

Surface structures in ammonia synthesis

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Ammonia synthesis is one of the most structure sensitive catalytic reactions. Reaction studies using single crystals showed the open (111) and (211) crystal faces of iron and the (11 $\bar{2}$ 1) and (11 $\bar{2}$ 0) crystal faces of rhenium to be most active, while the close packed iron (110) and rhenium (0001) crystal faces were almost inactive. These studies suggest that seven (C_7) and eight (C_8) metal atom coordinated surface sites, which are available only on the active surfaces, are very active for the dissociation of dinitrogen, the limiting factor in the reaction rate under most experimental circumstances. In this paper, the experimental evidence for the existence of the C_7 sites in iron is reviewed. In addition, the role of potassium in creating a different active site which is less sensitive to the iron surface structure is discussed. Newly developed surface science techniques should permit investigations into the dissociation of dinitrogen at the C_7 sites and how the resulting chemisorbed nitrogen atoms are removed to allow for reaction turnover. Advances in LEED-surface crystallography, allowing detailed determination of relaxation in the clean metal surfaces and adsorbate induced restructuring of the metal surface, reopen the question of the real structure of the active sites in the presence of atomic nitrogen, or atomic nitrogen coadsorbed with potassium and oxygen. Investigation of the dynamics of surface restructuring involving the movements of both the substrate metal atoms and the chemisorbed atoms by surface diffusion becomes feasible by the availability of the high pressure/high temperature STM system built in our laboratory. Studies of the surface structures of the model iron catalysts under dynamic conditions, using 0.1 ms time resolution and atomic spatial resolution under reaction conditions are now possible.

Keywords: ammonia synthesis; surface structure; structure sensitivity; iron; rhenium; STM

1. Introduction

The formation of ammonia from molecular nitrogen and hydrogen over iron has been the cradle and testing ground of chemical concepts since the beginning of this century [1,2]. It served as a test for chemical equilibrium, the third law of thermodynamics, and led to the discovery of transition from physisorption to chemisorption through the activated dissociation of dinitrogen (N_2). The importance of the surface structure of iron surfaces in preparing active catalysts to optimize the rate of this reaction was discovered early and structural promoters (e.g. alumina) were used as additives to produce and stabilize the active surface structure. Other

promoters, potassium for example, were thought to modify the bonding of reactants and reaction intermediates although their beneficial effects on the iron surface structure could not be determined.

With the advent of modern surface science techniques, major studies were initiated in several laboratories to identify the surface sites where molecular nitrogen dissociates and to uncover the molecular details of the reaction steps of N_2 and dihydrogen that ultimately lead to ammonia formation and subsequent desorption from the metal surface. Field ion microscopy (FIM) studies [3,4] indicated that the (111) iron crystal face is particularly active for atomizing N_2 , and was probably responsible for the surface structure sensitivity of the reaction discovered earlier. The dissociation probability of N_2 was found to be small [5], even on the active (111) iron surface (of the order of 10^{-5}) and was found to decrease by orders of magnitude for other iron crystal surfaces. Using the high pressure/low pressure reactor [6] developed in our laboratory, catalytic reaction rates were measured on different crystal faces of iron, and were found to vary by orders of magnitude (with the (111) and (211) iron crystal faces being the most active by far). The results of these studies are shown in fig. 1. Additionally, the observed reaction rates correlate well with the variation of the dissociation probability for N_2 from face to face. This information suggests that seven (C_7) and eight (C_8) metal atom coordinated surface sites (see fig. 1), which are available only on the active surfaces, control the reaction rate under most experimental circumstances. In addition, the correlation of the reaction rate with the dissociation probability of N_2 implies that the dissociation of N_2 is the rate limiting step.

In this paper we shall examine the experimental evidence and the current understanding of three important questions related to the roles of iron surface structures in ammonia synthesis: (1) How strong is the evidence for the C_7 site as the most active site for N_2 dissociation. (2) How does the catalytic reaction occur with strongly chemisorbed nitrogen atoms blocking the C_7 sites? (3) How does potassium promote ammonia synthesis? There is evidence, we believe, for a second active site for N_2 dissociation involving potassium and oxygen (K-O-Fe). After addressing these questions, we suggest future directions of research now available due to recent advances in surface science.

2. Evidence for the C_7 site as the active site

The top view of the geometric surface structures for various iron single-crystal surfaces, derived from the projection on the bulk structure, which were used in the study of ammonia synthesis are shown in fig. 1. Low energy electron diffraction (LEED)-surface crystallography studies clearly indicate that the surfaces of most clean metals relax inward [7,8]. The rougher the surface (the more open the surface structure), the greater the relaxation. Fig. 2 shows the (111) and (211) iron surface structures as determined by LEED-surface crystallography [9,10]. There is a large

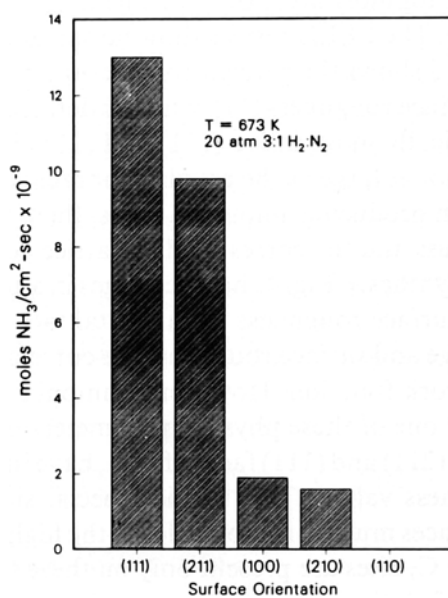
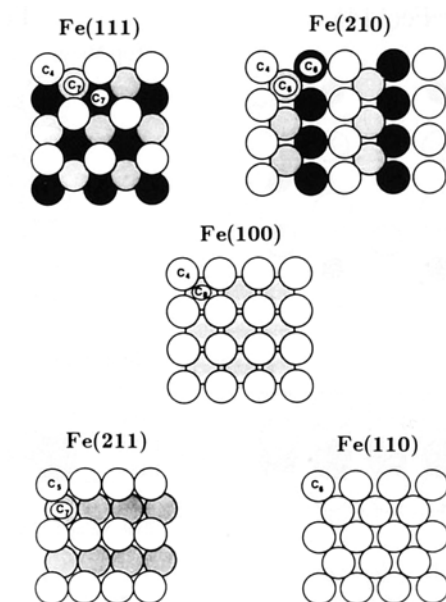


Fig. 1. The rate of ammonia synthesis on five iron surfaces studied exhibiting the structure sensitivity of ammonia synthesis [12,13].

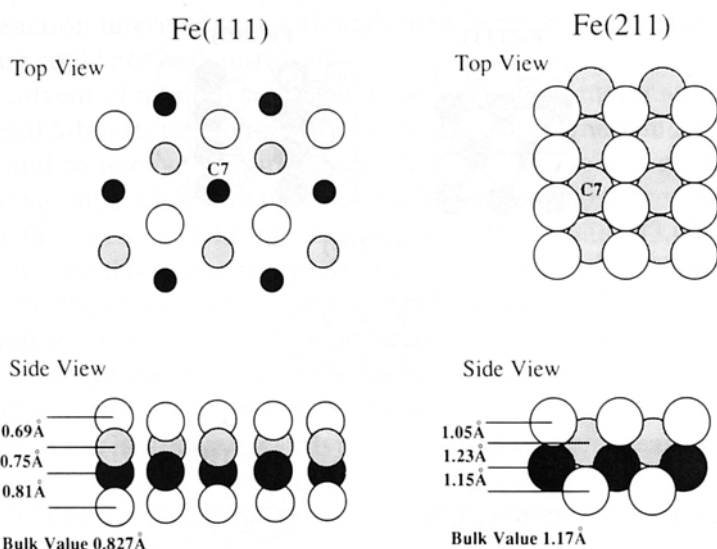


Fig. 2. Surface structures of the (111) and the (211) faces of iron determined by LEED crystallography [9,10].

inward relaxation in the topmost layer of both surfaces, bringing the exposed C_7 sites closer to the surface. The LEED results show no surface reconstructions in the X - Y surface plane. Fig. 3 shows the percent contraction in iron single-crystal surfaces as a function of surface roughness [11], which is defined as one-over-the packing density. The catalytically most active (111) and (211) iron crystal faces show large contractions, but not as large as the roughest or most open (210) iron surface that is much less active in producing ammonia. Thus, there is no direct correlation between surface roughness and the corresponding lattice contraction, and catalytic activity in ammonia synthesis. Fig. 4 shows changes in ammonia synthesis activity, work function and surface roughness from crystal face to crystal face [12,13]. The work function change and surface roughness are correlated; the more open the surface, the lower the work function. However, ammonia synthesis activity does not correlate with either one of these physical parameters of the iron system. The most active surfaces, the (211) and (111) faces of iron, have intermediate work function and surface roughness values. This implies special sites on the most active (111) and (211) iron surfaces must be responsible for the highest catalytic activity in ammonia synthesis. The C_7 sites are present only on these two iron surfaces. This behavior is unlike that of platinum where the catalytic activity for carbon-carbon or carbon-hydrogen bond-breaking correlates with surface roughness. The lack of this type of correlation with surface roughness is perhaps our best evidence that C_7 sites play unique roles in ammonia synthesis.

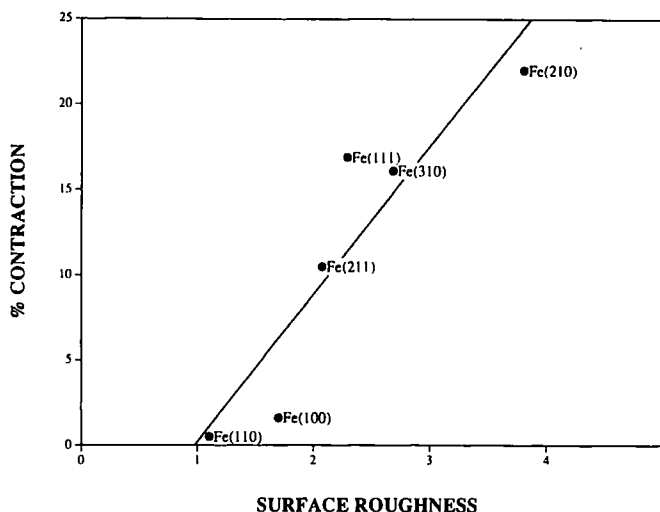


Fig. 3. The first layer contraction versus the surface roughness for different iron surfaces [10].

Unfortunately, there is no LEED-crystallography data on nitrogen chemisorbed on these most active (111) and (211) crystal surfaces of iron. There is data on atomic nitrogen chemisorbed on the (100) iron surface [14]. In this study it was found that nitrogen is adsorbed in a four-fold hollow site and its height above the surface and bond distances to the metal atoms have been determined. Thus chemisorption of nitrogen atoms in high coordination sites is expected. As long as there is no LEED-crystallography data available, based on this scant evidence one could propose that atomic nitrogen is likely to occupy the C_7 sites on both the (111) and (211) iron surfaces. It is hoped that LEED-crystallography of the nitrogen chemisorption system on (111) and (211) iron surfaces will be studied in the near future.

There are no studies of hydrogen chemisorption on (111) and (211) iron surfaces by LEED-crystallography. However, there are two hydrogen structures reported

- Ammonia Synthesis Activity*
(111) > (211) > (100) > (210) > (110)
- Work Function
(210) < (111) < (211) < (100) < (110)
- Surface Roughness**
(210) > (111) > (211) > (100) > (110)

Fig. 4. Variation of (a) the rate of ammonia synthesis, (b) the work function and (c) the surface roughness for iron surfaces from crystal face to crystal face [5,12].

on the catalytically inactive (110) closest packed iron surface. Hydrogen is believed to occupy a three-fold site on this surface [15]. It will be important to study hydrogen chemisorption and the ordering of hydrogen on the most catalytically active iron crystal surfaces. It is our hope that coadsorption of nitrogen and hydrogen will reveal the way the nitrogen location on the metal surface is varied as it becomes successively hydrogenated to NH , NH_2 and then to ammonia.

The structural role of alumina has been explored [16] on various iron single-crystal surfaces. Experimental results (fig. 5) show that even the least active (110) face of iron becomes as active as the (111) iron crystal face after the addition of alumina, and subsequently annealed in oxygen and water vapor. Furthermore, electron microscopy, thermal desorption and other studies indicate that during ammonia synthesis all iron surfaces restructure in the presence of alumina. A proposed mechanism, supported by X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and electron microscopy studies [13], for this restructuring is shown in fig. 6. Alumina first forms an FeAl_2O_4 iron aluminate on the surface. This new surface then serves as a template on which iron grows with (111) or (211) orientation upon exposure to the reaction mixture during ammonia synthesis. There is evidence that after heating in water vapor the iron growth orientation on the iron aluminate becomes (111) during ammonia synthesis [12]. The structural stability of the iron surface in the presence of ammonia is another ques-

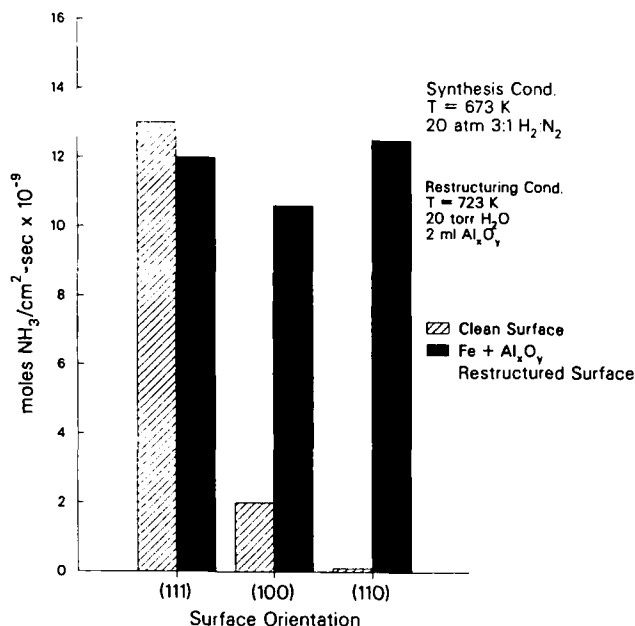


Fig. 5. The rate of ammonia synthesis of different iron surfaces showing that the addition of alumina and annealing in water and oxygen produce an active surface on the least active (110) face of iron [16].

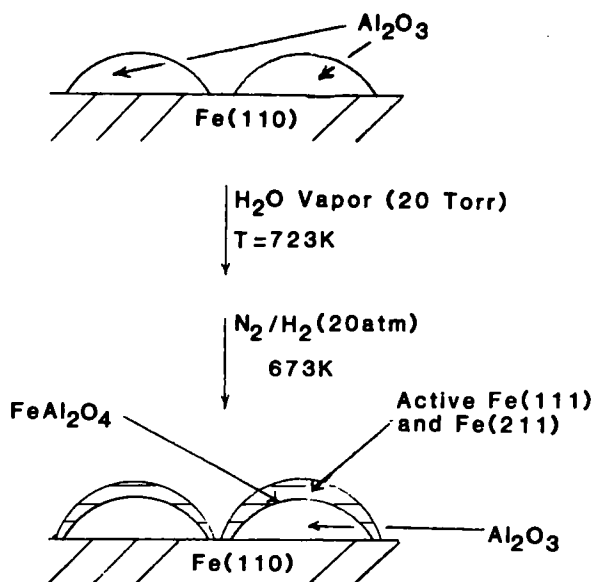


Fig. 6. A schematic depicting the mechanism of restructuring of iron induced by water vapor in the presence of aluminum oxide [16].

tion. Upon heating in ammonia, all iron surfaces most likely restructure to (211) crystal faces, with or without the presence of alumina [17].

3. Effects of potassium on ammonia synthesis

Fig. 7 shows the changes in dissociation probability of N₂ in the presence of potassium. The addition of potassium to the (111) iron crystal face, which possesses C₇ sites, increases the dissociation probability eight-fold. On the (100) iron face there is a 280-fold increase in N₂ sticking probability, while on the (110) iron face an even larger increase has been observed [5]. These two surfaces, the (100) and

	Factor
Fe(111)	8
Fe(100)	280
Fe(110)	~ 10 ³

Fig. 7. The increase in the N₂ sticking probability caused by co-adsorbed potassium on iron crystal surfaces [5].

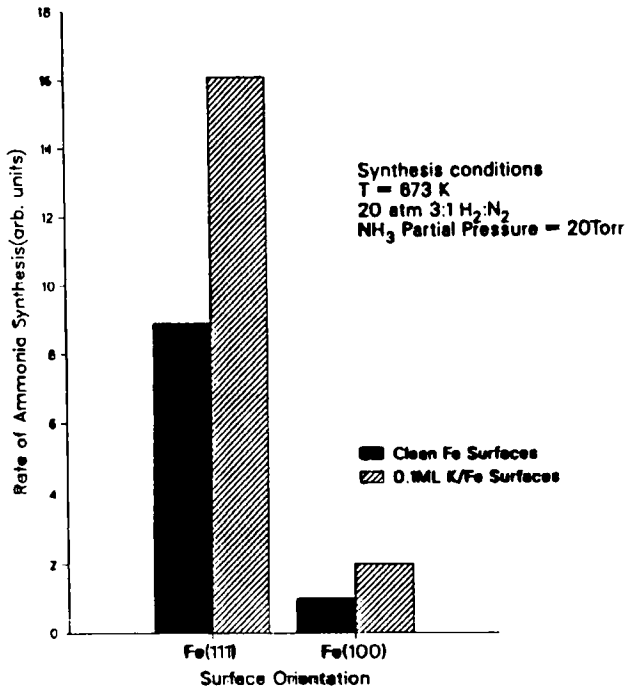


Fig. 8. The effect of potassium on the rate of ammonia synthesis on an iron single crystal surface [18].

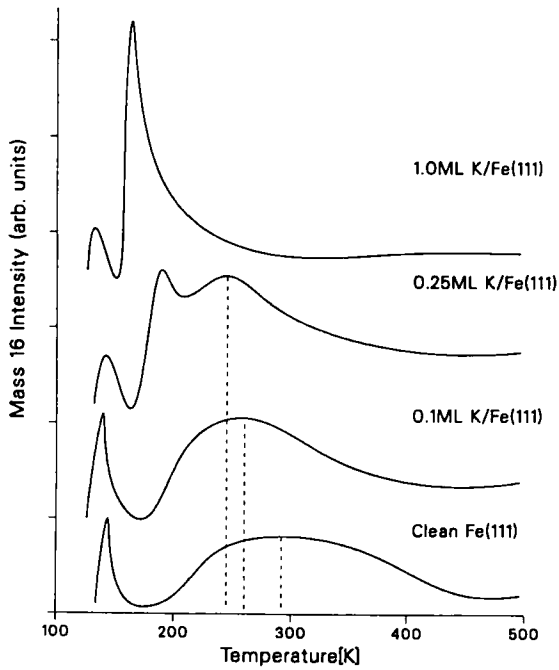


Fig. 9. Ammonia temperature-programmed desorption from the (111) iron surface with and without co-adsorbed potassium [18].

(110) faces of iron, do not contain C_7 sites. We believe these results indicate that potassium creates its own active sites on iron for N_2 dissociation. These sites appear to be independent of the metal surface structure and are not dependent on the presence of C_7 sites (at least not on the (100) and (110) faces of iron) which are believed to be responsible for the dissociation of N_2 on the clean surface. However, the enhancement in the catalytic activity of various crystal surfaces caused by the presence of potassium does not correlate in this circumstance with the increasing dissociation probability of N_2 . As fig. 8 shows, both (111) and (100) iron surfaces exhibit an eight-fold increase in reaction rates after the addition of potassium. This increase in reaction rate contrasts the two-fold and 280-fold increases in the dissociation probability of N_2 induced by potassium [18] on the (111) and the (100) faces, respectively. We believe the major impact of potassium is its effect on the bonding of ammonia. Detailed TPD studies from our laboratory show the heat of adsorption for ammonia is reduced by 2.4 kcal when ammonia is coadsorbed with potassium. Fig. 9 shows the TPD peaks and their shift on the (111) iron crystal face when ammonia is coadsorbed with potassium [18]. The important effect of this small decrease, due to the repulsive adsorbate-adsorbate interaction between potassium and ammonia (molecules that are both electron donors), appears at high partial pressures of ammonia when the reaction is carried out closer to equi-

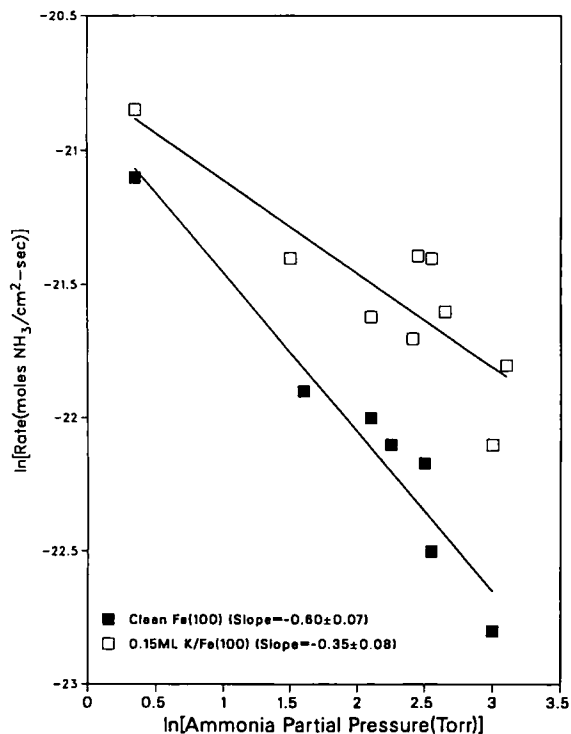


Fig. 10. The effect of potassium on the ammonia pressure dependence of ammonia synthesis [18].

brium. As fig. 10 shows, when we plot the log of the reaction rate, as a function of the logarithm of the ammonia partial pressure, there is a different negative partial pressure dependence, with or without potassium. In the presence of potassium the pressure dependence is negative order of -0.35 , while in the absence of potassium it is negative order -0.60 . This large difference in the slopes, evident even though there is some scatter, indicates a much higher conversion to ammonia in the presence of potassium at high ammonia partial pressures [18]. There are also small changes in the hydrogen pressure dependence of the ammonia formation rates, as shown in fig. 11. The consequence of the potassium and ammonia repulsive interaction is an equilibrium shift [18] of adsorbed ammonia toward the gas phase (shown in fig. 12). If one plots the ratio of the rate of ammonia formation with potassium to that without potassium as a function of ammonia partial pressure, the curve shows the change in equilibrium constant by a factor of 2 when potassium is present, toward gas phase ammonia [18]. That is, the lower ammonia heat of adsorption will lower the surface concentration of ammonia, thereby shifting the equilibrium toward the gas phase. Since adsorbed ammonia is likely to block the active sites, a weaker heat of adsorption makes the surface more active and produces higher turnovers for ammonia synthesis. The activation energy for ammonia synthesis does not change in the presence of potassium [18]. This is shown in

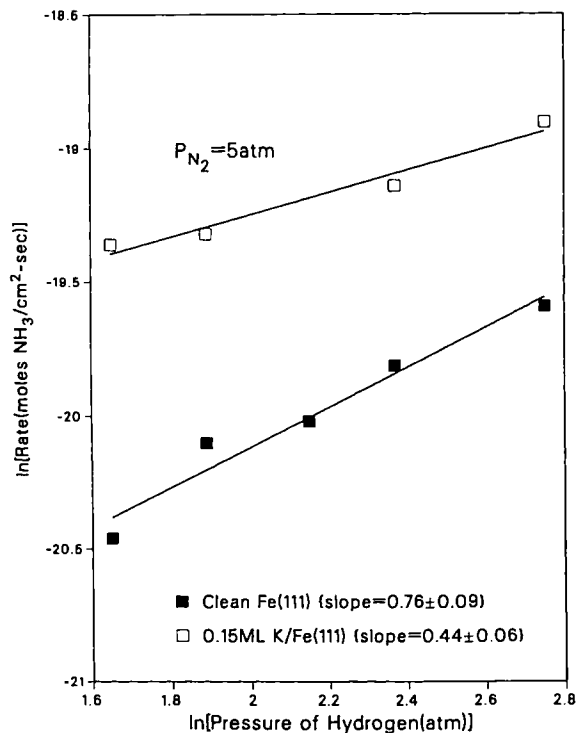


Fig. 11. The effect of potassium on the hydrogen pressure dependence of ammonia synthesis [18].

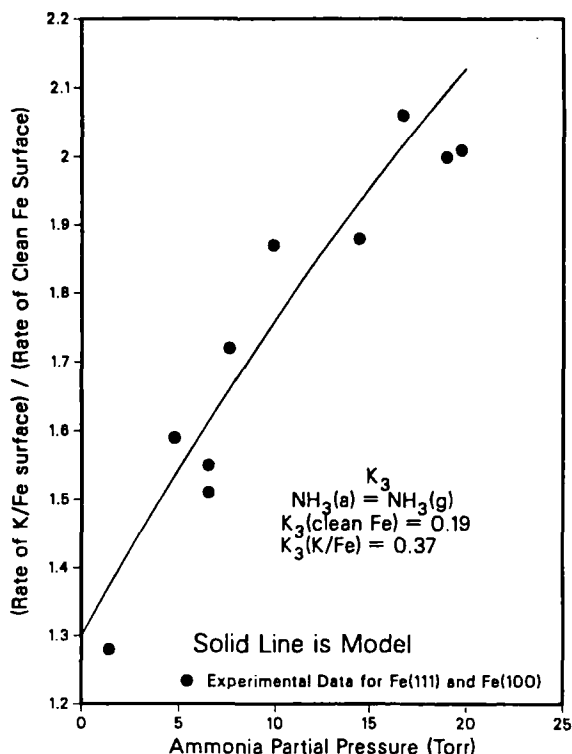


Fig. 12. The experimental fit of the reaction rate on iron with or without potassium to a model which allows for the blocking of the catalytic sites by both adsorbed ammonia and atomic nitrogen [18].

fig. 13, where the two parallel lines indicate no change in activation energy, even though the scatter of the data for potassium is quite large compared to that of the clean surface data. However, the rate enhancement is clearly visible in the presence of potassium. This implies that the addition of potassium to the surface does not effect the rate limiting step.

The major effects of potassium cannot be considered without the possibility of oxygen bound to iron surfaces also associated with potassium. It was found that oxygen stabilizes potassium on iron by substantially reducing the desorption rate of potassium. Nevertheless, the presence of oxygen does not seem to alter the effect of potassium on the dissociation probability of N_2 . The promotional activity of potassium for increasing the dissociation probability of N_2 on any iron single-crystal surface remains intact in the presence of oxygen. In addition, oxygen also restructures the iron surface [13,19]. It is possible that part of the potassium induced formation of new active sites is associated with oxygen. Oxygen along with potassium helps to restructure the iron surface in order to create new sites capable of dissociating N_2 . These sites, although different from the C_7 sites present on the (111) and (211) iron crystal surfaces, play very important roles for ammonia formation activity (especially at high ammonia partial pressures). Fig.

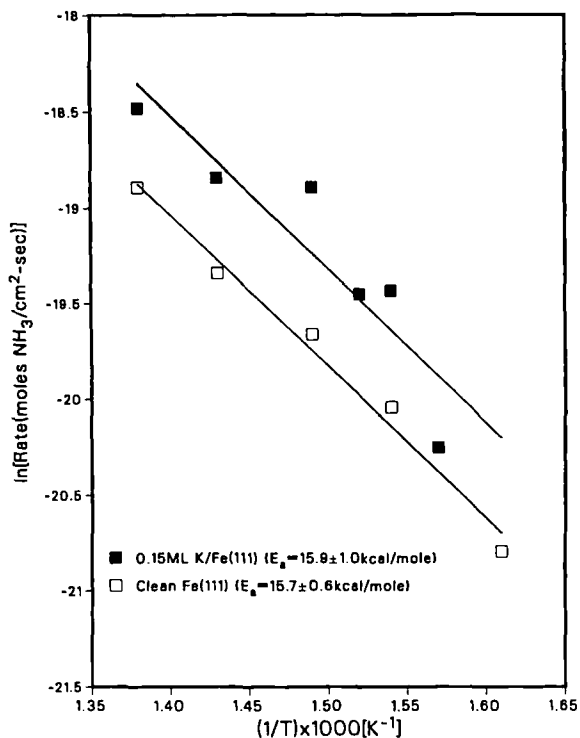


Fig. 13. The effect of potassium on the activation energy of ammonia synthesis between 623 and 723 K [18].

14 shows that the (110) face can be restructured to be of high activity by heating it in oxygen. However, if oxygen is not replenished the surface anneals back and loses its oxygen induced activity [13]. The purpose of fig. 14 is to show that oxygen does cause restructuring. Therefore, it is likely that oxygen tied to potassium could also cause restructuring of iron single-crystal surfaces and the creation of a new active site.

During the past few years, STM has appeared as a major new tool for studying surface structures, and perhaps extending its use to study surfaces under catalytic reaction conditions. One such apparatus has been built in our laboratory and is shown in fig. 15. The STM is surrounded by a furnace where the sample can be heated at high pressures while the STM tip scans the surface [20]. Early studies using a platinum (110) single crystal show the surface dramatically restructuring when heated in atmospheric pressures of hydrogen, oxygen and carbon monoxide [21]. This restructuring is shown in fig. 16. Our hope is to investigate the structural changes occurring on iron single-crystal surfaces, especially on the (111) and (211) iron surfaces during ammonia synthesis, using such a high temperature/high pressure STM apparatus.

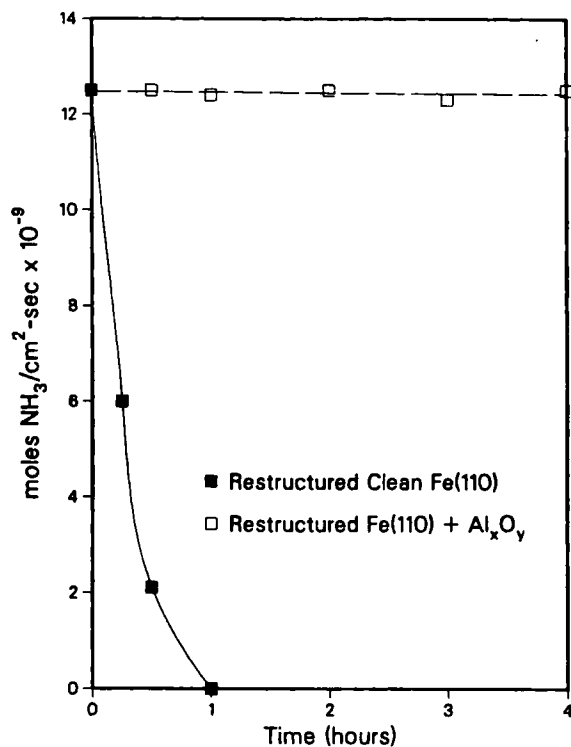


Fig. 14. The deactivation of the oxygen restructured (110) iron surface along with the restructured (110) iron surface with alumina added [13].

4. Strongly chemisorbed nitrogen atoms blocking the C₇ sites

STM is not only able to detect surface structures and changes at high pressures and temperatures, it can also show the movement of adsorbed atoms on molecules as other molecules are coadsorbed with them. This is demonstrated by our recent STM studies on rhenium single-crystal surfaces [22]. When sulfur is adsorbed on the (0001) face of rhenium at low coverages, to form a c(2 × 2) structure, and then carbon monoxide is added to this system, carbon monoxide adsorbs by compressing the sulfur to higher coverage domains, thereby freeing up metal sites where carbon monoxide can adsorb. This is shown in fig. 17. When carbon monoxide desorbs, the sulfur diffuses back to form the lower coverage low compression surface structure. Thus, coadsorption can lead to the movement of atoms from one adsorption site to another. It is likely that in the presence of hydrogen, nitrogen is moved from C₇ sites, which it occupies on the (111) and (211) faces of iron. After hydrogen reacts to form NH or NH₂ species, these species will have different bonding when compared to atomic nitrogen. These species are likely to move to new

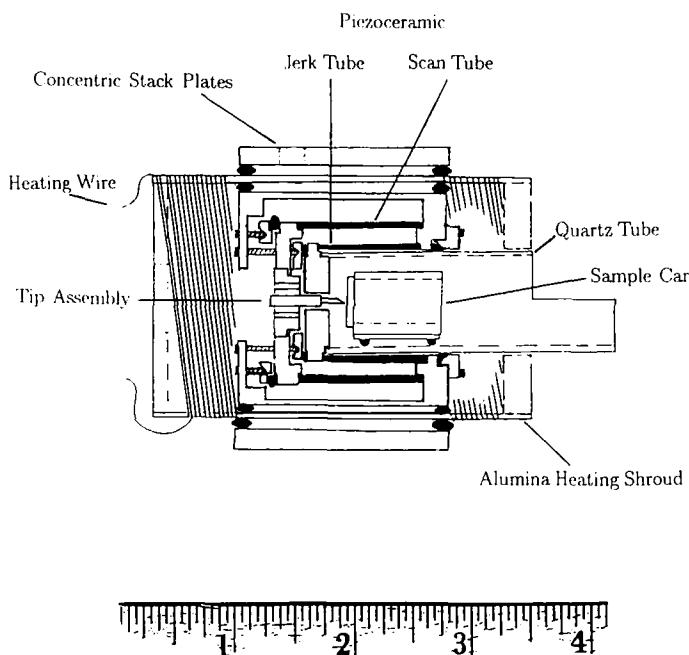


Fig. 15. The high temperature/high pressure scanning tunneling microscope (STM) [20].

locations, thereby freeing up the C_7 sites for the dissociation of the next N_2 molecule to adsorb at the C_7 site. Hopefully, STM will soon be used in investigating how and where nitrogen is located and how it reacts with hydrogen and whether it is removed from the C_7 adsorption sites.

The surface diffusion of adsorbed atoms can also be studied by STM by rapidly scanning the surface with a scanning rate of $\sim 100 \text{ \AA}/10^{-4} \text{ s}$. At this scanning rate, S appears to be disordered on the (0001) face of rhenium due to its rapid diffusion (fig. 18). By studying diffusion rates at various temperatures and using a spatial correlation imaging technique, the activation energy for S diffusion along the surface was determined to be about 0.8 eV [23,24]. It is our hope that we will be able to study the diffusion of nitrogen or NH groups on iron surfaces by STM at high temperatures and high N_2 and dihydrogen pressures. Recent studies of hydrocarbon diffusion on platinum surfaces revealed that hydrocarbon fragments can diffuse on platinum surfaces at high hydrogen and hydrocarbon pressures [25]. Depending on the degree of dehydrogenation, the diffusion rate of these hydrocarbon fragments is altered. The more hydrogen it contains, the faster it moves along the surface. Such studies with the nitrogen, NH and NH_2 systems could give us fundamental information about the dynamics of the movements of reaction intermediates during ammonia synthesis.

Pt(110) under atmospheric pressures

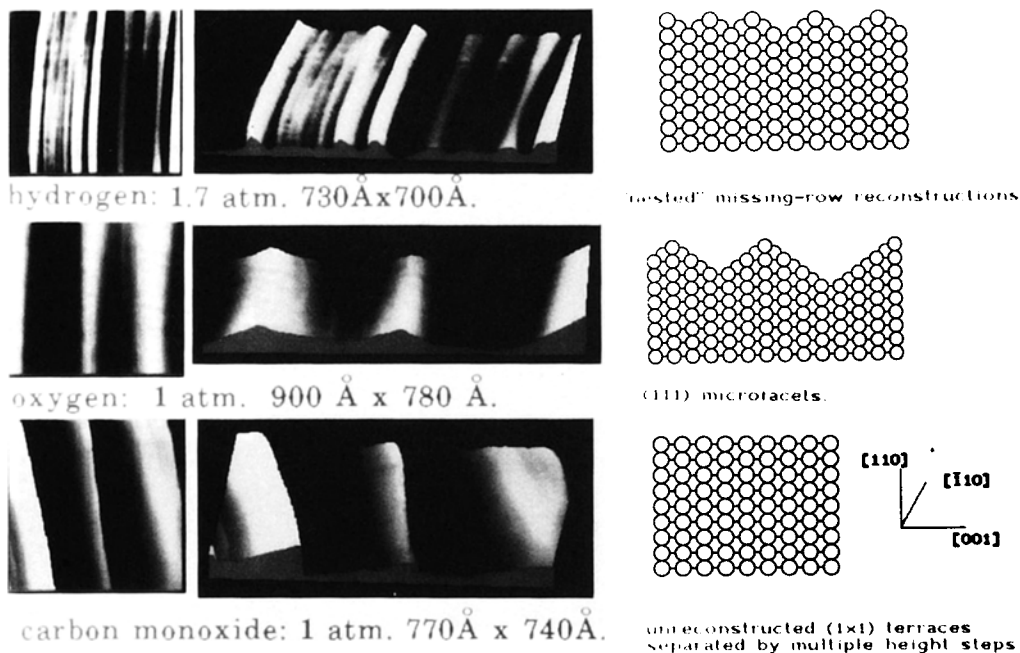


Fig. 16. Reconstruction of Pt(110) under atmospheric pressures of O₂ and H₂ observed by the high temperature/high pressure STM [21].

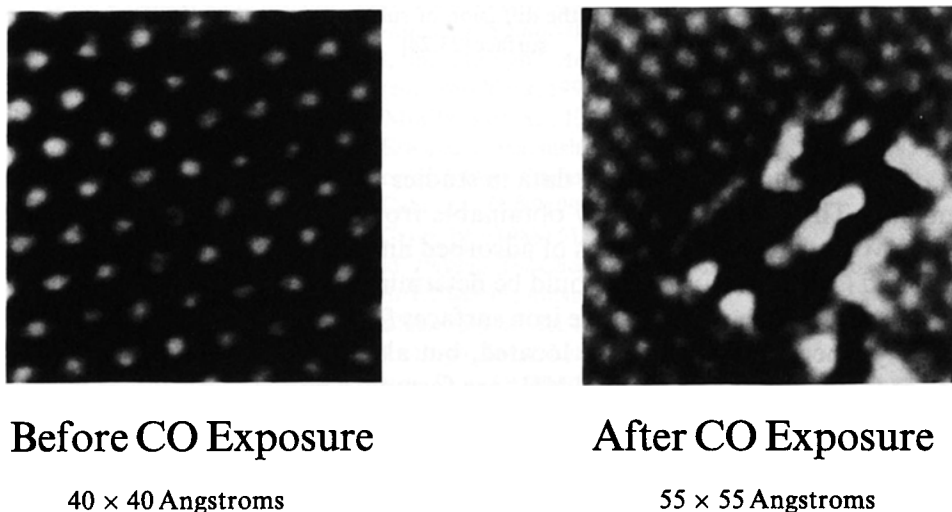


Fig. 17. Compression of the sulfur overlayer by carbon monoxide co-adsorption as detected by scanning tunneling microscopy (STM) [22].

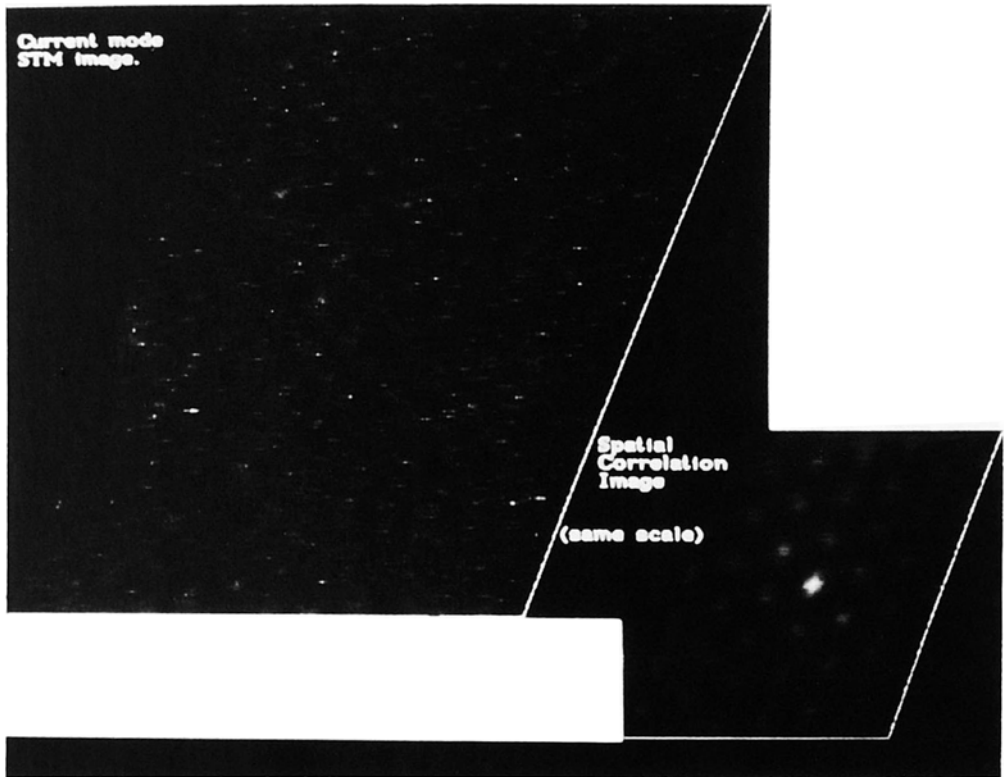


Fig. 18. The apparent disorder due to the diffusion of sulfur atoms on the (0001) rhenium crystal surface [23,24].

5. Summary

Let us summarize the missing data in studies of the surface science of ammonia synthesis. This data is presently obtainable from LEED-surface crystallography and STM studies. The structures of adsorbed nitrogen and hydrogen atoms on the (111) and (211) iron surfaces should be determined. The coadsorption of nitrogen and hydrogen on these two active iron surfaces for ammonia synthesis could tell us not only where these atoms are located, but also how they interact and perhaps change their location as NH and NH_2 are formed. The coadsorption of potassium and nitrogen may reveal the nature of the active sites which form by potassium adsorption on the iron single-crystal surfaces. Additionally, coadsorption of potassium, oxygen and nitrogen would tell us whether the effect of oxygen is restructuring, or how oxygen participated in the formation of the potassium induced active sites for ammonia synthesis on the various iron single-crystal surfaces. Finally, we should carry out high temperature/high pressure STM studies on the (111) and

(211) iron single-crystal surfaces under reaction conditions to explore the role of surface structure and its dynamic changes during ammonia synthesis.

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