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AMMONIA SYNTHESIS OVER IRON SINGLE CRYSTAL CATALYSTS: THE EFFECTS OF ALUMINA AND POTASSIUM PROMOTION

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Abstract

The effects of potassium and aluminum oxide in increasing the rate of ammonia synthesis from nitrogen and hydrogen have been investigated over model iron single crystal catalysts at 20 atm reactant pressure. Elemental potassium does not remain on the iron surface under reaction conditions but a small amount of potassium can be stabilized on the surface by coadsorption with oxygen. Substantially more potassium can be stabilized at higher temperatures by coadsorption with aluminum oxide. The cooperative interaction between the potassium and oxidized aluminum may be due to compound formation. A massive restructuring of a Fe(110) surface, induced by the presence of aluminum oxide and 5 atm nitrogen at 450 C, was observed. This restructured surface exhibits substantial ammonia synthesis activity, which may be due to the formation of crystallites of (111) planes during the restructuring. There is no increase in ammonia synthesis activity (promotion) for a Fe(110) surface following nitrogen treatment alone, nor any promotional effect for an iron single crystal surface with submonolayer amounts of oxidized aluminum and potassium adsorbed without nitrogen treatment.

1. INTRODUCTION

The catalytic synthesis of ammonia from its elements is one of the most important industrial reactions. The modern ammonia synthetic catalyst is similar to the original industrial catalyst in regard to the basic composition (1). It is made from iron oxide (Fe_3O_4) to which a few percent by weight of other oxides are added as promoters i.e. additives which increase the rate of ammonia production compared to metallic iron alone. Although there is considerable variation in the bulk composition of the catalysts (dependent upon the particular synthesis conditions employed), the oxides usually employed are those of aluminum, potassium and calcium. In addition, oxides of silicon and magnesium are now added whereas they were only present as impurities in the raw materials in the early catalysts.

Even though this reaction has been studied for over 80 years, a detailed understanding of the effect that the promoters play in the reaction is not known , and there have been many ideas put forward over the years (2). The promoters are generally divided into two classes: (i) structural promoters and (ii) electronic promoters. Since this is not the place for a detailed critical review of the various mechanisms of the promoters that have been proposed, the types of effects will be briefly reviewed without comment. The oxides of aluminum, magnesium and silicon are thought of as structural modifiers. For example in the case of aluminum oxide, during the reduction of the Fe_3O_4 to the active metallic phase (-Fe) the presence of Al ions inhibit the rate of diffusion of iron ions in the magnetite lattice and nucleation of small iron particles proceeds quickly compared with their growth rate. This leads to the formation of small crystallites and thereby a very porous structure with high surface area (10-20 m^2g^{-1}) (1,3). It has also been postulated that alumina also inhibits,

or makes difficult, the conversion of crytallographic planes with high catalytic activity (the Fe(111) planes (4)) into those less active ((100) and (110) planes respectively (4)).

Potassium oxide, however, is considered as an electronic promoter which can increase the specific activity of the Fe surface (activity per Fe atom) (2). Indeed, in a series of chemisorption studies of potassium and nitrogen on Fe single crystals in ultra-high vacuum, Ertl was able to show that the presence of submonolayer amounts of elemental potassium increased the dissociative sticking probability of nitrogen (the rate limiting step in the ammonia synthesis reaction (2,5,6)) by two orders of magnitude, and that of potassium coadsorbed with oxygen,(see later discussion), by an order of magnitude (7,8). Related to this is the chemical state of potassium under ammonia synthesis conditions, which has also been the subject of much debate (2). An alternative opinion as to the mechanism of the potassium promoter effect was given by Frankenburg (2d) who suggested that the alkali oxide neutralizes weakly acidic centers on the surface of the catalyst, thus preventing the catalyst surface from being blocked by adsorbed NH_3 molecules or species such as NH or NH_2. Support for this proposal comes from the observation that potassium improves the catalyst performance better at high pressures (i.e. high ammonia concentration) than at lower pressures (1).

The industrial catalyst is obviously a very complex system. In an attempt to understand the effects of alumina and potassium promoters in more detail, a simpler model system was studied using Fe single crystals as catalysts. Studies of the industrial catalyst itself have usually been carried out in reactors operating at pressures greater than 1 atm (1 atm = 101.3 kN m^{-2}) (2b-d), while indirect studies of the adsorption of nitrogen etc. on iron

single crystals have been performed under ultra-high vacuum (UHV) conditions where pressures do not exceed 10^{-4} Torr (1 Torr = 133.3 N m^{-2}) (2a). The former approach suffers from a lack of direct information on the nature of the catalyst surface and the UHV approach 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. This approach has been shown to be successful in many catalytic reaction systems (9).

In this paper we report the initial results of the promotional effect of potassium and alumina on Fe(111),(100) and (110) single crystals. We find that elemental potassium is not stable on the iron surface under our reaction conditions but a maximum of ten percent of a monolayer of K can be stabilized by coadsorption with oxygen. Substantially more potassium can be stabilized, and at higher temperatures, by coadsorption with aluminum oxide. This stabilization may be due to compound formation on the iron surface. However, no promotional effect is observed with submonolayer amounts of the stabilized K-Al_2O_3. A massive surface restructuring of an Fe(110) surface onto which Al_2O_3 had been deposited in a nitrogen environment was observed. Whereas the clean Fe(110) surface is inactive under our ammonia synthesis conditions, the restructured surface becomes as active as the clean Fe(100).

2. EXPERIMENTAL

The experiments were performed in a diffusion pumped stainless steel ultra-high vacuum (UHV) chamber with a base pressure of $1x10^{-9}$ Torr, which is described in detail elsewhere (4). The chamber is equipped with a retarding field analyzer for Auger electron spectroscopy (AES) and Low Energy Electron Diffraction (LEED), a mass spectrometer for temperature programmed desorption (TPD), an ion gun for sample cleaning, and a hydraulically operated high pressure cell that constitutes part of a microbatch reactor . The ionizer of the mass spectrometer is enclosed in a gold-plated tube with an aperture at the end to enhance the sensitivity and to permit sampling of gas desorbed almost exclusively from the front face of the crystal. When the high pressure cell is enclosed over the crystal this completes a loop that can be pressurized to 20 atm, and the gases can be circulated over the crystal with a positive displacement pump. A typical reaction sequence would be as follows. The crystal is cleaned and characterized in UHV, the high pressure cell is closed and pressurized to 20 atm with a 3:1 stoichiometric mixture of hydrogen and nitrogen. Then, while the gases are circulating over the crystal, the crystal is brought to the desired reaction temperature. Once this temperature is reached gas samples are periodically taken from the loop via a sampling valve and into a photoionization detector (PID) (4). The PID signal is directly proportional to only the ammonia partial pressure. After a given reaction time the loop is evacuated, the cell opened and the composition and structure of the surface analyzed in UHV.

Three single crystal faces of iron were studied: the (111),(100) and (110) surfaces. Both sides of the single crystals were oriented and polished by standard techniques. Prior to inserting each crystal into the vacuum chamber,

the near-surface concentration of the major contaminant, sulfur, was substantially reduced by heating the crystal in a vacuum furnace to 650 C in 1 atm hydrogen for 36 hours. The crystal was spot-welded to two 0.25 mm platinum support wires and was resistively heated. The temperature was monitored using a chromel-alumel thermocouple spot-welded to one side of the sample. During a reaction the crystal temperature could be controlled to 2 K of the desired temperature.

The reactant gases, research purity nitrogen and hydrogen were further purified by passing them through molecular sieve and a liquid-nitrogen cooled coil before they entered the reaction loop.

A Saes Getters source mounted close to the sample was used for evaporating potassium. The amount of potassium on the surface was measured by AES. The relationship between the potassium Auger signal and the coverage was obtained using potassium uptake curves. After cleaning the crystal the desired amount of potassium was deposited by controlling the deposition time. Due to the base pressure of the system being of the order $1x10^{-9}$ Torr, coadsorption of water (oxygen) could not be completely avoided. The effect of coadsorbed oxygen is discussed in the text.

A Knudsen-type cell was used for evaporation of aluminum. Due to the fact that the absolute intensity of the 67 eV Al LVV Auger peak was unreliable due to its location on the large secondary electron background of the RFA, a more reliable estimate of the amount of adsorbed aluminum was obtained by using carbon monoxide chemisorption. CO does not adsorb on aluminum oxide at room temperature (2b,10) , therefore the amount of Al-free Fe surface could be estimated by taking the difference in the integral areas of the TPD peaks of CO

from a initially clean Fe surface and that with Al evaporated. ^{13}CO was used for this calibration to separate the CO TPD peak from nitrogen which surface segregates and desorbs from the bulk of the Fe sample in the same temperature range. After initial outgassing both the K and Al sources proved to be clean and efficient sources of the respective metals. Submonolayer amounts of Al were easily and rapidly oxidized to Al_2O_3 on the Fe surface by heating to 600 C in $5x10^{-8}$ Torr oxygen for 60 seconds. Following this procedure the minimum of the second derivative of the LVV Al Auger peak moved from 67 eV to 53 eV indicating complete oxidation, in good agreement with Al_2O_3 thin films and bulk alumina (11,12). No splitting of the 47 eV LVV Fe peak was observed indicating that the Fe substrate was not being oxidized (13). If monolayer amounts of oxygen were present on the Fe surface it is known that under the synthesis conditions the oxygen would rapidly be removed. In fact even a heavily oxidized iron single crystal is readily reduced to metallic Fe under our ammonia synthesis conditions such that the activity is the same as that of the clean surface (4). In a separate study a polycrystalline Al foil was inserted into the UHV chamber and was heavily oxidized ($5 x10^{-6}$ Torr O_2 at 450 C for 15 min). The same shift in the Al LVV Auger peak was observed, and moreover the intensity ratio of the peak-to-peak heights of the LVV Al peak to the oxygen 520 eV peak was about 0.2 (Al peak recorded using 1 V p-p modulation, O peak using 7 V p-p), which was the same ratio as that observed for oxidized aluminum on the Fe(100) single crystal.

3. RESULTS AND DISCUSSION

3.1 STABILIZATION OF K UNDER REACTION CONDITIONS

3.1.1 Potassium on Iron

The ammonia synthesis reaction was studied firstly on clean Fe(111),(100) and (110) single crystals in order to corroborate and compare the results with previously obtained data on these surfaces (4). By using standard reaction conditions of a stoichiometric mixture of nitrogen and hydrogen (1:3) at 20 atm total pressure, and a temperature of 400 C, good agreement was reached as to the initial rates of ammonia formation on these surfaces; the Fe(111) being the most active by far. The relative activity was in good agreement with the previously obtained ratios of 400:25:1. Additionally, an apparent activation energy for the reaction of 18.8 0.5 kcal/mol was determined using a Fe(100) crystal in good agreement with our previously determined value of 19.4 kcal/mol (4).

Having established the structure sensitivity of the ammonia synthesis reaction the next stage was to investigate the role of the potassium promoter. Using a Fe(100) crystal elemental potassium was evaporated onto both sides of the crystal in UHV to give coverages between 0.05 and 1.0 monolayer. The crystal was then enclosed in the high pressure cell and the synthesis reaction performed at 400 C using 20 atm 3:1 hydrogen to nitrogen and the rate of ammonia production determined. For all coverages of potassium the rate of ammonia formation was the same as the clean Fe(100). Moreover, no potassium signal was detectable by AES at the end of the reaction. Thus it can be concluded that under our reaction conditions (and therefore most likely those of the industrial synthesis) elemental potassium is not stable at any coverage, and simply

volatilizes from the surface. This conclusion is in agreement with detailed UHV studies characterizing the adsorption of K on Fe single crystals where it was determined that potassium desorbs in the temperature range 450-850 K, depending upon the coverage of potassium present (14). Thus, even though the Fe-K bond is strongly ionic in character in the low to medium coverage regime resulting in thermal desorption of potassium at temperatures much higher than sublimation of bulk potassium, this effect is not enough to keep elemental potassium on the surface under our reaction conditions.

3.1.2 Potassium and Oxygen on Iron

The promoter that is added to the industrial catalyst, however, is not metallic potassium but potassium oxide. Further, UHV studies of K adsorption on Fe single crystals have shown that coadsorption of oxygen with the potassium stabilizes the potassium to higher temperatures such that even after briefly heating to 1000 K some potassium remains on the surface (8,15), although these conditions are quite different from the industrial synthesis conditions where the catalyst is kept at temperatures of 300-600 C in 150-300 atm of reactant gases for peroids of 8 years or more. In an attempt to stabilize potassium on the Fe(100) surface under our conditions coadsorption of potassium with oxygen was examined. Figure 1 sumarizes the results in the form of Auger electron spectra before and after the synthesis reaction. An Auger spectrum corresponding to that of a complete monolayer of K which had subsequently been exposed to oxygen in UHV is shown together with a spectrum recorded from the same surface after performing the synthesis reaction at 400 C at 20 atm total pressure of a stoichiometric mixture of N_2 and H_2 for 30 min. The potassium signal is substantially reduced after the reaction and corresponds to approximately ten percent of a monolayer. If the reaction is performed at higher temperatures, up

to 600 C, substantially less potassium is stabilized on the surface. Several different initial potassium coverages, in the range from 0.1 to 1.0 monolayer, and oxygen exposures, in addition to the order of exposure (i.e. K + O or O + K) were studied, all with the same conclusion. Namely that at 400 C a maximum of ten percent of a monolayer of K could be stabilized, this value decreasing rapidly as the reaction temperature is increased. More importantly, the measured initial rate of NH_3 formation in moles per cm^2 per second was unchanged from that of the clean Fe(100) for all the K + O adlayers investigated. If the rate were now to be calculated in terms of moles per exposed surface iron atom per second then the rate would be increased due to the fact that the potassium and oxygen are covering some of the surface iron atoms. The results of a more detailed study of K + O adlayers on the ammonia synthesis reaction will be published elsewhere (16).

3.1.3 Potassium and Oxidized Aluminum on Iron

Remembering that the industrial catalyst is a complex system of many promoter oxides it is to be expected that there will be some cooperative interactions between the various oxides. In order to explore this possibility we have also investigated the stability of potassium in a mixed adlayer of potassium with aluminum oxide. The Auger spectrum recorded at the end of a 30 min. synthesis reaction at 400 C with 20 atm 3:1 hydrogen:nitrogen, after first depositing 40% of a monolayer of Al_2O_3 followed by a complete monolyer of potassium in UHV, is shown in Figure 1. Comparing this spectrum with that of a K + O adlayer it can clearly be seen that substantially more potassium is stabilized. In fact the potassium AES signal corresponds to approximately 40% of a monolayer of potassium.

To further investigate the cooperative behaviour between the oxidized aluminum and potassium, resulting in the increased stability of the potassium, the following experiment was performed. A known amount of Al_2O_3 was deposited onto the Fe(100) crystal, followed by a coverage of K corresponding to a complete monolayer. The crystal was then heated to 400 C in UHV and the intensity of the K Auger signal recorded periodically. The results are summarized in Figure 2 where the relative concentration of potassium is shown as a function of time at 400 C for several different Al_2O_3 coverages. A rapid initial decrease in the ammount of K is observed in all cases but then a steady state is reached, the value of which depends upon the amount of Al_2O_3 present. In fact it can be seen that there is an approximate 1:1 correlation between the amount of potassium that is stabilized and the amount of aluminum oxide present. (On recording the Auger spectra during the run with no Al_2O_3 present there was some oxygen contamination,therefore 10% of a monolayer of K is stabilized, as shown in Figure 2). The 1:1 correlation is better observed in Figure 3 where the relative concentration of potassium remaining on the surface after heating to 400 C in UHV for 25 mins is plotted versus the relative concentration of oxidized aluminum. In all cases the amount of K that is stabilized in UHV is also stable under our reaction conditions (20 atm total pressure, 400-550 C). If the K + Al_2O_3 covered Fe(100) is heated above 600 C, then potassium is lost from the stabilized surface overlayer. This decomposition temperature agrees well with the temperature at which an industrial catalyst looses potassium from the surface, as monitored by X-ray photoelectron spectroscopy (2a).

As mentioned in the introduction, the nature of the stabilized potassium species in the industrial ammonia synthesis has been the cause for much debate for many years. There are sporadic references throughout the literature that the

Al_2O_3 + K_2O promoter pair is in the form of a potassium aluminate ($KAlO_2$). While we cannot conclude from the present data that a surface potassium aluminate is present, the 1:1 ratio of K to Al supports the idea. We can certainly infer that there is at least some cooperative association between the two on the Fe(100) surface which stabilizes the potassium to higher temperatures under our reaction conditions. The structure and characterization of this Al_2O_3 + K adlayer is undergoing further investigation.

Figure 4 summarizes the results of the initial rate of ammonia synthesis on a Fe(100) surface with submonolayer amounts of stabilized oxidized aluminum and potassium. The data is shown as the rate of ammonia synthesis versus the percentage of free iron surface (as determined by ^{13}CO TPD). The reactions were performed at 450 C with a 20 atm stoichiometric mixture of nitrogen and hydrogen. There is an approximate linear decrease in the rate of NH_3 synthesis with decrease in the amount of exposed iron surface, (no ammonia production was detected from a surface completely covered with alumina and potassium). The results indicate that there is no promotional effect per exposed surface iron atom at any of the surface concentrations of the Al_2O_3 + K layer that was studied. All that is observed is a site-blocking type effect on the rate. The same observation is found if submonolayer amounts of oxidized aluminum alone are added to the Fe(100) surface, and the same is also observed for alumina and potassium on a Fe(110) surface; no promotional effect is observed. Thus, even though the potassium can be stabilized to reaction temperatures (400-550 C) and at pressures up to 20 atm the nature of the promotional effect is uncertain at this time and is undergoing further study.

3.2 THE ALUMINA INDUCED RESTRUCTURING OF THE Fe(110) SURFACE

During the course of this study a very interesting phenomenum was observed, namely a restructuring of the surface of a Fe(110) single crystal onto which oxidized aluminum had been deposited. More importantly, the ammonia synthesis activity of this restructured surface is greatly enhanced compared to the clean Fe(110).

Specifically, if a Fe(110) crystal precovered with approximately 1.5 monolayers of aluminum oxide is heated to 450 C in 5 atm nitrogen gas for 30 min there is a massive surface restructuring leading to increased ammonia formation. Figure 5 displays the relative ammonia synthesis activity of clean Fe(111),(100) crystals and that from the nitrogen pretreated oxidized aluminum covered Fe(110). It can be seen that the activity of the latter surface is close to that of a clean (100) single crystal. (Reaction conditions: 20 atm 3:1 H_2:N_2, 400 C). Also shown in Figure 5 are the relative rates of clean (111),(100) crystals and that from a nitrogen pretreated (110) with no aluminum oxide present (nitrogen treatment: 5 atm, 450 C, 30 min). It is observed that nitrogen pretreatment of a clean (i.e. no Al_2O_3) Fe(110) surface has no effect on the measured initial rate of ammonia formation: no ammonia is detected. In addition there is no massive restructuring of the Fe(110) surface simply by heating in nitrogen. In fact when the LEED pattern is examined following this latter treatment a complex pattern is observed which is the same as that described by Bozso et al.(6), and can be interpreted due to the formation of a surface reconstruction (not a <u>restructuring</u>, see below) due to the formation of a surface nitride (6).

The restructuring and enhanced rate has been observed on three separate

Fe(110) single crystals, and the rate shown in Figure 5 is the average of the rates an all three. The enhanced rate of ammonia formation is not a transient effect. The same initial rate is obtained on the restructured surface on repeating the reaction many times over a period of several days, and the same rate is observed after 4 hours of reaction (after trapping out the ammonia formed (17)). The restructuring of the surface manifests itself in the fact that the surface of the crystal looks optically dull (the mirror finish is lost), and there is no LEED pattern. The nature of the restructuring can be observed by comparing Scanning Electron Micrographs recorded before and after the transformation (Figure 6). The scale of both the clean Fe(110) and restructured surface is the same and is indicated in the figure. The clean Fe(110) surface is smooth and featureless, while the restructured (110) is rough and an outer layer on top of the iron substrate is visible. Some crystallites on top of this outer layer are also visible. (Both samples were exposed to the atmosphere prior to taking the SEM photographs).

Although the exact nature and cause of the restructuring is still undergoing investigation several facts are known. (i) The restructuring only occurs in the presence of nitrogen gas. Five atmospheres of hydrogen or 5 atm of synthesis gas (H_2:N_2, 3:1) do not affect the alumina covered Fe(110) at 450 C. (ii) The restructuring is dependent upon the alumina concentration in the near surface region. Depositing 20% of a monolayer of Al_2O_3 had no effect, depositing a further 20% had no effect, but depositing an additional complete monolayer caused the restructuring shown in Figure 6. (iii) The restructuring has a considerable activation energy. Heating a Fe(110) crystal covered with 1.5 monolayers of alumina in 5 atm nitrogen for 30 min at 400 C did not result in any change, but heating the same composition to 450 C for 30 min resulted in the transformation. (iv) An equilibrium transformation is reached after 30 min at

450 C as heating for 10 hours at the same temperature did not result in any further modification of the surface or any change in the NH_3 synthesis rate.

An Auger spectrum recorded after depositing and oxidizing the aluminum shows only an Al signal at 53 eV (due to Al_2O_3), Fe signals at 47, 598, 652 and 702 eV and an oxygen signal at 510 eV. After nitrogen treatment at 450 C the spectrum is changed somewhat in that the Al peak is substantially reduced in intensity, or in fact is sometimes absent, and a nitrogen signal is observed at 381 eV. The reduction in the aluminum signal is indicative of the aluminum oxide diffusing into the near surface region during the restructuring. It is expected that this processes would have a considerable activation energy. This diffusion problem has an analogy in studies of metal support interactions where TiO_2 and Al_2O_3 have been deposited onto a Rh substrate. On heating in vacuum to temperatures above 500 C an active overlayer is formed where it is thought that the metal oxide has diffused into the Rh metal (18). In this case however it is purely the top one or two layers that are involved and there is no massive restructuring. In the Auger spectrum recorded after the transformation there was no indication of a peak at 60 eV due to aluminum nitride (11),(we also nitrided an aluminum foil in situ and observed the Al LVV signal shift from 67 eV to 60 eV in good ageement with the published value), thus the transformation is probably not be due to a surface expansion due to nitridation of the aluminum.

If the restructured surface is Ar^+ sputtered and annealed until only peaks representative of clean iron are observed in the Auger electron spectrum, the rate of ammonia synthesis under our standard conditions is identical to the rate before sputtering. The sputtered and annealed surface still exhibits no LEED pattern and about 15-20% less ^{13}CO adsorbs compared to a clean

(unrestructured) Fe(110) crystal. The apparent activation energy on the restructured surface was also determined. On recording the initial rate of ammonia synthesis on such a surface with a 20 atm stoichiometric mixture of nitrogen and hydrogen between 400-550 C an activation energy of 17.9 kcal/mol was calculated. This is within the error bars of the value calculated on a clean iron single crystal, 18.8 0.5 kcal/mol.

The fact that the rate of ammonia synthesis is the same on the restructured surface before and after sputtering (and annealing), i.e. with or without aluminum present in the Auger spectrum, suggests that the active component for the ammonia synthesis on the restructured surface is still elemental iron and not an active Fe-Al phase. Also supportive of this conclusion is the fact that the apparent activation energy for the reaction is the same on the restructured iron surface as on clean iron single crystals. The restructured surface has an activity about the same as that of a clean Fe(100) and yet the CO TPD results show that the restructured surface adsorbs <u>less</u> CO compared to the clean Fe(110) surface, indicating that its chemisorptive surface area has decreased. These results suggest that the increase in activity on the restructured surface is due to the formation of crystallites with orientations active towards ammonia synthesis, possibly (111) planes, which have been shown to be stabilized in the presence of nitrogen (19). The postulations that aluminum oxide either helps create iron crystallites which are more active towards ammonia synthesis or inhibits the conversion of such planes into less active ones during the reduction process of the industrial catalyst have been made in the literature in the past. Here we have presented some indirect evidence that this is also the case for an oxidized aluminum covered Fe(110) surface which is heated in nitrogen. It is possible that the aluminum oxide stabilizes a Fe-N phase which would otherwise not be stable in the presence of

hydrogen i.e. under ammonia synthesis conditions.

There are several references in the literature with regard to the reconstruction of iron surfaces induced by nitrogen. For example, as already mentioned, the Fe(110) surface reconstructs as evidenced by LEED after nitrogen exposure to give a surface nitride (6). Boudart et al. (20) concluded that ammonia treatment of small iron particles supported on MgO leads to the creation of C_7 sites (as present on a Fe(111) surface), and Loffler and Schmidt (21) observed extensive faceting of an iron wire which could be observed by SEM after heating in 0.5 Torr ammonia. While the formation of a surface nitride on the Fe(110) crystal after nitrogen exposure is a surface reconstruction, involving only the top one or two atomic layers, the magnitude of the effect in the latter two cases described above, and indeed in our case of Fe(110)-Al_2O_3/N, is better described as surface restructuring and is a more macroscopic phenomenum.

Experiments are underway to try and better identify the new surface phase formed during the aluminum oxide and nitrogen induced restructuring of the Fe(110), and also to understand the mechanism of the restructuring itself.

4. SUMMARY

The initial results of a model system of the effects of potassium and alumina promoters on the ammonia synthesis reaction have been discussed. We find that elemental potassium is not stable on the surface of an iron single crystal under our reaction conditions. However, by coadsorbing oxygen with the potassium up to ten percent of a monolayer of K can be stabilized at 20 atm synthesis gas pressure at the lower temperatures of the reaction (400 C), although this amount decreases continually with increase in reaction temperature. Substantially more

potassium can be stabilized under our reaction conditions, and at much higher temperatures, by firstly depositing submonolayer amounts of aluminum oxide on the surface of the iron single crystal and then evaporating potassium on top of this. The cooperative interaction between the potassium and alumina may be due to compound formation. No promotional effect is observed with submonolayer amounts of the stabilized Al_2O_3-K. A massive surface restructuring of an Fe(110) surface onto which approximately 1.5 monolayers of aluminum oxide had been deposited was observed after heating such an overlayer in 5 atm nitrogen at 450 C. Although the nature, and cause , of this restructuring is not fully understood at present, what is known is that the clean Fe(110) is inactive towards ammonia synthesis whereas the restructured surface has substantial activity.

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FIGURE CAPTIONS

FIGURE 1

Auger electron spectra of promoted Fe(100) surfaces before and after ammonia synthesis reaction. Conditions given in the text.

FIGURE 2

Relative concentration of potassium on a Fe(100) surface as a function of time at 400 C in UHV for several different oxidized aluminum coverages.

FIGURE 3

Relative concentration of potassium stabilized after heating the crystal at 400 C for 25 mins. in UHV versus the amount of oxidized aluminum present. The dotted line corresponds to a 1:1 correlation between the amount of potassium and oxidized aluminum.

FIGURE 4

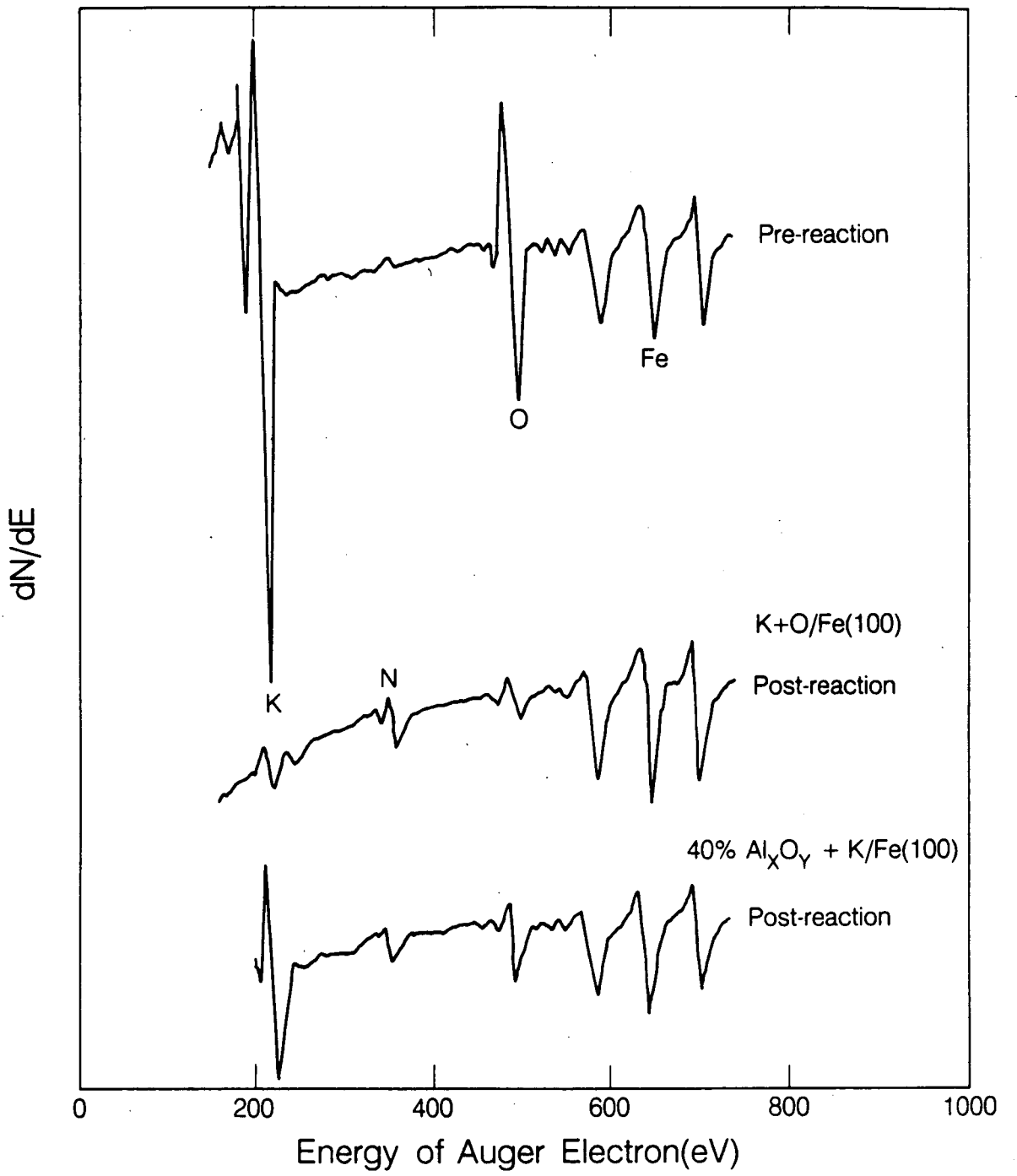
Initial rate of ammonia synthesis on a Fe(100) surface with submonolayer amounts of stabilized oxidized aluminum and potassium, shown as the rate of NH_3 synthesis versus percentage of free iron surface as determined by ^{13}CO TPD. Conditions given in the text.

FIGURE 5

The rate of ammonia synthesis for nitrogen pretreated Fe(110) surfaces. (i) Nitrogen pretreated clean Fe(110). (ii) Nitrogen pretreated Al_xO_y covered Fe(110). Also shown are the relative rates for clean Fe(111) and (100) (without nitrogen treatment). Conditions given in the text.

FIGURE 6

Scanning electron micrographs of (a) restructured Fe(110) surface (b) clean Fe(110) surface.



XBL 858-8961

FIGURE 1

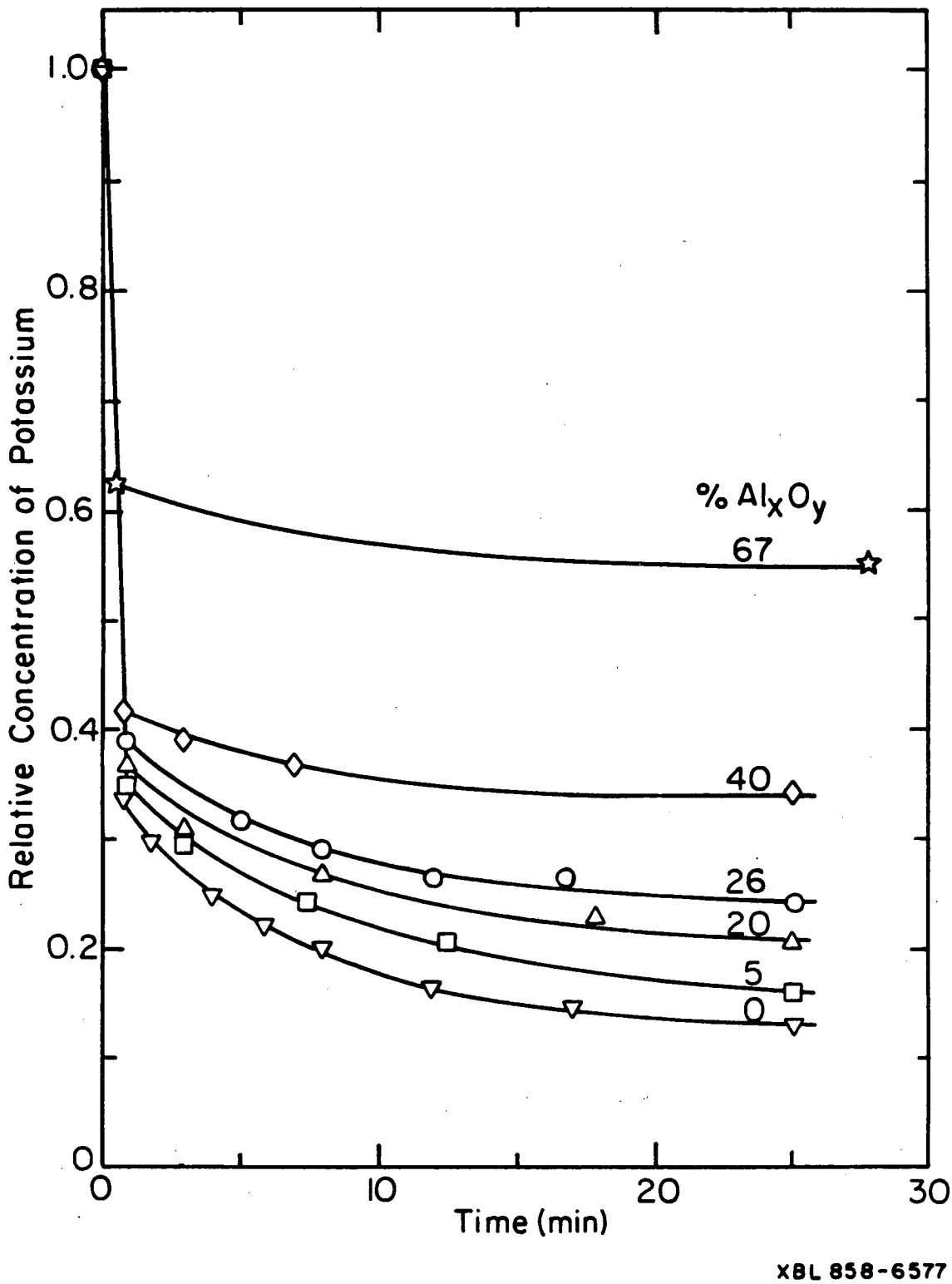

1.0
0.8
0.6
0.4
0.2
0
Relative Concentration of Potassium
% Al_xO_y
67
40
26
20
5
0
0
10
20
30
Time (min)
XBL 858-6577

FIGURE 2

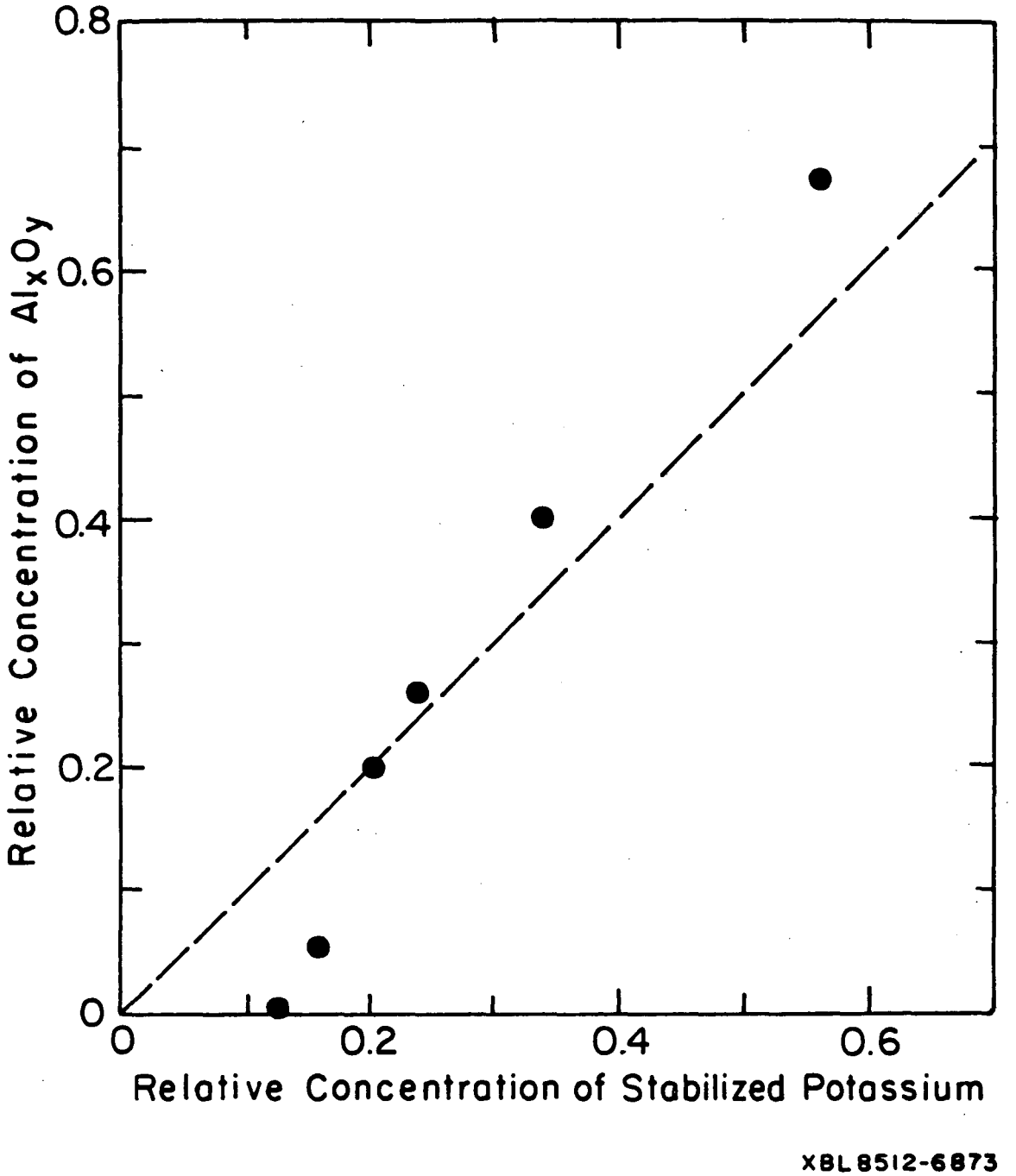
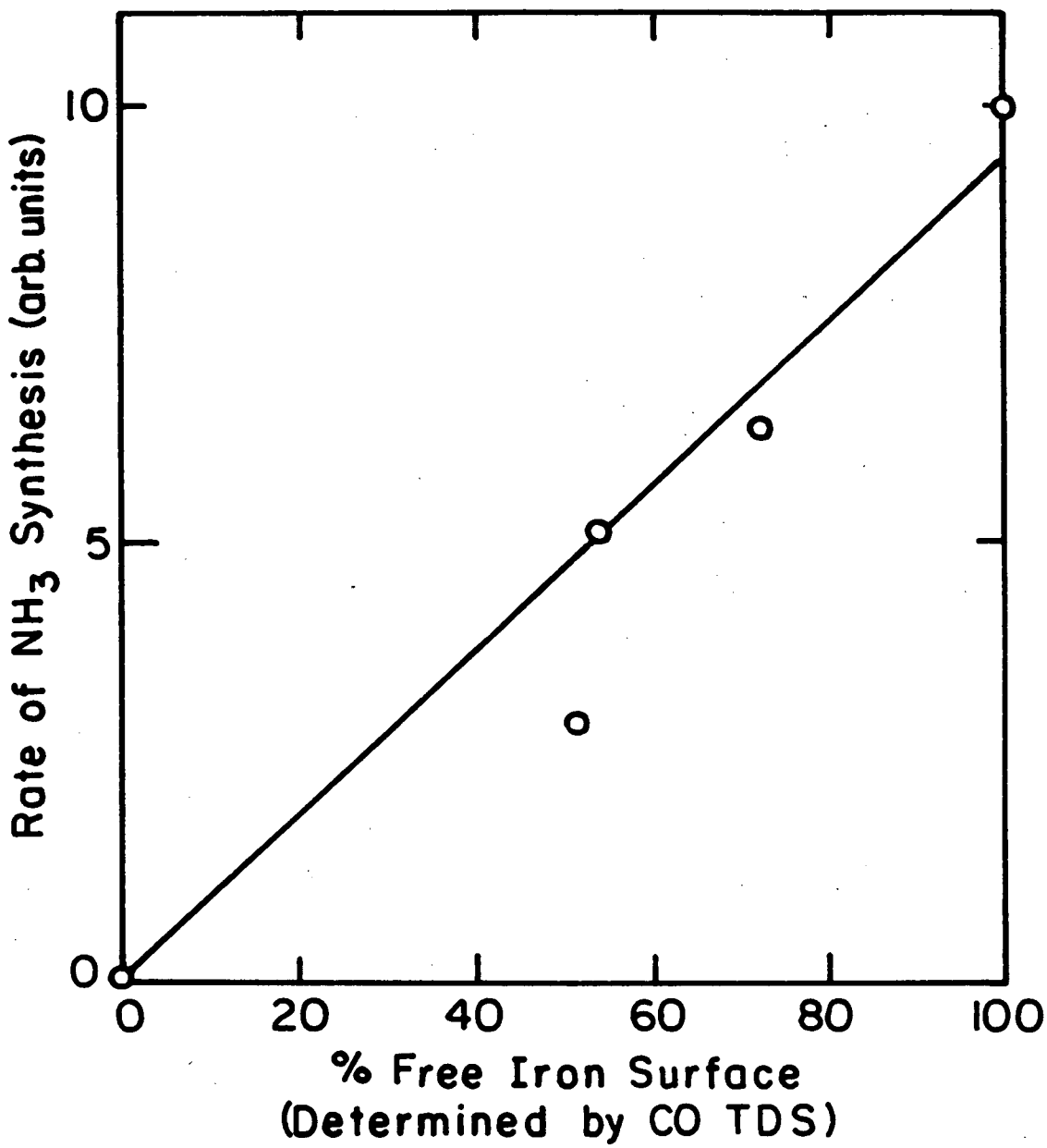

0.8
0.6
0.4
0.2
0
Relative Concentration of Al_xO_y
0
0.2
0.4
0.6
Relative Concentration of Stabilized Potassium
XBL8512-6873

FIGURE 3



XBL858-6578

FIGURE 4

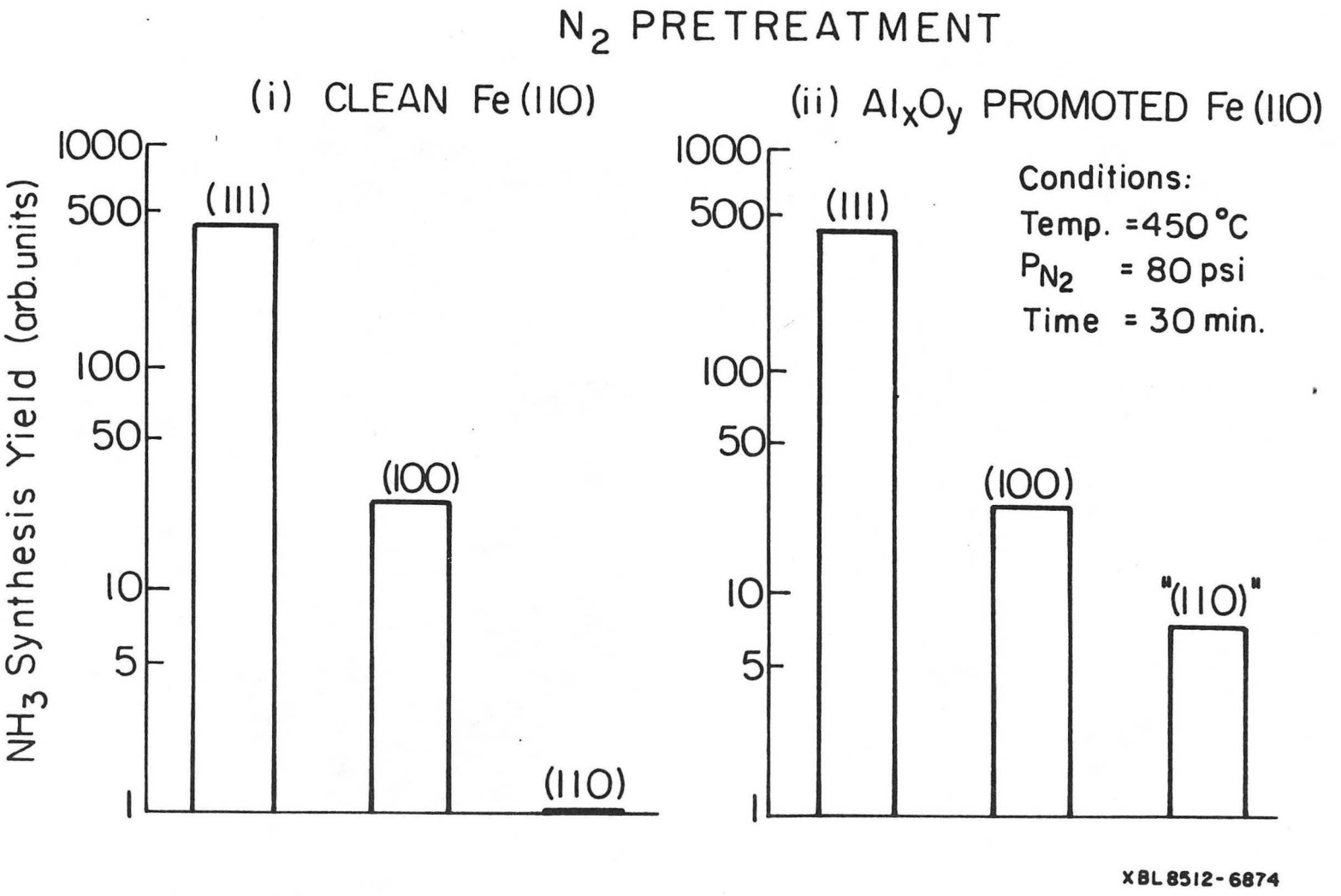
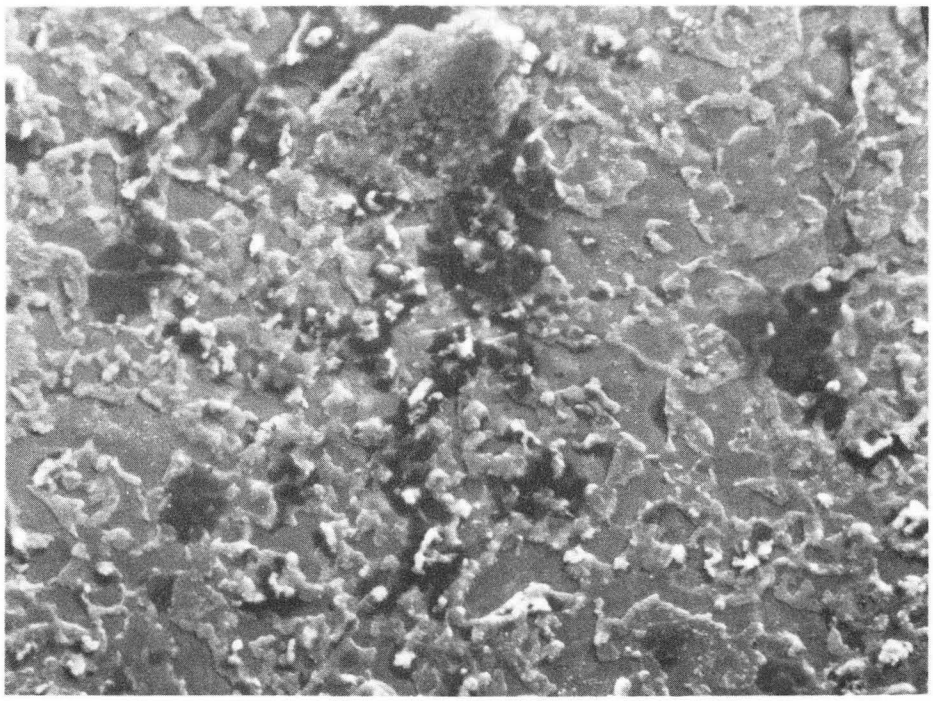

N2 PRETREATMENT
(i) CLEAN Fe (110)
(ii) AlxOy PROMOTED Fe (110)
NH3 Synthesis Yield (arb. units)
1000
500
100
50
10
5
1
(111)
(100)
(110)
"(110)"
Conditions:
Temp. =450 °C
PN2 = 80 psi
Time = 30 min.
XBL 8512-6874

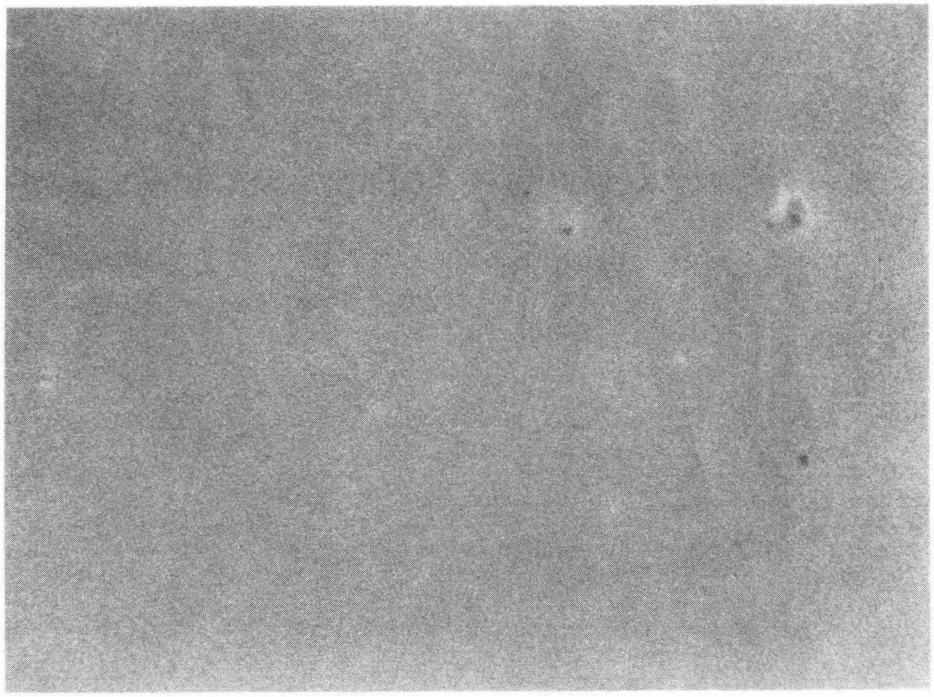
FIGURE 5

A



4.85μ

B



XBB 850-10233

FIGURE 6

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