LBL-18200
Preprint c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
JAN 7 1985
LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

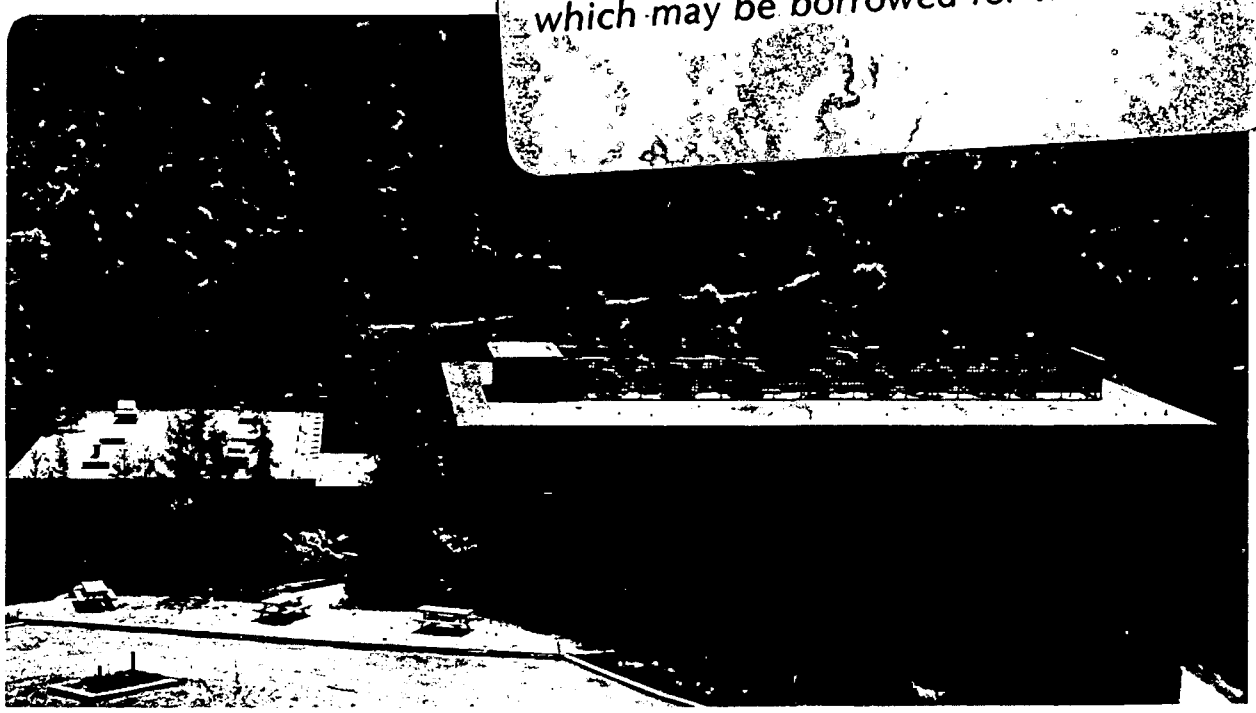
Submitted to the Journal of Catalysis

THE AMMONIA SYNTHESIS OVER RHENIUM SINGLE CRYSTAL CATALYSTS: STRUCTURE SENSITIVITY, KINETICS AND THE EFFECTS OF K AND O

M. Asscher, J. Carrazza, M.M. Khan, K.B. Lewis, and G.A. Somorjai

October 1984

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks



LBL-18200 c.2

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

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-18200

THE AMMONIA SYNTHESIS OVER RHENIUM SINGLE CRYSTAL CATALYSTS: STRUCTURE SENSITIVITY, KINETICS AND THE EFFECTS OF K AND O.

M. Asscher,* J. Carrazza, M.M. Khan,
K.B. Lewis, 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.

*Present Address: Department of Physical Chemistry
The Hebrew University of Jerusalem
Jerusalem 91904, ISRAEL

THE AMMONIA SYNTHESIS OVER RHENIUM SINGLE CRYSTAL CATALYSTS: STRUCTURE SENSITIVITY, KINETICS AND THE EFFECTS OF K and O.

M. Asscher,* J. Carrazza, M.M. Khan,
K.B. Lewis, 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 ammonia synthesis was investigated over model single crystal and polycrystalline foil rhenium catalysts at 20 atm reactants pressure and in the temperature range of 720-900K. The structure sensitivity of this reaction on four rhenium single crystals was studied. A remarkable sensitivity to the catalysts' surface structure was observed with reactivity ratio of 1:94:920:2820 for the Re(0001), Re($10\bar{1}0$), Re($11\bar{2}0$) and the Re($11\bar{2}1$) crystal faces respectively. The importance of high coordination metal atom sites both in the first and in the second layers are clearly indicated by these results. An apparent activation energy for the reaction of 20.4 ± 1.1 kcal/mole was observed, regardless of the catalyst surface structure. Kinetic data, pressure dependence analysis, and isotope effect indicate that, as with the iron catalyst, the rate limiting step for the reaction is the dissociative chemisorption of the nitrogen molecule. Potassium atoms on the clean rhenium catalysts were found neither to promote nor to poison the reaction. The coadsorption of potassium with oxygen does not suppress the reactivity of the catalyst and stabilization of the potassium atoms on the surface occurs. The presence of oxygen alone appears to increase the reaction rate.

INTRODUCTION

The synthesis of ammonia over iron has been studied in detail by generations of workers in the field of catalysis (Haber, Emmett,[1] Ozaki,[2] Boudart,[3] Tamaru...) and more recently by those engaged in surface science studies. (Brill,[4] Ertl,[5] Somorjai[6]) The kinetic parameters of the reaction have been determined and the structure sensitivity have been well documented by studies using single crystal surfaces. The effect of potassium in greatly enhancing the reaction rate is well established.

Recently we reported[7] that rhenium also exhibits remarkably high activity for ammonia synthesis. Using polycrystalline rhenium foils of $\sim 1 cm^2$ area we determined reaction rates in the range of 10^{17} molecules cm^{-2} sec^{-1} in the temperature range of 850 - 900K in our high pressure-low pressure apparatus at a total reactant pressure of 20 atm. that compare well with the activity of the most active iron(111) crystal surface under similar experimental conditions. In this paper we report the results of further studies of the ammonia synthesis over rhenium that were extended to single crystal surfaces; and over a much wider temperature range of 720 - 900K. We also determined the kinetic parameters of ammonia production for each crystal surface, detected a deuterium isotope effect and uncovered that potassium has a much smaller promotion effect of ammonia synthesis over rhenium than over iron catalysts.

Of the four single crystal surfaces of rhenium that were studied (0001), $(10\bar{1}0)$, $(11\bar{2}0)$ and $(11\bar{2}1)$ the $(11\bar{2}1)$ crystal face was found to be the most active, about 2800 times over the least active (0001) crystal face. Just as in the case of iron the more open crystal

faces are the most active in dissociating N_2. This observation points to the important catalytic role of highly coordinated metal atoms that are located in the second layer under the surface but are still accessible to adsorbed nitrogen on the open crystal faces. The seven coordinated metal sites that are thought to be the most active for bcc iron (in the second layer under the surface) are not playing unique roles for the hcp rhenium since the most active $(11\bar{2}1)$ surface does not possess any of these sites.

The kinetic orders and the activation energies found over rhenium are sufficiently similar to those found over iron to indicate a great similarity in the reaction mechanisms. However, potassium is not such a good promoter of ammonia synthesis over rhenium as it is over iron. If the beneficial influence of potassium is associated with aiding the reconstruction of iron to (111) orientation crystallites the absence of any major effect of K on rhenium is due to the much slower rates of restructuring of this high melting point metal under the reaction conditions.

EXPERIMENTAL

The apparatus used[8] consisted of an ultra high vacuum chamber with a base pressure of $1\text{-}3 \times 10^{-9}$ torr. It was equipped with a four grid retarding field analyzer for low energy electron diffraction (LEED) and Auger electron spectroscopy measurements to determine surface structure and chemical composition respectively. A quadrupole mass spectrometer was used for gas analysis and an ion sputtering gun for sample cleaning. A high pressure cell which enclosed the sample and separated it from the rest of the UHV chamber was connected to an external gas manifold. The twenty atmosphere mixture of reactant and product gases were continuously circulated over the single crystal samples via a positive displacement pump. The temperature of the sample could be

maintained by resistive heating within ± 2 ^{o}C. The edge of the single crystal sample was covered by spot welded platinum foil in order to minimize reactions taking place there. The sample was supported by a pair of platinum wire mounts. The temperature of the sample was controlled and monitored by spotwelding a Pt/Pt-5%Rh thermocouple at the edge.

Gas samples were periodically withdrawn through a sampling valve into a photoionization detector, having 10.2eV photons, to determine the partial pressure of ammonia. A recording integrator was used to measure the signal as a function of the reaction time.

The single crystal samples were typically 1 cm^2 discs of 1 mm thickness that were oriented and then polished on both sides by standard metallurgical techniques. The major contaminants were carbon and silicon, which could be readily removed by Ar^+ ion sputtering ($8x10^{-6}$ A/cm^2 at 500V) followed by annealing at 1250 ^{o}C for 7 minutes and then, if necessary, an additional oxygen treatment at $2x10^{-7}$ torr for 2 minutes with the crystal heated at 500 ^{o}C. The removal of Si could be best effected by Ar^+ ion sputtering at the same ion density at 1500V and 1000 ^{o}C followed by a similar annealing treatment. Surface structures were then verified using LEED.

RESULTS

The production of ammonia from nitrogen and hydrogen over clean polycrystalline rhenium foil was reported earlier at catalysts' temperature range of 603-713K.[7] In this study we have extended the temperature range to 900K in order to be able to monitor the production of NH_3 from the less active Re surfaces. These included polycrystalline

foils as well as four different single crystal surfaces. The isotopic effect due to the use of D_2 instead of H_2 and the effect of potassium promoters was studied here as well.

In Fig. 1, a typical ammonia production as a function of time is presented for two of the most active rhenium single crystal surfaces at 870K. Note the deviation from linearity of the production rate of NH_3 partial pressures higher than 6 Torr. This effect was noted earlier[7] for the polycrystalline catalysts and was attributed to a reversible poisoning by the ammonia product. Note also in Fig. 1 the higher activity of the Re(11$\bar{2}$1) single crystal face as compared with the Re(11$\bar{2}$0) surface. The structure sensitivity of this reaction will be discussed below.

The catalysts' temperature dependence of the rate of the ammonia synthesis was measured for two different polycrystalline foils and the Re(11$\bar{2}$0) single crystal face. Although different activities were measured for the two different foils and for the single crystal catalyst, the apparent activation energies, as obtained from Arrhenius plots, were the same, 20.4±1.1 kcal/mole for all three samples. In Fig. 2 a plot of the logarithm of the rate vs. the reciprocal of catalysts' temperature is shown for a polycrystalline foil and th Re(11$\bar{2}$0) single crystal catalyst.

A. Structure Sensitivity

The first evidence for structure sensitivity in the NH_3 synthesis over rhenium came from large differences in the activity of polycrystalline foils of different origin. Variations in activity of up to a factor of five were observed. The possibility that on polycrystalline foils one may have several crystal planes which are exposed with various and uncontrolled distributions led us to study the reaction over different single crystal faces as catalysts.

We have studied the ammonia synthesis yield over four different single crystal surfaces at identical conditions of 870K with total reactants pressure of 20 atm, $P_{H_2} : P_{N_2}$ =3:1. The crystals were the closed packed basal plane, Re(0001), Re(10$\bar{1}$0), Re(11$\bar{2}$0) and the Re(11$\bar{2}$1) faces. In all cases the crystals were polished in both sides and LEED patterns which are characteristic of those planes were obtained. No sign of reconstruction of any of these surfaces after Ar^+ sputtering and annealing at 1600K for 7 min. in vacuum could be detected. The same pattern was observed also after the high pressure reaction, if the crystal was kept hot during the high pressure loop pump down period, prior to opening it to UHV.

The LEED spots were sharp with the Re(0001) and Re(11$\bar{2}$0) samples while the Re(10$\bar{1}$0) and Re(1121) patterns were somewhat diffused even after longer annealing periods. This suggests that for these samples the ordering of the surface atoms was not as long range as in the case of the former two planes. The temperature of the crystals during the reaction was higher than the typical ammonia synthesis conditions using iron catalysts,[1] since we tried to obtain conditions in which some activity would be detectable even with the least active (0001) plane. By keeping the same experimental conditions for the more active crystals as well, an accurate comparative study is possible.

To calibrate the sensitivity of the detection system, a Pt foil, comparable in size to the Re samples $\sim cm^2$, was cleaned, annealed and then heated to 870K with the 20 atm. of reactants at the regular reaction conditions. This way the baseline for the detection of ammonia was determined and thus the detection limits could be established. A rate of $(5\pm4)\bullet10^{13}$ NH_3 molec/$cm^2\bullet$sec. was our experimental detection limit.

The Re(0001) sample produced undetectable amounts of NH_3 with the reactants circulating at the reaction conditions for about one hour. If sputtered by Ar^+ bombardment, 5μA at 500V for 5 min. each side of the crystal without subsequent annealing, an initial rate more than an order of magnitude higher than the detection limit was measured. This rate decreased after few minutes possibly due to partial annealing. When the sample was annealed at 1300K for 5 min., the rate was already reduced substantially to only about a factor of two higher than the detection limit. The production rate dropped to (or below) the detection limit when the sample was annealed at 1640K for 7 minutes.

Next we cut the Re single crystal rod to the $(10\bar{1}0)$ orientation which is slightly more open than the close packed basal plane. The activity here was much higher but still lower than the reactivity measured using the polycrystalline foil. A rate of $(4.7\pm1.5)\bullet10^{15}$ was measured. Since the reactivity was still more than an order of magnitude lower than that of the foil, we cut the more open crystals - $Re(11\bar{2}0)$ and $Re(11\bar{2}1)$ where atoms of second layers are exposed and more space is available between the topmost surface atoms. The rates were $(4.6\pm0.5)\bullet10^{16}$ and $(14\pm2)\bullet10^{16}$ NH_3 molec/$cm^2\bullet$sec for the $Re(11\bar{2}0)$ and the $Re(11\bar{2}1)$ respectively. For comparison the rate with the polycrystalline foil under identical conditions is $(18\pm1)\bullet10^{16}$ NH_3 molec/$cm^2\bullet$sec.

A bar graph summary of the structure sensitivity among the single crystal catalysts is shown in Fig. 3. In parenthesis the rates are given as turnover frequencies (T.F.), taking into account the number of surface atoms per unit cell. The relative activity ratios obtained are thus 1:94:920:2820 for the Re(0001), $Re(10\bar{1}0)$, $Re(11\bar{2}0)$ and the $Re(11\bar{2}1)$ crystals respectively.

B. Reaction Kinetics

Reactants Pressure Dependence. In order to study the order of the reaction with respect to the reactants, the dependence of the overall rate of the synthesis on the pressure of the reactants were measured. The order of the synthesis with respect to nitrogen is obtained by plotting the logarithm of the overall rate vs. the logarithm of the N_2 pressure. In Fig. 4 a plot of this kind is shown with a polycrystalline rhenium foil at 736K. In these experiments the H_2 pressure was kept constant at 16 atms, while the N_2 pressure was varied in the range of 0.8 - 11.2 atms. The slope of the straight line determines the order of the reaction with respect to nitrogen and it was found to be first order (n=1.02). A similar experiment, this time with the nitrogen pressure kept constant at 5.4 atm and the hydrogen pressure is varied between 3.4 to 17.0 atms, was performed in order to determine the order of the reaction with respect to hydrogen. In Fig. 5, the logarithm of rate vs. the logarithm of hydrogen pressure plot with a Re(1120) catalyst at 870K is shown. The slope or the order of the reaction with respect to hydrogen is m=0.67.

Isotope Effect. The reaction rate was also studied as a function of the sample temperature with deuterium. Arrhenius plots of the ammonia synthesis over a polycrystalline Re foil are shown in Fig. 6 for H_2 and D_2 as reactants. A very small difference in the activation energy of the reaction, 19.4 kcal/mole and 21.5 kcal/mole for H_2 and D_2 respectively is observed, which is within the experimental error. The yield of the reaction with deuterium is also higher by about 30-50% over the temperature range of this study which was 730-810K.

C. Effects of Potassium and Oxygen

In the industrial ammonia synthesis catalyst there is an important role for the K_2O additive, which is believed to act as an electronic promoter of the iron catalyst.[1] In this work we have studied the effect of predosing pure potassium on top of the clean Re surfaces and the effect of potassium coadsorbed with oxygen, on the activity of these catalysts. We have used the Seas' getters potassium sources to generate pure atomic potassium vapours and calibrated the surface coverage using the relative Auger peak intensities of Re(167) and K(250). The peaks ratios were compared to the values obtained for potassium on Pt[9], such that Re(172)/K(252)≅0.35 corresponds to a coverage of one monolayer of potassium. At the highest sample temperature of 870K, the post run coverage of potassium was 0.15 of a monolayer. The effect of the pure K atoms was typically very small, the largest promotion effect of 23% was found with the Re(1121) single crystal. The results of pure K promotion of the ammonia synthesis rates over three of the catalysts, the polycrystalline Re foil, the Re(11$\bar{2}$0) and Re(11$\bar{2}$1) single crystal surfaces are presented in Table 1. Also in Table 1 are the results of potassium coadsorbed with oxygen. Several experiments were carried out in order to study the effect of oxygen coadsorbed with a constant K coverage of 15% of a monolayer: (i) Dosing the Re+K(0.15Θ) with 100L O_2 in the UHV chamber. (ii) Mixing 1 Torr of O_2 gas with the circulating 20 atmospheres of N_2 and H_2. (iii) Mixing 2- Torr O_2 with the reactants. In the first procedure, the oxygen seems to stabilize the potassium on the surface while some of the oxygen ~35% is removed from the surface during the 15 minutes run at 870K. There is, however, a clear enhancement of reactivity of the Re(11$\bar{2}$1) and the Re foil. With the second type of experiments with 1-2.5 Torr oxygen circulating in the high pressure loop, there was more stabilization of the K on the surface with a large oxygen coverage post run, estimated at 1/2 of a monolayer. The activity was reduced only slightly

in the Re(11$\bar{2}$0) case while some enhanced activity was evident with the Re polycrystalline foil. Certainly no poisoning is detected. Finally with about 20 Torr oxygen in the loop, the activity is reduced to half the rate, yet about 0.2 of a monolayer of K is left on the surface with oxygen coverage close to one monolayer (see Table 1).

DISCUSSION

A. Structure sensitivity

The structure sensitivity of the iron catalyst for the ammonia synthesis was recognized for some time. It was found by field electron emission[4] that the more open Fe(111) crystal face adsorbs nitrogen much faster than the other more close packed low Miller index planes and that the (100) and the (110) faces restructure (facet) to form the (111) plane upon exposure to nitrogen[4]. This effect was later suggested as an evidence that the Fe(111) is the most active plane for the synthesis of ammonia as well. The same (111) plane was also predicted to be more stable on the iron microcrystallites which are formed supported iron catalysts during the course of the reaction[3]. The results of these and other studies, using Mossbauer spectroscopy and CO adsorption techniques[3], suggested the importance of the exposed C_7 coordination atoms in the second layer as the active site for ammonia synthesis. Other ultra high vacuum studies of the adsorption kinetics of nitrogen on low Miller index planes of clean iron single crystals[10], all supported the hypothesis that the Fe(111) plane, having C_7 coordination atoms in the second layer is the most active for the ammonia synthesis. Finally, the most direct evidence for this assumption came from the experiments by Spencer et al.[11] who

studied the ammonia synthesis at high pressures (20 atms.) over iron single crystals and found an activity ratio of 418:25:1 for the (111), (100) and the (110) single crystal planes of iron respectively[11].

The choice of rhenium single crystal planes for this study of activity toward ammonia synthesis, was guided by the observations of the activity of specific iron sites. After observing no activity with the close packed (0001) basal plane and only small activity (relative to the polycrystalline foil) with the Re(10$\bar{1}$0) plane, we tried the Re(11$\bar{2}$0) face that exposes C_7 coordination atoms. Since rhenium is a hexagonal closed packed metal the environment of surface atoms is very different from that in iron with a body centered cubic structure. The (11$\bar{2}$0) rhenium single crystal plane exposes C_7 coordination atoms - two in a unit cell, - but unlike the bcc(111) structure in which the two C_7 atoms in a unit cell are in the second layer, those atoms are in the topmost layer. Here the second layer consists of C_{11} coordination atoms. The activity of this plane as shown in Fig. 3 is rather high, but still smaller than that measured with the polycrystalline foil. The similarity between the (111) face of the iron and the rhenium (11$\bar{2}$0) is not limited, however, to the presence of C_7 coordination atoms. Shown in Fig. 7, a schematic top and side view of the unreconstructed Fe(111), Re(11$\bar{2}$0) and the Re(11$\bar{2}$1) single crystal surfaces. It is clear that the Fe(111) and the Re(11$\bar{2}$0) are similar also in the distance between adjacent atoms on the surface. Both are quite open surfaces on which once a nitrogen molecule adsorbs and dissociates the adsorbed atoms formed may diffuse along troughs away from each other and thus recombination is prevented. The higher activity of these open and corrugated surfaces imply that the dissociation of the nitrogen molecules is facilitated by the possibility to interact with both first and second atomic layers of the metal. This microscopic view of the rate limiting step of the ammonia synthesis suggests

that the rough structure and openess are important for the ammonia synthesis, perhaps more so than the presence of C_7 sites. In order to test the lack of need for C_7 sites for high synthesis activity we cut the $(11\bar{2}1)$ plane of Re which, as shown in Fig. 7, contains no C_7 atoms but is as open as the $(11\bar{2}0)$ face, though having rougher second layer structure. As mentioned in the results section, this crystal showed a somewhat more diffuse LEED pattern, indicating considerable surface disorder that make our results only suggestive, but the 3-fold higher activity of this plane when compared with the $(11\bar{2}0)$ face indicate that at least for rhenium the presence of C_7 coordination atoms are not essential for ammonia synthesis. The validity of a detailed structural analysis of the surface obtained under UHV conditions of course is not necessarily applicable under high pressure reaction conditions. In the case of iron, the low Miller index planes and in particular the more open ones are known to relax in vacuum. Reconstruction of the (100) and the (110) planes of iron in the presence of nitrogen was reported as well[4] and it is always possible that a reversible reconstruction under high pressure conditions occur during the synthesis. The results from the high pressure synthesis mentioned previously with iron single crystals[11] however seem to indicate that the structure under high pressure conditions is the same as the surface structure detected in vacuum, otherwise such a dramatic structure sensitivity correlation would not be possible[11]. In the case of rhenium, which is a much harder material, information is not available on the possible reconstruction of the low Miller index planes. The LEED pattern of the $Re(11\bar{2}0)$ crystal plane after the high pressure synthesis was identical to that observed before the reaction; no irreversible reconstruction occurred during ammonia synthesis at 20 atm. Since atom self-diffusion rates in the bulk or on the surface can be correlated to melting temperatures, the higher melting rhenium is expected to have lower diffusion rates than iron under similar reaction conditions. Thus, most restructuring processes that require atomic diffusion would likely be much slower for rhenium than for iron.

The observation of the remarkable structure sensitivity of rhenium for ammonia synthesis permits us to obtain conclusions on the surface structure of rhenium crystallites on silica supported rhenium catalysts. When we compare the rates observed with single crystals, to those reported for a supported Re on SiO_2 [12], which were conducted at lower temperature 700K, we obtain (after extrapolation to the same temperature) much lower turnover frequencies. These rate values correspond to the activity of a mixture of Re(0001) and the Re($10\bar{1}0$) planes. This implies that the supported rhenium particles tend to form crystallites predominantly with (0001) and ($10\bar{1}0$) planes.

B. Kinetic Parameters and Reaction Mechanism

The kinetics and mechanism of ammonia synthesis over iron based catalysts was extensively studied over the last decades. Discussions of the kinetic aspects and the mechanism of the reaction can be found in the literature[1,2,5,10,13] contain valuable information which may be usefully compared with the results obtained here for the ammonia synthesis over rhenium catalysts. The ammonia synthesis over rhenium is first order with respect to nitrogen pressure, 0.67 order with respect to H_2 and has an activation energy of 19.4±1.1kcal/mole of ammonia.

The reaction is first order with respect to nitrogen pressure (see Fig. 3) for both iron and rhenium. This indicates that similar to the mechanism of ammonia synthesis on iron catalysts, the rate limiting step involves the adsorption of nitrogen molecules on the Re surface:

$$N_2(g) \rightarrow N_2(ad) \qquad [1]$$

$$N_2(ad) \rightarrow 2N(ad) \qquad [2]$$

In the case of iron catalysts, the second step is considered the rate limiting step of the synthesis[2,5,10,11]. With the data available in this study we cannot distinguish between the two processes. It is known, however, that as in the case of iron[14,15], the dissociative sticking probability of nitrogen molecules on rhenium surfaces is very low, of the order of $10^{-6} - 10^{-8}$ [16]. It is reasonable to speculate that the rate limiting step, if an activated process, would be the dissociation step[1] rather than the adsorption of the molecule which is not expected to be activated. Based on the assumption that the dissociation of the nitrogen molecule is the rate limiting step of the ammonia synthesis over rhenium, we may adopt rate expressions that were suggested for the iron catalysts. A successful and widely used one is that due to Temkin and Pyzhev[17] and the extension by Temkin[18] which takes into account the dependence of rate constants on the pressure and corrects for deviation from ideal gas behavior at high pressures:

$$\frac{d(NH_3)}{dt} = \left[k_1^o a_{N_2}\left(\frac{a_{H_2}^3}{a_{NH_3}^2}\right)^{\alpha} - k_2^o\left(\frac{a_{NH_3}^2}{a_{H_2}^3}\right)^{\beta}\right]\exp[-(\bar{V}_a - \alpha\bar{V}_s)P/RT] \qquad [3]$$

Here a_{N_2}, a_{H_2} and a_{NH_3} are the activities of nitrogen, hydrogen and ammonia respectively, k_1^o and k_2^o are the pressure independent rate constants for ammonia synthesis and decomposition respectively. The exponent includes the partial molar volumes of the adsorbed nitrogen $\bar{V}_a$ and the transition state $\bar{V}_s$ and the total pressure P. Application of this equation to our experimental conditions, i.e. low conversion (less than 0.2%) and a small catalyst surface area (1 cm^2), reduces eq. [3] to only the first part of it, where we neglect reverse reaction that leads to ammonia decomposition.

$$\frac{d(NH_3)}{dt} \cong k_1^o a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^{\alpha} \qquad [4]$$

Similar expression is obtained if the formula suggested by Ozaki et al.[19] for a uniform surface covered mostly by N atoms is used. An extension of Ozaki's expression by Nielsen[20] would result in an identical formula, only two new adjustable parameters ω and α are introduced. Nielsen's formula which takes into account the reverse reaction as well is considered more general since it combines the four different conditions discussed by Ozaki et al[19] into a single expression[20]:

$$\frac{d(NH_3)}{dt} = \frac{k_2^o(a_{N_2} K_a^2 - a_{NH_3}^2/a_{H_2}^3)}{(1 + K_3 a_{NH_3}/a_{H_2}^{\omega})^{2\alpha}} \qquad [5]$$

According to Nielsen et al[20], at conversions higher than 0.1% on the iron catalyst, the right hand term in the denominator is greater than unity. Assuming that the same relations apply for rhenium, where K_3 represents the rate determining step, then eq. [5] rearranges to an expression almost identical to eq. [4], with some differences in the constants and the meaning of the adjustable parameters α in eq.[5] vs. ω and α from eq.[4]. It is important to note that from Ozaki's[19] and Nielsen's[20] derivations it turns out that if $\omega = 1.5$ then the most important intermediate on the surface should be atomic nitrogen, while if $\omega = 1.0$, it should be the NH fragment[(19, 20)].

These rate expressions seem to correlate well with the observed first order dependence (see Fig. 3) of the overall ammonia synthesis over rhenium with respect to nitrogen pressure. The order of the reaction with respect to hydrogen seems to be different for rhenium as compared to iron catalysts. With Re, the overall order is 0.67

(see Fig. 4) which means that $\alpha = 0.22$ if eq. [4] is used. The α value obtained for the iron catalyst using eq. 4 was 0.64[20]. The other significant difference is the apparent activation energy for the synthesis of 42.3 kcal/mole which was obtained by using eq. [3] with $\alpha = 0.64$[18]. It is interesting to note, however, that under identical experimental conditions to those of this study, using clean Fe(111) single crystal as the catalyst, an apparent activation energy of 19.4 kcal/mole was measured[21] which is very close to the one measured here. It is also important to note that when the activation energy for the rate limiting step only was measured, on a promoted iron catalyst, an activation energy of 20 kcal/mole was obtained[19, 20]. If eq.[5] is used, in the approximate form applied at low conversions, one should find the dependence of the rate on the partial pressure or activity of ammonia, in order to solve for the two unknowns - ω and α. This was obtained by extending our experiments shown in Fig. 1 to longer times and higher ammonia partial pressures, (up to about 10 Torr ammonia in the 20 atm total pressure), and the rates of the synthesis were taken at various ammonia partial pressures, rather than measuring the initial rates, as usually was done. Such ammonia partial pressure dependence on the overall rate was carried out on two single crystals - the Re(11$\bar{2}$1) and the Re(11$\bar{2}$0). The results yielded $\alpha = 0.23$ on both crystals if we used eq.[5], which is identical to the value obtained from Temkin's equation from the hydrogen pressure dependence on the Re(1120). With this value of α we obtained the second parameter $\omega = 1.45$ from the order of the reaction with respect to hydrogen (0.67). If we use the arguments which lead to eq.[5], we should have the rhenium surface covered mostly with N_{ad} species.

This rather indirect way of obtaining information on the surface composition, needs of course further confirmation from more direct experimental studies. It should be noted that quite different interpretations and results as to the dominant species on the surface

during ammonia synthesis were obtained and discussed in the literature when using iron based catalysts. The presence of NH_{ad} was concluded mostly from isotopic studies on a doubly promoted iron[19,22], while others found evidence for the N_{ad} species on differently promoted[18,20,23] or pure[24] iron catalysts. It was noted, however, that the nature of the dominant nitrogen containing species on the surface is very sensitive to parameters such as surface uniformity, temperature, reactants' pressure and the extent of oxygen removal from the surface[19].

Isotope Effect. Several isotope effect studies in the ammonia synthesis over iron based catalysts appear in the literature, many of those due to Ozaki et al[19,22,23]. In the first study over a doubly promoted catalyst - $Fe/Al_2O_3/K_2O$, the rate of reaction increased by a factor of 3-4 when H_2 was replaced by D_2. This was somewhat unexpected since the rate limiting step of the reaction was already then accepted to involve the nitrogen dissociative chemisorption without any hydrogen bond formation or breaking. The sequential hydrogenation of the adsorbed N_{ad} [20] or NH_{ad} [19] species are believed to occur very rapidly. The explanation for the significant inverse isotope effect arises from the difference in the adsorption rate constants K_H and K_D of the ammonia product on the catalyst surface. Since the rate of the synthesis is slowed down by the presence of the ammonia product, which undergoes dissociative chemisorption under the reaction conditions, the isotope effect indicates that NH_3 adsorbs and dissociates faster than ND_3, thus the overall synthesis rate is slower when using H_2 [22]. The magnitude of the inverse isotope effect was calculated by estimating the ammonia adsorption rate constants from partition functions and zero point vibrational energies of NH_3/ND_3 vs. H_2/D_2 [22], and was found to be temperature dependent: $K_D/K_H = 74.2$ at 273K and is only 4.32 at 573K. If one extrapolates these calculations to our experimental conditions, with catalyst

temperature of 800K, the isotope ratio is expected to be $K_D/K_H \sim 1.6$. In Fig. 5 it is shown that at 800K the synthesis activity with D_2 is about a factor of 1.5 higher than the corresponding H_2 activity in good agreement with the calculations. The overall isotope effect should be similar on iron and on rhenium catalysts because the molecular properties which are important for the determination of the isotope effects are those of the gas phase molecules[22]. The slightly higher activation energy observed with D_2 (barely beyond the experimental error) cannot be readily explained.

D. The Effects of Potassium and Oxygen

The role of the K_2O additive in the industrial iron catalyst is considered very important and different from the other two typical additives[1]. The Al_2O_3 and CaO are believed to act as structural promoters which prevent sintering and thus the reduction of active surface area of the reduced metallic iron[1]. The K_2O effect was unclear until recently recently when low pressure experiments by Ertl et al.[5,25-27] have shown a dramatic effect of potassium on the rate of nitrogen chemisorption on iron single crystal surfaces. The increased heat of adsorption and dissociative rate of N_2 in the presence of potassium was thought to reflect an increase of the local free electron density of the metal near the potassium site, which facilitates backdonation to the $2\pi^*$ orbitals of the nitrogen molecules and thus enhance its bonding and its dissociation rate[28]. Since the nitrogen dissociative chemisorption is the rate limiting step in the ammonia synthesis, these observations at low pressures seem to explain, at least in part, the electronic promotion effect of potassium on the industrial catalyst that operates at high reactant pressures. As mentioned earlier field electron emission studies indicate the possibility of surface restructuring to the more active (111) crystal face in the presence of nitrogen and

potassium. If this occurs it could induce an increased activity in addition to the electronic promotion effect on the bonding of nitrogen. The role of oxygen coadsorbed with K was studied as well, since in the industrial iron catalyst case there is no pure potassium on the surface. It was observed that the presence of oxygen reduced the electronic promotion effect of pure potassium[25], i.e. the nitrogen is adsorbed at a lower rate. The important role of the coadsorbed oxygen species, however, is in thermally stabilizing the potassium ions on the catalyst's surface[22].

The results obtained in our studies of the rhenium catalysts are quite different. The overall synthesis rate at temperatures up to 870K, where the potassium is still stable on the surface, does not change much as compared with the clean Re catalysts. As shown in Table 1 the effect of pure potassium is maximum with the Re $(11\bar{2}1)$ and even then it causes less than 25% increase in activity. The potassium on the other hand does not have any poisoning effect that might be expected when covering the active transition metal surface with a chemically inactive metal. Up to coverages of 25% of a monolayer at lower crystal temperatures in which such coverages are stable during the reaction, no decrease in the activity of the catalyst could be detected when compared with the clean catalyst.The other striking difference when compared with the iron studies, is the positive effect of oxygen on the rhenium synthesis rate. As seen in Table 1, even at oxygen partial pressures of several Torr in the high pressure loop, there is no poisoning of the reaction as observed with iron. On the contrary, a significant enhancement of the rate is observed for rhenium foils when compared with the clean or the pure potassium covered catalysts. The nature of the surface compound that forms between potassium and oxygen is not well known and requires further investigation. The results seem to indicate, however, that both the pure potassium and the surface compound with oxygen are mobile on the surface, or

certainly do not block the active sites, thus enabling the dissociative chemisorption of nitrogen molecules to proceed without any significant poisoning up to rather high additive coverages.

If potassium or oxygen or their compound influence the catalytic activity of iron for ammonia synthesis by catalyzing the restructuring of the surface to expose the highly active (111) orientation this restructuring effect must be absent for rhenium. This would not be surprising since atom diffusion along the surface is needed for massive restructuring to take place. The high melting point rhenium should have much lower surface self-diffusion rates than iron under the same experimental conditions that would prohibit such restructuring process.

The role of alkali metal additives on the ammonia synthesis activity of several supported transition metals was studied as well[29-31]. It was found that when supported on activated carbon the promotion by alkali metals had a remarkable effect of enhancing the synthesis rates[20-31]. Ru was found to be the most active catalyst under conditions of low temperature (250°c) and low pressure (600 Torr) and also most sensitive to the alkali additives. A supported Re sample was studied as well and was found to be among the least active catalysts[28]. Under these conditions the apparent activation energies of the various metals were 9, 13 and 18 kcal/mole for Rh, Ir and Pt(27) while the most active catalyst - Ru when promoted with K atoms, had 21 kcal/mole apparent activation energy. It is not clear why Re was so inactive under these experimental conditions, but it is possible that the active carbon as a support deactivated the Re catalyst more than some of the other metals. We have found that carbon, if accumulated on the surface, could poison the reaction quite effectively. An alternative explanation that was given before

invokes the structure sensitivity of the reaction that leads to an inactive rhenium catalyst if the carbon silica or alumina[30] supported metal crystallites are composed of (0001) and $(10\bar{1}0)$ crystal surfaces.

ACKNOWLEDGMENTS

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 No. DE-AC03-76SF00098.

REFERENCES

1. P.H. Emmet in "The Physical Basis for Heterogeneous Catalysis" E. Dranglis and R.I. Jaffe eds., Pg. 3, Plenum Press, New York, (1975).

2. A. Ozaki and K. Aika in "Catalysis: Science and Technology" J.R. Anderson and M. Boudart eds.; Springer, Berlin, (1981).

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

4. R. Brill, E.L. Richter and R. Ruch; Agnew Chem. Int. Ed. Engl. 6, 882, (1967).

5. G. Ertl, Proc. XXV Conf. of the R. Welch Foundation Conf. on Chemical Research: Heterogeneous Catalysis. Houston, Texas, November 9-11, (1981).

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

7. N.D. Spencer and G.A. Somorjai; J. Catal., 78, 1112 (1982).

8. A.L. Cabrera, N.D. Spencer, E. Kozak, P. Davies and G.A. Somorjai, Rev. Sci. Instrum. 53, 1893 (1982).

9. E. Garfunkel and G.A. Somorjai; Surf. Sci., 115, 441 (1982).

10. G. Ertl; Catal. Rev. Sci. Engr. 21, 201 (1980).

11. N.D. Spencer and G.A. Somorjai; Reports on Progress in Physics, Vol 46, 1, (1983).

12. W.K. Shiflett and J.A. Dumesic; J. Catal., 77, 57 (1982).

13. A. Nielsen, Catal. Rev. Sci. & Engr, 23, 17 (1981).

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

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

16. R. Lin and G. Ehrlich; J. Vac. Sci. Technol., 13, 310 (1976).

17. M.I. Temkin and V. Pyzhev; Acta Physicochim (U.R S S), 12, 327 (1940).

18. M.I. Temkin; J. Phys. Chem. (U.R.S.S.) 24, 1312 (1950).

19. A. Ozaki, H. Taylor and M. Boudart; Proc. Royl Soc. (London) A258, 47 (1960).

20. A. Nielsen, J.Kjaer and B. Hansen, J. Catal., 3, 68 (1964).

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

22. A. Ozaki; "Isotopic Studies of Heterogeneous Catalysis", Academic Press, New York, (1977).

23. K. Aika and A. Ozaki; J. Catal , 19, 1058 (1974).

24. K. Aika and A. Ozaki; J. Catal., 13, 232 (1969).

25. Z. Paal, G. Ertl, S.B. Lee; Appl. Surf. Sci., 8, 231 (1981).

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

27. G. Ertl, S.B. Lee and M. Weiss; Surf. Sci., 114, 527 (1982).

28. G. Ertl, J. Vac. Sci. Technol. A, 1, 1247 (1983).

29. K. Aika, H. Hori and A. Ozaki; J. Catal., 27, 424 (1972).

30. K. Aika, J. Yamaguchi and A. Ozaki; Chem. Lett. (Japan), pp. 161 (1973).

31. A. Ozaki, K. Aika and H. Hori., Bull. Chem. Soc. (Japan) 44, 3216 (1971).

FIGURE CAPTIONS

Fig. 1: The partial pressure of NH_3 is plotted vs. time with two Re single crystal catalysts at 870K, total pressure of 20 atms, $P_{H_2}:P_{N_2}=3:1$, Re(11$\bar{2}$1) (triangles) and Re (11$\bar{2}$0 (open circles). The turnover frequency (T.F.=NH_3 molecules/surface atom•sec) were obtained from the initial rates (solid lines).

Fig. 2: Arrhenius plots for ammonia synthesis over Re foil (triangles) and a Re(11$\bar{2}$0) single crystal (open circles) catalysts.

Fig. 3: Structure sensitivity in the ammonia synthesis over Re single crystal faces. The turnover frequency (T.F.) is given as (NH_3 molecules/ cm^2•sec).

Fig. 4: Nitrogen pressure dependence of the ammonia synthesis over a Re polycrystalline foil at 736K. The hydrogen pressure is 16 atms.

Fig. 5: Hydrogen pressure dependence of the ammonia synthesis over Re (11$\bar{2}$0) single crystal catalyst at 870K. The nitrogen pressure was 5.4 atms.

Fig. 6: Isotope effect in the synthesis of ammonia over Re polycrystalline foil. The filled circles represent the reaction with deuterium while the open circles are with hydrogen at the same conditions. Total pressure is 20 atm; $P_{H_2}:P_{N_2}=3:1$.

Fig. 7: Schematic atomic structures of the Fe(111), Re(11$\bar{2}$1) and the Re(11$\bar{2}$0) crystal surfaces from side and top views. The solid circles are topmost atoms, the dotted circles are second layer atoms and the shaded circle is an atomic nitrogen. The circles' sizes represent roughly the relative Van Der Waals radii of the corresponding atoms.

Table 1: Effect of clean K and K coadsorbed with oxygen on the ammonia synthesis rates (NH_3 molec/cm^2•sec) x 10^{-16} .

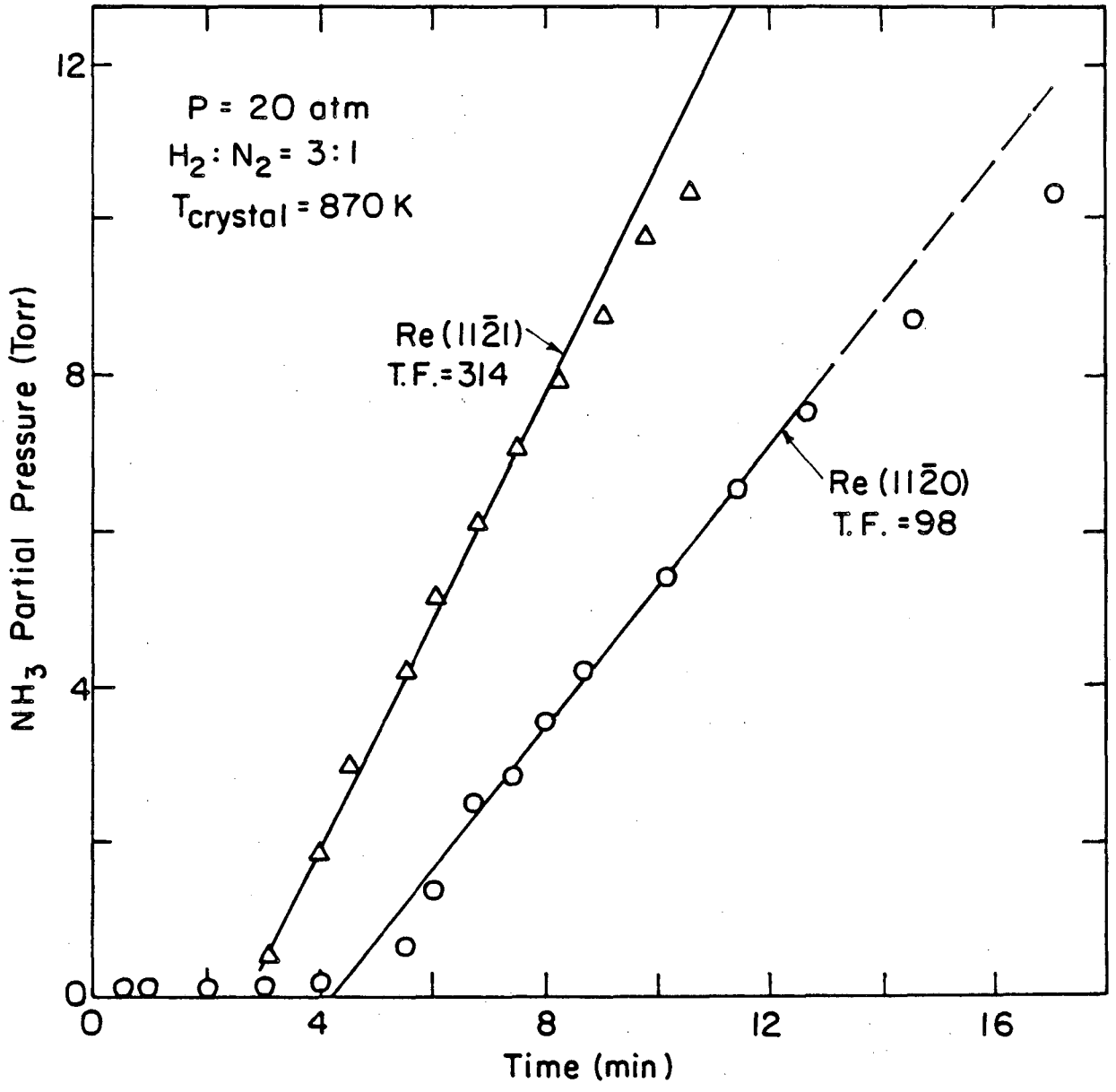
	Re (11$\bar{2}$0)	Re(11$\bar{2}$1)	Re(foil)
clean	4.6	14.1	18.4
K^a	4.6	17.4	19.4
K^a+O^b	4.6	18.2	22.0
K^a+O^c	4.3	-	23.2
K^a+O^d	2.3	-	-

a - 0.15 monolayer; b-100 Langmuir O_2 with K preadsorbed.

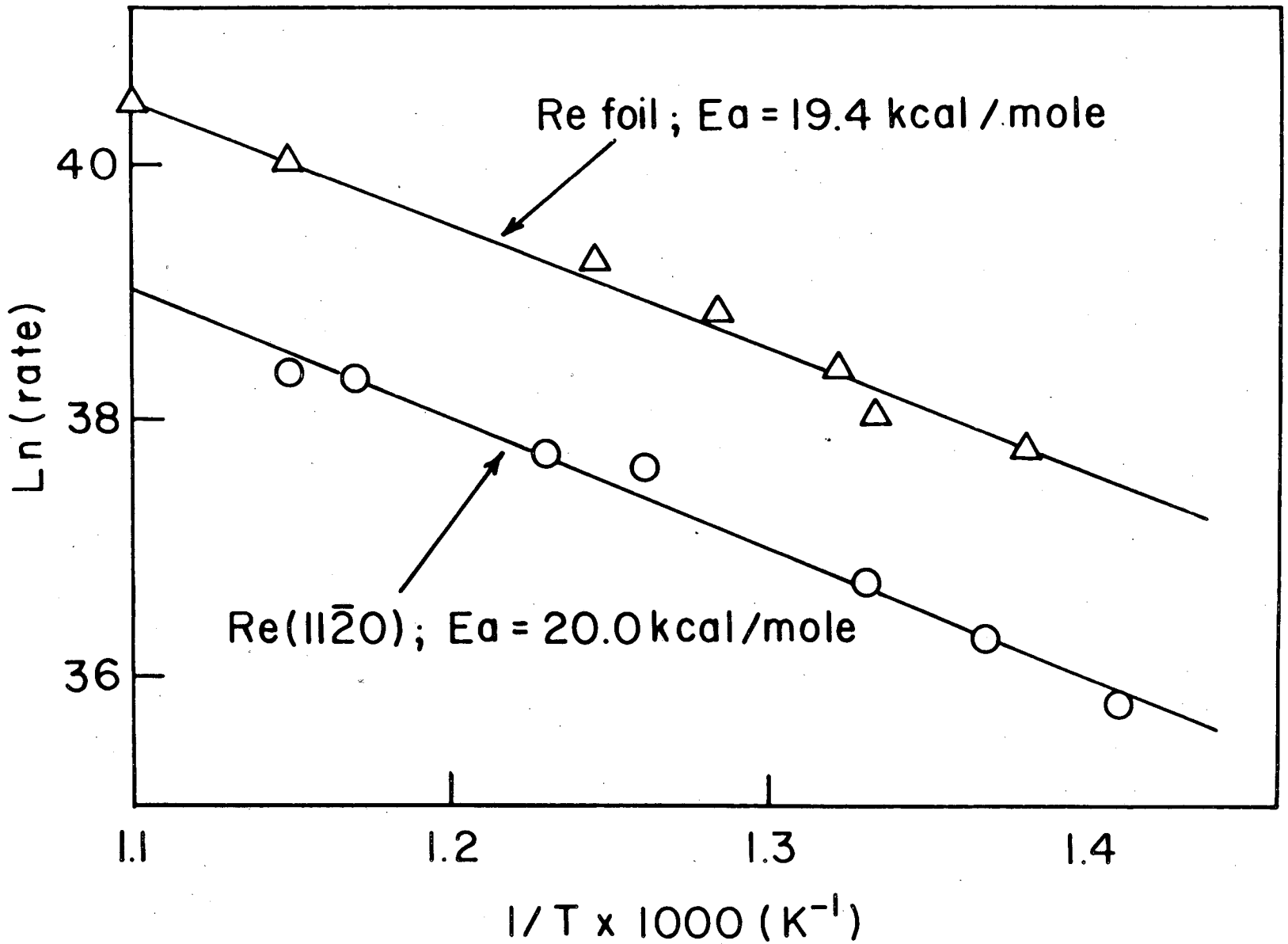
c-1 Torr O_2 in the high pressure loop; d - 20 Torr O_2 in the high pressure loop.

e - Catalyst temperature = 870K, P_{total} =20atm.; P_{H_2} : P_{N_2} =3:1.

Fig. 1



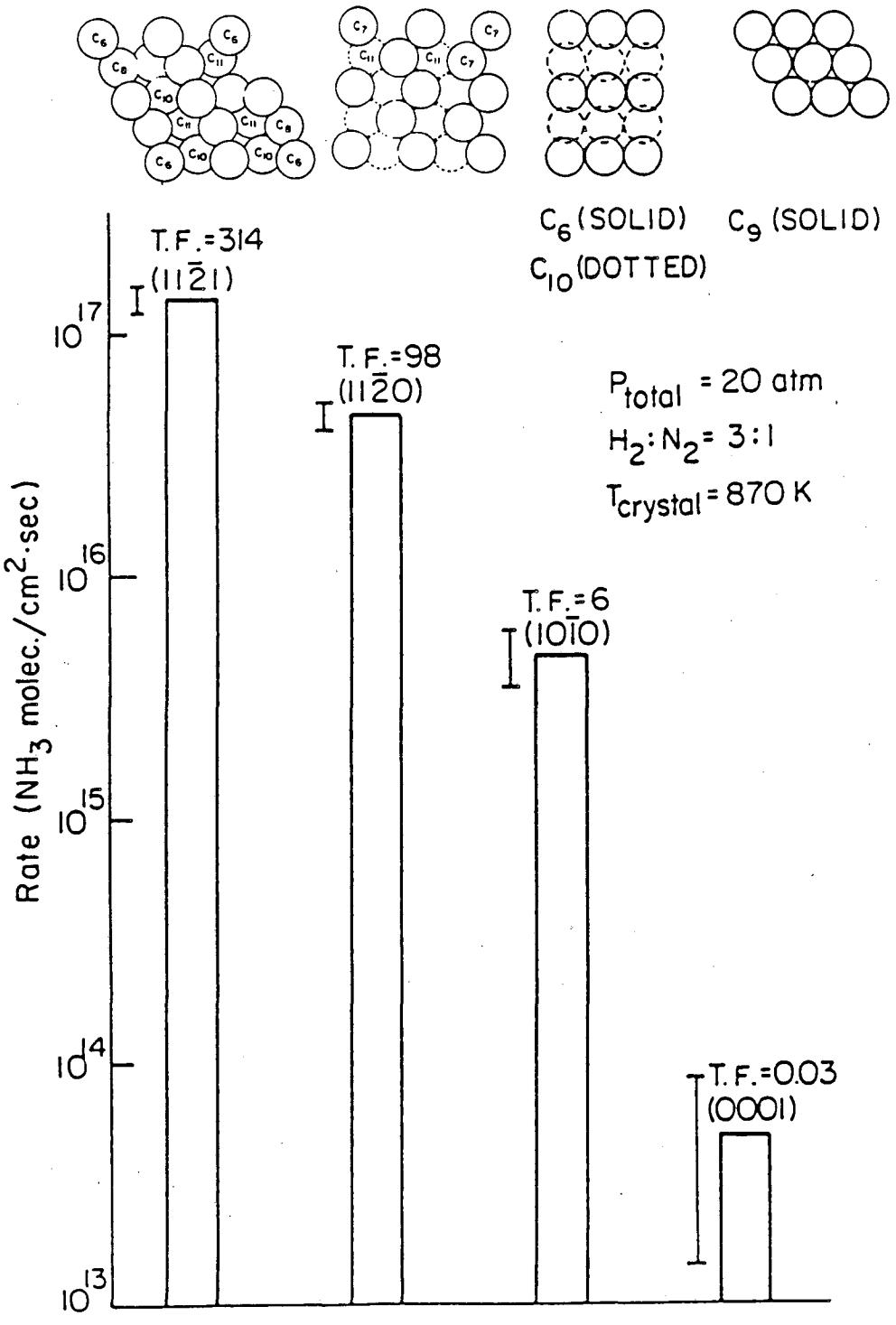
XBL843-6699



XBL 8410-4067

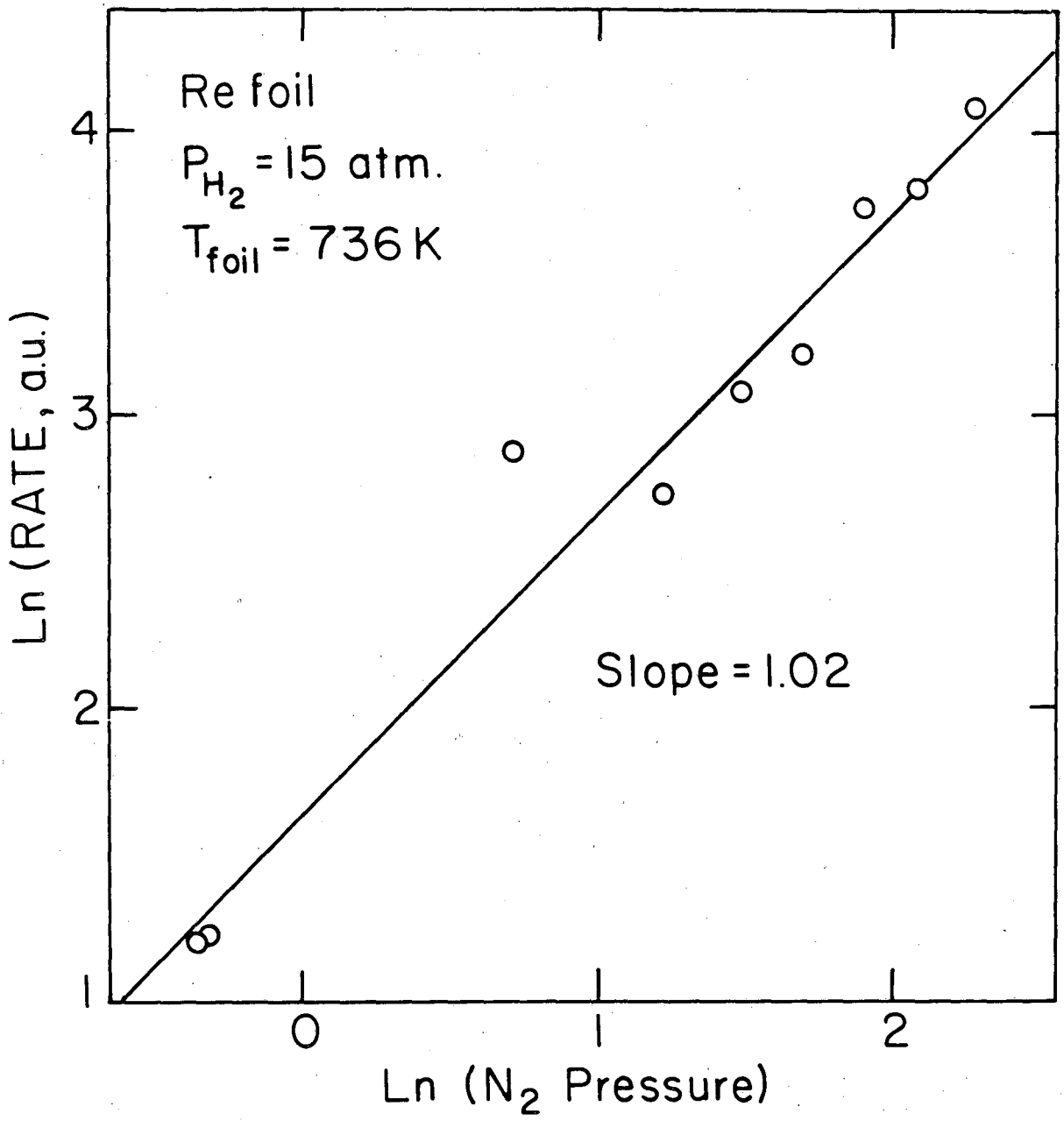
Fig. 2

Fig. 3



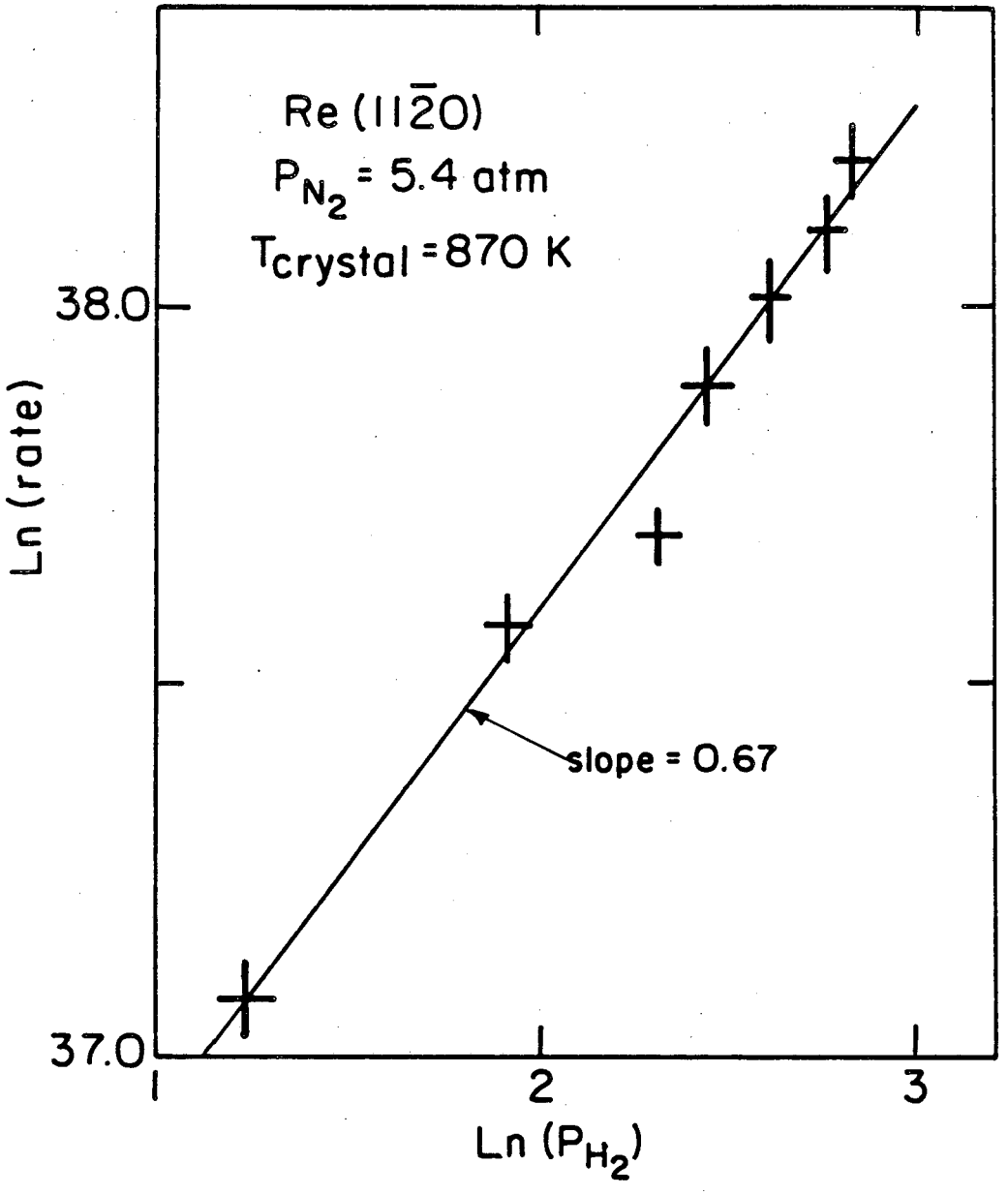
XBL 845-1900

Fig. 4



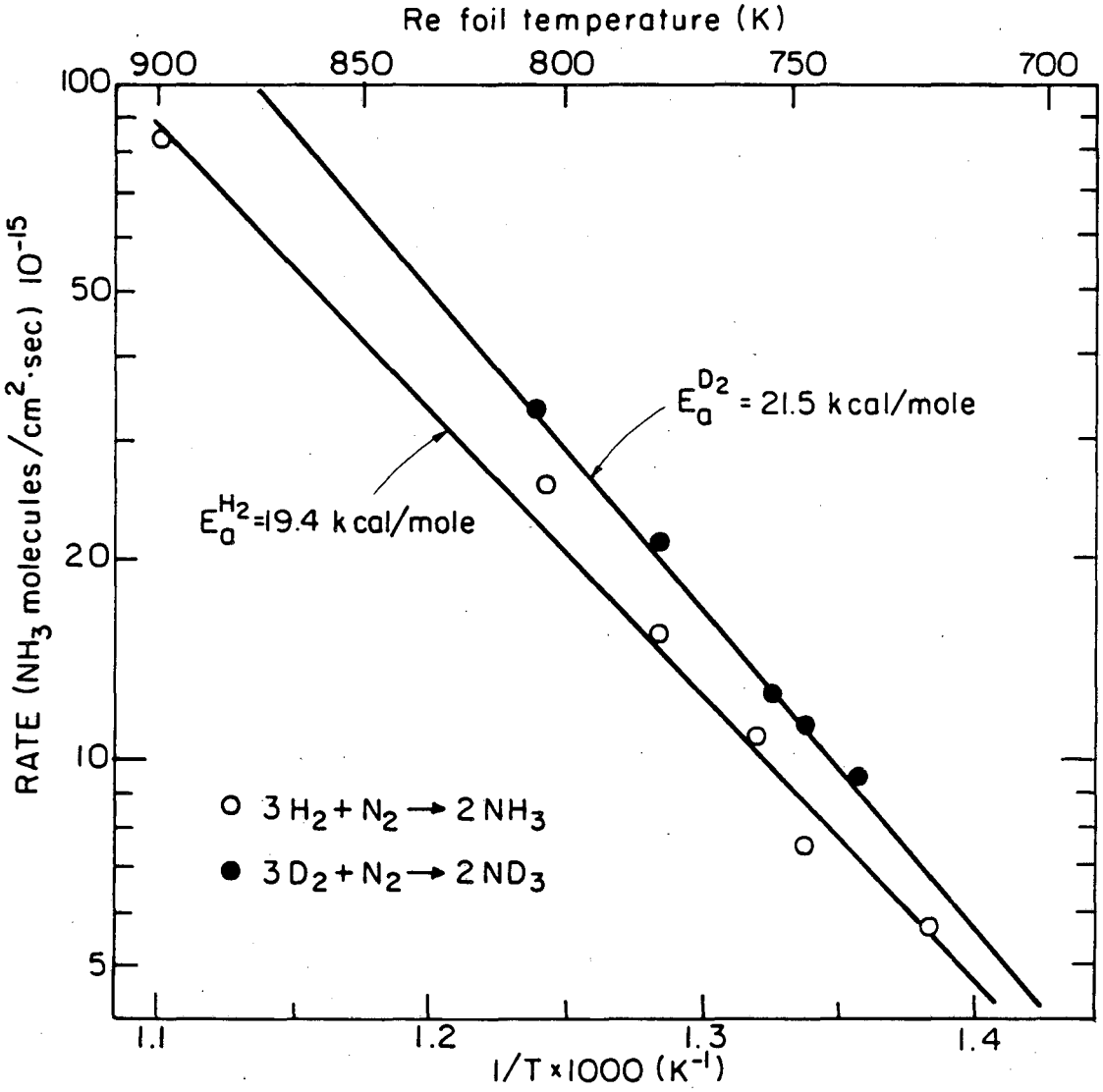
XBL 8410-4066

Fig. 5



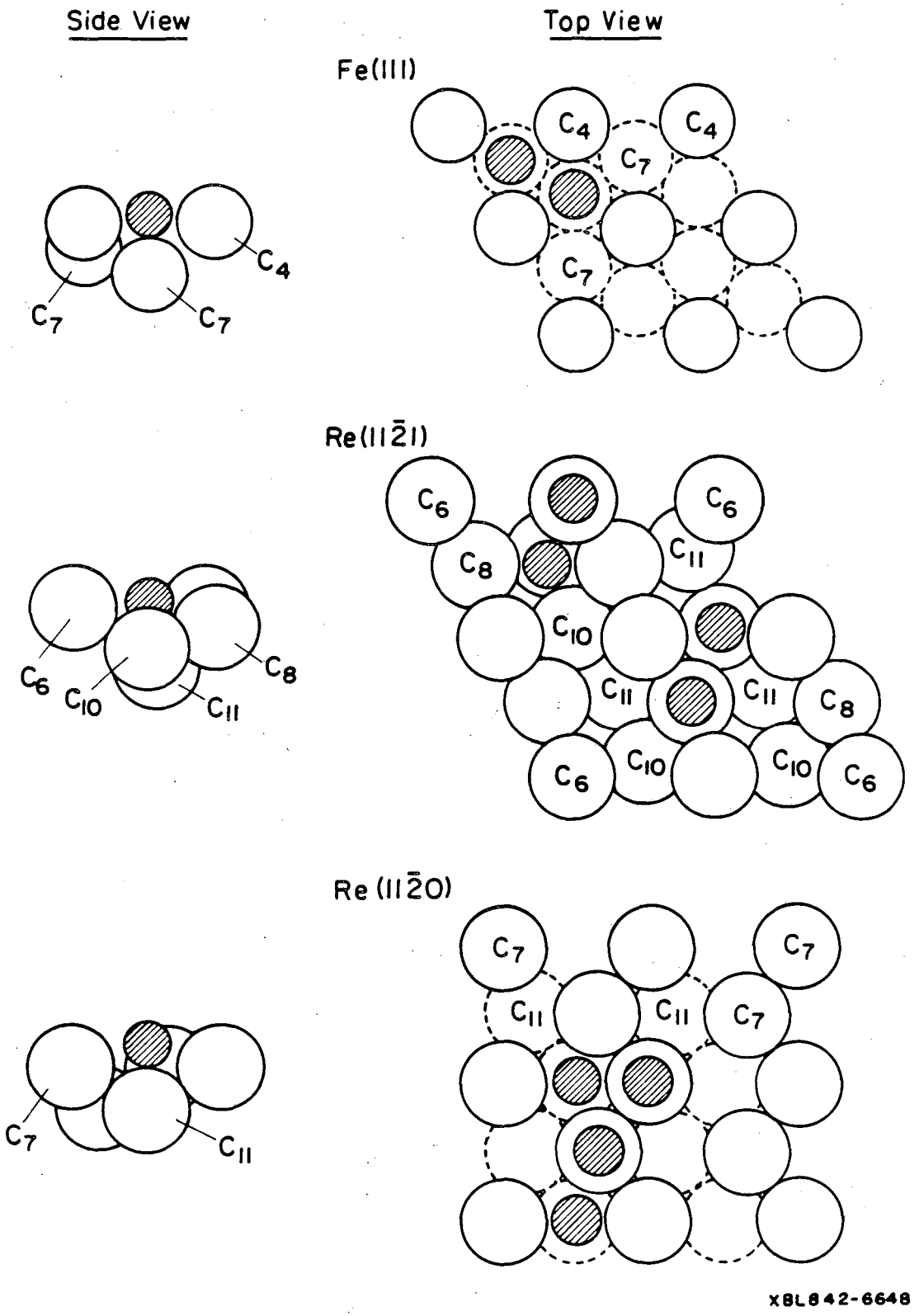
XBL843-6698

Fig. 6



XBL 8310-6516

Fig. 7


Side View
Top View
Fe(111)
C4
C7
Re(11$\bar{2}$1)
C6
C8
C10
C11
Re (11$\bar{2}$0)
C7
C11
XBL842-6648

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.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720