

# Selective Oxidation of Ammonia on Ruthenium to Form p(2 x 2) Nitrogen Layer

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## **Abstract**

Oxidation of ammonia was used to prepare a p(2 x 2) nitrogen layer on the Ru(0001) surface as verified by temperature-programmed desorption (TPD) and low energy electron diffraction (LEED). The process takes place in an ultra-high vacuum (UHV) chamber. The surface is precovered with oxygen and then exposed to ammonia at low temperature. Upon heating, the ammonia is oxidized to form water, which desorbs at low temperature to leave a nitrogen-covered surface. The resulting layer can be used in a variety of surface chemical studies, including a hydrogenation reaction, which is an important part in the study of the Haber-Bosch process, in which ruthenium is used as a catalyst.

## Introduction

Heterogeneous catalysis is an important part of industrial processes. One important heterogeneous catalytic reaction is the Haber-Bosch process (depicted by equation 1), which is the synthesis of ammonia.



This reaction provides the ammonia that is used in fertilizers and is essential to life. In 2010, a total of 131,000,000 metric tons of ammonia was produced worldwide [1]. Industrially, an iron-based catalyst is used in this process because it is relatively inexpensive. However, this catalyst requires high pressure and temperature conditions. Ruthenium is known to be a better catalyst but its high cost makes it unsuitable for industrial applications [2]. For this reason, it is beneficial to study the details of the process over ruthenium (the ideal process) so that a more efficient yet still inexpensive catalyst may be proposed.

An important part of ammonia synthesis is the hydrogenation of nitrogen. To study this process, an ordered nitrogen layer needs to be prepared on the ruthenium surface. One way to do this is through oxidation of ammonia, as shown by equation 2 [3]:



Oxydehydrogenation of ammonia can be performed over ruthenium by pre-covering the surface with oxygen and then introducing ammonia. Ammonia is known to desorb from oxygen-covered ruthenium near 175 K, H<sub>2</sub> is known to desorb near 375 K, and N<sub>2</sub> near 750 K [4]. The importance of these temperatures is that somewhere between 375 K and 750 K, solely nitrogen will be on the surface of ruthenium. The adsorption structure of the nitrogen can be identified by low-energy electron diffraction (LEED).

This method of oxidation of ammonia has been studied on several metal surfaces, including platinum. In the study of Pt(111), it was found that the formation of an atomic nitrogen layer depended on both the amount of oxygen and ammonia. The ideal exposures for the gases were 2.0 L of O<sub>2</sub> and 0.4 L of NH<sub>3</sub> [5] (1 Langmuir = 10<sup>-6</sup> Torr for 1 second). Along with the products and reactants of equation (2), the study also found desorption of NO in some of the trials with NH<sub>3</sub> exposures of less than 0.4 L. Also at a lower exposure of NH<sub>3</sub>, they found a second peak for molecular oxygen (desorption peak for recombinative oxygen after N<sub>2</sub> has desorbed), which implies that not all of the oxygen was consumed in the process. The maximum amount of surface nitrogen was found at the ideal conditions above. It was confirmed to be a well-structured p(2 x 2) nitrogen layer using Auger electron spectroscopy (AES) and LEED. The nitrogen layer can also be hydrogenated (using an exposure of H<sub>2</sub>) and the resulting N-H stretch in the RAIR spectrum was observed [5].

Nitrogen layers can also be prepared on ruthenium by plasma discharge of N<sub>2</sub> [6] or dissociative adsorption of NH<sub>3</sub> [7], but since the sticking coefficient of nitrogen on ruthenium is so small (10<sup>-12</sup>) [8], a large exposure of gas is required, which elevates the pressure in the chamber and makes these methods impractical.

The presence of atomic nitrogen on ruthenium would be an ideal condition for the Haber-Bosch process since the dissociation of  $N_2$  is the rate-limiting step of the reaction [9]. The desired outcome of this study is an atomic layer of nitrogen on the ruthenium crystal after performing the oxydehydrogenation of equation (2) in a UHV (ultra-high vacuum) chamber and stopping the heating before  $N_2$  desorbs from the ruthenium surface. This nitrogen layer may be further used to study its hydrogenation to form  $NH$ . From this, the reaction temperature and kinetics of the process may be found. If the  $NH$  is found to be stable, it can be hydrogenated to  $NH_2$ . Through this type of study, it may be determined if surface  $NH_3$  can be formed by hydrogenating atomic N on Ru(0001). This method has been used previously to study the hydrogenation of N on platinum [4].

## Experimental Methods

A Ru(0001) crystal is used in this study in a UHV chamber equipped with a Hiden HAL 201/3F quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), an ion gun for sputtering, a Bruker IFS 66 v/s Fourier transform infrared (FTIR) spectrometer for reflection-absorption infrared spectroscopy (RAIRS), and LEED optics. The crystal is spot-welded to two short tantalum wires for resistive heating up to 900 K. It can also be heated to higher temperatures (up to 1500 K) by using electron beam heating from a thoriated tungsten filament adjacent to the sample. The electrons emitted by the heated filament are accelerated to the sample by positively biasing the sample to 600 V. The chamber is pumped by a turbomolecular pump backed by a mechanical pump to keep the pressure around  $1 \times 10^{-10}$  Torr. Gases are let into the system through a variable leak valve connected to a gas manifold.

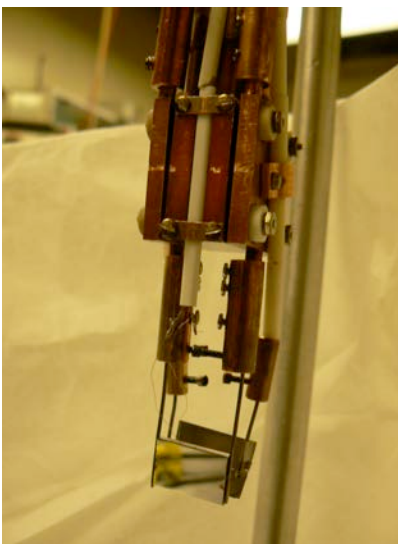


Figure 1. Ruthenium crystal on the sample holder.  
Sample is connected to two tantalum wires and a thermocouple.

### *Cleaning the Sample*

The crystal was cleaned with two cycles of Ar<sup>+</sup> ion sputtering and annealing. The first cycle was sputtering at 1 kV followed by annealing to 1500 K for 30 seconds. The second cycle was sputtering at 0.5 kV followed by annealing to 850 K for 1 min. The pressure of the argon in the chamber during sputtering was  $5 \times 10^{-5}$  Torr. The sample was rotated 5 degrees every 2 minutes for 15-16 minutes to ensure uniform sputtering. One of the main purposes of this procedure is to eliminate any carbon impurities on the surface. If there were any carbon on the surface, an introduction of oxygen in the chamber would oxidize the carbon, forming CO. In order to prove the absence of carbon impurities after cleaning, the sample was saturated with oxygen and TPD data was taken (heating rate of 2 K/sec). This data is used to check for the existence of a recombinative CO peak.

### *Formation of Nitrogen Layer*

After cleaning, the sample was cooled down to 150 K using liquid nitrogen. It was annealed to 600 K to remove any residual CO and was then cooled down to around 90 K. Varying amounts of O<sub>2</sub> were introduced to the chamber (0.2 L, 0.5 L, 1 L, 2 L, 5 L) at the beginning of each trial. Time was allowed to let the pressure decrease and equilibrate. 5 L of ammonia was then put on the crystal and the pressure was again allowed to decrease. TPD data was taken (heating rate of 2 K/sec, ranging from 150 K to 950 K) to find the amount of O<sub>2</sub> that is enough to saturate the surface. This data was also used to find the temperature at which everything except nitrogen desorbs. This was the temperature used in the next part of the experiment. The following desorption products were monitored in the TPD data: H<sub>2</sub> (m/z = 2), NH<sub>3</sub> (m/z = 17), H<sub>2</sub>O (m/z = 18), N<sub>2</sub>/CO (m/z = 28), NO (m/z = 30), N (m/z = 14), and C (m/z = 12). Masses 12 and 14 were monitored to distinguish the desorption of N<sub>2</sub> from that of CO, since both have the same mass of 28. The estimated desorption temperatures are 175 K for NH<sub>3</sub>, 375 K for H<sub>2</sub>, and 750 K for N<sub>2</sub> [4].

### *Checking the Structure of the Nitrogen Layer*

To check that the nitrogen layer is present and well ordered, LEED (low-energy electron diffraction) was used to observe the structure of the layer. After cleaning with sputtering and annealing, the sample was prepared by cooling down to 150 K using liquid nitrogen and annealing to 600 K to remove adsorbed CO. For the clean surface, the sample was cooled to 90 K and then LEED was taken. For the surface with the nitrogen layer, the sample was cooled down to 90 K and enough oxygen to saturate the surface was added (2 L). Time was given to allow the pressure to decrease. 5 L of ammonia was then added and the pressure was allowed to decrease again. The sample was heated to 457 K for 60 s so that all components except nitrogen had desorbed. It was cooled again to 90 K before the LEED picture was taken.

## **Results and Discussion**

After cleaning the sample with sputtering and annealing and saturating it with oxygen, the TPD data was taken and used to check its purity. The sample was proven clean by comparing the data to that of a sample that has carbon impurities. It is known that molecular CO (not from the carbon impurities) will desorb from ruthenium at 350-450 K [10] so this will

appear in the data whether the sample is clean or not. The recombinative CO that is formed from the oxidation of carbon impurities on the surface begins to desorb at around 530 K [11]. Shown in Figure 2, the absence of recombinative CO desorption from an oxygen-saturated surface indicates the cleanliness of the surface. Cleaning with two cycles of sputtering and heating was done before every experiment to ensure that there was no residual carbon interfering with the reactions.

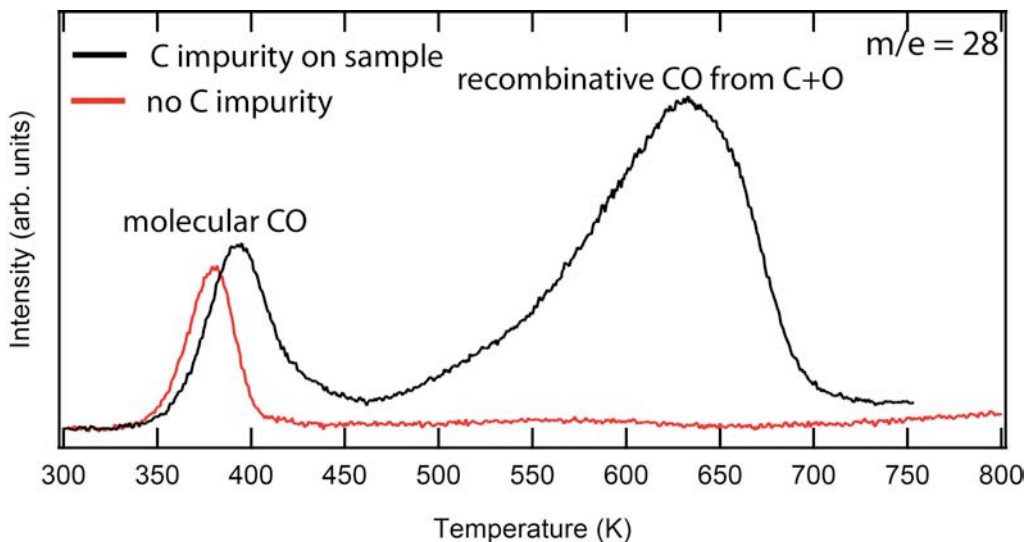


Figure 2. TPD data of the clean ruthenium surface without carbon impurities compared to that of one that does have carbon impurities.

The first set of experiments tested the production of nitrogen with varying amounts of oxygen on the surface. The surface was pre-covered with oxygen and then 5 L of ammonia was put on the surface. Both gases were put on the surface at 90 K because the sticking coefficient is higher at low temperatures [8]. The sample was heated while TPD data was taken. The TPD data of mass 28 from these experiments are shown in Figure 3.

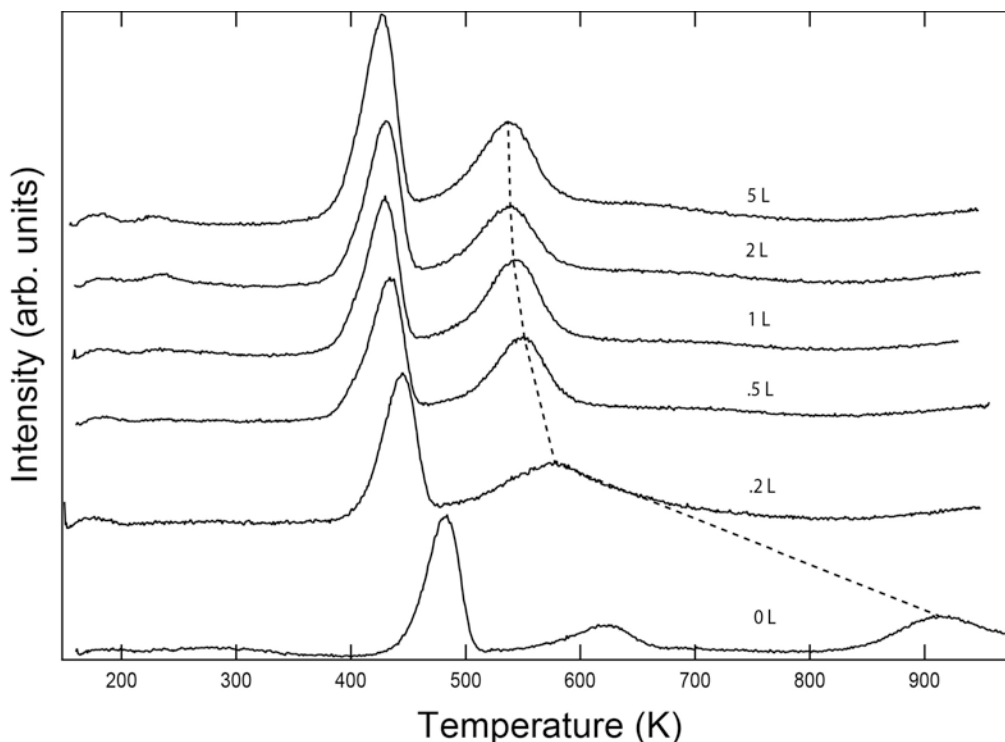


Figure 3. Mass 28 TPD data with varying amounts of oxygen. All data was collected after 5 L of ammonia was put on the surface. Both oxygen and ammonia were exposed at 89 K. The dotted line connects the nitrogen peaks to show the decrease in desorption temperature as the amount of oxygen is increased.

As the amount of oxygen increases, the desorption temperature of nitrogen decreases (as shown by the dotted line) and the intensity of the peak increases slightly, meaning more nitrogen is being formed. The peaks at 425-475 K are due to molecular CO, which is an irrelevant part of this experiment (CO is always present in the background). In the data with no oxygen added, there is a small peak at 625 K. This represents the small amount of recombinative CO. The data with oxygen are not suspected to have much or any recombinative CO. This is proven by monitoring mass 12 with TPD. Mass 12 corresponds to the carbon atom fragment of CO. A mass 12 peak aligning with a mass 28 peak indicates desorption of CO. There is a small peak for mass 12 at 625 K when there is no pre-covering of oxygen, but is absent when there is a pre-covering of oxygen.

Peaks are attributed to nitrogen in the same manner. Both mass 12 and mass 14 are monitored to distinguish CO peaks from N<sub>2</sub> peaks in the mass 28 data. An example is shown in Figure 4.

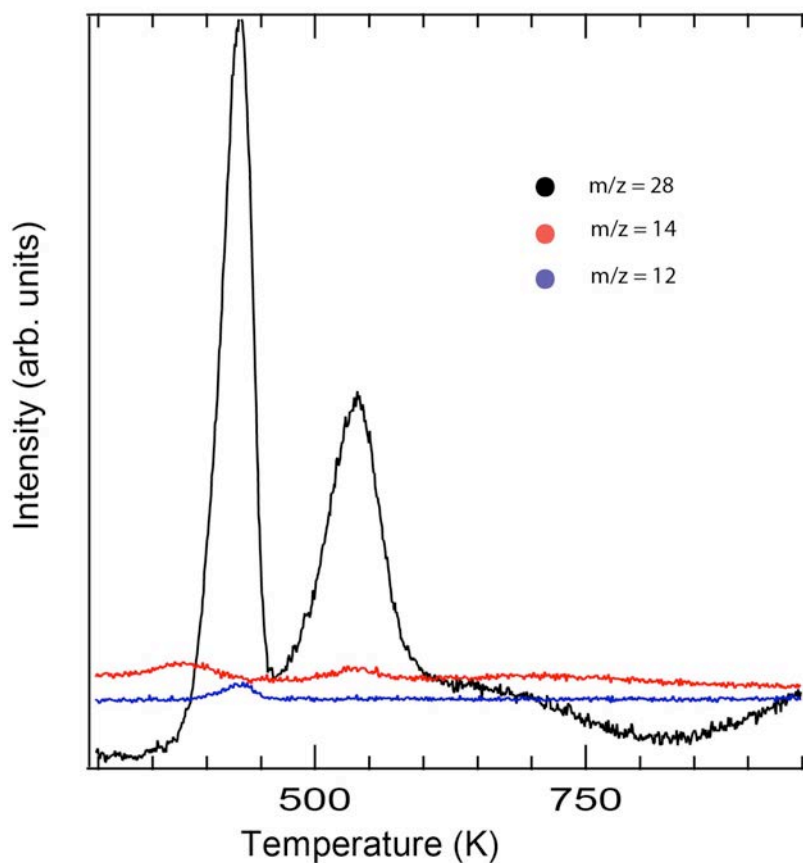


Figure 4. TPD data for masses 28, 14, and 12 to distinguish  $N_2$  from CO. Data was taken with a pre-covering of 2 L of oxygen and exposure of 5 L of ammonia, both at 89 K.

The data above proves that the mass 28 peak around 430 K can be attributed to CO (since it aligns with a mass 12 peak) and the mass 28 peak around 540 K can be attributed to  $N_2$  (since it aligns with a mass 14 peak). The mass 14 peak around 375 K aligns with molecular ammonia desorption and is not associated with mass 28.

Another way to prove that reaction (2) is occurring is by monitoring mass 18 in TPD to discern any water being produced. Mass 18 was observed after ammonia was put on the surface both with and without oxygen. The results are shown in Figure 5.

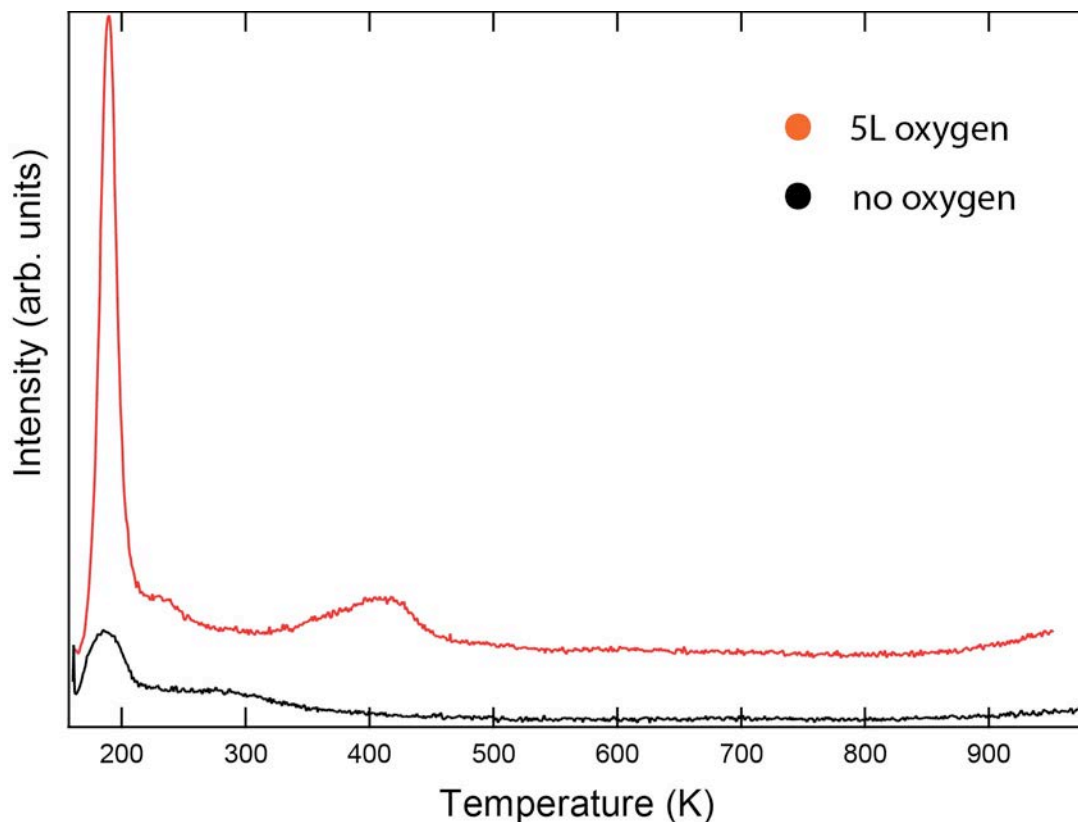


Figure 5. Mass 18 TPD data with and without oxygen to discern the desorption of water. All data was taken with ammonia exposure of 5L.

Without a pre-covering of oxygen, there should be no water forming because there should not be any presence of oxygen in the chamber. However, there is a small peak around 180 K when there is no oxygen present. This is attributed to water in the background gases that adsorb to the surface at 88 K. However, the mass 18 peak for the oxygen-precovered surface is significantly larger than that without oxygen, suggesting that water is being produced in the reaction. The presence of a distinct peak for both water and nitrogen is a strong indicator that reaction (2) is indeed occurring since both products are present.

The structure of the nitrogen layer was observed using LEED. To prepare the sample for LEED, the procedure for TPD was followed. The only difference being that the heating was stopped just before the nitrogen desorbs ( $\sim 457\text{K}$ ). This ensures that everything but nitrogen desorbs. Figure 6 shows the desorption data for all the components of equation (2). It is clear that at  $\sim 457\text{K}$ , only nitrogen should remain on the surface. The small  $\text{NH}_3$  peak at  $\sim 700\text{K}$  is likely from ammonia desorption from the sample holder. After the sample was cooled back down to 90 K, the LEED picture was taken and compared to a LEED picture of a clean Ru(0001) crystal.



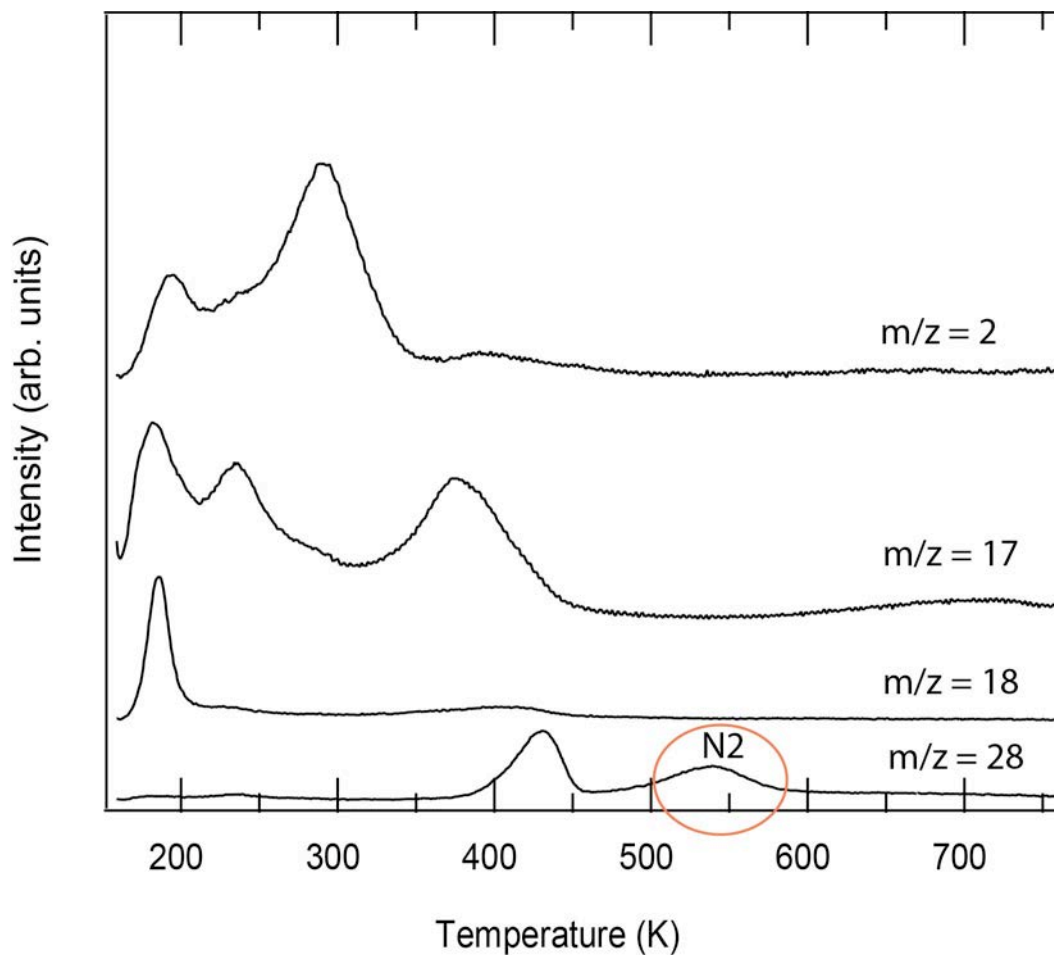


Figure 6. Desorption data for all components of equation (2). All data is from exposure to 2 L O<sub>2</sub> and 5 L NH<sub>3</sub> (which are the conditions for LEED).

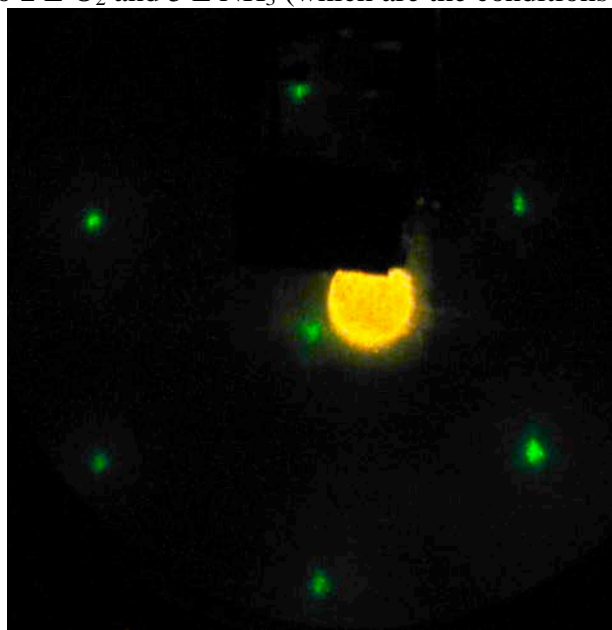


Figure 7a. LEED of clean crystal taken at 90 K

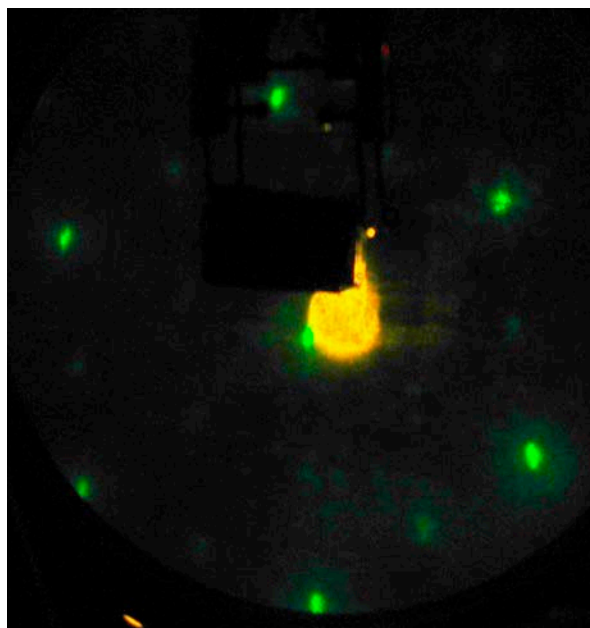


Figure 7b. LEED of crystal with nitrogen layer taken at 90 K

- Pattern from Ru
- Pattern from nitrogen

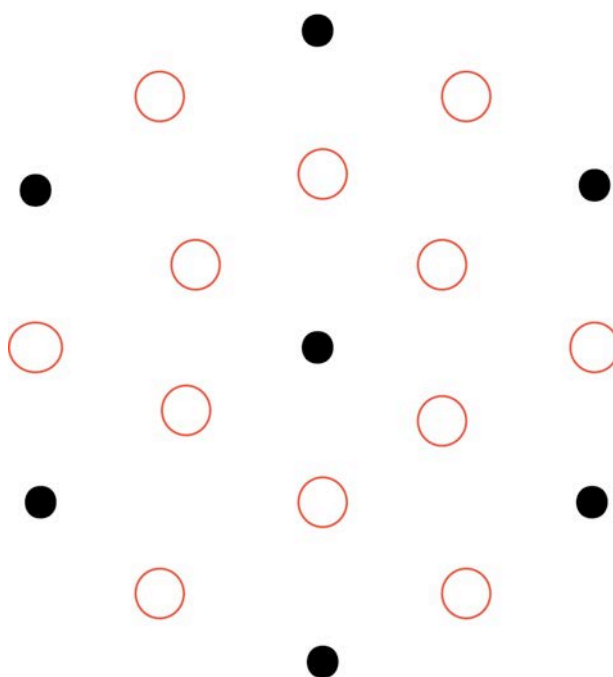


Figure 7c. Schematic of a well-structured (2 x 2) nitrogen layer LEED

Figure 7 compares the LEED picture from the clean Ru(0001) surface with that of the N-covered surface. The latter shows additional spots indicative of a p(2x2) LEED pattern from the atomic nitrogen layer. The weakness of the spots could be caused by a low coverage of the atomic nitrogen layer. It has been shown that 5 L exposure of NH<sub>3</sub> produces less than 0.05 monolayers (ML) of nitrogen on Ru(0001) [12]. Oxygen pre-coverage of the surface does increase the amount of desorbed N<sub>2</sub>, as shown in Figure 3, but not by much. Therefore, the amount of nitrogen produced on the surface is likely much lower than the saturation amount. However, the observation of a p(2x2) LEED pattern still proves the N layer to be well structured. Figure 7c shows what a well structured p(2 x 2) layer should look like. The additional spots are aligned with those of the ruthenium crystal and are symmetric. Figure 7b shows that the LEED of the N layer also has these properties.

## Conclusion

This study used TPD and LEED to prove the formation of an atomic nitrogen layer on ruthenium resulting from the oxidation of ammonia. Ammonia is known to decompose on Ru(0001) into atomic nitrogen and hydrogen, which desorb as N<sub>2</sub> and H<sub>2</sub> at 800 and 400 K, respectively. However, when the surface is pre-covered with oxygen, the nitrogen desorption peak is lowered in temperature and increased in intensity, indicating that the presence of adsorbed oxygen facilitates NH<sub>3</sub> decomposition on Ru(0001) and decreases the activation energy required for N<sub>2</sub> desorption. These results have been corroborated by other research [4]. An exposure of 2 L of oxygen was found to be enough to saturate the surface. Without oxygen, the desorption temperature was around 915 K; with 2 L of oxygen, the desorption temperature was around 540 K. The assignment of mass 28 desorption at ~ 550 K to N<sub>2</sub> instead of CO is supported by the observation of mass 14 (N) and the absence of mass 12 (C) at the same temperature. In addition, the observation of water desorption at ~180 K confirms the production of water from reaction (2). The LEED data showed the presence of a well ordered p(2x2) N layer. This method of nitrogen layer formation is effective and credible.

## Acknowledgements

The funding from the National Science Foundation grant #1062943 is gratefully acknowledged. The help of Christos Takoudis, Greg Jursich, and Arman Butt is also much appreciated.

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