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Publication Date

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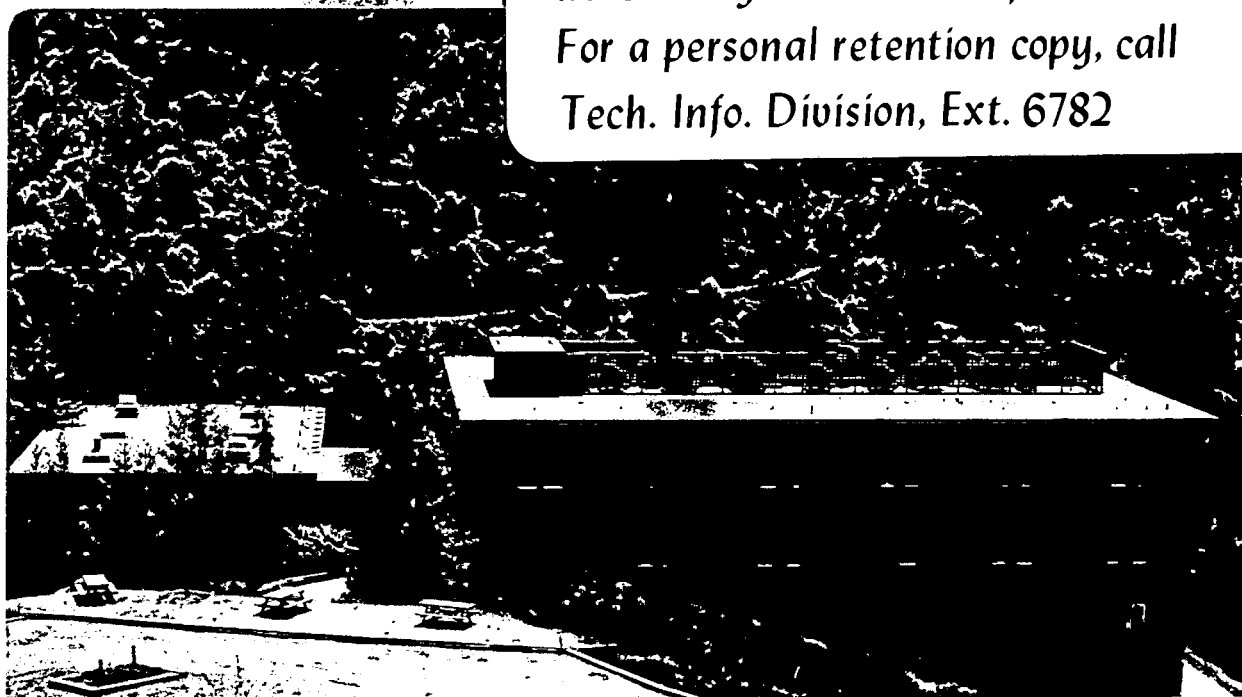
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August 1981

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IRON SINGLE CRYSTALS AS AMMONIA SYNTHESIS CATALYSTS:
EFFECT OF SURFACE STRUCTURE ON CATALYST ACTIVITY

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Abstract

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.

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This work was supported by the director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

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 kNm⁻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 Nm⁻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. 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 Mossbauer 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 et al. [3] and Boszo 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)

and Fe(110), respectively, but because of thermodynamic limitations they were unable to investigate actual ammonia synthesis under the low pressure conditions ($P_{N_2} < 10^{-4}$ torr) that were employed.

The present study is the first which directly and unambiguously probes the iron 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 4-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 was typically 10 torr, which at 723 K would be about 1.5% of the equilibrium value.

The high pressure loop consisted primarily of 1/4" (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 $\sim 157 \text{ cm}^3\text{s}^{-1}$ 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. 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 Figure 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, 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 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 during a typical synthesis run at 736 K is shown in Figure 2. The shape of the initial portion of the curve is the result of slow diffusion and adsorption 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 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/C_4 surface atom/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 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 was not obtained.

As is evident from the Auger spectra (Fig.4) taken before and after the run shown in Figure 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 non-iron 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 not simply 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 similar temperature to that used in the synthesis 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 an identical rate to that obtained on the clean surface. When an initially clean crystal was heated at 673 K in 5×10^{-4} torr of ammonia for 10 hours to produce several layers of Fe_4N [10], the subsequent Auger spectrum of the sample strongly resembled Figure 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 in 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 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 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 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 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 ($1.5 \times 10^{-5} \text{ Acm}^{-2}$ for 10 minutes at 500 V) without subsequent annealing of the Fe(110) surface increased its catalytic activity by nearly an order of magnitude although it was still far below that of the Fe(111) surface. Exposure to catalytic conditions produced a significant nitrogen signal in the Auger spectrum 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 that of the (111) and (110) faces. It was found to have an activity of approximately 1/16 that of the 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 Fe(111):Fe(100):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 Fe(111) is by far the most active and Fe(110) the least active plane in ammonia synthesis catalysis, Fe(100) having 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 $19.4 \text{ kcal mole}^{-1}$. 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 affecting the catalytic activity of the Fe(111) surface, was found to increase that 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 $4.6 \times 10^{-8} \text{ moles cm}^{-2} \text{ s}^{-1}$ 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 ($10\text{-}30 \text{ kcal mole}^{-1}$, 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 is still not certain. Although a considerable amount of surface nitrogen appeared in the Auger spectrum after all 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 hydrogen. It is possible that the post-run surface nitrogen (which may be a thin layer of Fe_4N 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.

The dependence of the rate of ammonia production on hydrogen partial pressure (Table 1) at overall conversion which is far from equilibrium is somewhat puzzling. Because we have not investigated this effect in detail, it is only possible to suggest that its origins may be the result of hydrogen enhancement of dissociative chemisorption of nitrogen at the conditions of high pressure and temperature under which these experiments were carried out [13,14].

Acknowledgements

We gratefully acknowledge Prof. P.H. Emmett, Prof G. Ertl, Prof. M. Boudart, and Dr. M. Grunze for useful discussions during the preparation of this paper.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

We are also indebted to the Dow Chemical Company for financial support.

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Figure Captions

Figure 1. Low index planes of iron

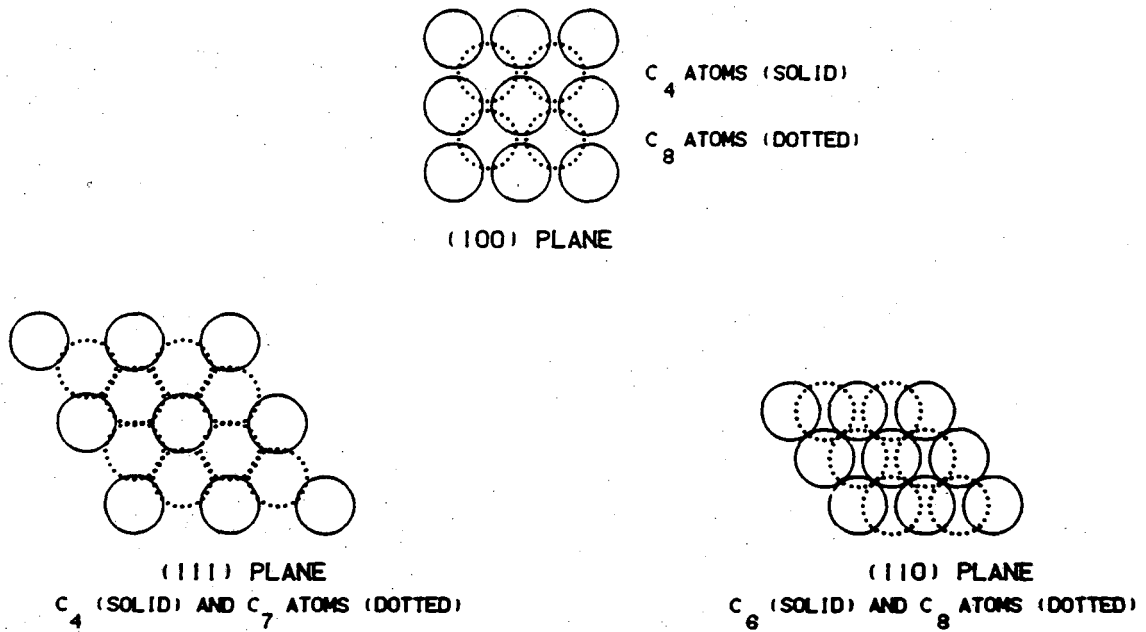
Figure 2. Increase in ammonia concentration in loop during run.

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

Figure 4. Auger spectra (a) before sythesis run

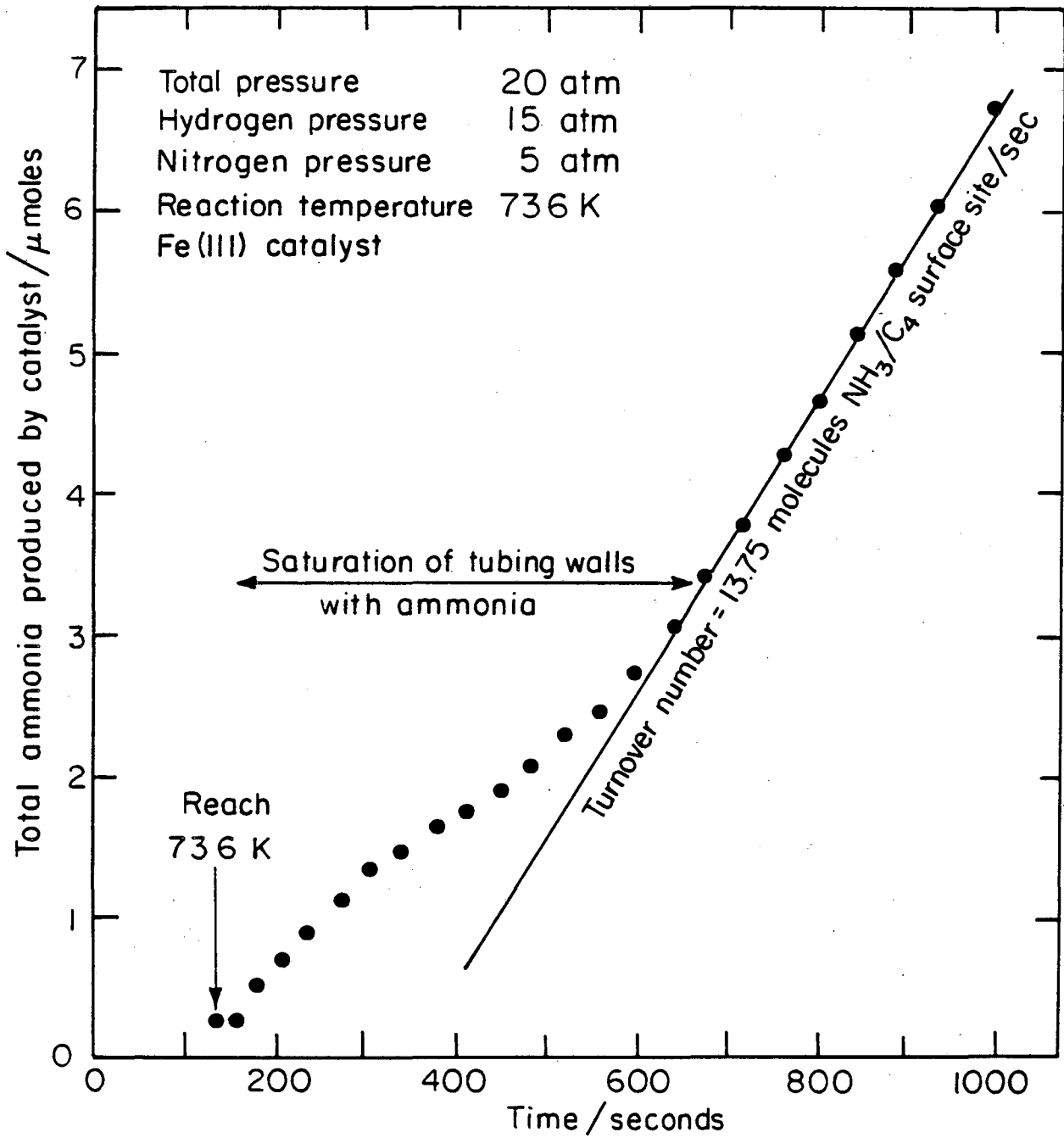
(b) after synthesis run.

LOW-INDEX PLANES OF IRON



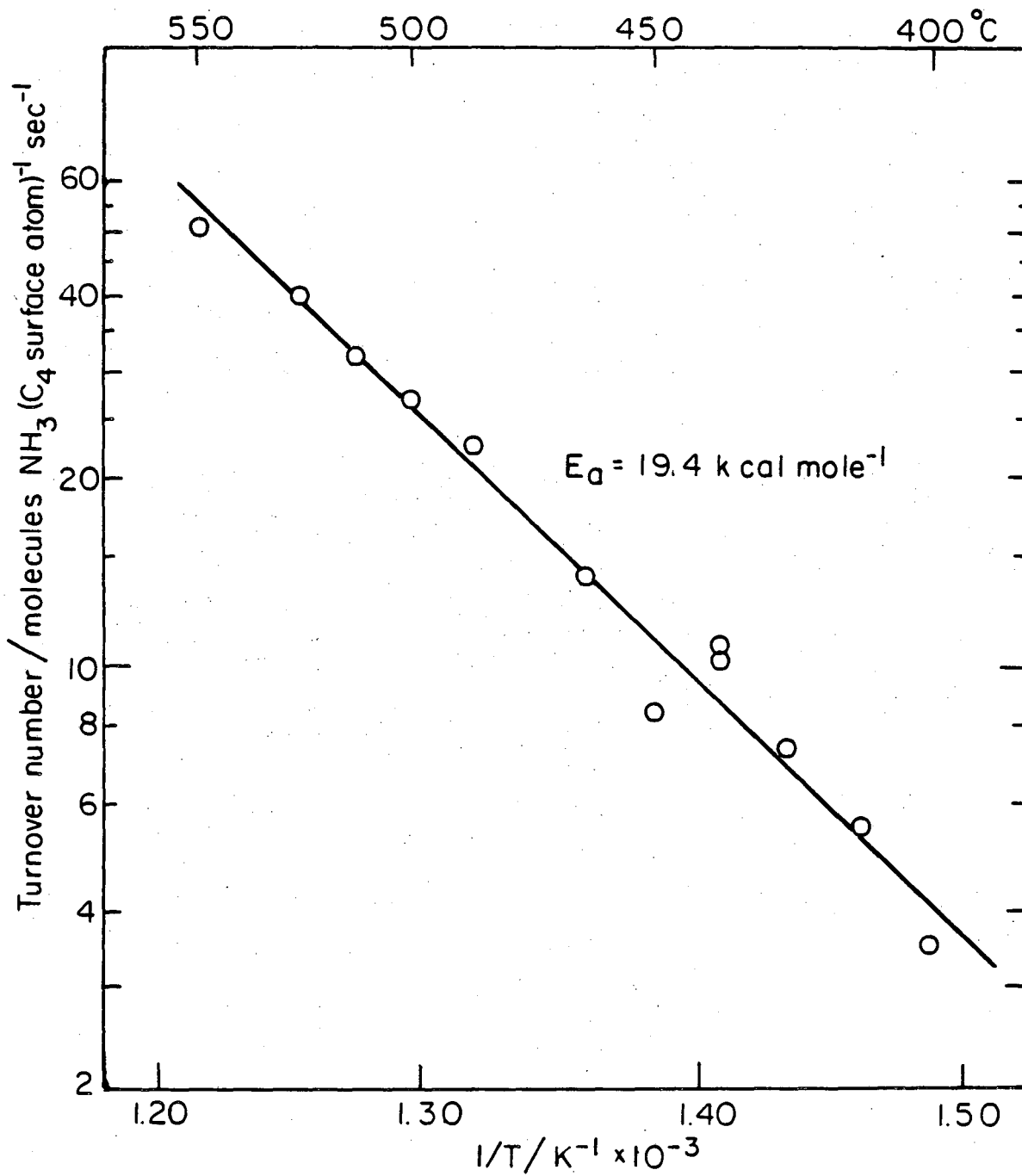
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Fig.1



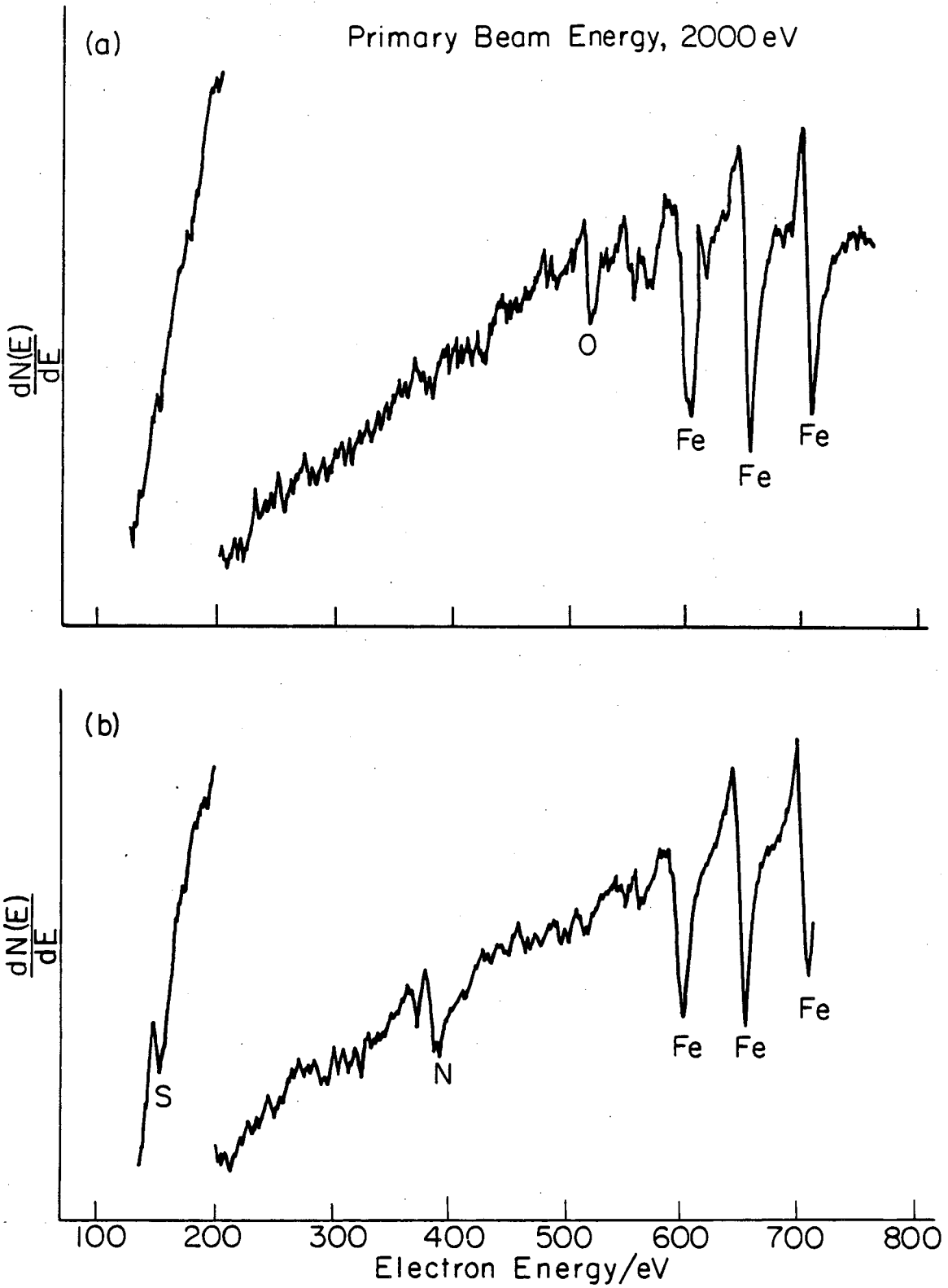
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Fig.2



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Fig.3



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Fig.4

Table 1. Effect of Changing Reactant Partial Pressures

| Run Temperature K | $P_N / \text{atm.}$ 2 | $P_H / \text{atm.}$ 2 | $P_{Ar} / \text{atm.}$ | $P_{\text{total}} / \text{atm.}$ | Turnover Number/ $\text{molec. NH}_3(\text{C}_4\text{atom})^{-1} \text{s}^{-1}$ |
|-------------------|--------------------------|--------------------------|------------------------|----------------------------------|--|
| 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 |

Table 2. Ammonia Synthesis Surface Structure Sensitivity

| Catalyst Surface | Area/cm ² | Rate ^a /moles NH ₃ cm ⁻² s ⁻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 MN^{-2}), $P_H / P_N = 3/1$, Temp. = 798 K
2 2

b Detection limit of Photoionization Detector

c Argon ion bombardment ($1.5 \times 10^{-5} \text{ Acm}^{-2}$ for 600 s at 500 V)

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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