The Effects of Potassium on Ammonia Synthesis over Iron Single-Crystal Surfaces

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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 0.3% 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. 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 shows that the adsorption energy of ammonia is significantly reduced when coadsorbed with potassium. A model is proposed in which the decrease of 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. © 1988 Academic Press, Inc.

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 yet found is iron "promoted" with 1–3% by weight of aluminum oxide and potassium oxide, which further increase the rate of ammonia production (*1–3*). An understanding of how the catalyst system works on the atomic scale 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 are influenced by the presence of promoters.

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 can not be examined on the atomic level. Surface science studies of the catalyst on the atomic scale require a high vacuum, in which the synthesis of ammonia does not occur at a detectable rate.

The development in our laboratory of a unique high-pressure/ultrahigh-vacuum (UHV) apparatus 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) $\gg$ Fe(100) > Fe(210) $\gg$ 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 phases of iron, such as Fe(100) and Fe(110), with water vapor in the presence of aluminum oxide produces new surfaces, which are as active as Fe(111) and Fe(211) for ammonia synthesis, by restructuring.

The studies reported in this paper elucidate the effects of potassium in ammonia synthesis. 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/ultrahigh-vacuum apparatus (5–8). 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 diffraction (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 then it was enclosed in the high-pressure cell. The micro-batch reactor was then pressurized with 5 atm of nitrogen and 15 atm 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 10.2-eV lamp. The PID signal was directly proportional to the ammonia partial pressure in the loop and has a detection limit of 1×10^{-10} mol 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 TPD experiments were done at a base pressure of 2×10^{-9} Torr. The sample was typically at about 130 K during ammonia adsorption. The crystal was heated in a linear fashion (8 K/sec) and mass 16 was monitored (NH_2^+) to avoid any interference by water.

The single crystals used in this study were typically 1-cm^2 disks about 1 mm thick. They were cut and polished by stan-

dard metallurgical techniques. Platinum support wire (0.25-mm 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 (4–5×10^{-6} A/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 of research purity. Further purification of the gases was accomplished by passing the gases through a molecular sieve and then 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 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 because of 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 47-eV MVV iron Auger peak split into a 42- and a 52-eV peak, indicative of iron oxide (11). Even with this high initial surface 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 kept under reaction conditions for only 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.

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),
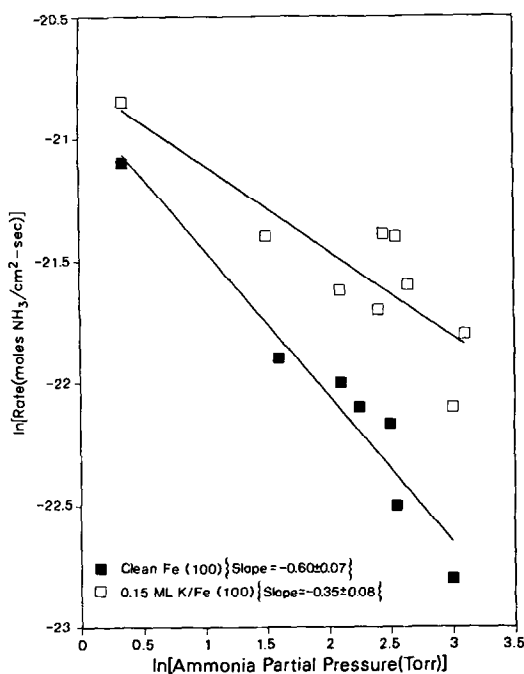
FIG. 1. The pressure dependence of ammonia synthesis in ammonia over Fe(100) and K/Fe(100). The rate measurements at the lowest conversions represent the average of many experimental values. When potassium is present the apparent order in ammonia becomes less negative. This suggests that less gas-phase ammonia adsorbs to 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).

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 Fig. 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 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.

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 ± 0.6 kcal/mol for clean Fe(111) and 15.9 ± 1.0 kcal/mole for K/Fe(111) (Fig. 3). The experimental error in E_a for K/Fe(111) is higher than that for clean Fe(111) because the potassium cover-
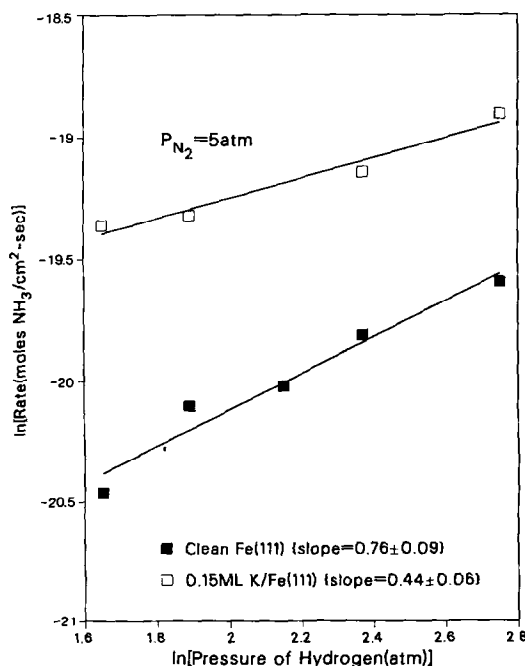

FIG. 2. The hydrogen pressure dependence for the ammonia synthesis reaction over Fe(111) and K/Fe(111). The addition of potassium to Fe(111) lowers the apparent order of hydrogen.
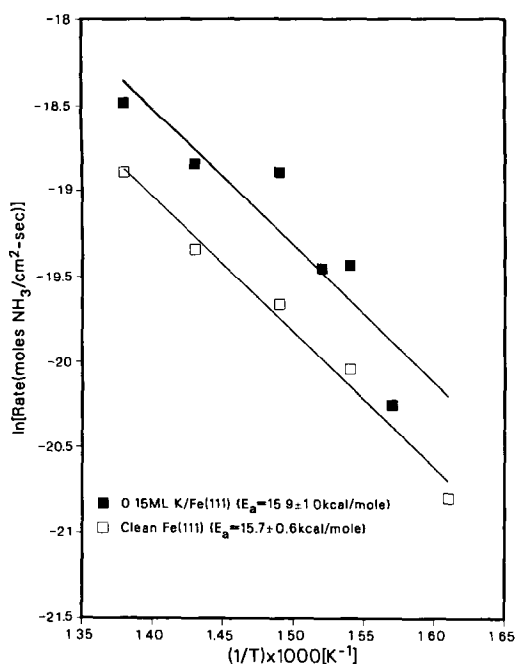
FIG. 3. The activation energy (E_a) for ammonia synthesis over Fe(111) and K/Fe(111). There is no change in E_a, within experimental error, when potassium is present, suggesting that the promoter effect of potassium is due largely to changes in the reaction order of ammonia and hydrogen. Similar E_a values for Fe(111) and K/Fe(111) imply that the mechanism of ammonia synthesis is not altered by the addition of potassium.

age 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 0.1-Langmuir (L) dose (1 L = 1 × 10⁻⁶ Torr-sec) on clean Fe(111) and K/Fe(111) is shown in Fig. 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 about 40 K. The peak

maximum shifts continuously to lower temperatures 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 desorption 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 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).
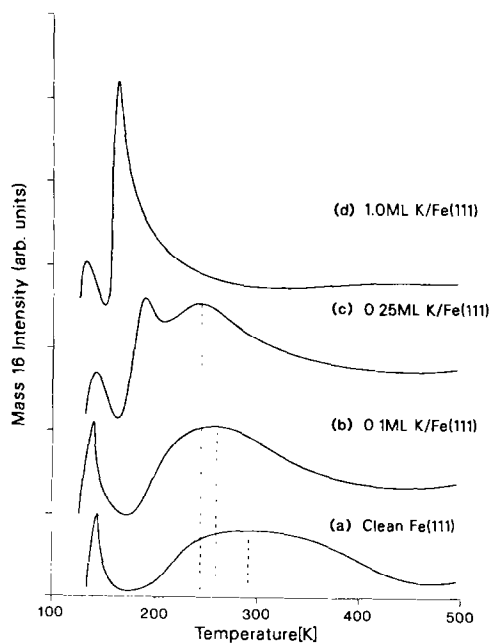

FIG. 4. Ammonia temperature-programmed desorption results on Fe(111) and K/Fe(111) (heating rate = 8 K/sec) after a 0.1-L dose. (a) Clean Fe(111); (b) a 0.15-ML coverage of potassium shifts the ammonia desorption peak down in temperature by 40 K, suggesting that potassium lowers the adsorption energy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

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 the amount of gas phase ammonia (<2 Torr) is insufficient to poison the reaction significantly. 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 (ΔH_{ad}) on iron $(\tau \alpha e^{\Delta H_{ad}/RT})$ (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 then 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 0.10-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 (17), then the 40-K shift corresponds to a 2.4-kcal/mol 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 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 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 (12). 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 postreaction Auger data. Within experimental error, there is no change in the intensity of the nitrogen Auger peak between an Fe 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 ultrahigh-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 that the process requires two open sites on the catalyst surface (2, 7, 9). Using Langmuir–Hinshelwood kinetics the rate of ammonia synthesis (r), in this case, can be written as

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

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)

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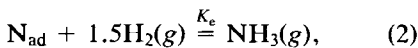
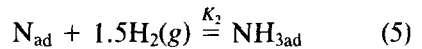where K_e is the equilibrium constant. Following the method of Langmuir,

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

θ_N is substituted into Eq. (1) so that
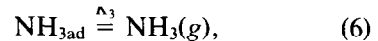
$$r = \frac{k_1 P_{N_2}}{[1 + (1/K_e)(P_{NH_3}/P_{H_2}^{1.5})]^2} (16). \qquad (4)$$

The data can be represented accurately by Eq. (4). Fitting of the experimental data to the equation (i.e., solving for K_e) is done by setting $d(\ln r)/d(\ln P_{NH_3})$ 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 Eq. (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 suggest that a promoter effect of potassium is to lower the concentration of ammonia on the catalyst surface. In this case the fraction of vacant sites is $1 - \theta_N - \theta_{NH_3}$, where θ_N and θ_{NH_3} are determined by the equilibria

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

and

$$NH_{3ad} \overset{K_3}{=} NH_3(g), \qquad (6)$$

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

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

The constants K_3 and K_2 can be obtained by fitting Eq. (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 dinitrogen, the only role of hydrogen in the rate expression (Eq. (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 equilibria expressions (Eqs. (5) and (6)). This is reflected in the lowering of the apparent order in hydrogen when potassium is added to the iron surface.

The concept 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, 18–21) contend that the effect of potassium on doubly promoted industrial catalysts (containing 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 (containing only aluminum oxide) and doubly promoted catalysts are similar when a total of 1 atm of nitrogen and hydrogen is used, suggesting that the ammonia partial pressure is not great enough at these conditions to reveal the effect of potassium. In another study (20), in which higher reactant pressures (5–200 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 became ever 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 with a singly or a doubly promoted catalyst was found not to differ.

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 rate over clean Fe 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, then 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, then a 30% increase in rate corresponds to a 0.35-kcal/mol 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 showed that the activation energy for
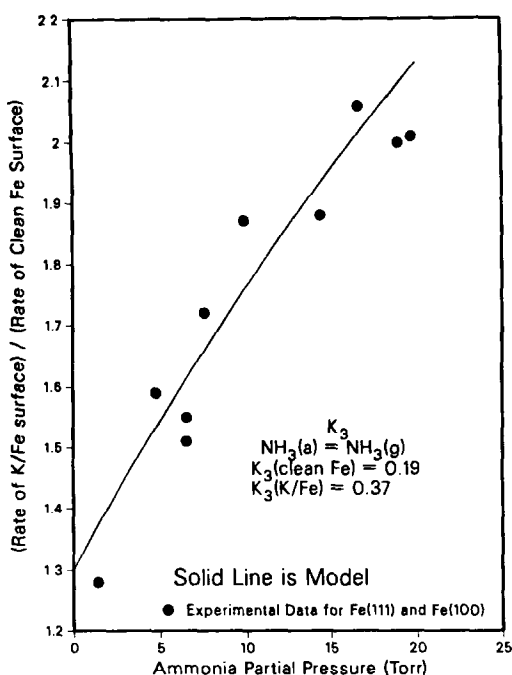
FIG. 5. The experimental rate data fit to a model which allows for the blocking of catalytic surface sites by adsorbed ammonia as well as by atomic nitrogen. The promoter effect of potassium at zero ammonia partial pressure is due to an increase in the rate of dissociative nitrogen chemisorption and at higher conversions it is due to an enhancement in the equilibrium constant K_3.

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, allowing more electron density to be transferred to dinitrogen and thus lowering its adsorption energy and the activation energy for dissociation on the iron. The coadsorption of oxygen was found to be of prime importance for thermally stabilizing 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 (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 our studies. The extent of promotion by potassium on dinitrogen dissociation under industrial conditions (~100 atm 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 0.15 ML 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 0.3% 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 being changed.

A model has been presented and it is consistent with 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, making more sites available to chemisorb dinitrogen dissociatively and 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.

ACKNOWLEDGMENTS

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