/mol was determined, which could be translated into an activation energy of 76 kJ/mol for the hydrogenation from NH₂ to NH₃.

Introduction

The reduction of NO₃ on rhodium is one of the key reactions that occurs in the automotive exhaust gas converter. Although the greater part of the NO is reduced by reaction with CO, a substantial part is reduced by hydrogen, which is present in exhaust gas and is moreover formed on the surface of the metal particles by the decomposition of hydrocarbons.¹,² NO reduction by H₂ may yield three different N-containing products, viz. N₂, N₂O, and NH₃, of which the last two are undesirable from an environmental point of view.

Kinetic studies of the NO + H₂ reaction have been performed on Pt foil,³ Rh foil,⁴ Pt/Rh single crystals,⁵,⁶ Rh/SiO₂,⁷ and Rh/Al₂O₃.⁸ These studies have shown that the reactivity of atomic nitrogen, which is formed by the dissociation of NO, plays a key role in the selectivity issue of the NO + H₂ reaction. Whereas reactions such as the NO dissociation⁹⁻¹¹ and recombination of atomic nitrogen to N₂¹²,¹³ have been studied extensively, the microscopic mechanisms of N₂O and NH₃ formation are still unknown. NH₃ formation is commonly described by the stepwise hydrogenation of atomic nitrogen.¹⁴ Indeed, many reports on NH and NH₂ species exist. On Rh(100)¹⁵ and Pt/Rh(100)⁶,¹⁰ evidence was found by electron energy loss spectroscopy (EELS) for an NH intermediate that could be translated into an activation energy of 76 kJ/mol for the hydrogenation from NH₂ to NH₃.

Experimental Section

Temperature-programmed desorption (TPD) and SIMS experiments were done in a stainless steel ultrahigh vacuum (UHV) system pumped with a 360 L/s turbomolecular pump and a water-cooled titanium sublimation pump. The base pressure was typically around 5 × 10⁻¹¹ mbar, and mass spectra of the residual gas indicated the presence of mainly H₂, CO, and CO₂. The system is equipped with a Leybold SSM 200 quadrupole mass spectrometer.
mass spectrometer for TPD and SIMS and a Leybold EA 10 hemispherical energy analyzer for Auger electron spectroscopy (AES) and ∆E measurements. Both analyzers are interfaced with a PC for data storage.

SIMS measurements were carried out in the static (low-damage) mode. Typically, we used a defocused 5 keV primary Ar+ beam with a current density of 1−10 nA/cm². To average eventual anisotropies in the secondary ion emission process, we applied a target bias of +45 V and an extractor voltage of −300 V on the entrance lens of the quadrupole system.

The UHV system contained a rhodium crystal that was cut in the [111] orientation within 0.5° and polished according to standard procedures. The temperature was measured by a chromel−alumel thermocouple spot-welded on the back of the crystal. The standard cleaning procedure consisted of an argon sputter treatment (900 K, 1.5 keV, 5 μA/cm²) followed by annealing in 2×10⁻² mbar O₂ (900−1100 K) and a final annealing treatment in vacuum at 1420 K. The gases, NO (Messer Griesheim, 99.5%) and H₂ (Messer Griesheim, 99.995%), were used without further treatment. Exposures are reported in langmuirs (1 langmuir = 1.33×10⁻⁶ mbar·s), and coverages are expressed with respect to the number of Rh surface atoms (1 monolayer (ML) =1.6×10¹⁵ cm⁻²).

Atomic nitrogen layers with a coverage of 0.10 ML were obtained by adsorbing 0.25 langmuir NO at 120 K and selectively removing the atomic oxygen at 375 K by reaction with 2×10⁻⁸ mbar hydrogen during 160 s. The atomic nitrogen layers were exposed to H₂ at various pressures and temperatures. The amount of nitrogen remaining after the hydrogenation experiment was determined by TPD. Although the surface also contained NH₃ intermediates, N₂ was the only nitrogen-containing desorption product observed. We mention here that the experiments were only possible with an excellent background pressure (p < 5×10⁻¹¹ mbar), where CO adsorption during the reaction procedure can be prevented.

Results

Preparation of Atomic Nitrogen Layers on Rh(111). For all the experiments we started from an atomic nitrogen layer with a coverage of 0.10 ML (±3%). Figure 1 illustrates the procedure for preparing atomic nitrogen with SIMS spectra of the Rh(111) surface after NO adsorption at 120 K, heating to 375 K to dissociate the NO, and after reaction with hydrogen at 375 K to remove the oxygen.

The presence of molecularly adsorbed NO at 120 K is indicated in the SIMS spectrum by the appearance of the Rh₃NO⁺ cluster ion at m/e = 236. Heating to 375 K results in complete dissociation of the adsorbed NO molecules. This is evidenced by the appearance of the Rh₃N⁺ and Rh₂O⁺ cluster ions (at m/e = 220 and m/e = 222), which are representative for atomic N and O, respectively, and by the disappearance of the Rh₂NO⁺ cluster ion. The removal of atomic oxygen by reaction with hydrogen is clearly illustrated by the disappearance of the Rh₂O⁺ peak. Although removing the oxygen results in a large decrease of the SIMS intensities, the presence of atomic nitrogen remains clearly visible by the Rh₃N⁺ peak at m/e = 220. Temperature-programmed desorption confirms that the hydrogen treatment to remove the oxygen does not result in a decrease of the atomic nitrogen coverage, since the N₂ TPD peak areas before and after the H₂ reaction are equal. The removal of the atomic oxygen is also illustrated by the N₂ desorption behavior. As Figure 1 shows, removal of atomic oxygen results in a shift of the N₂ desorption spectrum to higher temperature, attributed to the disappearance of repulsive interactions between oxygen and nitrogen atoms on the surface.

Hydrogenation of Atomic Nitrogen at Constant Temperature and H₂ Pressure. In this section we show how the coverage of an atomic nitrogen layer decreases when it is exposed to a constant H₂ pressure at a fixed temperature. The decrease of the atomic nitrogen coverage was determined by comparing the N₂ TPD area after a hydrogenation experiment with the N₂ TPD area of the initial atomic nitrogen layer.

As we will show in the discussion section, hydrogen adsorption is readily at equilibrium under our reaction conditions. We have restricted the upper temperature limit to 400 K in order to prevent N₂ formation and desorption. We found that up to 400 K the atomic nitrogen coverage remained unchanged when the crystal was kept isothermally in vacuum for several minutes. Under these conditions the rate of ammonia formation equals the decrease of the atomic nitrogen coverage and can be written as

\[
\frac{d\theta_{NH₃}}{dt} = k_{eff} \theta_{N}^n \theta_{H₂}^m = k'_{eff} \theta_{N}^n
\]

The decrease of the nitrogen coverage with time is determined by the nth-order dependence of the ammonia formation rate on the nitrogen coverage. Figure 2 shows the decrease of the nitrogen coverage with time at T = 375 K and pH₂ = 2×10⁻⁷ mbar and at T = 400 K and pH₂ = 5×10⁻⁷ mbar. Although the nitrogen coverage continues to decrease below 0.04 ML, the data are not shown in Figure 2, since the relative error in the remaining Nads coverage determination by TPD becomes too large.

The decreasing slope of the \( \theta_N \) coverage versus time curve indicates a positive order \( n \) of the ammonia formation rate in the nitrogen coverage. If the order \( n \) is assumed to be unity, integration of eq 1 yields

\[
\ln[\theta_N(t)/\theta_N(0)] = -k'_{eff} t
\]

where \( \theta_N(t) \) and \( \theta_N(0) \) are the nitrogen coverages after and before reaction, respectively. The inset of Figure 3 confirms that a linear relation is obtained if the logarithm of the coverage ratio is plotted versus time. This indicates that the ammonia formation rate is proportional to the nitrogen coverage.
the H₂ pressure dependence would be at most a square root
the first hydrogenation step is not rate limiting. In that case,
the H₂ pressure at 375 K. The curve shows that for pressures
below 5 × 10⁻⁷ mbar, the dependence is close to linear whereas
the dependence levels off above ~5 × 10⁻⁷ mbar H₂.

Dependence of the NH₃ Formation Rate on the H₂
Pressure. The H₂ pressure dependence of the NH₃ formation
rate can give information on the rate-determining step in the
subsequent hydrogenation of atomic nitrogen to NH₃.

Under the applied reaction conditions, the hydrogen coverage
is expected to be small (θ₁H ≪ 1), and therefore, it is proportional
to the square root of the H₂ pressure. In this case the following
general dependence is expected:

\[ \ln(\theta_H(t)/\theta_H(0)) = -k_{eff} \theta_H m t = -k'_{eff}p_{H2}^{m/2}t \]  

The pressure dependence of the hydrogenation rate was
investigated by keeping the reaction time constant at 160 s and
varying the H₂ pressure in the range between 2 × 10⁻⁵ and 1 × 10⁻⁶ mbar. Figure 3 shows a plot of the logarithm of the ratio of the remaining and initial N ads coverage versus the hydrogen pressure at 375 K. The curve shows that for pressures below 5 × 10⁻⁷ mbar, the dependence is close to linear whereas the dependence levels off in the pressure range from 5 × 10⁻⁷ to 1 × 10⁻⁶ mbar. A similar experiment at 400 K showed a similar H₂ pressure dependence.

Based on these results only, assignment of the rate-determining step is not possible. However, we definitely conclude that the first hydrogenation step is not rate limiting. In that case, the H₂ pressure dependence would be at most a square root dependence. Figure 3, however, shows a linear dependence for H₂ pressures below 5 × 10⁻⁷ mbar.

Identification of NH₃ Reaction Intermediates by SIMS.
For elucidating the hydrogenation mechanism of atomic nitrogen
to NH₃, the identification of surface intermediates is of great
significance. In previous studies, SIMS has successfully been
applied to identify NH₃-like intermediates on the surface.\(^{35,36}\) This section presents the SIMS results of the Rh(111) surface
during N hydrogenation. The collection time for a SIMS
spectrum was 15 s, which is about 10% of the time scale of a
typical hydrogenation experiment. Spectra were taken after 20 s
of reaction to be sure that equilibration was reached between the
NH₃ intermediates and to compare different reaction conditions with similar nitrogen coverages.

Figure 4 shows two characteristic mass regions of a SIMS
spectrum of the Rh(111) surface taken after 20 s of reaction at
5 × 10⁻⁷ mbar H₂ and 375 K. The presence of NH₃ on the
surface is evidenced by the appearance of the Rh(NH₃)⁺ cluster
ion at m/e = 120. In the high-mass range, N_{ads} and NH₂_{ads} are observed as predominant surface species by the appearance of the Rh₂N⁺ and Rh₂(NH₂)⁺ cluster ions at m/e = 220 and m/e = 222, respectively. From a previous investigation we know that the Rh₂(NH₂)⁺ cluster ion is not a consequence of the presence of NH₃ on the surface.\(^{36}\) The presence of hydrogen on the surface is evidenced by the appearance of the Rh₂H⁺ peak at m/e = 207, which is not fully resolved from the Rh⁺ peak, however. To facilitate the assignment of the SIMS peaks, H₂ was exchanged for D₂, which resulted in the expected mass shifts, as Figure 4 shows. In this case also a small peak at m/e = 222 is resolved. Whether this peak stems from the presence of ND on the surface or results from fragmentation of ND₂ is unknown.

Although the presence of N, NH₂, and NH₃ on the surface is
clearly established by the spectra in Figure 4, interpretation of
the peak intensities in terms of surface coverages is rather
complicated. Previous studies have shown that SIMS peak
intensity ratios can give quantitative information about coverages of adsorbates.\(^ {36-38}\) However, it should be noted that occasion-
ally nonlinear correlations between intensity ratios and coverage
are observed. Therefore, careful calibration is required in order
to obtain quantitative information from SIMS measurements.
For NH₃ we have been able to do such a calibration by studying
the adsorption of NH₃ on Rh(111).\(^ {36}\) In the case of NH₃,
intermediates, however, calibration is much more difficult, since
no methods are at hand to prepare well-defined coverages of
NH₃ species on the surface. We have therefore assumed that the Rh₂NH₃⁺/Rh²⁺N⁺ peak ratio reflects at least qualitatively the coverage ratio of NH₂ and N on the surface. The intensity of the Rh₂⁺ peak was not used as a reference, since it was not fully resolved from the Rh₂H⁺ peak.

Figure 5 shows the H₂ pressure dependence of the Rh(NH₃)⁺/Rh⁺ and Rh(NH₃)⁺/RhN⁺ peak intensity ratios at a constant temperature of 375 K. The SIMS spectra were taken after 20 s of reaction. The Rh(NH₃)⁺/RhN⁺ peak intensity ratio increases in the H₂ pressure regime between 1 × 10⁻⁸ and ~5 × 10⁻⁷ mbar but becomes constant at higher H₂ pressures. The Rh(NH₃)⁺/Rh⁺ peak intensity ratio increases over the whole pressure regime. Thus, NH₃ is the predominant NH species during the hydrogenation of atomic nitrogen while small amounts of NH₃ are present as well. The coverage of both NH₂ and NH₃ increases with increasing H₂ pressure, but for NH₂ the dependence levels off to a constant at a pressure of about 5 × 10⁻⁷ mbar.

We have also investigated the influence of the temperature on the presence of the intermediates on the surface. Figure 6 shows the dependence of the Rh(NH₃)⁺/Rh⁺ and Rh(NH₂)⁺/RhN⁺ peak intensity ratios on temperature at a constant H₂ pressure of 1 × 10⁻⁶ mbar and also after 20 s of reaction. The Rh(NH₂)⁺/Rh⁺ peak ratio increases somewhat up to temperatures of 365 K, whereafter it decreases rapidly. Except for the measurement at 325 K, the Rh(NH₂)⁺/RhN⁺ peak ratio remains more or less constant over the entire temperature range.

Evidence for NH₃ Intermediates from TPD. In the literature, much of the evidence for the existence of NH₃ intermediates is based on the appearance of a reaction-limited H₂ desorption state. To make the comparison to our results, we have frozen the intermediates present under reaction conditions by rapid cooling (4 K/s) under H₂ atmosphere to 275 K, after which the system was evacuated for 2 min and a TPD experiment was performed. Figure 7 shows the H₂ and N₂ TPD spectra obtained by freezing the reaction at 350 K and 5 × 10⁻⁷ mbar H₂ after 20 s. The H₂ desorption spectrum clearly shows two desorption states. The low-temperature desorption state with a peak maximum at 330 K represents the common second-order desorption-limited state. The H₂ desorption state with a peak maximum around 415 K corresponds to a reaction-limited state, which is attributed to the decomposition of NH₃ intermediates.

The only nitrogen-containing product that was observed during TPD was N₂, whereas no NH₃ and N₂H₂ could be detected. Furthermore, it appeared that all NH had decomposed before N₂ desorption started at around 500 K. Figure 7 also shows a SIMS spectrum of the surface before TPD was performed, which indicates the presence of N, NH₂, and NH₃ on the surface.

The ratio of the atomic nitrogen coverage to the amount of hydrogen desorbing in the reaction-limited desorption state at 415 K is of interest because it can give additional information about the composition of the NH₃ intermediate. Comparison of the N₂ and H₂ TPD peak areas and correcting for differences in ionization probabilities (S₁/N₂ ≈ 0.45) yields an overall N:H ratio of 1:1.1 for the NH₃ intermediates. A different way to determine the N:H ratio is by relating the N₂ and H₂ TPD areas to the NO and H₂ uptake curves. In this way, the atomic nitrogen coverage was estimated to be 0.10 ML and the amount of hydrogen desorbing from the reaction-limited state was 0.11 ML, which results in the same overall N:H ratio of 1:1.1 for the NH₃ intermediates.

Note that the H:N ratio of 1.1 reflects the overall composition of the surface after 20 s of hydrogenation at 350 K, excluding the atomic hydrogen, and has no bearing on the composition of the NH₃ species themselves.

Dependence of the NH₃ Formation Rate on Temperature. To determine the effective Arrhenius parameters, we investi-
gated the rate of NH₃ formation in the temperature range 325–400 K. In these experiments the H₂ pressure was kept constant at 1 × 10⁻⁶ mbar. Figure 8 shows the logarithm of the hydrogenation rate versus the reciprocal temperature. The slope of the curve corresponds to an effective activation energy of 40 kJ/mol, while the effective pre-exponential equals 10² s⁻¹.

We use the terms effective activation energy and pre-exponential, since several equilibrium and rate constants may be involved depending on the rate-limiting step. At least the hydrogen adsorption equilibrium has to be incorporated, since the H₂ pressure is kept constant while the temperature changes, which results in varying hydrogen coverages.

Discussion

Mechanism and Kinetic Description of NH₃ Formation on Rh(111). With respect to the kinetic mechanism of the stepwise hydrogenation of atomic nitrogen to NH₃, the following experimental results are pertinent. (1) The rate of ammonia formation is linearly proportional to the hydrogen pressure below 5 × 10⁻⁷ mbar H₂. (2) SIMS spectra indicate that N and NH₂ are the predominant surface species under reaction conditions, whereas NH₃ and possibly NH are present only in very small amounts. (3) The reaction-limited H₂ desorption state, emanating from NHₓ decomposition, indicates the presence of signifi-
cantly amounts of NH$_3$ on the surface under reaction conditions; the average H:N ratio in the NH$_3$ intermediates is 1.1:1.

Concurrently, these results point to the hydrogenation of NH$_2$ as the rate-determining step. We therefore propose the following sequence of steps with the associated equilibrium constants:

\[
\begin{align*}
\text{H}_2(g) + 2\theta &= 2\text{H}_\text{ads} & K_1 = \frac{\theta_H^2}{\theta_H^2 P_{\text{H}_2}} \\
\text{N}_\text{ads} + \text{H}_\text{ads} &= \text{NH}_\text{ads} + \theta & K_2 = \frac{(\theta_{\text{NH}} \theta_H)}{(\theta_{\text{H}} \theta_H)} \\
\text{NH}_\text{ads} + \text{H}_\text{ads} &= \text{NH}_2\text{ads} + \theta & K_3 = \frac{(\theta_{\text{NH}_2} \theta_H)}{(\theta_{\text{NH}} \theta_H)} \\
\text{NH}_2\text{ads} + \text{H}_\text{ads} &\rightarrow \text{NH}_3\text{ads} + \theta & r_{\text{NH}_3} = k_2 \theta_{\text{NH}_2} \theta_H \\
\text{NH}_3\text{ads} &\rightarrow \text{NH}_3(g) + \theta & r_{\text{NH}_3} = k_3 \theta_{\text{NH}_3}
\end{align*}
\]

We will justify and discuss this kinetic mechanism in the following. Under our experimental conditions, i.e., $2 \times 10^{-8} < P_{\text{H}_2} < 1 \times 10^{-6}$ mbar and $325 < T < 400$ K, both the rate of hydrogen adsorption and desorption are fast compared to the NH$_3$ formation rate. Furthermore, hydrogen adsorption is sufficiently fast to supply hydrogen for the conversion of atomic nitrogen into NH$_2$ species. Therefore, we conclude that H$_2$ adsorption rapidly reaches equilibrium (on the order of seconds).

Although initially all the nitrogen on the surface is present as N$_\text{ads}$, exposure to hydrogen results in the conversion of part of the atomic nitrogen into NH species. It is difficult to determine the exact time scale upon which equilibrium between the NH$_2$ intermediates is reached. However, the rapid buildup of the NH$_2$ intermediates and the absence of an induction period in the time-dependent hydrogenation experiments indicate that equilibrium conditions apply for the major part of the time scale of the hydrogenation experiments. In the final step, NH$_3$ desorption can be neglected, since the NH$_3$ production rate is slow compared to the pumping speed of the vacuum system, resulting in a negligible NH$_3$ background pressure.

Under the assumption that equilibrium conditions apply for both H$_2$ adsorption and the NH$_2$ intermediates up to NH$_3$, the following kinetic expression can be derived for the decrease of the nitrogen coverage with time (which is equal to the NH$_3$ formation rate):

\[
\frac{d\theta_{\text{N}\text{tot}}(t)}{dt} = -k_2 \theta_{\text{NH}_2}(t) \theta_H
\]

\[
\frac{d\theta_{\text{N}\text{tot}}(t)}{dt} = K_2 K_3 (K_{\text{H}_2})^{1/2} \theta_{\text{NH}_2}(t) \theta_H
\]

\[
= \frac{K_2 K_3 (K_{\text{H}_2})^{1/2}}{1 + K_2 (K_{\text{H}_2})^{1/2} + K_3 (K_{\text{H}_2})^{1/2} + (K_{\text{H}_2})^{1/2}}
\]

\[
(5)
\]

The number of empty sites available for hydrogen adsorption equals

\[
\theta_e = 1 - \theta_H - \sum \theta_{\text{NH}_2}
\]

For the derivation of eq 5 we have made the assumption that $\theta_e \approx 1 - \theta_H$. This has the advantage that two independent factors are obtained for the H$_2$ pressure dependence of the hydrogen adsorption equilibrium and the equilibria of the NH$_2$ intermediates (last and second factor in eq 5, respectively). The choice of the number of empty sites available for hydrogen adsorption is quite arbitrary anyway, so we have assumed it to be unity in accordance with the situation on the empty surface.

In fact, the number of empty sites increases during the hydrogenation experiment because of the decrease of the nitrogen coverage. However, the decrease of the atomic nitrogen coverage in a typical hydrogenation experiment was on the order of 0.05 ML, and therefore, the increase of the number of empty sites is relatively small. Hence, eq 5 should be valid under the conditions employed in this work.

**H$_2$ Pressure Dependence of the NH$_3$ Formation Rate.** As the second factor in eq 5 indicates, the order in the H$_2$ pressure of the NH$_3$ coverage can vary between 0 and 1. As stated previously, the hydrogen coverage is small under our reaction conditions and therefore proportional to $P_{\text{H}_2}^{1/2}$. This can easily be seen from the last factor in eq 5, which represents the hydrogen coverage and reduces to $(K_{\text{H}_2})^{1/2}$ if $K_{\text{H}_2} \ll 1$. In consequence of this, the order of the NH$_3$ formation rate in the H$_2$ pressure can vary between 1/2 and 3/2 as extremes.

Figure 5 shows that the NH$_2$ coverage increases with increasing H$_2$ pressures below $\sim 5 \times 10^{-7}$ mbar, whereas the NH$_2$ coverage becomes constant at higher H$_2$ pressures. From a kinetic point of view, the observed H$_2$ dependence of the NH$_2$ coverage and the NH$_3$ formation rate is consistent. At pressures below $5 \times 10^{-7}$ mbar both the NH$_2$ and the hydrogen coverage depend on the H$_2$ pressure, resulting in an overall first-order dependence of the NH$_3$ formation rate on the H$_2$ pressure. Above $5 \times 10^{-7}$ mbar, the NH$_2$ coverage becomes constant and the H$_2$ pressure dependence of the NH$_3$ formation rate is determined solely by the pressure dependence of the hydrogen coverage ($\sim P_{\text{H}_2}^{1/2}$).

**Presence of NH$_2$ Intermediates on the Surface under Reaction Conditions.** The SIMS results of the surface under reaction conditions indicate that N and NH$_2$ are the predominant nitrogen surface species. Drechsler et al., 35 using SIMS, have demonstrated that NH is the main surface species during the NH$_3$ decomposition on Fe. We may therefore conclude that the absence of NH in our SIMS spectra is not caused by a poor sensitivity but is due to a low surface coverage of NH. NH$_2$ is also detected but only in very small amounts. A previous study on the adsorption of NH$_3$ on Rh(111) 36 indicated that an NH$_3$ coverage as small as 0.01 ML resulted in a SIMS Rh(NH$_3$)$^+$/Rh$^+$ peak intensity ratio as large as $\sim 7$. In the present case the SIMS Rh(NH$_3$)$^+$/Rh$^+$ peak intensity ratio does not exceed a value of 0.25 (see Figure 5), which points to a negligibly low coverage. In fact the NH$_3$ steady-state coverage is determined by the ratio of NH$_3$ production to the desorption rate:

\[
\text{NH}_2\text{ads} + \text{H}_\text{ads} \rightarrow \text{NH}_3\text{ads} \rightarrow \text{NH}_3\text{gas}
\]
Under steady-state conditions, the rate of NH$_3$ formation is equal to the rate at which the nitrogen coverage decreases. As Figure 2 shows, a typical value for the decrease of the nitrogen coverage is 0.0002 ML/s. For the NH$_3$ desorption rate, an activation energy of 81.5 kJ/mol was found if a pre-exponential factor of 10$^{13}$ was assumed. By use of these values, an NH$_3$ steady-state coverage of 4 × 10$^{-6}$ ML is calculated at 375 K. Since this coverage is very small, we must be conscious about the role that surface defects might play. If NH$_3$ is for instance adsorbed more strongly to defect sites, the coverage might become significantly higher.

Equation 6 predicts that the NH$_3$ steady-state coverage increases if the NH$_2$ formation rate increases. This is in line with the results in Figure 5, which shows that the NH$_3$ steady-state coverage for a given temperature increases with increasing H$_2$ pressure.

Since no reference is available, it is difficult to give a precise estimate of the NH$_3$:N surface coverage ratio on the basis of the SIMS Rh$_2$NH$_3$+/Rh$_2$N$^+$ peak intensity ratio. Quantification is complicated, since the relative SIMS sensitivities for N and NH$_2$, and the fragmentation of the Rh$_2$NH$_3$+ cluster ion to Rh$_2$N$^+$, are unknown. Nevertheless, it is remarkable that the SIMS Rh$_2$NH$_3$+/Rh$_2$N$^+$ peak intensity ratio becomes independent of the H$_2$ pressure above 5 × 10$^{-7}$ mbar at 375 K (see Figure 5, and note the logarithmic pressure scale) and is also independent of the temperature at a constant H$_2$ pressure of 1 × 10$^{-6}$ mbar (see Figures 6). In all cases, the Rh$_2$NH$_3$+/Rh$_2$N$^+$ peak intensity ratio saturated at a value of ~0.43. This might indicate that not all nitrogen is accessible to hydrogen. Yamada et al. reported that hydrogen exposure to a c(2 × 2) N adlayer on Rh(100) only resulted in NH$_3$ formation at the edges of nitrogen islands. From our results we have no direct evidence for island formation, but it could explain why the NH$_2$ coverage saturates while the Rh$_2$NH$_3$+/Rh$_2$N$^+$ ratio remains small.

In the literature, most of the information concerning the stability of NH$_2$ intermediates stems from decomposition experiments. Bassignana et al. showed that on Ni(110), NH$_2$ is the predominant intermediate formed during thermal NH$_3$ decomposition at 350 K. An activation energy of 20 kcal/mol was reported for NH$_3$ decomposition into N or NH. Also, Rausher et al. reported NH$_2$ as a stable intermediate on Ru(001) between 280 and 300 K during N$_2$H$_4$ decomposition. The NH$_2$ intermediate was found to decompose into NH at higher temperatures. On Rh(111), Wagner and Schmidt reported a reaction-limited H$_2$ desorption peak at 430 K when studying the reactions of oxygen with NH$_2$ and N$_2$H$_4$. This reaction-limited H$_2$ desorption peak seems identical with the one we observed during TPD of the Rh(111) surface containing the NH$_2$ intermediates formed during the hydrogenation of N$_{ad}$ (see Figure 7). However, Wagner and Schmidt attributed the H$_2$ formation to decomposition of NH rather than to NH$_2$. This latter assignment has been made in a previous investigation by the same authors Wagner and Schmidt, where they investigated the decomposition of H$_2$NCHO, D$_2$NCHO, N$_2$H$_4$, and NH$_3$ on Rh(111). Decomposition of D$_2$NCHO showed that the reaction-limited H$_2$ (D$_2$) peak at 430 K stemmed from decomposition of the amino NH$_2$ (ND$_2$) group. Similar to our findings, they determined an overall N:H ratio of 1:1.08 when comparing the N$_2$ and reaction-limited H$_2$ (D$_2$) desorption peak areas. From this result they concluded that decomposing NH$_2$ species was NH. A reaction-limited NH$_3$ desorption state was also observed in these experiments, which was explained by hydrogenation of NH$_3$. It should be noted that their results could of course also be explained by assuming that the surface contained N and NH$_3$ in a 1:1 ratio.

**Kinetic Parameters of NH$_3$ Formation.** Figure 7 shows that at a H$_2$ pressure of 1 × 10$^{-6}$ mbar the Rh$_2$NH$_3$+/Rh$_2$N$^+$ peak ratio is almost independent of the temperature and equal to the saturation value. If we assume that the Rh$_2$NH$_3$+/Rh$_2$N$^+$ peak ratio is a measure of the NH$_2$ coverage, the latter is also temperature independent. This greatly simplifies the interpretation of the measured activation energy, since the temperature dependence of the NH$_3$ equilibrium is not incorporated. In this case, the effective rate constant that is measured equals the product of the elementary rate constant for the reaction from NH$_2$ to NH and the square root of the H$_2$ adsorption equilibrium constant, $k_{eff} = k_2f_{H_2}$ (see eq. 5). Under these assumptions, the activation energy for the reaction of NH$_2$ to NH$_3$ equals

$$E_{act,NH_2-NH_3} = E_{act,eff} + \frac{1}{2}E_{des,H_2} = 40 + 36 = 76 \text{ [kJ/mol]}$$

H$_2$ TPD experiments yielded an activation energy and pre-exponential of 72 kJ/mol and 10$^{11}$ s$^{-1}$, respectively, for desorption in the low-coverage limit, in good agreement with the literature.

The only activation energy reported in the literature on NH$_3$ formation stems from Hirano et al. They found an effective activation energy of 55 kJ/mol for NH$_3$ formation by the reaction of NO + H$_2$ on a Pt$_{0.25}$/Rh$_{0.75}(100)$ single crystal. Comparison with our value is difficult, since it is not clear which reaction constants contribute to the effective activation energy. Shustorovich and Bell have studied the synthesis and decomposition of NH$_3$ on transition metal surfaces by a bond-order-conservation-Morse-potential analysis and concluded that the first hydrogenation step, i.e., the reaction from N to NH, is rate limiting in NH$_3$ formation on Pt. Furthermore, they concluded that both NH$_2$ and NH$_3$ are more stable surface intermediates than NH and that NH$_3$ desorption is favored above NH$_2$ decomposition. Although the calculations are performed for Pt(111), the discrepancies with our findings and those of other authors are striking. First, it contradicts the H$_2$ pressure dependence we observed for the NH$_3$ formation rate on Rh(111), and second, it cannot explain the buildup of significant amounts of NH$_2$ intermediates, either during NH$_3$ decomposition or NH$_3$ formation.

**Conclusions**

Atomic nitrogen layers with well-determined coverage can be prepared by adsorbing NO at low temperature followed by thermal dissociation and selective removal of the atomic oxygen by reaction with hydrogen. When the atomic nitrogen layer is exposed to H$_2$ at constant temperature and pressure, the rate at which the atomic nitrogen coverage decreases appears to be first order in the atomic nitrogen coverage. The rate of NH$_3$ formation is first order in the H$_2$ pressure between 1 × 10$^{-8}$ and 5 × 10$^{-7}$ mbar, but the order decreases between 5 × 10$^{-7}$ and 1 × 10$^{-6}$ mbar. SIMS spectra of the surface under reaction conditions indicate, by the appearance of Rh$_2$N$^+$ and Rh$_2$NH$_3$+ peaks at $m/e = 220$ and 222, respectively, that N and NH$_2$ are the predominant surface intermediates. Small amounts of NH$_3$ could be monitored on the surface by the appearance of the RhNH$_3^+$ cluster ion in the SIMS spectra. The NH$_2$ coverage increased with increasing H$_2$ pressure between 1 × 10$^{-8}$ and 5 × 10$^{-7}$ mbar at 375 K. In the pressure range between 5 × 10$^{-7}$ and 1 × 10$^{-6}$ mbar the NH$_2$ coverage became constant. At a pressure of 1 × 10$^{-6}$ mbar H$_2$, the NH$_2$ steady-state
coverage was independent of the temperature. The presence of NH$_2$ species was also evidenced by the appearance of a reaction-limited H$_2$ desorption state at 415 K attributed to decomposition of NH$_3$.

From the temperature dependence of the NH$_3$ formation rate, an effective pre-exponential and activation energy of $10^2$ s$^{-1}$ and 40 kJ/mol were calculated. The experimental results can best be explained by assuming that the third hydrogenation step, i.e., the hydrogenation from NH$_2$ to NH$_3$, is rate limiting. The activation energy of this step is 76 kJ/mol.

References and Notes