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Ammonia-Pretreatment-Induced Restructuring of Iron Single-Crystal Surfaces: Its Effects on Ammonia Synthesis and on Coadsorbed Aluminum Oxide and Potassium

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The effects of ammonia pretreatment on the structure and activity of iron single-crystal surfaces for ammonia synthesis are examined. Treatment of the (110), (100), and (111) planes of iron with 5 or 50 Torr of ammonia (723 K, 30 min) causes surface restructuring as evidenced by changes in ammonia synthesis activity (20 atm total pressure), and in temperature-programmed desorption, and by the appearance of new surfaces as seen by scanning electron microscopy. The (110) plane of iron is inactive for ammonia synthesis under the conditions used in this study, but the ammonia-pretreatment-restructured Fe(110) surface becomes about twice as active as the Fe(100) face. The restructured Fe(100) surface becomes about four times more active than the clean, unrestructured (100) surface. Restructuring the active Fe(111) face in ammonia results in a slight decrease in ammonia synthesis activity. The kinetic data, temperature-programmed desorption, and scanning electron microscopy suggest that Fe(110) and Fe(100) are restructured to surfaces containing C_7 sites, such as Fe(111) and Fe(211). A stereographic analysis of the restructured Fe(111) surface, using scanning electron microscopy, taken together with the reaction rate measurements suggests that {211} surface planes are formed upon ammonia treatment. The high concentrations of near-surface nitrogen that is deposited by the ammonia pretreatment does not block catalytic sites for the synthesis of ammonia. The presence of aluminum oxide on any of the iron single-crystal surfaces inhibits the ammonia-induced restructuring process, while the presence of potassium has no observable effect on the process. These results suggest a method of activating iron with both ammonia and water vapor restructuring in the presence of aluminum oxide and potassium to achieve a catalyst with optimal activity for ammonia synthesis.

1. INTRODUCTION

The synthesis of ammonia from its elements over iron is a structure-sensitive reaction (*1–3*). A major concern in the preparation of an industrial catalyst is to preferentially create and stabilize surface orientations (i.e., Fe(111) and Fe(211)) (*4, 5*). This objective is usually accomplished in the chemical technology by combining magnetite (Fe_3O_4) with about 2% by weight of potassium oxide (K_2O) and aluminum oxide (Al_2O_3) and then reducing the catalyst precursor in a stoichiometric mixture of hydrogen and nitrogen or in an ammonia–hydrogen flow (*6*). Catalytic studies have found that the industrial iron catalyst is more active when reduced in a stoichiometric mixture of nitrogen and hydrogen than in pure hydrogen (*7*). Also, by treating the catalyst with ammonia, so as to achieve a higher partial pressure of nitrogen (through the complete dissociation of ammonia), a nitrogen-induced restructuring results in an enhancement in ammonia-synthesis activity (*2*).

The interaction of nitrogen with iron in forming iron nitride has been thought for a long time to create surfaces which would be active in ammonia synthesis (*1, 2, 8*). Extensive surface-science research has been carried out to explore how the structure of

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iron is modified by its interaction with nitrogen and ammonia. Field emission studies dealing with nitrogen on iron suggested that the adsorption of nitrogen occurs more readily on the (111) face of iron and that the (110) and (100) planes, which are not as active as Fe(111), are actually transformed to the (111) face in the presence of nitrogen (*9*). This study by Brill *et al.* was one of the first examples of adsorbate-induced restructuring.

Nitrogen adsorption on Fe(111) and Fe(110) under ultrahigh vacuum (UHV) has been found to cause structural rearrangements of the iron surface atoms (a wide range of LEED patterns can be obtained) (*10, 11*), while adsorption on Fe(100) produces a simpler c(2 × 2) superstructure. Adsorption of nitrogen on Fe(12, 1, 0) causes extensive reconstruction resulting from the formation of a surface nitride similar to bulk Fe_4N (*12*).

Ammonia completely decomposes on Fe(111), Fe(100), and Fe(110) at temperatures above 400 K (hydrogen desorbs) (*13, 14*), producing a higher virtual pressure of atomic nitrogen than can be obtained by dosing iron with nitrogen under UHV. For example, adsorption of NH_3 at elevated temperatures on Fe(100) caused faceting of the (100) surface producing monoatomic steps in contrast to the c(2 × 2) superstructure obtained by the adsorption of nitrogen. Higher pressures of ammonia (0.05–1 Torr) cause extensive bulk faceting of polycrystalline iron at temperatures between 600 and 1250 K (*15*).

The use of a combined high-pressure/UHV chamber, developed in our laboratory, allows the study of the effects of nitrogen-induced restructuring of iron single-crystal catalysts for ammonia synthesis under both the UHV and high-pressure (20 atm total pressure) environments. This experimental approach has shown its power in studies of the structure sensitivity of ammonia synthesis (*1, 5*) and the effects of both aluminum oxide and potassium in this reaction over iron. These earlier studies have implicated the C_7 site (*5*) (Fe surface atoms with seven nearest neighbors) for the high activity of Fe(111) and Fe(211) for ammonia synthesis (activity of (111) $>$ (211) $\gg$ (100) $>$ (210) $>$ (110)) and have indicated that the promotional effect of aluminum oxide in the ammonia-synthesis catalyst is to create and stabilize surfaces which contain C_7 sites through its interaction with iron oxide prior to reduction (*4*). The effect of potassium has been shown to be twofold. It promotes ammonia synthesis over iron by increasing dissociative nitrogen chemisorption (rate-limiting step), and reduces the surface concentration of product ammonia, creating more available catalytic sites for the rate-limiting step. It has also been shown that to fully realize the promotional effects of both aluminum oxide and potassium on iron the catalyst should be restructured with aluminum oxide prior to the addition of potassium (*16*). If potassium is present along with aluminum oxide in the preparation stage of the iron catalyst, potassium aluminate forms and the aluminum oxide-induced restructuring of iron or iron oxide is inhibited.

This paper reports the effects of nitrogen on inducing restructuring and on the ammonia synthesis activity of Fe(110), Fe(100), and Fe(111) crystal surfaces. We find that by treating the (110) and (100) faces of iron with ammonia prior to ammonia synthesis these surfaces restructure, losing their original surface orientation. The restructured Fe(110) and Fe(100) crystal faces approach the activity of the most active Fe(111) surface for ammonia synthesis. The ammonia-pretreated Fe(111) surface also restructures, but shows only a small decrease in activity for ammonia synthesis. The presence of high bulk and surface concentrations of nitrogen after the ammonia treatment does not affect the catalytic surface, suggesting that the presence of strongly bound nitrogen and its diffusion to the iron surface from the bulk is not a factor in explaining ammonia-synthesis kinetics. The presence of aluminum oxide inhibits the ammonia-induced restructuring of iron, while the presence of potassium has no observable effect on the process.

2. EXPERIMENTAL

The apparatus used in this study has been described in detail elsewhere (*1*). Briefly, the experiments were performed in a combined ultrahigh vacuum (UHV)/high pressure apparatus. Ultrahigh vacuum was achieved in a stainless-steel chamber with a base pressure less than 2×10^{-9} Torr. The UHV chamber was equipped with a four-grid retarding field analyzer for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The primary electron beam (2000 eV) for AES is provided by a glancing-incidence electron gun.

The relative nitrogen coverage, $C_N = N_{381}$ eV/Fe_{652} eV, will be used to represent the nitrogen coverage at the surface and in the iron near-surface region. To quantify the C_N values, obtained in this study, it will be assumed that $C_N = 0.9$ corresponds to a surface concentration (surface nitrogen atoms/surface iron atoms) θ equal to 0.5 arrived at in a previous study (*10*) on Fe(100). This calibration will be applied to obtain θ_N values for the Fe(111) surface. The iron surface density on the Fe(111) surface is less than the Fe(100) surface; thus the θ_N values used for the Fe(111) surface are actually lower limits for the nitrogen surface concentration. A linear correspondence between changes in C_N and θ_N will be assumed in this study. Nitrogen is absorbed by iron and thus C_N is an average of the concentration of nitrogen in the near-surface region and at the surface. An outermost surface nitrogen coverage could not be determined in this study, but ion-scattering spectroscopy experiments are being planned to quantify the surface nitrogen coverage. All N_{381} eV/Fe_{652} eV ratios are attained by using a 14-volt modulation on the retarding grid.

A quadrupole mass spectrometer was used to analyze the residual gas composition in the chamber and to perform temperature-programmed desorption (TPD). A hydraulically operated high-pressure cell was also present in the chamber, which when closed constituted part of a microbatch reactor.

Sources for the evaporation of Al and K are also available. Aluminum is evaporated from a ceramic crucible wrapped with tungsten wire which is resistively heated. The Al is oxidized by water vapor in the UHV chamber (5×10^{-8} Torr) and its coverage on the Fe surface is determined by carbon monoxide TPD (*17*). Potassium is evaporated from a conventional SAES Getter source and it is rapidly oxidized in UHV with 5×10^{-8} Torr of water vapor. The coadsorbed oxygen stabilizes the potassium during ammonia synthesis (*17*).

Ammonia pretreatment of the iron surfaces was performed by enclosing the sample in the high-pressure cell and then equilibrating the desired pressure of ammonia in the reaction loop. All pretreatments were carried out at 723 K for 30 min (only the pressure of ammonia will be used to describe the pretreatments mentioned throughout the text).

The single-crystal samples used were on the average 1 cm^2 disks about 1 mm thick. They were cut and polished by standard metallurgical techniques. The single crystals were spot-welded between 0.51-mm-diameter platinum wire. The crystal was heated resistively and its temperature was monitored with a chromel–alumel thermocouple spot-welded to the edge of the crystal. Sulfur impurity in the sample was removed by prolonged argon ion sputtering (4–5 $\times 10^{-6}$ A/cm^2) while the sample was at 873 K. Carbon was removed by treating the sample with 1×10^{-7} Torr of oxygen while sputtering.

The reactant gases (N_2 and H_2) were research purity and were further purified by passing them through a molecular sieve trap and a liquid-nitrogen-cooled coil. Anhydrous ammonia (Matheson, 99.9% purity) was used without further purification.

A typical reaction sequence would occur

by preparing and characterizing an iron single-crystal sample in UHV by LEED, TPD, and AES. The sample was enclosed by the high-pressure cell to form an external reaction loop. Ammonia pretreatments were performed by introducing 5 or 50 Torr of ammonia into the loop while heating the sample to 723 K for 30 min. The sample was cooled and the loop evacuated. Reactant gases (15 atm of hydrogen and 5 atm of nitrogen) were introduced and circulated over the sample by a positive displacement pump. The sample was heated to 673 K and ammonia production was monitored by periodically passing samples from the reaction loop through a photoionization detector (PID), sensitive only to the ammonia partial pressure. After reaction the crystal was cooled to 373 K in the reaction mixture, the reactant gases evacuated from the loop, and the sample returned to UHV. TPD was performed by heating the sample at 10 K/sec while monitoring mass 15 (NH^+ fragment) with the mass spectrometer. Mass 15 is monitored instead of mass 17 (NH_3^+) to eliminate any contribution to the signal from residual water which adsorbs on the sample during pumpdown.

3. RESULTS

3.1. *Reaction-Rate Studies*

3.1.2. Clean iron single crystals pretreated with ammonia prior to ammonia synthesis. Rates of ammonia synthesis over initially clean (110), (100), and (111) faces of iron are shown in Fig. 1, along with the rates obtained after the treatment of the Fe(110), Fe(100), and Fe(111) crystals with 5 Torr of ammonia at 723 K for 30 min prior to the ammonia synthesis reaction. The Fe(110) and Fe(100) surfaces show large increases in activity for ammonia synthesis (Fig. 1) after ammonia pretreatment. The initially inactive Fe(110) face becomes about half as active as the clean Fe(111) surface. The activity of the Fe(100) surface, for ammonia synthesis, increases by a factor of 4 and the Fe(111) surface shows only a small decrease in activity after ammonia pretreatment. Further treatment of the restructured single crystals with 50 Torr of ammonia leads to no further change in ammonia synthesis rates.

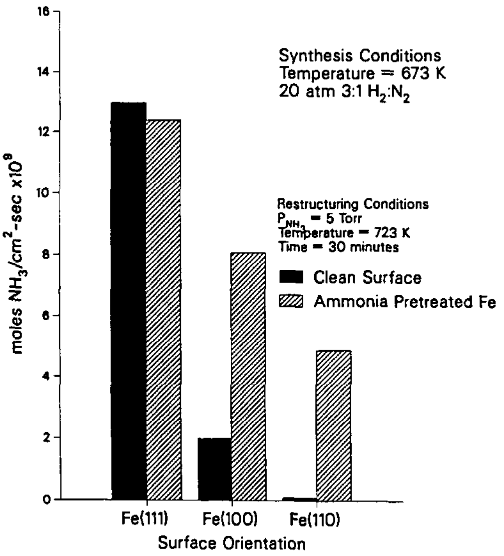


FIG. 1. Rates of ammonia synthesis over clean Fe single crystals of (111), (100), and (110) orientation and those pretreated in ammonia prior to ammonia synthesis. Ammonia pretreatment greatly enhances the activities of Fe(110) and Fe(100), while it has little effect on the ammonia synthesis activity of Fe(111).

3.2. *The Effects of Adsorbed Nitrogen on Fe Surfaces for Ammonia Synthesis*

3.2.1. The surface composition of the ammonia-pretreated iron single-crystal surfaces. After treatment of the iron single crystals with ammonia, a large concentration of nitrogen was detected by AES in the iron near-surface region ($C_N = 1$, $\theta = 0.6$) and no LEED pattern was obtained. The surfaces could be briefly sputtered to remove surface nitrogen, but the rate of synthesis over these surfaces was identical to those with the high initial nitrogen surface concentrations. Post-reaction AES showed a nitrogen-to-iron ratio of approximately 0.2 ± 0.02. To recover the high surface concentration of nitrogen (C_N) the samples could be heated to temperatures greater than 973 K, where nitrogen surface segregates and begins to desorb from the surface. However, this high-temperature purging starts to deactivate the restructured (100), and (110) surfaces, as evidenced by a decrease in ammonia synthesis activity. Removing all the bulk nitrogen, at elevated temperatures, deactivated the restructured surfaces to the respective clean surface through this annealing process.

3.2.2. The coverage of nitrogen at high ammonia synthesis conversions over Fe(111) and K/Fe(111). Experiments were performed to study the effect of adsorbed nitrogen on a Fe(111) surface. Conditions were carefully avoided which would lead to substantial bulk concentrations of nitrogen (see ammonia pretreatment). The Fe(111) and K/Fe(111) surfaces were exposed to mixtures of nitrogen, hydrogen, and ammonia which represented ammonia-synthesis reaction conversions of 0.1%, 0.3% (P_{NH_3} = 20 Torr), 2.5% (P_{NH_3} = 200 Torr), and 5% (P_{NH_3} = 400 Torr) at 673 K. Rates of ammonia production over the 1 cm^2 surfaces were too low to measure; instead the coverage of nitrogen on the iron surfaces was monitored by post-reaction AES. The ratio of the 381-eV-nitrogen peak to the 652-eV-Fe Auger peak ranged from 0.17 ± 0.02 to 0.39 ± 0.03 for the 0.1% and 5% reaction conversions, respectively. In absolute nitrogen coverages these C_N values range from $\theta_N = 0.09$ to $\theta_N = 0.21$ for C_N equal to 0.17 and 0.39, respectively. The relative concentrations of nitrogen to iron was the same on the K/Fe surfaces, within experimental error. To rule out the possibility that nitrogen might adsorb on the Fe(111) surface during evacuation of the reaction cell, the sample was kept at 373 K and 673 K during this step, after two separate reactions. The nitrogen concentration measured by AES after each reaction was identical at each temperature.

As was mentioned before, rates of ammonia formation at high reaction conversion (>0.5%) were not attainable, due to the small iron catalyst surface area. It has also been shown that high nitrogen concentrations, attained at high reaction conversion, were stable in UHV after evacuation of the reaction cell. Surfaces prepared in this way were then returned to the reaction cell and initial rates of synthesis were recorded. In all cases the N/Fe(111) surfaces prepared at high conversion showed identical rates to clean Fe(111) at a conversion of 0.1%. Post-reaction Auger showed that all Fe(111) surfaces exhibited similar nitrogen-to-iron ratios (0.17, $\theta_N = 0.09$), suggesting that high coverages of nitrogen achieved at high conversion (5%) were rapidly removed at 0.1% conversion. However, this loss of surface nitrogen was not observed as an increase in ammonia production when the Fe surfaces prepared at high reaction conversions were run at 0.1% reaction conversion. Thus, the post-reaction surface concentration of nitrogen is only a function of the ammonia partial pressure during ammonia synthesis, when the partial pressure of nitrogen and hydrogen are held constant.

3.2.3. Fe surfaces with Al_xO_y and/or potassium additives pretreated with ammonia prior to reaction. The addition of Al_xO_y to the (111), (100), and (110) surfaces of iron decreases the rate enhancement for ammonia synthesis over (110) and (100) which occurs upon ammonia pretreatment. As increasing amounts of Al_xO_y are added to the surface the amount of restructuring decreases as evidenced by decreases in the ammonia synthesis activity. At 1 ml coverage of Al_xO_y the ammonia-induced restructuring of the iron single-crystal surfaces is entirely inhibited. Post-reaction AES finds that the surface concentration of Al_xO_y after the ammonia pretreatment is identical to the initial Al_xO_y surface concentration.

The presence of potassium adsorbed alone or coadsorbed with Al_xO_y has no inhibiting effect on the restructuring process. Iron surfaces with coverages of potassium ranging from 0.1 to 1 ml pretreated with ammonia showed the same initial rate of ammonia synthesis as those surfaces pretreated without potassium.

3.3 Structural Characterization of the Restructured Iron Surfaces

3.3.1. Temperature-programmed desorption. The desorption of ammonia from iron single crystals, after a high-pressure ammonia synthesis reaction, is sensitive to surface structure (*4*). Both Fe(111) and Fe(211) are found to exhibit two desorption peaks with peak maxima at 570 and 650 K. The Fe(100) and Fe(110) faces of iron show only ammonia desorption at 650 K.

When Fe(111), Fe(100), and Fe(110) are treated with 5 Torr of ammonia prior to reaction there are marked changes in the post-reaction TPD. Both Fe(100) and Fe(110) develop the low-temperature peak at 570 K that is characteristic of Fe(111) or Fe(211) orientations (*4*), while the 650 K peak shows little change.

3.3.2. Scanning-electron microscopy. The microscopic appearance of all ammonia-pretreated iron surfaces was studied by scanning electron microscopy (SEM). The SEM micrographs of the ammonia-treated (110), (100), and (111) faces of iron are shown in Fig. 2 (the clean surfaces are smooth and featureless). In the case of the (111) surface the new features which appear upon ammonia pretreatment were large enough and sufficiently separated from each other to allow a stereographic investigation to determine what crystallographic planes were being created upon ammonia treatment.

Figure 3 shows an isolated feature with the projection of the ⟨110⟩ crystallographic axis onto the (111) surface indicated (determined by Laue X-ray crystallography). By determination of the base length (D_0) and height of the feature (Z_c) by SEM, the angle in which plane (*a*) intersects the (111) plane could be determined. The base length, D_0, was determined by measuring the distance in the SEM micrograph taken at 0° tilt (the electron beam is perpendicular to the (111) surface). The distance, D_r, was then determined from a SEM micrograph, taken when the sample was tilted 20° from the electron beam. The height of the feature was determined (see Fig. 4) from the geometric relation (*18*)

$$Z_c = \frac{(D_r - D_0 \cos 20°)}{(\sin 20°)}. \qquad (1)$$

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

4. DISCUSSION

The results presented in this paper lead to several conclusions. 1) Perhaps the most important is that high partial pressures of ammonia restructure Fe(110), Fe(100), and Fe(111) surfaces. The ammonia-induced restructuring of Fe(110) and Fe(100) produces new surfaces which contain C_7 sites, while restructuring Fe(111) results in the creation of Fe(211) surfaces. 2) The high concentrations of nitrogen in the iron bulk and on the surface, which are present after the ammonia-induced restructuring, do not affect ammonia-synthesis activity. This result suggests that the strongly bound nitrogen does not sit on active catalytic sites in ammonia synthesis and that diffusion of nitrogen from the bulk to the iron surface is unimportant during ammonia synthesis. (The possibility that the nitrogen observed by AES is mostly beneath the outermost surface cannot be ruled out by the experments presented in this research.) 3) Alu-

TABLE 1

Summary of SEM Results

No.	α (°)	D_0 (μm)	D_r (μm)	Z_c (μm)	θ (°)	Crystal face
1	0	2.86		.958	18.5	(112)
1	20		2.36	—	—	—
2	0	2.52		.842	18.5	(112)
2	20		2.08	—	—	—
3	0	2.70		.869	17.9	(112)
3	20		2.24	—	—	—

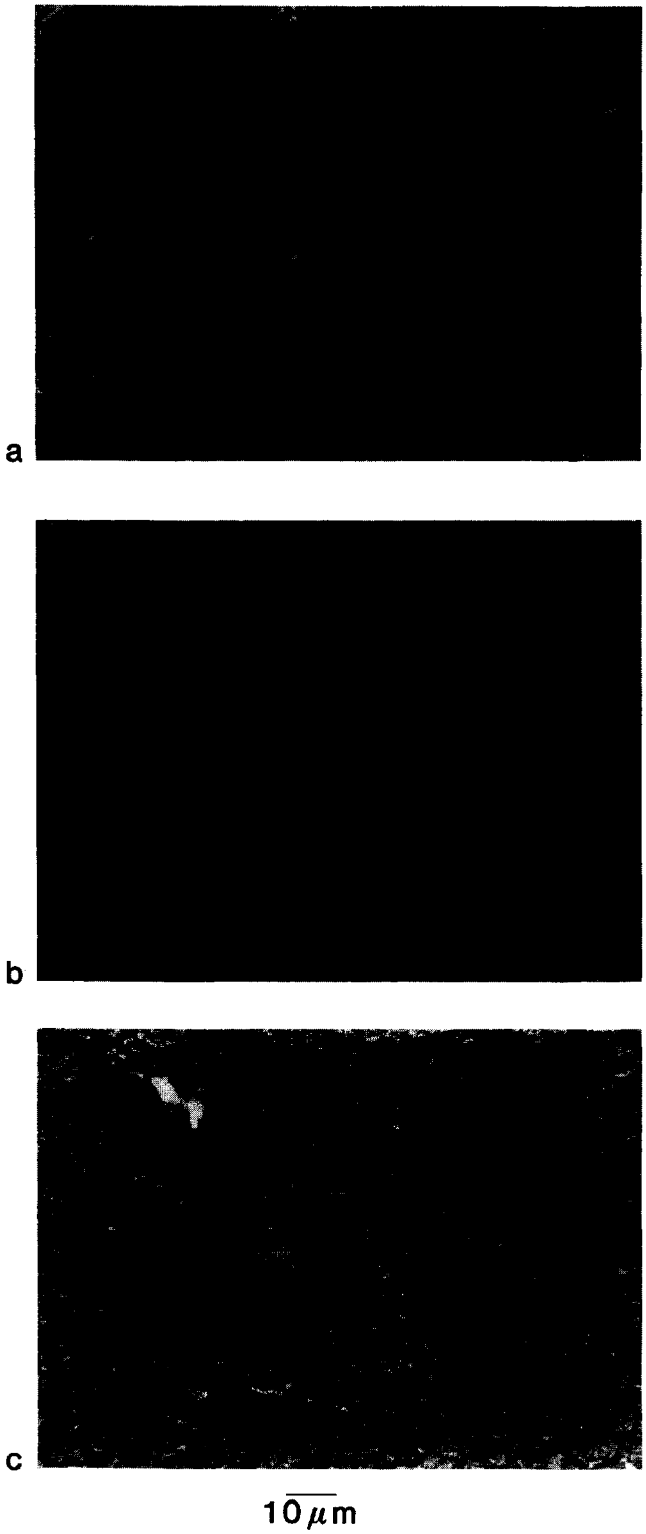


FIG. 2. Scanning electron micrographs of the (a) Fe(111), (b) Fe(100), and (c) Fe(110) surfaces after they were treated in 5 Torr of ammonia at 723 K for 30 min indicating the restructuring of all three crystal orientations. Single-crystal surfaces which have not been ammonia treated appear smooth and featureless in SEM.

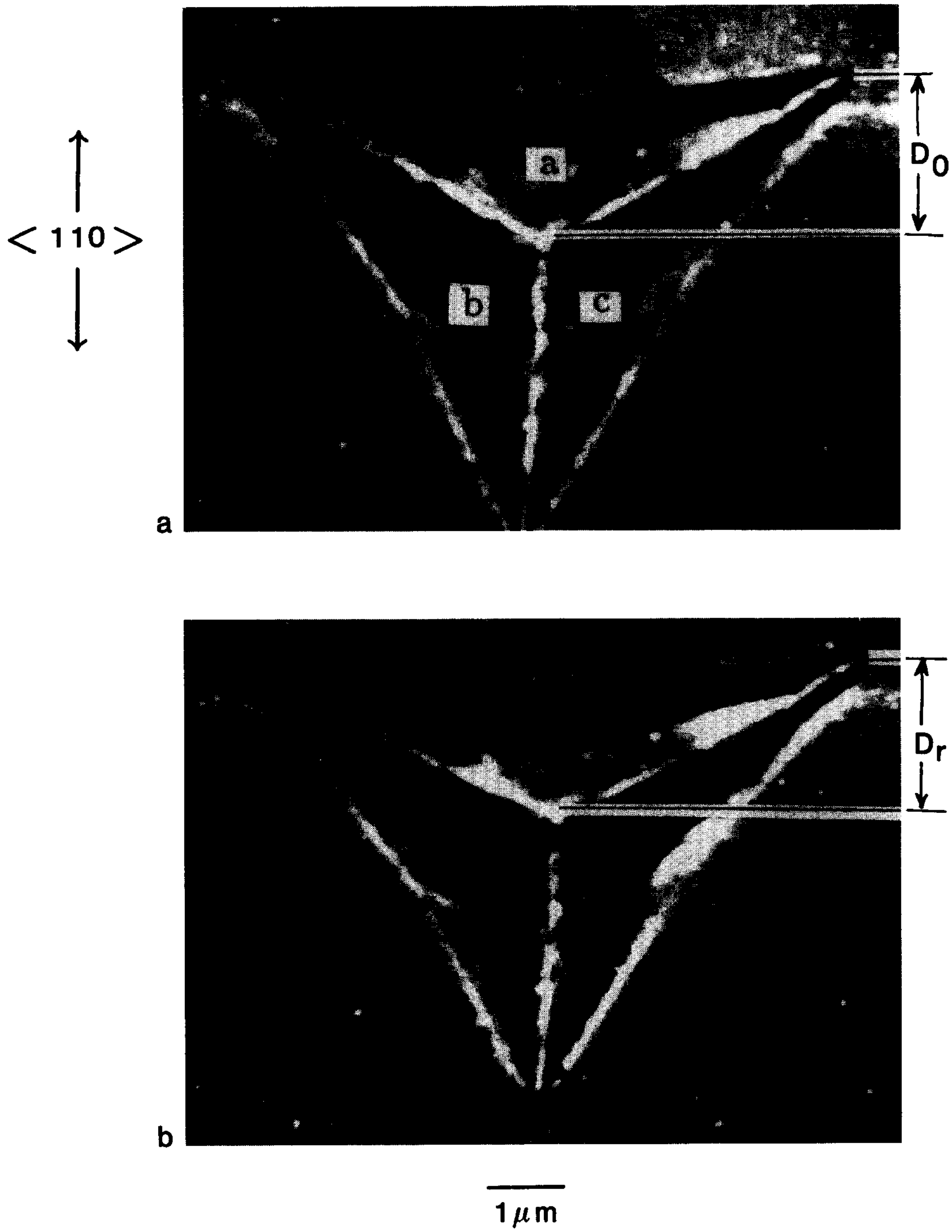
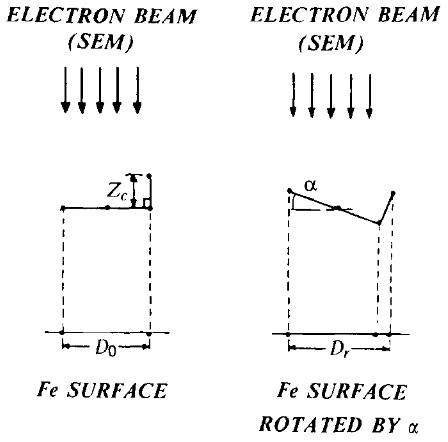


FIG. 3. Magnified view of restructured Fe(111) surface at (a) $\alpha = 0°$ tilt and (b) $\alpha = 20°$ tilt. Parameters used in the stereo pair study are shown in the figure along with the ⟨110⟩ crystallographic direction (determined by Laue X-ray crystallography).



$$D_r = D_0 \cos\alpha + Z_c \sin\alpha$$

$$Z_c = \frac{D_r - D_0 \cos\alpha}{\sin\alpha}$$

FIG. 4. Stereo pair geometry and equations solved for tilt angle α.

minum oxide and potassium exhibit different behavior during ammonia pretreatment. Potassium shows no inhibiting effect while aluminum oxide inhibits ammonia-induced restructuring of iron single-crystal surfaces.

4.1. Nitrogen-Induced Restructuring of Fe(110) and Fe(100)

Analysis of the reaction-rate results, temperature-programmed desorption data, and scanning electron microscopy suggest that Fe(100) and Fe(110) are restructured to surfaces which contain highly coordinated iron surface atoms. The most active site for ammonia synthesis is usually accepted to be the C_7 site which is present on the highly active Fe(111) and Fe(211) surfaces. The presence of the C_7 site on ammonia-restructured Fe(100) and Fe(110) is supported by the temperature-programmed desorption results. The growth of a low-temperature peak on restructured (100) and (110), similar to the peak found on clean Fe(111) and Fe(211), suggests that C_7 sites are being formed during the ammonia pretreatment. This low-temperature peak was found to appear on Al_xO_y/Fe surfaces which had been restructured in the presence of water vapor. In our previous study (*4*) restructuring Al_xO_y/Fe(100) and Al_xO_y/Fe(110) in water vapor produced surfaces as active as Fe(111). Thus, water vapor treatment of Al_xO_y/Fe surfaces creates more active surfaces than those restructured in ammonia. However, in both cases, the restructured Fe(100) and Fe(110) exhibit high activity due to the creation of C_7 sites.

4.2. SEM Analysis of the Restructured Fe(111) Surface

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

(211) surface is only slightly less active than the (111) face of iron (*5*).

The activity of the (111) and (211) faces of iron is usually attributed to the presence of C_7 sites (Fe atoms with seven nearest neighbors) which are able to enhance the rate-limiting step in the ammonia-synthesis reaction, the dissociation of nitrogen. The presence of these highly coordinated sites might also explain the increased dissociation rate of ammonia over the (111) plane of *bcc* tungsten relative to W(110) and W(100) (*20*). It seems then that surfaces which expose C_7 sites are stabilized by the chemisorption of atomic nitrogen and it would be thermodynamically favorable for the Fe(111) surface, with a surface free energy (γ) of 1460 ergs/cm^2, to restructure to the more densely packed Fe(211) plane (γ_{211} = 1350 ergs/cm^2) (*21*) (which contains C_7 sites) in the presence of ammonia.

4.3. *The Effects of Adsorbed and Dissolved Nitrogen on Iron During Ammonia Synthesis*

The presence of adsorbed nitrogen, present during ammonia synthesis, seems not to affect ammonia-synthesis activity under the conditions used in this study. Surfaces restructured in ammonia produce high near-surface concentrations of nitrogen, but these surfaces are no more active than surfaces where the near-surface nitrogen has been removed prior to ammonia synthesis. This suggests that at 673 K, where ammonia synthesis is carried out, the diffusion of nitrogen from the bulk is not an important process, in agreement with recent theoretical work (*19*). These results also suggest that the nitrogen detected in UHV does not reside on catalytic sites during ammonia synthesis, since rates are the same over nitrogen-free and nitrided Fe surfaces after ammonia pretreatment. For example the rate over an Fe(111) surface with a nitrogen surface concentration of $\theta_N = 0.6$ is identical to an Fe(111) surface with a $\theta_N = 0.09$. Also, our studies of adsorbed nitrogen on Fe(111) which had not undergone ammonia pretreatment agree with the idea that the surface concentration of nitrogen on Fe is determined by the gas-phase ammonia concentration, since N/Fe(111) surfaces prepared at high conversion (5%, P_{NH_3} = 400 Torr) are not stable at low conversion (0.1% or 0.3%).

4.4. *The Effects of Aluminum Oxide and Potassium on the Restructuring of Fe*

The presence of Al_xO_y on the Fe surface inhibits the restructuring process induced by ammonia. Aluminum oxide seems to block the iron surface which could otherwise dissociate ammonia. This blocking of the restructuring process by Al_xO_y is in sharp contrast to the case where aluminum oxide catalyzes the restructuring of iron in the presence of water vapor prior to ammonia synthesis (*4*). In this circumstance iron oxide is found to migrate on top of the aluminum oxide overlayer as a result of the oxidizing environment (water vapor). The major driving force for this structural transformation is most likely compound formation between iron oxide and aluminum oxide.

When nitrogen is the restructuring agent it is not thermodynamically favorable for iron nitride to cover aluminum oxide, probably because of the absence of a strong chemical interaction between iron nitride and aluminum oxide. Hence, AES finds aluminum oxide on the iron surface after Al_xO_y/Fe surfaces have been pretreated in ammonia. Contrary to this, in the case of restructuring in water vapor, AES finds that Al_xO_y leaves the iron surface region, residing underneath the active iron surface.

The presence of potassium on Fe during ammonia pretreatment has no additional effect on the restructuring process when adsorbed alone or when coadsorbed with Al_xO_y. Thus, potassium does not seem to affect the structural promotion of ammonia-synthesis catalyst under our experimental conditions, during either ammonia or water-vapor treatment. However, the presence of potassium on an Al_xO_y/Fe surface during water-vapor pretreatments inhibits restructuring. A likely explanation for this observation is that the formation of potassium aluminate blocks the interaction between iron oxide and aluminum oxide (*16*). These results argue against potassium being a structural promoter. Instead, promotion by potassium in ammonia synthesis seems to be solely electronic in nature, since potassium has been shown to increase the rate of nitrogen dissociation (rate-limiting step) (*22, 23*) and to decrease the concentration of ammonia product, thus opening up more active surface for the rate-limiting step (*16, 23*).

Tables 2 and 3 summarize the effects of water-vapor and ammonia pretreatment on the initial rate of ammonia synthesis over Fe, Al_xO_y/Fe, and K/Al_xO_y/Fe surfaces. The tables show that the presence of aluminum oxide promotes the restructuring of iron during the water-vapor pretreatment, but it inhibits the ammonia-induced restructuring. The presence of potassium shows no effect in the ammonia pretreatment and it inhibits water-vapor-induced restructuring of iron. These results suggest that to form the most active ammonia-synthesis catalyst from an iron single-crystal surface by utilizing both pretreatments, the iron should first be restructured in ammonia before aluminum oxide is added. After aluminum oxide is added the surface should be treated in water vapor and finally potassium should be added to serve as a promoter at high ammonia-synthesis-reaction conversions. However, it is not clear whether the ammonia pretreatment is required in the activation of the iron single crystal, since optimal activity can also be achieved by using the water-vapor pretreatment alone.

TABLE 2

Surface	Rate[a] clean surface	Rate[a] after NH_3 pretreatment of		
		Clean surface	0–1 ml Al_xO_y on Fe surface	0–1 ml K on Al_xO_y/Fe surface
Fe(111)	1.3	1.2	1.2–<0.01	1.2–<0.01
Fe(100)	0.2	0.8	0.8–<0.01	0.8–<0.01
Fe(110)	<0.01	0.5	0.5–<0.01	0.5–<0.01

[a] Initial rate × 10^8 moles NH_3/cm^2 – sec.

TABLE 3

Surface	Rate[a] clean surface	Rate[a] after NH_3 pretreatment of		
		Clean surface	2 ml Al_xO_y on Fe surface	0–1 ml K on Al_xO_y/Fe surface
Fe(111)	1.3	1.3	1.2	1.2–<0.01
Fe(100)	0.2	0.2	1.1	0.8–<0.01
Fe(110)	<0.01	<0.01	1.2	1.2–<0.01

[a] Initial rate × 10^8 moles NH_3/cm^2 – sec.

5. SUMMARY

The ammonia-induced restructuring of Fe(110), Fe(100), and Fe(111) surfaces has been reported. The restructured (110) surface becomes twice as active as the Fe(100) surface while the restructured Fe(100) surface increases by a factor of 4 over the respective clean surface. The Fe(111) surface shows only a small decrease in ammonia-synthesis activity upon ammonia-induced restructuring. The kinetic data and temperature-programmed desorption results suggest that Fe(100) and Fe(110) restructure to highly active surfaces, which contain C_7 sites, in the presence of ammonia. High coverages of nitrogen dissolved in the bulk and adsorbed on the surface after ammonia pretreatment do not affect ammonia-synthesis kinetics.

A stereographic investigation of the restructured Fe(111) surface suggests that surface planes of {211} orientation (which have been found to be highly active in ammonia synthesis) are developing on the surface due to the high virtual pressure of nitrogen provided by the ammonia decomposition. The growth of the (211) surface orientations on the restructured (111) surface is invoked to explain the absence of a significant change in ammonia-synthesis activity when the Fe(111) surface is restructured.

The presence of aluminum oxide on the iron surface during ammonia pretreatment inhibits restructuring, while the presence of potassium produces no observable effect on the restructuring process. The results suggest that to combine both ammonia and water-vapor pretreatment (*4*) the following procedure should be used. The iron surface should be treated in ammonia with the subsequent addition of aluminum oxide. Water-vapor treatment of the surface then activates the promoter effects of aluminum oxide and the further addition of potassium promotes the iron surface at high ammonia-synthesis-reaction conversions.

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REFERENCES

1. Spencer, N. D., Schoonmaker, R. C., and Somorjai, G. A., *J. Catal.* **74,** 129 (1982).

2. Dumesic, J. A., Topsoe, H., and Boudart, M., *J. Catal.* **37,** 513 (1975).

3. Brunauer, S., and Emmett, P. H., *J. Amer. Chem. Soc.* **62,** 1732 (1940).

4. Strongin, D. R., Bare, S. R., and Somorjai, G. A., *J. Catal.* **103,** 289 (1987).

5. Strongin, D. R., Carrazza, J., Bare, S. R., and Somorjai, G. A., *J. Catal.* **103,** 213 (1987).

6. Ozaki, A., "Catalysis, Science and Technology," Vol. 1, Chap. 3. Springer–Verlag, Berlin/New York, 1981.

7. Brill, R., and Kurzidim, J., *Colloq. Int. C.N.R.S.* **187,** 99 (1969).

8. Richard, M. A., and Vanderspurt, T. H., *J. Catal.* **94,** 563 (1985).

9. Brill, R., Richter, E., and Ruch, E., *Angew. Chem. Int. Ed. Engl.* **6,** 882 (1967).

10. Bozso, F., Ertl, G., Grunze, M., and Weiss, M., *J. Catal.* **49,** 18 (1977).

11. Bozso, F., Ertl, G., and Weiss, M., *J. Catal.* **50,** 519 (1977).

12. Dowben, P. A., Grunze, M., and Jones, R. G., *Surf. Sci. Lett.* **109,** L519 (1981).

13. Weiss, M., Ertl, G., and Nitschke, F., *Appl. Surf. Sci.* **2,** 614 (1979).

14. Grunze, M., Bozso, F., Ertl, G., and Weiss, M., *Appl. Surf. Sci.* **1,** 241 (1978).

15. Loffler, D. G., and Schmidt, L. D., *J. Catal.* **44,** 244 (1976).

16. Strongin, D. R., and Somorjai, G. A., *Catal. Lett.* **1,** 61 (1988).

17. Bare, S. R., Strongin, D. R., and Somorjai, G. A., *J. Phys. Chem.* **90,** 4726 (1986).

18. Fior, G. O., Ph.D. thesis, University of California, Berkeley, CA, 1982.

19. Stoltze, P., and Norskov, J. K., *Phys. Rev. Lett.* **55,** 2502 (1985).

20. McAllister, J., and Hansen, R. S., *J. Chem. Phys.* **59,** 414 (1973).

21. Johnson, R. A., and White, P. J., *Phys. Rev.* **13,** 13 (1976).

22. Ertl, G., "Robert Welch Conferences on Chemical Research," Vol. XXV, "Heterogeneous Catalysis," p. 179. Houston, 1981.

23. Strongin, D. R., and Somorjai, G. A., *J. Catal.* **109,** 51 (1988).