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# Formation of NH<sub>3</sub> and N<sub>2</sub> from atomic nitrogen and hydrogen on rhodium (111)

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Reactions of adsorbed N atoms on Rh(111) to N<sub>2</sub> and NH<sub>3</sub> were studied with temperature programmed desorption, temperature programmed reaction spectroscopy, and static secondary ion mass spectrometry. For N-atom coverages below  $\approx 0.15$  monolayers, desorption of N<sub>2</sub> follows simple second-order kinetics, but at higher coverages the desorption traces broaden to higher temperatures. Hydrogenation to NH<sub>3</sub> can be described by a stepwise addition of H atoms to N<sub>ads</sub> in which the reaction from NH<sub>2,ads</sub> + H<sub>ads</sub> to NH<sub>3,ads</sub> determines the rate. The activation energy for the rate determining step is 76 kJ/mol. The desorption of NH<sub>3</sub> from Rh(111) was studied separately. The kinetic parameters for desorption at low NH<sub>3</sub> coverage are 81 kJ/mol and 10<sup>13</sup> s<sup>-1</sup>, but the rate of desorption increases rapidly with increasing NH<sub>3</sub> coverage. It is argued that the remarkable coverage dependence of the desorption rate is unlikely to be caused by lateral repulsive interactions but may be due to a coverage dependence of the pre-exponential factor. © 1997 American Vacuum Society. [S0734-2101(97)56303-2]

## I. INTRODUCTION

The most important function of rhodium in a three-way catalyst is to reduce nitrogen oxides from automotive exhausts to harmless nitrogen.<sup>1</sup> The key step in the reduction of NO is the dissociation of NO into adsorbed nitrogen and oxygen atoms, N<sub>ads</sub> and O<sub>ads</sub>, for which all surfaces of rhodium have satisfactory reactivity.<sup>2-5</sup> Exhaust gas contains several constituents (CO, H<sub>2</sub>, and several hydrocarbons) that readily remove oxygen from the surface. The fundamentally important question then remains is how the N atoms react. The desirable pathway is that to N<sub>2</sub>, but reactions to NH<sub>3</sub> (Ref. 6) and HCN (Ref. 7) are conceivable as well.

The purpose of this article is to present and compare kinetic parameters for the reactions of atomic nitrogen to N<sub>2</sub> and to NH<sub>3</sub> on rhodium (111). Temperature programmed desorption (TPD), temperature programmed reaction spectroscopy (TPRS), and static secondary ion mass spectrometry (SSIMS) have proven to be a successful combination for studying such reactions in real time.<sup>3,4,6-9</sup> First, we describe how submonolayers of N<sub>ads</sub> can be prepared in a controlled way. Then we discuss the desorption of N<sub>ads</sub> to N<sub>2</sub>, and next the hydrogenation of N<sub>ads</sub> to NH<sub>3</sub>. Finally, we briefly discuss the desorption of NH<sub>3</sub>. The work has yielded activation energies and pre-exponential factors of a number of elementary surface reactions of adsorbed N atoms.

## II. EXPERIMENT

Experiments were done in an ultrahigh vacuum UHV system (base pressure around 1 × 10<sup>-10</sup> mbar) equipped with a Leybold SSM 200 quadrupole mass spectrometer for TPD and SSIMS measurements that is described elsewhere.<sup>3</sup> The rhodium crystal, cut in the [111] orientation within 0.5° and

polished by standard procedures, was mounted on a moveable stainless steel manipulator with 0.3-mm-thick tantalum wires, where it could be cooled to liquid nitrogen temperature and resistively heated up to 1500 K. Temperatures were measured with a Chromel–Alumel thermocouple spotwelded on the backside of the crystal. Small amounts of bulk impurities, such as sulphur, chlorine, and boron, were removed by cycles of argon sputtering (1.5 keV, 5 μA/cm<sup>2</sup>) at 900 K and annealing to 1400 K. Carbon was removed by annealing the crystal in 2 × 10<sup>-8</sup> mbar O<sub>2</sub> and slowly varying the temperature between 900 and 1100 K. Oxygen was removed from the surface by a short anneal to 1425 K. Hydrogen (Messer Griesheim, 99.999% pure), NO (Messer Griesheim, 99.5% pure), and NH<sub>3</sub> (Ucar, 99.995% pure) were used without further purification; gas exposures are reported in langmuirs (L) (1 L = 1.33 × 10<sup>-6</sup> mbar s); coverages are reported in monolayers (ML being the number of adsorbates per Rh surface atom).

## III. RESULTS AND DISCUSSION

### A. How to prepare atomic nitrogen

As N<sub>2</sub> does not chemisorb dissociatively on rhodium (111), one has to resort to other sources of N atoms. We have used NO in combination with H<sub>2</sub> at 400 K. The SIMS spectra in Fig. 1 show that the approach works: The lower spectrum is the SIMS between 200 and 250 atomic mass units (amu) of 3.0 L NO adsorbed on Rh(111) at 120 K. It shows ions of Rh<sub>2</sub><sup>+</sup> (206 amu) and Rh<sub>2</sub>NO<sup>+</sup> (236 amu) that are characteristic of molecularly adsorbed NO. Next, the surface is heated to 400 K to dissociate NO and to desorb the excess NO that cannot be dissociated.<sup>3</sup> The SIMS spectrum confirms that all NO has disappeared and that the surface instead contains N and O atoms, as indicated by the Rh<sub>2</sub>N<sup>+</sup> (220 amu) and Rh<sub>2</sub>O<sup>+</sup> (222 amu) secondary ions, respectively.

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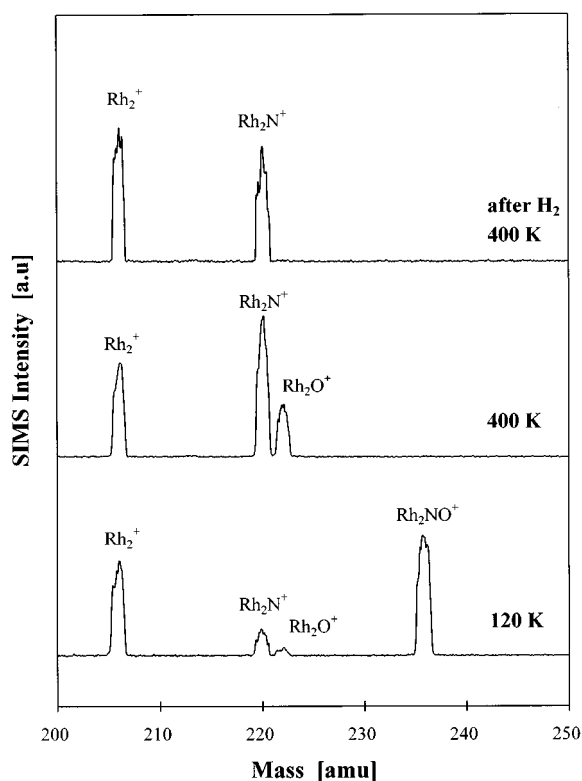


FIG. 1. SIMS spectra of the Rh(111) surface after the different reaction steps to produce  $\text{N}_{\text{ads}}$ ; adsorption of 3.0 L NO at 120 K, thermal NO dissociation at 400 K, and reaction with  $2.10^{-8}$  mbar  $\text{H}_2$  for 160 s to remove atomic oxygen.

Treatment in  $2 \times 10^{-8}$  mbar  $\text{H}_2$  at 400 K during 160 s removes all O atoms, as confirmed by the SIMS spectrum of Fig. 1 (top), which only contains peaks due to  $\text{Rh}_2^+$  and  $\text{Rh}_2\text{N}^+$ . Checking the N-ads coverage by means of thermal desorption indicated that virtually no N atoms are lost due to hydrogenation at 400 K. Thus,  $\text{N}_{\text{ads}}$  layers on Rh(111) are readily prepared by decomposing molecularly adsorbed NO at 400 K, followed by hydrogenation of O atoms at the same temperature. If one starts with NO coverages below 0.20 ML, where all the NO dissociates,<sup>3</sup> the eventual coverage of N atoms equals that of the initially molecular NO.

## B. Desorption of $\text{N}_2$

Recombinative desorption to form  $\text{N}_2$  is the desired reaction pathway of N atoms in the context of automotive exhaust catalysis. Figure 2 shows thermal desorption spectra of  $\text{N}_2$  from Rh(111) surfaces with coverages of  $\text{N}_{\text{ads}}$  in the range of 0–0.25 ML. Initially, the spectra follow the expected second-order desorption behavior, in agreement with the literature.<sup>10,11</sup> Chan–Aris–Weinberg analysis<sup>12</sup> indicates an activation energy of  $118 \pm 10$  kJ/mol and a pre-exponential factor of  $10^{10 \pm 1}$   $\text{s}^{-1}$  in the limit of zero coverage. The fact that the pre-exponential factor is smaller than  $kT/h$  ( $\sim 1.4 \times 10^{13}$   $\text{s}^{-1}$  at 650 K) indicates loss of entropy going from the free reactants to the transition state.

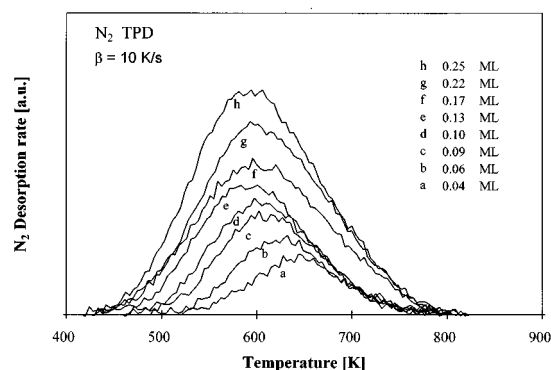
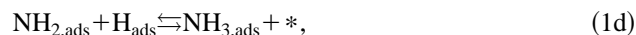
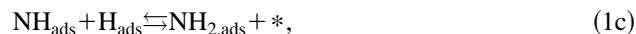


FIG. 2.  $\text{N}_2$  TPD spectra obtained from a Rh(111) surface covered with various amounts of atomic nitrogen. For atomic nitrogen coverages larger than 0.15 ML the  $\text{N}_2$  desorption peaks broaden towards the high temperature side.

For  $\text{N}_{\text{ads}}$  coverages of 0.15 ML and higher, however, the desorption traces broaden towards the *high* temperature side, indicating the population of sites from which the desorption proceeds is considerably slower than for the first 0.15 ML of N atoms. One explanation for the delayed  $\text{N}_2$  desorption might be formation of the N-induced ( $1 \times 2$ ) added row reconstruction of the Rh(111) surface, which was recently reported by Xu and Ng.<sup>13</sup>

## C. Hydrogenation of $\text{N}_{\text{ads}}$

Starting with a Rh(111) surface and a certain coverage  $\theta_{\text{N}}$  and exposing it to a background pressure of  $\text{H}_2$ , we can expect the following sequence of elementary steps:



The overall rate expressed in terms of a power rate law becomes

$$r_{\text{NH}_3} = - \frac{d\theta_{\text{N}}}{dt} = k_{\text{eff}} \cdot \theta_{\text{N}}^n \times p_{\text{H}_2}^m. \quad (2)$$

The rate of ammonia formation is too small to be measured directly with acceptable precision by a mass spectrometer, but the rate of reaction can accurately be determined by measuring the decrease in the coverage of  $\text{N}_{\text{ads}}$  by means of thermal desorption after hydrogenation.

The order of ammonia formation in the coverage of N atoms equals  $n = 1$ , as follows from the straight line plot of  $\ln \theta_{\text{N}}$  versus time, measured at 375 K and a constant pressure of  $2 \times 10^{-7}$  mbar of  $\text{H}_2$ .<sup>6</sup> The order in hydrogen was determined at 375 K and  $\text{H}_2$  pressures between  $5 \times 10^{-8}$  and  $10^{-6}$  mbar, for a fixed reaction time of 160 s, (see Fig. 3). In the low pressure regime (i.e., below  $4 \times 10^{-7}$  mbar), the rate

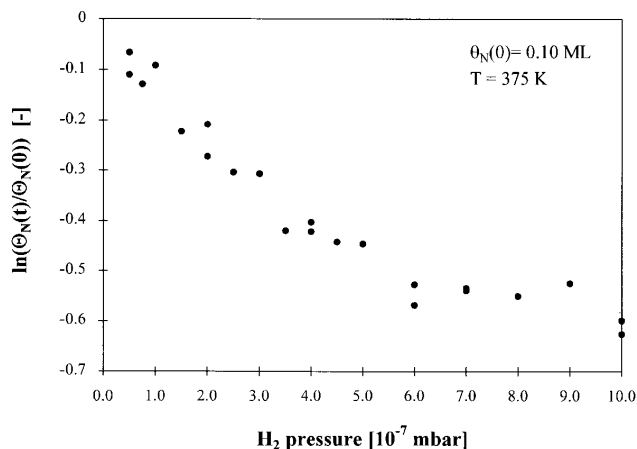


FIG. 3. The influence of  $\text{H}_2$  pressure on the hydrogenation rate, indicated by plotting the  $\ln[\theta_{\text{N}}(t)/\theta_{\text{N}}(0)]$  after 160 s of reaction vs  $\text{H}_2$  pressure. Initially the hydrogenation rate is linearly proportional to the  $\text{H}_2$  pressure, but the dependence levels off above  $\approx 5.10^{-7}$  mbar  $\text{H}_2$ .

is approximately first order in hydrogen. As the coverage of H atoms  $\theta_{\text{H}}$  is proportional to  $p(\text{H}_2)^{1/2}$  or lower, an order in  $\text{H}_2$  equal to 1 implies that the first hydrogenation step, reaction (1a) in the scheme above, does *not* determine the rate.

Hence, either step (1c), (1d), or (1e) should be considered rate determining.

In order to identify a rate determining step, one needs to establish which species reside on the surface during hydrogenation. Static SIMS can provide this information, although in a qualitative way. The SIMS spectrum in the left panel of Fig. 4, measured during hydrogenation at 375 K and  $5.10^{-7}$  mbar  $\text{H}_2$ , shows peaks of  $\text{Rh}_2^+$ ,  $\text{Rh}_2\text{H}^+$ ,  $\text{Rh}_2\text{N}^+$ , and  $\text{Rh}_2\text{NH}_2^+$ . SIMS measurements of the N hydrogenation by means of deuterium give better mass separation and confirm the assignments. The fact that the Rh(111) surface contains a significant concentration of  $\text{NH}_2$  species during the hydrogenation of  $\text{N}_{\text{ads}}$  clearly points to the reaction between  $\text{NH}_{2,\text{ads}}$  and  $\text{H}_{\text{ads}}$ , step (1d) in the scheme above, as the rate-determining step. The right panel of Fig. 4 shows the SIMS intensity ratio  $\text{Rh}_2\text{NH}_2^+/\text{Rh}_2\text{N}^+$  when measured as a function of  $\text{H}_2$  pressure. Note that, from a kinetic point of view, the decreasing  $\text{H}_2$  dependence of the  $\text{Rh}_2\text{NH}_2^+/\text{Rh}_2\text{N}^+$  ratio above  $5.10^{-7}$  mbar  $\text{H}_2$  agrees with the decreasing  $\text{H}_2$  dependence of the hydrogenation rate (see Fig. 3).

It is interesting that not all N atoms are converted to  $\text{NH}_2$ . If the reaction of Fig. 4 is stopped and the surface cooled down and subsequently heated in a TPD experiment, the atomic hydrogen desorbs below 380 K, but at 415 K a reaction limited desorption peak of hydrogen arises, mainly due to the decomposition of  $\text{NH}_{2,\text{ads}}$ , while the N atoms de-

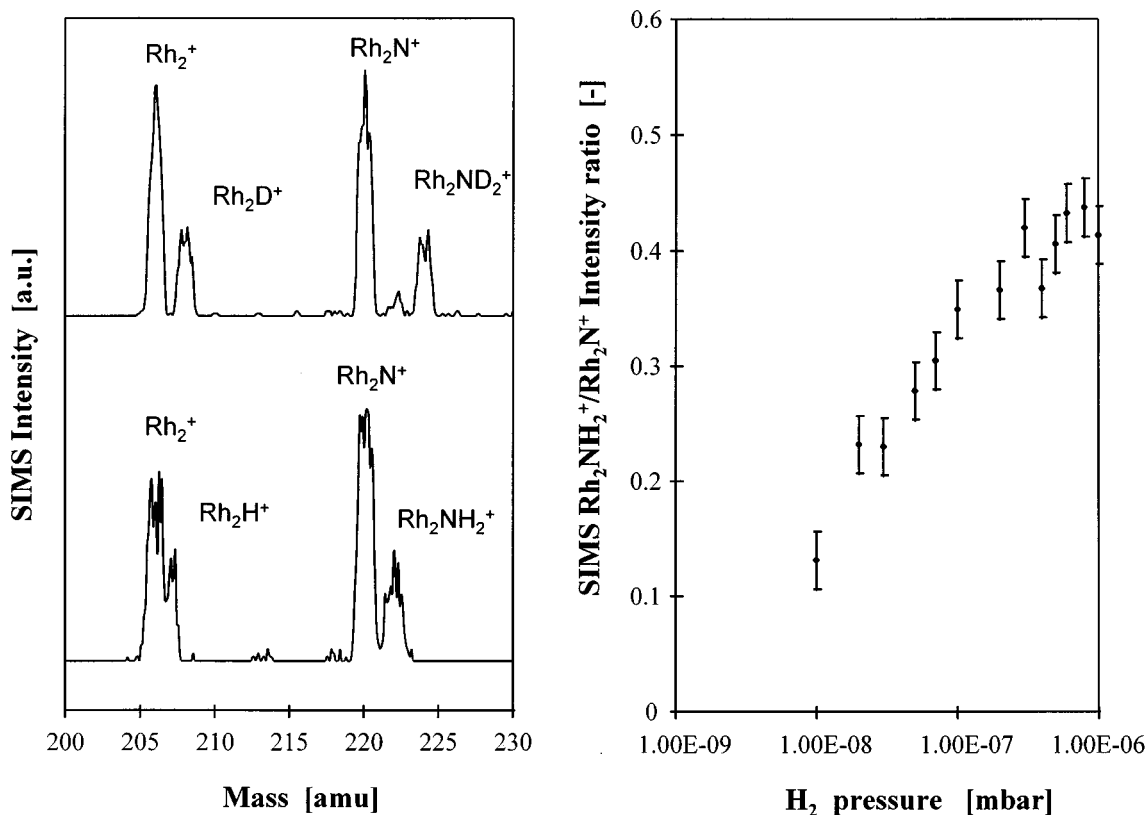


FIG. 4. (Left) SIMS spectrum of the Rh(111) surface during a hydrogenation experiment showing the presence of H, N, and  $\text{NH}_2$ , as reaction intermediates. Peak assignments were verified by using  $\text{D}_2$  instead of  $\text{H}_2$ . The spectrum was taken after 20 s of reaction; the  $\text{H}_2$  pressure was  $5.10^{-7}$  mbar and  $T=375$  K. (Right)  $\text{H}_2$  pressure dependence of the SIMS  $\text{Rh}_2\text{NH}_2^+/\text{Rh}_2\text{N}^+$  peak intensity ratio which initially increases with  $\text{H}_2$  pressure but reaches a saturation value of 0.43 above  $5.10^{-7}$  mbar.

sorb as in Fig. 2. The experiment suggests a stoichiometry of  $\text{N}:\text{H}=1:1$ , implying that half of the nitrogen is present as  $\text{NH}_{2,\text{ads}}$  during hydrogenation at 350 K. These findings suggest that N atoms are present in islands, whereas hydrogenation is limited to the edges of these islands.

Finally, measuring the temperature dependence of the rate yields an effective activation energy of 40 kJ/mol and a pre-exponential factor of  $100 \text{ s}^{-1}$ . If we write the rate of reaction as

$$r = k_4 \times \theta_{\text{NH}_2} \times \theta_{\text{H}} \approx k_4 \times K_{\text{H}_2}^{1/2} \times \theta_{\text{NH}_2} \times p_{\text{H}_2}^{1/2}, \quad (3)$$

while the heat of adsorption of  $\text{H}_2$  equals 72 kJ/mol, the true activation energy of the rate determining step (1d) becomes 76 kJ/mol.

#### D. Temperature programmed desorption of $\text{NH}_3$ from Rh(111)

Desorption of  $\text{NH}_3$  is kinetically insignificant in the hydrogenation scheme described above, but can of course be studied separately. Temperature programmed desorption spectra were measured at a heating rate of 5 K/s after adsorption of  $\text{NH}_3$  at 120 K. In order to check whether ammonia decomposes, the mass channels  $m/e=2(\text{H}_2)$ ,  $m/e=17(\text{NH}_3)$ ,  $m/e=28(\text{N}_2)$ , and  $m/e=30(\text{N}_2\text{H}_2)$  were monitored. In all cases,  $\text{NH}_3$  was the only detectable N-containing desorption product. Some  $\text{H}_2$  desorption was indeed observed, but this was attributed to adsorption of small amounts of  $\text{H}_2$  from the background.

The  $\text{NH}_3$  desorption spectra in Fig. 5 show three distinct desorption states depending on the  $\text{NH}_3$  coverage. The first low coverage state, denoted by  $\alpha_1\text{-NH}_3$ , has a maximum around 320 K which broadens significantly to lower temperature with increasing  $\text{NH}_3$  coverage. Application of the Redhead method<sup>14</sup> to the low coverage peak at 320 K yields a desorption energy of  $81.5 \pm 3 \text{ kJ/mol}$  for  $\alpha_1\text{-NH}_3$  if a pre-exponential factor of  $10^{13} \text{ s}^{-1}$  is assumed. Other analysis methods that in general give more reliable answers<sup>15</sup> appeared unsuitable because of the strong dependence of the desorption energy on the coverage.

The transition to the second desorption state  $\alpha_2\text{-NH}_3$ , which maximizes at 155 K, takes place very gradually. Above  $\text{NH}_3$  exposures of  $\approx 0.45 \text{ L}$ , a third desorption state,  $\beta\text{-NH}_3$ , is observed by a very sharp peak at 130 K. Application of the Redhead method yields a desorption energy of 32 kJ/mol for this  $\beta\text{-NH}_3$  if, again, a pre-exponential factor of  $10^{13} \text{ s}^{-1}$  is assumed.

The adsorption of  $\text{NH}_3$  on Rh(111) greatly resembles that on the hexagonally close-packed surfaces of other group VIII metals, such as Pt(111), Ru(0001), and Ni(111).<sup>16–19</sup> All systems exhibit the remarkable decrease of the  $\alpha_1\text{-NH}_3$  desorption temperature with increasing  $\text{NH}_3$  coverage. This was formerly attributed to a decrease of the desorption energy caused by repulsive lateral interactions between  $\text{NH}_3$  molecules.<sup>19</sup> One problem with this explanation is that the dramatic influence of the coverage on the desorption energy is by no means recognized in the coverage dependent behavior of the work function. As is shown elsewhere,<sup>20</sup> the work

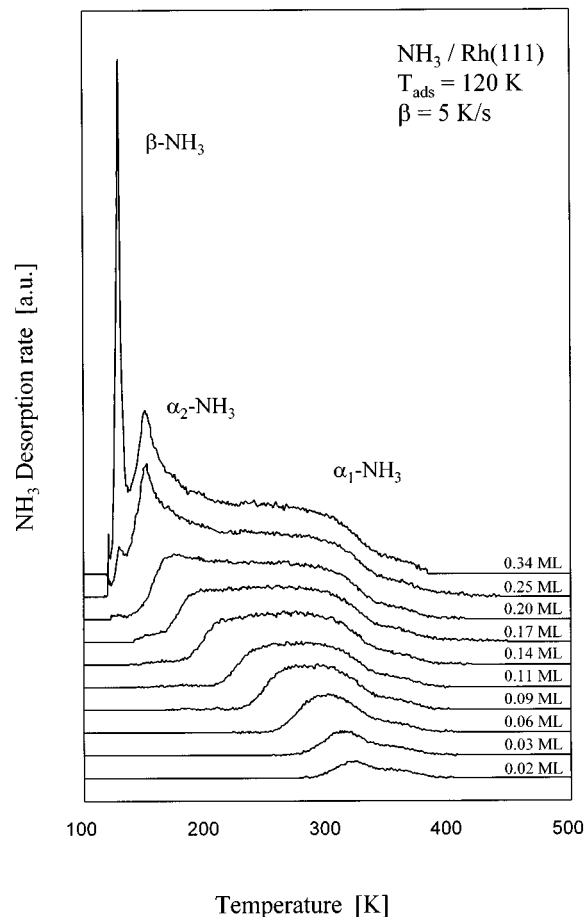


FIG. 5. TPD spectrum of  $\text{NH}_3$  obtained after exposure of various amounts of  $\text{NH}_3$  at 120 K. The heating rate was 5 K/s.

function decreases linearly with the  $\text{NH}_3$  coverage up to a coverage of  $\approx 0.15 \text{ ML}$ , implying that the work function change and, consequently, the average dipole per adsorbed  $\text{NH}_3$  molecule, is constant. If repulsive lateral interactions were responsible for the large decrease in the desorption energy, the average dipole of the  $\text{NH}_3$  molecules would be expected to be influenced as well. We therefore wonder if an alternative explanation in terms of entropy effects could be given.

According to conventional transition state theory, the rate of desorption equals<sup>21</sup>

$$r_{\text{des}} = \frac{k_B T}{h} \frac{p f^\ddagger}{p f} e^{-E_{\text{des}}/RT} \theta_{\text{NH}_3}, \quad (4)$$

where  $k_B$  = Boltzmann's constant,  $T$  = temperature,  $h$  = Planck's constant,  $p f^\ddagger$  and  $p f$  are the partition functions of the transition state and the ground state, respectively,  $E_{\text{des}}$  = desorption energy,  $R$  = gas constant, and  $\theta_{\text{NH}_3}$  =  $\text{NH}_3$  coverage.

If the adsorption energy and, hence,  $E_{\text{des}}$  are constant, a coverage dependence of the desorption rate constant can still be caused by the ratio of the partition functions. For example, let us suppose that adsorbed ammonia molecules are mobile in the high temperature/low coverage regime of the

TABLE I. Kinetic parameters of several elementary surface reactions.

Reaction	$E_{\text{act}}$ (kJ/mol)	$\nu$ (s <sup>-1</sup> )	Source
NO <sub>ads</sub> + * → N <sub>ads</sub> + O <sub>ads</sub>	65 ± 6	10 <sup>11 ± 1</sup>	Ref. 3
N <sub>ads</sub> + N <sub>ads</sub> → N <sub>2</sub> + 2*	118 ± 10	10 <sup>10 ± 1</sup>	This work
NH <sub>2,ads</sub> + H <sub>ads</sub> → NH <sub>3,ads</sub> + *	76 ± 6	...	This work; Ref. 6
NH <sub>3,ads</sub> → NH <sub>3</sub> + *	81 ± 5	10 <sup>13</sup> (assumed)	Ref. 20

TPD spectra, and that the transition state for desorption is mobile as well, then the ratio of the partition functions  $pf^{\ddagger}/pf$  is on the order of 1 and the molecule desorbs with a pre-exponential factor on the order of  $e \times k_B \times T/h = 10^{13} \text{ s}^{-1}$ .<sup>21</sup> As the coverage becomes higher, the translational partition function of the ground state decreases, whereas that of the transition state may remain high. The result is that the ratio  $pf^{\ddagger}/pf$  in (4) increases, causing the pre-exponential to go up with coverage, while the adsorption energy remains constant until the adsorbate molecules start to interact, that is, in the  $\alpha_2$  state. Note that, if the above interpretation is correct, the estimate of the low coverage adsorption energy on the basis of the Redhead formula, 81 kJ/mol, should be correct, as the pre-exponential factor would indeed be on the order of  $10^{13} \text{ s}^{-1}$ .

#### IV. CONCLUSIONS

- (1) N<sub>ads</sub> layers of well determined coverage on Rh(111) can be prepared by using the NO+H<sub>2</sub> reaction.
- (2) The desorption of N<sub>ads</sub> from Rh(111) to N<sub>2</sub> initially follows second-order kinetics, with rate parameters as in Table I. The broadening of the TPD traces to higher temperatures at coverages above 0.15 ML is tentatively explained by a N-induced (1 × 2) reconstruction of the Rh(111) surface.
- (3) The hydrogenation of N<sub>ads</sub> on Rh(111) can be described as a stepwise addition of H atoms, in which the addition of the third H atom determines the rate (kinetic parameters in Table I). The overall hydrogenation is a slow

reaction ( $E_{\text{act}}^{\text{eff}} = 40 \text{ kJ/mol}$ ;  $\nu^{\text{eff}} = 10^2 \text{ s}^{-1}$ ). Some evidence has shown that hydrogenation occurs at the edges of N islands only.

- (4) The rate of NH<sub>3</sub> desorption from Rh(111) depends strongly on coverage, as it does on other group VIII metals. It is argued that the coverage dependence may be dominated by the pre-exponential factor due to a mobile ground state of the NH<sub>3</sub> molecule at the desorption temperature.

#### ACKNOWLEDGMENTS

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