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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 NH₃ 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. 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, Rh foil, Pt/Rh single crystals, PtO₂ and Rh/Al₂O₃. 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 dissociation and combination of atomic nitrogen to N₂ 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. Indeed, many reports on NH and NH₃ species exist. On Rh(100) and Pt/Rh(100) evidence was found by electron energy loss spectroscopy (EELS) for an NH intermediate that was reversibly formed when a c(2 × 2)-N adlayer was exposed to H₂. Zemlyanov et al. observed an NH intermediate during the NO + H₂ reaction on Pt(100) by EELS. Prasad and Gland explained the formation of diimide N₂H₂ during the decomposition of NH₃ on N₂H₄ on Rh foil by the coupling of NH species on the surface. NH₂ intermediates were also observed in NH₃ and N₂H₄ decomposition studies on Ni, Pt, Rh, and Ru.

Recently, the NO + H₂ reaction regained interest in the field of synthetic gas conversion. Several methods have been developed for the preparation of atomic nitrogen layers. Belton et al. prepared N_ads layers by dissociation of NO with an electron beam and a subsequent removal of O_ads by reaction with CO. Bugyi et al. used a discharge tube to atomize nitrogen before adsorption. Another alternative to preparing N_ads layers is exposure of the surface to NH₃ at temperatures above ~400 K. All the above-mentioned preparation methods have the disadvantage that it is difficult to deposit a well-defined amount of atomic nitrogen. Since we want to derive the rate of ammonia formation indirectly from the decrease of the atomic nitrogen coverage, it is essential to know the initial N_ads coverage accurately. For this reason, we have prepared atomic nitrogen layers by adsorbing NO at low temperature and removing the O atoms selectively by reaction with H₂ at temperatures where N atoms are not yet hydrogenated or desorbed as N₂. Finally, secondary ion mass spectrometry (SIMS), applied under reaction conditions, reveals that NH₃_ads is the dominant NH₃ species on the surface during the N hydrogenation.

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
A defocused 5 keV primary beam with a PC for data storage.

Typically, we used a defocused 5 keV primary beam with a PC for data storage.

Nitrogen layers were exposed to H₂ at various pressures and 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 with 2 × 10⁻⁵ mbar and 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 H₂ during 160 s. The atomic nitrogen layers were exposed to H₂ at various temperatures. The amount of nitrogen remaining after the sputter treatment (900 K, 1.5 keV, 5 × 10⁻ⁱ⁵ cm⁻²) followed by thermal NO dissociation at 375 K, and reaction with H₂ to remove atomic oxygen. The right panel shows a comparison between the N₂ TPD spectra obtained from a surface covered with 0.10 ML atomic nitrogen and 0.10 ML NO. The absence of atomic oxygen results in a shift of the N₂ desorption maximum to higher temperature.

The 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

\[ r_{N\text{H}_3} = -\frac{d\theta_N}{dt} = k'_{\text{eff}} \theta_N^n \theta_H^m = k'_{\text{eff}} \theta_N^n \]

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 \( T = 375 \text{ K} \) and \( p_{\text{H}_2} = 2 \times 10^{-7} \text{ mbar} \) and at \( T = 400 \text{ K} \) and \( p_{\text{H}_2} = 5 \times 10^{-7} \text{ mbar} \). 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 \( N_{\text{ads}} \) 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

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

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.
Based on these results only, assignment of the rate-determining step is not possible. However, we definitely conclude that the hydrogenation step is rate limiting. In that case, the H₂ pressure dependence would be at most a square root dependence. The inset shows that a linear relation is obtained when the ratio of the initial to remaining atomic nitrogen coverage is plotted versus the time, indicating that the hydrogenation rate is first order in the atomic nitrogen coverage.

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 (Θ_H < 1), and therefore, it is proportional to the square root of the H₂ pressure. In this case the following general dependence is expected:

\[
\ln[\Theta_{N}(t)/\Theta_{N}(0)] = -k_{\text{eff}} \rho_{H} m t = -k'_{\text{eff}} p_{H2}^{m/2} t
\]

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 \(2 \times 10^{-5}\) and \(1 \times 10^{-6}\) 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 \(5 \times 10^{-7}\) mbar, the dependence is close to linear whereas the dependence levels off in the pressure range from \(5 \times 10^{-7}\) to \(1 \times 10^{-6}\) 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 \(5 \times 10^{-7}\) 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 NH₂-like intermediates on the surface. 

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 equilibrium 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 \(5 \times 10^{-7}\) 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. The presence of hydrogen on the surface is evidenced by the appearance of the RhH⁺ 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. However, it should be noted that occasionally 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). In the case of NH₂ 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+/Rh2N+ peak ratio reflects at least qualitatively the coverage ratio of NH3 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(NH3)+/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(NH3)+/Rh+ peak ratio increases somewhat up to temperatures of 365 K, whereafter it decreases rapidly. Except for the measurement at 325 K, the Rh(NH3)+/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 (S_{N2}/S_{N} = 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 NH$_3$ formation in the temperature range 325 - 400 K. In these experiments the H$_2$ pressure was kept constant at $1 \times 10^{-6}$ 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 $10^2$ 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 H$_2$ pressure is kept constant while the temperature changes, which results in varying hydrogen coverages.

Discussion

Mechanism and Kinetic Description of NH$_3$ Formation on Rh(111). With respect to the kinetic mechanism of the stepwise hydrogenation of atomic nitrogen to NH$_3$, the following experimental results are pertinent. (1) The rate of ammonia formation is linearly proportional to the hydrogen pressure below $5 \times 10^{-7}$ mbar H$_2$. (2) SIMS spectra indicate that N and NH$_2$ are the predominant surface species under reaction conditions, whereas NH$_3$ and possibly NH are present only in very small amounts. (3) The reaction-limited H$_2$ desorption state, emanating from NH$_x$ decomposition, indicates the presence of signifi-
cant amounts of NH₃ on the surface under reaction conditions; the average H:N ratio in the NH₃ intermediates is 1.1:1.

Concurrently, these results point to the hydrogenation of NH₃ as the rate-determining step. We therefore propose the following sequence of steps with the associated equilibrium constants:

\[
\begin{align*}
H₂(g) + 2* & \rightleftharpoons 2H_{ads} \\
N_{ads} + H_{ads} & \rightleftharpoons NH_{ads} + * \\
NH_{ads} + H_{ads} & \rightleftharpoons NH₂_{ads} + * \\
NH₂_{ads} + H_{ads} & \rightleftharpoons NH₃_{ads} + * \\
NH₃_{ads} & \rightleftharpoons NH₂_{g} + * \\
N_{tot}(t) & \rightleftharpoons N_{ads}(t)
\end{align*}
\]

We will justify and discuss this kinetic mechanism in the following. Under our experimental conditions, i.e., \(2 \times 10^{-8} < P_{H₂} < 1 \times 10^{-6}\) mbar and 325 < \(T < 400\) K, both the rate of hydrogen adsorption and desorption are fast compared to the NH₃ formation rate. Furthermore, hydrogen adsorption is sufficiently fast to supply hydrogen for the conversion of atomic hydrogen into NH₃ species. We therefore conclude that H₂ adsorption rapidly reaches equilibrium (on the order of seconds).

Although initially all the nitrogen on the surface is present as \(N_{ads}\), exposure to hydrogen results in the conversion of part of the atomic nitrogen into NH₃ species. It is difficult to determine the exact time scale upon which equilibrium between hydrogenation and desorption are fast compared to the NH₃ formation rate. Furthermore, hydrogen adsorption is sufficiently fast to supply hydrogen for the conversion of atomic hydrogen into NH₃ species. We therefore conclude that H₂ adsorption rapidly reaches equilibrium (on the order of seconds).

Under the assumption that equilibrium conditions apply for both H₂ adsorption and NH₃ intermediates up to NH₃, the following kinetic expression can be derived for the decrease of the nitrogen coverage with time (which is equal to the NH₃ formation rate):

\[
\frac{dθ_{N_{tot}}(t)}{dt} = -k_4θ_{NH}(t)θ_H
\]

\[
\frac{dθ_{N_{tot}}(t)}{dt} = -k_4θ_{N_{tot}}(t)θ_H + \frac{K_3K_5(K_pθ_H)}{1 + K_2(K_pθ_H)^{1/2} + K_3(K_pθ_H)^{1/2}} + (K_pθ_H)^{1/2}
\]

(5)

The number of empty sites available for hydrogen adsorption equals

\[
θ_e = 1 - θ_H - \sum θ_{NH_i}
\]

For the derivation of eq 5 we have made the assumption that \(θ_e \approx 1 - θ_H\). This has the advantage that two independent factors are obtained for the H₂ pressure dependence of the hydrogen adsorption equilibrium and the equilibria of the NH₃ 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.

\[\text{Figure 8. Dependence of the hydrogenation rate, determined as } ln(θ_{H}(t)/θ_{H}(t)) \text{ after } 160 \text{ s of reaction at } 1 \times 10^{-6} \text{ mbar, on the temperature. The effective activation energy was } 40 \text{ kJ/mol, and the effective pre-exponential was } 10^2 \text{ s}^{-1}.\]

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.

**H₂ Pressure Dependence of the NH₃ Formation Rate.** As the second factor in eq 5 indicates, the order in the H₂ pressure of the NH₃ coverage can vary between 0 and 1. As stated previously, the hydrogen coverage is small under our reaction conditions and therefore proportional to \(P_{H₂}^{1/2}\). This can easily be seen from the last factor in eq 5, which represents the hydrogen coverage and reduces to \((K_pθ_H)^{1/2}\) if \(K_pθ_H \ll 1\). In consequence of this, the order of the NH₃ formation rate in the H₂ pressure can vary between 1/2 and 3/2 as extremes.

Figure 5 shows that the NH₂ coverage increases with increasing H₂ pressures below \(\sim 5 \times 10^{-1}\) mbar, whereas the NH₂ coverage becomes constant at higher H₂ pressures. From a kinetic point of view, the observed H₂ dependence of the NH₂ coverage and the NH₃ formation rate is consistent. At pressures below \(5 \times 10^{-7}\) mbar both the NH₂ and the hydrogen coverage depend on the H₂ pressure, resulting in an overall first-order dependence of the NH₃ formation rate on the H₂ pressure. Above \(5 \times 10^{-7}\) mbar H₂, the NH₂ coverage becomes constant and the H₂ pressure dependence of the NH₃ formation rate is determined solely by the pressure dependence of the hydrogen coverage (\(\sim P_{H₂}^{1/2}\)).

**Presence of NH Intermediate on the Surface under Reaction Conditions.** The SIMS results of the surface under reaction conditions indicate that N and NH₂ are the predominant nitrogen surface species. Drechsler et al.\(^{35}\) using SIMS, have demonstrated that NH is the main surface species during the NH₃ 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. NH₂ is also detected but only in very small amounts. A previous study on the adsorption of NH₃ on Rh(111)\(^{36}\) indicated that an NH₃ coverage as small as 0.01 ML resulted in a SIMS Rh(NH₃)\(^+\)/Rh\(^+\) peak intensity ratio as large as \(\sim 7\). In the present case the SIMS Rh(NH₃)\(^+\)/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 NH₃ steady-state coverage is determined by the ratio of NH₃ production to the adsorption rate:

\[\text{NH}_2_{ads} + H_{ads} \rightarrow \text{NH}_3_{ads} \rightarrow \text{NH}_3_{gas}\]
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$_3$ 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$_2$:N surface coverage ratio on the basis of the SIMS data of Bassignana et al. They reported that on Ni(110) NH$_2$ formation at a pressure of 1 × 10$^{-6}$ mbar is almost independent of the temperature and equal to the saturation value. If we assume that the RH$_2$NH$_2$/$Rh_2N^+$ 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$_2$ 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$_2$ and the square root of the H$_2$ adsorption equilibrium constant, $k_{eff} = k_e K_{H_2}^{1/2}$ (see eq 5). Under these assumptions, the activation energy for the reaction of NH$_2$ to NH$_3$ equals

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

(7)

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$_2$ desorption is favored above NH$_3$ 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$_3$ intermediates, either during NH$_3$ decomposition or after 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$_2$ 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 RhN$^+$ 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 NH₂ species was also evidenced by the appearance of a reaction-limited H₂ desorption state at 415 K attributed to decomposition of NH₂.

From the temperature dependence of the NH₃ formation rate, an effective pre-exponential and activation energy of 10² 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 NH₂ to NH₃, is rate limiting. The activation energy of this step is 76 kJ/mol.

References and Notes