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D.R. Strongin
(Ph.D. Thesis)

June 1988

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SURFACE SCIENCE AND CATALYTIC STUDIES ON THE EFFECTS OF ALUMINIUM OXIDE AND POTASSIUM ON AMMONIA SYNTHESIS OVER IRON SINGLE CRYSTAL SURFACES

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Ph.D. Thesis

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Abstract

The effects of aluminum oxide and potassium on ammonia synthesis over Fe(110), Fe(100), Fe(111), Fe(210), and Fe(211) single crystal surfaces have been investigated by surface science and high pressure catalytic studies (20 atm reactant pressure of nitrogen and hydrogen). It has been found that a pretreatment of the iron single crystal catalysts, in the presence of water vapor, must be performed prior to ammonia synthesis for aluminum oxide to enhance the rate of ammonia formation. In this circumstance the less active Fe(110) and Fe(100) surfaces are restructured into stable and highly active surfaces (i.e. Fe(111) and Fe(211)) for ammonia synthesis.

Potassium exhibits two distinct effects on ammonia synthesis over iron single crystals. The addition of potassium to Fe(100) and Fe(111) increases the rate of
nitrogen dissociation (the rate limiting step) and inhibits catalyst poisoning, which results from readsorption of gas phase ammonia product. A model is presented to explain potassium promotion. It is consistent with the finding of a changing apparent reaction order in ammonia and hydrogen, lower adsorption energy of ammonia on iron, and unchanged activation energy for ammonia synthesis with the addition of potassium to Fe(111) and Fe(100). The Fe(110) surface is inactive with or without adsorbed potassium under the ammonia synthesis conditions used in this research.

It is shown that coadsorption of potassium with aluminum oxide during the water vapor pretreatment inhibits the restructuring process due to the formation of potassium aluminate. Thus, to fully exploit the effects of both aluminum oxide and potassium, the iron catalyst should first be restuctured with aluminum oxide in the presence of water vapor and then potassium should be added.

It is also shown that iron can be restuctured in the presence of ammonia. This nitrogen catalyzed restructuring causes enhancement in both Fe(110) and Fe(100) ammonia synthesis activity, but little change is found on Fe(111). The growth of highly active surfaces on ammonia restuctured Fe(110) and Fe(100), which contain highly coordinated surface atoms (Fe(211)& Fe(111)), are implicated. The research also indicates that ammonia treatment of Fe(111) induces the formation of Fe(211) planes. Aluminum oxide and potassium have little effect on the ammonia induced restucturing process.
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Dedication

To my family, Myron, Arlene, Alisa, Dave & Joanne, and Smokey, I dedicate this thesis. Their love for me, and their support in both the personal and scientific facets of my life, have made possible everything I have achieved. To them I say “I love you and thank you for everything”.
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Chapter 1
Introduction

1.1 Preface

Modern-day ammonia synthesis is the product of close to a century of research. Much of the effort has been directed toward elucidating the promoter effects of potassium and aluminum oxide on the rate of ammonia synthesis over iron. Out of this work has evolved a multitude of techniques, concepts, and ideas which have profoundly affected catalytic chemistry. Many reviews have been written on this subject [1,2,3], but it becomes evident from them that a molecular level understanding of the effects of the promoters is still lacking. A principal reason for this deficiency is that the bulk of this early research has used indirect methods to study the catalyst. A large amount of kinetic data relating the gas phase ammonia concentration to the surface concentration of promoters has been obtained [4,5]. This type of data is important for optimizing the concentration of promoters, but it fails to reveal the atomic level effects of the promoters on the working catalyst. With the advent of combined surface science / high pressure systems, high pressure reaction data (>1 atmosphere) can be correlated to the atomic structure of the catalyst surface, which is determined in the ultra-high vacuum (UHV) environment.
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(< 10^{-8} \text{ Torr}). The combination of surface science and high pressure catalysis provides powerful tools in the study of the reactivity and structure of surfaces. This thesis will be devoted to describing how surface science studies, combined with high pressure data, has elucidated the structure sensitivity and the role of potassium and aluminum oxide in ammonia synthesis.

1.2 Historical Perspective

1.2.1 Development of Ammonia Synthesis

It was recognized in the late 19th century, by Sir William Crookes, that ultimately the world population would surpass the available food supply if crop yields, specifically wheat, were not improved [6]. In a speech to the British Association for the Advancement of Science Crookes stated the following [7]:

"It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty. Before we are in the grip of actual dearth the chemist will step in and postpone the day of famine to so distant a period that we and our sons and grandsons may legitimately live without undue solicitude for the future".

One solution to the problem was to create an economical and efficient means of fixating nitrogen, since it was already known that the use of nitrogen containing compounds in fertilizer improved crop yield substantially.

This goal was realized by Fritz Haber (in 1908) [8,9] who synthesized ammonia, in substantial yield, from nitrogen and hydrogen with an osmium catalyst at a total pressure of reactant gas of 185 atm at a temperature of 870 K. The apparatus
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yielded about 90 grams of ammonia per hour with about 98 grams of osmium catalyst [6,10,11]. Soon after, at BASF in Germany, Alwin Mittasch (in 1910), found an economically feasible alternative to the costly and rare osmium catalyst. He discovered that iron with the addition of alumina (Al₂O₃) and potash (K₂O) was the most suitable catalyst for the large-scale synthesis of ammonia.

At this stage of development there existed a sizable gap between Haber’s apparatus and the one which would be required to produce tons of ammonia per day. The major problem was that high pressure of reactant gas was needed to make the synthesis of ammonia a commercially feasible process. This technological breakthrough was pioneered by Carl Bosch of BASF in 1913 who oversaw the first factory dedicated to ammonia synthesis in Oppau, Germany [12,13,14]. This equipment was designed to produce 30 tons of ammonia per day with 300 kg catalyst and 200 atm total pressure of nitrogen and hydrogen.

Both Fritz Haber and Carl Bosch received nobel prizes for their work. Haber, in 1919 for his research on the catalytic synthesis of ammonia and Bosch in 1931 for his development of high pressure technology, which allowed the realization of ammonia synthesis as a commercial process.

Since this time there have been major developments in improving ammonia synthesis, both in technology and catalyst design. Advances in pressure containment equipment and synthesis gas (N₂ and H₂) production have made ammonia synthesis more efficient and cost effective. The development of improved catalyst, than what was first used by Mittasch or Bosch, has allowed the use of lower pressures (80 atm) for the production of ammonia [6]. It is remarkable that, even though seventy years have elapsed, since the work of Haber and Bosch, the basic composition of the catalyst has remained unaltered.
1.2.2 Ammonia Synthesis Catalyst

In determining that iron was the most efficient and economical catalyst for the synthesis of ammonia, Mittasch and coworkers had surveyed over 20,000 catalyst formulations for ammonia synthesis. Figure 1.1 shows ammonia synthesis activity for several elements [15]. Osmium, the element Haber used originally is actually slightly more active than iron, but it was found to be extremely sensitive to water or oxygen impurities in the feed gas (N₂ and H₂). Iron was found to be the most efficient and economical catalyst.

1.2.3 Previous Work on Ammonia Synthesis Catalyst

The work by Haber, Bosch, and Mittasch on ammonia synthesis catalysts was of an extremely empirical nature. It was primarily directed towards a systematic survey of the periodic table to find the most efficient catalyst. Later work, which focused on understanding catalyst structure and activity paved the way for modern day catalytic studies. The pioneering work of Paul Emmett and coworkers during the 1930's initiated the use of gas adsorption to study the structure and reactivity of catalytic surfaces [16,17,18]. Emmett was the first to use gases such as carbon monoxide, carbon dioxide, and nitrogen to characterize the catalytic surface. Low temperature nitrogen adsorption [19] (the BET method) enabled the total surface area of a catalyst to be determined, while carbon monoxide and carbon dioxide chemisorbed only on the iron and potassium surfaces respectively. Using these probes Emmett concluded that about 50% of the catalyst surface was covered with the aluminum oxide and potassium promoters [16]. His work on nitrogen chemisorption showed that the rate of nitrogen adsorption on the catalyst was
Figure 1.1: The percent ammonia in the exit gas as a function of element at a pressure of 10 MPa at 823 K (60 litres hour$^{-1}$ over 2 g of metals) [2].
similar to the rate of ammonia synthesis [20]. This result was the first evidence for nitrogen dissociation being the rate limiting step in ammonia synthesis, and led to the first kinetic analysis of ammonia synthesis.

### 1.2.4 Ammonia Synthesis Kinetics

Even before the nitrogen dissociation step was implicated to be rate limiting in ammonia synthesis, Winter [21] had studied the decomposition of ammonia over iron. He found that the rate of ammonia decomposition ($V$) could be expressed as:

$$V = k P_{NH_3}^{0.9} / P_{H_2}^{1.5}$$

over iron foil. The data was interpreted by assuming the equilibrium:

$$NH_3 = \frac{3}{2} H_2 + N_{adsorbed}$$

where the rate limiting step for the decomposition of ammonia was the desorption of nitrogen.

Emmett later showed that the rate of nitrogen adsorption on "doubly promoted" iron (catalyst which contains both aluminum oxide and potassium) was of the same order of magnitude as the ammonia synthesis rate [20], and that the rates of hydrogen dissociation and hydrogenation of iron nitride were much faster processes [22,23]. The hydrogenation step could proceed at room temperature even though ammonia synthesis occurs at temperatures close to 673 K. These results led to a reaction scheme as follows (this scheme has been supported by numerous catalytic and modern surface science measurements) [2]:
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\[ N_{2\text{gas}} \rightarrow 2N_{\text{adsorbed}} \quad (1.3) \]

\[ H_{2\text{gas}} = 2H_{\text{adsorbed}} \quad (1.4) \]

\[ N_{\text{adsorbed}} + H_{\text{adsorbed}} = NH_{\text{adsorbed}} \quad (1.5) \]

\[ NH_{\text{adsorbed}} + H_{\text{adsorbed}} = NH_2_{\text{adsorbed}} \quad (1.6) \]

\[ NH_2_{\text{adsorbed}} + H_{\text{adsorbed}} = NH_3_{\text{adsorbed}} \quad (1.7) \]

\[ NH_3_{\text{adsorbed}} = NH_3_{\text{gas}}. \quad (1.8) \]

Using the work of Winter and Emmett, Temkin and Pyzhev published a paper entitled "Kinetics of Ammonia Synthesis on Promoted Iron Catalysts" [4] which improved upon Winter's model and brought order to ammonia synthesis kinetic data. In this work it was assumed that during ammonia synthesis, nitrogen was the majority surface species and that its concentration was determined by the gas phase hydrogen and ammonia concentrations. Thus, the equilibrium established under ammonia synthesis conditions was:

\[ N_{\text{adsorbed}} + \frac{3}{2}H_{2\text{gas}} = NH_3_{\text{gas}}. \quad (1.9) \]

Temkin used the Frumkin-Slygin isotherm [24]:

\[ \theta_N = \frac{1}{f} \ln a_0 P_{\text{N}_2}, \quad (1.10) \]
to represent the surface coverage of atomic nitrogen ($\theta_N$) on "doubly promoted" iron. The values $f$ and $a_0$ are constants and are defined by the Zeldowitch equation [25] for rate of adsorption ($V_a$):

$$ V_a = k_a P_{N_2} \exp(-g \theta_N) $$

and the Langmuir equation [26] for the rate of desorption ($V_d$):

$$ V_d = k_d \exp(h \theta_N) $$

where $h$ and $g$ are constants. At the adsorption equilibrium $V_a = V_d$ and $f$ and $g$ are obtained by setting $f=g+h$ and $a_0 = \frac{k_a}{k_d}$.

Temkin [4] used the Frumkin-Slygin isotherm to express $\theta_N$ as:

$$ \theta_N = \frac{1}{f} \ln(a_0 K(P_{N_2}^2/P_{H_2}^3)) $$

where $\frac{1}{K}$ is the equilibrium constant of reaction 1.9. By substituting $\theta_N$ into the expressions for $V_a$ and $V_d$ the overall rate of ammonia synthesis, $V_{\text{synthesis}} = V_a - V_d$, is given by:

$$ V_a = k_a P_{N_2}[a_0 K P_{N_2}^3/P_{H_2}^2]^{\alpha} - k_d[P_{N_2}^2/P_{H_2}^3]^1-\alpha $$

where $\alpha = g/f = g/(g+h)$ and describes the relative change of the activation energy ($E_a$) and heat of adsorption ($Q$) of nitrogen, $\Delta E_a / \Delta Q$, with $\theta_N$. The nitrogen heat of adsorption is assumed to vary inversely with $\theta_N$ [27].

The basic framework of the equation can be derived using Langmuir kinetics and by assuming a homogeneous surface (nitrogen heat of adsorption is independent of coverage). Now the forward rate of synthesis ($r$) can be written as:

$$ r = k P_{N_2}(1 - \theta_N)^2 $$
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and, using the equilibrium expression 1.9, $\theta_N$ can be solved for and written as

$$\theta_N = \frac{KP_{NH_3}/P_{H_2}^{1.5}}{1 + KP_{NH_3}/P_{H_2}^{1.5}}. \quad (1.16)$$

Substituting $\theta_N$ into equation 1.15 shows that the rate of synthesis is:

$$r = \frac{kP_{N_2}}{[1 + KP_{NH_3}/P_{H_2}^{1.5}]^2}. \quad (1.17)$$

At Temkin's conditions of high conversion:

$$K\frac{P_{NH_3}}{P_{H_2}^{1.5}} >> 1 \quad (1.18)$$

and

$$r = kP_{N_2}\left[\frac{H_2^{1.5}}{KP_{NH_3}}\right]^2 [5] \quad (1.19)$$

which is closely related to the forward rate, $V_a$, in the Temkin equation, but lacks the surface heterogeneity factor, $\alpha$.

1.3 Composition and Structure of Industrial Catalyst

Since the realization of industrial scale ammonia synthesis in 1913, there have been no major changes in the composition of the iron catalyst [2,6]. In catalyst preparation, potassium oxide and aluminum oxide are fused with magnetite (Fe$_3$O$_4$) at about 1873 K followed by reduction. This catalyst is referred to as "doubly promoted" iron, while a catalyst which only contains Al$_2$O$_3$ is called "singly promoted". The industrial catalyst might also employ the oxides of Ca, Mg, or Si in the iron depending on the reaction conditions [2].
1.3.1 Unreduced Catalyst

During fusion, some Al₂O₃ dissolves into the magnetite and grows substitutionally with the Fe₃O₄ spinel lattice [28,29,30]. Unlike aluminum oxide, potassium oxide does not grow in the spinel structure and hence, does not dissolve in the magnetite lattice. Thus, the major fraction of aluminum oxide and a minor portion of the potassium oxide forms a solid solution in the magnetite.

1.3.2 Reduced Catalyst

The ammonia synthesis catalyst precursor is reduced, by treating the oxidized catalyst with a stoichiometric mixture of nitrogen and hydrogen [1,31]. The temperature and extent to which this is carried out is dependent on the concentration of potassium and aluminum oxide in the iron oxide.

Many changes in “singly” and “doubly promoted” iron occur upon reduction. The major change is the removal of oxygen, as water, from the magnetite. This occurs without shrinkage of the catalyst and hence a very porous structure results, with a BET surface area of about 10 m²/g-cat [2]. Many techniques including gas adsorption, X-ray broadening, and transmission microscopy have shown that the reduced magnetite exists as metallic iron crystallites which are less than 40 nm in diameter [32].

1.3.3 Effects of Promoters on Catalyst Surface Area

The surface area of “singly promoted” iron increases about 20 times with increasing Al₂O₃ loading, up to 2.5% Al₂O₃, at which point the surface area plateaus.
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at about 20 m²/g-cat (see figure 1.2 a) [33,34]. The addition of K₂O to “singly promoted” iron is crucial for enhancing catalytic activity, but its presence in “doubly promoted” iron actually reduces the surface area [17]. Typically, the BET surface area of “doubly promoted” iron is 10 m²/g-cat, while “singly promoted” iron is 20 m²/g-cat [2].

1.3.4 Distribution of Promoters

Even though the bulk loading of Al₂O₃ and K₂O is between 1% and 3%, their surface concentration is high. As was stated before, Emmett showed that between 40% and 60% of the catalyst surface of “doubly promoted” iron is decorated with promoter. It was also shown by Emmett that most of the potassium and aluminum oxide on the surface exists as potassium aluminate. Emmett used gas adsorption to show this, but additional proof for this is the observation that potassium is much less volatile on the catalyst when Al₂O₃ is present [18].

1.3.5 Effects of Promoters on Catalyst Activity

Emmett showed that at 90 K, CO adsorbs to iron, but does not adsorb on either Al₂O₃ or K₂O, thus the amount of CO which the catalyst adsorbs is proportional to free iron surface [16,18]. It has also been shown that the catalytic activity of “doubly promoted” iron is directly proportional to free iron surface. This surface is not covered with promoter and can be accurately measured by carbon monoxide adsorption isotherms.

It is shown in figure 1.2 a that the BET surface area plateaus at 2.5% Al₂O₃ for “singly promoted” iron, while CO adsorption studies show that the amount
Figure 1.2: (a) The surface area of "singly promoted" iron increases about 20 times with increasing Al₂O₃ loading, up to 2.5% Al₂O₃, at which point the surface area plateaus at about 20 m²/g-cat. (b) Ammonia synthesis activity increases up to 2.5% Al₂O₃ loading and then decreases due to Al₂O₃ blocking active catalyst [2].
of free iron surface increases up to 2.5% Al₂O₃ and then starts to decrease (see figure 1.2 b) [34,35]. The rate of ammonia synthesis is proportional to the amount of free iron surface, so the decrease in activity at >2.5% Al₂O₃ loading is due to excess aluminum oxide starting to cover the iron surface, without further enhancement in iron surface area. Aluminum oxide is called a structural promoter, since it only seems to create high surface area without becoming involved directly with ammonia synthesis.

The behavior of the catalyst surface area and activity is much different in the case of K₂O. The addition of potassium oxide actually decreases the surface area of the catalyst, but the activity of the surface for ammonia synthesis is increased (figure 1.3) [17]. Thus, potassium increases the specific activity of iron, and is called an electronic promoter. Maximum activity is achieved when about 20% of the surface is covered by potassium oxide [17]. Higher coverages start to decrease activity, because of surface blocking of iron.

1.3.6 Structure of Ammonia Synthesis Catalyst

After fusion of Al₂O₃ with magnetite, the aluminum oxide is distributed homogeneously throughout the Fe₃O₄ [2]. After reduction most of the Al₂O₃ segregates out of the metallic iron lattice. This effect produces the high concentration of surface Al₂O₃, which is observed. However, the high surface area of the promoted iron is thought to be due to small amounts of Al₂O₃ in the Fe crystallites [2,36]. This conclusion is drawn from x-ray measurements which show that the diffraction lines of pure α-Fe are broadened when Al₂O₃ is present. It is concluded that iron aluminate (FeAl₂O₄) is present in the α-Fe particles [37,38]. This conclusion is supported by calculations which show that FeAl₂O₄ can exist in a α-Fe particle.
Figure 1.3: (a) Shows the activity enhancement upon K₂O loading and (b) that the surface area of ammonia synthesis catalyst decreases with potassium addition [2].
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by replacing 7 iron atoms with only minor distortions [39].

1.4 The Need for a Model System

It is apparent that the ammonia synthesis catalyst is a complex mixture of iron, potassium, aluminum, and oxygen, and that the promotion by Al₂O₃ and K₂O comes through an interaction with the active iron component [31]. If a complex system such as this is to be understood it is advisable to study a model system. In this case, iron single crystals prepared and characterized in UHV, serve as model catalysts for the active component of the industrial catalyst. By quantitatively adding potassium, aluminum and oxygen to the single crystal surface in UHV and then carrying out high pressure ammonia synthesis (20 atm of nitrogen and hydrogen), a direct correlation can be made between the reactivity and surface structure of the catalyst.

1.5 Organization of Thesis

The primary problems this thesis will address are concerned with understanding promotion by aluminum oxide and potassium, on the molecular level, for ammonia synthesis over iron. Before this is done it is necessary to summarize, in chapter 2, the experimental techniques used in this thesis. It is also important to review important surface science results in chapter 3 and to develop the concept of structure sensitivity in chapter 4. Chapters 5 and 6 present results and discussion, which lead to a full understanding of both potassium and aluminum oxide promotion on iron. Chapter 7 is concerned with the means by which aluminum oxide
and potassium promote iron when they are coadsorbed, and a recipe for creating active "doubly promoted" iron is given. Chapter 8 discusses the effects of dissolved and adsorbed nitrogen, during ammonia synthesis, in altering the structure of iron with and without promoter. Chapter 9 deals with bimetallic surfaces, containing iron, for ammonia synthesis, and finally chapter 10 summarizes the insight gained from this thesis work regarding ammonia synthesis.

References


REFERENCES


Chapter 2

EXPERIMENTAL

2.1 Preface

Experiments in this thesis have been carried out in a combined ultra-high vacuum (UHV) / high pressure apparatus, shown in figure 2.1. The UHV environment was usually $1 \times 10^{-9}$ Torr, which allowed for structure and reactivity of surfaces to be probed by modern surface science techniques. The UHV chamber was pumped by a liquid nitrogen trapped diffusion pump. A high pressure cell allowed for high pressure catalysis (20 atm) to be performed over the single crystal samples [1]. The combined UHV / high pressure apparatus included:

- A 50 liter bakeable, stainless steel chamber.
- A 6 inch, liquid nitrogen trapped diffusion pump (Varian: VHS-6) capable of obtaining a base pressure of $7 \times 10^{-10}$ Torr.
- A rotatable manipulator (LBL) capable of heating a single crystal sample to 2000 K and cooling to 80 K.
- A hydraulically operated high pressure cell and external reaction loop to perform high pressure ammonia synthesis.
- Evaporation sources for deposition of aluminum, potassium, and iron.
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Figure 2.1: Photograph of combined UHV / high pressure apparatus.
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- Four grid retarding field analyzer (Varian: 981-0127) for Auger electron spectroscopy (AES) and low energy electron diffraction (LEED).

- A glancing incidence electron gun used as the excitation source for AES.

- A quadrupole mass spectrometer (UTI: 100C) to analyze residual gases in UHV and to perform temperature programmed desorption (TPD).

- Two precision leak valves (Varian: 951-5106) for the introduction of controlled amounts of gases into the UHV chamber.

- An ion sputtering gun (PHI: 4-161) for sample cleaning.

Some of the experiments presented in Chapter 9 were carried out in a separate UHV chamber, which allowed photoemission to be performed on Fe/Re(10\(\bar{1}0\)) surfaces. The chamber included:

- A He I (21.2 eV) source to perform ultra-violet photoelectron spectroscopy (UPS).

- A double pass cylindrical mirror analyzer (CMA, PHI: 15-256) for AES and UPS.

2.2 Mounting and Preparation of Single Crystals

Single crystals of iron with (110), (100), (111), (211), and (210) surface orientations were used in this work. In addition Re(10\(\bar{1}0\)), Re(11\(\bar{2}1\)), Re(0001), Ag(100), and Mo(100) single crystals were used. The single crystals were spark cut from single crystalline rod (iron was obtained from Monocrystals company and Noah chemicals) to 1° of the desired orientation and were polished on both sides with 25 \(\mu\text{m}\) diamond paste. Proper orientation of the crystals was confirmed by Laue
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x-ray back diffraction. The single crystal samples used were on the average 1 cm² disks about 1 mm thick.

All single crystals were mounted on a rotatable manipulator, as shown in the center of figure 2.2. The single crystals were spot welded to 0.020 inch diameter platinum wire (Livermore stock). The platinum wire was spot-welded to 0.050 inch platinum posts which were mounted to the manipulator via copper feedthroughs. The sample could be resistively heated, and typically about 10 amperes was needed to heat a 1 cm² iron sample to 873 K in UHV (such a sample is shown in figure 2.2). The design of the manipulator also allowed efficient cooling of the sample. The copper feedthroughs were hollow, so that \( \frac{1}{8} \) inch teflon tube could be inserted up to the platinum post. Passing liquid nitrogen through this tube allowed cooling of the sample down to 80 K. The temperature of the sample was measured by a chromel-alumel thermocouple which was spot-welded to the crystal edge.

Figure 2.2 also exhibits the high pressure cell, in the open position, extending down from the top of the chamber, the aluminum source in the lower left, and the potassium source in the lower right side of the figure. The 4-grid LEED optics is shown in the back of the chamber.

2.2.1 High Pressure Cell

The UHV environment is necessary to utilize surface sensitive techniques, as explained in the next section, but it is not possible to have measurable rates for ammonia synthesis in UHV. This high pressure requirement is satisfied by the use of a hydraulically operated high pressure cell, capable of containing 20 atm of reactant gas. A picture of the cell fully open and closed over the single crystal sample is shown in figure 2.3. When closed, the cell seals itself with a knife edge against a copper gasket, with about 1800 psi external pressure supplied by compressed nitrogen. This seal isolates the sample from the UHV environment and by opening a Nu-Pro valve above and below the cell an external reactor loop is developed. Typically, if the UHV chamber is \( 1 \times 10^{-9} \) Torr, then the introduction
Figure 2.2: Photograph of the interior of the UHV / high pressure apparatus.
Figure 2.3: Photographs of the high pressure cell in the open, partially closed and closed positions.
of 20 atm of nitrogen and hydrogen in the reactor loop causes the pressure to increase to $5 \times 10^{-9}$ Torr.

### 2.2.2 High Pressure Reaction Loop

The external reaction loop is composed of $\frac{1}{4}$ inch stainless steel tubing with a total volume of 170 cm$^3$ (includes the volume of the 1 inch diameter high pressure cell). A schematic of the reaction loop is shown in figure 2.4. A positive displacement pump (Whitey, model LP10) circulates the high pressure gas around the loop. A pressure gauge (Heise, model H33814) is also present which is calibrated for gas pressures between 0 atm and 50 atm. The loop is evacuated, before and after reaction, by a rotary mechanical pump to $10^{-2}$ Torr, at which time the cell can be opened to the main UHV chamber (the valves below and above the high pressure cell are also closed at this time).

### 2.2.3 Detection of Ammonia Product

An 8-way Whitey valve is installed in the loop, allowing periodic sampling of the high pressure loop during reaction. The sample size is $\frac{1}{4}$ cc and is passed through a photoionization detector (PID) (HNU Systems, model 52-02) with a photon output of 10.2 eV. This photon energy ionizes ammonia (ionization potential = 9.8 eV) while leaving nitrogen (15.6 eV) and hydrogen (15.4 eV) unionized. The ionized ammonia is accelerated to a detection plate held at 200 eV, producing a current. The current output of the PID is a function of only ammonia partial pressure in the reaction loop and is a linear function in the 0 Torr - 20 Torr range of NH$_3$, as shown in figure 2.5. The current is in the nanoampere range and can be detected with a picomometer. The current is converted to a 0-10 volt output, which is converted into a peak area by an integrator (Spectra-Physics minigrator: 21947-01). Thus, rates of ammonia synthesis can be determined by taking periodic samples.
Figure 2.4: Schematic representation of the reaction loop used to perform high pressure ammonia synthesis.
Figure 2.5: Output of the PID as a function of ammonia partial pressure.
2.2.4 Aluminum and Potassium Evaporation Source

Aluminum was evaporated from a \( \frac{3}{8} \) inch diameter and 1 inch long alumina crucible which contained aluminum wire pieces (purity >99.99%). The crucible was wrapped with 0.020 inch diameter tungsten wire which could be resistively heated. It is very important to use an ultra-pure alumina crucible for the source, since during evaporation of the aluminum the tungsten wire is white hot and if the crucible is not ultra-pure then deposition of contaminants, along with the aluminum, is substantial. (When an aluminum evaporation source was first put in the chamber, standard purity alumina was used and substantial amounts of potassium, sodium, and calcium were deposited along with the aluminum). The aluminum could be oxidized by admitting controlled amounts of oxygen or water vapor into the UHV chamber through a leak valve.

Potassium was deposited on the iron sample by a commercial SAES Getter source. It consists of a nicrome boat filled with potassium dichromate and an 16% Al, 84% Zr alloy. Upon Heating (\( \approx 873 \) K) the Al-Zr alloy reduces the dichromate and potassium metal is liberated.

2.2.5 Iron Evaporation Source

The iron evaporation source consisted of 0.02 inch high purity iron wire wrapped around 0.03 inch diameter tungsten wire. The source was heated by passing about 35 amperes through the tungsten wire. Outgassing of the source required it to be run at 30 amperes for about 12 hours. This procedure reduced contamination by carbon and sulfur, which evolved initially from the source region.
2.3 Surface Sensitive Techniques

2.3.1 Mean Free Path of Electrons in a Solid

Most of the surface science techniques used in this work required electrons, as the probe particle. Electrons offer advantages over photon techniques, in that electrons have a relatively small mean free path in a solid. Figure 2.6 plots the mean free path of electrons in various elements as a function of energy. (This curve is usually referred to as the universal curve, since the mean free path of the electron is independent of the element.) The curve shows that electrons are a surface sensitive probe, since they cannot penetrate far into the solid in the range of energies between 10 eV and 2500 eV. For example, electrons with energies of 100 eV must originate at about 4 Å or less in the solid to escape from the solid without a loss in energy. Of course, mean free path is only an average distance and the contribution from electrons at a distance t in the solid is \(\exp(-t/\lambda)\), where \(\lambda\) is the mean free path obtained from the universal curve.

2.3.2 Auger Electron Spectroscopy (Sample Composition and Coverage)

In 1925 P. Auger noticed that small quantities of electrons were emitted from a photoplate when irradiated by hard x-rays [2]. These electrons (so called Auger electrons) were found to compete against the x-ray emittance process and occurred when a core electron was ejected from an atom by x-rays, and higher level electrons filled the core level hole. This process was found to be a much more general phenomenon, in that Auger electrons can be produced whenever incident radiation, photons, electrons or ions has energy greater than a core electron in an atom (K, L, M,..levels). If the interaction of one of these particles with an atom leaves an excited state with a core hole in the atom, then de-excitation will occur. Two processes by which the highly unstable excited state can relax from the L
Figure 2.6: Mean free path of an electron in a solid as a function of energy.
level are shown in figure 2.7, where the core hole is in the K level. A higher level electron will fill the core hole and this process will either yield an x-ray or an Auger electron. In the x-ray process the energy, released by the filling of the core hole, is carried by a photon. In the Auger process the energy released by the relaxation is given to another electron, an Auger electron, through a radiationless process. In the case where a metal surface is the source, then the kinetic energy of the emitted Auger electron ($E_{ke}$), detected by the analyzer, from the process depicted in figure 2.7 is:

$$E_{ke} = E_K - E_{L_{III}} - e\phi$$  \hspace{1cm} (2.1)

where $\phi$ is the work function of the electron analyzer. The work function being the energy required to move an electron from the Fermi level of a metal to the vacuum level.

Auger electron spectroscopy is a powerful analytical tool, in that the energy with which the Auger electron is emitted from the surface is a function of the element it evolved from. Thus, by detecting the energy of the Auger electron surface composition can be determined. (Since the Auger process is a three electron process hydrogen and helium can not be detected.)

2.3.3 The Excitation Source

As was mentioned before, Auger electron spectroscopy can be performed with any type of radiation which is capable of ionizing inner electronic shells of atoms. In the research carried out in this thesis, the primary excitation source was an electron gun, which produced emission currents of about 0.4 milliamperes, with an electron energy of 2000 eV. The energy of the Auger electron is not a function of the primary beam energy, but a general rule of thumb is that the primary beam energy should be about three times the energy of the Auger electron to be detected for maximum sensitivity. (In this study the Auger electrons with the
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Figure 2.7: Auger and x-ray fluorescence processes.
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highest energy were those which originated from iron with an energy of 702 eV, which is an Fe MVV transition.)

To achieve maximum surface sensitivity a glancing incidence electron gun was used to generate the 2000 eV electrons. It has been found that the Auger yield from the top most atomic layer of a surface is greatly enhanced if the angle between the primary electron beam and the surface is about $10^\circ$. This can be understood by noting that at grazing incidence more atoms at the surface are excited than those atoms deeper in the bulk.

The use of electrons, as the primary source of excitation, makes AES an extremely sensitive surface probe, since the atomic ionization cross section for electron impact is in the range of $10^{-20}$ cm$^2$ [3]. The use of X-rays as the excitation source should, in principle, make AES even more sensitive, since the ionization cross section of core electrons is higher with x-rays. However, the use of electrons have two major advantages. The first is that electron sources are much easier to construct and install in UHV than x-ray sources. The second reason is that electron fluxes ($\approx 6 \times 10^{12}$ electrons/second) are usually much higher than the x-ray fluxes ($\approx 10^6$ photons/second) which are produced in a standard UHV chamber.

One disadvantage with AES is that the Auger electron peaks sit on a high background, caused by a high yield of secondary electrons. The energy of these secondary electrons, on which the Auger electrons sit, have little correlation with the energetics of the process by which they evolved from, since they have gone through many scattering events with the near surface region before they are detected. Thus, for maximum sensitivity the Auger electrons should be separated from this background.

2.3.4 Detection of Auger Electrons

Using a four grid retarding field analyzer, Auger electrons can be energy resolved. The experimental set-up is shown in figure 2.8. Only electrons with energies greater than the electrostatic potential applied to the second and third
Figure 2.8: Experimental set-up to energy analyze electrons in AES.
grids can be detected (the 1st and 3rd grids are grounded to remove capacitance coupling). The current detected by the collector is:

\[ i(V_r) \propto \int_{E=E_{V_r}}^{\infty} N(E) dE. \]  

(2.2)

The energy distribution \([N(E)]\) is just proportional to \(dN(E)/dE\). To differentiate equation 2.2 electronically the potential \(V_r\) is modulated with a small ac voltage \(V_m \sin \omega t\). The current which is detected at the collector \([i(V_r + V_m \sin \omega t)]\) can be approximated by the first three terms of a Taylor expansion around \(i(V_r)\):

\[ i(V_r = V_m \sin \omega t) = i(V_r) + i'(V_r) \times V_m \sin \omega t + \frac{i''(V_r)}{2!} \times V_m^2 \sin^2 \omega t \]  

(2.3)

where

\[ \sin^2 \omega t = \frac{1}{2}[1 - \cos 2\omega t]. \]  

(2.4)

By detecting the amplitude of the ac signal which has frequency \(\omega\), the first derivative \((i')\) spectrum can be obtained, as shown in figure 2.9. As can be seen, the \(N(E)\) distribution has small peaks on a large background so what is usually done is to record the ac component of the signal with frequency \(2\omega\), by using a lock-in amplifier tuned to \(2\omega\). This signal is proportional to \(dN(E)/dE\). This can be seen by noting that \(\sin^2 \omega t = \frac{1}{2}[1 - \cos 2\omega t]\) (see equation 2.4).

2.3.5 Determination of Growth Mechanisms with AES

The coverage of an adsorbate on a surface can be determined with AES by monitoring the adsorbate growth mechanism. Typically, there are three mechanisms by which an adsorbate can grow on a substrate [4], as shown in figure 2.10. The first is the Frank - van der Merwe mechanism where the adsorbate grows layer by layer. The Stranski - Krastanov mechanism describes the case where one or more atomic layers (monolayer) grow on the substrate, with subsequent growth of three dimensional crystallites. Volmer - Weber growth is one in which the adsorbate grows in three dimensional islands on the surface.
Figure 2.9: Auger spectrum proportional to $\omega$ (distribution) and $2\omega$ (derivative of distribution) [3].
Figure 2.10: Growth mechanisms detectable by AES.
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The basic principle behind AES determination of these growth mechanisms is that when an adsorbate grows on a surface the substrate Auger electrons are attenuated, because of their finite mean free path in a solid. From an analysis of how these Auger electrons attenuate as a function of deposition time or exposure to the adsorbate, the growth mechanism can be determined. Representative plots of each type of growth are shown in figure 2.10. In the Volmer-Weber mechanism the substrate intensity \( I_s \) decreases exponentially with adsorbate concentration. In this circumstance \( I_s \) reaches zero very slowly, since there is always bare substrate exposed. The Frank-van der Merwe mechanism exhibits linear attenuation when \( I_s \) is plotted against adsorbate coverage, but with a different slope for each layer. Hence, each break in the line indicates the beginning of a new monolayer. The Volmer-Weber plot is just a combination of layer by layer and three dimensional crystallite growth. Thus, a linear attenuation is observed for the layer by layer growth, and the attenuation becomes nonlinear where three dimensional growth begins.

2.3.6 Chemical Shifts in AES

The chemical environment of a surface atom can often affect the energy distribution of Auger electrons. This may be an energy shift, lineshape change, or attenuation of energy loss features associated with the main Auger peak.

Strong charge transfer between atoms, such as in the aluminum-oxygen system, may change the Auger spectrum drastically [5]. Metallic aluminum exhibits a LVV (V denotes valence band) at 68 eV, but upon nitridation and oxidation the peak shifts to 60 eV and 51 eV respectively (see figure 2.11). Thus, this peak shift will be used in this thesis to verify the oxidation of aluminum. Lineshape changes in the carbon 281 eV, KVV, Auger transition can be used to distinguish between graphitic and carbidic carbon, as shown in figure 2.11 [6]. These are just a couple of examples of AES being used to study chemical shifts. A more complete treatment of this subject is given in Briggs et. al. [7].
Figure 2.11: Examples of chemical shifts detectable by AES.
2.3.7 Temperature Programmed Desorption

Paul Redhead, in 1962, published a paper on the "Thermal Desorption of Gases", which to this day remains the classic paper on the subject [8]. The Redhead analysis allows for the determination of activation energy, rate constant and the order of reaction, by monitoring the desorption rate of gases from a surface which is heated in a well defined way.

Desorption of a gas from a surface, in vacuum, can be defined by the following relation defining the pressure, $P$, observed from the desorption:

\[ \frac{dP^*}{dt} + \frac{p^*}{\tau} = aN(t) \]  

(2.5)

where $p^* = p - p_{\text{equilibrium}}$. The residence time of molecules in the vacuum chamber is $\tau$, $N(t)$ the desorption rate and $a$ is a function of the sample area and chamber volume. For high pumping speeds, ($\tau \to 0$, which is assumed to be the case in most systems) the change in pressure is $p^* = a\tau N(t)$. Thus, the pressure change in the vacuum chamber recorded by a mass spectrometer is proportional to the rate of desorption of gas from a surface.

2.3.8 Determining Kinetic Parameters from TPD

The rate of desorption from unit surface area is:

\[ N(t) = -\frac{d\sigma}{dt} = \nu_n\sigma^n \exp(-E/RT) \]  

(2.6)

where $\sigma$ is surface coverage (molecules/cm$^2$) of adsorbate, $\nu_n$ is the rate constant, $n$ the order of reaction, and $E$ the activation energy of desorption. In most cases the activation energy of adsorption is close to zero, so to a good approximation $E$ is equal to the heat of adsorption. To exploit this relation experimentally, the sample with the adsorbed gas is heated with a linear heating rate, $T = T_0 + \beta t$,
where $\beta$ is the temperature rise per unit time. By differentiating $N(t)$ with respect to temperature and setting $\frac{dN(t)}{dt} = 0$ the following relations can be obtained:

\[
\frac{E}{RT_P^2} = (\nu_1/\beta) \exp(-E/RT_P), n = 1 \tag{2.7}
\]

\[
\frac{E}{RT_P^2} = (2\sigma_P \nu_2/\beta) \exp(-E/RT_P), n = 2 \tag{2.8}
\]

\[
\frac{E}{RT_P^2} = \frac{\sigma_0 \nu_2}{\beta} \exp(-E/RT_P), n = 2 \tag{2.9}
\]

where $\sigma_0$ is the initial surface coverage of an adsorbate and $\sigma_P$ is the surface coverage at the temperature where the maximum rate of desorption occurs ($T_P$). By recording a trace of the rate of desorption (mass spectrometer output) versus temperature, and using a linear temperature ramp (usually between 10 K/sec - 50 K/sec), $T_P$ can be obtained.

For a first order reaction (equation 2.7), obtaining $T_P$, allows for $E$ to be calculated if a value of $\nu_1$ is assumed. To a good approximation:

\[
\frac{E}{RT_P} = \ln \frac{\nu_1 T_P}{\beta} - 3.64 \tag{2.10}
\]

when $10^{13} > \frac{\beta}{\nu_1} > 10^8$ (K$^{-1}$), which is usually the case for desorption from a surface. For second order desorption ($n=2$) the situation is a little more complicated, since $\sigma_0$ must be known.

2.3.9 Low Energy Electron Diffraction

Davisson and Germer, in 1925, observed the first example of the wave nature of electrons. They observed distinct maxima and minima in the angular distribution of backscattered electrons from a nickel surface. This observation was published in 1927 in the paper “The Diffraction of Electrons by a Crystal of Nickel” [9]. The data was interpreted by utilizing the de Broglie relation:
where \( h \) is Planck’s constant.

This early experiment by Davisson and Germer involved angularly resolving the backscattered electrons, by moving a Faraday cup around the sample and recording current as a function of position. The modern day LEED setup was pioneered by Lander in 1962. It involves accelerating the elastically scattered electrons to a phosphor screen, which gives an image of the entire diffraction pattern. The experimental setup used in this thesis is shown in figure 2.12. The monoenergetic beam of electrons varied from 20 eV (\( \lambda = 7.5 \) Å) to 150 eV (\( \lambda = 1 \) Å). The 2nd and 3rd grids of the RFA (figure 2.12) were held at a voltage about 5 eV less than the primary beam. This arrangement only allowed elastically backscattered electrons to reach the phosphor screen, reducing background intensity.

Since electron energies of 20 eV - 150 eV are used for the primary beam the technique is extremely surface sensitive (see section on electron mean free path). Thus, LEED is just the two dimensional analog of x-ray diffraction and it gives information on the symmetry, size of the unit cell, as well as information on the ordering of adsorbates.

2.3.10 Ultra - Violet Photoelectron Spectroscopy (UPS)

The use of monochromatic uv photons allows for the characterization of the density of states (DOS) near the Fermi level of a solid. In this research, the He I (21.2 eV) line was used as the ultra-violet source. The photoelectrons emitted from the solid and detected by the CMA have kinetic energy (\( E_{\text{kin}} \)):

\[
E_{\text{kin}} = h\nu - E_B - e\phi,
\]

where \( h\nu \) is 21.2 eV for the He I line, \( E_B \) the binding energy of the electron, and \( \phi \) is the work function of the spectrometer. Energy resolving all the photoelectrons
Figure 2.12. Experimental set-up for LEED.
allows the density of states profile to be determined.

2.3.11 Work Function Measurements by UPS

Another use of UPS is to determine the surface work function:

$$\phi_{sur} = h\nu - (E_{\text{fermi}} - E_{BH})$$  \hspace{1cm} (2.13)

where $\phi_{sur}$ is the surface work function, $E_{\text{fermi}}$ are those electrons which are emitted from the solid with the highest $E_{\text{kin}}$, and $E_{BH}$ are those electrons which escape the solid with $E_{\text{kin}} = 0$ eV. In practice the sample is usually biased with about -6 eV to allow detection of the low energy photoelectrons. In this thesis changes in $\phi_{sur}$ due to surface composition are obtained. It will be shown in chapter 9, by UPS, that the adsorption of Fe on Re(1010) surface lowers the surface work function.

2.4 Preparation of Iron Single Crystal Samples

2.4.1 Cleaning Iron Single Crystals

In iron, bulk impurities such as sulfur and carbon are common. Before the sample is mounted in UHV the crystal is heated to about 873 K in a hydrogen furnace to help deplete the bulk of sulfur. The cleaning procedure is continued in UHV, where a combination of argon ion sputtering and chemical treatment is used.

Sputtering the iron at 873 K for a prolonged period of time removes the sulfur, but treatment of the sample in about $1 \times 10^{-7}$ Torr of oxygen at 673 K is needed to rid the sample of carbon. The iron surface is considered clean if Auger electron spectroscopy (AES) shows no impurities and if a low energy electron diffraction pattern (LEED) is obtained, which is representative of the bulk crystal orientation.
2.4.2 Deposition of Aluminum Oxide and Potassium

Aluminum is evaporated on the iron crystal surface by passing 10 amperes through 0.02 inch diameter tungsten wire which heats a ceramic crucible containing aluminum wire. The aluminum is oxidized on the iron surface by leaking about $1 \times 10^{-8}$ Torr of water vapor into the UHV chamber. Oxidation of the aluminum is confirmed by the shift of the 67 eV LVV Auger transition, representative of elemental aluminum, to 54 eV in the oxide [5]. The coverage of aluminum oxide is determined by titrating the surface with carbon monoxide ($^{13}$CO is used so that CO can be distinguished from residual N$_2$, which desorbs from the surface, with the mass spectrometer tuned to 29 amu). At room temperature CO chemisorbs on metallic iron, but not on aluminum oxide [10,11]. By adsorbing and desorbing CO, and by comparing the integral areas from both clean iron and Al$_x$O$_y$/Fe surface TPD spectra, the relative amount of free iron can be calculated, as shown in figure 2.13. Aluminum oxide is denoted by Al$_x$O$_y$, because of uncertainty in the aluminum and oxygen stoichiometry. The Auger spectrum can be calibrated using this data so that coverages of aluminum oxide can be alternatively determined by AES. In this work, one monolayer corresponds to the point at which CO can no longer adsorb on the surface. Thus, one monolayer might correspond to more than one atomic layer, since aluminum oxide will be shown later to grow in three-dimensional islands on the iron surface [12].

The deposition of potassium is accomplished by using a SAES getter source. Coverages of potassium are determined by a potassium uptake curve. It was shown in a previous work [13] that at room temperature no more than one monolayer of alkali metal at 373 K or above will be stable on a transition metal in UHV, because of the low sublimation energy of the alkalis. The ratio of the 252 eV potassium Auger peak to the iron 652 eV peak was equal to four at saturation and this is assumed to be one monolayer (ML) coverage.
Figure 2.13: The coverage of Al$_2$O$_y$ is calculated by comparing the integral areas from the clean Fe and Al$_x$O$_y$/Fe surface CO TPD spectra.
Table 2.1: Reactant gas purity and supplier.

<table>
<thead>
<tr>
<th>Reactant Gas</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>LBL - Matheson</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>LBL - Matheson</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Matheson</td>
<td>Anhydrous(&gt;99.99%)</td>
</tr>
<tr>
<td>Water</td>
<td>LBL</td>
<td>Triply Distilled(Freeze-thaw)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>LBL - Matheson</td>
<td>&gt;99.99%</td>
</tr>
</tbody>
</table>

2.4.3 Reactant Gases

The reactant gases used in this thesis are listed in table 2.1. Both nitrogen and hydrogen were purified by passing the gas through a molecular sieve trap and a liquid nitrogen cooled coil before introduction into the reaction loop. The anhydrous ammonia from Matheson was used as is and the water was triply distilled and was given three freeze-thaw cycles before use. Carbon monoxide used in this thesis was obtained from LBL - Matheson and was used without further purification.

2.4.4 Performing High Pressure Ammonia Synthesis

After the sample is prepared and characterized in UHV it must be transferred to a different environment if ammonia synthesis is to be studied, since the rate of ammonia production from its elements would be negligible in UHV. Having a UHV chamber equipped with a high pressure cell [1] provides the necessary environment while never exposing the sample to the ambient atmosphere. A typical experiment would proceed as follows. The sample is cleaned and potassium and aluminum oxide are added in the desired concentrations on the iron surface. The single crystal is enclosed in a high pressure cell which constitutes part of a micro-batch reactor, isolating the sample from the UHV environment. High pressures of gases (15 atm of
hydrogen and 5 atm of nitrogen) are introduced and the sample is resistively heated to reaction temperature (673 K unless otherwise noted). Ammonia production is monitored by periodically taking samples from the reaction loop and passing them through a photoionization detector with a 10.2 eV lamp. This photon energy ionizes ammonia, but not nitrogen and hydrogen. Thus, the PID signal is only proportional to the ammonia partial pressure in the loop. By taking these samples at known times, rates of ammonia synthesis are determined. After the reaction is completed, the sample is cooled to 373 K in the reactant gas, the reaction loop is evacuated and the cell opened, returning the sample to the UHV environment. Surface characterization is then performed with AES, LEED, and temperature programmed desorption (TPD).

References


Chapter 3
Structure Sensitivity

3.1 Structure Sensitivity of Ammonia Synthesis

Since single crystals have surfaces with well defined geometries the structure sensitivity of a reaction can be probed directly. This approach has proved effective in many systems [1] where it has been found that surface geometries influence catalytic reactions. This influence is best exemplified in ammonia synthesis where differences of up to two orders of magnitude are found between crystallographic planes [2]. The rates of ammonia synthesis over five iron single crystal orientations are shown in figure 3.1. The Fe(111) and Fe(211) surfaces are by far the most active in ammonia synthesis, and they are followed in reactivity by Fe(100), Fe(210), and Fe(110) [3]. Schematic representations of the idealized unit cells for these surfaces are shown in figure 3.2, along with coordination numbers for exposed surface atoms. Examination of the unit cell structures for the five different iron single crystal surfaces suggests two possible reasons for the high activity of the (111) and (211) faces compared to the (210), (100) and (110) orientations; surface roughness or active sites. It is shown in this chapter that ammonia synthesis over iron shows a strong correlation with the coordination number of exposed iron surface atoms,
CHAPTER 3: STRUCTURE SENSITIVITY

Figure 3.1: Structure Sensitivity of Ammonia Synthesis Over Iron.

T = 673 K
20 atm 3:1 H₂:N₂

[Diagram showing ammonia synthesis rates for different surface orientations]

moles NH₃/cm²·sec x 10⁹

(111) (211) (100) (210) (110)

Surface Orientation
but activity for ammonia synthesis is not related to surface roughness.

The (111) surface can be considered a rough surface, since it exposes second and third layer atoms to reactant gases in contrast to the (110) surface which only exposes first layer atoms. Work functions are related to the roughness of a surface [4] and it is useful to quantify the corrugation of a plane in this way. The work functions of all the iron faces are not available but they are for tungsten [5], another bcc metal which shows structure sensitivity for ammonia decomposition [6]. The order of decreasing work function ($\phi$) is as follows: $\phi_{110} > \phi_{211} > \phi_{100} > \phi_{111} > \phi_{210}$. Open faces, like the (111) surface, have lower work functions than close packed faces such as the (110) surface. The significance of this for ammonia synthesis might be that the dissociation of nitrogen (the rate limiting step [7,8]) proceeds faster on a surface with a low work function. This is supported by theory [7], which calls for transfer of electronic charge from the d band of iron into the $2\pi^*$ antibonding orbitals of nitrogen for dissociation, a process which might be aided by a low surface work function (this theory is discussed further in chapter 4).

The second possible explanation for the structure sensitivity involves active sites. The (111) and (211) faces of iron are the only surfaces which expose $C_7$ sites (iron atoms with seven nearest neighbors) to the reactant gases. Theoretical work by Falicov et. al. [9] suggests that highly coordinated surface atoms would show increased catalytic activity, due to low energy charge fluctuations in the d bands of highly coordinated surface atoms. Examination of the results suggest that the later argument of active sites is the key to the structure sensitivity of ammonia synthesis over iron.

The reaction rates, in figure 3.1, show that the (211) face is almost as active as the (111) plane of iron, while Fe(210) is less active than Fe(100). The Fe(210) and Fe(111) faces are open faces which expose second and third layer atoms. The
Figure 3.2: Idealized representations of Fe unit cells. The coordination number of each surface atom is indicated.
Fe(211) face is more close packed, but it exposes C_7 sites. If surface roughness or a low work function was the important consideration for an active ammonia synthesis catalyst, then the Fe(210) would be expected to be the most active face. Instead Fe(111) and Fe(211) are much more active, indicating that the presence of C_7 sites are more important than surface roughness in an ammonia synthesis catalyst.

The idea of C_7 sites being the most active site in ammonia synthesis on iron has been suggested in the past. Dumesic et. al. [10] found that the turnover number for ammonia synthesis was lower on small iron particles than larger ones. Pretreatment of an Fe/MgO catalyst with ammonia enhanced the turnover number over small iron particles, but did not affect the turnover number over larger particles. This result was explained by noting that the concentration of C_7 sites would be expected to be higher on the larger iron particles and that the ammonia induced restructuring enhanced the number of these sites on the smaller particles in the catalyst. This was supported by the fact that the restructured catalyst chemisorbed 10% less CO than the unrestructured catalyst. Highly coordinated sites, such as C_7, would chemisorb less CO than less coordinated sites, because of steric considerations. Thus, it was concluded that C_7 sites are the most active iron atoms for ammonia synthesis.

Additional research which supports the contention that highly coordinated surface sites are most active for ammonia synthesis has been carried out on rhenium [11]. In this study rates of ammonia synthesis over the (0001), (10\bar{1}0), (1\bar{1}20), and (11\bar{2}1) faces were determined, as shown in figure 3.3. Here, as for iron, the face with the highest activity, the (11\bar{2}1) plane, is the surface which exposes the most highly coordinated sites. Figure 3.3 also shows that the (11\bar{2}1) face exposes C_{11} and C_{10} sites while the next active (1\bar{1}20) face exposes C_{11} and C_7 sites. This
Figure 3.3: Structure sensitivity over rhenium [11].
research in combination with the work on the iron crystal faces, supports the contention that highly coordinated sites are the most active for ammonia synthesis and that surface roughness is only important to the extent that it can expose these active surface atoms to the gas phase nitrogen and hydrogen.

References


Chapter 4

Surface Science Studies of K/Fe, K/N₂/Fe, and K/NH₃/Fe Systems

4.1 Surface Science Studies of K/Fe, K/N₂/Fe, and K/NH₃/Fe Systems

This chapter summarizes a large amount of work which has been performed external to this thesis, but which serves as an important background into the effects of potassium on iron. The structure and bonding strength of potassium will be discussed along with the effects of potassium on the dissociative chemisorption of nitrogen on iron single crystal surfaces.

4.1.1 The Structure of Potassium on Iron Single Crystal Surfaces

The structure of potassium overlayers on well-defined single crystal surfaces [1,2] has been investigated. Potassium shows no ordered structures on the (100) face of iron at any surface coverage. Ordered overlayers have been observed for potassium
adsorbed on Fe(110) and Fe(111).

At a saturation coverage of potassium, an ordered overlayer with hexagonal close-packed symmetry has been observed on the (110) face of iron. A lack of ordering by potassium is found at lower coverages and this is usually explained by noting that the mobility of the alkali metal on the iron surface is high. This allows only small ordered domains to exist which cannot be observed by LEED. At higher coverages lateral interactions between neighboring adsorbed potassium atoms result, and hence the potassium resides in energetically favorable surface sites which form an ordered structure.

In contrast, the (111) surface of iron exhibits an ordered potassium structure only at low potassium coverages, where a (3x3) structure is observed. At higher coverages of potassium, the diffraction pattern corresponding to the (3x3) structure deteriorates and a (1x1) structure with a high background appears, indicating the presence of a disordered potassium overlayer.

4.1.2 The Stability of Potassium on Iron in UHV

The strength of the interaction between iron and potassium has been studied by temperature programmed desorption [1,2]. Potassium TPD spectra from the (111), (100), and (110) faces of iron show the same qualitative features. At low coverages of potassium ($\theta_K \approx 0.07$, where $\theta_K$ is equal to the number of potassium atoms divided by the number of surface Fe atoms), desorption occurs $\approx 800$ K, but at higher coverages ($\theta_K \approx 0.8$) of potassium, the maximum rate of desorption decreases to about 550 K (figure 4.1). This type of behavior is common for alkalis on transition metals. Reneutralization of the alkali metal begins to occur [4] as higher coverages of potassium are achieved, resulting in a lower iron
Figure 4.1: K TPD spectra for potassium adsorbed on a polycrystalline Fe surface suggest that potassium will not be stable under stationary ammonia synthesis conditions (T ≈ 673 K) [3].
- potassium interaction, and hence a reduction in the desorption energy. Using the Redhead analysis [5], the desorption energies of potassium on the various iron crystal faces are as follows: Fe(110), 57±2 kcal/mole; Fe(100), 54±2 kcal/mole; Fe(111), 52±2 kcal/mole. These values are obtained by extrapolating to zero coverage and they represent the upper limits for the strength of the potassium - iron bond. Desorption energies become lower at higher coverages of potassium, but the detailed data necessary to determine the potassium desorption energy as a function of coverage is not available.

Coadsorption of oxygen thermally stabilizes potassium on the iron surface, as exhibited in figure 4.2. These TPD spectra show that for high coverages of potassium, the coadsorption of oxygen appreciably raises the desorption temperature. For a potassium adlayer without oxygen, the maximum desorption rate occurs at 550 K and the desorption is complete by 900 K. When oxygen is present, the temperature at which the maximum rate of desorption occurs is increased to 750 K, and even at 1000 K, part of the potassium-oxygen adlayer is thermally stable on the iron surface. It is also evident from the figure that the order of adsorption of potassium and oxygen does not significantly change the thermal stability of the adlayer at high coverages. However, at lower coverages of potassium and oxygen, the order of adsorption of the additives changes the thermal stability of the layer. If oxygen is predosed (Y₀=0.48, \(\frac{\text{Intensity of } O\text{ }510\text{ eV Auger peak}}{\text{Intensity of } Fe\text{ }650\text{ eV Auger peak}}\)) on polycrystalline iron, followed by the addition of potassium \((n_K=1.48\times10^{14}\text{ cm}^{-2})\), then the maximum rate of potassium desorption occurs at 750 K. On a surface where potassium is added first \((n_K=1.55\times10^{14}\text{ cm}^{-2})\), followed by oxygen addition \((Y_0=0.89)\), the maximum rate of potassium desorption occurs at about 800 K. In addition, a much larger fraction of the potassium desorbs above 1000 K when potassium is present on the surface before the addition of oxygen.
Figure 4.2: The presence of oxygen thermally stabilizes potassium. (a) $n_K = 2.45 \times 10^{14}$ cm$^{-2}$, (b) $n_K = 2.06 \times 10^{14}$ cm$^{-2}$, $Y_0 = 0.90$ (O adsorbed first), and (c) $n_K = 2.61 \times 10^{14}$ cm$^{-2}$, $Y_0 = 0.62$ (K adsorbed first). $Y_0$ is defined in text.
CHAPTER 4: SURFACE SCIENCE STUDIES OF K/Fe

The nature of the K + O adlayer is uncertain, but research [6] on Fe(110), using x-ray photoelectron spectroscopy (XPS) and UPS, has shown that oxygen is directly bound to the iron surface. The interaction between potassium and oxygen, which is probably responsible for the thermal stability of the layer, was observed as a shift in the potassium 2p level in the XPS studies. These results suggest either that both potassium and oxygen exist as an adlayer, in which they are both chemisorbed directly to the iron surface, or in a configuration where the potassium atoms sit on top of an oxygen layer. The fact that the adlayer is more stable when potassium is adsorbed on the iron before the addition of oxygen is strong evidence for the former argument. The formation of a bulk potassium compound, such as K₂O, is extremely unlikely, since this compound is known to decompose at about 620 K. This decomposition temperature is well below 1000 K, the temperature at which the potassium - oxygen layer completely desorbs at, in the TPD experiments.

4.1.3 The Effect of Potassium on the Dissociative Chemisorption of Nitrogen on Iron Single Crystal Surfaces in UHV

The rate determining step in ammonia synthesis is accepted to be the dissociation of nitrogen [7,8,9]. Thus, the interaction between nitrogen and iron has been studied [10,11], along with the addition of submonolayer amounts of potassium [3,7,12]. All the work that will be mentioned has been carried out in a UHV chamber, limiting the pressure range to between 10⁻⁴ Torr and 10⁻¹⁰ Torr.

Using iron single crystals and polycrystalline foils, the sticking probability of nitrogen on iron was found to be on the order of 10⁻⁷. This result reveals
why, in addition to thermodynamic considerations, ammonia synthesis from the elements is favored at high reactant gas pressures. Since the sticking probability of dissociating nitrogen is so low on iron, higher pressures of nitrogen enhances the kinetics of the rate limiting step in ammonia synthesis. The structure sensitivity of the reaction (see chapter 3) is also revealed in the nitrogen chemisorption studies. It was found that the Fe(111) surface dissociatively chemisorbs nitrogen 20 times faster than the Fe(100) surface and 60 times faster than the Fe(110) surface. This agrees well with the structure sensitivity of ammonia synthesis and adds more credence to the idea that dissociative chemisorption of nitrogen is the rate limiting step in ammonia synthesis. The addition of submonolayer amounts of elemental potassium has drastic effects on the nitrogen chemisorption properties of the (110), (100) and (111) faces of iron.

Figure 4.3 [12] shows the effect of potassium on the initial sticking coefficient ($\sigma_0$) of nitrogen on a Fe(100) surface. For clean Fe(100), $\sigma_0 \approx 1.4 \times 10^{-7}$, but with the addition of potassium $\sigma_0$ increases almost linearly, until a potassium concentration of $1.5 \times 10^{14}$ K atoms/cm$^2$, where $\sigma_0$ reaches a maximum value of $3.9 \times 10^{-5}$; a factor of 280 enhancement over clean Fe(100). Higher coverages of potassium start to decrease $\sigma_0$, presumably due to potassium blocking iron sites which would otherwise dissociatively chemisorb nitrogen. The maximum increase in $\sigma_0$, due to potassium adsorption, on Fe(111) is about a factor of 8 ($\sigma_0 = 4 \times 10^{-5}$) at a potassium concentration of $2 \times 10^{14}$ K atoms/cm$^2$ (figure 4.4). The potassium induced enhancement of $\sigma_0$ on the Fe(110) surface is greater than that observed on either Fe(111) or Fe(100), so that the differences in activities for nitrogen dissociation, seen on the clean surfaces, are eliminated in the presence of potassium.

The mechanism by which potassium promotes nitrogen chemisorption is usually attributed to the lowering of the surface work function in the vicinity of a
Figure 4.3: The variation of $\sigma_0$ with the addition of potassium to Fe(100) at 430 K. $\sigma_0$ is enhanced by a factor of 280 relative to clean Fe(100) [12].
Figure 4.4: $\sigma_0$ as a function of potassium coverage on Fe(111) at 430 K. $\sigma_0$ can be enhanced by a factor of 8 in the presence of potassium [12].
potassium atom. This effect is greatest at low potassium coverages ($\lesssim 0.15$), where the potassium - iron bond has strong ionic character and the lowering of the local ionization potential, induced by the potassium, is greatest. This allows for more electron density to be transferred, from the surface, into the nitrogen $2\pi^*$ antibonding orbitals. This phenomenon increases the adsorption energy of molecular nitrogen and simultaneously lowers the activation energy for dissociation. For example, on the Fe(100) surface the addition of $1.5 \times 10^{14}$ K atoms/cm$^2$ decreases the work function by about 1.8 eV and increases the rate of nitrogen dissociation by more than a factor of 200. This enhancement in rate is accompanied by an increase in the adsorption energy of nitrogen on Fe(100) by 11.5 kcal/mole, which in the presence of potassium decreases the activation barrier for dissociation from 2.5 kcal/mole to about 0 kcal/mole. Figure 4.5 shows a proposed potential energy surface for the $N_2$ interaction with Fe(100) and K/Fe(100) surfaces. The presence of potassium increases the adsorption energy of nitrogen on Fe and reduces the activation energy for dissociation to atomic nitrogen.

The coadsorption of oxygen has been found to decrease the promoter effect of potassium on the rate of nitrogen dissociation over iron. Figure 4.6 shows that $\sigma_0$ decreases continuously with increasing oxygen coverage on a polycrystalline iron sample. The effect of the oxygen on nitrogen adsorption, in this study, is attributed to the physical blockage of iron surface, since if $\sigma_0$ is normalized to the amount of iron surface which is accessible to nitrogen, then $\sigma_0$ remains fairly constant as oxygen coverages are increased. This result implies that the promoter effect of potassium is not significantly affected by the presence of oxygen. It is also strong evidence for an adlayer where both potassium and oxygen interact directly with the iron surface, since potassium sitting on top of oxygen would not be expected to exert the same promotion as potassium adsorbed alone.
Figure 4.5: Potential energy diagram for the interaction of \( N_2 \) with Fe(100) and K/Fe(100) surfaces [7].
Figure 4.6: The effect of oxygen on $\sigma_0 (= \frac{S_0}{10^5})$ for a K/Fe (polycrystalline) surface. The decrease in $\sigma_0$ is attributed to the physical blockage of surface sites by oxygen. $Y_0$ is defined as the ratio between the oxygen Auger intensity and iron Auger intensity ($Y_0 = \frac{I_{O(310 \text{ eV})}}{I_{Fe(550 \text{ eV})}}$) [3].
4.2 Summary of Surface Science Results

Many conjectures on the chemical state and role of potassium in ammonia synthesis can be made from the surface science results. The potassium TPD results clearly show that elemental potassium will not be stable at the temperatures necessary to perform the synthesis of ammonia. The industrial reaction is usually run between 673 K and 748 K and the TPD results show that elemental potassium would rapidly desorb at these temperatures. With the coadsorption of oxygen, potassium can be thermally stabilized up to temperatures greater than 1000 K. Bulk potassium compounds such as K₂O or KOH would not be stable under ammonia synthesis conditions [13]. This suggests that the addition of K₂O to the industrial catalyst results in a chemisorbed potassium and oxygen adlayer, stable under industrial ammonia synthesis conditions.

The (111) face of iron has been shown to dissociatively chemisorb nitrogen 20 times faster than Fe(100) and 60 times faster than Fe(110). The addition of potassium increases the rate of nitrogen dissociation over Fe(100) and Fe(110) by more than an order of magnitude. The effect over Fe(111) is much less pronounced, so that the differences in activities, observed over the clean surfaces, is eliminated in the presence of potassium.

Although vital for thermally stabilizing potassium, the presence of oxygen decreases the rate of nitrogen dissociation on iron, because it physically blocks iron surface. A rough inverse proportionality is observed between σ₀, the initial sticking coefficient of nitrogen on K/Fe, and the coverage of oxygen. The K + O adlayer is expected to promote ammonia synthesis by enhancing the rate limiting step. The high pressure studies presented next suggest that a more important promoter
effect of potassium involves lowering the concentration of adsorbed ammonia on
the iron catalyst, thus making more sites available for the dissociation of nitrogen.
This will be shown to be consistent with ammonia TPD results, presented in the
next chapter, which show that potassium substantially decreases the adsorption
energy of ammonia on iron.

References

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Chapter 5

Combined Surface Science and Catalytic Study of the Effects of Potassium on Ammonia Synthesis

5.1 Introduction

As was mentioned earlier, in chapter 1, the most efficient catalyst found to synthesize ammonia is iron “promoted” with 1-3% by weight of aluminum oxide and potassium oxide [1,2,3]. Iron based catalysts used in ammonia synthesis usually perform at high pressures (>1 atm) where ammonia production proceeds at a significant rate [2,3]. Under these conditions the catalyst surface cannot be examined on the atomic level. Surface science studies of the catalyst on the atomic-scale require high vacuum where the synthesis of ammonia does not occur at a detectable rate.

The studies reported in this chapter elucidate the effects of potassium in ammonia synthesis. It is shown that potassium fails to exhibit a promoter effect on the Fe(110), which is inactive under the ammonia synthesis conditions used in this study. A promoter effect by potassium is observed on the Fe(100) and Fe(111) surfaces and the effect is enhanced as the reaction conversion increases. This re-
result is consistent with previous research [4] in this laboratory, which found that potassium fails to exhibit a significant promoter effect at close to zero reaction conversion. The activation energy at low conversion for the reaction is unaltered with the addition of potassium, but there are marked changes in the apparent reaction order of ammonia and hydrogen for ammonia synthesis. Temperature programmed desorption studies show that potassium lowers the adsorption energy of ammonia on iron.

A model is presented which explains the surface science and kinetic data. It assumes that adsorbed ammonia, as well as atomic nitrogen, blocks active sites which would otherwise dissociate nitrogen (the rate limiting step in ammonia synthesis) [2,5,6]. When the model is fit to the kinetic data it suggests that the promotional effect of potassium involves lowering the concentration of adsorbed ammonia on the catalyst, thereby making more active sites available for the dissociation of nitrogen. The model also suggests that an additional effect of potassium is to increase the rate constant for dissociative nitrogen chemisorption on Fe(111) and Fe(100) by 30%.

5.2 Results

5.2.1 The Stability of Potassium on Iron Under Ammonia Synthesis Conditions

Rates of ammonia synthesis were monitored over the Fe(111), Fe(100), and Fe(110) surfaces with and without potassium. In all cases in which the effect of potassium was studied, an initial coverage of 1 ML was deposited on the single crystal surface. After reaction about 0.15 ML of potassium was left as concluded from post-reaction AES. Surface oxygen was always detectable after reactions
which were performed over K/Fe surfaces; presumably due to oxygen and water impurities in the reactant gases. However, the oxygen was necessary to stabilize the potassium on the iron surface under reaction conditions [4]. Heating a K/Fe surface to 673 K in UHV and then introducing the surface to ammonia synthesis conditions, in the high pressure cell, led to a post reaction surface which had no adsorbed potassium. Reactions were carried out over K/Fe surfaces which had been oxidized in UHV until the 47 eV MVV iron Auger peak split into a 42 eV and 52 eV peak, indicative of iron oxide [7]. Even with this high initial surface oxygen concentration, only 0.15 ML of potassium was left after a high pressure ammonia synthesis reaction.

Experiments were also performed in which 1.0 ML of potassium was deposited on the iron single crystal and the sample was only kept under reaction conditions for a few minutes. When the sample was returned to UHV, AES showed a potassium coverage of 0.15 ML suggesting that the low steady-state coverage of potassium was established quickly, under reaction conditions, by evaporation of the excess potassium.

AES always showed the presence of nitrogen after high pressure ammonia synthesis reactions. Within experimental error, the coverage of nitrogen (intensity of the 381 eV nitrogen Auger peak) was the same on Fe and K/Fe surfaces after a reaction.

5.2.2 The Ammonia Partial Pressure Dependence Over Iron Single Crystal Surfaces

Ammonia synthesis rates, as a function of ammonia partial pressure, were calculated for the Fe(100), Fe(111), K/Fe(100), and K/Fe(111) surfaces. The Fe(110)
and K/Fe(110) surfaces were inactive (ammonia production was below the detection limit of the PID) under the conditions used in this study. Typically reactions performed on Fe(111) and Fe(100) were carried out until an ammonia partial pressure of 20 Torr had been established in the reaction loop. Figure 5.1 plots the logarithm of the ammonia synthesis rate versus the logarithm of the ammonia partial pressure for Fe(100). The slope of this plot (apparent reaction order in ammonia) is -0.6±0.07 for clean Fe(100) and -0.35±0.07 for the K/Fe(100) surface. The same experiments were carried out for Fe(111) and K/Fe(111). The apparent reaction order was found to be -0.49±0.08 for Fe(111) and -0.34±0.07 for K/Fe(111), which is within experimental error of the ammonia pressure dependences found for Fe(100) and K/Fe(100) surfaces respectively.

5.2.3 The Hydrogen Partial Pressure Dependence Over Iron Single Crystal Surfaces

The apparent reaction order for hydrogen on Fe(111) and K/Fe(111) surfaces is shown in figure 5.2. The apparent order for the clean Fe(111) surface is 0.76±0.09, but the value decreases to 0.44±0.06 for the K/Fe(111) surface. In these experiments the partial pressure of hydrogen was varied from 5 atm to 15 atm while the nitrogen pressure was kept constant at 5 atm. All rates were taken as close to zero conversion as possible, but depending on the activity of the surface being studied the partial pressure of ammonia varied from 0 to 3 Torr.

The apparent order in hydrogen for the Fe(100) surface was not determined, since the activity of this face at the hydrogen pressures needed to obtain a partial pressure plot was too low to be reliable at a catalyst temperature of 673 K.
Figure 5.1: The pressure dependence of ammonia synthesis in ammonia over Fe(100) and K/Fe(100). Potassium increases the apparent reaction order for ammonia.
CHAPTER 5: EFFECTS OF POTASSIUM

Figure 5.2: The hydrogen pressure dependence for the ammonia synthesis reaction over Fe(111) and K/Fe(111). The addition of potassium to Fe(111) lowers the apparent reaction order of hydrogen.
5.2.4 The Activation Energies for Clean Fe and K/Fe Surfaces

The initial rate of ammonia synthesis was determined for clean Fe(111) and K/Fe(111) at every 15 K interval between 638 K and 723 K. Using an Arrhenius plot, the apparent activation energy \( (E_a) \) was found to be 15.7±0.6 kcal/mole for clean Fe(111) and 15.9±1.0 kcal/mole for K/Fe(111), as shown in figure 5.3. The experimental error in \( E_a \) for K/Fe(111) is higher than for clean Fe(111), because the potassium coverage changed as the temperature of the sample was varied to obtain the Arrhenius plot. To minimize this effect, \( E_a \) was determined in a narrow temperature range. Within error, \( E_a \) does not change upon the addition of potassium.

5.2.5 Ammonia Temperature Programmed Desorption Studies

The temperature programmed desorption of ammonia, after a 1 langmuir (L) dose (1 L = 1×10\(^{-6}\) Torr-sec), on clean Fe(111) and K/Fe(111) is shown in figure 5.4 (heating rate = 8 K/sec). Ammonia desorbs through a wide temperature range, resulting in a broad peak with a maximum rate of desorption occurring at around 300 K. With the addition of 0.1 ML of potassium the peak maximum shifts to a lower temperature by about 40 K. The peak maximum continuously shifts to lower temperature with increasing amounts of coadsorbed potassium. At a coverage of 0.25 ML a new desorption peak grows in at about 189 K. Increasing coverages of potassium now increase the intensity of the new peak (it also shifts to lower temperatures) and decreases the intensity of the original ammonia desorp-
Figure 5.3: The activation energy ($E_a$) for ammonia synthesis over Fe(111) and K/Fe(111).
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Figure 5.4: Ammonia temperature programmed desorption results on Fe(111) and K/Fe(111) (heating rate = 8K/sec) after a 1 L dose.
CHAPTER 5: EFFECTS OF POTASSIUM

ion peak. At a potassium coverage of about 1.0 ML only a weakly bound ammonia species is present with a maximum rate of desorption occurring at 164 K. This observation, that the ammonia adsorption energy decreased with the coadsorption of potassium on iron, is similar to that found for ammonia desorption from nickel and ruthenium with adsorbed sodium [8,9].

5.3 Discussion

The results reported in this chapter show that the promoter effect of potassium becomes more pronounced at higher partial pressures of ammonia. This is reflected in the ammonia partial pressure dependence studies, which show that the apparent order in ammonia increases from -0.6 for the clean Fe(100) surface to -0.35 for the K/Fe(100) surface. Within experimental error, the same ammonia partial pressure dependences are found for Fe(111) and K/Fe(111). These changes in the reaction orders for ammonia and hydrogen occur without a change in activation energy. This implies that potassium does not change the elementary reaction steps for ammonia synthesis. These results, taken together with the temperature programmed desorption results (which show that potassium decreases the adsorption energy of ammonia on iron), suggest that potassium is promoting ammonia synthesis by keeping gas phase ammonia from adsorbing and poisoning the synthesis reaction at higher conversions or higher partial pressures of ammonia. This interpretation explains why previous work [4] failed to find a potassium promoter effect when initial rates of ammonia synthesis were determined over clean Fe and K/Fe surfaces. During initial rate measurements there is not a sufficient amount of gas phase ammonia (<2 Torr) to significantly poison the reaction. Thus, the promoter effect of potassium was not discernable.
5.3.1 The Effect of Potassium on the Adsorption of Ammonia on Iron Single Crystal Catalysts During Ammonia Synthesis

Poisoning of the catalyst by gas phase ammonia must involve readsoption of the product molecule on the iron surface. Once adsorbed, the ammonia has a certain residence time ($\tau$) on the catalyst, which is determined by its adsorption energy ($\Delta H_{\text{ad}}$) on iron ($\tau \propto e^{\Delta H_{\text{ad}}/RT}$) [10]. During this residence on the catalyst, the ammonia can either diffuse on the surface or decompose to atomic nitrogen and hydrogen [11,12]. In both cases the species produced by the ammonia might reside on surface sites which would otherwise dissociatively chemisorb gas phase nitrogen, thus decreasing the rate of ammonia synthesis [11,12]. The promoter effect of potassium then involves lowering the adsorption energy of the adsorbed ammonia so that its surface concentration is decreased. This interpretation is supported by the temperature programmed desorption results which show that ammonia desorption from Fe(111) shifts to lower temperatures when potassium is adsorbed on the surface. Even at a 0.10 ML coverage of potassium (coverage which is similar to that stable under ammonia synthesis conditions) the temperature at which the maximum rate of ammonia desorption occurs decreases by about 40 K. If first order kinetics for ammonia desorbing from the iron is assumed, and the Redhead analysis used [13], then the 40 K shift corresponds to a 2.4 kcal/mole drop in the adsorption energy. Thus, the residence time for the adsorbed ammonia is reduced and more of the active sites are available for the dissociation of nitrogen. At higher coverages of potassium the adsorption energy of the ammonia decreased to an even greater extent, but these coverages could not be maintained under ammonia synthesis conditions. There also seems to be an additional adsorption site for the ammonia
CHAPTER 5: EFFECTS OF POTASSIUM

when adsorbed on iron at high coverages of potassium, as indicated by the TPD results. The development of a new desorption peak, with coverages of potassium greater than 0.25 ML, might result from ammonia molecules interacting directly with potassium atoms; the negative end of the ammonia dipole interacting with the potassium ion on the iron surface [8]. This interaction appears to be weaker, since at a potassium coverage of 1 ML, ammonia desorbs from the surface at about 164 K.

Additional experimental evidence supporting the notion that ammonia blocks active sites comes from the post-reaction Auger data. Within experimental error, there is no change in the intensity of the nitrogen Auger peak between an Fe surface and a K/Fe surface after a high pressure ammonia synthesis reaction. This observation suggests that potassium does not change the coverage of atomic nitrogen, but instead the presence of potassium helps to inhibit the readsorption of molecular ammonia on the catalyst. High pressure reaction conditions are probably needed to stabilize this ammonia product on the iron surface at 673 K, so it will not be present in the ultra-high vacuum environment. Thus, only the more strongly bound atomic nitrogen will be detected by AES in UHV.

5.3.2 Modeling the Kinetic Data with a Rate Equation

To model a catalytic reaction some knowledge of the elementary reaction steps must be assumed. For ammonia synthesis it is usually accepted that the dissociative chemisorption of nitrogen is rate-limiting and that the process requires two open sites on the catalyst surface [2,14,5]. Using Langmuir-Hinshelwood kinetics, the rate of ammonia synthesis (r) can be written as:

\[ r = k_1 P_{N_2}(1 - \theta_N)^2 \]  \hspace{1cm} (5.1)
where \( k_1 \) is the rate constant for nitrogen dissociative chemisorption and \( 1 - \theta_N \) is the fraction of vacant sites (\( \theta_e \)) on the surface, if atomic nitrogen is assumed to be the most abundant species. The fraction of sites covered by nitrogen, \( \theta_N \), is calculated by assuming the equilibrium [11,12]:

\[
N_{ad} + 1.5H_2(g) \rightleftharpoons NH_3(g)
\] (5.2)

where \( K_e \) is the equilibrium constant. Following the method of Langmuir:

\[
\theta_N = \frac{(1/K_e)(P_{NH_3}/P_{H_2})}{[1 + (1/K_e)(P_{NH_3}/P_{H_2})]^2}.
\] (5.3)

\( \theta_N \) is substituted into equation 5.1 so that:

\[
r = \frac{k_1P_{N_2}}{[1 + (1/K_e)(P_{NH_3}/P_{H_2})]^2} \] [12]. (5.4)

The data can be accurately represented by equation 5.4. Fitting of the experimental data to the equation (i.e. solving for \( K_e \)) is done by setting \( dlnr/dlnP_{NH_3} \) equal to the apparent order of ammonia, and by using the values \( P_{N_2} = 5 \) atm, \( P_{H_2} = 15 \) atm, and \( P_{NH_3} = 0.013 \) atm. This method yields a value of \( K_e = 0.5 \times 10^{-4} \) for clean Fe surfaces and \( K_e = 1 \times 10^{-3} \) for K/Fe surfaces. This model implies that the equilibrium constant \( K_e \) increases with the adsorption of potassium, pushing the equilibrium in equation 5.2 to the gas phase ammonia side, and as a result lowers the fraction of sites covered by adsorbed nitrogen, increasing the rate of ammonia synthesis.

It is instructive now to take the case where both adsorbed nitrogen and ammonia can block catalytic sites, since the kinetic data suggests that a promoter effect of potassium is to lower the concentration of ammonia on the catalyst surface. In this case \( \theta_e = 1 - \theta_N - \theta_{NH_3} \), where \( \theta_N \) and \( \theta_{NH_3} \) are determined by the equilibria:

\[
N_{ad} + 1.5H_2(g) \rightleftharpoons NH_3(g)
\] (5.5)
and

\[ NH_{3ad} \xrightleftharpoons[K_2]{[\text{5.6}]} NH_3(g) \]

where \( K_2 \) and \( K_3 \) are equilibrium constants (note \( K_e = K_2K_3 \)). Now the rate of ammonia synthesis is:

\[ r = \frac{k_1P_{N_2}P_H^{3}}{[P_H^{1.5} + (P_{NH_3}/K_3)(K_2^{-1} + P_H^{1.5})]^2}. \]  

(5.7)

The constants, \( K_3 \) and \( K_2 \), are calculated by fitting equation 5.7 to the experimental data. For the clean surface \( K_3 = 0.19 \) and \( K_2 = 2.6 \times 10^{-3} \). When potassium is present, \( K_3 = 0.37 \) and \( K_2 = 2.6 \times 10^{-3} \). This model, which accounts for adsorbed ammonia blocking active sites, suggests that the enhancement in ammonia synthesis rate seen over the K/Fe surfaces is due to an increase in the equilibrium constant \( K_3 \), or a shift in the equilibrium from adsorbed to gas phase ammonia. The increase in \( K_3 \) might be due to the decreased adsorption energy of ammonia when potassium is present, as evidenced by the temperature programmed desorption results. The decrease in the apparent order of hydrogen is also consistent with the increase in \( K_3 \) induced by potassium. Since the rate limiting step in ammonia synthesis is the dissociation of nitrogen, the only role of hydrogen in the rate expression (equation 5.7) is to create available sites for this step. In the presence of potassium, \( K_3 \) increases making more sites available, as shown by the equilibrium expressions 5.5 and 5.6. This is reflected in the lowering of the apparent order in hydrogen when potassium is added on the iron surface.

The contention that potassium increases the rate of ammonia synthesis by lowering the concentration of adsorbed ammonia product, on the iron catalyst, might explain earlier work which was carried out on the industrial catalyst. Numerous reports in the literature [2,15,16,17,18] contend that the effect of potassium on "doubly promoted" industrial catalysts (catalysts that contain both aluminum
oxide and potassium) becomes more pronounced as higher reaction conversions are achieved. It has been shown previously [16] that the turnover number over “singly promoted” catalyst (those that contain only aluminum oxide) and “doubly promoted” catalysts are similar when a total of one atmosphere of nitrogen and hydrogen is used, suggesting that the ammonia partial pressure is not great enough at these conditions to make the effect of potassium important. In another study [17], where higher reactant pressures (5 atm - 200 atm) were used, the promoter effect of potassium became significant on the industrial catalyst. It was found that as the concentration of gas phase ammonia was increased, catalysts containing potassium increasingly became more active than catalyst which contained no potassium. This implies that on the industrial catalyst the apparent order in ammonia becomes less negative when potassium is present. Also, in the same study the activation energy for ammonia synthesis was found to be the same for “singly” and “doubly promoted” catalyst.

The experimental results, presented in this chapter and carried out on well defined Fe and K/Fe surfaces, agree well with what was found on the industrial catalyst. It seems likely that the mechanism of potassium promotion involving the lowering of the ammonia adsorption energy, suggested by these experiments, occurs on the industrial catalyst.

5.3.3 The Effect of Potassium on Nitrogen Dissociation Under Ammonia Synthesis Conditions

In addition to hindering ammonia adsorption on the iron catalyst, potassium might also enhance nitrogen dissociation during ammonia synthesis. Figure 5.5 shows the experimentally determined ratio of the clean Fe rate to the rate over
CHAPTER 5: EFFECTS OF POTASSIUM

K/Fe surfaces as a function of ammonia partial pressure. The ratio continuously increases as more ammonia is present in the gas phase (i.e. the promoter effect of potassium is enhanced). If the only role of potassium was to keep ammonia off the catalyst surface, then in the limit of zero ammonia partial pressure, the ratio should be unity. Instead the fit of the model to the experimental data is best when the ratio is 1.3 at zero ammonia partial pressure. This result implies that potassium increases \( k_1 \), the rate constant for nitrogen chemisorption, by 30% on both Fe(111) and Fe(100). If the pre-exponential factor for \( k_1 \) is assumed to be the same for clean Fe and K/Fe surfaces, then a 30% increase in rate corresponds to a 0.35 kcal/mole decrease in the activation energy \( (E_a) \) for the rate limiting step. This change in \( E_a \) is too small to be resolved in the experiments performed in this chapter. A small change in \( E_a \) such as this might also explain observations with an industrial catalyst, that the activation energy for ammonia synthesis was only slightly higher on “singly promoted” (aluminum oxide) iron than it was on “doubly promoted” (aluminum oxide and potassium oxide) catalysts [17,19].

Enhancement of the rate limiting step in high pressure ammonia synthesis by potassium is supported by surface science studies [20,21], which investigated the influence of potassium on the rate of dissociative chemisorption of nitrogen \( (k_1) \) on iron single crystals (chapter 4). The activity ratio for nitrogen dissociation was found to be 60:3:1 for the Fe(111), Fe(100), and Fe(110) surfaces respectively. Potassium removed the difference in activities between the (110), (100), and (111) faces of iron by lowering the activation energy for nitrogen dissociation markedly on Fe(110) and Fe(100). The effect of potassium on Fe(111) is less pronounced, but on all three iron surfaces the effect of potassium was attributed to the same mechanism. In the vicinity of a potassium atom the local work function on the surface is lowered and this allows more electron density to be transferred to ni-
Figure 5.5: The experimental rate data fit to a model which allows for the blocking of catalytic surface sites by adsorbed ammonia as well as atomic nitrogen.
trogen, thus increasing its adsorption energy and lowering the activation energy for dissociation on the iron. The coadsorption of oxygen was found to be of prime importance for thermally stabilizing potassium [22], but the presence of adsorbed oxygen decreased the effect of potassium on the rate of nitrogen dissociation.

Under the conditions used in this study (20 atm reactant pressure and a catalyst temperature of 673 K) oxygen is needed to stabilize potassium. The presence of the oxygen probably accounts for the small effect of potassium on $k_1$ in the present studies. The promotion by potassium, of nitrogen dissociation under industrial conditions ($\approx$100 atm reactant pressure), will probably be similar to the effect seen under the conditions used in this chapter, since it is well documented in the literature [18,23] that potassium is in intimate contact with oxygen on the commercial catalyst.

5.4 Summary of Effects of Potassium

The promoter effects of potassium on ammonia synthesis have been investigated over the Fe(110), Fe(100), and Fe(111) surfaces under high pressure conditions. A coverage of 0.15 ML is the maximum amount of potassium that can be stabilized on the iron single crystals under the conditions used in this chapter. Adsorbed potassium has no promotional effect on the inactive Fe(110) surface. Potassium, however, increases the rate of ammonia synthesis markedly over the Fe(111) and Fe(100) crystal faces. The promotional effect becomes enhanced as the reaction conversion increases. For example, at a reaction conversion of 0.3% there is a twofold increase in the rate of ammonia synthesis over Fe(111) and Fe(100) in the presence of potassium. The presence of potassium changes the ammonia reaction order from -0.6 to -0.35 and the hydrogen reaction order from
0.76 to 0.44, on the (100) and (111) faces of iron. However, there is no change in the activation energy, within experimental error, when potassium is present, suggesting that the mechanism for ammonia synthesis is not changed.

A model has been presented which is consistent with the high pressure kinetic and surface science studies. The model accounts for the blocking of catalytic sites, which have the ability to dissociate nitrogen, by adsorbed ammonia and atomic nitrogen. The presence of potassium lowers the concentration of adsorbed ammonia on the surface, which makes more sites available to dissociatively chemisorb nitrogen, increasing the rate of ammonia synthesis. The model suggests that an additional promoter effect by potassium is a 30% enhancement of the rate of nitrogen dissociation on Fe(111) and Fe(100), further increasing the rate of ammonia production.

References


REFERENCES


Chapter 6

Combined Surface Science and High Pressure Studies on the Effects of Aluminum Oxide in Ammonia Synthesis

6.1 Introduction

Most early research on aluminum oxide, in relation to ammonia synthesis, suggests that the use of aluminum oxide for ammonia synthesis simply increases the surface area of the iron catalyst and inhibits sintering, which usually occurs with high surface area metallic particles [1,2]. This interpretation is supported by work which showed, by BET measurements, that the surface of the industrial ammonia synthesis catalyst increased ten-fold when aluminum oxide was added in the preparation phase [1]. Other workers have asserted that aluminum oxide, in addition to increasing surface area, prevents the conversion of active planes, such as Fe(111), to less active surfaces (i.e. Fe(100) and Fe(110)) during ammonia synthesis [1]. However, this contention could not be shown, because of the lack of surface structure probes in this previous work. Recent surface science and
high pressure results will now be described which directly investigated the iron-aluminum oxide system for ammonia synthesis over Fe(110), Fe(100), and Fe(111) model single crystal catalysts [3].

This chapter reports a study on the effects of promoter, aluminum oxide, on the synthesis of ammonia over single crystal iron surfaces of (111), (100), and (110) orientation. It is found that a pretreatment of the iron catalyst, in the presence of aluminum oxide, using water vapor must be performed prior to the ammonia synthesis for aluminum oxide to function as a promoter. In this circumstance the rates of the reaction over the less active (110) and (100) faces increases markedly, to attain the rate observed over the most active Fe(111) face. The presence of aluminum oxide helps to maintain this high activity, which is caused by the restructuring of the less active crystal faces to surfaces as active as the Fe(111) or Fe(211) faces [4].

6.2 Results

6.2.1 Auger Electron Spectroscopy and Low Energy Electron Diffraction Studies

The growth of oxidized aluminum on the iron single crystals was studied by AES and LEED. There was no indication of any long-range ordering of the Al\textsubscript{x}O\textsubscript{y} at any coverage on the Fe(111), Fe(100), and Fe(110) planes. Using AES, the 67 eV aluminum transition intensity was plotted against the iron 47 eV and 652 eV peak intensities. In both cases no breaks in the curves were found, indicating three dimensional Al\textsubscript{x}O\textsubscript{y} island growth.

AES was used to estimate the coverage of Al\textsubscript{x}O\textsubscript{y} in the near surface region on the three different iron surfaces used in this study before and after the various
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water vapor treatments. On both the Fe(110) and Fe(111) surfaces an initial concentration of two monolayers of Al$_x$O$_y$ decreases to about 50% of a monolayer after being treated with 0.05 Torr of water vapor, with subsequent reduction in the H$_2$ and N$_2$ synthesis gas mixture. A more drastic reduction in the Al$_x$O$_y$ coverage was observed if the sample was treated with 0.4 Torr of water. In this case the Al$_x$O$_y$ was barely detectable by AES (about 5% of a monolayer). Argon ion sputtering the surface ($4 - 5 \times 10^{-6}$ amperes/cm$^2$) at room temperature uncovered additional Al$_x$O$_y$. Sputtering the sample at 823 K revealed less Al$_x$O$_y$, because the Al$_x$O$_y$ diffused into the iron bulk or iron had migrated on top of the Al$_x$O$_y$. Prolonged sputtering at 823 K eventually caused a (1x1) LEED pattern to appear on both the Fe(111) and Fe(110) surfaces.

The behavior of Al$_x$O$_y$ on the Fe(100) face is different than that on the (110) and (111) planes. After a treatment with 0.05 Torr or 0.4 Torr of water vapor the ratio of the aluminum Auger signal to the iron signal was unchanged, indicating that no Al$_x$O$_y$ had left the surface. After a 20 Torr treatment of water vapor about 50% of a monolayer of Al$_x$O$_y$ was left on the Al$_x$O$_y$/Fe(100) surface.

Auger peak positions were used to study the cooperative interaction between the Al$_x$O$_y$ and iron in the presence of water vapor, because the energy of an Auger transition of an element is often sensitive to the chemical environment [5]. Metallic iron has a MVV Auger transition at 47 eV which splits into a 42 eV and 52 eV doublet in the oxide (the 42 eV peak has been attributed to the participation of oxygen 2p electrons and the 52 eV Auger peak to the influence of iron d electrons) [6]. Elemental aluminum exhibits a LVV Auger peak at 68 eV, which shifts to 54 eV in the oxide [7]. When Al$_x$O$_y$ is deposited on the iron substrate only 47 eV and 54 eV peaks are present. When the Al$_x$O$_y$ surface is treated with water vapor the 42 eV peak, representative of iron oxide, shifts to 39 eV (Figure 6.1),
possibly indicating an alteration of the iron-oxygen bond and a chemical interaction between \( \text{Al}_2\text{O}_3 \) and iron in an oxidizing environment (i.e. \( \text{Fe} + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} = \text{FeAl}_2\text{O}_4 + \text{H}_2 \)).

6.2.2 Reaction Rate Studies

The initial rate of ammonia synthesis was determined over the clean Fe(111), Fe(100), and Fe(110) surfaces (Figure 6.2). The addition of aluminum oxide on the (110), (100), and (111) faces of iron decreases the rate of ammonia synthesis in direct proportion to the amount of surface covered by the additive (figure 6.3). All aluminum oxide is doing in this case is blocking iron surface which is active for ammonia synthesis. Remembering that the industrial catalyst is prepared by fusing aluminum oxide with iron oxide (\( \text{Fe}_3\text{O}_4 \)), rates of ammonia synthesis were also obtained over these different surfaces after they had been pretreated with water vapor.

6.2.3 Clean Fe Single Crystals Treated with Water Vapor Prior to the Ammonia Synthesis Reaction

Treatment of the clean (110), (100), and (111) surfaces at water vapor pressures of 0.05 Torr or 0.4 Torr produces heavily oxidized surfaces, as shown by the splitting of the 47 eV MVV iron Auger peak into 44 eV and 52 eV peaks [6]. The oxidized surfaces are readily reduced under the conditions used for the ammonia synthesis reaction, and the respective Fe(110), Fe(100), and Fe(111) surfaces are regenerated.

Treatment of a clean Fe(110) surface with 20 Torr of water vapor followed
Figure 6.1: AES spectra of oxidized iron and a partially oxidized iron-aluminum oxide surface. Note the shift of the 42 eV iron peak to 39 eV when aluminum oxide is coadsorbed on the oxidized surface.
Figure 6.2: Ammonia synthesis rates over clean iron single crystals and restructured Al₂O₃/Fe surfaces.
Figure 6.3: Addition of aluminum oxide to iron single crystals decreases the rate of ammonia synthesis in direct proportion to the amount of iron surface covered by the additive.
by reduction under synthesis conditions leaves a restructured surface (no \((1 \times 1)\) LEED pattern is obtained), whose initial ammonia synthesis activity is close to that of the \((111)\) plane of iron. Visual inspection of the crystal shows that the initial mirror finish of the crystal is lost and a dull luster is now apparent. If this surface is kept under ammonia synthesis conditions for one hour the surface again becomes inactive (Figure 6.4), and a \((1 \times 1)\) LEED pattern representative of the \(\text{Fe}(110)\) surface appears.

A 20 Torr water vapor pretreatment also restructures the \((111)\) and \((100)\) planes of iron. The restructured \(\text{Fe}(111)\) surface (broad and diffuse \((1 \times 1)\) LEED spots are obtained) shows a small decrease (about 5\%) in its ammonia synthesis activity (figure 6.2). The restructured \(\text{Fe}(100)\) plane (no LEED pattern is obtained) becomes almost as active as the \((111)\) face of iron (figure 6.2). Like the restructured \(\text{Fe}(110)\) face, the activity of the restructured \((111)\) and \((100)\) surfaces return to their respective clean surface activity after one hour of ammonia synthesis. Sharp \((1 \times 1)\) LEED patterns for both surfaces are observed at this time.

6.2.4 \(\text{Al}_2\text{O}_y/\text{Fe}\) Surfaces Pretreated in Water Vapor Prior to the Ammonia synthesis Reaction

Treatment of \(\text{Al}_2\text{O}_y\) (0.5-1.5 monolayers)/\(\text{Fe}\) surfaces with 0.05 or 0.4 Torr of water vapor, produced no restructuring as judged by the ammonia synthesis rate on the \((111)\), \((100)\), and \((110)\) faces of iron.

Major changes in the activity of ammonia production for the \(\text{Fe}(110)\) face occurs when two or more monolayers of \(\text{Al}_2\text{O}_y\) were deposited on the surface prior to the water vapor treatment. After a water vapor treatment of 0.05 Torr the \(\text{Al}_2\text{O}_y/\text{Fe}(110)\) surface restructures. The restructured surface is now about
Figure 6.4: The effect of \( \text{Al}_x\text{O}_y \) on the activity of the restructured Fe(110) surface under ammonia synthesis conditions.
as active as the Fe(100) plane (Figure 6.2). If two monolayers of Al\textsubscript{x}O\textsubscript{y} were deposited on a new Fe(110) surface, then exposure to 0.4 Torr or 20 Torr of water vapor produced a restructured surface almost as active as the Fe(111) crystal face (figure 6.2). The restructured Al\textsubscript{x}O\textsubscript{y}/Fe(110) surface retained its high ammonia synthesis activity for longer than four hours under ammonia synthesis conditions (figure 6.4).

A Fe(111) surface with two monolayers of Al\textsubscript{x}O\textsubscript{y} shows no noticeable change in activity when pretreated with 0.05 Torr of water vapor. Exposure to 0.4 Torr or 20 Torr of water vapor restructures the surface, producing a slight decrease (about 5%) in ammonia synthesis activity (figure 6.2).

The Al\textsubscript{x}O\textsubscript{y}/Fe(100) surface exhibited no restructuring when exposed to 0.05 Torr or 0.4 Torr of water vapor (conditions which restructured the Al\textsubscript{x}O\textsubscript{y}/Fe(110) and Al\textsubscript{x}O\textsubscript{y}/Fe(111) surfaces). Treatment of the Al\textsubscript{x}O\textsubscript{y}/Fe(110) surface with 20 Torr of water vapor caused restructuring and enhanced activity for the ammonia synthesis reaction. The synthesis rate over the restructured Al\textsubscript{x}O\textsubscript{y}/Fe(100) surface was similar to that of the clean Fe(111) surface activity (figure 6.2). No deactivation was observed for the restructured Al\textsubscript{x}O\textsubscript{y}/Fe(100) surface after four hours of ammonia synthesis.

All the restructured Al\textsubscript{x}O\textsubscript{y}/Fe surfaces maintained their activity even after any surface Al\textsubscript{x}O\textsubscript{y} was removed by ion sputtering, as monitored by AES. A \textsuperscript{13}CO titration could not be used to determine the Al\textsubscript{x}O\textsubscript{y} coverage, since all the restructured surfaces (after the surface Al\textsubscript{x}O\textsubscript{y} had been removed by argon ion sputtering) chemisorbed substantially less carbon monoxide than the respective clean, unstructured surfaces. For example, the restructured Fe(110) and Fe(100) surfaces chemisorbed approximately 40% less CO than the clean Fe(110) and Fe(100) faces respectively. Prolonged sputtering (2-4 hours at 823 K) caused the restructured
surfaces to exhibit (1×1) LEED patterns and ammonia synthesis activities representative of the clean, unrestructured surfaces (no Al₂O₃ was present at this time as judged by AES).

6.2.5 Activation Energy for the Ammonia Synthesis Reaction Over Clean and Restructured Iron

The initial rate of ammonia synthesis was determined for the restructured Al₂O₃/Fe(110) and restructured clean Fe(110) surface at 25 K intervals, between 673 K and 823 K. Using an Arrhenius plot, the apparent activation energy of both restructured surfaces was found to be 18.6±1 kcal/mole, in close agreement with the value of 19.4±0.5 kcal/mole obtained for the clean single crystal surfaces [8].

6.2.6 Surface Structure characterization

The synthesis of ammonia from its elements is a structure sensitive reaction over iron and variation of rates observed in this study due to the pretreatments suggests that new surface orientations are being created. In an attempt to characterize the structure of the new surfaces scanning electron microscopy (SEM) and temperature programmed desorption were performed on the clean and restructured surfaces. SEM gave information on the microscopic appearance of the surfaces while TPD gave insight into the nature of the crystal orientations present on the restructured surfaces.

6.2.7 Scanning Electron Microscopy
The development of a clean Fe(110) single crystal surface into a restructured surface was followed by SEM. Figure 6.5 shows micrographs taken of restructured Al\textsubscript{x}O\textsubscript{y}/Fe(110) surfaces (a clean, unrestructured iron single crystal showed only a flat and featureless surface). At an exposure of 0.05 Torr of water vapor the formation of crystallites, about one micron in diameter, appear on the Al\textsubscript{x}O\textsubscript{y} (figure 6.5 a). Using 0.4 Torr of water vapor reconstructs the entire surface as can be seen in figure 6.5 b.

A Fe(110) surface restructured in 20 Torr of water vapor is shown in figure 6.6 a. The surface appears uniform in appearance, unlike the Al\textsubscript{x}O\textsubscript{y}/Fe(110) restructured surface. Figure 6.6 b shows the same surface after one hour of ammonia synthesis. The surface now shows less pronounced features, similar to the unrestructured Fe(110) plane. This conclusion is supported by the appearance of a (1×1) Fe(110) LEED pattern and inactivity towards the production of ammonia in the synthesis reaction.

### 6.2.8 Temperature Programmed Desorption

Ammonia adsorption and desorption has been studied in UHV on the Fe(111), Fe(100), and Fe(110) surfaces [9,10]. Molecular ammonia completely desorbs from all the iron surfaces by 400 K. In contrast to this result it has been found in this study that after the high pressure ammonia synthesis reaction, ammonia desorbs in the 400 K - 750 K temperature range from all the iron single crystal surfaces studied. The desorbing ammonia, detected during these TPD experiments, results from surface species which adsorbed on the catalyst during ammonia synthesis, or during the pump-down sequence, where the sample is kept at a temperature of 373 K (see chapter 2.4.4). The mechanism has not been studied in detail,
Figure 6.5: SEM of the restructured $\text{Al}_x\text{O}_y/\text{Fe}(110)$ surface. (a) After a 0.05 Torr treatment of water vapor and reduction in ammonia synthesis gas. (b) After a 0.04 Torr treatment of water vapor with subsequent reduction.
Figure 6.6: SEM of restructured Fe(110) surface (a) after a 20 Torr water vapor treatment or (b) after 1 hour of ammonia synthesis.
but more important to this work is that the ammonia desorption can be used to probe the different surface orientations, since different TPD spectra are observed following ammonia synthesis for the (110), (100), (111), and (211) iron single crystal surfaces. The Fe(211) TPD spectrum is included, because it helps support a conclusion presented later.

Ammonia TPD spectra for the four surfaces are shown in Figure 6.7. The Fe(110) surface displays one desorption peak ($\beta_3$) with a peak maximum at 658 K. Two desorption peaks are observed for the Fe(100) surface ($\beta_2$ and $\beta_3$) at 556 K and 661 K. The Fe(111) surface exhibits three desorption peaks ($\beta_1$, $\beta_2$, and $\beta_3$) with peak maxima at 495 K, 568 K, and 676 K. The Fe(211) plane has two desorption peaks ($\beta_2$ and $\beta_3$) at 570 K and 676 K. Temperature programmed desorption spectra for the Al$_2$O$_y$/Fe(110), Al$_2$O$_y$/Fe(100), and Al$_2$O$_y$/Fe(111) surfaces restructured in 20 Torr of water vapor are shown in Figure 6.8. A new desorption peak, $\beta_2$, develops on the restructured Al$_2$O$_y$/Fe(110) surface and an increase in the $\beta_2$ peak occurs on the restructured Al$_2$O$_y$/Fe(100) surface. The $\beta_2$ peaks from the restructured Al$_2$O$_y$/Fe(110) and Al$_2$O$_y$/Fe(100) surfaces grow in the same temperature range as the Fe(111) and Fe(211) $\beta_2$ peaks. Deactivation of the restructured surfaces by prolonged sputtering at 832 K reduces the intensity of the $\beta_2$ peaks on the restructured Al$_2$O$_y$/Fe(110) and Al$_2$O$_y$/Fe(100) surfaces to the same level as found for the respective clean surfaces.

The clean Fe(110), Fe(100), and Fe(111) surfaces restructured with 20 Torr of water vapor produce the same TPD spectra as the Al$_2$O$_y$ restructured surfaces. Deactivation of the (100) and (110) clean restructured iron surfaces is rapid under the ammonia synthesis conditions and the $\beta_2$ peaks become equivalent in intensity to those on the respective clean surfaces within one hour of ammonia synthesis.
Figure 6.7: Ammonia TPD from clean iron single crystals (heating rate is 10 K/sec) after ammonia synthesis. Mass 15 (NH\textsuperscript{+} fragment) is monitored to avoid detecting water contamination, which adsorbs during pump-down after ammonia synthesis, and then desorbs during TPD.
Figure 6.8: Ammonia TPD from restructured iron single crystals. The growth of the \( \beta_2 \) peaks on restructured Al\(_x\)O\(_y\)/Fe(110) and Al\(_x\)O\(_y\)/Fe(100) are attributed to the creation of C\(_7\) sites.
6.3 Discussion

Examination of the results reveals several effects of $\text{Al}_2\text{O}_3$ on iron single crystal surfaces in the presence of water vapor. Perhaps the most significant is that $\text{Al}_2\text{O}_3$ prevents the reconversion of the restructured, active surfaces to ones less active in the ammonia synthesis (i.e. Fe(110) and Fe(100) surfaces). Another effect of $\text{Al}_2\text{O}_3$ is its ability to restructure iron single crystals to new surface orientations, active in ammonia synthesis, at water vapor pressures lower than those needed to restructure clean iron single crystal surfaces. The fact that the activation energy for ammonia synthesis over the restructured $\text{Al}_2\text{O}_3$ surfaces is the same as over the clean surface implies that iron is still the active phase for the synthesis of ammonia.

The nature of the restructuring of $\text{Al}_2\text{O}_3$/Fe surfaces is indicated by the kinetic and TPD results. Kinetic data shows that through restructuring the activity towards ammonia synthesis of the Fe(110) and Fe(100) planes approaches that of the clean Fe(111) or Fe(211) planes, while the Fe(111) plane is not affected greatly by restructuring. The activity of the clean Fe(111) and Fe(211) planes is usually attributed to the presence of $C_7$ sites (Fe atoms with seven nearest neighbors) [8,4,11]. The clean Fe(100) and Fe(110) plane lack these sites, and this observation suggests that restructuring in water vapor produces highly coordinated $C_7$ sites on the restructured Fe(110) and Fe(100) surfaces. The increase in rates over the restructured Fe(110) and Fe(100) planes is not attributable to an increase in surface area, since less CO is adsorbs on these surfaces than on the respective clean surfaces. A similar decrease in CO adsorption has also been observed on iron ammonia synthesis catalysts that have been restructured with ammonia [11].
(chapter 3). These results were interpreted as due to the formation of C₇ sites, which are not able to adsorb as much CO as lower coordinated sites, because of steric reasons. This explanation is applicable to the present study and it further supports the idea of formation of C₇ sites upon water vapor restructuring.

While not as convincing as the kinetic data, the ammonia TPD results certainly point towards the formation of surface orientations which contain C₇ sites after restructuring. The growth of the β₂ peaks upon restructuring of the Fe(110) and Fe(100) surfaces suggests that the surfaces change orientation upon water vapor treatment. The β₂ peaks also are observed in the same temperature range as the Fe(111) β₂ peak. It seems likely that the TPD peaks in this temperature range act as a signature for the C₇ site, since the Fe(211) surface (figure 6.7), which contains C₇ sites and is highly active in the ammonia synthesis reaction, also exhibits a β₂ peak after the ammonia synthesis, with a peak maximum at 570 K. These results suggest that surface orientations which contain C₇ sites, such as the Fe(111) and Fe(211) planes, are formed during the reconstruction of clean and Al₂O₃ treated iron surfaces, but only in the presence of Al₂O₃ does the active restructured surface remain stable under the ammonia synthesis conditions.

The process by which iron restructures seems to involve both oxidation and reduction. Initial oxidation by water vapor destroys the original morphology of the iron surface. Reduction with N₂ and H₂ removes the oxygen, and the resulting metallic iron is left in orientations (i.e. Fe(111) and Fe(211)) active for ammonia synthesis. If no support phase is present (i.e. Al₂O₃), reconversion of the iron into less active orientations is rapid under ammonia synthesis conditions. It has been shown in UHV [12,13] that the oxidative process on the Fe(110) plane is more facile than on the Fe(100) surfaces, and this agrees with the fact that the Fe(110) surface can restructure, in this study, with lower water vapor pressures than are
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needed for the Fe(100) plane.

With the addition of Al$_2$O$_y$ the mobility of the iron is increased, and restructuring can occur at lower pressures of water vapor. The SEM micrographs suggest that iron is forming crystallites on top of the restructured Al$_2$O$_y$/Fe(110) surface (opposed to the uniform appearance of the restructured clean Fe(110) surface). AES finds little Al$_2$O$_y$ on the surface, suggesting that the iron has diffused on top of the Al$_2$O$_y$. This restructuring process may be understood by considering wetting properties and the minimization of the free energy for the iron oxide-aluminum oxide system.

In vacuum or in a reducing environment (i.e. ammonia synthesis conditions), metallic iron will not spread over aluminum oxide (metallic iron has a higher surface tension than aluminum oxide [14]). Conversely, in an oxidizing environment (i.e. the water vapor treatments) iron oxide forms (the surface tension of the oxide will be lower than the metal [14,15]) and a chemical interaction between iron and aluminum oxide might result, as inferred from the AES results. Both these considerations favor iron wetting the aluminum oxide. Using transmission electron microscopy, it has been shown that iron wets alumina (Al$_2$O$_3$) in an oxidizing environment or even in the presence of hydrogen which contains trace amounts of water vapor [16]. From microelectron diffraction data, the formation of iron aluminate (i.e. FeAl$_2$O$_4$) in the presence of an oxygen source was also postulated [16].

Whereas 20 Torr of water vapor was needed to restructure clean iron single crystals, only 0.4 Torr of water vapor is needed to restructure an Al$_2$O$_y$/Fe surface, since Al$_2$O$_y$ provides an alternate and apparently more facile mechanism for the migration of iron. Upon reduction, metallic iron is left in highly active orientations (i.e. Fe(111) and Fe(211)) for the ammonia synthesis reaction. The Al$_2$O$_y$ now stabilizes the active iron, since if the Al$_2$O$_y$ was not present the iron would move...
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to positions coincident with the bulk periodicity.

Figure 6.9 is a schematic representation of the proposed restructuring process which is consistent with the experimental findings. Oxidation of iron in water vapor induces spreading of the iron oxide over the aluminum oxide islands. The major driving force, for this process, being the the formation of iron aluminate, a conclusion which is supported by the AES work. In nitrogen and hydrogen the iron oxide is reduced, but iron aluminate remains, providing a template for the growth of active surface orientations of iron, such as Fe(111) and Fe(211). The thickness of the iron layer after restructuring can not be quantified, but it probably is about 3 or 4 layers. This conclusion is supported by the experimental result that the active iron layer can quickly be removed by ion sputtering (exposing aluminum oxide). Furthermore, an active surface for ammonia synthesis will require at least three layers of iron to produce highly coordinated, active sites (see figure 3.2).

The formation of iron aluminate during reconstruction of the iron surface may be responsible for the stability of the restructured Al₂O₃/Fe surfaces. The formation of iron aluminate has been postulated in XPS studies on Fe-Al₂O₃ and Fe₃O₄-Al₂O₃ systems [17,18] as well as in numerous studies on the industrial ammonia synthesis catalyst [19,20,21]. The volume of an FeAl₂O₄ molecule is approximately equal to the volume of seven iron atoms in a bcc lattice [19] so that FeAl₂O₄ can exist as a skeleton in the iron lattice with little distortion. The low coverages of Al₂O₃ on the restructured surfaces suggest that the support effect might be coming through inclusions of FeAl₂O₄ in the near surface region. This contention is supported by the fact that ion sputtering the restructured surfaces reveal subsurface Al₂O₃.
Figure 6.9: Schematic representation of the restructuring process which is induced by aluminum oxide and water vapor.
6.4 Summary of Aluminum Oxide Results

Treating the (110), (100), and (111) faces of iron with 20 Torr of water vapor causes surface restructuring. The restructured Fe(110) and Fe(100) surfaces become as active as the clean Fe(111) surface in ammonia synthesis. The restructured Fe(111) exhibits a slight decrease (about 5%) in activity when compared to the clean Fe(111) surface. The restructured (110), (100), and (111) surfaces reconvert to their unrestructured orientations within one hour of ammonia synthesis.

The same restructuring on the Fe(110), Fe(100), and Fe(111) surfaces can be performed with water vapor in the presence of aluminum oxide. In this case 20 Torr of water vapor restructures the Al₂O₃/Fe(110) and only 0.4 Torr of water vapor is needed to restructure the Al₂O₃/Fe(110) surface, so that they become as active as the Fe(111) face in ammonia synthesis. The restructured Al₂O₃/Fe(110) and Al₂O₃/Fe(100) surfaces maintain their activity for longer than four hours under ammonia synthesis conditions. The formation of iron aluminate in the iron near surface region is invoked to explain the stability of the restructured Al₂O₃/Fe surfaces.

The reaction rate studies and ammonia temperature programmed desorption results suggest that planes containing C₇ sites, such as the Fe(211) and Fe(111) surfaces, are created during the water vapor pretreatments with or without aluminum oxide. Only when aluminum oxide is present will these active surfaces remain stable and not reconvert to less active surfaces (i.e. Fe(110) and Fe(100) planes).
References


Chapter 7

Combined UHV/High Pressure Studies on the Interaction Between Aluminum Oxide and Potassium Coadsorbed on Iron

7.1 Introduction

The iron ammonia synthesis catalyst that is utilized in industry is usually mixed with potassium oxide and aluminum oxide additives that further increase the rate of ammonia synthesis (see chapter 1). It is found that aluminum oxide additives alone increase the rate of ammonia synthesis by increasing the active surface area of the iron [1]. Potassium addition decreases the iron surface area, but still increases the rate by a factor of three to ten [1]. The "doubly promoted" iron catalyst surface consists of regions where potassium oxide resides alone and areas where it interacts with aluminum oxide [1,2]. Combined high pressure and ultra-high vacuum studies presented in chapters 5 and 6 have elucidated the mechanisms by which aluminum oxide [3] or potassium [4] adsorbed alone increases the rates of ammonia synthesis over Fe(111), Fe(100), and Fe(110) single crystal surfaces. This
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The chapter reports on the combined effects of coadsorbed potassium and aluminum oxides, commonly used in preparing the industrial iron catalyst.

This chapter shows that while aluminum oxide can stabilize much more potassium on the iron surface (as compared to the 0.15 monolayers on the clean iron), probably by forming a potassium aluminate compound (i.e. $\text{KAIO}_2$) [5], it does not improve the activity of the catalyst any further. This observation is due in part to the blocking of the active iron surface by potassium aluminate and in part to the inhibiting effect of potassium on the aluminum oxide induced restructuring of iron [3]. It is experimentally shown that the most active ammonia synthesis catalyst is produced by first restructuring iron with water vapor in the presence of aluminum oxide and then adding potassium.

7.2 The Stability of Potassium on Iron when Coadsorbed with Aluminum Oxide

Figure 7.1 shows Auger spectra for a K/Fe(100) surface prepared prior to carrying out ammonia synthesis, a K/Fe(100) surface after reaction, and a post-reaction K/40%Al$_x$O$_y$/Fe(100) surface. It is apparent that the surface with aluminum oxide can retain more potassium during ammonia synthesis conditions than the surface without aluminum oxide. This suggests that aluminum oxide binds directly to potassium, or there is an interaction mediated through the iron surface. To probe these interactions, experiments were performed in which a known amount of Al$_x$O$_y$ was deposited on a Fe(100) surface. About 1 ML of potassium was evaporated on the crystal, and the sample was heated to 673 K in UHV. The potassium Auger signal was monitored periodically. A rapid decrease occurs in the potassium Auger signal initially, which is due to the low desorption energy of potassium at high
Figure 7.1: AES spectra of promoted Fe(100) surfaces before and after ammonia synthesis. The pre-reaction potassium signal corresponds to 1 ML.
CHAPTER 7: EFFECTS OF COADSORBED AlₓOᵧ AND POTASSIUM coverages. After about 20 minutes a steady state concentration of potassium was established. The final coverage of potassium was approximately equal to the initial coverage of aluminum oxide. This result is represented in figure 7.2, where the relative concentration of stabilized potassium is plotted against the relative concentration of aluminum oxide. An approximate 1:1 ratio is found between the surface concentration of potassium and aluminum oxide, and this is suggestive of compound formation between the two additives (i.e. KAlO₂), as opposed to a non-stoichiometric AlₓOᵧ-K surface layer [5].

7.3 Water Vapor Treatment of K/AlₓOᵧ/Fe and Fe Single Crystal Surfaces

Coverages between 0.1 ML and 1.0 ML of potassium, adsorbed alone on the (111), (100), and (110) faces of iron, failed to produce any promotional effects after pretreatments of 0.05 Torr, 0.4 Torr, and 20 Torr of water vapor. After water vapor treatments, the coverage of potassium was never more than 0.4 ML, and it did not exceed 0.1 ML after the ammonia synthesis reaction, in agreement with research presented in chapter 5.

The same coverages of potassium coadsorbed with two monolayers of aluminum oxide on the Fe(110), Fe(100), and Fe(111) surfaces hindered the restructuring process in water vapor (see chapter 6). As increasing amounts of potassium were coadsorbed, more aluminum oxide was detected by AES after water pretreatments of 20 Torr, and less restructuring of the iron occurred (rates of ammonia synthesis over these surfaces were less than those for surfaces which were restructured with just aluminum oxide). There is a one to one ratio between aluminum oxide and potassium on the surface. In the case where one monolayer of potassium was
Figure 7.2: The relative concentration of stabilized potassium plotted against the relative concentration of aluminum oxide present. The dotted line corresponds to a 1:1 ratio of potassium to aluminum oxide.
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deposited on two monolayers of aluminum oxide, AES showed that no aluminum oxide or potassium left the iron surface after a 20 Torr water vapor pretreatment, and restructuring failed to occur.

7.4 The Effects of Coadsorbed Potassium and Aluminum Oxide on the Clean, Unrestructured Fe(100) Surface for Ammonia Synthesis

In these experiments conditions that would induce restructuring of iron (treatment of the AlₓOᵧ/Fe(100) surface with water vapor at 723 K (chapter 6)) were carefully avoided. Thus, the Fe(100) surface structure remained unaltered during these experiments. Figure 7.3 shows the partial pressure of ammonia, in the reaction loop, as a function of ammonia synthesis reaction time for a clean Fe(100), 0.15 ML K/Fe(100), 0.25 ML K/25%AlₓOᵧ /Fe(100), and a 25%AlₓOᵧ /Fe(100) surface. The initial rate of ammonia synthesis (0 Torr - 3 Torr of ammonia is in the loop during this time) over the AlₓOᵧ/Fe(100) and K/AlₓOᵧ /Fe(100) surfaces have been shown to decrease roughly in proportion to the amount of iron catalyst surface covered by the additives (see chapter 6 and figure 6.3) [5]. Thus, potassium aluminate [5] does not increase the activity of the catalyst in this circumstance. As the reaction conversion increases, the promoter effect of potassium becomes apparent. Thus, the 0.25 ML K/25%AlₓOᵧ /Fe(100) surface increasingly becomes more active than the 25%AlₓOᵧ /Fe(100) surface. This is the same behavior as is observed when comparing the reaction rates over the K/Fe(100) and Fe(100) surfaces in the same figure [4]. The addition of potassium reduces the adsorption energy of adsorbed ammonia and leads to a lower surface concentration of ammonia on the catalyst by shifting the equilibrium NH₃(ad) → NH₃(g) to the gas.
Figure 7.3: The partial pressure of ammonia in the reaction loop is plotted against time of ammonia synthesis for four different surfaces.
phase ammonia side (i.e. the equilibrium constant $K_3$ increases). With less adsorbed ammonia the number of available sites for the dissociation of nitrogen, the rate limiting step in ammonia synthesis [6,7], is increased and this increase causes an increase in the rate of ammonia production. In addition, potassium enhances the rate of nitrogen dissociation by approximately 30% over Fe(111) and Fe(100) under ammonia synthesis conditions (see chapter 5).

It has been shown that the concentration of aluminum oxide and potassium exist in an approximate 1:1 ratio under ammonia synthesis conditions [5]. Even though high coverages of potassium can be stabilized with aluminum oxide, the promotional effect never exceeds the effect attained on the 0.15 ML K/Fe(100) surfaces, as reported on in chapter 5. Thus, the potassium that is tied up by the aluminum oxide in a compound (KAlO$_2$) seems to be rendered catalytically inactive. The 0.25 ML K/25%Al$_2$O$_3$/Fe(100) surface exhibits roughly the same rate of ammonia synthesis as the 0.15 ML K/Fe(100) surface at all ammonia partial pressures used in this study, as indicated by the slopes of the curves in figure 7.3. Stabilizing more than 0.25 ML of potassium with Al$_2$O$_3$ begins to decrease the promoter effect of potassium. One reason for this is that high coverages of potassium block catalytic sites for nitrogen dissociation [5,8].

7.5 **The Effects of Coadsorbed Potassium and Aluminum Oxide on the Restructured Fe(100) Surface for Ammonia Synthesis**

Figure 7.4 shows ammonia accumulation, as a function of reaction time, for the clean Fe(100), for 25%Al$_2$O$_3$/Fe(100) that was restructured by 20 Torr of water vapor at 723 K, and for 0.25 ML K/25%Al$_2$O$_3$/Fe(100) that was restructured first
in the presence of aluminum oxide alone, before the potassium was added. The studies in chapter 6 suggest that aluminum oxide catalyzes restructuring of Fe(100) and Fe(110) to crystal faces, such as Fe(111) and Fe(211), which are about an order of magnitude more active than the unrestructured Fe(100) and Fe(110) faces [9]. Potassium addition to the restructured surface further enhances the rate over the restructured iron, which becomes predominant at high ammonia conversions. In this way the promotional effects of both aluminum oxide and potassium can be fully realized. It should be noted that if both aluminum oxide and potassium are added before restructuring in water vapor, the extent of surface restructuring (Fe(100) → Fe(111) and Fe(211)) is decreased. The potassium aluminate that forms on the surface seems to prevent the aluminum oxide-iron interaction, which is necessary for reconstruction of the iron surface morphology.

The motivation behind the work carried out in this thesis has primarily consisted of trying to understand the promotional effects of aluminum oxide and potassium in the industrial catalyst. By using model iron single crystal surfaces as catalysts, it has been shown that the promoter effect of aluminum oxide results from the interaction with iron oxide during the preparation stage of the industrial catalyst [3]. After the activation of the catalyst (i.e. reduction in N₂ and H₂), aluminum oxide stabilizes the iron in active orientations, such as Fe(111) and Fe(211) [3,9], for ammonia synthesis. Potassium does not seem to be involved in this structural promotion [3], but its presence on the catalyst surface promotes ammonia synthesis on these active crystal orientations by increasing the rate of nitrogen dissociation and by lowering the concentration of adsorbed ammonia, thus making more catalytic sites available for nitrogen dissociation [4].
Figure 7.4: Ammonia partial pressure in the reaction loop is plotted against time of reaction for clean Fe(100) and restructured Fe(100) with Al\textsubscript{x}O\textsubscript{y} and potassium.
REFERENCES

References


Chapter 8

Ammonia Pretreatment Induced Restructuring of Iron Single Crystal Surfaces for Ammonia Synthesis

8.1 Introduction

It has been shown in this thesis (chapter 3) that the synthesis of ammonia from its elements is a structure sensitive reaction over iron [1,2,3]. Thus, a major concern in the preparation of an industrial catalyst is to preferentially create and stabilize active surface orientations (i.e. Fe(111) and Fe(211)) [4,5]. This objective is usually accomplished in the chemical industry by combining magnetite (Fe$_3$O$_4$) with about two percent by weight of potassium oxide (K$_2$O) and aluminum oxide (Al$_2$O$_3$) and then reducing the catalyst precursor in a stoichiometric mixture of hydrogen and nitrogen, or in an ammonia - hydrogen flow [6]. Catalytic studies have found that the industrial iron catalyst is more active when reduced in a stoichiometric mixture of nitrogen and hydrogen than in pure hydrogen (see chapter 1) [7]. Also, by treating the catalyst with ammonia, so as to achieve a
high virtual pressure of nitrogen (through the complete dissociation of ammonia), a nitrogen induced restructuring results, thereby leading to an enhancement in ammonia synthesis activity [2].

The interaction of nitrogen with iron in forming iron nitride has for a long time been thought to create surfaces which would be active in ammonia synthesis [1,2,8]. An extensive amount of surface science research has been devoted to understanding the interaction of nitrogen and ammonia on the structure of iron. Field emission studies dealing with nitrogen on iron suggested that the adsorption of nitrogen occurs most readily on the (111) face of iron and that the (110) and (100) planes, which are not as active as Fe(111), are actually transformed to the (111) face in the presence of nitrogen [9].

Nitrogen adsorption on Fe(111) and Fe(110) in UHV has been found to cause structural rearrangements of the iron surface atoms (a wide range of LEED patterns can be obtained) [10,11], while adsorption on Fe(100) produces a simpler c(2×2) superstructure. Adsorption of nitrogen on Fe(12,1,0) causes extensive reconstruction, which results from the formation of a surface nitride, similar to that found in bulk Fe₄N [12].

Ammonia completely decomposes on Fe(111), Fe(100), and Fe(110) at temperatures above 400 K (hydrogen desorbs) [13,14], producing a higher virtual pressure of atomic nitrogen than can be obtained by dosing iron with nitrogen in UHV. For example, adsorption of NH₃ at elevated temperatures on Fe(100) caused faceting of the (100) surface, producing monatomic steps, in contrast to the c(2×2) superstructure obtained by the adsorption of nitrogen. Higher pressures of ammonia (0.05 Torr - 1 Torr) cause extensive bulk facetting of polycrystalline iron at temperatures between 600 K and 1250 K [15].

This chapter reports on the effect of nitrogen induced restructuring on the
ammonia synthesis activity and the structure of well defined Fe(110), Fe(100), and Fe(111) surfaces. It is found in this study that by treating the (110) and (100) faces of iron with ammonia prior to ammonia synthesis that the surfaces restructure, losing their original surface orientation. The restructured Fe(110) and Fe(100) faces approach the activity of the Fe(111) surface. The ammonia pretreated Fe(111) surface shows only a small decrease in activity for ammonia synthesis. The presence of potassium and aluminum oxide do not influence the restructuring process. The presence of high bulk and surface concentrations of nitrogen after the ammonia treatment does not affect the catalytic surface suggesting that the presence of strongly bound nitrogen and bulk diffusion of nitrogen to the iron surface is not a factor in explaining ammonia synthesis kinetics.

8.2 Results

8.2.1 Reaction Rate Studies

8.2.2 Clean Iron Single Crystals Pretreated with Ammonia Prior to Ammonia synthesis

Rates of ammonia synthesis over initially clean (110), (100), and (111) faces of iron are shown in Figure 8.1. The rates, quoted in the figure were obtained after the treatment of the Fe(110), Fe(100), and Fe(111) crystals with 5 Torr of ammonia at 723 K for 30 minutes prior to the ammonia synthesis reaction. The Fe(110) and Fe(100) surfaces show large increases in activity for ammonia synthesis (figure 8.1) after ammonia pretreatment. The initially inactive Fe(110) face becomes about as active as the clean Fe(100) surface. The activity of the Fe(100) surface, for ammonia synthesis, increases by a factor of four and the Fe(111) surface shows only a small decrease in activity after ammonia pretreatment. Further treatment
CHAPTER 8: AMMONIA INDUCED RESTRUCTURING

Synthesis Conditions
Temperature = 673 K
20 atm 3:1 H₂:N₂

Restructuring Conditions
P$_{NH₃}$ = 5 Torr
Temperature = 723 K
Time = 30 minutes

Figure 8.1: Rates of ammonia synthesis over clean Fe single crystals and ones pretreated in ammonia prior to ammonia synthesis. Ammonia pretreatment restructures Fe(110) and Fe(100) to surfaces containing C₇ sites. Restructuring of Fe(111) has little change on ammonia synthesis activity.
CHAPTER 8: AMMONIA INDUCED RESTRUCTURING

of the restructured single crystals with 50 Torr of ammonia leads to no further change in ammonia synthesis rates.

8.3 The Effects of Adsorbed Nitrogen on Fe Surfaces for Ammonia Synthesis

8.3.1 The Surface Composition of the Ammonia Pretreated Iron Single Crystal Surfaces

After treatment of the iron single crystals with ammonia, a large concentration of nitrogen was detected by AES in the iron near surface region \((N_{381} \, eV/Fe_{652} \, eV = 1)\), and no LEED pattern was obtained. The surfaces could be briefly sputtered to remove surface nitrogen, but the rate of synthesis over these surfaces were identical to those with the high nitrogen surface concentrations. Post reaction AES showed a nitrogen to iron ratio of approximately 0.2±0.02. To recover the high surface concentration of nitrogen \((N \, to \, Fe \, AES \, ratio \, of \, 1)\) the samples could be heated to temperatures \(\sim 973 \, K\), where nitrogen surface segregates and begins to desorb from the surface. However, this high temperature purging starts to deactivate the restructured \((100)\), and \((110)\) surfaces, as evidenced by a decrease in ammonia synthesis activity. Hence, removing all the bulk nitrogen, at elevated temperatures, will deactivate the restructured surfaces to the respective clean surface through annealing.

8.3.2 The Coverage of Nitrogen at High Ammonia Synthesis Conversions Over Fe(111) and K/Fe(111)

Experiments were performed to study the effect of adsorbed nitrogen on a well
defined Fe(111) surface. Conditions were carefully avoided which would lead to substantial bulk concentrations of nitrogen (see ammonia pretreatment section). The Fe(111) and K/Fe(111) surfaces were exposed to mixtures of nitrogen, hydrogen, and ammonia which represented ammonia synthesis reaction conversions of 0.1%, 0.3%, 2.5%, and 5% at 673 K. Rates of ammonia production were too low over the 1 cm² surfaces to measure. Instead the coverage of nitrogen on the iron surfaces was monitored by post-reaction AES. The ratio of the 381 eV nitrogen peak to the 652 eV Fe Auger peak ranged from 0.17±0.02 to 0.39±0.03 for the 0.1% and 5% reaction conversions respectively. The relative concentration of nitrogen to iron was the same on the K/Fe surfaces, within experimental error. To rule out the possibility that nitrogen might adsorb on the Fe(111) surface during evacuation of the reaction cell, the sample was kept at 373 K and 673 K during this step. The nitrogen concentration measured by AES was identical at each temperature.

At conversions as low as 0.1%, bulk nitrogen becomes apparent. For example, the surface nitrogen which is stable in UHV after a 0.1% conversion can be removed by sputtering and annealing, at which time a sharp (1x1) LEED pattern representative of clean Fe(111) is obtained. However, annealing at elevated temperatures (≈973 K) causes nitrogen to appear on the surface suggesting that bulk nitrogen is formed even at relatively low reaction conversions.

At high conversions (2.5% and 5%) the rates of ammonia production were too low for measurement, over Fe(111). To study the ammonia synthesis activity over these Fe(111) surfaces, which had acquired a high surface concentration of nitrogen at high conversion, initial rates of ammonia synthesis were determined (15 atm H₂ and 5 atm N₂). In all cases the N/Fe(111) surfaces, prepared at high conversion, showed identical rates to clean Fe(111), at a conversion of 0.1%. Post reaction
Auger showed that all Fe(111) surfaces exhibited similar nitrogen to iron ratios. The high coverages of nitrogen, achieved at high conversion (5%), were rapidly removed at 0.1% conversion. Thus, the post reaction surface concentration of nitrogen is only a function of the reaction conversion, at which ammonia synthesis was carried out at.

8.3.3 Fe Surfaces with Al₂O₃ and/or Potassium Pretreated with Ammonia Prior to Reaction

The addition of Al₂O₃ to the (111), (100), and (110) surfaces of iron decreases the rate enhancement over (110) and (100), which occurs upon ammonia pretreatment. As increasing amounts of Al₂O₃ are added to the surface the amount of restructuring decreases, as evidenced by decreases in the ammonia synthesis activity. Post reaction AES finds that no Al₂O₃ has left the near surface region after the ammonia pretreatment. This is different behavior than found for Al₂O₃/Fe surfaces which have been restructured in water vapor [4] (chapter 6). In the water vapor case, iron is found to cover Al₂O₃ during the water vapor pretreatment.

The presence of potassium adsorbed alone or coadsorbed with Al₂O₃ has no effect on the restructuring process.

8.4 Structural Characterization of the Restructured Iron Surfaces

8.4.1 Temperature Programmed Desorption

The desorption of ammonia from iron single crystals, after a high pressure ammonia synthesis reaction, is sensitive to surface structure [4]. Both Fe(111) and
Fe(211) are found to exhibit two desorption peaks with peak maxima at 570 K ($\beta_2$) and 650 K ($\beta_3$, see figures 6.7 and 6.8). The Fe(100) and Fe(110) faces of iron show only ammonia desorption at 650 K.

When Fe(111), Fe(100), and Fe(110) are treated with 5 Torr of ammonia prior to reaction there are marked changes in the post-reaction TPD. Both Fe(100) and Fe(110) develop the low temperature peak ($\beta_2$) at 570 K, while the 650 K peak ($\beta_3$) shows little change.

8.4.2 Scanning Electron Microscopy

The appearance of all ammonia pretreated iron surfaces were studied by scanning electron microscopy (SEM) [16]. The SEM micrographs of the ammonia treated (110), (100), and (111) faces of iron are shown in figure 8.2 (the clean surfaces are smooth and featureless). In the case of the (111) surface the new features, which appear upon ammonia pretreatment, were large enough and sufficiently separated from each other to permit a stereographic investigation to determine what crystallographic planes were created upon ammonia treatment.

Figure 8.4 shows an isolated feature with the projection of the $<110>$ crystallographic axis onto the (111) surface indicated (determined by Laue x-ray crystallography). By determining the base length ($D_0$) and height of the feature ($Z_c$) by SEM, the angle in which plane a intersects the (111) plane could be determined, as shown in figure 8.3. The base length, $D_0$ (defined in figure 8.4 a), was determined in the SEM micrograph taken at 0° tilt (the electron beam is perpendicular to the (111) surface). The distance, $D_r$, was then determined from a SEM micrograph, taken when the sample was tilted 20° from the electron beam (figure 8.4 b). The height of the feature was then determined from the geometric relation (see
Figure 8.2: Scanning electron micrographs of the (a) Fe(111), (b) Fe(100), and (c) Fe(110) surfaces after they were treated in 5 Torr of ammonia at 723 K for 30 minutes. Single crystal surfaces which have not been ammonia treated appear smooth and featureless by SEM.
Figure 8.3: Stereo pair geometry and equations solved for tilt angles $\pm \alpha$. 

\[ D_r - D_l = \frac{P}{2 \sin \alpha} \]

\[ D_l = D_c \cos \alpha - Z_c \sin \alpha \]

\[ D_r = D_c \cos \alpha + Z_c \sin \alpha \]


The angle, $\theta$, at which plane $a$ intersected the (111) surface is equal to $\tan^{-1}(Z_c/D_0)$. This analysis was done on three different features and the $\theta$ values were 18.5°, 18.5°, and 17.9° (see table 8.1). The crystal orientation that most closely agrees with an average value of 18.2°± 0.5° is the (112) face, which intersects the (111) plane at 19.5°.

8.5 Discussion

8.5.1 Nitrogen Induced Restructuring of Fe(100) and Fe(110)

Analysis of the reaction rate results, temperature programmed desorption data, and scanning electron microscopy suggest that Fe(100) and Fe(111) are restructured to surfaces which contain highly coordinated iron surface atoms. The most active site for ammonia synthesis is usually accepted to be the C$_7$ site, which is present on highly active Fe(111) and Fe(211). The presence of the C$_7$ site on the ammonia restructured Fe(100) and Fe(110) is supported by the temperature programmed desorption results. The growth of a low temperature peak ($\beta_2$, see figures 6.7 and 6.8) on restructured (100) and (110), which is similar to the peak found on clean Fe(111) and Fe(211) suggests that C$_7$ sites are being formed by the high nitrogen concentration. This low temperature peak was also found to appear on Al$_x$O$_y$/Fe surfaces which had been restructured in the presence of water vapor. In this previous study (chapter 6), restructured Al$_x$O$_y$/Fe(100) and Al$_x$O$_y$/Fe(110) become as active as Fe(111). Thus, water vapor treatment of Al$_x$O$_y$/Fe surfaces create more active surface than those restructured in ammonia. However, in both
Figure 8.4: Isolated view of restructured Fe(111) surface at: (a) 0° tilt and (b) 20° tilt. Parameters used in the stereo pair study are shown in the figure along with the <110> crystallographic direction (determined by Laue X-ray crystallography).
cases, the restructured Fe(100) and Fe(110) exhibit high activity due to the creation of C₇ sites.

8.5.2 The Effect of Adsorbed and Dissolved Nitrogen on Iron During Ammonia Synthesis

The presence of adsorbed nitrogen, present during ammonia synthesis, seems not to affect ammonia synthesis activity under the conditions used in this study. Surfaces, restructured in ammonia, produce high near surface concentrations of nitrogen, but these surfaces are no more active than surfaces where the near surface nitrogen had been removed prior to ammonia synthesis. (The possibility that there is no surface nitrogen and that the nitrogen seen by Auger is actually subsurface nitrogen can not be ruled out.) This result suggests that at 673 K, where ammonia synthesis is carried out, the diffusion of nitrogen from the bulk is not an important process, in agreement with recent theoretical work [18]. These results also suggest that the nitrogen detected in UHV does not reside on catalytic sites during ammonia synthesis, since rates are the same over nitrogen-free and nitrided Fe surfaces after ammonia pretreatment. Also, studies (section 8.3.2) of adsorbed nitrogen on Fe(111), which had not undergone ammonia pretreatment, agree with the idea that the surface concentration of nitrogen on Fe is determined by the gas phase ammonia concentration. N/Fe(111) surfaces prepared at high conversion (5%) are not stable at low conversion (0.1% or 0.3%); the excess nitrogen being removed at low conversion.
8.5.3 SEM Analysis of the Restructured Fe(111) Surface

In the case of the (111) face of iron the ammonia synthesis rate and stereographic analysis help to characterize the restructured surface. The stereographic work gives an average angle of 18.2° ± 0.5° between plane a (figure 8.4) and the (111) surface. If the orientation of plane a is to be described by the Miller indices h, k, and l, then h and k must be equivalent, since the vector describing plane a (h,k,l), is in the same plane as the <111> and <110> vectors. Considering planes which have Miller indices ranging from 0 to 3 and using the condition that h and k are equal leads to the conclusion that the orientation of plane a is (112), which intersects the (111) plane at an angle of 19.5°. (Planes which have values of h, k, and l greater than 3 were not considered due to the high surface free energy associated with such rough surfaces.) All the other planes considered fall well outside the value of 18.4° ± 0.5° arrived at by the SEM work performed in this study. The three-fold symmetry of the features (planes a, b, and c are equivalent) and the (111) surface require that planes b and c be the (211) and (121) surfaces which are equivalent to the (112) plane. The reaction rate studies support this assignment, since the restructured (111) surface shows only a small decrease in ammonia synthesis activity when compared to the clean Fe(111) surface. Research, presented in chapter 3, showed that the (211) surface is only slightly less active than the (111) face of iron.

The high activities of the (111) and (211) faces of iron are usually attributed to the presence of C7 sites (Fe atoms with seven nearest neighbors) which are able to enhance the rate limiting step in the ammonia synthesis reaction, the dissociation of nitrogen. The presence of these highly coordinated sites might also explain
the increased dissociation rate of ammonia over the (111) plane of bcc tungsten relative to W(110) and W(100) [19]. It seems then that surfaces which expose C7 sites are stabilized by the chemisorption of atomic nitrogen and it would be thermodynamically favorable for the Fe(111) surface, with a surface free energy (\(\gamma\)) of 1460 ergs/cm\(^2\), to restructure to the more densely packed Fe(211) plane (\(\gamma_{211} = 1350\) ergs/cm\(^2\)) [20], which contains C7 sites, in the presence of ammonia.

8.5.4 The Effects of Aluminum Oxide and Potassium on the Restructuring of Fe

The presence of Al\(_2\)O\(_3\) on the Fe surface does not seem to affect the restructuring process. Its presence is actually detrimental to the process, since the Al\(_2\)O\(_3\) seems only to block iron surface which could otherwise dissociate ammonia. This restructuring process is in sharp contrast to the case where aluminum oxide restructures iron in the presence of water vapor prior to ammonia synthesis [4]. In this circumstance iron oxide is found to migrate on top of the aluminum oxide overlayer as a result of the oxidizing environment (water vapor). The major driving force for this structural transformation is most likely compound formation between iron oxide and aluminum oxide.

When nitrogen is the restructuring agent it is not thermodynamically favorable for iron nitride to cover aluminum oxide, probably resulting from the absence of a strong chemical interaction between iron nitride and aluminum oxide. Hence, AES finds aluminum oxide on the iron surface after Al\(_2\)O\(_3\)/Fe surfaces have been pretreated in ammonia. In the case of water vapor restructuring, AES finds that Al\(_2\)O\(_3\) leaves the iron surface region and resides under the active iron surface.

The presence of potassium on Fe during ammonia pretreatment has no effect
CHAPTER 8: AMMONIA INDUCED RESTRUCTURING

Table 8.1: Results of SEM stereographic analysis of ammonia restructured Fe(111) surface.

<table>
<thead>
<tr>
<th>Stereo Pair</th>
<th>Tilt</th>
<th>D_{z}(\times10^3 \text{ mm})/5KX</th>
<th>Z_{z}(\times10^4 \text{ mm})</th>
<th>\theta(\circ)</th>
<th>Crystal Face</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0°</td>
<td>2.86</td>
<td>9.58</td>
<td>18.5</td>
<td>(112)</td>
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<tr>
<td>–</td>
<td>20°</td>
<td>2.36</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>0°</td>
<td>2.52</td>
<td>8.42</td>
<td>18.5</td>
<td>(112)</td>
</tr>
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<td>20°</td>
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<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
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<td>0°</td>
<td>2.70</td>
<td>8.69</td>
<td>17.8</td>
<td>(112)</td>
</tr>
<tr>
<td>–</td>
<td>20°</td>
<td>2.24</td>
<td>–</td>
<td>–</td>
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</tr>
</tbody>
</table>

on the restructuring process when K is adsorbed alone or coadsorbed with Al_{x}O_{y}. Thus, potassium does not seem to affect the structural promotion of ammonia synthesis catalyst either during ammonia treatment or when Al_{x}O_{y} surfaces are treated in water vapor, as shown previously in chapter 6.

8.6 Summary

The ammonia induced restructuring of Fe(110), Fe(100), and Fe(111) surfaces has been reported. The restructured (110) surface becomes twice as active as the Fe(100) surface, while the restructured Fe(100) surface increases by a factor of four over the respective clean surface. The Fe(111) surface shows only a small decrease in ammonia synthesis activity upon ammonia induced restructuring. The kinetic data and temperature programmed desorption results suggest that Fe(100) and Fe(110) restructure to highly active surfaces, which contain C_{7} sites, in the presence of ammonia. High coverages of nitrogen dissolved in the bulk and adsorbed on the surface, after ammonia pretreatment, does not affect the ammonia synthesis kinetics.
A stereographic investigation of the restructured Fe(111) surface suggests that surface planes of \{211\} orientation (which have been found to be highly active in ammonia synthesis) are developing on the surface, due to the high virtual pressure of nitrogen provided by the ammonia decomposition. The growth of the (211) surface orientations on the restructured (111) surface is invoked to explain the absence of a significant change in ammonia synthesis activity when the Fe(111) surface is restructured.

References


REFERENCES


Chapter 9

Fe/Re, Fe/Mo, and Fe/Ag
Bimetallic Systems for Ammonia Synthesis

9.1 Introduction

Most of this thesis has dealt with an atomic understanding of structure sensitivity, and the effects of aluminum oxide and potassium on iron ammonia synthesis catalysts. "Doubly promoted" iron is the most commercially used catalyst, because of its activity and cost efficiency for the synthesis of ammonia. Improvement of this catalyst, through an understanding of the promoter effects, was the ultimate goal of this thesis, and chapter 7 dealt with this aspect. A slightly different approach for the improvement of ammonia synthesis catalyst is presented now. This chapter presents surface science and catalytic results on bimetallic iron - rhenium, iron - molybdenum, and iron - silver surfaces for ammonia synthesis.

Rhenium has been shown previously [1] to be active for ammonia synthesis and to be more resistant to poisoning by oxygen and sulfur than iron. Thus, it is of practical as well as fundamental importance to study the Fe/Re surface, which might prove to be more active and poison resistant than "doubly promoted" iron.
Molybdenum is a substrate which is known to be more reactive than iron in most surface reactions [2] and forms nitrides facially. The dissociation of nitrogen is accepted to be the rate limiting step over iron, so it is interesting to study a system where dissociation can occur over one component (i.e. Mo), and the hydrogenation of the nitrogen over another (i.e. iron).

An interesting aspect of ammonia synthesis is structure sensitivity. By using Ag as a substrate (inactive alone for ammonia synthesis under the conditions used in this study), the effect of different numbers of iron layers on ammonia synthesis activity can be studied.

The approach taken in studying these systems is to deposit submonolayer to multilayer concentrations of iron on rhenium, molybdenum, and silver single crystals. This procedure allows the growth mode, geometric structure and electronic structure of iron to be studied on the three different substrates. After characterization, high pressure ammonia synthesis is performed to study the bimetallic catalyst's activity.

9.2 Results
9.2.1 Growth Mechanism of Fe on Re, Mo, and Ag

The growth of iron on Re(10\(\overline{1}0\)) has been studied by Auger electron spectroscopy and LEED. Figure 9.1 shows an AES uptake curve for Fe on Re(10\(\overline{1}0\)), where the intensity of the Re(10\(\overline{1}0\)) is plotted against Fe dose time (evaporation rate of Fe is constant). The plot shows three linear segments with different slopes, characteristic of layer by layer growth (see experimental section). The completion of the first monolayer of Fe occurs at 2 minutes evaporation time, while the second
Figure 9.1: Fe uptake plot on Re(1010). Clear breaks in the plot are seen at 2, 4, and 6 minutes indicating the completion of the 1st, 2nd, and 3rd layers.
and third layers occur at 4 and 6 minutes respectively. The same uptake curves were applied to obtain coverages of Fe on Re(1121) and Re(0001).

Figure 9.2 shows uptake curves for Fe on Mo(100) and Ag(100). The figure shows that Fe grows layer by layer for at least three layers on Mo, and for two layers in the case of Ag. Previous work also showed that Fe exhibits an epitaxial layer by layer growth on Ag(100) for three layers, at which point island growth of the iron begins [3].

9.2.2 Structure of Fe on Re(1010), Re(0001), and Ag(100)

Figure 9.3 shows low energy electron diffraction patterns obtained for the clean Re(1010) surface and for a surface with 1 ML and 4 ML of iron. The rectangular symmetry of the Re(1010) surface is observed in the LEED pattern, and with the evaporation of 1 ML of iron, the (1×1) diffraction pattern is maintained, but with slight streaking between the substrate spots. This diffraction pattern persists up to 4 ML Fe coverage, but with an continuously increasing background intensity. This observation of an increasing background, suggests that the iron is starting to restructure, on the Re substrate, at high coverages (4 ML) of iron. Figure 9.3 shows that at coverages above 4 ML the diffraction pattern changes, producing a diffraction pattern, showing hexagonal symmetry.

Deposition of Fe on Re(0001) produced no superstructures. The only change which occurred was dimming of the Re substrate diffraction spots and an increase in the LEED background intensity.

A LEED study was not performed in this research for Fe/Ag surfaces, but a previous study [3] has shown that Fe grows in the fcc (100) orientation on Ag(100) for the first three layers at room temperature. It was concluded in this previous
CHAPTER 9: Fe/Re, Fe/Ag, and Fe/Mo for Ammonia Synthesis

a) Fe Uptake on Mo(100)

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b) Fe Uptake on Ag(100)

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<table>
<thead>
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<th>Deposition Time [Minutes]</th>
<th>Ag 356 eV Auger Intensity [Arb. Units]</th>
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Figure 9.2: Iron uptake plots on (a) Mo(100) and (b) Ag(100). Iron grows layer by layer for at least three layers in the case of Mo(100) and for two layers on the Ag(100) surface.
Figure 9.3: LEED patterns for (a) clean Re(1010), (b) 1 ML Fe/Re(1010), and (c) ≈4 ML Fe/Re(1010).
work that fcc Fe, which exists between 1173 K and 1673 K, grew with an 11% lattice expansion over bulk fcc iron (interatomic spacing of 2.57 Å).

9.2.3 Electronic Structure of Fe/Re

Ultra-violet photoelectron spectroscopy was used to characterize changes in the Re valence band structure, upon Fe deposition. Figures 9.4 and 9.5 show the density of states (DOS) profile for a clean Re(1010) surface and for Fe/Re(1010) surfaces. The most noticeable feature is the electronic state about 2 eV below the Fermi level. At ½ ML Fe coverage a state appears close to the fermi level, representative of the iron DOS profile. At 1 ML coverage the state is fully developed, and higher coverages of Fe cause little change in the UPS spectrum.

Figure 9.6 shows the work function change, \( \Delta \phi \) (by UPS), as a function of Fe coverage. There is a rapid decrease in the work function until the Fe coverage reaches about 1 ML. After the maximum \( \Delta \phi \), of -0.6 eV at \( \approx 1 \) ML coverage, there is a rise in the work function as higher Fe coverages are achieved. At low Fe coverage there is a large dipole set up, between the Fe and Re, which lowers the surface work function. As higher Fe coverages are obtained the work function starts to increase, since repulsion between neighboring dipoles result and charge transfer from the Fe to Re is decreased. At multilayer concentrations of Fe the surface work function becomes similar to that of bulk iron.

9.3 Ammonia Synthesis Reaction Rate Studies

Figure 9.7 shows the rate of ammonia synthesis over Fe/Re(1010), as a function of iron coverage (determined by AES). The addition of iron, up to 4 ML, to
Figure 9.4: UPS spectra of: (a) clean Re(10\bar{1}0) and (b) $\frac{1}{2}$ ML Fe/Re(10\bar{1}0) surfaces.
Figure 9.5: UPS spectra of: (a) 1 ML Fe/Re(10\bar{1}0) and (b) 8 ML Fe/Re(10\bar{1}0) surfaces.
Figure 9.6: Change in work function, $\Delta \phi$, induced by varying coverages of Fe on Re(1010).
Figure 9.7: Rate of ammonia synthesis versus the coverage of adsorbed iron on Re(1010).
Re(10\bar{1}0) continuously enhances ammonia synthesis activity. The maximum rate increase, about a factor of 2.5, is achieved at an iron coverage of 4 ML. Further additions of iron starts to decrease activity. This decrease in activity occurs at the point at which Fe converts from its (10\bar{1}0) hexagonally close packed structure to bcc iron, probably with a (110) orientation, because the LEED pattern has three-fold symmetry.

The activity of Fe(100) under identical conditions is \(8 \times 10^{-9} \text{ moles NH}_3 \text{ cm}^{-2} \text{ sec}^{-1}\), while the initial rate of ammonia synthesis for Re(10\bar{1}0) is \(7.5 \times 10^{-9} \text{ moles NH}_3 \text{ cm}^{-2} \text{ sec}^{-1}\). The activity of 4 ML Fe/Re(10\bar{1}0) is \(1.6 \times 10^{-9} \text{ moles NH}_3 \text{ cm}^{-2} \text{ sec}^{-1}\), a factor of 5 less active than Fe(100).

The Re(11\bar{2}1) surface has an activity of \(1.5 \times 10^{-9} \text{ moles NH}_3 \text{ cm}^{-2} \text{ sec}^{-1}\). Figure 9.8 shows the partial pressure of ammonia in the reaction loop, as a function of reaction time for different Fe/Re surfaces. The maximum rate enhancement which could be achieved was at an Fe coverage of 3 ML. Even at this concentration the activity was \(3.74 \times 10^{-9} \text{ moles NH}_3 \text{ cm}^{-2} \text{ sec}^{-1}\), still much less active than the (111) face of iron. Higher coverages of Fe could not be stabilized under ammonia synthesis conditions.

The Re(0001) surface was inactive with and without the addition of Fe during ammonia synthesis. This result suggests that Fe grows close packed on the Re basal plane, a conclusion which is consistent with the lack of activity.

Similar to Fe/Re(0001), the Fe/Mo(100) and Fe/Ag(100) surfaces were found to be inactive. Both the Fe/Mo(100) and Fe/Ag(100) showed changes in the Fe coverages under reaction conditions. In the case of Mo, when 2 or more monolayers of Fe were deposited initially, the post ammonia synthesis AES showed an increase in the Mo 186 eV peak and a decrease in the Fe 652 eV peak. What was also observed, was a nitrogen 381 eV Auger peak, more intense than that which could be obtained on either Re or Fe single crystals. This result is expected, because of the stability of molybdenum nitride. A possible explanation for the increase
Figure 9.8: Accumulation of ammonia in the reaction loop as a function of time and coverage of Fe on Re(1121). Rate of ammonia synthesis is proportional to the slope of the line for each surface.
in the Mo AES peak is that the formation of the nitride removed the interaction between Mo and Fe, causing the Fe to form three dimensional islands. Dissolution of the Fe into the Mo bulk is unlikely, since in UHV, where no nitrogen is present on the surface, the Mo and Fe Auger peaks show no change in intensity when the surface is heated to 773 K. In the case of Ag no more than 2 ML of iron could be stabilized on the Ag(100) surface under reaction conditions (773 K), even if 5 ML - 6 ML of iron were deposited at room temperature prior to ammonia synthesis.

9.4 Discussion

9.4.1 Growth of Fe on Re(10\overline{1}0)

Characterization of Fe growth has been carried out most extensively on Re(10\overline{1}0). Auger electron spectroscopy shows distinct breaks in the Fe uptake plot (see figure 9.1). At the completion of the first monolayer the Re 176 eV Auger peak is attenuated by about 70\%, in agreement with behavior of other bimetallic systems [4]. The observation that the Re 176 eV signal is attenuated to such a great extent at the completion of the first monolayer, and almost fully after the third monolayer, supports layer by layer growth of the Fe. If Fe grew as three dimensional crystallites on the Re(10\overline{1}0) surface, attenuation of the Re substrate Auger signal would occur much more slowly (see experimental AES section).

Further support for layer by layer growth is provided by the LEED results. Up to an iron coverage of 4 ML, the (1\times1) pattern representative of hcp (10\overline{1}0) symmetry persists. This observation suggests that the interaction between the Re and Fe is strong enough to make it energetically favorable for Fe to grow hcp rather than bcc, its structure in the pure Fe system. The streaking between
the diffraction spots is probably due to the lattice mismatch between Fe and Re. Above 4 ML Fe coverage, the influence of the Re substrate is insufficient to affect the structure of the iron. This appears as a change in the LEED pattern, which shows that the iron collapses to the bcc structure, probably of (110) orientation. Iron growing in the (110) bcc structure would explain the decrease in ammonia synthesis activity at high coverages of iron (> 4 ML).

9.4.2 Active Sites or Surface Work Function: Fe/Re(1010) and Fe/Ag(100)

In chapter 3, it was concluded that the presence of highly coordinated sites on a surface are more important than a low surface work function or an open surface structure. This conclusion is also supported by the present work on the Fe/Re(1010) and Fe/Ag(100) surfaces.

Figure 9.6 shows that the minimum work function for the Fe/Re surface is achieved at about 1 ML. Figure 9.7 shows that the maximum rate of ammonia synthesis occurs at 4 ML Fe coverage and that this surface is about 1.5 times more active than the 1 ML Fe/Re(1010) surface, which has the lowest surface work function. Thus, the results presented in both figures show that there is no correlation between ammonia synthesis activity and surface work function. What seems to be important is the geometric structure of the surface. This conclusion is strongly supported by the rate measurements shown in figure 9.7, which show that the activity of the Fe/Re(1010) surface keeps increasing as more and more layers of Fe are deposited, up to 4 ML. This result implies that as Fe layers are deposited sites active for ammonia synthesis (highly coordinated surface atoms) are produced. For example, if Fe(111) could be grown on an inert substrate, then
it would take 3 or 4 layers of iron to produce ammonia, since it takes this much Fe to produce \( C_7 \) sites.

The same conclusion is reached in the Fe/Ag(100) case. Even though 2 ML of iron can be stabilized on the Ag(100) surface under ammonia synthesis conditions there is no measurable ammonia synthesis rate. This result suggests that not enough iron can be stabilized to form an active surface.

### 9.5 Summary

The structure and ammonia synthesis activity of Fe/Re, Fe/Mo, and Fe/Ag surfaces has been studied. It is found that the addition of Fe to the (10\( \overline{1} \)0), and (11\( \overline{2} \)1) faces of Re enhance the activity relative to the respective clean Re surfaces. In the case of Re(10\( \overline{1} \)0), the adsorbed Fe is found to adopt a hcp (10\( \overline{1} \)0) geometry for the first 4 ML. Higher coverages cause the iron overlayer to reconstruct to the bcc (110) face. It is also found that ammonia synthesis over Fe/Re(10\( \overline{1} \)0) is not a function of surface work function, but instead it is a function of surface geometric structure. This conclusion is also supported by work on the Fe/Ag(100) surface, which is inactive with Fe concentrations up to 2 ML, suggesting that more iron layers are required to produce active sites (\( \gtrsim 4 \) ML).

The Re(0001) surface, with or without adsorbed Fe, is inactive for ammonia synthesis at 773 K. The Mo(100) and Fe/Mo(100) surfaces are also found to be inactive for ammonia synthesis. Iron grows layer by layer on the Mo(100) surface for at least three layers. Under ammonia synthesis conditions a strong Mo nitride is formed which causes the interaction between Fe and Mo to be removed, causing the Fe to adopt a three dimensional island configuration.
References


Chapter 10
Summary

10.1 Structure Sensitivity of Ammonia Synthesis Over Iron

High pressure kinetic results, presented in chapter 3, for ammonia synthesis over Fe(210) and Fe(211) surfaces, in addition to the Fe(111), Fe(100), and Fe(110) surfaces, show that the presence of highly coordinated sites are more important than surface roughness for high catalytic activity. Both the (111) and (211) faces of iron, which expose C7 sites, were found to be of comparable activity and had much greater activity than the (210), (100), and (110) faces, which fail to expose highly coordinated sites. It was concluded that surface roughness on iron ammonia synthesis catalysts is only important to the extent that it can expose highly coordinated sites.

Research carried out in chapter 9, on the structure and ammonia synthesis activity on bimetallic Fe/Re(10\bar{1}0) and Fe/Ag(100) surfaces, supports the contention that active sites (i.e. C7 sites) are more important than surface roughness. It is shown that the activity of the Fe/Re(10\bar{1}0) surface is independent of surface work function, but strongly dependent on the number of iron layers adsorbed on the
CHAPTER 10: SUMMARY

Re(1010) surface. It is also shown that only 2 ML of iron can be stabilized on the Ag(100) surface (Ag alone is inactive for ammonia synthesis) during ammonia synthesis. The two layers of iron are found to be inactive for ammonia synthesis, again implying that more layers of iron are needed to produce active sites.

10.2 Promoter Effects of Potassium

The promoter effects of potassium on ammonia synthesis have been investigated over the Fe(110), Fe(100), and Fe(111) surfaces under high pressure conditions. A coverage of 0.15 ML is the maximum amount of potassium that can be stabilized on the iron single crystals under ammonia synthesis conditions. Adsorbed potassium has no measurable effect on the inactive Fe(110) surface. However, adsorbed potassium increases the rate of ammonia synthesis markedly over the Fe(111) and Fe(100) crystal faces. The promotional effect becomes enhanced as the reaction conversion increases. For example, at an ammonia partial pressure of 20 Torr there is a two-fold increase in the rate of ammonia synthesis over Fe(111) and Fe(100), in the presence of potassium. The presence of potassium changes the ammonia reaction order from -0.60 to -0.35 on the (100) and (111) faces of iron. Adsorbed potassium decreases the reaction order in hydrogen from 0.76 to 0.44 on Fe(111). However, within experimental error, there is no change in the activation energy, when potassium is present, suggesting that the mechanism for ammonia synthesis is not changed.

The kinetic data is explained by a model which accounts for the blocking of catalytic sites, which have the ability to dissociate nitrogen, by adsorbed ammonia and atomic nitrogen. Potassium lowers the concentration of adsorbed ammonia on the surface, making more sites available to dissociatively chemisorb nitrogen. The
model suggests that an additional promoter effect by potassium is a 30\% enhancement of the rate of nitrogen dissociation on Fe(111) and Fe(100), further increasing the rate of ammonia production. This conclusion is in qualitative agreement with nitrogen chemisorption studies on Fe and K/Fe surfaces in UHV (chapter 4).

10.3 Promoter Effects of Aluminum Oxide

Treating the (110), (100), and (111) faces of iron with 20 Torr of water vapor causes surface restructuring. The restructured Fe(110) and Fe(100) surfaces become as active as the clean Fe(111) surface for ammonia synthesis. The restructured Fe(111) exhibits a slight decrease (about 5\%) in activity when compared to the clean Fe(111) surface. The restructured (110), (100), and (111) surfaces reconvert to their unrestructured orientations within one hour of ammonia synthesis.

The same restructuring on the Fe(110), Fe(100), and Fe(111) surfaces can be performed with water vapor in the presence of aluminum oxide. In this case, 20 Torr of water vapor restructures the Al$_2$O$_x$/Fe(100) and only 0.4 Torr of water vapor is needed to restructure the Al$_2$O$_x$/Fe(110) surface, so that they become as active as the Fe(111) face in ammonia synthesis. The restructured Al$_2$O$_x$/Fe(110) and Al$_2$O$_x$/Fe(100) surfaces maintain their activity for longer than four hours under ammonia synthesis conditions. The formation of iron aluminate in the iron near surface region is invoked to explain the stability of the restructured Al$_x$O$_y$/Fe surfaces.

The reaction rate studies and ammonia temperature programmed desorption results suggest that planes containing C$_7$ sites, such as the Fe(211) and Fe(111) surfaces, are being created during the water vapor pretreatments, with or without aluminum oxide. However, only when aluminum oxide is present will these active
surfaces remain stable, and not reconvert to less active surfaces (i.e. Fe(110) and Fe(100) planes).

10.4 Coadsorbed Aluminum Oxide and Potassium

The coadsorption of potassium with the aluminum oxide inhibits the restructuring process. Thus, to realize the full promotional effects of aluminum oxide and potassium the surfaces should be restructured with only aluminum oxide and potassium should be added afterwards. Using this procedure, the activity of the Fe(110) surface can be increased to such an extent that it exceeds the activity which is observed over clean Fe(111), at an ammonia partial pressure of 20 Torr (P_{N_2}=5 \text{ atm} \text{ and } P_{H_2}=15 \text{ atm}). Restructuring with Al_2O_3 produces a surface as active as Fe(111), and potassium contributes an additional two-fold increase.

The application of these results to the industrial catalyst seems to be warranted. The industrial catalyst is prepared by fusing 1-3% by weight of aluminum oxide and potassium to iron oxide. This catalyst precursor is reduced, to the active catalyst, in a stoichiometric mixture of nitrogen and hydrogen. This procedure has been reproduced in the combined UHV / high pressure studies presented in this thesis. The promoter effects of aluminum oxide in the industrial catalyst result from its interaction with the iron oxide during the preparation stage. This interaction probably results in iron aluminate formation, and this prevents planes such as Fe(111) and Fe(211), formed during reduction, from converting to more thermodynamically stable planes, such as the less active Fe(110) and Fe(100) surfaces. The presence of potassium seems to have little to do with this structural promotion. Actually, its presence during this step might inhibit the full promo-
tional effect of aluminum oxide from being realized. Its interaction with aluminum oxide seems to form a potassium aluminate, which retards the interaction between iron oxide and aluminum oxide, during the restructuring process.

10.5 Ammonia Induced Restructuring of Iron

Ammonia, like water vapor, has been found to restructure Fe(110), Fe(100), and Fe(111) surfaces. Treatment of Fe(110) and Fe(100), prior to ammonia synthesis (50 Torr, 723 K, 30 min) enhances their ammonia synthesis activity. The restructured Fe(110) becomes as active as unrestructured Fe(100), while ammonia pretreatment of Fe(100) increases its activity four-fold. Temperature programmed results and the kinetic data suggest that C₇ sites are created during the ammonia pretreatment. Treatment of Fe(111) with ammonia produces surface morphology changes, as observed by SEM, but ammonia synthesis activity is unaltered. The post reaction ammonia TPD is also unchanged, when compared to unrestructured Fe(111). An SEM stereographic analysis shows that Fe(211) planes are formed on the Fe(111) surface during the restructuring process. This is consistent with the results already presented, which show that Fe(211) ammonia synthesis activity is similar to Fe(111) and the Fe(211) ammonia TPD profile is also similar to Fe(111).

Furthermore, it was shown that ammonia restructured surfaces have high concentrations of dissolved and adsorbed nitrogen. Removal of surface nitrogen does not influence the catalytic activity of the iron, suggesting that this strongly bound nitrogen is not important in explaining ammonia synthesis kinetics.
Appendix A

Ion Scattering Spectroscopy With UTI Mass Spectrometer

A.1 ISS With Mass Spectrometer

Most surface science techniques, which yield information about composition, such as AES or x-ray photoelectron spectroscopy (XPS), are not capable of giving solely top atomic layer sensitivity. For example, electrons which are generated in the Auger process might have sufficient kinetic energy to escape the solid, and be detected from the first 4-5 layers, if the Auger electron has an energy of about 600 eV (see chapter 2 on mean free path of electrons).

The use of Ion Scattering spectroscopy (ISS) can alleviate this dilemma, because information obtained from this technique is from the outermost layer [1]. The technique involves bombarding a surface with low energy ions (usually 500 eV - 2000 eV ions) and detecting the energy of the ion after it has scattered from the surface. The ion loses a characteristic amount of energy at a surface, which depends on the mass of the surface atom it scattered off of. By detecting the energy of the scattered ions, surface composition of the outermost atomic layer can be determined. The surface sensitivity results partly from the size of the ion and
its low initial energy, but the major reason for the surface sensitivity is due to the high probability of reneutralization of He⁺ that scatters from more than one surface atom (multiple scattering) or penetrates past the top layer. Thus, the fact that only the fraction of He⁺ which stays ionized after its collision with the surface is detected accounts for the surface sensitivity of the technique.

Assuming that the ion undergoes only one scattering event at the surface and using conservation of energy and momentum the energy of the scattered ion (E) can be accurately determined by the following relation:

\[
E = E_0 \frac{1}{(1 + A)^2} [\cos \phi \pm \sqrt{A^2 - \sin^2 \phi}]^2
\]  

(A.1)

where \(A = \frac{M_1}{M_2}\), \(M_1\) is the mass of the surface atom, \(M_2\) is the ion mass, \(E_0\) is the primary ion energy, and \(\phi\) is the scattering angle.

A.2 Experimental Equipment

To perform the ISS experiment a standard ion source is used along with a cylindrical mirror analyzer (CMA) or hemispherical analyzer for energy resolving the scattered ions. This has restricted ISS, in the past, to UHV chambers which include high resolution and costly analyzers. However, most systems include a quadrupole mass spectrometer and a method is described in the next section which shows that the mass spectrometer can be modified, so that it can energy resolve ions, as well as mass resolve them.
A.3 Modification of Mass Spectrometer

Figure A.1 shows a schematic representation of an UTI mass spectrometer which was modified for energy resolution. Between the ionizer section and the quadrupole mass filter is mounted a four grid retarding analyzer, similar to the RFA which is used in AES. Schematics of the grid system are shown in figures A.2 - A.4. The first and fourth grids are grounded and the second and third grids, which are mounted on the top and bottom of plate 2 are used to apply an electrostatic potential.

The UTI mass spectrometer electron multiplier is replaced with a channeltron and the feedthrough, in the base plate of the probe, which used to supply voltage to the Faraday cup of the electronmultiplier, is used instead to apply voltage to the retarding grids.

A.4 Performing ISS

The experiment is performed by ramping the second and third grids from $U_r=0\,\text{eV}$ to $U_r=E_0$. As in AES, the retarding potential, $U_r$, is modulated with an about 30 volts (peak to peak) ac with a frequency, $\omega$, of 2500 Hz. The quadrupole filter is tuned to the ion mass and the signal from the channeltron is put into a lock-in amplifier, with the reference channel tuned to $\omega$. The ionizing filaments are kept off in the ISS mode, since reionizing helium, which becomes neutralized at the surface, will decrease the surface sensitivity of the technique (see section A.1).

By tuning to $\omega$, the lock-in amplifier output is proportional to the number of
Figure A.1: Schematic of modified UTI mass spectrometer.
Figure A.2: Grid plate #1.

APPENDIX A: ISS With Mass Spectrometer
Figure A.3: Grid plate # 2.
Figure A.4: Grid plate # 3.
ions at energy E (N(E)). Experimental data for ISS of Pt, with > 1 ML adsorbed potassium, and tungsten oxide is shown in figure A.5, where N(E) is plotted against ion kinetic energy. The appearance of only K from the K/Pt surface, and oxygen from the tungsten oxide surface, exhibits the surface sensitivity of the technique. The ability of this setup to obtain an ISS spectrum by using signal analysis, similar to that used in AES, is an advantage over ISS experiments performed with a CMA or hemispherical analyzer. Using a CMA or hemispherical analyzer necessitates the use of pulse counting electronics, since the ion transmission through these analyzers is low relative to the quadrupole in a mass spectrometer (transmission through the added retarding grids is \( \approx 80\% \)). This makes data acquisition easier for the present system.

The increased signal with the energy resolving mass spectrometer also suggests that lower incident primary beams can be used, minimizing surface damage caused by the scattering technique. This might require pulse counting the signal, obtaining the spectrum, \( \int_{E_i}^{\infty} N(E)dE \), and then differentiating the spectrum with a computer giving the standard N(E) spectrum. This has not yet been tried, but might prove to be the most useful feature of using the modified mass spectrometer for ISS.

A.5 Mass Resolution of Ions

Mass resolution is needed in the ISS experiment, because ions scattering off the surface sputter surface atoms. The use of He\(^+\) as the scattering ion minimizes damage to the surface. The sputtered atoms will increase background, so they are removed with the quadrupole mass filter. This is a major advantage of modifying a mass spectrometer for energy analysis, rather than using a CMA to perform
Figure A.5: ISS data with mass spectrometer (a) clean Pt, (b) K adsorbed on Pt, and (c) oxygen on tungsten. Scattering angle, $\phi = 60^\circ$. 
ISS. When a CMA is used there is no mass selection and this leads to a high background signal, due to sputtered fragments from the surface at low energies. For example, He$^+$ scattering off Li is difficult to see, if only a CMA is used [2], since the low energy He$^+$ which results after scattering is lost in the background signal.

For maximum mass resolution in the UTI mass spectrometer, an ion should have an energy of about 25 eV when it enters the quadrupole section. Most sputtered fragments which come off the surface have energies in this range, so they are effectively filtered out and do not interfere with the scattered ion signal.

However, the scattered ion in ISS can enter the quadrupole region at energies ranging from 0 eV to 500 eV, depending on the surface composition, and assuming a 500 eV initial beam energy. As the energy of the ion increases, the number of oscillations the ion undergoes in the quadrupole electric field is decreased. Thus, resolution of the ions decreases with increasing kinetic energy. For He$^+$ scattering, mass 4 gives a strong signal, but tuning to masses below 2 and above 6 give no signal, suggesting that even high energy helium ions can be resolved fairly well. Resolution becomes progressively worse for heavier ions such as Ne$^+$ and Ar$^+$. In the case of Ar$^+$ scattered ions can be detected between 0 amu and 100 amu. A way to correct this is to float the quadrupole rod at a voltage, $V_c$, where $U_t - V_c \approx 25$ eV. This will give the ion an energy of $\approx 25$ eV as it enters the quadrupole region.

What must be considered, if each ion does not have the same pass energy, is whether the transmission of the ion through the quadrupole region will change as a function of energy. To test this, experiments were performed with He$^+$ and Ne$^+$ in which the detection system was tuned to mass 4 and 20 respectively and where the quadrupole region was grounded so there was no mass resolution. At least, for
He$^+$ and Ne$^+$ the ISS spectra did not seem to change greatly. This is most likely due the high transmission (almost 100%) of light ions through the quadrupole region.

A.6 Use as a Mass Spectrometer

When not being used for ISS the system can be once again be used as a mass spectrometer with minor changes. The ionizer filaments are now turned on and the retarding grids (2$^{nd}$ and 3$^{rd}$) are grounded or floated at a negative energy ($\approx$ 20 eV) to extract the ions from the ionizer region. The signal from the channeltron is led into the UTI mass spectrometer.

To rapidly change between ISS and mass spectrometer mode it is convenient to splice two of the cables on the probe connector head. The collector signal and faraday cup cables can be spliced and SHV connectors installed on both sides. In ISS mode the cables are separated enabling the cable which carries the signal to be plugged into the lock-in amplifier and the modulated voltage to be connected to the 2$^{nd}$ and 3$^{rd}$ grids through the faraday cup cable. In the mass spectrometer mode the cables are simply reconnected.

References

