The Synthesis of Ammonia over a Ruthenium Single Crystal

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The ammonia synthesis rate over a ruthenium single crystal has been studied in the temperature range 598–898 K. Ammonia was synthesized from a stoichiometric ($3H_2 : N_2$) gas-mixture at a pressure of approximately 2 bar. The ammonia production rate was measured in two ways: with the reactor isolated (batch mode) and under constant gas flow (flow mode). The overall activation energy was measured to be 101 ± 4 kJ/mol, and the turnover frequency was 2×10^{-2} s^{-1} at 673 K. After synthesis, the primary adsorbed species was nitrogen and there was evidence of hydrogen in the bulk of the crystal. © 1998 Academic Press

1. INTRODUCTION

Industrially, ammonia is generally synthesized in a catalytic reaction between nitrogen and hydrogen over an iron based catalyst. This catalytic system which has been known for 80 years has been studied extensively and there exist considerable knowledge about it even at the atomic level (1–5). As an alternative to this traditional iron catalyst, ruthenium based catalysts have also been studied (6–10). Some of these have shown promising activity and stability. Like on the iron-based catalyst, alkali metals are strong promoters on the ruthenium based catalysts. The most electropositive of the alkali metals, Cs, has been found to give the best activity (6).

The main advantage of the Ru-based catalysts is that they are less sensitive to poisoning by ammonia than Fe-based catalysts. Instead, they are inhibited by hydrogen (7, 8) which is not the case for Fe-based catalysts (3). For this reason the Ru-based catalysts have a higher activity when used at lower H_2/N_2 ratios than at the stoichiometric one, which however is less favorable since it gives a lower ammonia content at equilibrium conditions. Thus the optimum H_2/N_2 ratio and gas pressure for Ru-based catalysts is a balance between activity and equilibrium (8).

Several studies have reported turnover frequencies of catalytic reactions over single crystal surfaces, which are in agreement with the turnover frequencies obtained over high surface area catalysts. Examples of such studies are on the ammonia synthesis reaction over Fe (5), the metha-nation reaction over Ni (11), and the methanol synthesis over Cu (12–14), and they clearly demonstrate that single crystal surfaces can serve as models for the active part of a catalyst despite the so-called structure gap between the small particles in high surface area catalysts and the single crystal surfaces. An advantage of using single crystal surfaces is that the surface can be very well characterized with surface science techniques, giving the possibility to pinpoint the exact reasons for changes in the catalytic activity of the surface. The present study is the first step in using this procedure on the ammonia synthesis over clean and modified Ru surfaces.

Here we report on the synthesis of ammonia over a well-defined clean ruthenium single crystal. The ammonia was synthesized from a stoichiometric ($3H_2 : N_2$) gas mixture at a pressure of approximately 2 bar and in the temperature range 598–898 K. The results obtained are compared to results from experiments on ruthenium based catalysts, as well as to a single experiment done with the same apparatus over a Fe(111) surface (15).

2. METHODS

The experiments were carried out in a stainless steel UHV system with a base pressure of 1×10^{-10} mbar. A micro reactor, built to withstand 10 bar, was contained within the UHV system, allowing direct transfer of the sample from vacuum into the micro reactor, Fig. 1. The setup, which was equipped with an X-ray photoelectron spectrometer, a differentially pumped quadrupole mass spectrometer, a differentially pumped ion sputter gun, and a gas doser, has been described previously in an ammonia synthesis study over polycrystalline iron (16). In the present study the sample was a Ru(0001) single crystal, of about 1 cm in diameter and 2-mm thick. It was mounted on a 0.6-mm tungsten wire, which was also used for resistively heating the crystal. The temperature of the crystal was measured with a chromel–alumel thermocouple spot welded to the edge of the crystal. After the experiments were carried out, Laue X-ray diffraction showed that the crystal was miscut by 4° in the [1 1 $\overline{2}$ 0] direction and, therefore, has approximately one
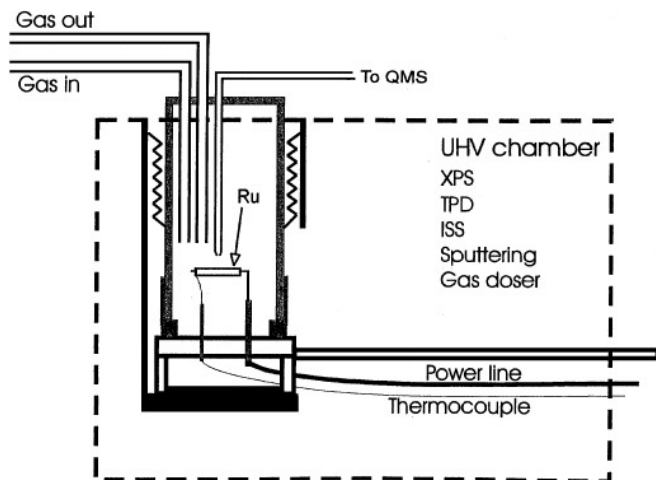
FIG. 1. Sketch of the experimental setup. The micro reactor is shown in the situation when it is isolated from the UHV chamber.

single atomic step for every 12 terrace atoms, and the steps are made of atoms in zigzag rows. The proper name for the crystal front facet is Ru(1 1 $\overline{2}$ 45).

The crystal was cleaned at one face by sputtering with 1 keV Ar$^+$ ions, cyclic heating in 3×10^{-8} mbar of O_2, followed by annealing at 1525 K in vacuum. Unfortunately, this treatment was found to clean the entire surface of the crystal, so that not only the front but also the sides and the back of the crystal were cleaned and therefore active in the synthesis experiments. Attempts to passivate the sides and the back of the crystal with sulfur was not successful, since the sulfur was mobile in the synthesis experiment and therefore ended up contaminating the front of the crystal as well. A method for eliminating this problem is at present under development.

The crystal surface cleanliness was monitored by X-ray photoelectron spectroscopy (XPS). Since the C_{1s} and Ru_{3d} binding energies are similar, XPS cannot be used to measure the presence of carbon containing species. Instead, the surface was tested for carbon impurities by adsorbing oxygen and monitoring the thermal desorption of CO and CO_2. Inside the micro reactor, schematically depicted in Fig. 1, a quartz capillary orifice with a submicron hole was positioned about 3 mm above the crystal surface, allowing a controlled leak between the micro reactor and the mass spectrometer (17). The glass-lined tube connecting the capillary and the mass spectrometer was kept at about 425 K to minimize the adsorption of ammonia on the internal walls of the tube. The micro reactor was cleaned by exposing the crystal to the gas mixture at the highest crystal temperature repeatedly for long time. After this initial treatment experiments could be repeated in the micro reactor without significant loss of activity during the experiments.

A stoichiometric gas mixture ($3H_2 : N_2$) containing 5% He and 5% Ne was used in the synthesis experiments. The He and Ne was used for calibration of the mass spectrometer signals, since the amount of gas leaked to the mass spectrometer depends on crystal temperature. The gas mixture was cleaned by passing it over hot Ni and Cu catalysts and thereafter a dry ice cooled molecular sieve. The total pressure during the synthesis experiments was approximately 2.3 bar. The synthesis experiments were started by isolating the cleaned ruthenium crystal in the micro reactor and then a flow of synthesis gas was let through the micro reactor. The ammonia synthesis rate was measured by two methods; batch mode and flow mode. A typical "batch mode" experiment proceeded as follows: The sample temperature was raised to the appropriate level. When the signals monitored by the mass spectrometer had stabilized the micro reactor was isolated from the gas flow and the increase in ammonia partial pressure was measured for 30–180 min. depending on temperature. After this, synthesis gas was flowed through the reactor in order to remove most of the synthesized ammonia. The experiment was then repeated at another temperature or it was stopped. A "flow mode" run was done as follows: The gas flow was measured. It was between 10 and 20 Nml/min. The temperature of the crystal was raised to the desired level and left at that temperature for 200–800 min, long enough to reach steady state for the ammonia concentration in the reactor. After this the temperature was raised and the procedure was repeated. At last the crystal was allowed to cool to 330 K and after approximately 1000 min the zero point for the ammonia signal was established and the experiment was stopped.

After the rate measurements had ended the gas flow was stopped, the micro reactor was evacuated by a turbo molecular pump and finally the crystal was removed from the micro reactor for analysis in the UHV chamber.

The gas phase contents of the micro reactor was monitored with the mass spectrometer throughout the synthesis experiments. A large number of masses were monitored, however, the only significant intensity changes were observed for those masses related to ammonia and water. The water signal was mainly due to water produced in the mass spectrometer since it had no effect on the ammonia synthesis rate that the water signal decreased as more synthesis experiments were carried out. It was therefore necessary to compensate the mass spectrometer signal for overlap of masses between ammonia and water. The concentration of ammonia as measured by the mass spectrometer was calibrated against an infrared sensitive detector (Leybolds BINOS). This calibration could be checked, in the cases where the ammonia concentration was getting very close to equilibrium. It was found that there was good agreement between the ammonia concentration found from the calibration and the equilibrium concentration calculated from thermodynamic data (18) (see Fig. 2). The error in the measured ammonia concentration was always found to be less than 20%.
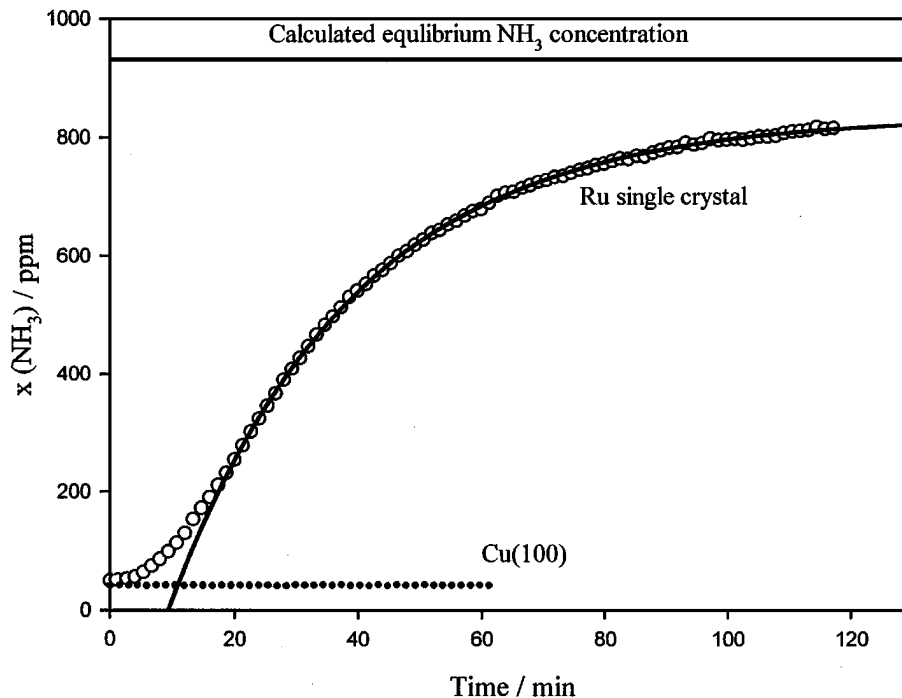
FIG. 2. Results from batch mode experiments at 873 K with the Ru crystal and a Cu(100) crystal. The full line is a fit to the Ru crystal data. The ammonia concentration is not zero-point corrected since it has no influence on the slope. The horizontal line is the calculated equilibrium concentration of ammonia at the given temperature and pressure. See text for discussion.

In order to check that no parts inside the micro reactor, other than the Ru crystal, were active in synthesizing ammonia, a few batch-mode experiments were carried out with the ruthenium crystal replaced by a Cu(100) crystal. In Fig. 2, the ammonia signal as a function of time is shown for both the ruthenium crystal and the Cu(100) crystal under identical experimental conditions. The lack of ammonia production observed for the Cu(100) surface, not only shows that copper is a very poor ammonia catalyst, but also that the other hot surfaces, such as the hot tungsten filament and the thermocouple in the micro reactor, did not produce ammonia.

To find out if the hot tungsten filament heating the ruthenium crystal was a serious problem, we performed a model experiment by heating a crystal under ambient conditions. We found that the maximum temperature difference between the crystal and the tungsten filament was 120 K when the crystal temperature was approximately 770 K. This difference increased to 200 K when an air flow was introduced to mimic the greater heat conductivity of the synthesis gas containing hydrogen. The hot region was at a short distance from where the tungsten filament entered into the holes of the crystal. To estimate the effect of these two hot spots, one has to know the distance that the hot gas will travel before it is in equilibrium with the rest of the gas. The translational and rotational relaxation is fast but the vibrational relaxation is quite slow—up to 10^8 collisions per gas molecule

is needed before the vibrations have equilibrated with the surrounding gas (19). Since the mean free path for the gas molecules was about 100 nm we find that the mean diffusion length of the molecules was well below 1 mm before they relaxed. This diffusion length implies that at maximum 2% of the crystal was affected by the vibrational hot gas. The molecular beam results of Romm *et al.* (20) indicate that this area of the crystal was up to 10 times as active as the rest of the crystal, giving rise to a maximum 20% increase in total activity, which is within the experimental uncertainty. We believe that the high N$_2$ sticking coefficient on Ru(0001) reported in (21, 22), when the ion gauge was switched on, is due to electronically excited or dissociated N$_2$ which by no means can be obtained by a filament slightly hotter than the crystal. The model experiment also clearly showed that the convection was pronounced, an effect that will further reduce any effect of the slightly hotter filament.

3. RESULTS

At temperatures higher than approximately 800 K the concentration of ammonia in the micro reactor during a synthesis experiment was close to the equilibrium concentration of ammonia. This is, for instance, seen in Fig. 2 where the ammonia signal measured during a batch mode experiment at 873 K is shown. When the ammonia concentration approached equilibrium the decrease in the apparent

rate of ammonia production was caused by the increase in ammonia decomposition as the ammonia concentration increased. Alternatively, the increase in ammonia concentration could lead to site blocking on the surface reducing the rate. However, this was not believed to be the case since the reaction order for ammonia is close to zero for ammonia synthesis with Ru-powder (9, 23). The fit to the curve seen in Fig. 2 was based on the assumption that the decomposition of ammonia was first order in the ammonia concentration under these conditions. This is in agreement with measurements by Tsai and Weinberg (24) on the decomposition of ammonia over a Ru(0001) surface. They found that the decomposition was first order in P_{NH_3} for temperatures above 750 K. The time dependence of the ammonia concentration used in the fit in Fig. 2 is thus

$$x_{NH_3} = x\mathrm{sat}_{NH_3}(1 - \exp(-k(t - t_o))) \qquad [1]$$

were $x\mathrm{sat}_{NH_3}$ is the ammonia concentration at equilibrium at the given conditions. t_0 is a shift in time, which is discussed below. In order to get a good estimate of the reaction rate at zero ammonia concentration (rate$_0$ $\propto$ the slope at zero ammonia concentration in Fig. 2) it was necessary to correct for the decomposition of ammonia at nonzero ammonia concentration for temperatures above 800 K. From the kinetics for the ammonia decomposition one gets the following correction formula:

$$rate_0 = rate(x_{NH_3}) \Big/ \left(1 - \frac{x_{NH_3}}{x\mathrm{sat}_{NH_3}}\right). \qquad [2]$$

When the temperature was lower than 800 K no correction was needed since the ammonia concentration was less than 10% of the equilibrium concentration.

In Fig. 2 it is seen that the measured ammonia concentration did not start increasing at once when the reactor was closed at $t = 0$. This was due to a time constant caused by a lack of complete mixing in the high pressure cell and the adsorption of ammonia on the interior walls of tubes and the micro reactor. To compensate for this the fit was shifted in time. The problems with adsorption and mixing and the fact that the average gas temperature in the micro reactor was unknown make it somewhat difficult to calculate the absolute ammonia synthesis rate in the batch mode experiments. This obstacle was overcome by using a reaction rate from the flow mode experiment as a reference, as discussed below.

A typical flow mode experiment is shown in Fig. 3. The decrease in activity seen at 873 K was due to surface contamination by sulfur possibly originating from the micro reactor walls. The amount of sulfur was normally so small that it was undetectable with XPS after a standard synthesis experiment, but it could be detected after prolonged experiments (several hours) at high temperatures. Generally the deactivation rate decreased for every time synthe-
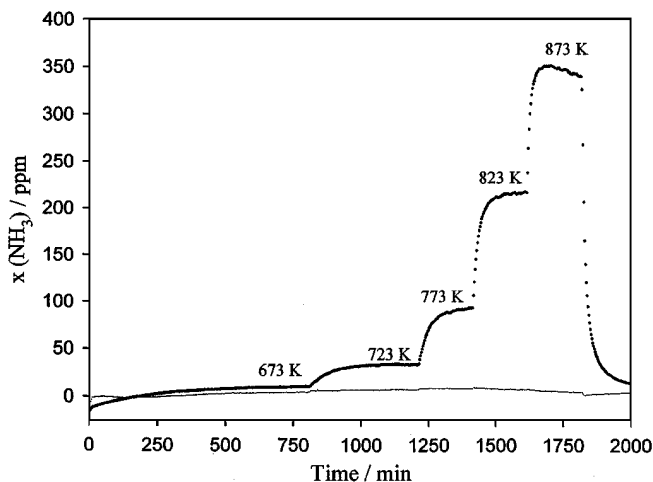
FIG. 3. Flow mode experiment on ammonia synthesis over the Ru crystal. The total pressure of H_2 and N_2 was 2.1 bar and the gas flow through the reactor was 15 Nml/min. The thin line is the water signal. All concentrations have been shifted according to the zero point found at a crystal temperature of 330 K. The ammonia concentration starts below this zero point since it took a while before the mass spectrometer was conditoned after the four orders of magnitude increase in pressure when the gas was let into the micro reactor.

sis was carried out at the highest temperatures, so it would have been totally eliminated by synthesis for several days at 873 K or higher. In order to establish a zero point for the ammonia signal, the crystal was kept at 330 K for a long period of time.

Arrhenius plots of the rates of ammonia synthesis are shown in Fig. 4 for the batch-mode experiments and in Fig. 5 for the flow-mode experiments. The absolute rates for the batch mode experiments were found by setting the rate at 773 K, equal to the rate at that temperature in the flow-mode experiment. As seen in the two figures there is a satisfactory agreement between the two activation energies.

The overall activation energy for the synthesis was on average found to be 101 ± 4 kJ/mol. Assuming that the whole crystal was active and that the density of surface sites was equal to the surface density of atoms for the Ru(0001) surface, the turnover frequency was found to be approximately 2×10^{-2} s^{-1} at 673 K.

After synthesis the crystal was characterized with XPS and temperature programed desorption (TPD). Sometimes there was more than 1% sulfur on the surface and, if this was the case, the results from the preceding synthesis experiment were rejected. XPS always showed that there was oxygen and nitrogen on the surface after synthesis.

In Fig. 6 the thermal desorption products from the crystal after an ammonia synthesis experiment are shown and it is seen that CO (mass 12 and mass 28) and N_2 (mass 14 and mass 28) were desorbing from the surface. The synthesis experiments were performed at temperatures above the desorption temperature of CO, so the CO observed was
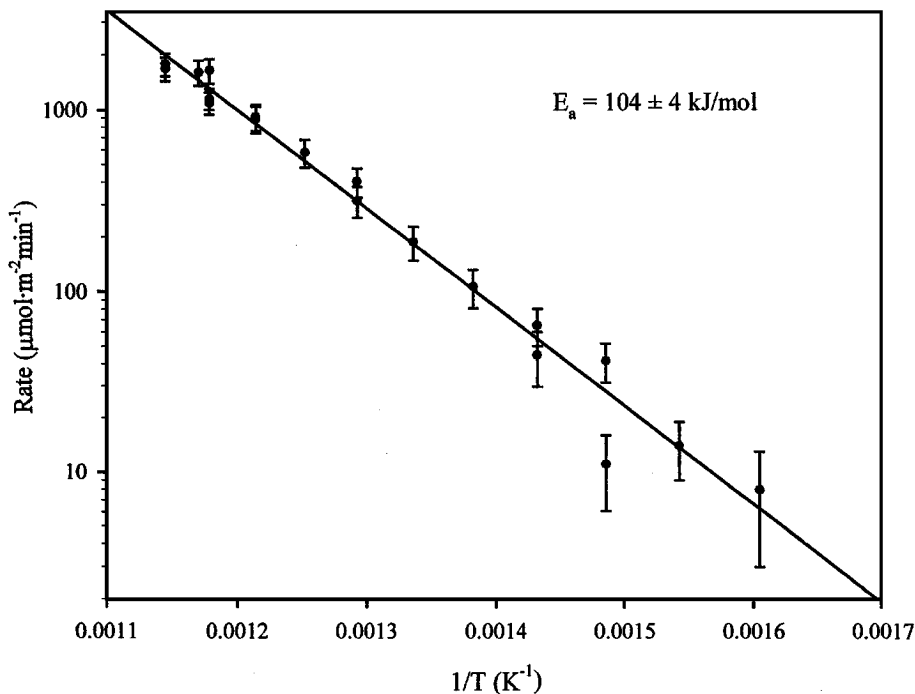
FIG. 4. Arrhenius plot for ammonia production rates measured in batch mode.

adsorbed after the synthesis experiments. This was clearly reflected by the fact that the size of the CO signal depended strongly on the time between synthesis and TPD, as well as the quality of the UHV background between synthesis and TPD. This CO also explains the oxygen observed on the sur-

face with XPS after a synthesis experiment. The desorption of N$_2$ between 700 K and 825 K is in agreement with work on Ru(0001) (21). Like CO, there is a problem with nitrogen adsorption after the synthesis experiments. The sticky nature of ammonia caused the removal of ammonia to be
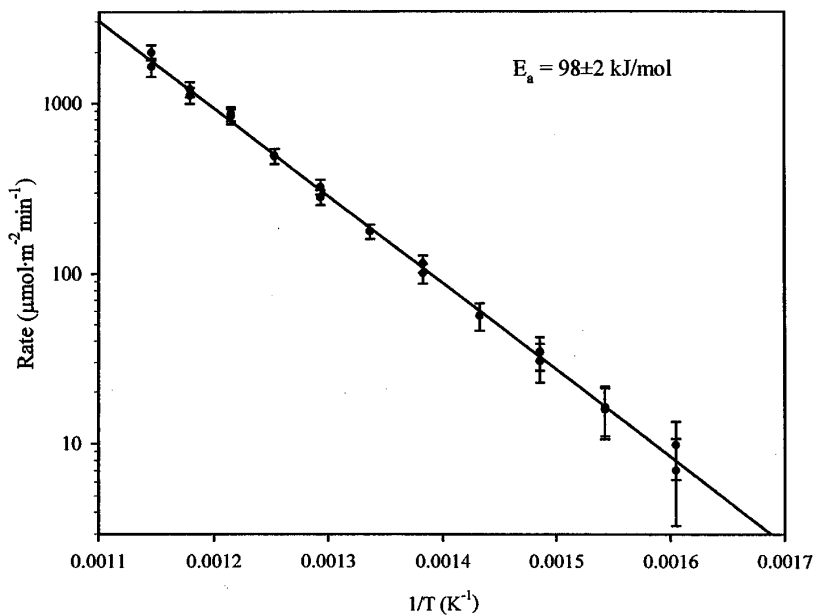

FIG. 5. Arrhenius plot for ammonia production rates measured in flow mode.
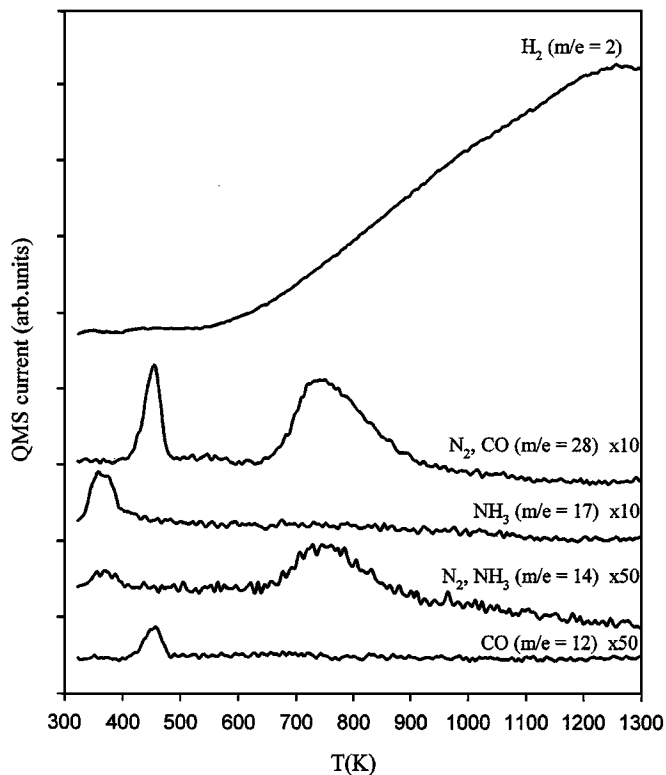
FIG. 6. TPD spectra from the Ru crystal after ammonia synthesis. The heating rate was 2 K/s. The zero points are shifted.

slow, which gave the possibility for increasing the nitrogen coverage by adsorption of ammonia after the crystal was cooled in the synthesis gas, and also after the micro reactor was evacuated. Thus the amount of nitrogen on the surface observed after the synthesis experiment could not be used as a measure of the nitrogen coverage during synthesis. Normally H_2 desorption is observed at temperatures below 500 K on Ru(0001) (25, 26). After ammonia synthesis, desorption of H_2 was seen high above these temperatures and the amount of H_2 desorbing corresponds to much more than one monolayer. Therefore it is believed that the desorbing hydrogen originated from the bulk of the crystal, indicating that hydrogen was dissolved in the bulk during ammonia synthesis at high pressures. This has also been observed for hydrogen in copper (27).

4. DISCUSSION

There is a general consensus that the rate limiting step for ammonia synthesis on ruthenium is the dissociative adsorption of N_2 like it is in the case of iron (1–3). This is concluded from the fact that the reaction order for N_2 has always been found to be close to 1 for ruthenium based catalysts and Ru-powder (7–9, 23) and that the dissociative adsorption of N_2 is activated on ruthenium (22, 28). For iron the dissociative adsorption of N_2 and the ammonia synthesis

activity has been seen to be sensitive to the surface structure [4, 5, 28–30]. Recently Dietrich *et al.* measured the dissociative sticking coefficient for N_2 on Ru(0001), Ru(10$\bar{1}$0), and Ru(11$\bar{2}$1) and found a value of approximately 10^{-12} at 300 K for all three surfaces (22). Hence, whitin the limits of these experiments no structure sensitivity was seen for the dissociative adsorption of N_2 on Ru at 300 K. In a later publication (31) it is considered that the above-mentioned sticking coefficients were mostly caused by trace amounts of Cs on the surfaces. This will explain the difference between the single crystal results and the results obtained over a Ru/Al_2O_3 catalyst argued to correspond to unpromoted Ru (32). The setup used in this study was employed, a few years ago, in an investigation of the promotional effect of potassium on the ammonia synthesis activity of iron (16). For that reason we cannot exclude the presence of trace amounts of potassium on the ruthenium surface below the detection limit of XPS, as suggested in Ref. (31). On the other hand, we never observed any evidence for this.

In a density functional calculation study of N_2 dissociation on a Ru(0001) surface Mortensen *et al.* calculated the ground state energy as function of reaction coordinate for the process. The activation energy was found to be 131 kJ/mol. The transition state was characterized by a very stretched molecule where one of the nitrogen atoms is diffusing from a fcc site to a hcp site on the surface [28]. The fact that the surface to some extent was covered by reaction intermediates during synthesis will give rise to a higher activation energy for the synthesis reaction than for the rate-limiting step (3). Therefore, the agreement between the overall activation energy of 101 kJ/mol measured for the present ammonia synthesis study and the theoretical activation energy for the dissociative chemisorption is not very good.

If it is ruled out that the reason for the lower activation energy is steps and other defects present at the surface, as indicated by the lack of surface structure sensitivity for the dissociative adsorption of N_2 (22), an explanation could be that nitrogen molecules in vibrational exited states will give rise to an apparent lower barrier. This is plausible due to the late barrier for the dissociation found in the density functional calculation [28]. In support of this explanation Romm *et al.* (20) have seen in a molecular beam experiment on dissociative chemisorption of N_2 on Ru(0001) that an increase in vibrational energy will increase the sticking more than the same increase in translational energy. An example of vibrational excitation giving rise to a lower apparent activation barrier was seen in the dissociation of methane over a Ni(100) surface (33, 34). Here molecular beam investigations suggest an energy barrier of approximately 90 kJ/mol for the translational energy [33], whereas the apparent activation energy in a thermal experiment is 58 kJ/mol (34). A barrier of 61 kJ/mol for N_2 dissociation on the Ru/Al_2O_3 catalyst was derived from transient kinetic

TABLE 1

Ammonia Synthesis Activity of a Selection of Single Crystals and Ru-Based Catalysts

Catalyst	TOF[a]	Pressure	Activation energy (kJ/mol)	Ref.
Ru single crystal	2×10^{-2} [b]	2.1 bar	101	—
Fe(111)	3 [c]	2.2 bar	—	[15]
Ru-powder	1.6×10^{-3}	600 torr	117	[9]
Ru/MgO (2%)	3.2×10^{-3}	1 bar	126	[6]
Cs-Ru /MgO	2×10^{-2}	1 bar	113	[6]
Ru/MgO (5%)	3.7×10^{-3}	1 bar	69 (68[d])	[8]
	8.8×10^{-3}	20 bar	78	
Ru/Al₂O₃	6.5×10^{-4}	1 bar	70 (100[e])	[8]
	2.5×10^{-3}	20 bar	76	
Cs-Ru/MgO	4.8×10^{-2}	20 bar	109	[8]
Cs-Ru/Al₂O₃	2.8×10^{-3}	1 bar	103	[8]
	3.6×10^{-3}	20 bar	101	

[a] The turnover frequencies are extrapolated to 673 K based on the observed activation energies. The activation energies are obtained from constant flow measurements if nothing else is stated.

[b] Calculated from the surface atom density of Ru(0001): $15.7 * 10^{14}$ cm⁻².

[c] Calculated from the surface atom density of Fe(111): $7.04 * 10^{14}$ cm⁻².

[d] Activation energy if ammonia concentration was between 500 ppm and 1250 ppm.

[e] Activation energy if ammonia concentration was between 150 ppm and 600 ppm.

experiments (32). This barrier is not in any conflict with the present data since it is lower than the apparent activation energy for the ammonia synthesis reaction. It has been suggested that preadsorbed hydrogen enhances the rate of N_2 chemisorption on supported Ru catalysts (10). This could explain the difference between the DFT calculations and the experiments, but it could not be confirmed or rejected by the present experiments. It will have to await experiments designed for this purpose.

A selection of data from Ru-based catalysts are shown in Table 1. Care should be taken when comparing with these data, since they were normally obtained at a higher ammonia pressure and a lower temperature than used in the present study. The activation energies in Table 1 were normally obtained at constant gas flow and as the reaction order for ammonia is not always exactly zero this has an effect on the value of the activation energy, as is seen for the Ru/Al₂O₃ catalyst in Table 1. The Ru/Al₂O₃ catalyst is, as mentioned above, considered to correspond to unpromoted Ru (32) so comparison between this catalyst, Ru-powder, and the Ru single crystal is most relevant. The activation energies are in fair agreement, especially the value of 100 kJ/mol found for Ru/Al₂O₃ at "constant" ammonia concentration and the value of 101 kJ/mol for the Ru single crystal. The turnover frequency for the Ru single crystal is, however, high, compared to both Ru-powder and the Ru/Al₂O₃ catalyst. The fact that the turnover frequencies for the Ru-powder and the Ru/Al₂O₃ catalyst were

obtained at a higher ammonia pressure could be an explanation for this discrepancy. In the case of Ru/Al₂O₃ in Table 1 the ammonia concentration was about 20 times larger than in the present study when the synthesis temperature was 673 K. Since the turnover frequency is defined as the rate of reaction per site, the way of counting the number of active sites will affect its value. For our single crystal the number of active sites was obtained from the geometric surface area of the ruthenium crystal and the Ru(0001) surface atom density, 15.7×10^{14} cm⁻², which is the surface facet of ruthenium with the highest surface atom density. The number of active sites on the catalysts were found by hydrogen chemisorption assuming a 1 : 1 ratio between ruthenium surface atoms and adsorbed hydrogen. Uncertainties in the number of active sites by both methods could account for some of the discrepancies in the turnover frequencies.

From the turnover frequency, the N_2 pressure and the gas temperature the probability for turning an N_2 molecule hitting the surface into two NH_3 molecules can be calculated to be 3×10^{-10} at 673 K. We used the crystal temperature as gas temperature since at the pressure used the mean free path of the gas molecules was so small ($\simeq$100 nm) that the crystal and the gas molecules hitting the surface were assumed to be in thermal equilibrium. Extrapolating to 300 K by using an activation energy of 101 kJ/mol results in a sticking probability of 4×10^{-20}. This is much lower than the sticking probability of 1×10^{-12} observed at 300 K by Dietrich *et al.* (22). If the dissociative sticking of N_2 is the rate limiting step, then these numbers are only consistent if there is a high coverage of reaction intermediates during synthesis. The inhibiting effect of hydrogen observed for Ru-powder suggests that the most important intermediate blocking the surface would be hydrogen. The sticking coefficient for dissociative N_2 chemisorption derived from the molecular beam experiments was roughly 10^{-6} when the tranlational energy was about 0.1 eV, which was the lowest energy used (20). This energy corresponds to a thermal temperature of 1000 K. At that temperature the turnover frequency in this work corresponds to a sticking coefficient of 10^{-7}.

For comparison we have also included in Table 1 the ammonia synthesis activity of a Fe(111) surface (15). This Fe(111) activity is in good agreement with the earlier studies of ammonia synthesis by Fe single crystals (5), when it is taken into account that these studies where conducted at 20 bar. Fe(111) is the iron surface believed to be the active surface in ammonia synthesis with Fe-based catalysts (35). We found that the Fe(111) surface is approximately 70 times more active than the ruthenium single crystal at 673 K. Thus at the low ammonia concentration obtained in the present studies Fe(111) is superior to ruthenium. The fact that Ru-based catalysts can be as good as Fe-based catalysts under industrial conditions is due to the negative effect of high concentrations of ammonia on the Fe-based catalysts and

probably the stronger effect of alkali metal promoters on ruthenium than on iron.

5. SUMMARY

The present study of the synthesis of ammonia over a ruthenium single crystal from a stoichiometric ($3H_2 : N_2$) gas-mixture at a pressure of approximately 2 bar and in the temperature range 598–898 K gives rise to the following conclusions: The overall activation energy for the synthesis reaction was measured to be 101 ± 4 kJ/mol, and the turnover frequency was $2 \times 10^{-2} s^{-1}$ at 673 K. After synthesis, the primary adsorbed species was nitrogen and there was evidence of hydrogen in the bulk of the crystal. The Fe(111) surface was 70 times more active at 673 K than the ruthenium surface under the present conditions of low ammonia concentration.

ACKNOWLEDGMENT

REFERENCES

1. Nielsen, A., "An Investigation on Promoted Iron Catalyst for the Synthesis of Ammonia." Gjellerup, Copenhagen, 1968.
2. Stoltze, P., and Nørskov, J. K., *Phys. Rev. Lett.* **55**, 2502 (1985).
3. Stoltze, P., *Phys. Scr.* **36**, 824 (1987).
4. Ertl, G., *in* "Catalytic Ammonia Synthesis Fundamentals and Practice" (J. R. Jennings, Ed.), p. 109, Plenum, New York, 1991.
5. Strongin, D. R., and Somorjai, G. A., *in* "Catalytic Ammonia Synthesis Fundamentals and Practice" (J. R. Jennings, Ed.), p. 133. Plenum, New York, 1991.
6. Aika, K., Takano, T., and Murata, S., *J. Catal.* **136**, 126 (1992).
7. Tennison, S. R., *in* "Catalytic Ammonia Synthesis Fundamentals and Practice" (J. R. Jennings, Ed.), p. 303. Plenum, New York, 1991.
8. Rosowski, F., Hornung, A., Hinrichsen, O., Herein, D., Muhler, M., and Ertl, G., *Appl. Catal. A* **151**, 443 (1997).
9. Aika, K., Kumasaka, M., Oma, T., Kato, O., Matsuda, H., Watanabe, N., Yamazaki, K., Ozaki, A., and Onishi, T., *Appl. Catal.* **28**, 57 (1986).
10. Fastrup, B., *Catal. Lett.* **48**, 111 (1997).
11. Goodman, D. W., Kelly, R. D., Madey, T. E., and Yates, J. T., *J. Catal.* **63**, 226 (1980).
12. Rasmussen, P. B., Holmblad, P. M., Askgaard, T., Ovesen, C. V., Stoltze, P., Nørskov, J. K., and Chorkendorff, I., *Catal. Lett.* **26**, 373 (1994).
13. Fujitani, T., Nakamura, I., Watanabe, T., Uchijima, T., and Nakamura, J., *Catal. Lett.* **35**, 297 (1995).
14. Yoshihara, J., and Campbell, C. T., *J. Catal.* **161**, 776 (1996).
15. Dahl, S., Törnqvist, E., and Chorkendorff, I., to be published.
16. Törnqvist, E., and Chen, A. A., *Catal. Lett.* **8**, 359 (1991).
17. Kasemo, B., *Rev. Sci. Instrum.* **50**, 1602 (1979).
18. Barin, I., "Thermochemical Data of Pure Substances," Part II, p. 942. VCH, Weinheim, 1989.
19. Henriksen, N. E., Billing, G. D., and Hansen, F. Y., *J. Phys. Chem.* **96**, 223 (1992).
20. Romm, L., Katz, G., Kosloff, R., and Asscher, M., *J. Phys. Chem. B* **101**, 2213 (1997).
21. Shi, H., Jacobi, K., and Ertl, G., *J. Chem. Phys.* **99**(11), 9248 (1993).
22. Dietrich, H., Geng, P., Jacobi, K., and Ertl, G., *J. Chem. Phys.* **104**(1), 375 (1996).
23. Rambeau, G., and Amariglio, H., *J. Catal.* **72**, 1 (1981).
24. Tsai, W., and Weinberg, W. H., *J. Phys. Chem.* **91**, 5302 (1987).
25. Shi, H., and Jacobi, K., *Surf. Sci.* **313**, 289 (1994).
26. Danielson, L. R., Dresser, M. J., Donaldson, E. E., and Dickingson, J. T., *Surf. Sci.* **71**, 599 (1978).
27. Rasmussen, P. B., Holmblad, P. M., Christoffersen, H., Taylor, P. A., and Chorkendorff, I., *Surf. Sci.* **287/288**, 79 (1992).
28. Mortensen, J. J., Morikawa, Y., Hammer, B., and Nørskov, J. K., *J. Catal.* **169**, 85 (1997).
29. Spencer, N. D., Schoonmaker, R. C., and Somorjai, G. A., *Nature* **294**, 643 (1981).
30. Alstrup, I., Chorkendorff, I., and Ullmann, S., *J. Catal.* **168**, 217 (1997).
31. Jacobi, K., Dietrich, H., and Ertl, G., *Appl. Surf. Sci.* **121/122**, 558 (1997).
32. Hinrichsen, O., Rosowski, F., Hornung, A., Muhler, M., and Ertl, G., *J. Catal.* **165**, 33 (1997).
33. Holmblad, P. M., Wambach, J., and Chorkendorff, I., *J. Chem. Phys.* **102**, 8255 (1995).
34. Ølgaard, B., Luntz, A. C., Holmblad, P. M., and Chorkendorff, I., *Catal. Lett.* **32**, 15 (1995).
35. Schütze, J., Mahdi, W., Herzog, B., and Schlögl, R., *Topics Catal.* **1**, 195 (1994).