

The Ammonia Synthesis over Rhenium Single-Crystal Catalysts: Kinetics, Structure Sensitivity, and Effect of Potassium and Oxygen

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The ammonia synthesis from nitrogen and hydrogen has been investigated over model single-crystal and polycrystalline foil rhenium catalysts at 20 atm reactant pressure and in the temperature range 720–900 K. The reaction rate is remarkably sensitive to the catalyst surface structure. A reactivity ratio of 1:94:920:2820 was found for the Re(0001), Re(1010), Re(1120), and Re(1121) crystal faces, respectively. The catalytic activity of rhenium for ammonia synthesis is higher the more open and rough the surface is. An apparent activation energy of 19.4 ± 1.1 kcal/mol was observed, regardless, of the catalyst surface structure. Kinetic data, reactant pressure dependence, and deuterium isotope effect indicate that, as in the case of iron, the rate-determining step is the dissociative chemisorption of the nitrogen molecule. Potassium metal adsorbed on the clean rhenium surface does not have any effect on the reaction rate. The coadsorption of potassium with oxygen does not suppress the reactivity of the catalyst and stabilization of potassium on the surface OCCURS. © 1986 Academic Press, Inc.

INTRODUCTION

The synthesis of ammonia over metallic iron has been studied over both polycrystalline (1–3) and single-crystal catalysts (4–6). Expressions for the reaction rate have been determined by several authors (7–10), assuming that the dissociation of nitrogen on the surface is the rate-determining step. Studies on single-crystal surfaces have shown that the rate is strongly dependent on the catalyst surface structure (6). Also, a potassium promoter effect has been established on the industrial catalyst (polycrystalline iron) by several authors (1).

Ammonia synthesis activity over several other transition metals has also been studied (11–13). Ruthenium supported on carbon was found to be very active and sensitive to alkali additives under conditions of low temperature (523 K) and low pressure (600 Torr). Under these conditions, sup-

ported ruthenium catalysts showed a ten-fold increase in activity compared to the conventional doubly promoted iron catalyst (Fe–Al₂O₃–K₂O). A silica-supported rhenium catalyst was studied under the same conditions described above and was found to be among the least active (13). Recently, however, work done in our laboratory at 20 atm and 713 K has shown that rhenium is remarkably active for ammonia synthesis (14). The rate over a polycrystalline rhenium foil was as high as over the most active iron single-crystal face studied so far [Fe(111)].

In this study, we report further results on the synthesis of ammonia over rhenium. Polycrystalline foils and four single-crystal rhenium surfaces have been studied: Re(0001), Re(1010), Re(1120) and Re(1121). Kinetic parameters for ammonia production have been obtained for each surface between 720 and 900 K. As in the case of iron, a strong structure sensitivity is observed. The catalyst activity can be related to the roughness and openness of the sur-

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face. The kinetic dependence on the reactant gases and the activation energy found over rhenium are sufficiently close to those of iron to indicate a great similarity in the reaction mechanism. The dissociative chemisorption of nitrogen is considered the rate-determining step of the reaction. Potassium metal deposited alone on the rhenium metal surface does not promote the synthesis of ammonia. If the effect of potassium on iron is associated with aiding to its reconstruction to the (111)-orientation crystallites, the absence of any major effect of potassium on rhenium is due to the much slower rates of reconstruction of this high-melting-point metal under reaction conditions.

EXPERIMENTAL

The apparatus used in these studies consisted of an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-9} Torr (15). Surface structure and chemical composition were determined by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), respectively. A retarding field analyzer was used for both techniques. A quadrupole mass spectrometer was used for gas analysis and an ion sputtering gun for sample cleaning. The sample could be enclosed in a cell and separated from the UHV chamber, to carry out reactions at high pressures (20 atm). The cell was part of a loop connected to an external gas manifold. During reaction, gases were continually circulated over the single-crystal sample via a positive displacement pump. For a typical experiment, after the composition and structure of the surface were determined, the sample was isolated from UHV by closing the high pressure cell. Hydrogen was then introduced into the loop, keeping the crystal at room temperature. Nitrogen was introduced next, while the gases were being circulated through the loop. After the desired gas mixture was obtained, the catalyst was heated resistively to reaction temperature. The

temperature was controlled and monitored by a Pt/Pt-5%Rh thermocouple spotwelded to the edge of the crystal. During experiments, variations on the sample temperature were within ± 2 K.

Gas samples were periodically withdrawn from the reaction loop through a sampling valve into a photoionization detector, equipped with a 10.2-eV UV lamp. Ammonia was the only reaction product. At this photon energy, ammonia was also the only gas ionized. Thus, the detector signal was directly proportional to the ammonia partial pressure. A recording integrator was used to measure the signal as a function of reaction time. To calibrate the sensitivity of the detection system, a platinum foil comparable in size to the rhenium samples (~ 1 cm²) was cleaned, annealed, and then heated to 870 K under 20 atm of reactants under the regular reaction conditions. Since the platinum does not catalyze the synthesis of ammonia from nitrogen and hydrogen, the baseline for the detection of ammonia could be determined and thus the detection limit established. A rate of $(5 \pm 4) \times 10^{13}$ NH₃ molec/cm² · sec was our detection limit.

Studies were performed on both polycrystalline and single-crystal surfaces of ~ 1 cm² total area. Four single-crystal surfaces were studied: Re(0001), Re(10 $\bar{1}$ 0), Re(11 $\bar{2}$ 0), and Re(11 $\bar{2}$ 1). Both sides of the single-crystal samples were oriented and then polished by standard metallurgical techniques. The major contaminants were silicon and carbon. When the sample was used for the first time, silicon was removed by Ar⁺ sputtering (8×10^{-6} A/cm² at 1500 eV) for several hours followed by annealing at 1523 K for 7 min. Carbon was removed by oxygen treatment at 2×10^{-7} Torr for 2 min with the crystal at 723 K. After this initial cleaning procedure, all the contaminants after reaction could be removed by Ar⁺ sputtering (8×10^{-6} A/cm² at 500 V) for a few minutes, followed by annealing at 1523 K for 7 min. The sample was cleaned after every experiment. After no contaminants were detected by AES, in the case of single-crystal sam-

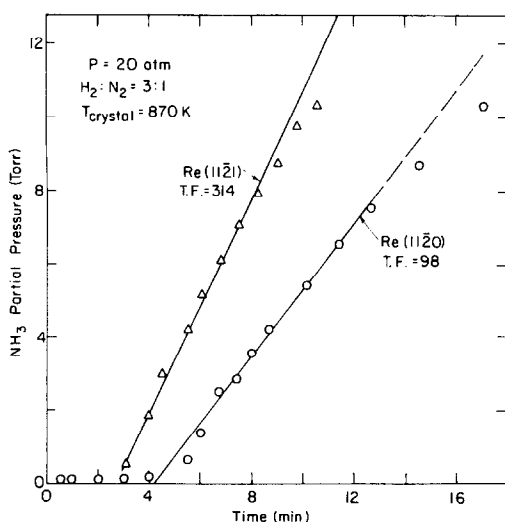


FIG. 1. Amount of ammonia produced as a function of time for two single-crystal catalysts: Re(1121) (triangles) and Re(1120) (open circles). The crystal temperature is 870 K; the total reactant pressure is 20 atm ($p_{N_2}:p_{H_2} = 1:3$). The turnover frequency (TF) was obtained from the initial rates (solid line). (TF = NH_3 molecules/surface atom \times sec).

ples, the surface structure was verified using LEED.

The LEED spots were sharp for the Re(0001) and Re(11 $\bar{2}$ 0) samples while the Re(11 $\bar{2}$ 1) and Re(10 $\bar{1}$ 0) patterns were somewhat diffused even after longer annealing periods. This suggests that the order of the surface atoms in these two samples had a shorter range than in the case of the former two. No sign of reconstruction of any of the single-crystal surfaces after Ar^+ sputtering and annealing could be detected. The same pattern was also observed after high pressure reaction, if adsorption of gases on the surface was avoided by keeping the crystal at reaction temperature while the high pressure cell was evacuated, prior to opening to UHV.

RESULTS

A. Reaction Kinetics

Temperature dependence. The production of ammonia from nitrogen and hydrogen over clean polycrystalline rhenium foil

was reported earlier between 603 and 713 K (14). In this study the temperature range was extended to 900 K in order to be able to monitor the production of ammonia from the less active rhenium surfaces.

In Fig. 1 a typical plot of the total pressure of ammonia produced as a function of time at 870 K is presented for the two most active rhenium single-crystal surfaces. Note the deviation from linearity of the production of ammonia with time at partial pressures higher than 6 Torr. This effect was noted earlier for the polycrystalline foil 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 later. The apparent "induction period" of 3–4 min is the time needed to saturate the surfaces of the stainless-steel reactor with ammonia.

The temperature dependence of the rate of ammonia synthesis was measured for two different polycrystalline foils and the Re(11 $\bar{2}$ 0) single-crystal face. In Fig. 2, Arrhenius plots are shown for a polycrystalline foil and the Re(11 $\bar{2}$ 0) single crystal. Although different activities were measured for the two different foils and for the single crystal, the apparent activation energies as obtained from Arrhenius plots were the same for all three samples, within experimental error ($E_a = 19.4 \pm 1.1$ kcal/mol).

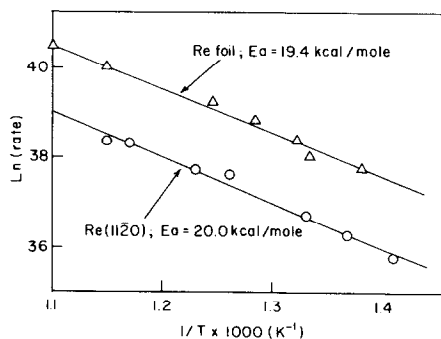


FIG. 2. Arrhenius plots for ammonia synthesis over rhenium foil (triangles) and Re(1120) single-crystal (open circles) catalysts.

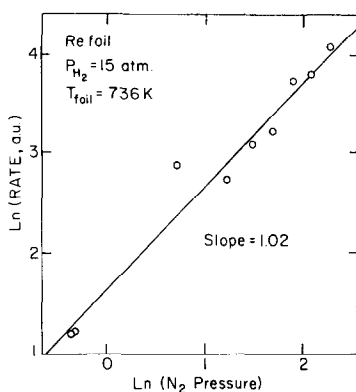


FIG. 3. Nitrogen pressure dependence of the ammonia synthesis over a rhenium polycrystalline foil at 736 K. The hydrogen pressure was 15 atm.

Reactant pressure dependence. The reaction rate dependence on both hydrogen and nitrogen have been determined. The dependence of the reaction rate on the nitrogen partial pressure is shown in Fig. 3. In these experiments, the hydrogen partial pressure was kept constant at 16 atm and the nitrogen partial pressure was varied between 0.8 and 11.2 atm. The reaction rate was found to be first order on nitrogen ($n = 1.02$). A similar experiment was performed to determine the reaction order on hydrogen. This time the nitrogen pressure was kept constant at 5.4 atm and the hydrogen

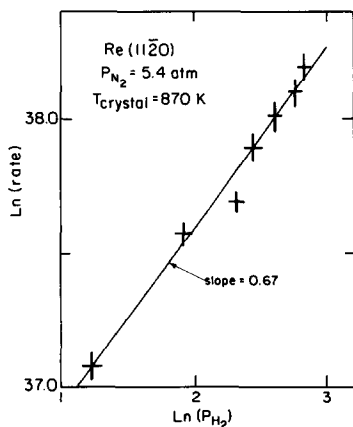


FIG. 4. Hydrogen pressure dependence of the ammonia synthesis over Re(1120) single-crystal catalyst at 870 K. The nitrogen pressure was 5.4 atm.

pressure was varied between 3.4 and 17.0 atm. The results obtained, shown in Fig. 4, indicate that the reaction order with respect to hydrogen is equal to 0.67.

Isotope effect. The reaction rate was also studied as a function of temperature, using deuterium as a reactant instead of hydrogen. Arrhenius plots of the ammonia synthesis over polycrystalline foil are shown in Fig. 5. The rate of reaction increased by about 30 to 50% over the temperature range studied when deuterium was used instead of hydrogen. A very small difference in activation energy of the reaction is observed ($E_a = 19.4$ and 21.5 kcal/mol for NH_3 and ND_3 formation, respectively).

B. Structure Sensitivity

The first evidence for structure sensitivity in the ammonia synthesis over rhenium came from the large variations in activity of several polycrystalline foils of different origin. Variations in activity of up to a factor of 5 were observed. The possibility that dif-

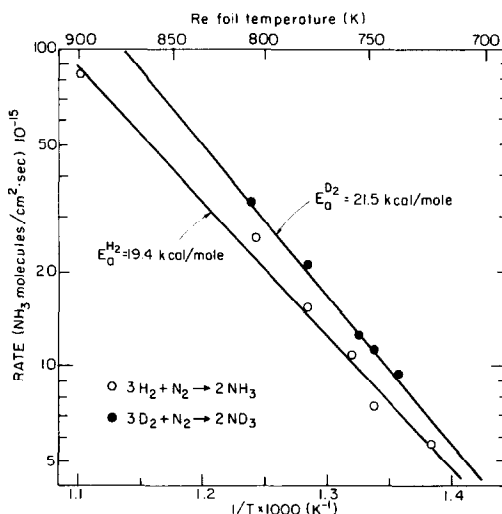


FIG. 5. Arrhenius plots for ammonia synthesis over polycrystalline rhenium foil, using either hydrogen or deuterium as reactant. The dots represent the reaction rates using deuterium and the open circles represent the ones using hydrogen. The reaction conditions are the same in both cases: total reactant pressure of 20 atm and ratio of nitrogen to hydrogen or deuterium equal to 1:3.

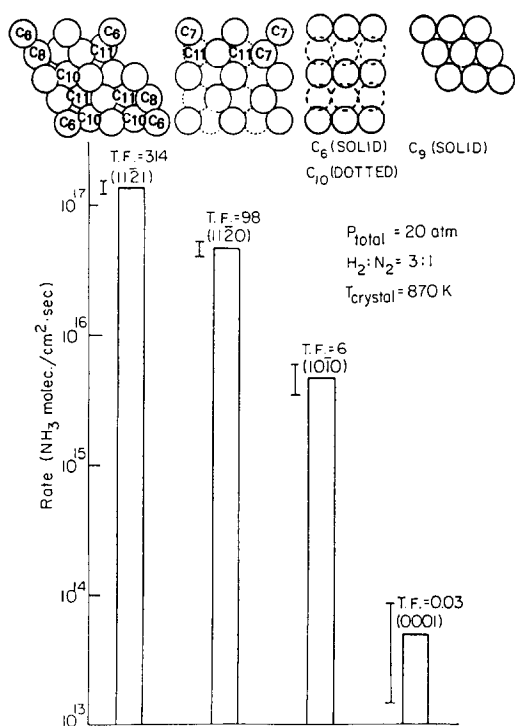


Fig. 6. Structure sensitivity in the ammonia synthesis over rhenium single-crystal faces. The turnover frequencies (TF) are given as NH_3 molec./ $\text{cm}^2 \times \text{sec}$. Schematics of the atomic structure of each surface are given above each bar.

ferent foils may expose several crystal faces with an uncontrollable distribution led us to study the reaction over various single-crystal faces as catalysts.

The synthesis of ammonia was studied over four different single-crystal surfaces at 870 K and a total reactant pressure of 20 atm ($p_{\text{H}_2}:p_{\text{N}_2} = 3:1$). The surface planes studied were Re(0001) (the closest packed basal plane), Re(1010), Re(1120), and Re(1121). Geometric representations of the faces studied are given in Fig. 6. A bar graph summary of the reaction rates over the four catalyst faces studied is also given in Fig. 6. The rates are given as turnover frequencies, considering all the surface atoms exposed as active sites. The relative activity ratio obtained is 1:94:920:2820 for the Re(0001), Re(1010), Re(1120), and Re(1121) surfaces, respectively. The results indicate that the catalytic activity for am-

monia synthesis can be related to the roughness and openness of the surface. This relation could also be obtained from the following results. The rhenium closest packed surface [Re(0001)] produced almost undetectable amounts of ammonia at 870 K under normal reaction conditions. When both sides of the Re(0001) crystal were sputtered by Ar^+ bombardment ($5 \times 10^{-6} \text{ A}$ at 500 V for 5 min) without subsequent annealing, an initial rate more than an order of magnitude higher than the detection limit was measured. This rate decreased after a few minutes possibly due to partial annealing. When the sample was annealed at 1300 K for 5 min, the rate was already reduced to only about a factor of 2 higher than the detection limit. The production rate dropped to (or below) the detection limit when the sample was annealed at 1640 K for 7 min.

C. Effect of Potassium and Oxygen

The effect of predosing potassium alone and potassium coadsorbed with oxygen on the catalytic activity for ammonia synthesis of several rhenium surfaces has been studied. A Saes getters potassium source was used to generate pure atomic potassium vapors. Surface coverages were determined using the relative Auger peak intensities of Re (167 eV) and K (250 eV). The peaks ratios were compared to the values obtained for potassium on platinum (16), such that $\text{Re}(167 \text{ eV})/\text{K}(250 \text{ eV}) = 0.35$ corresponds to a coverage of one monolayer of potassium. The ammonia synthesis rates were determined over three rhenium surfaces, a polycrystalline foil, and the Re(1120) and Re(1121) single crystals. The results are presented in Table 1. In all three cases, under reaction conditions, most of the potassium desorbs from the rhenium surface when it is deposited alone. At 870 K, only coverages of potassium lower than 0.15 of a monolayer were observed. The effect of potassium on the reaction rate was typically very small. The largest promotion effect, a 23% increase in rate, was found with

TABLE 1

Effect of Potassium Adsorbed Alone and Potassium Coadsorbed with Oxygen on the Ammonia Synthesis Rates over Rhenium Metal Catalysts^a

| Surface composition | Surface structure | | |
|---------------------------------|-------------------|----------|----------|
| | Re(1120) | Re(1121) | Re(foil) |
| Clean | 4.6 | 14.1 | 18.4 |
| K ^b | 4.6 | 17.4 | 19.4 |
| K ^b + O ^c | 4.5 | 18.2 | 22.0 |
| K ^b + O ^d | 4.3 | n.a. | 23.2 |
| K ^b + O ^e | 2.3 | n.a. | n.a. |

Note. Reaction conditions: catalyst temperature = 870 K, $p_{\text{total}} = 20$ atm, $p_{\text{N}_2} : p_{\text{H}_2} = 3 : 1$.

^a Values in (NH_3 molec/cm² $\times 10^{-16}$).

^b 0.25 monolayer of potassium.

^c Adsorption of 100 liters O₂ previous to reaction.

^d Addition of 1.0 Torr of O₂ to the reactant gases.

^e Addition of 20.0 Torr of O₂ to the reactant gases.

the Re(1121) single crystal. On the Re(1120) surface no promotion effect was observed.

The results of potassium coadsorbed with oxygen are also shown in Table 1. In all the experiments, 25% of a monolayer of potassium was adsorbed on the surface previous to reaction. Oxygen was adsorbed on the surface using one of three different procedures: (i) dosing the Re + K (0.25 θ) surface with 100 liters of oxygen gas in the UHV chamber, (ii) mixing 1.0 Torr of oxygen with the reactant gases, or (iii) mixing 20.0 Torr of oxygen with the reactant gases. The presence of oxygen in all cases stabilized the potassium on the rhenium surface under reaction conditions. When the first procedure was used to adsorb the oxygen (UHV adsorption), a clear enhancement of the reaction rate was observed when the Re(1121) and rhenium foil catalysts were used. Some oxygen was removed from the rhenium surface (~35%) after 15 min at 870 K under reaction conditions. With the second type of experiment (1.0 Torr of oxygen circulating in the high pressure loop) a large postreaction oxygen coverage was observed. The activity was reduced only slightly in the Re(1120) case while some enhancement in activity was evident with the polycrystalline foil. Certainly no poisoning

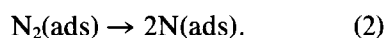
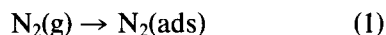
was detected. Finally with about 20 Torr of oxygen in the loop, the activity is reduced to half, with a postreaction oxygen coverage close to one monolayer.

DISCUSSION

A. Kinetic parameters and reaction mechanism

Studies done in this work show that the ammonia synthesis over rhenium is first order with respect to nitrogen pressure and 0.67 order with respect to hydrogen and has an activation energy of 19.4 ± 1.1 kcal/mol, regardless of the surface structure of the catalyst. Since these values are similar to those obtained for iron, it is useful to compare these two catalysts.

The reaction is first order with respect to nitrogen for both iron and rhenium. This indicates that the rate-determining step, in both cases, involves the adsorption of nitrogen on the surface:



In the case of iron, the second step is considered the rate-determining step for the synthesis of ammonia (2, 5, 17, 18). In the case of rhenium, 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, the dissociative sticking probability of nitrogen on the rhenium surface is very low (19) (of the order of 10^{-6} to 10^{-8}). It is reasonable to speculate then that the rate-determining step would be the dissociation of nitrogen [Eq. (2)] rather than the adsorption step [Eq. (1)], which is not expected to be activated. Based on the assumption that the dissociation of the nitrogen molecule is the rate-determining step over rhenium, rate expressions that have been suggested for the iron catalyst can be used. A successful and widely used expression has been developed by Temkin and Pyzhev (7, 8):

$$\frac{d(p_{\text{NH}_3})}{dt} = k_1 p_{\text{N}_2} \left(\frac{p_{\text{H}_2}}{p_{\text{NH}_3}^2} \right)^\alpha - k_2 \left(\frac{p_{\text{NH}_3}^2}{p_{\text{H}_2}} \right)^\beta. \quad (3)$$

Here p_{N_2} , p_{H_2} , and p_{NH_3} are the pressures of nitrogen, hydrogen, and ammonia respectively, and k_1 and k_2 are the pressure independent rate constants for ammonia synthesis and decomposition, respectively. Under our experimental conditions, i. e., low conversions (less than 0.2%) and a small catalyst surface area (1 cm²), the second part of Eq. (3), which considers the decomposition of ammonia, can be neglected. We then obtain

$$\frac{d(p_{NH_3})}{dt} = k_1 p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2} \right)^\alpha \quad (4)$$

Ozaki *et al.* (9) and Nielsen *et al.* (10) have developed several expressions for the rate of ammonia synthesis over iron, depending on the major species present on the surface. All the expressions can be combined into a single one if two adjustable parameters, α and ω , are introduced.

$$\frac{d(p_{NH_3})}{dt} = \frac{kp_{N_2}}{(1 + K(p_{NH_3}/p_{H_2}^\omega))^{2\alpha}} \quad (5)$$

If the surface is covered mostly by N_{ads} species, then ω is equal to 1.5. If it is covered by NH_{ads} species, then ω is equal to 1.0. Nielsen *et al.* proved that at ammonia conversions larger than 0.1%, on the iron catalyst, the right-hand term in the denominator of Eq. (5) is much larger than one (10). Note that in this case, the expression derived by Temkin and Pyzhev [Eq. (4)] is obtained for the case of a surface covered mostly by N_{ads} species.

These rate expressions, derived for the iron catalyst, correlate very well with the observed first-order dependence of the rate over rhenium with respect to the nitrogen pressure. The order of the reaction with respect to hydrogen is different for the rhenium and iron catalysts. With rhenium, the overall order is 0.67 (see Fig. 4) which means that α is equal to 0.22 if Eq. (4) is used. The α value obtained for the iron catalyst using Eq. (4) is 0.64 (10).

The activation energies for iron and rhenium are very similar. Spencer *et al.* (6)

found an apparent activation energy of 19.4 kcal/mol, using an Fe(111) single crystal as a catalyst under experimental conditions identical to ours. This value is the same as the one obtained in this study for rhenium catalysts. On a promoted iron catalyst, an apparent activation energy of 20 kcal/mol has been determined (9, 10). This is in excellent agreement with the previous results.

As was mentioned earlier, the value of the parameter ω in Eq. (5) is indicative of the major species present on the surface under reaction conditions. In order to find the two adjustable parameters α and ω in Eq. (5), the dependence of the rate on the partial pressure of ammonia must be determined. This was done by carrying out experiments for longer times and higher ammonia partial pressures than in those shown earlier in Fig. 1. The rates of ammonia synthesis were taken at various ammonia pressures, rather than measuring the initial rates, as was done previously. The experiments were carried out on two single crystals, Re(11 $\bar{2}$ 1) and Re(11 $\bar{2}$ 0). The results yielded an α value equal to 0.23 on both crystals when Eq. (5), was used. This is identical to the α value obtained from Temkin's equation [Eq. (4)] using the hydrogen pressure dependence on Re(1120). With this value of α a value of ω equal to 1.45 was obtained from the order of the reaction with respect to hydrogen ($m = 0.67$). As was mentioned before, this suggests that the rhenium surface is covered mostly by N_{ads} species under the reaction conditions of ammonia synthesis.

This rather in direct way of obtaining information on the surface composition requires, of course, further confirmation from more direct experimental studies. Quite different interpretations about the dominant species on the surface during ammonia synthesis have been obtained and discussed in the literature, using iron-based catalysts. The presence of NH_{ads} has been concluded mostly from isotopic studies on the doubly promoted iron (9, 20), while others have found evidence for N_{ads} species on singly

promoted or pure catalysts (8, 10, 21). It should be noted, however, that the nature of the predominant species on the surface is very sensitive to parameters such as surface uniformity, temperature, reactant pressure, and extent of oxygen removal from the surface (9).

Isotope effect. Several isotope effect studies in the ammonia synthesis over iron-based catalysts have appeared in the literature. In a study over doubly promoted catalyst (Fe–Al₂O₃–K₂O), the rate of reaction increased by a factor of 3 when hydrogen was replaced by deuterium (9, 20, 21). This was somewhat unexpected since the rate-determining step of the reaction was already then accepted to involve the nitrogen dissociative chemisorption without any hydrogen bond formation and/or breaking. The sequential hydrogenation of the N_{ads} or NH_{ads} species is 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 synthesis is slowed down by the presence of the ammonia product, which undergoes dissociative chemisorption under the reaction conditions, the isotope effect indicates that NH₃ adsorbs and dissociates faster than ND₃; thus the overall synthesis rate is slower when using hydrogen. 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 NH₃/ND₃ vs H₂/D₂ (20). It was found to be temperature dependent: K_D/K_H equals 74.2 at 273 K and is only 4.32 at 573 K. If one extrapolates these calculations to our experimental conditions, i.e., 800 K, the isotope ratio is expected to be $K_D/K_H = 1.6$. In Fig. 5 it is shown that at 800 K the synthesis activity with deuterium is about a factor of 1.5 higher than the corresponding value using hydrogen, in good agreement with the calculations. The overall isotope effect should be similar on iron and on rhenium catalysts

because the molecular properties that are important for the determination of the isotope effects are those of the gas-phase molecules. The slightly higher activation energy observed with deuterium (barely beyond experimental error) cannot be readily explained.

B. Structure sensitivity

The structure sensitivity of iron for ammonia synthesis has been extensively studied. Brunauer and Emmett (22), in 1940, proposed that the Fe (111) surface was the most active for this reaction. Since then, several studies (3, 4, 18) have suggested the importance of exposed C₇ coordination atoms in the second layer of the Fe(111) surface as the active sites for ammonia synthesis. In our laboratory, Spencer *et al.* (6) studied the ammonia synthesis at high pressures (20 atm) over several iron single-crystal surfaces. They found an activity ratio of 418 : 25 : 1 for the (111), (100) and (110) single-crystal planes of iron, respectively. This is the most direct evidence reported so far for the structure sensitivity of iron for ammonia synthesis.

The choice of rhenium single-crystal planes for this study was guided by the observations of the activity of specific iron sites. After observing no activity on the close-packed (0001) basal plane and only a low activity on the slightly more open Re(10 $\bar{1}$ 0) plane (relative to the polycrystalline foil), the Re(11 $\bar{2}$ 0) face that exposes C₇ coordination atoms was chosen. As in the case of the (111) face of iron, the (11 $\bar{2}$ 0) face of rhenium has two C₇ coordination atoms per unit cell. But, since rhenium has a hexagonal close-packed structure, these two C₇ coordination atoms are in the topmost layer, in contrast to the (111) body-centered-cubic surface of iron, where the C₇ atoms are in the second layer (See Fig. 7). The activity of this plane, as shown in Fig. 3, is higher than that of the (0001) and (10 $\bar{1}$ 0) surfaces. The similarity of the (111) face of iron and the rhenium (11 $\bar{2}$ 0) is not limited only to the presence of C₇ coordina-

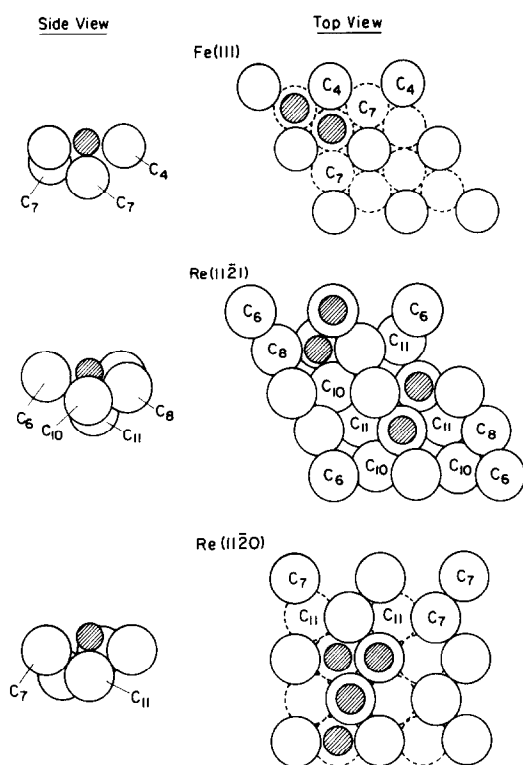


FIG. 7. Schematic atomic structures of Fe(111), Re(1121), and Re(1120) crystal surfaces from side and top views. The solid circles are topmost atoms, the dotted circles are the second layer atoms, and the shaded circles are the nitrogen atoms. The size of the circles roughly represents the relative Van der Waals ratio of the corresponding atoms.

tion atoms. As shown in Fig. 7, both surfaces are quite open. The higher activity of these open and corrugated surfaces implies that the dissociation of nitrogen molecules is facilitated by their possibility to interact with both the first and second atomic layers of the metal. Once a nitrogen molecule adsorbs and dissociates on such a surface, the adsorbed atoms just formed may diffuse along troughs away from each other and thus recombination is prevented. Remember that when the almost inactive close-packed surface [Re(0001)] was sputtered without subsequential annealing, a tenfold increase in activity was observed. All these suggest that the increase in activity on the (1120) surface with respect to the (0001) and

(1010) surfaces might be due to the roughness and openness of the surface, instead of the presence of C_7 sites. In order to test this hypothesis, the (1121) plane of rhenium was studied. As shown in Fig. 7, this surface plane does not contain C_7 atoms. It is as open as the (1120) face and it has a rougher second layer structure. This surface showed a threefold increase in activity compared with the (1120) face. This clearly shows that C_7 coordination sites are not indispensable for the catalytic activity of rhenium for ammonia synthesis and the activity of a particular surface can be related to its openness and roughness. We should mention, however, that the Re(1121) crystal showed a slightly more diffuse LEED pattern than the Re(1120), indicating a larger surface disorder. This does not affect the previous conclusion, but makes the absolute value of the difference in rates of these two surfaces only approximate.

It is possible that the surface structures present under UHV conditions are not present 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 vacuo* (23). Reconstruction of the (111) and (100) planes of iron in the presence of nitrogen has been reported (24), and it is always possible that a reversible reconstruction under high pressure conditions occurs under the reaction conditions for ammonia synthesis. Studies over iron single crystals at high pressure (6) indicate, however, that this is not the case. Otherwise, such a dramatic structure sensitivity correlation would not be possible. In the case of rhenium, information is not available on the possible reconstruction of the low Miller index planes. The LEED pattern of the Re(1120) crystal plane after the high pressure reaction was identical to that observed before the reaction. Thus, 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 point tempera-

tures, the higher melting point rhenium is expected to have lower diffusion rates than iron under similar reaction conditions. Thus, reconstructing 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 allows us to infer something about the surface structure of the crystallites in the previous work on silica-supported rhenium catalysts (13). The rates reported for this catalyst correspond, after extrapolation to the same temperature, to a value between the rates obtained with the Re(0001) and Re(10 $\bar{1}$ 0) single-crystal surfaces. This suggests that the supported rhenium particles tend to form crystallites of closely packed exposed surfaces.

C. The Effect of Potassium and Oxygen

The role of potassium oxide (K₂O) additive in the industrial iron catalyst is considered very important (1). The effect of K₂O is, however, still unclear. Recently, low pressure experiments by Ertl *et al.* (5, 25–27) have shown a dramatic effect of potassium on the rate of nitrogen dissociative chemisorption on iron single-crystal surfaces due to an electronic effect. Since the nitrogen dissociative chemisorption is the rate-determining 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. On the other hand, field electron emission studies indicate that iron surfaces tend to reconstruct to the more active (111) crystal face in the presence of nitrogen and potassium (4). Thus the promotion effect of potassium on iron can be due to an electronic effect on the bonding of nitrogen and a structural effect. The role of oxygen coadsorbed with potassium has been studied, since in the industrial iron catalyst there is not pure potassium on the surface. It was observed that the presence of oxygen reduced the electronic effect of

pure potassium; i.e., the nitrogen is adsorbed at a lower rate (25). The important role of the coadsorbed oxygen species, however, is to thermally stabilize the potassium ions on the catalyst surface (21).

The results obtained in this study on the rhenium catalyst are different from those on iron. The overall synthesis rate at temperatures up to 870 K does not change much as compared with the clean rhenium catalyst. As shown in Table 1, the effect of pure potassium is maximum with the Re(1121) and even then it causes less than a 25% increase in activity. Potassium, on the other hand, does not have any poisoning effect. This might be expected, since the active transition metal surface is being covered by a chemically inactive one. The other striking difference between rhenium and iron is the positive effect of oxygen over the reaction rate when coadsorbed with potassium on the surface. As seen in Table 1, even at oxygen partial pressures of 1 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. The nature of the surface compound that is formed between potassium and oxygen is not well known and requires further investigation. The results seem to indicate, however, that both 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 to proceed without significant poisoning up to rather high additive coverages.

If potassium or oxygen or their compound influences the catalytic activity of iron for ammonia synthesis by catalyzing the reconstruction of the surface to expose the highly active (111) orientation, this reconstructing effect is absent on rhenium. This is not surprising since atom diffusion along the surface is needed for massive reconstruction to take place. The high melting point rhenium should have much lower surface self-diffusion rates than iron under

the same experimental conditions, inhibiting such a reconstructing process.

SUMMARY

The results presented in this study show that rhenium is an excellent catalyst for ammonia synthesis. The kinetic data suggest that, as in the case of iron, the rate-limiting step is the dissociative chemisorption of nitrogen. The rate is strongly dependent on the surface structure of the catalyst. The activity of a rhenium catalyst is higher the more open and rough its surface is. No promotion effect of potassium was observed.

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