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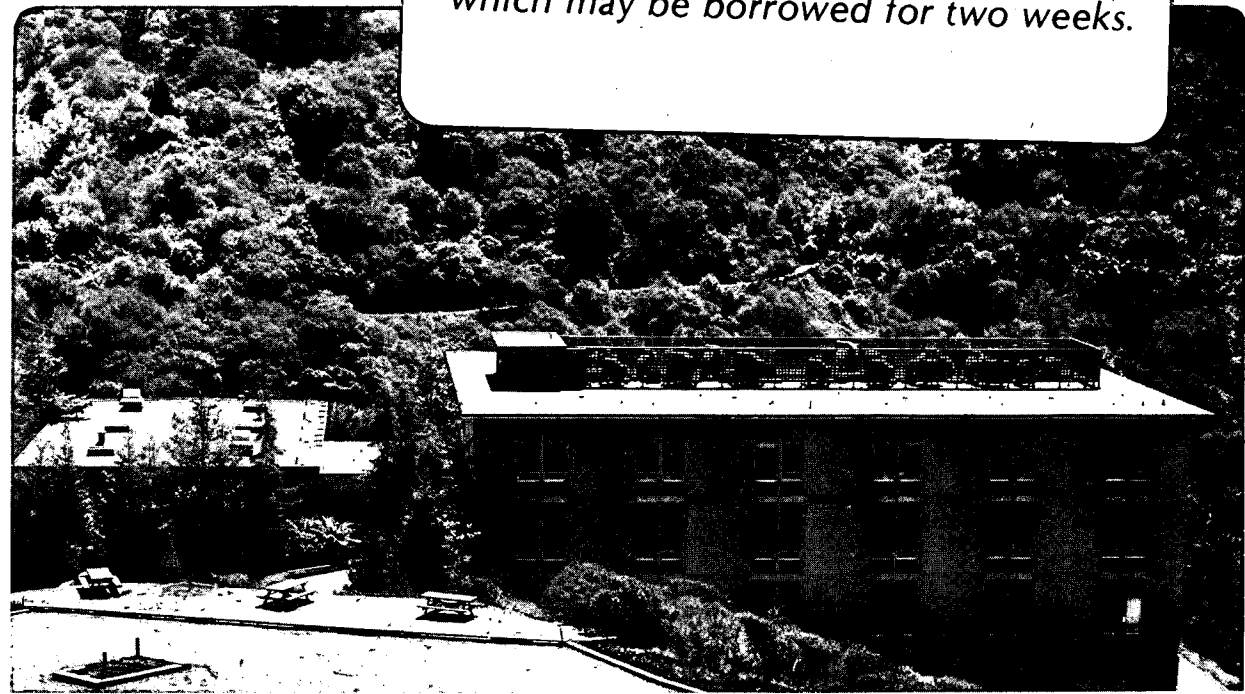
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The Effects of Potassium on the Ammonia Synthesis Over Iron Single Crystal Surfaces

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Abstract

The effects of potassium on ammonia synthesis over model iron single crystal catalysts of (111), (100), and (110) orientation have been studied under high pressure reaction conditions(20 atm reactant pressure of nitrogen and hydrogen). Under these conditions, no more than 0.15 monolayers(ML) of potassium can be stabilized on the iron surfaces.

The Fe(110) surface shows no activity for ammonia synthesis in this study with or without adsorbed potassium. The presence of potassium on the Fe(111) and Fe(100) surfaces increases the rate of ammonia synthesis markedly. At a low reaction conversion of 0.5% the rate over Fe(111) and Fe(100) is enhanced by a factor of two in the presence of potassium. The effect of potassium on Fe(111) and Fe(100) is enhanced as higher reaction conversions(i.e. increasing ammonia partial pressures) are achieved because potassium induces changes in the reaction orders for both ammonia and hydrogen. This is the first study which shows that the activity of the clean Fe(111) surface can be improved upon. No change in the activation energy for the reaction is observed with potassium, suggesting that the reaction mechanism has not been altered. Temperature programmed desorption show that the adsorption energy of ammonia is significantly reduced when coadsorbed with potassium.

A model is proposed whereby the decrease of the ammonia adsorption energy, induced by potassium, reduces the concentration of ammonia on the iron surface. This effect decreases the number of active sites blocked by the ammonia product thereby increasing the rate of ammonia synthesis. The model also suggests that an additional effect of potassium is to increase the rate of nitrogen dissociative chemisorption by about 30% over Fe(111) and Fe(100) under ammonia synthesis conditions.

1 Introduction

The synthesis of ammonia from its elements, nitrogen and hydrogen, is one of the most studied and important catalytic reactions. The most efficient catalyst found was iron "promoted" with 1-3% by weight of aluminum oxide and potassium oxide that further increase the rate of ammonia production[1,2,3]. An atomic scale understanding of how the catalyst system works is of prime importance and is possible by utilizing modern surface science techniques. Model studies using single crystal iron surfaces with added aluminum oxide and potassium oxide should reveal how the catalyst surface structure and reactivity is influenced by the presence of promoters.

Iron based catalysts used in ammonia synthesis usually perform at high pressures ($>$1atm) where ammonia production proceeds at a significant rate[2,3]. Under these conditions the catalyst surface can not 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 development of a unique high pressure / ultra-high vacuum(UHV) apparatus in our laboratory bridges this pressure gap[4]. This equipment allows the structure and composition of the catalyst surface to be determined in UHV while the catalytic activity of the surface can be monitored under high pressure conditions(20 atm of reactant pressure). Work in our laboratory using this apparatus studied the structure sensitivity of ammonia synthesis(Fe(111) $>$Fe(211) $>>$Fe(100) $>$Fe(210) $>>$Fe(110))[5,6] and has suggested that C_7 sites(Fe atoms with seven nearest neighbors) are responsible for the high activity of Fe(111) and Fe(211)[6]. More recent studies[7] have elucidated the effects of aluminum oxide in ammonia synthesis. Treatment of the less active faces of iron, such as Fe(100) and Fe(110), with water vapor in the presence of aluminum oxide produces new surfaces by restructuring, which are as active as Fe(111) and Fe(211) for ammonia synthesis.

The studies reported in this paper elucidate the effects of potassium in ammonia

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synthesis. It is shown that potassium fails to exhibit a promoter effect on the inactive Fe(110) surface under our conditions. 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 result is consistent with previous research[8] in this laboratory which found that potassium fails to exhibit a significant promoter effect at close to zero reaction conversion. The activation energy for the reaction is unaltered with the addition of potassium but there are marked changes in the apparent 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 dinitrogen(the rate limiting step in ammonia synthesis)[2,9,10]. 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 dinitrogen. 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%.

2 Experimental

All experiments presented in this paper were performed in a unique high pressure / ultra-high vacuum apparatus[5,6,7,8]. The stainless-steel chamber was capable of reaching a base pressure of 1×10^{-9} Torr. Mounted in the center of the chamber was a hydraulically operated high pressure cell. When closed the cell constituted part of a micro-batch reactor.

The UHV chamber was also equipped with a retarding field analyzer which was used to perform Auger electron spectroscopy(AES) and low energy electron diffrac-

tion(LEED). A quadrupole mass spectrometer was used to perform temperature programmed desorption experiments(TPD).

Typical high pressure ammonia synthesis reactions were carried out as follows. The sample was characterized in UHV by AES and LEED and than it was enclosed in the high pressure cell. The micro-batch reactor was than pressurized with 5atm of nitrogen and 15atm of hydrogen. The sample was resistively heated to 673 K and ammonia formation was monitored by periodically passing gas samples through a photo-ionization detector(PID) with a 10.2eV lamp. The PID signal was directly proportional to the ammonia partial pressure in the loop and it had a detection limit of 1×10^{-10} moles NH_3/cm^2-sec. After reaction the loop was evacuated and the sample was returned to UHV where AES, LEED, and TPD were performed.

Ammonia temperature programmed desorption experiments were done with a base pressure of 2×10^{-9} Torr. The sample was typically at about 130K during ammonia adsorption. The crystal was heated in a linear fashion(8K/sec) and mass 16 was monitored(NH_2^+) to avoid any interference by water.

The single crystals used in this study were typically $1cm^2$ disks about 1mm thick. They were cut and polished by standard metallurgical techniques. Platinum support wire(0.25mm diameter) was spot-welded around the single crystal sample. The crystal was resistively heated and a chromel-alumel thermocouple was used to monitor the sample temperature. Carbon and sulfur impurities present in a freshly cut iron single crystal were removed by argon ion sputtering($4\text{-}5 \times 10^{-6}$amperes/cm^2) in 1×10^{-7} Torr of oxygen while the sample was held at 873 K.

A Saes Getter source was used to deposit potassium on the single crystal samples. The coverage of potassium was determined by a potassium uptake curve which plotted the intensity of the 252-eV potassium Auger peak against dose time(the evaporation rate of the source was held constant). The coverage of potassium will be referred to in monolayers(ML) throughout the text.

The reactant gases(N_2 and H_2) were research purity. Further purification of the gases was accomplished by passing the gases through molecular sieve and than a liquid nitrogen cooled coil. The ammonia used for the TPD experiments was

obtained from Matheson(99.9% purity). It was used without further treatment.

3   Results

3.1   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 1ML was deposited on the single crystal surface. After reaction about 0.15ML 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. The oxygen, however, was necessary to stabilize the potassium on the iron surface under reaction conditions[8]. Reactions were carried out over K/Fe surfaces which had been oxidized in UHV until the 47eV MVV iron Auger peak split into a 42eV and 52eV peak, indicative of iron oxide[11]. Even with this high initial surface concentration only 0.15ML of potassium was left after a high pressure ammonia synthesis reaction.

Experiments were also performed in which 1.0ML 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 0.15ML 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 381eV nitrogen Auger peak) was the same on Fe and K/Fe surfaces after a reaction.

3.2 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 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 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 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.

3.3 The Hydrogen Partial Pressure Dependence Over Iron Single Crystal Surfaces

The apparent order in hydrogen for Fe(111) and K/Fe(111) surfaces is shown in figure 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 5atm to 15atm while the nitrogen pressure was kept constant at 5atm. 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.

3.4 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±0.6kcal/mole for clean Fe(111) and 15.9±1.0kcal/mole for K/Fe(111). The experimental error in E_a for K/Fe(111) is higher than clean Fe(111) in that 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.

3.5 Ammonia Temperature Programmed Desorption Studies

The temperature programmed desorption of ammonia after a 0.1langmuir(L) dose(1L = 1×10^{-6}Torr-sec) on clean Fe(111) and K/Fe(111) is shown in figure 4(heating rate = 8K/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 0.1ML of potassium the peak maximum shifts about 40 K. The peak maximum continuously shifts to lower temperature with increasing amounts of coadsorbed potassium. At a coverage of 0.25ML 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 desorption peak. At a potassium coverage of about 1.0ML only a weakly bound ammonia species is present with a maximum rate of desorption occurring at 164 K. This observation of the ammonia adsorption energy decreasing with the coadsorption of potassium on iron is similar to what is found for ammonia desorption from nickel and ruthenium with adsorbed sodium[12,13].

4 Discussion

The results reported in this paper 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) respectively. 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 poisoning the synthesis reaction at higher conversions or higher partial pressures of ammonia. This explains why previous work in our laboratory[8] 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.

4.1 The Effect of Potassium on the Adsorption of Ammonia to Iron Single Crystal Catalysts During Ammonia Synthesis

Poisoning of the catalyst by gas phase ammonia must involve readsorption of the product molecule on the iron surface. Once adsorbed the ammonia has a certain residence time(τ) on the catalyst which is determined by its adsorption energy(H_{ad}) on iron($\tau \propto e^{H_{ad}/RT}$)[14]. During this residence on the catalyst the ammonia can

either diffuse on the surface or decompose to atomic nitrogen and hydrogen[15,16]. 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[15,16]. The promoter effect of potassium than involves lowering the adsorption energy of the adsorbed ammonia so that the concentration of adsorbed ammonia is decreased. This 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 0.10ML 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[17] than the 40 K shift corresponds to a 2.4kcal/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 dinitrogen. At higher coverages of potassium the adsorption energy of the ammonia decreased to a 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 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 0.25ML 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[12]. This interaction appears to be weaker, since at a potassium coverage of 1ML, 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 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.

4.2   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 dinitrogen is the rate-limiting step and the process requires two open sites on the catalyst surface[2,7,9]. Using Langmuir-Hinshelwood kinetics the rate of ammonia synthesis(r) can be written as

$$r = k_1 P_{N_2}(1 - \theta_N)^2 \tag{1}$$

where k_1 is the rate constant for nitrogen dissociative chemisorption and $1 - \theta_N$ is the fraction of vacant sites on the surface, if atomic nitrogen is the most abundant species. The fraction of sites covered by nitrogen, θ_N, is determined by assuming the equilibrium[15,16];

$$N_{ad} + 1.5H_2(g) \overset{K_e}{=} NH_3(g) \tag{2}$$
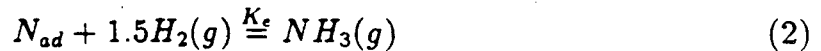
where K_e is the equilibrium constant. Following the method of Langmuir;

$$\theta_N = \frac{(1/K_e)(P_{NH_3}/P_{H_2}^{1.5})}{[1 + (1/K_e)(P_{NH_3}/P_{H_2}^{1.5})]}. \tag{3}$$

θ_N is substituted into (1) so that

$$r = \frac{k_1 P_{N_2}}{[1 + (1/K_e)(P_{NH_3}/P_{H_2}^{1.5})]^2}[16]. \tag{4}$$

The data can be accurately represented by equation 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}=5atm, P_{H_2}=15atm, and P_{NH_3}=0.013atm. This method yields a value of K_e=0.5×10^{-4}atm$^{-0.5}$ for clean

Fe surfaces and $K_e = 1 \times 10^{-3} atm^{-0.5}$ for K/Fe surfaces. This model implies that the equilibrium constant K_e increases with the adsorption of potassium pushing the equilibrium in eqn.2 to the gas phase ammonia side, thus lowering the fraction of sites covered by adsorbed nitrogen and 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 $\theta_v = 1 - \theta_N - \theta_{NH_3}$ where θ_N and θ_{NH_3} are determined by the equilibria

$$N_{ad} + 1.5H_2(g) \overset{K_2}{\rightleftharpoons} NH_{3ad} \tag{5}$$

and

$$NH_{3ad} \overset{K_3}{\rightleftharpoons} NH_3(g) \tag{6}$$

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

$$r = \frac{k_1 P_{N_2} P_{H_2}^3}{[P_{H_2}^{1.5} + (P_{NH_3}/K_3)(K_2^{-1} + P_{H_2}^{1.5})]^2} \tag{7}$$

The constants K_3 and K_2 can now be obtained by fitting equation 7 to the experimental data. For the clean surface $K_3 = 0.19 atm^{-1}$ and $K_2 = 2.6 \times 10^{-3} atm^{-1.5}$. When potassium is present $K_3 = 0.37 atm^{-1}$ and $K_2 = 2.6 \times 10^{-3} atm^{-1.5}$. 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 dinitrogen, the only role of hydrogen in the rate expression(equation 6) is to create available sites for this step. In the presence of potassium, K_3 increases making more sites available as

shown by the equilibria expressions (5) and (6). This is reflected in the lowering of the apparent order in hydrogen when potassium is added to the iron surface.

The contension that potassium increases the rate of ammonia synthesis by lowering the concentration of adsorbed ammonia product on the iron catalyst might explain earlier work carried out on the industrial catalyst. Numerous reports in the literature[2,18,19,20,21] contend that the effect of potassium on doubly promoted industrial catalysts(contain both aluminum oxide and potassium) becomes more pronounced as higher reaction conversions are achieved. It has been shown previously[19] that the turnover number over singly(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 see the effect of potassium. In another study[20], where higher reactant pressures(5 - 200atm) 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 not to change when going from a singly to a doubly promoted catalyst.

The experimental results, obtained in our laboratory 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 our experiments, occurs on the industrial catalyst.

4.3   The Effect of Potassium on Dinitrogen Dissociation Under Ammonia Synthesis Conditions

In addition to hindering ammonia adsorption on the iron catalyst, potassium

might also enhance dinitrogen dissociation during ammonia synthesis. Figure 5 plots the experimentally determined ratio of the clean Fe rate to the rate over 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, than in the limit of zero ammonia partial pressure, the ratio should be unity. Instead the best fit of the model to the experimental data occurs when the ratio is 1.3 at zero ammonia partial pressure. This implies that potassium increases k_1(rate constant for dinitrogen 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 than a 30% increase in rate corresponds to a 0.35kcal/mole decrease in the activation energy(E_a) for this step. This change in E_a is too small to be resolved in our experiments. A small change in E_a such as this might also explain work that has been done on the industrial catalyst which found 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[20,22].

Enhancement of the rate limiting step in high pressure ammonia synthesis by potassium is supported by surface science studies[23,24] which investigated the influence of potassium on the rate of dissociative chemisorption of nitrogen(k_1) on iron single crystals. The activity ratio for dinitrogen dissociation was 60:3:1 for the Fe(111), Fe(100), and Fe(110) surfaces respectively. It was found that potassium removed the difference in activities between the (110), (100), and (111) faces of iron by lowering the activation energy for dinitrogen 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 dinitrogen, thus lowering its adsorption energy and activation energy for dissociation on the iron. The coadsorption of oxygen was found to be of prime importance for thermally stabilizing

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potassium[25], but the presence of oxygen decreased the effect of potassium on the rate of dinitrogen dissociation.

Under the conditions used in this study(20atm reactant pressure and a catalyst temperature of 673K) oxygen is needed to stabilize potassium. The presence of the oxygen probably accounts for the small effect of potassium on k_1 in our studies. The extent of promotion by potassium, on dinitrogen dissociation under industrial conditions($\approx$100atm reactant pressure), will probably be similar to the effect seen under our conditions since it is well documented in the literature[21,26] that potassium is in intimate contact with oxygen on the commercial catalyst.

5 Summary

The promoter effect of potassium on ammonia synthesis has been investigated over the Fe(110), Fe(100), and Fe(111) surfaces under high pressure conditions. A coverage of 0.15ML is the maximum amount of potassium that can be stabilized on the iron single crystals under our conditions. 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 0.5% 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 in not being changed.

A model has been presented and it 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 dinitrogen, 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 dinitrogen, further increasing the rate of ammonia synthesis. The model suggests that an additional promoter effect by potassium is a 30% enhancement of the rate of dinitrogen dissociation on Fe(111) and Fe(100), further increasing the rate of ammonia production.

Acknowledgement

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6 Figure Captions

Figure 1. The pressure dependence of ammonia synthesis in ammonia over Fe(100) and K/Fe(100). When potassium is present the apparent order in ammonia becomes less negative. This suggests that less gas phase ammonia adsorbs and poisons the catalyst in the presence of potassium. Thus, the ammonia synthesis rate is enhanced because more surface sites are open for the dissociative chemisorption of dinitrogen(rate limiting step).

Figure 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 order of hydrogen.

Figure 3. The activation energy(E_a) for ammonia synthesis over Fe(111) and K/Fe(111). There is no change in E_a, within experimental error when potassium is present suggesting that the promoter effect of potassium is largely due to changes in the reaction order of ammonia and hydrogen. Similar E_a values for Fe(111) and K/Fe(111) imply that the mechanism of ammonia synthesis is not altered by the addition of potassium.

Figure 4. Ammonia temperature programmed desorption results on Fe(111) and K/Fe(111)(heating rate = 8K/sec) after a 0.1L dose. (a) clean Fe(111); (b) a 0.15ML coverage of potassium shifts the ammonia desorption peak down in temperature by 40 K suggesting that potassium lowers the adsorption energy of ammonia on iron; (c) at a potassium coverage of 0.25ML a new desorption peak appears at 189 K; (d) at a 1.0ML coverage of potassium ammonia is weakly adsorbed and it desorbs at 164 K.

Figure 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. The

promoter effect of potassium at zero ammonia partial pressure is due to an increase in the rate of dissociative nitrogen chemisorption and at higher conversions it is due to an enhancement in the equilibrium constant K_3.
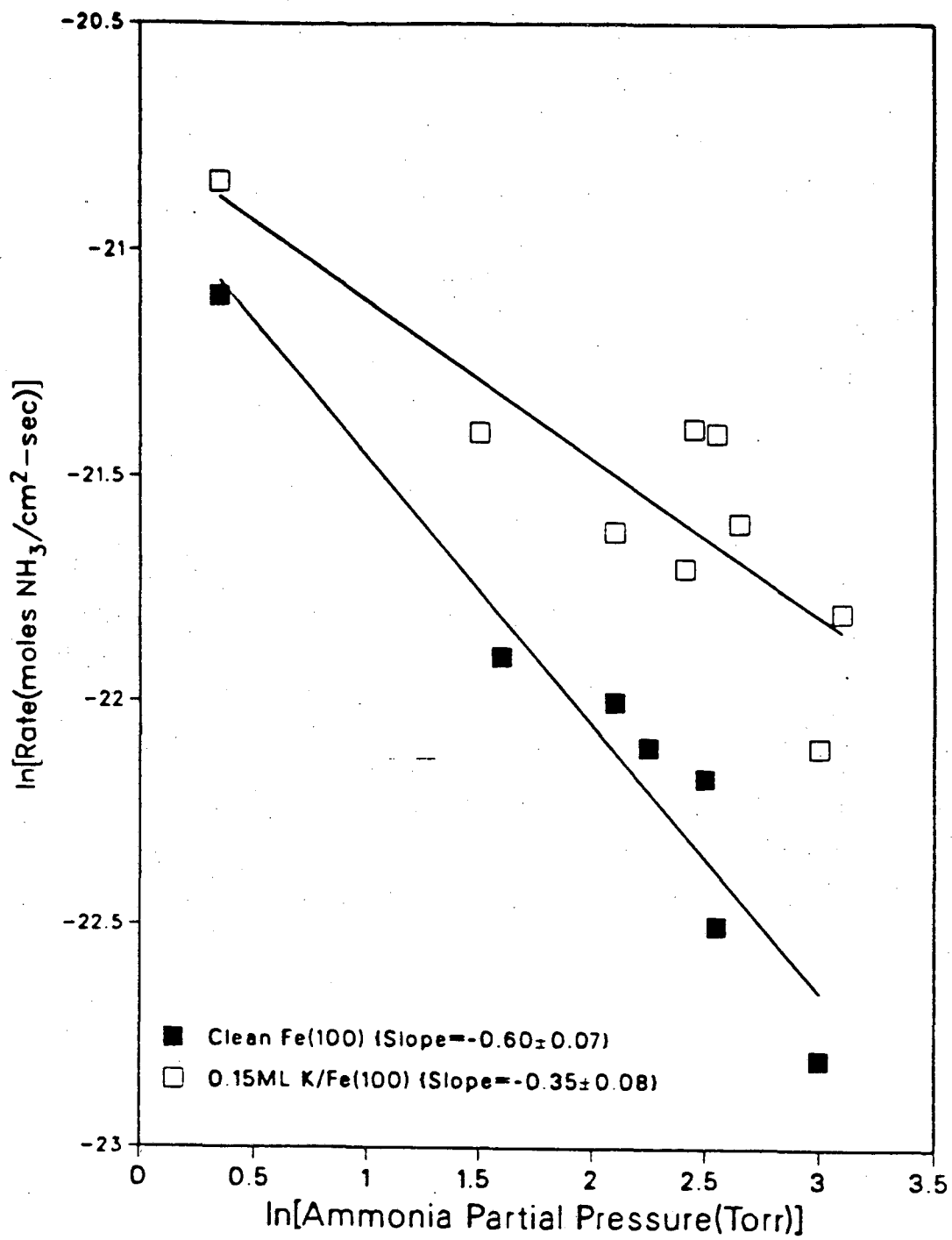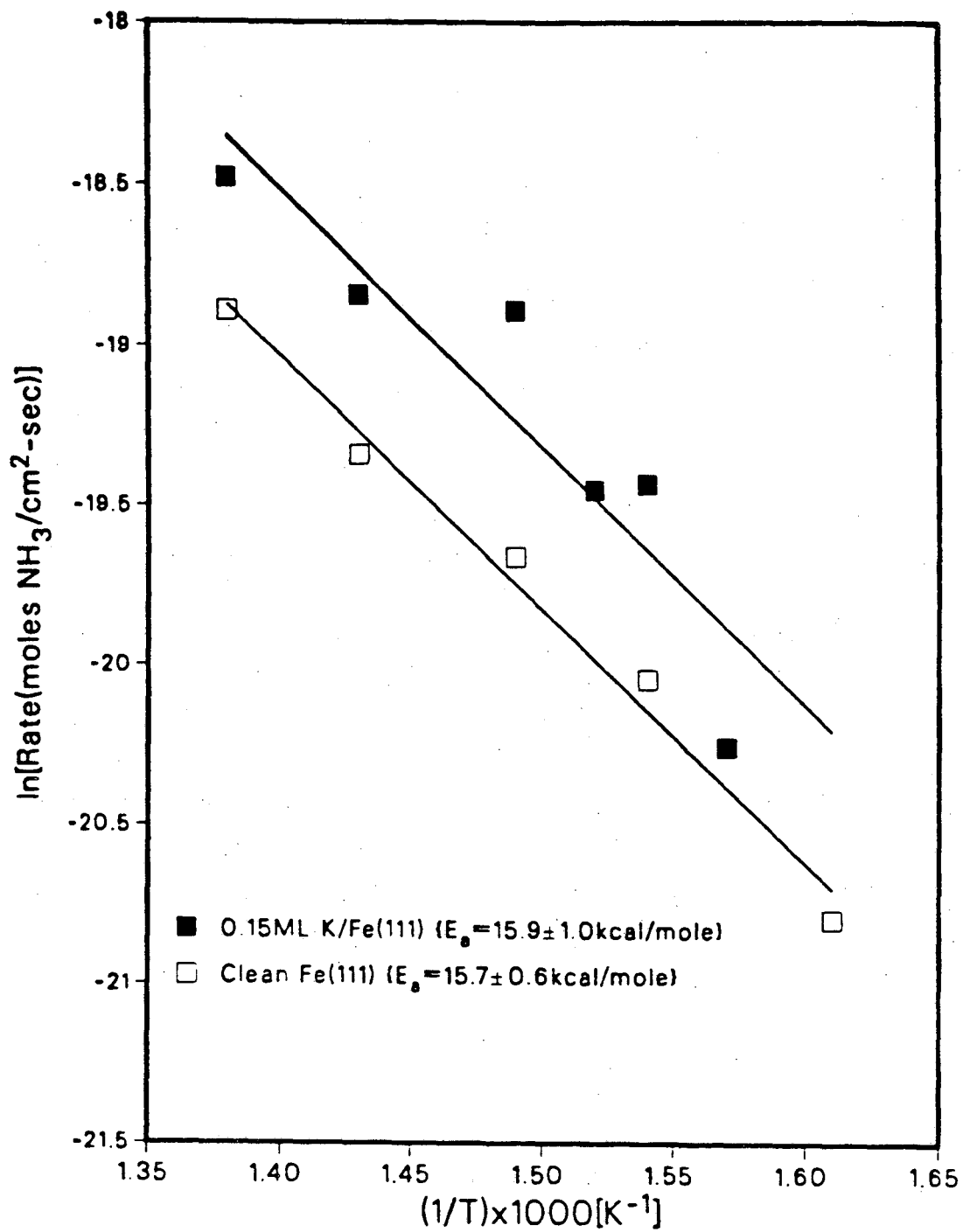
Fig. 1
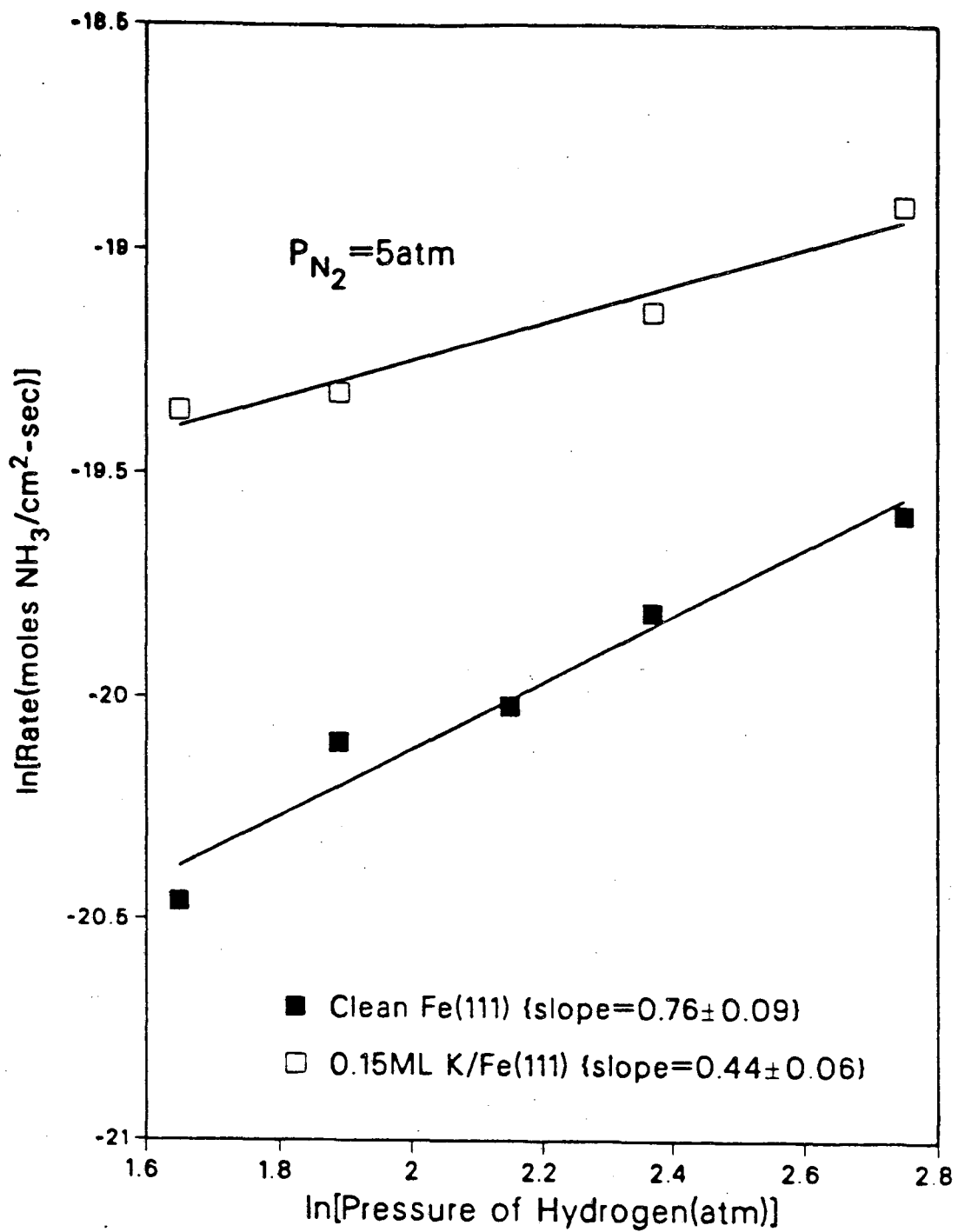
Fig. 2

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Fig. 3

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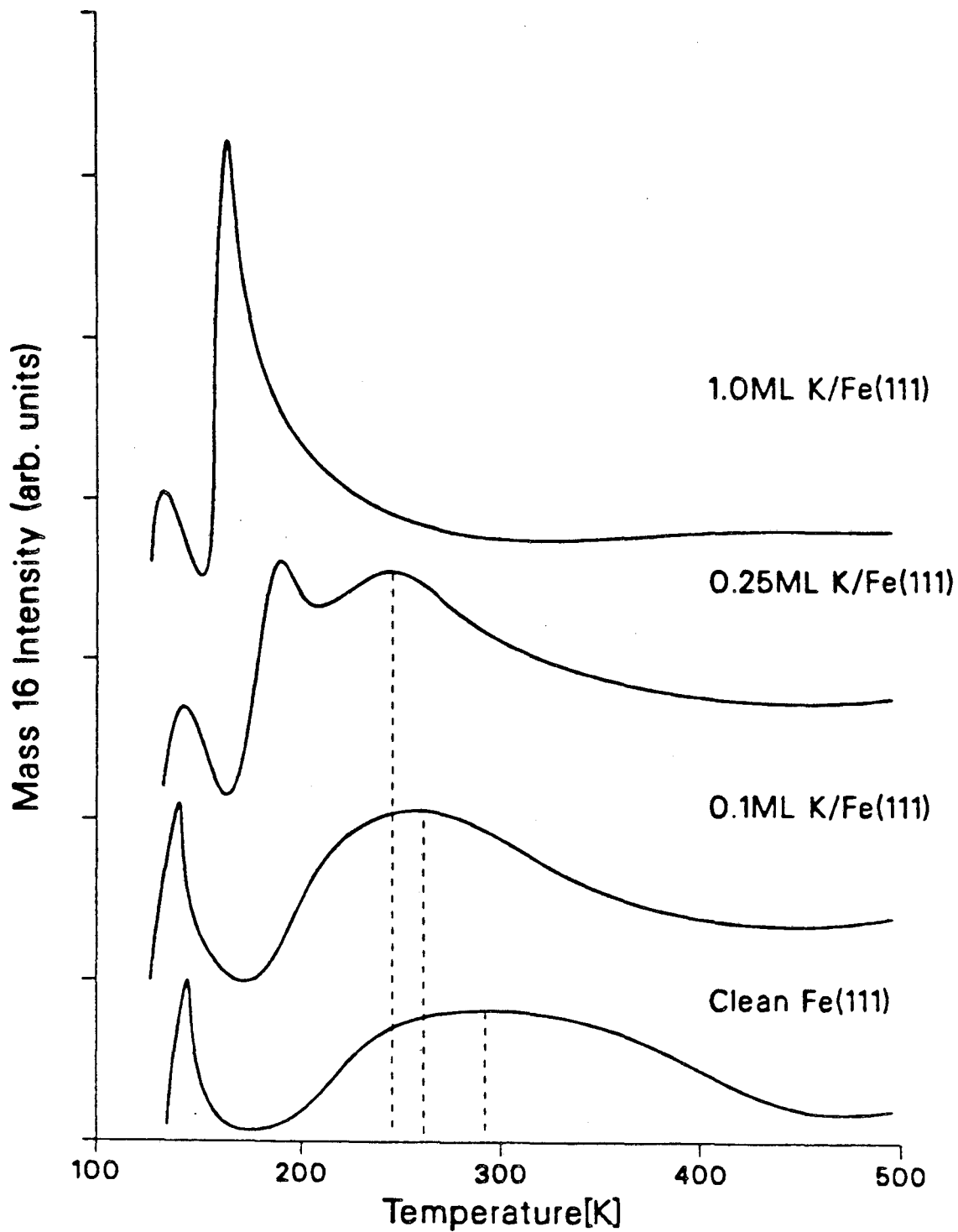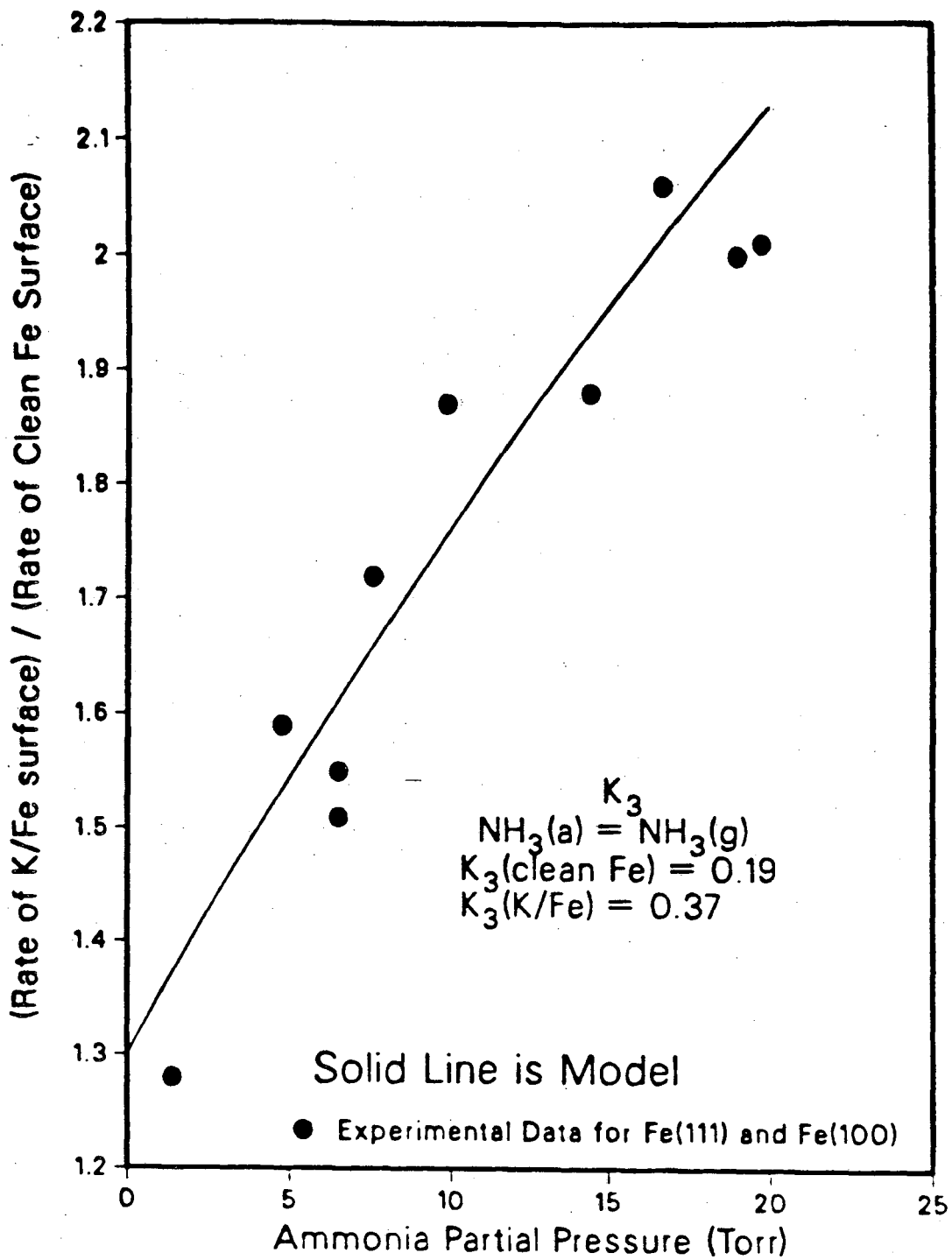23

Ammonia TPD From Clean Fe(111) and K/Fe(111) surfaces

Fig. 4

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Fig. 5

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