Title

THE EFFECTS OF ALUMINUM OXIDE IN RESTRUCTURING IRON SINGLE CRYSTAL SURFACES FOR AMMONIA SYNTHESIS

Authors

Strongin, D.R.
Bare, S.R.
Somorjai, G.A.

Publication Date

1986-11-01

Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

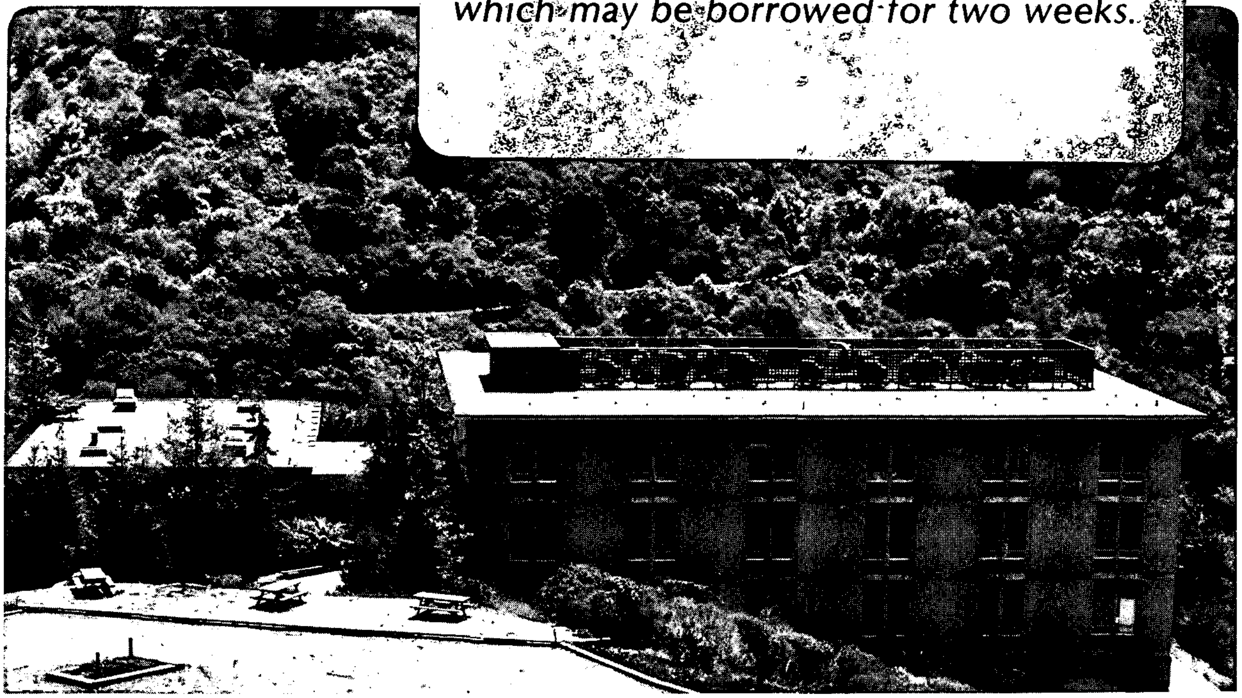
Materials & Chemical Sciences Division

Submitted to Journal of Catalysis

THE EFFECTS OF ALUMINUM OXIDE IN RESTRUCTURING IRON SINGLE CRYSTAL SURFACES FOR AMMONIA SYNTHESIS

D.R. Strongin, S.R. Bare, and G.A. Somorjai

November 1986



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL-21836

The Effects of Aluminum Oxide in Restructuring Iron Single Crystal Surfaces for Ammonia Synthesis

D.R. Strongin, S.R. Bare and G.A. Somorjai

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720, U.S.A.

Abstract

The effect of aluminum oxide and potassium on the ammonia synthesis over the (111), (100), and (110) faces of iron has been investigated. A restructuring of the Fe(110) and Fe(100) surfaces, induced by the presence of aluminum oxide and 20 Torr of water vapor takes place making the restructured surfaces almost as active as the clean Fe(111) plane in the ammonia synthesis reaction (20 atm reactant pressure of hydrogen and nitrogen). The high activity of the restructured surfaces is maintained for over four hours of ammonia synthesis. Without the presence of aluminum oxide treatment of the Fe(110) and Fe(100) surfaces with 20 Torr of water vapor again produces restructured surfaces which are almost as active as the Fe(111) plane for a short period. However, in this case deactivation of the restructured surfaces into the respective clean, unrestructured surfaces occurs within one hour of ammonia synthesis. Restructuring of the Fe(111) with 20 Torr of water vapor produces only a slight decrease in ammonia synthesis activity. The enhancement in rate of the restructured Fe(110) and Fe(100) surfaces, with or without aluminum oxide, might be explained by the formation of active surface orientations for ammonia synthesis (i.e. Fe(111) and Fe(211)), which contain C_7 sites (iron atoms with seven nearest neighbors), during the water vapor treatments. These Restructured surfaces are only stable in the ammonia synthesis conditions when aluminum oxide is present.

Potassium adsorbed alone of with coadsorbed aluminum oxide exhibits no promotional effects under the water vapor pretreatment conditions used in this study.

Introduction

The industrial synthesis of ammonia occurs over an iron catalyst promoted with the oxides of potassium (K_2O), aluminum (Al_2O_3), calcium (CaO) and silicon (SiO_2). The preparation of the catalyst involves the fusing of about two percent by weight of the promoters with Fe_3O_4 (magnetite) followed by reduction. Over seventy years of work has gone into elucidating the effects of the potassium oxide and aluminum oxide since they are thought to represent the two different types of effects (electronic and structural promotion) exhibited by the promoters. Studies on the industrial catalyst have shown that the addition of Al_2O_3 increases the surface area of the catalyst from an initial value of $1m^2$/g-cat. (unpromoted iron) to a value of $25m^2$/g-cat. The addition of K_2O decreases the surface area to about $10m^2$/g-cat. but increases the ammonia synthesis rate by a factor of three (1,2). Recent surface science work (3,4) has shown that the addition of potassium to a Fe(100) face increases the rate of dissociative nitrogen chemisorption, the rate limiting step in the ammonia synthesis reaction (5,6,7), to a level equivalent to the most active Fe(111) plane.

The catalytic studies carried out on the industrial catalyst have usually been performed in systems which operate at pressures greater than one atmosphere (1,6). In this type of environment the surface of the working catalyst can not be characterized directly. Surface science studies on the adsorption of nitrogen on iron single crystals have been carried out in ultra-high vacuum systems where pressures do not exceed 10^{-4} Torr (1 Torr = $133.3 N/m^2$) (3,4) and the synthesis of ammonia does not proceed at a detectable rate. The development of combined high pressure/ultra-high vacuum systems in our laboratory bridges this pressure gap and allows the study of catalytic reaction rates and selectivity on well characterized single crystal surfaces. In ultra-high vacuum an iron sample can be characterized by surface sensitive techniques and at high pressure ammonia synthesis conditions (20 atm of a stoichiometric mixture of N_2 and H_2) rates of ammonia production can be determined as a function of surface compostion and structure. Our studies of the ammonia synthesis on the (111), (100), and (110) crystal faces of iron revealed the marked structure sensitivity of this reaction (Fe(111) Fe(100) Fe(110)) (8). Recent studies in our laboratory which included the (211) and (210) crystal faces (9) clearly implicated the unique activity of seven coordinated sites for ammonia synthesis that are only present in the (111) and (211) crystal faces to dissociate dinitrogen (the rate limiting step for this reaction).

We report the study of the effects of promoters, aluminum oxide and potassium, on the synthesis of ammonia on single crystal iron surfaces of (111), (100), and (110) orientation. We find that a pretreatment of the iron catalyst, in the presence of aluminum oxide, using water vapor must be performed prior to the ammonia synthesis for aluminum oxide to function as a promoter. In this circumstance the rates of the reaction over the less active (110) and (100) faces increases markedly to attain the rate observed over the most active Fe(111) face. The presence of aluminum oxide helps to maintain this high activity which is caused by the restructuring of the less active crystal faces to surfaces as active as the Fe(111) or Fe(211) faces (9). Under our conditions of pretreatment and reaction reported here potassium alone or together with aluminum oxide has no discernable effects on the catlyst activity.

Experimental

The experiments in this study were performed in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure less than $2x10^{-9}$ Torr. The chamber is equipped with a retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) and a hydraulically operated high pressure cell which constitutes part of a micro-batch reactor. A mass spectrometer is used to monitor residual gases in the chamber and to perform temperature programmed desorption (TPD). The ionizer on the mass spectrometer is enclosed by a gold plated tube with an opening (0.25 cm diameter) at the end. This whole assembly was mounted on a bellows so that during TPD experiments the aperature could be brought close to a face of the sample. This procedure improved sensitivity and eliminated the detection of gases desorbing from the support wires.

A typical reaction sequence would occur as follows. The sample is prepared and characterized in UHV by LEED and AES and is enclosed by the high pressure cell to form an external reaction loop. The loop is than pressurized with the reactant gases (20 atm of 3:1 mixture of H_2 and N_2) which are circulated by a positive displacement pump and the sample is heated to the reaction temperature (all ammonia synthesis reactions were run at 673K unless otherwise noted). Ammonia formation is monitored by periodically taking samples from the reaction loop and passing them through a photoionization detector (PID) sensitive only to the ammonia partial pressure. After reaction the crystal is cooled to 373K, in the reaction mixture, and the reactant gases are than evacuated from the cell. The sample is returned to the UHV environment where AES, LEED, and TPD are performed.

Water vapor treatment of the iron surfaces was performed by enclosing the sample in the high pressure cell and than equilibrating the desired pressure of water vapor within the external loop. All the treatments were carried out at 723K for 30 minutes (only the pressure of water vapor will be used to describe the treatments mentioned throughout the text).

The single crystal samples used were on the average 1cm^2 disks about 1mm thick. They were cut and polished by standard metallurgical techniques. The sample was spot-welded between 0.25mm 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 sample. The major impurities in the iron single crystals were sulfur and carbon. The sulfur was removed by prolonged argon ion sputtering ($4-5\times10^{-6}$ amperes/cm^2) while the sample was held at 873K. Carbon was removed by treating the crystal with 1×10^{-7} Torr of oxygen while sputtering.

A Knudsen cell was used for the evaporation of aluminum. The aluminum was oxidized to Al_xO_y (aluminum oxide will be denoted as Al_xO_y due to the uncertainty in the aluminum and oxygen stoichiometry) by heating the surface to 673K in 5×10^{-8} Torr of water. The extent of aluminum oxidation was verified by the shift of the 67eV aluminum LVV auger peak to 54eV representative of bulk Al_2O_3 (10). coverages of Al_xO_y were determined by titrating the surface with ^{13}CO. Since CO chemisorbs on iron and not Al_2O_3 (11) the relative amount of free iron surface could be obtained by taking the difference in integral areas between CO/Fe and CO/Al_xO_y/Fe TPD peaks. Rates of ammonia synthesis reported throughout this paper were determined by taking into account the amount of free iron surface on each crystal. Coverages above one monolayer(ml) were estimated by dividing the evaporation time by the time it took to evaporate one monolayer of Al_xO_y (defined as the point where no CO chemisorbs to the sample). It is proposed later in this paper (see section 3.1) that Al_xO_y grows in three dimensional islands on the iron surface, thus the point where CO can no longer chemisorb on the sample might actually correspond to more than one atomic layer. The ratio of intensities of the 47eV iron and 54eV Al_xO_y auger peaks were calibrated against the CO titration data so that coverages of aluminum oxide could alternatively be determined by AES. Potassium was deposited onto the single crystals by a Saes Getters source. The potassium coverage was determined from uptake curves where the intensity of the 252eV potassium auger peak was plotted against dose time (the evaporation rate was constant in these experiments).

The reactant gases (N_2 and H_2) were research purity. They were further purified by passing them through a molecular seive trap and a liquid nitrogen cooled coil. The distilled water used in this study was outgassed by repeated freeze thaw cycles.

Iron samples were examined by scanning electron microscopy (SEM) after removal from the UHV chamber. Transfer in air to the microscope did not seem to alter the sample surfaces because identical micrographs were seen for samples after one day or one week exposure to air.

3.0 Results

3.1 Auger Electron Spectroscopy and Low Energy Electron Diffraction Studies

The growth of oxidized aluminum on the iron single crystals was studied by AES and LEED. There was no indication of any long-range ordering of the Al_xO_y at any coverage on the Fe(111), Fe(100), and Fe(110) planes. Using AES the 67eV aluminum transition intensity was plotted against the iron 47 and 652eV peak intensities. In both cases no breaks in the curves were found indicating three dimensional Al_xO_y island growth (12).

AES was used to estimate the coverage of Al_xO_y in the near surface region on the three different iron surfaces used in this study before and after the various water vapor treatments. On both the Fe(110) and Fe(111) surfaces an initial concentration of two monolayers of Al_xO_y decreases to about 50% of a monolayer after being treated with 0.05 Torr(50mTorr) of water vapor and subsequent reduction in the H_2 and N_2 synthesis gas mixture. A more drastic reduction in the Al_xO_y coverage was observed if the sample was treated with 0.4 Torr(400mTorr) of water. In this case the Al_xO_y was barely detectable by AES (about 5% of a monolayer). Argon ion sputtering the surface (4-5×10^{-6}amperes/cm^2) at room temperature uncovered additional Al_xO_y. Sputtering the sample at 823K revealed less Al_xO_y due to the diffusion of the Al_xO_y into the iron bulk or iron on top of the Al_xO_y. Prolonged sputtering at 823K eventually caused the (1x1) LEED pattern to appear on both the Fe(111) and Fe(110) surfaces.

The behavior of Al_xO_y on the Fe(100) face is different than that of the (110) and (111) planes. After a treatment with 0.05 or 0.4 Torr of water vapor the ratio of the aluminum Auger signal to the iron signal was unchanged indicating that no Al_xO_y had left the surface. After a 20 Torr treatment of water vapor about 50% of a monolayer of Al_xO_y is left on the

Al_xO_y/Fe(100) surface.

Auger peak positions were used to study the cooperative interaction between the Al_xO_y and iron in the presence of water vapor because the energy of an Auger transition of an element is often sensitive to the chemical environment (13). Metallic iron has a MVV Auger transition at 47eV which splits into a 42 and 52eV doublet in the oxide (the 42eV peak has been attributed to the participation of oxygen 2p electrons and the 52eV Auger peak to the influence of iron d electrons) (14). Elemental aluminum exhibits a LVV Auger peak at 68eV which shifts to 54eV in the oxide (10). When Al_xO_y is deposited on the iron substrate only 47 and 54eV peaks are present. When the Al_xO_y/Fe surface is treated with water vapor the 42eV peak, representative of iron oxide, shifts to 39eV (Fig.1) possibly indicating an alteration of the iron-oxygen bond and a chemical interaction between Al_xO_y and iron in an oxidizing environment (i.e. $Fe + Al_2O_3 + H_2O = FeAl_2O_4 + H_2$).

3.2 Reaction Rate Studies

The initial rate of ammonia synthesis was determined over the clean Fe(111), Fe(100), and Fe(110) surfaces (Fig. 2). The addition of aluminum oxide alone, elemental potassium coadsorbed with oxygen and aluminum oxide or potassium coadsorbed with aluminum oxide on the (110), (100), and (111) faces of iron decreases the rate of ammonia synthesis in direct proportion to the amount of surface covered by the additive in agreement with work that was reported recently (15). Rates of ammonia synthesis were also obtained over these different surfaces after they had been pretreated with water vapor.

3.2.1 Clean Fe Single Crystals Treated with Water Vapor Prior to the Ammonia Synthesis Reaction

Treatment of the clean (110), (100), and (111) surfaces to water vapor pressures of 0.05 or 0.4 Torr produces heavily oxided surfaces as shown by the splitting of the 47eV MVV iron Auger peak into 44 and 52eV peaks (14). The oxidized surfaces are readily reduced under the conditions used for the ammonia synthesis reaction, and the respective Fe(110), Fe(100), and Fe(111) surfaces are regenerated.

Treatment of a clean Fe(110) surface with 20 Torr of water vapor followed by reduction under synthesis conditions leaves a restructured surface (no (1x1) LEED pattern is obtained) whose initial ammonia synthesis activity is close to the (111) plane of iron. Visual inspection of the crystal shows that the initial mirror finish of the crystal is lost and a dull luster is now apparent. If this surface is kept under the ammonia synthesis conditions for one hour the surface again becomes inactive (Fig.3) and a (1x1) LEED pattern representative of the Fe(110) surface appears.

A 20 Torr water vapor pretreatment also restructures the (111) and (100) planes of iron. The restructured Fe(111) surface (broad and diffuse (1x1) LEED spots are obtained) shows a small decrease (about 5%) in its ammonia synthesis activity. The restructured Fe(100) plane (no LEED pattern is obtained) becomes almost as active as the (111) face of iron. Like the restructured Fe(110) face the activity of the restructured (111) and (100) surfaces return to their respective clean surface activity after one hour of ammonia synthesis. Sharp (1x1) LEED patterns for both surfaces are observed at this time.

3.3.3 Al_xO_y/Fe Surfaces Pretreated in Water Vapor Prior to the Ammonia synthesis Reaction

Treatment of Al_xO_y(0.5-1.5 monolayers)/Fe surfaces with 0.05 and 0.4 Torr of water vapor produced no restructuring as judged by the ammonia synthesis rate on the (111), (100), and (110) faces of iron.

Major changes in the activity of ammonia production for the Fe(110) face occurs when two or more monolayers of Al_xO_y are deposited on the surface prior to the water vapor treatment. After a water vapor treatment of 0.05 Torr the Al_xO_y/Fe(110) surface restructures. The restructured surface is now about as active as the Fe(100) plane (Fig.2). If two monolayers of Al_xO_y are deposited on a new Fe(110) surface than exposure to 0.4 torr or 20 Torr of water vapor produces a restructured surface almost as active as the Fe(111) crystal face (Fig.2). The restructured Al_xO_y/Fe(110) surface retains its high ammonia synthesis activity for longer than four hours under ammonia synthesis conditions (Fig.3).

A Fe(111) surface with two monolayers of Al_xO_y shows no noticable change in activity when pretreated with 0.05 of water vapor. Exposure to 0.4 or 20 Torr of water vapor restructures the surface producing a slight decrease (about 5%) in ammonia synthesis activity (Fig.3).

The Al_xO_y/Fe(100) surface exhibited no restructuring when exposed to 0.05 or 0.4 Torr of water vapor (conditions which restructured the Al_xO_y/Fe(110) and Al_xO_y/Fe(111) surfaces). Treatment of the Al_xO_y/Fe(110) surface with 20 Torr of water vapor caused restructuring and enhanced activity for the ammonia synthesis reaction. The synthesis rate over the restructured Al_xO_y/Fe(100) surface was similar to the clean Fe(111) surface activity (Fig.2). No deactivation was observed for the restructured Al_xO_y/Fe(100) surface after four hours of ammonia synthesis.

All the restructured Al_xO_y/Fe surfaces maintained their activity even after any surface Al_xO_y was removed by ion sputtering as monitored by AES. A ^{13}CO titration could not be used to determine the Al_xO_y coverage in that all the restructured surfaces (after the surface Al_xO_y had been removed by argon ion sputtering) chemisorbed substantially less carbon monoxide than the respective clean, unrestructured surfaces. For example, the restructured Fe(110) and Fe(100) surfaces chemisorbed approximately 40% less CO than the clean

Fe(110) and Fe(100) faces respectively. Prolonged sputtering (2-4 hours at 823K) caused the restructured surfaces to exhibit (1x1) LEED patterns and ammonia synthesis activities representative of the clean, unrestructured surfaces (no Al_xO_y was present at this time a judged by AES).

3.1.4 Water Vapor Pretreatment of Clean and Al_xO_y/Fe Single Crystal Surfaces in the Presence of Coadsorbed Potassium

Coverages of 0.1 to 1.0 monolayers of potassium adsorbed alone on the (111), (100), and (110) faces of iron failed to produce any promotional effects after pretreatments of 0.05, 0.4, and 20 Torr of water vapor (after the water vapor treatments the coverage of potassium was never more than 0.4 monolayers and it did not exceed 0.1 monolayers after the ammonia synthesis reaction in agreement with previous work (15)).

The same coverages of potassium coadsorbed with two monolayers of aluminum oxide on the Fe(110), Fe(100), and Fe(111) surfaces hindered the restructuring process in water vapor. As increasing amounts of potassium were coadsorbed more aluminum oxide was detected by AES after water pretreatments of 20 Torr and less restructuring of the iron occured (rates of ammonia synthesis over these surfaces were less than those surfaces which were restructured with just aluminum oxide). There was an one to one ratio between aluminum oxide and potassium on the surface (15) and in an extreme case where one monolayer of potassium was deposited on two monolayers of aluminum oxide AES showed that no aluminum oxide or potassium left the iron surface after a 20 Torr water vapor pretreatment and restructuring failed to occur.

3.2.4 Activation Energy for the Ammonia Synthesis Reaction Over Clean and Restructured Iron

The initial rate of ammonia synthesis was determined for the restructured Al_xO_y/Fe(110) and restructured clean Fe(110) surface at every 25K interval between 673K and 823K. Using an Arrhenius plot, the apparent activation energy of both restructured surfaces was found to be 18.6±1kcal/mole, in close agreement with the value of 19.4±0.5kcal/mole obtained for the clean single crystal surfaces (8).

3.3 Surface Structure characterization

The synthesis of ammonia from its elements is a structure sensitive reaction over iron and variation of rates observed in this study due to the pretreatments suggests that new surface orientations are being created. In an attempt to characterize the structure of the new surfaces scanning electron microscopy (SEM) and temperature programmed desorption were performed on the clean and restructured surfaces. SEM gave information on the microscopic appearance of the surfaces while TPD gave insight into the nature of the crystal orientations present on the restructured surfaces.

3.3.3 Scanning Electron Microscopy

The development of a clean Fe(110) single crystal surface into a restructured surface was followed by SEM. Figure 4 shows micrographs taken of restructured Al_xO_y/Fe(110) surfaces (a clean, unrestructured iron single crystal showed only a flat and featureless surface). At an exposure of 0.05 Torr of water vapor the formation of crystallites, about one micron in diamenter, appear on the Al_xO_y/Fe(110) surface (Fig.4a). Using 0.4 Torr of water vapor reconstructs the entire surface as can be seen in Figure 4b.

A Fe(110) surface restructured in 20 Torr of water vapor is shown in Fig. 5a. The surface appears uniform in appearence unlike the Al_xO_y/Fe(110) restructured surface. Figure 5b shows the same surface after one hour of ammonia synthesis. The surface now shows less pronounced features, similar to the unrestructured Fe(110) plane. This is supported by the appearance of a (1x1) Fe(110) LEED pattern and inactivity towards the production of ammonia in the synthesis reaction.

3.3.2 Temperature Programmed Desorption

Ammonia adsorption and desorption has been studied in UHV on the Fe(111), Fe(100), and Fe(110) surfaces (16,17). Molecular ammonia completely desorbs from all the iron surfaces by 400K. In contrast to this it has been found in this study that after the high pressure ammonia synthesis reaction ammonia desorbs in the 400-750K temperature range from all the iron single crystal surfaces studied. The mechanism hasn't been studied in detail but more important to this work is that the ammonia desorption can be used to probe the different surface orientations since different TPD spectra are observed following ammonia synthesis for the (110), (100), (111), and (211) iron single crystal surfaces. The Fe(211) TPD spectrum is included because it helps support a conclusion presented later (see section 4.0).

Ammonia TPD spectra for the four surfaces are shown in Figure 6. The Fe(110) surface displays one desorption peak (β_3) with a peak maximum at 658K. Two desorption peaks are seen for the Fe(100) surface (β_2 and β_3) at 556K and 661K. The Fe(111) surface exhibits three desorption peaks (β_1, β_2, and β_3) with peak maxima at 495K, 568K, and 676K and the Fe(211) plane has two desorption peaks (β_2 and β_3) at 570K and 676K. Temperature programmed desorption spectra for the Al_xO_y/Fe(110), Al_xO_y/Fe(100), and Al_xO_y/Fe(111) surfaces restructured in 20 Torr of water vapor are shown in Figure 7. A new desorption peak, β_2 develops on the restructured Al_xO_y/Fe(110) surface and an increase in the β_2 peak occurs on the restructured Al_xO_y/Fe(100) surface. The β_2 peaks from the restructured Al_xO_y/Fe(110) and Al_xO_y/Fe(100) surfaces grow in the same temperature range as the Fe(111) and Fe(211) β_2 peaks. Deactivation of the restructured surfaces by prolonged sputtering at 832K reduces the intensity of the β_2 peaks on the restructured Al_xO_y/Fe(110) and Al_xO_y/Fe(100) surfaces to the same level as the respective clean surfaces.

The clean Fe(110), Fe(100), and Fe(111) surfaces restructured with 20 Torr of water vapor produce the same TPD spectra as the Al_xO_y restructured surfaces. Deactivation of the (100) and (110) clean restructured iron surfaces is quick under the ammonia synthesis conditions and the β_2 peaks become equivalent in intensity to those on the respective clean surfaces within one hour of ammonia synthesis.

4.0 Discussion

Examination of the results reveals several effects of Al_xO_y on iron single crystal surfaces in the presence of water vapor. Perhaps the most significant is that Al_xO_y prevents the reconversion of the restructured, active surfaces to ones less active in the ammonia synthesis (i.e. Fe(110) and Fe(100) surfaces). Another effect of Al_xO_y is its ability to restructure iron single crystals to new surface orientations active in the ammonia synthesis at water vapor pressures lower than those needed to restructure clean iron single surfaces. The fact that the activation energy for ammonia synthesis over the restructured Al_xO_y/Fe surfaces is the same as over the clean surface implies that iron is still the active phase for the synthesis of ammonia.

The nature of restructuring of the Al_xO_y/Fe surfaces is indicated by the kinetic and TPD results. Kinetic data shows that through restructuring the activity towards ammonia synthesis of the Fe(110) and Fe(100) planes approaches that of the clean Fe(111) or Fe(211) planes while the Fe(111) plane is not affected greatly by restructuring. The activity of the clean Fe(111) and Fe(211) planes is usually attributed to the presence of C_7 sites (Fe atoms with seven nearest neighbors) (8,9,18). The clean Fe(100) and Fe(110) plane lack these sites. This suggests that restructuring in water vapor produces highly coordinated C_7 sites on the restructured Fe(110) and Fe(100) surfaces. The increase in rates over the restructured Fe(110) and Fe(100) planes is not attributable to an increase in surface area since less CO is adsorbed on these surfaces when compared to the respective clean surfaces. A similar decrease in CO adsorption has also been observed on iron ammonia synthesis catalysts that have been restructured with ammonia (18). These results were interpreted as due to the formation of C_7 sites which are not able to adsorb as much CO as lower coordinated sites because of steric reasons. This explanation is applicable to the present study and it further supports the idea of formation of C_7 sites upon water vapor restructuring.

While the ammonia TPD results are not as convincing as the kinetic data they certainly point towards the formation of surface orientations which contain C_7 sites during restructuring. The growth of the b_2 peaks upon restructuring of the Fe(110) and Fe(100) surfaces suggests that the surfaces change orientation upon water vapor treatment. The β_2 peaks also reside in the same temperature range as the Fe(111) β_2 peak. It seems likely that the TPD peaks in this temperature range act as a signature for the C_7 site since the Fe(211) surface (Fig.6), which contains C_7 sites and is highly active in the ammonia synthesis reaction (9) also exhibits a β_2 peak after the ammonia synthesis with a peak maximum at 570K. These results suggest that surface orientations which contain C_7 sites, such as the Fe(111) and Fe(211) planes, are being formed during the reconstruction of clean and Al_xO_y treated iron surfaces but only in the presence of Al_xO_y does the active restructured surface remain stable under the ammonia synthesis conditions.

The process by which iron restructures seems to involve both oxidation and reduction. Initial oxidation by water vapor destroys the original morphology of the iron surface. On reduction with synthesis gas the oxygen is removed and the resulting metallic iron is left in orientations (i.e. Fe(111) and Fe(211)) active for the ammonia synthesis. If no support phase is present (i.e. Al_xO_y) reconversion of the iron into less active orientations is rapid under ammonia synthesis conditions. It has been shown in UHV (19,20) that the oxidative process on the Fe(110) plane is more facile than on the Fe(100) surfaces and this agrees with the fact that the Fe(110) surface can restructure, in this study, with lower water vapor pressures than are needed for the Fe(100) plane.

With the addition of Al_xO_y the mobility of the iron is increased and restructuring can occur at lower pressure of water vapor. The SEM micrographs suggest that iron is forming crystallites on top of the restructured Al_xO_y/Fe(110) surface (opposed to the uniform appearance of the restructured clean Fe(110) surface). AES finds little Al_xO_y on the surface suggesting that the iron has diffused on top of the Al_xO_y islands. These findings can be explained by considering wetting properties and the minimization of the free energy for the iron oxide-aluminum oxide system.

In vacuum or in a reducing environment (i.e. ammonia synthesis conditions), metallic iron will not spread over aluminum oxide (metallic iron has a higher surface tension than aluminum oxide (21)). Conversely, in an oxidizing environment (i.e. the water vapor treatments) iron oxide forms (the surface tension of the oxide will be lower than the metal (21,22)) and a chemical interaction between iron and aluminum oxide might result as inferred from the AES results. Both these considerations favor iron wetting the aluminum oxide. Using transmission electron microscopy it has been shown that iron wets alumina (Al_2O_3) in an oxidizing environment or even in the presence of hydrogen which contains trace amounts of water vapor (23). Using micro electron diffraction the formation of iron aluminate (i.e. $FeAl_2O_4$) in the presence of an oxygen source was also postulated (23).

Whereas 20 Torr of water vapor was needed to restructure clean iron single crystals only 0.4 Torr of water vapor is needed to restructure an Al_xO_y/Fe surface since Al_xO_y provides an alternate and apparently more facile mechanism for the migration of iron. Upon reduction metallic iron is left in a highly active orientation (i.e. Fe(111) and Fe(211)) for the ammonia synthesis reaction. The Al_xO_y now stabilizes the active iron since if the Al_xO_y were not present the iron would move to positions coincident with the bulk periodicity.

The formation of an iron aluminate during reconstruction of the iron surface may be responsible for the stability of the restructured Al_xO_y/Fe surfaces. The formation of iron aluminate has been postulated in XPS studies on $Fe-Al_2O_3$ and $Fe_3O_4-Al_2O_3$ systems (24,25) as well as in numerous studies on the industrial ammonia synthesis catalyst (26,27,28). The volume of an $FeAl_2O_4$ molecule is approximately equal to the volume of seven iron atoms in a bcc lattice (26) so that $FeAl_2O_4$ can exist as a skeleton in the iron lattice with little distortion. The low coverages of Al_xO_y on the restructured surfaces suggests that the support effect might be coming through inclusions of $FeAl_2O_4$ in the near surface region. This is supported by the fact that ion sputtering the restructured surfaces reveal subsurface Al_xO_y.

A promoter effect by potassium still has not been observed on iron single crystal studies which have approached industrial conditions of 100 atm total reactant pressure. Previous work reported recently (15) observed no electronic promotion when potassium was adsorbed alone or coadsorbed with oxygen and Al_xO_y on the iron surfaces. The conditions used in this study revealed no promotional effects by potassium.

Potassium promotion seems to be extremely sensitive to the environment. UHV studies (3,4) showed that potassium increased the rate of dissociative nitrogen chemisorption by more than an order of magnitude over single crystals and polycrystalline foils but with the addition of oxygen the promotional effect decreased rapidly. The turnover number for unpromoted, singly promoted (Al_2O_3), and doubly promoted (K_2O and Al_2O_3) iron catalysts have been found to be roughly equivalent when a total pressure of one atmosphere of hydrogen and nitrogen is used for the ammonia synthesis conditions (29). The studies performed in this laboratory find no electronic or structural promotion by potassium at 20 atm of 3:1 H_2 and N_2. To understand the effect of potassium it seems necessary to reach the industrial synthesis conditions (100 atm total pressure). Combined UHV/high pressure experiments capable of reaching these conditions are being planed for the future.

5.0 Summary

Treating the (110), (100), and (111) faces of iron with 20 Torr of water vapor causes surface restructuring. The restructured Fe(110) and Fe(100) surfaces become as active as the clean Fe(111) surface in the ammonia synthesis. The restructured Fe(111) exhibits a slight decrease (about 5%) in activity when compared to the clean Fe(111) surface. The restructured (110), (100), and (111) surfaces reconvert to their unrestructured orientations within one hour of ammonia synthesis.

The same restructuring on the Fe(110), Fe(100), and Fe(111) surfaces can be performed with water vapor in the presence of aluminum oxide. In this case 20 Torr of water vapor restructures the Al_xO_y/Fe(100) and only 0.4 Torr of water vapor is needed to restructure the Al_xO_y/Fe(110) surface so that they become as active as the Fe(111) face in ammonia synthesis. The restructured Al_xO_y/Fe(110) and Al_xO_y/Fe(100) surfaces maintain their activity for longer than four hours in the ammonia synthesis conditions. The formation of iron aluminate in the iron near surface region is invoked to explain the stability of the restructured Al_xO_y/Fe surfaces.

The reaction rate studies and ammonia temperature programmed desorption results suggest that planes containing C_7 sites, such as the Fe(211) and Fe(111) surfaces, are being created during the water vapor pretreatments with or without aluminum oxide. Only when aluminum oxide is present will these active surfaces remain stable and not reconvert to less active surfaces (i.e. Fe(110) and Fe(100) planes).

Coadsorbing potassium with aluminum oxide or depositing potassium alone on iron single crystals produces no promotional effects under the water vapor pretreatments used in this study.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under contract number DE-AC03-76SF00098.

References

1. Nielsen, A., "An Investigation on promoted Iron Catalysts for the Synthesis of Ammonia", Jul. Gjellerups Forlag, 3rd Ed., Copenhagen (1968).

2. Ozaki, A., and Aika, K., "Catalysis, Science and Technology," Part 1, Chap. 3. Springer-Verlag, Berlin, 1981.

3. Ertl, G., Weiss, M., and Lee, S.B., Chem. Phys. Lett. 60, 391(1979).

4. Paal, Z., Ertl, G., and Lee, S.B., Appl. Surface Sci. 8, 231(1981).

5. Nielsen, A., Catal. Rev. 4, 1(1970).

6. Frankenburg, W.G., in "Catalysis Vol.3", (Ed. P.H. Emmett), Reinhold NY (1955), p.171.

7. Ertl, G., in "Robert Welch Conferences on Chemical Research XXV Heterogeneous Catalysis", Houston 179(1981).

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

9. Strongin, D.R., Bare, S.R., and Somorjai, G.A., submited to J. Catal.

10. Madden, H.H., and Goodman, D.W., Surface Sci. 150, 39(1985).

11. Emmett, P.H., in "The Physical Basis for Heterogenous Catalysis", (Eds. E. Drouglis and R.I. Jaffee), Plenum (1975), p.3.

12. Biberian, J.P., and Somorjai, G.A., Appl. Surface Sci. 2, 352(1979).

13. Wagner, C.D., in "Practical Surface Analysis" (D. Briggs and M.P. Seah, Eds.), Appendix 4, Wiley, New York, 1983.

14. Ertl, G., and Wandelt, K., Surface Sci. 50, 479(1975).

15. Bare, S.R., Strongin, D.R., and Somorjai, G.A., J. Phys. Chem., accepted.

16. Grunze, M., Bozso, F., Ertl, G., and Weiss, M., Appl. Surface Sci. 1, 241(1978)

17. Weiss, M., Ertl, G., and Nitschke, F., Appl. Surface Sci., 2, 614(1979).

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

19. Langell, M., and Somorjai, G.A., J. Vac. Sci. and Tech. 21,

858(1982).

20. Brundle, C.R., Surf. Sci. 66, 581(1977).

21. Overbury, S.H., Bertrand, P.A.,and Somorjai, G.A., Chem. Rev. 75(5), 547(1975).

22. Beruto, D., Baro, L.,and Passerone, A., in "Oxides and Oxide Films" (Ashok k. Vijh, Ed.), Vol. 6. Deckker, New York, 1981.

23. Sushumna, I.,and Ruckenstein, E., J. Catal. 94, 239(1985).

24. Paparazzo, E., Dormann, J.L.,and Fiorani, D., Phys. Rev. B

25. Paparazzo, E., Appl. Surf. Sci. 25, 1(1986).

26. Borghard, W.S.,and Boudart, M., J. Catal., 80, 194(1983).

27. Ludwiczek, H., Preisinger, A., Fischer, A., Hosemann, R., Schonfeld, A.,and Vogel, W., J. Catal. 51, 326(1978).

28. Fagherazzi, G., Galante, F., Garbassi, F.,and Pernicone, N., J. Catal. 26, 344(1972).

29. Khammouma, S., Ph.D. dissertation, Stanford Univ., 1972.

Figure Captions

Figure 1

AES spectra of oxidized iron and a partially oxidized iron-aluminum oxide surface. Note the shift of the 44eV iron peak to 39eV when aluminum oxide is coadsorbed on the oxided surface.

Figure 2

Ammonia synthesis rates over clean iron single crystals and restructured Al_xO_y/Fe surfaces (note that water vapor pressures are given in mTorr). A rate is given to the clean Fe(110) surface in this figure for clarity but in actuality the ammonia yield from this crystal face is below the detection limit of the PID (1×10^{-10}moles NH_3/cm^2-sec.) used in this study.

Figure 3

The effect of Al_xO_y on the activity of the restructured Fe(110) surface under the ammonia synthesis conditions. Deactivation of the clean restructured Fe(110) surfaces occurs within one hour. The restructured Al_xO_y/Fe(110) surface maintains its activity for greater than four hours.

Figure 4

SEM of the restructured Al_xO_y/Fe(110) surface: (a) An

Al_xO_y/Fe(110) surface after after a 0.05 Torr treatment of water vapor and subsequent reduction in the synthesis gas mixture; (b) An Al_xO_y/Fe(110) surface after a 0.4 Torr treatment of water vapor followed by reduction. The AES and SEM results indicate that aluminum oxide is located under the active iron surface during ammonia synthesis thereby avoiding blocking of the active catalytic iron sites.

Figure 5

SEM micrographs of the restructured Fe(110) surface: (a) taken after a 20 Torr treatment of water vapor; (b) taken after one hour of ammonia synthesis (note the smoothing out of the features which were observed after the initial restructuring). The features on these surfaces are much more uniform in appearance than those on the restructured Al_xO_y/Fe surfaces.

Figure 6

Ammonia TPD from clean iron single crystals (heating rate is 10 K/sec). Different TPD spectra are found for each surface. Only the Fe(111) and Fe(211) planes exhibit large desorption peaks in the temperature range 400K - 600K. These peaks are attributed to the presence of C_7 sites on the (111) and (211) planes of iron.

Figure 7

Ammonia TPD from restructured iron single crystals (heating rate is 10 K/sec). A β_2 state grows on the restructured Al_xO_y/Fe(110) surface and the restructured Al_xO_y/Fe(100) face in the same temperature range as the Fe(111) β_2 peak and the Fe(211) β_2 peak. This indicates that active planes for ammonia synthesis, containing C_7 sites (i.e. Fe(111) and Fe(211) surfaces), are forming upon the water vapor induced restructuring.

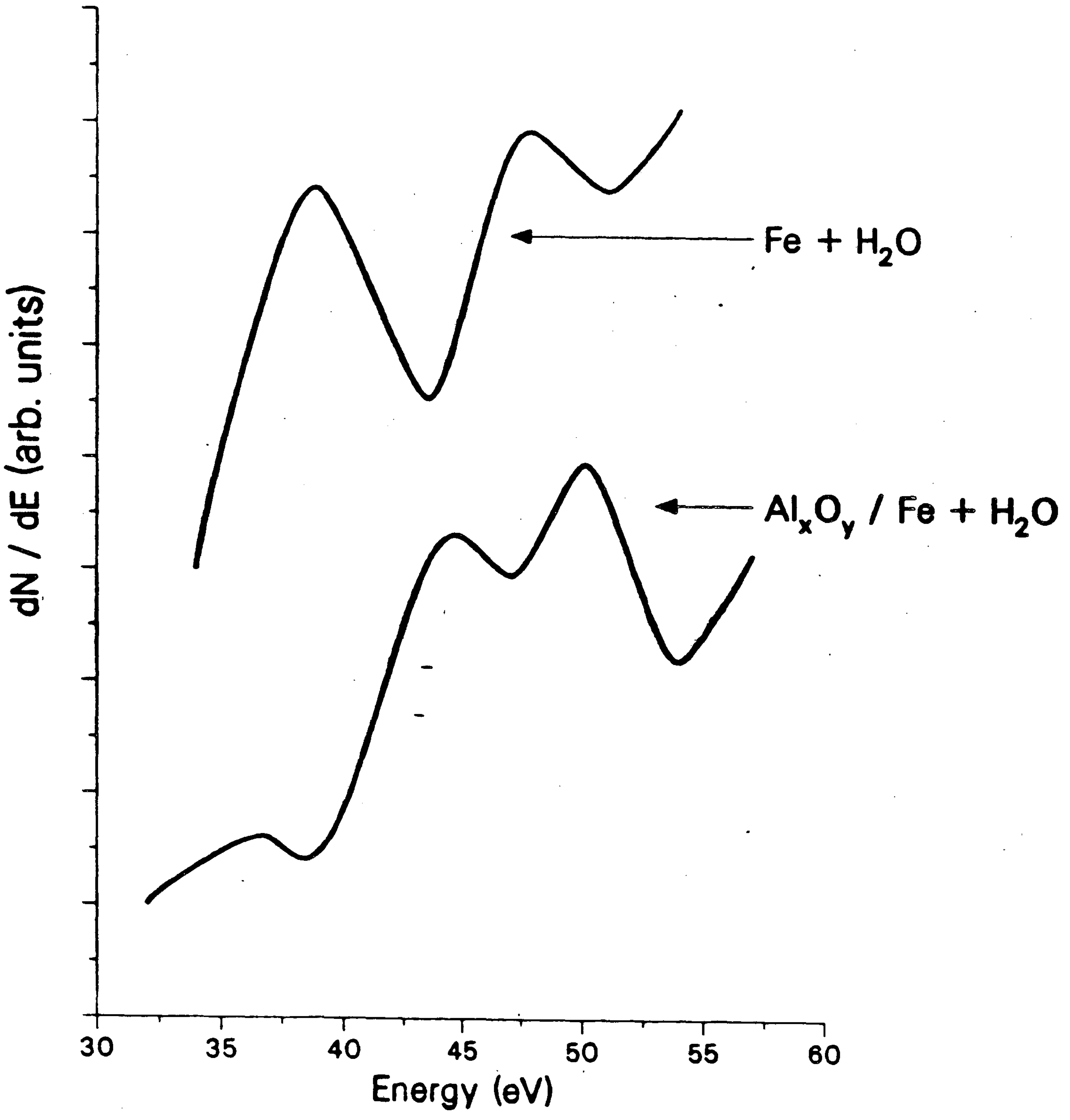


Figure 1

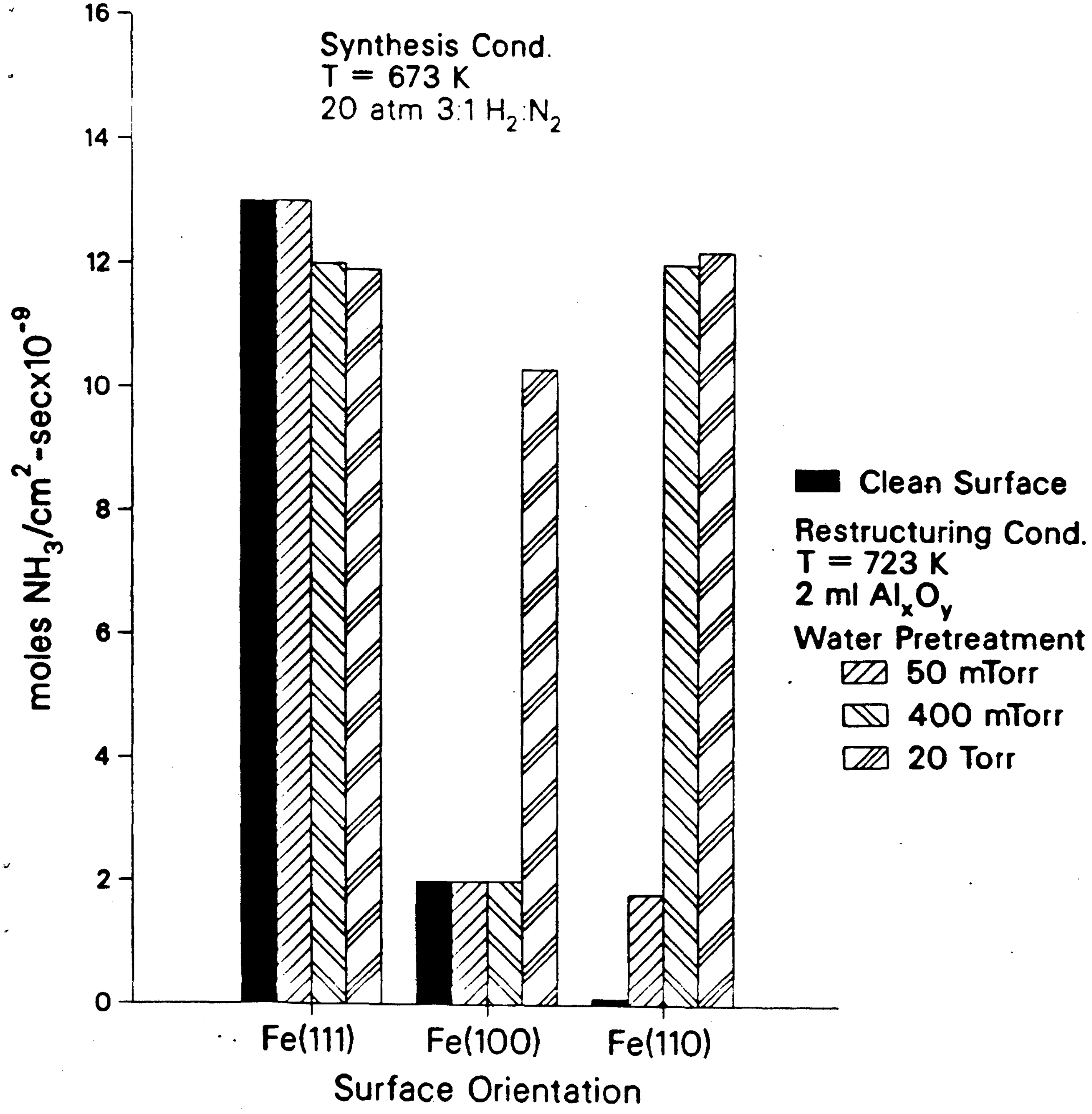

16
14
12
10
8
6
4
2
0
moles NH_3/cm^2-sec$\times 10^{-9}$
Synthesis Cond.
T = 673 K
20 atm 3:1 H_2:N_2
Fe(111)
Fe(100)
Fe(110)
Surface Orientation
Clean Surface
Restructuring Cond.
T = 723 K
2 ml Al_xO_y
Water Pretreatment
50 mTorr
400 mTorr
20 Torr

Figure 2

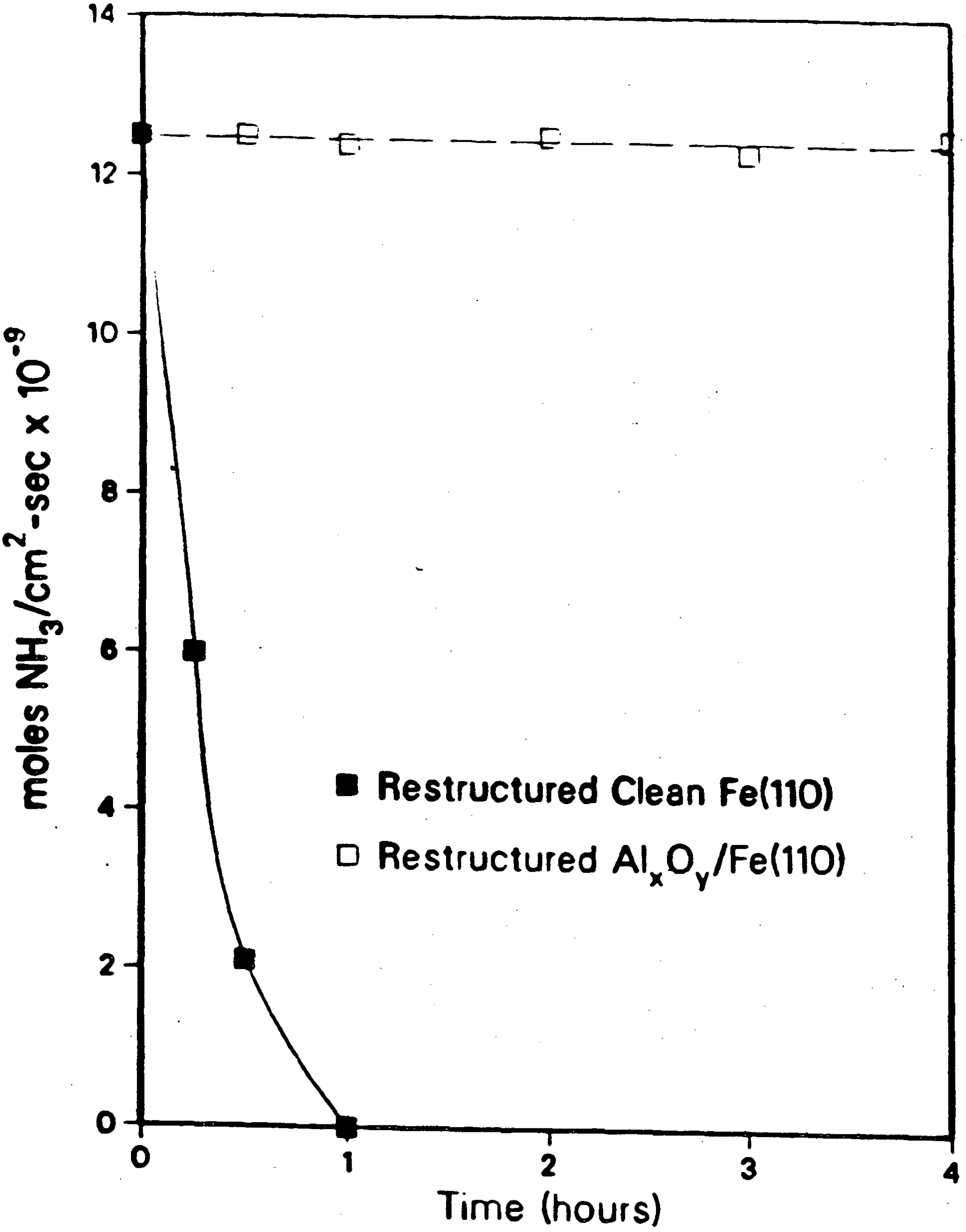
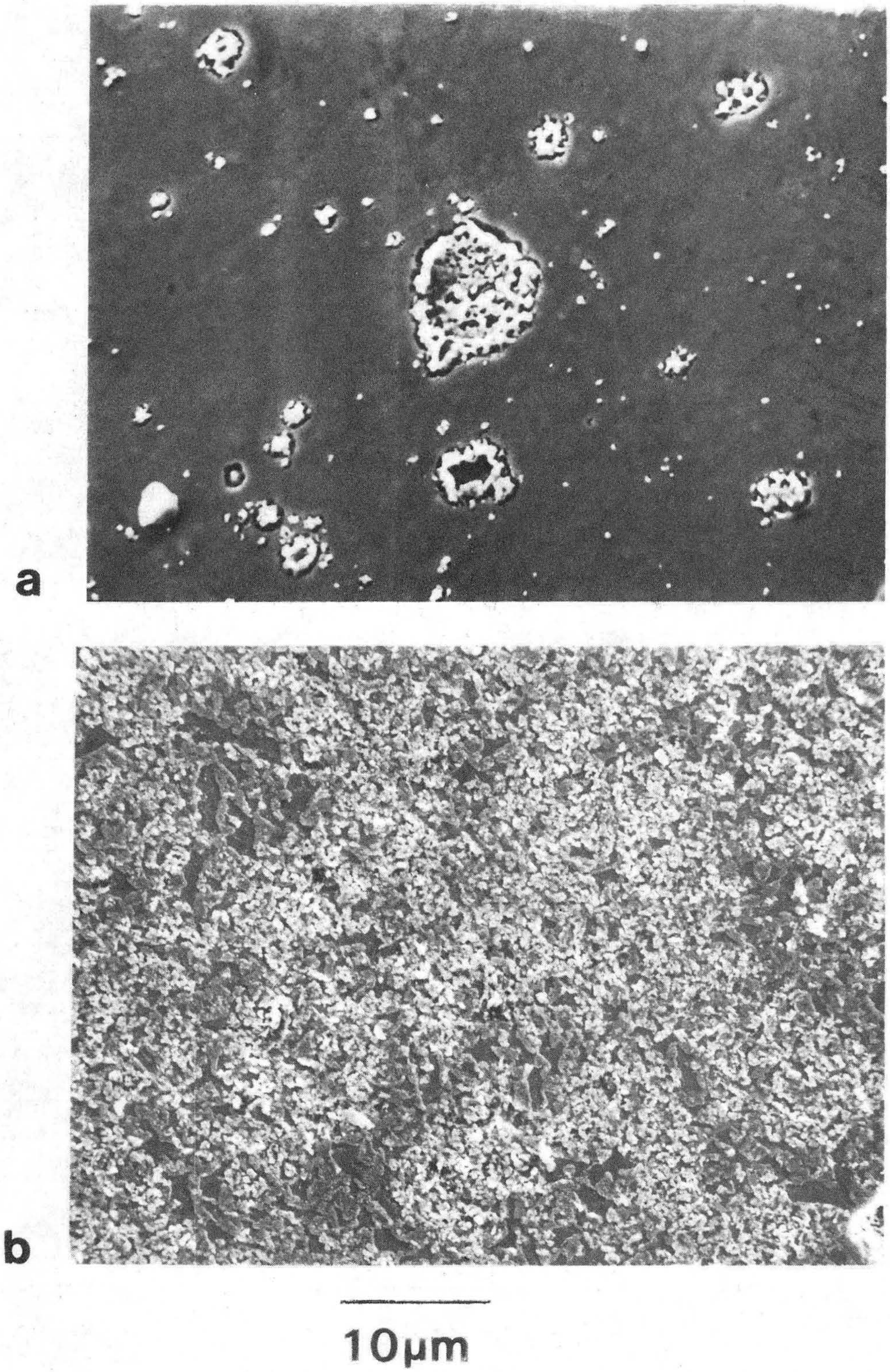
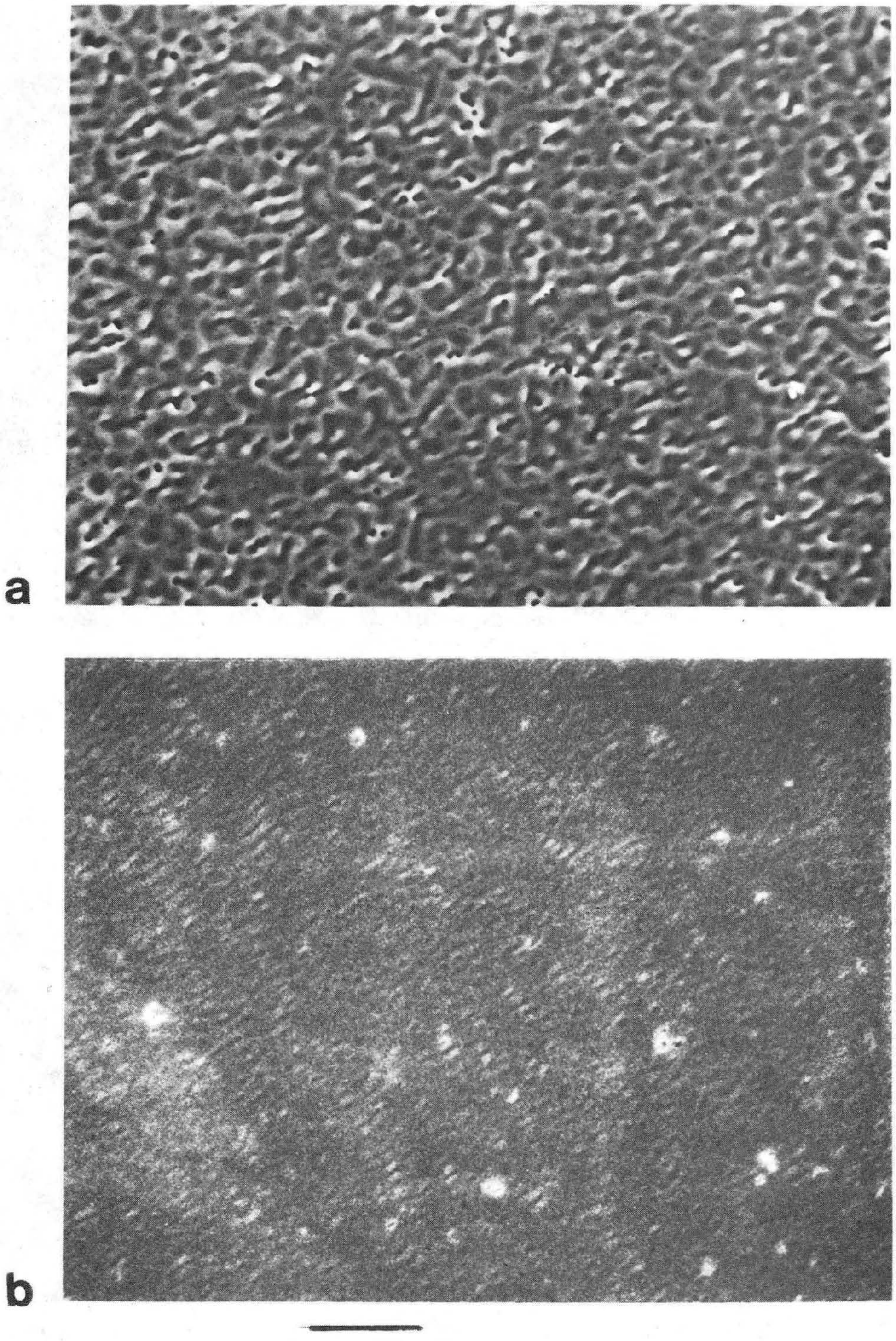

moles NH_3/cm^2-sec x 10^{-9}
14
12
10
8
6
4
2
0
0
1
2
3
4
Time (hours)
■ Restructured Clean Fe(110)
□ Restructured Al_xO_y/Fe(110)

Figure 3



XBB 866-4791

Figure 4



XBB 866-4790

Figure 5

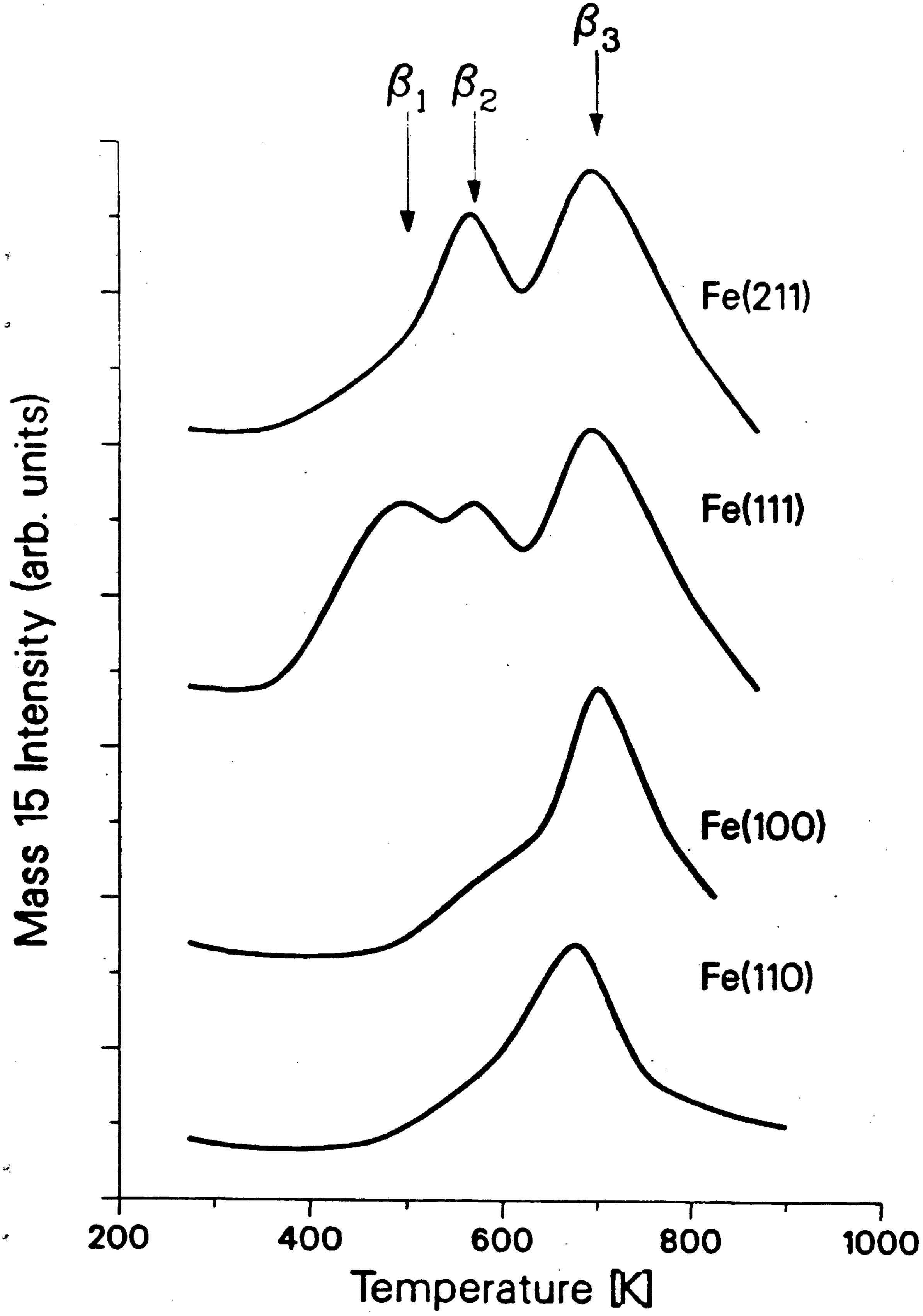
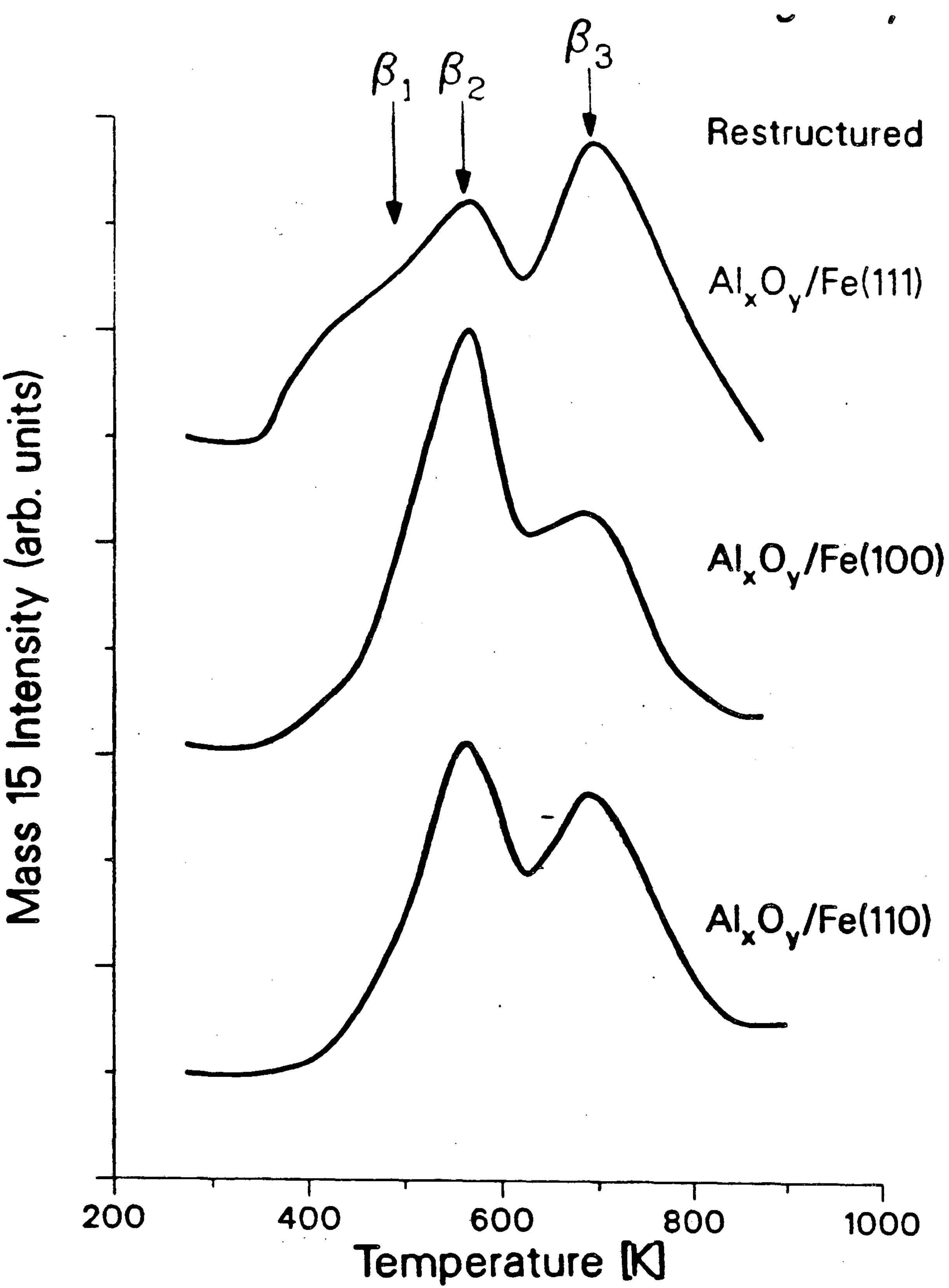

β_1
β_2
β_3
Fe(211)
Fe(111)
Fe(100)
Fe(110)
Mass 15 Intensity (arb. units)
200
400
600
800
1000
Temperature [K]

Figure 6



-- XBL 866-2296 --

Figure 7