

Iron Single Crystals as Ammonia Synthesis Catalysts: Effect of Surface Structure on Catalyst Activity

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The activity of three iron single-crystal faces with respect to their ability to catalyze ammonia synthesis was investigated. At 798 K and a total pressure of 20 atm of a stoichiometric mixture of hydrogen and nitrogen, the relative rates of ammonia formation were found to be 418:25:1 for Fe(111), Fe(100), and Fe(110) samples, respectively. The activation energy for ammonia synthesis on the Fe(111) surface was determined as 19.4 kcal mole⁻¹. Significant quantities of nitrogen were found to be present in the bulk and on the surface of the iron samples after catalytic runs. This is the first study in which ammonia synthesis activity has been directly correlated with surface crystallographic structure under well-defined, high-pressure conditions.

INTRODUCTION

Until recently, studies of the kinetics of ammonia synthesis have been carried out either under industrial conditions in reactors, operating at upwards of 1 atm (1 atm = 101.3 kN m⁻²) total pressure (1, 2), or indirectly in the clean environment of the ultrahigh-vacuum chamber (3) where pressures rarely exceed 10⁻⁴ Torr (1 Torr = 133.3 N m⁻²). While many useful results have come from both these approaches, the former method suffers from a lack of direct information on the nature of the catalyst surface and the latter, low-pressure, technique does not allow the synthesis of ammonia to occur to any measurable extent, since the thermodynamic equilibrium is unfavorable. The present investigation, using an apparatus which allows both UHV and high-pressure conditions to be obtained within the same chamber, bridges the pressure gap and enables the rate of formation of ammonia to be directly related to the state of the catalyst surface.

Reactor studies (1) have, with few exceptions, shown that the rate-determining step

in iron-catalyzed ammonia synthesis is the dissociative adsorption of nitrogen. Using field emission microscopy, Brill *et al.* (4) found that the (111) plane of iron preferentially adsorbed nitrogen and brief exposures to the gas resulted in the faceting of (110) and (100) planes to a (111) orientation. Furthermore, Brill and Kurzidim (5) made the suggestion, based on indirect evidence, that the Fe(111) plane of iron was the only one active in ammonia synthesis. Dumesic *et al.* (6), working with small iron particles in a reactor experiment using Mössbauer spectroscopy and CO chemisorption, came to the conclusion that seven-coordinated (C₇) iron atoms were active in ammonia synthesis. This is consistent with the work of Brill and Kurzidim (5), since the Fe(111) plane has the highest C₇ concentration. Ertl (3) and Bozso *et al.* (7, 8), using UHV techniques, reported initial rates of nitrogen adsorption at 550 K to be in the ratio 60:3:1 for Fe(111), Fe(100), and Fe(110), respectively, but because of thermodynamic limitations they were unable to investigate actual ammonia synthesis under the low-pressure conditions ($P_{N_2} \leq 10^{-4}$ Torr) that were employed.

The present study is the first which directly and unambiguously probes the iron

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catalyst surface structure sensitivity for the ammonia synthesis reaction under conditions of high temperature and pressure which approach those used in industry.

METHODS

The apparatus consisted of a bakeable stainless-steel ultrahigh-vacuum chamber of base pressure 10^{-9} Torr equipped with a four-grid retarding field analyzer for Auger electron spectroscopy, a quadrupole mass spectrometer for residual gas analysis, a sputter ion gun for specimen cleaning, and a hydraulically operated high-pressure cell (9) connected to an external stainless-steel loop. After closing the high-pressure cell, reactant and product gases at a total pressure of 20 atm were circulated over the heated iron crystal specimen by a positive displacement pump. Samples were periodically withdrawn using a gas chromatography-type sampling valve and swept by a nitrogen carrier gas into a photoionization detector (PID, lamp energy = 10.2 eV) in order to determine the amount of ammonia in the loop. With the photon energy employed, ammonia was the only species present which could be detected by the PID, rendering a separating column unnecessary. The detection system was calibrated by introducing known amounts of ammonia into the loop followed by pressurizing to 20 atm with a stoichiometric (1:3) mixture of nitrogen and hydrogen. The output signal of the PID was found to be a linear function of ammonia concentration in the regime encountered in our synthesis experiments: the partial pressure of ammonia produced in a synthesis run typically did not exceed 10 Torr, which at 723 K would be about 1.5% of the equilibrium value.

The high-pressure loop consisted primarily of $\frac{1}{4}$ -in (6.4 mm) stainless-steel tubing and had a total volume of 170 cm³. Initially, the loop was contaminated with oxygen and chlorine, which were removed by cooling an isolable condenser section with liquid nitrogen while circulating hydrogen gas at 6

atm pressure for several hours and by subsequently flushing the loop several times with 15 atm of hydrogen before each synthesis run. The usual flow rate of gas in the loop during a run was ~ 157 cm³ sec⁻¹ providing some laminar flow in the straight sections of loop ($N_{Re} = 200$), but turbulence and mixing at corners and constrictions. Reactants were mixed *in situ* by slowly bleeding nitrogen into circulating hydrogen, and product ammonia was allowed to build up in the high-pressure loop during the run. Pumping of the loop was achieved by a combination of mechanical and liquid nitrogen sorption pumps, and after most runs the crystal was maintained at reaction temperature until the loop was pumped out and the cell reopened to the UHV chamber.

Iron is a metal with a body-centered cubic lattice. The three low-index planes used in the present study are shown in Fig. 1. The Fe(110) plane is the closest-packed iron surface with only six-coordinated (C_6) atoms exposed. The Fe(100) plane is less closely packed and only has four-coordinated (C_4) atoms in its surface. The Fe(111) plane was the most open surface studied and has both C_4 and seven-coordinated (C_7) atoms exposed. Three approximately circular iron specimens were cut from a high-purity (4N) single-crystal rod and diamond polished, the final dimensions being approximately 6 mm diameter and 1 mm thickness.

The specimens were spot-welded to 0.25-mm platinum support wires which, in turn,

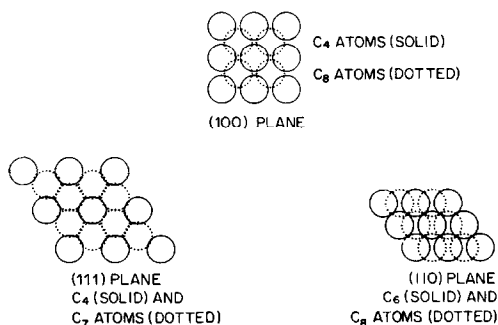


FIG. 1. Low-index planes of iron.

were spot-welded to 2-mm platinum rods on the manipulator. Platinum was chosen as a support material because of its inactivity as an ammonia synthesis catalyst. The crystal temperature was controlled to ± 0.5 K and monitored by a Chromel-Alumel thermocouple, spot-welded to the edge of the specimen. Sulfur and carbon were the principal contaminants in the iron, but the surface concentrations of these could be substantially reduced by several days of heating at 1070 K in 1 atm of hydrogen, prior to insertion into the chamber, followed by many cycles of argon ion bombardment (on both sides of the specimens) and annealing at 973 K. In order to minimize catalysis occurring on ill-defined iron surfaces, platinum foil was spot-welded to the rough edges of the specimens.

RESULTS

1. The (111) Crystal Face of Iron

The gradual buildup of ammonia in the high-pressure loop during a typical synthesis run at 736 K is shown in Fig. 2. The shape of the initial portion of the curve is the result of slow diffusion and adsorption

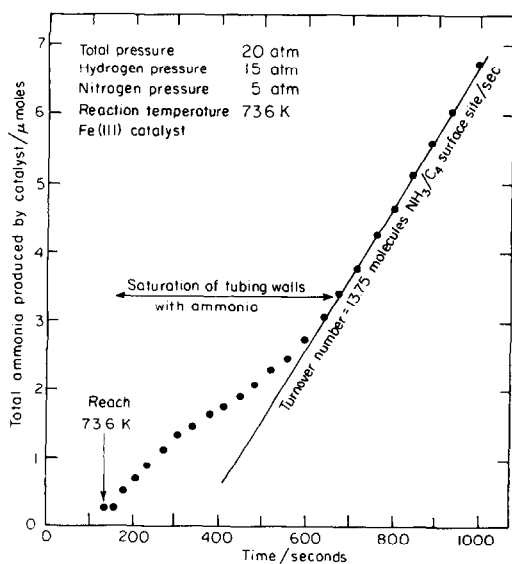


FIG. 2. Increase in ammonia concentration in loop during run.

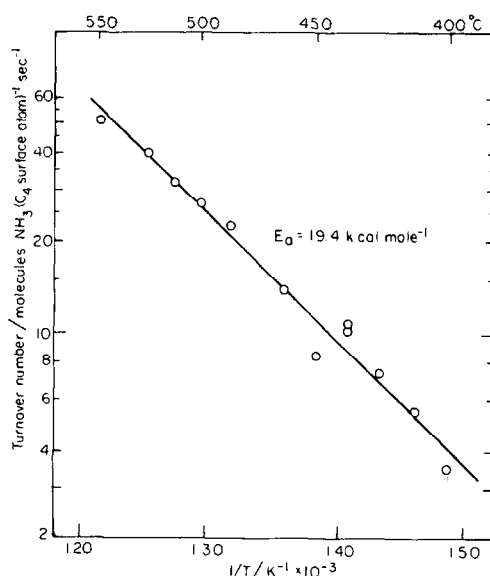


FIG. 3. Arrhenius plot for ammonia synthesis on Fe(111).

of ammonia on the walls of the loop. Although the initial increase in ammonia concentration nearly corresponds to the total rate of synthesis, there follows a period during which ammonia starts to adsorb on the walls of the loop and the detected rate of formation is equal to the actual rate only after the walls have become saturated. In order to test this hypothesis, enough ammonia (~ 1 Torr) was added to the initial reactant mixture to saturate the walls, with the consequence that the detected ammonia increased from the outset at a constant rate. A turnover number for the catalyst can be derived from the part of the curve where ammonia concentration increases linearly. In the case of Fe(111) at 736 K (Fig. 2), the turnover number is 13.75 molecules NH_3 per C_4 surface atom per second. The turnover numbers (based on the number of C_4 atoms) for the Fe(111)-catalyzed reaction were determined at several temperatures within a 150 K range and plotted vs reciprocal temperature in Arrhenius form (Fig. 3). The activation energy derived from the straight line so obtained was 19.4 kcal mole $^{-1}$. The gross kinetic effects of varying

TABLE I
Effect of Changing Reactant Partial Pressures

Run temperature (K)	P_{N_2} (atm)	P_{H_2} (atm)	P_{Ar} (atm)	P_{total} (atm)	Turnover number (molecules NH_3 (C_4 atom) $^{-1}$ sec $^{-1}$)
748	15	5	0	20	11.1 ± 2.0
748	5	15	0	20	12.7 ± 2.0
748	5	5	10	20	3.2 ± 1.0
748	5	5	0	10	5.0 ± 1.0

the partial pressure of the reactants at a crystal temperature of 748 K were also briefly investigated and the results are summarized in Table 1, where it can be seen that the turnover number is sensitive to both hydrogen and nitrogen partial pressures under these conditions, although extensive data which would be necessary to derive an exact kinetic expression were not obtained.

As is evident from the Auger spectra (Fig. 4) taken before and after the run shown in Fig. 2, the catalyst surface was clean prior to the synthesis reaction apart from a small amount of oxygen. This was removed during the run, presumably by the hydrogen as water. After the reaction, apart from a small amount of sulfur which had diffused out of the bulk iron (a process which appears to be enhanced by the presence of hydrogen) the only noniron surface species detected was nitrogen. This was always present after catalytic runs, even if they were terminated at a point where the first small ammonia production was observed. This nitrogen could not be removed by heating alone, which suggests that it is present not simply as an adsorbed species (7). Moreover, argon ion bombardment at room temperature, while cleaning the surface (as monitored by Auger spectroscopy), did not remove *all* nitrogen, which continued to be evolved at elevated temperatures. The nitrogen could, however, be removed by circulating 15 atm of hydrogen over the sample while it was being maintained at a temperature similar to that used in the syn-

thesis run. This procedure led to the formation of some ammonia which, although too low in concentration to be detected by the PID, was found in the background gas mass spectrum at a low level after the loop was evacuated and the high-pressure cell reopened to UHV. When a synthesis reaction was carried out immediately on the N-contaminated surface from a previous run, ammonia was produced at a rate identical to that obtained on the clean surface. When an

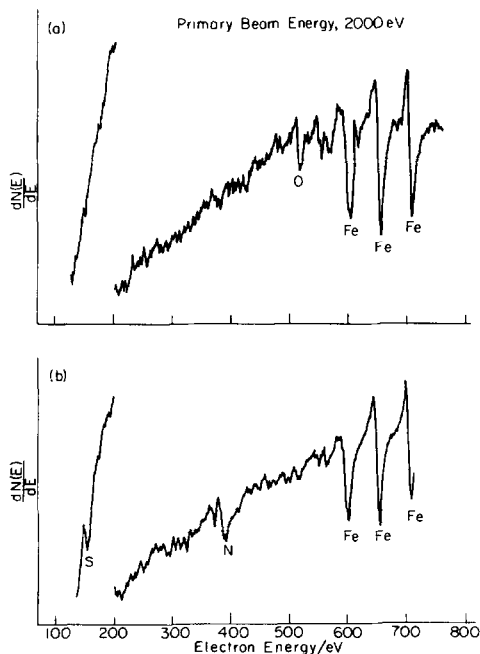


FIG. 4. Auger spectra: (a) before synthesis run; (b) after synthesis run.

initially clean crystal was heated at 673 K in 5×10^{-4} Torr of ammonia for 10 h to produce several layers of Fe_4N (10), the subsequent Auger spectrum of the sample strongly resembled Fig. 4b, which suggests that a similar amount of nitrogen was deposited during a normal catalytic run. A synthesis run carried out on the ammonia-treated sample showed catalytic activity which was comparable to that of the clean crystal.

If the sample was heated *in vacuo* for several hours at 973 K, large quantities of sulfur were found to segregate to the surface, presumably forming FeS (11). When treated in this way, the sample was totally inactive as an ammonia synthesis catalyst, as might be expected from industrial observations that sulfur is a serious poison of the real catalyst.

An attempt was made to study the catalytic activity of a heavily oxidized iron surface, but the oxide was found to be so short-lived under the reducing conditions of the reactant mixture that its activity could not be distinguished from that of clean iron. Addition of 5 Torr of water to the reaction mixture, however, completely suppressed catalytic activity, possibly suggesting that if it is continually replenished, the oxidized surface is inactive as a catalyst.

There was no effect on the turnover number (Table 2) when the $\text{Fe}(111)$ sample was argon ion bombarded on both sides for varying lengths of time before some of the catalytic runs. In order to test for the possibility that the stainless-steel high-pressure cell was catalyzing the reaction, the $\text{Fe}(111)$ crystal was replaced by a platinum sample of similar dimensions in order to reproduce, as closely as possible, the heat transfer between the crystal and the cell walls. When subjected to the usual synthesis reaction conditions at 773 K for many minutes, the platinum sample and cell walls produced no ammonia either as detected in the PID or as background gas in the mass spectrum after the cell was reopened to the UHV chamber.

2. The (110) (Close-Packed) Crystal Face of Iron

After thorough cleaning and annealing of the $\text{Fe}(110)$ specimen, it did not produce enough ammonia to be detected by the PID under the catalytic conditions used in the studies of ammonia synthesis on the $\text{Fe}(111)$ surface. It did catalyze the synthesis reaction to a small extent, however, since ammonia could be seen in the background mass spectrum after reopening the cell to the UHV chamber. If the detection limit of the PID is taken to be the upper limit on ammonia production for the $\text{Fe}(110)$ sample, the catalytic activity of the (111) specimen is at least 418 times larger than that of the (110) crystal. Brief argon ion bombardment (1.5×10^{-5} A cm^{-2} for 10 min at 500 V) without subsequent annealing of the $\text{Fe}(110)$ surface increased its catalytic activity by nearly an order of magnitude although it was still far below that of the $\text{Fe}(111)$ surface. Exposure to catalytic conditions produced a significant nitrogen signal in the Auger spectrum taken after the cell was reopened to UHV.

3. The (100) Crystal Face of Iron

The rate of ammonia synthesis on this crystal face lies between those of the (111) and (110) faces. It was found to have an activity of approximately $\frac{1}{16}$ th that of the $\text{Fe}(111)$ face, and its activity increased by nearly a factor of 2 after deliberate disordering of the surface by argon ion bombardment (Table 2). Using the PID limit of detection for activity on the (110) face, we obtain activity ratios of $\sim 418:25:1$ for $\text{Fe}(111):\text{Fe}(100):\text{Fe}(110)$. As with the other two surfaces, nitrogen was present in the Auger spectrum after all synthesis runs on this plane.

DISCUSSION

The results of the present study show clearly that $\text{Fe}(111)$ is by far the most active and $\text{Fe}(110)$ the least active plane in ammonia synthesis catalysis, $\text{Fe}(100)$ having in-

TABLE 2

Ammonia Synthesis Surface Structure Sensitivity

Catalyst surface	Area (cm ²)	Rate ^a (moles NH ₃ cm ⁻² sec ⁻¹)
Fe(111)	0.63	4.6×10^{-8}
Fe(100), ordered	0.80	2.8×10^{-9}
Fe(110), ordered	0.57	1.1×10^{-10} ^b
Fe(100), disordered ^c	0.80	4.5×10^{-9}
Fe(110), disordered ^c	0.57	9.7×10^{-10}

^a Total pressure, 20 atm (2.03 MNm⁻²), $P_{H_2}/P_{N_2} = 3/1$, temp. = 798 K.

^b Detection limit of photoionization detector.

^c Argon ion bombardment (1.5×10^{-5} A cm⁻² for 600 sec at 500 V).

intermediate activity and all three surfaces being partially covered with nitrogen after the reaction. The activation energy for ammonia synthesis has also been determined for the Fe(111) face as being 19.4 kcal mole⁻¹. The presence of surface nitrogen and oxygen did not appear to affect the performance of the single crystals as catalysts, the oxygen being rapidly removed as soon as the samples were heated in the reaction mixture. Both surface sulfur and small quantities of water in the reactant mixture were found to suppress all catalytic activity in the samples. Deliberate surface disordering by argon ion bombardment of the samples, while not noticeably affecting the catalytic activity of the Fe(111) surface, was found to increase those of the Fe(100) and Fe(110) specimens, the activity of the latter being enhanced by nearly an order of magnitude over the ordered surface value.

The actual activity ratio of Fe(111):Fe(100):Fe(110) at 798 K was found to be 418:25:1 for catalysis of ammonia synthesis, ammonia being formed at a rate of 4.6×10^{-8} moles cm⁻² sec⁻¹ on the Fe(111) face at this temperature. This is in broad agreement with the ratio obtained (3, 7, 8) for nitrogen dissociative chemisorption (60:3:1), the discrepancy probably being due to slight differences in crystal orientation (which would have a great effect in the case of the least active (110) crystal), temperature differences (the chemisorption results were obtained at 550 K, whereas the

present work was carried out at 798 K), and differences in nitrogen coverage (the chemisorption results refer to rates at zero coverage). The activation energy for the synthesis reaction is consistent with that obtained by Scholten and Zwietering (12) for nitrogen chemisorption on the real catalyst (10–30 kcal mole⁻¹, depending on the coverage). This, together with the similarity of the relative nitrogen adsorption and ammonia synthesis activities for the different crystal planes adds further support to the now generally accepted conclusion that nitrogen dissociative chemisorption is the rate-determining step in iron-catalyzed ammonia synthesis.

The state of the surface during the reaction and the nature of the catalytically active site are still not certain. Although a considerable amount of surface nitrogen appeared in the Auger spectrum *after* ammonia synthesis runs in the present study, we may not infer that nitrogen is necessarily present in significant quantities on the catalyst surface while ammonia is actually being synthesized. The fact that the nitrogen can be removed by hydrogen treatment implies that the surface nitrogen seen in the Auger spectrum is similar in nature to that which reacts to form ammonia during the synthesis run, and it should not be regarded as inactive. Nitrogen is known to dissolve in the bulk of iron (7), and during the reaction a considerable amount of atomic nitrogen presumably diffuses away from the catalyst surface into the bulk before it can react with surface hydrogen. It is possible that the postrun surface nitrogen (which may be a thin layer of Fe₄N as described by Ertl *et al.* (10) diffuses back from the bulk and segregates at the surface while the crystal is still at reaction temperature and the reactants are being pumped away. As has been suggested by Bozso *et al.* (7), the outward-diffusing nitrogen may cause a reconstruction at the surface to form a surface nitride. Such a surface may also be present during synthesis, but at present there is insufficient evidence to substantiate its existence.

It would appear (Table 2) that the close-packed Fe(110) plane contains few, if any, active sites, but that active sites are created by argon ion bombardment, where the term "active sites" is taken to mean sites upon which the catalytic reaction occurs or regions of the surface which may be converted to such sites (e.g., by the formation of a surface compound). Furthermore, it is clear that the total number of active sites on the Fe(111) plane is insensitive to argon ion bombardment. These observations are consistent with the hypothesis of Dumesic *et al.* (6) that C₇ iron atoms are components of the active site, since the inclusion of surface vacancies by argon ion bombardment can be envisioned as causing a substantial increase in the number of C₇ atoms on the close-packed Fe(110) surface (which initially has none) while not dramatically affecting the number on the open Fe(111) surface. However, owing to our inability to probe directly the nature of the catalyst surface during reaction, we cannot verify the details of the active site on the basis of the present data alone.

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