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Ammonia Synthesis Catalyzed by Rhenium

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Polycrystalline rhenium appears to be nearly an order of magnitude more active as an ammonia synthesis catalyst than the most active crystal plane of iron (Fe(111)) at low conversions and in the reactant pressure (20 atm) and temperature (603–713 K) regimes investigated. It displays an activation energy for ammonia synthesis of 16.2 kcal mole^{-1}, which is lower than that of Fe(111) (19.4 kcal mole^{-1}) under identical experimental conditions. Although rhenium becomes reversibly poisoned at 1–2 Torr of product ammonia, exposure to water or presulfidation has little effect on its catalytic activity. This is in marked contrast to the behavior of iron.

INTRODUCTION

Between Haber's initial discovery of the catalytic activity of iron for ammonia synthesis (*1*) in 1904, and the start-up in 1912 of the first large-scale ammonia plant to use the iron–alumina–potassium oxide catalyst developed by Mittasch *et al.* (*2*), many thousands of catalyst formulations were tested at the laboratories of BASF in Germany. We can be certain, however, that rhenium was not among these, since the element was not discovered until 1925, and was not readily available until many years later.

The literature pertaining to NH_3 synthesis over rhenium is sparse, the first reference to rhenium as an ammonia catalyst being made by Zenghelis and Stathis (*3*) in 1937. These workers found that the catalytic activity of rhenium was inferior to that of iron for ammonia synthesis. In 1971 Ozaki *et al.* (*4*) investigated the properties of a rhenium catalyst, promoted with charcoal and potassium, and found it to display activity for ammonia synthesis, with an activation energy of ~16.5 kcal mole^{-1}. These authors found similarly prepared iron and ruthenium catalysts to be more active, however, with activation energies of ~13.2 and 24.6 kcal mole^{-1}, respectively.

This paper deals with the ammonia synthesis activity of clean rhenium at low conversions (<2 Torr ammonia), at temperatures of between 603 and 713 K and at reactant pressures of ~20 atm. Under these conditions, rhenium was nearly an order of magnitude *more* active as an ammonia synthesis catalyst than the most active crystal plane of iron (Fe(111)) (*5*). Moreover, the effects of water and surface sulfur on the rhenium activity were found to be very slight, although these substances are known to suppress almost completely the catalytic activity of iron for this reaction.

EXPERIMENTAL

The high-pressure–low-pressure apparatus used to study ammonia synthesis has been described in detail elsewhere (*5, 6*). It consists of a stainless-steel ultrahigh vacuum (UHV) chamber containing an Auger spectrometer, a quadrupole mass spectrometer, and argon sputter-ion cleaning facilities. In addition, a high-pressure cell could be lowered around the catalyst sample and connected to an external circulation loop, enabling catalytic reactions to be run (and monitored) *in situ* at pressures of up to 20 atm. Ammonia was detected by means

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of a photoionization detector (lamp energy 10.2 eV) attached to the external loop, and reactant and product gases were circulated by means of a positive displacement pump. A switchable condenser was also attached to the circulation loop (Fig. 1). Using a slurry of isopentane as a coolant (equilibrium temperature 113 K), it was possible to trap almost all the ammonia present in the loop, while not significantly condensing the reactants (N_2, H_2). Thus, the apparatus combined the properties of a catalytic reactor with those of a UHV system.

The catalyst sample consisted of a 6 × 6-mm square polycrystalline rhenium foil (99.97% purity, Alfa Division, Ventron Corporation) of thickness 0.025 mm. The initial contaminants in the foil were found to be sulfur and carbon, the latter being the most tenacious. Cleaning was achieved by repeated argon ion bombardment (500 V, 1.5×10^{-5} Acm^{-2}) of both sides of the sample, interspersed with extended periods of annealing in vacuum at 1273 K.

The rhenium foil was spot-welded to 0.25-mm platinum support wires which, in turn, were spot-welded to 2-mm platinum rods on the manipulator. Platinum was chosen as a support material because of its ineffectiveness as a catalyst for ammonia synthesis. The catalyst temperature was monitored by means of a chromel-alumel thermocouple, spot-welded to one face of the foil.

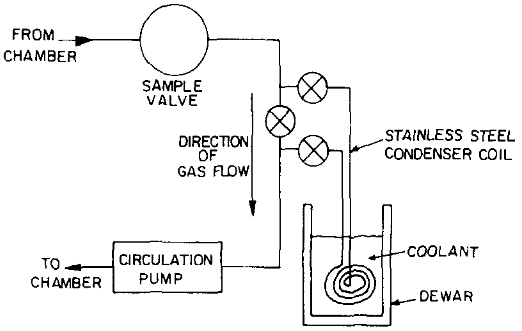

FIG. 1. Schematic diagram of a condenser used to remove ammonia selectively from the reactant-product mixture during ammonia synthesis.

RESULTS

Rhenium was investigated as an ammonia synthesis catalyst in a stoichiometric mixture of hydrogen and nitrogen at a pressure of 20 atm. Over the entire temperature range used (603–713 K), rhenium displayed an initial catalytic activity which was approximately an order of magnitude greater than that of the most active crystal plane of iron (Fe(111)) (*5*). At 673 K, the maximum turnover rate was 3.3×10^{-8} mole NH_3 s^{-1} cm^{-2} (of catalyst). However, the synthesis activity decreased as the ammonia partial pressure rose above ~1–2 Torr (Fig. 2), suggesting that "product poisoning" of the catalyst surface was occurring. In order to investigate the reversibility of this poisoning, a synthesis run was undertaken, in which the isopentane-cooled condenser (Fig. 1) was periodically opened to the circulation loop. This action reduced the ammonia concentration in the loop to a value well below that necessary to cause poisoning of the rhenium surface and, after closing the condenser, ammonia proceeded to build up again at the initial rate. This could be repeated many times (Fig. 3), the slight decrease in the slopes toward the end of the experiment probably being due to the slow poisoning of the surface by traces of carbon-containing substances in the reactant mixture (a small carbon signal was detectable in the post-run Auger spectrum). Thus it appears that the product poisoning of the rhenium surface is a reversible process, and some kind of equilibrium exists between the poisoning surface species and the gas phase ammonia.

The activation energy for ammonia synthesis on rhenium was calculated by plotting the logarithm of maximum activity (the slope of the straight-line section of the synthesis curve (Fig. 2)) vs reciprocal temperature. A straight line was obtained, yielding an activation energy of 16.2 kcal $mole^{-1}$. This is displayed in Fig. 4 together with comparable data obtained for Fe(111), the iron crystal plane found to be the most ac-

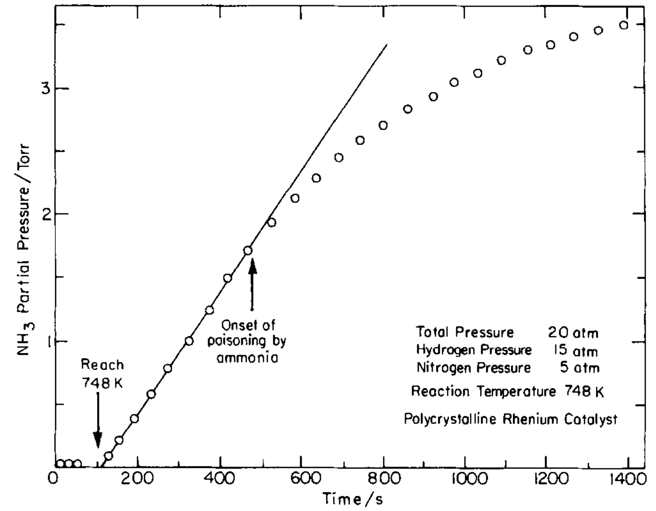

FIG. 2. Evolution of ammonia during synthesis reaction on a polycrystalline rhenium catalyst of surface area 0.72 cm^2 (reactor volume = 170 cm^3).

tive in ammonia synthesis (*5*). If it is assumed that the reactant surface coverages on both iron and rhenium catalysts are similar, then extrapolation of the straight lines indicates that the pre-exponential factors for both rhenium and iron(111)-catalyzed synthesis reactions are the same.

As was previously observed with iron catalysts (*5*), the postrun Auger spectra of the rhenium contained a strong nitrogen

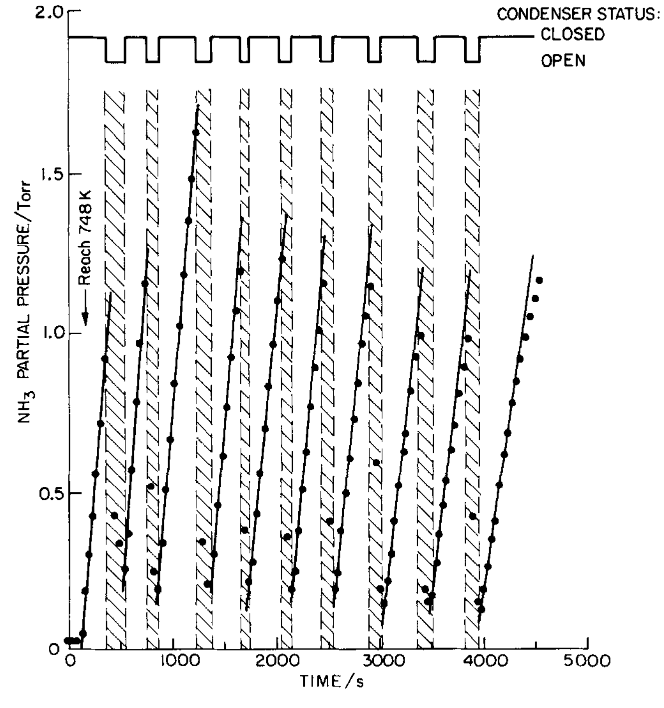

FIG. 3. Demonstration of the reversibility of product poisoning during ammonia synthesis on rhenium.

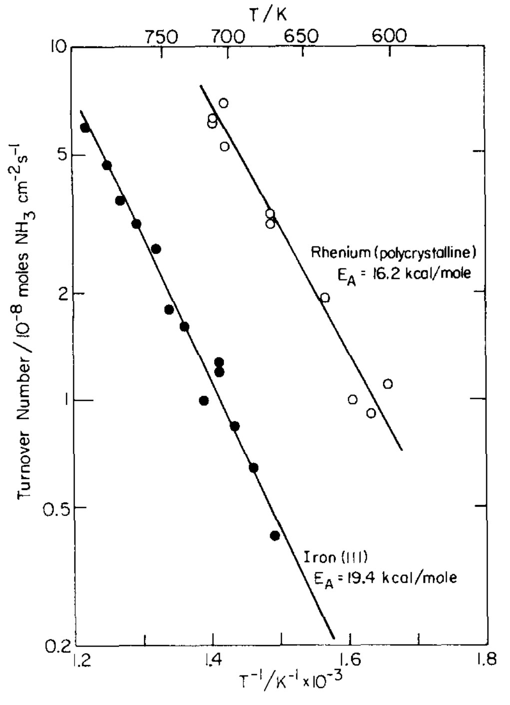

FIG. 4. Arrhenius plots for polycrystalline rhenium and Fe(111) ammonia catalysts.

signal. Restarted ammonia synthesis proceeded on such a nitrogen-containing surface at an identical rate to that observed on the initially clean rhenium, and, as with iron, is probably due to resegregation of atomic nitrogen on the metal surface which had dissolved in the bulk metal during the synthesis reaction (*5*).

Pretreatment of the rhenium sample with oxygen at 1273 K led to a clear uptake of oxygen, visible in the Auger spectra. However, as seen also with iron (*5*) this oxygen appeared to have no effect on the rate of subsequent ammonia synthesis, the oxygen being very rapidly removed on exposure to the nitrogen–hydrogen mixture at reaction temperatures.

Significant differences were observed between rhenium and iron with respect to their behavior in the presence of water and sulfur. Presulfidation of the iron specimens, or the inclusion of 10–20 Torr of water in the reactant mixture was found to suppress ammonia synthesis activity entirely. However, in the case of polycrystalline rhenium, neither presaturation of the surface with H_2S (monolayer coverage, as observed by AES) nor the inclusion of 20 Torr of water in the reactant mixture had a significant effect on catalytic activity, the subsequent ammonia synthesis rate merely being suppressed by 10–20%.

DISCUSSION

It appears that the mechanisms for the ammonia synthesis reaction on rhenium and iron(111) are similar, since they seem to have identical pre-exponential factors and comparable activation energies. The small difference in the latter (3.2 kcal mole^{-1}) would account for the observed differences in turnover rates. This is probably due to the different electronic properties of the metals, which, in turn, would affect the activation energy for the dinitrogen dissociation step.

The product poisoning behavior is most likely due to a blocking of catalytically active sites by intermediates in the decomposition pathway of ammonia, such as NH and NH_2. It would seem reasonable that the concentration of these species should be in equilibrium with the gas phase ammonia and therefore it is to be expected that the site-blocking species' concentration would be concomitantly reduced as the gaseous ammonia partial pressure is reduced by condensation. It is worthy of note that previous studies of ammonia decomposition on rhenium (*7*, *8*) have indeed suggested that NH or NH_2 species are involved in the rate-limiting step of the decomposition reaction.

The resistance of rhenium to poisoning by sulfur is well-known, and partially accounts for its use as a component of alloy hydrocracking and reforming catalysts in the petroleum industry. The exact nature of the interaction of rhenium with surface sulfur (to produce a chemisorbed overlayer or surface sulfide) is uncertain, however, and is at present the subject of investigation in our laboratory. The fact that rhenium did not become significantly poisoned in the presence of surface sulfur suggests either that the rhenium–sulfur species is as effective at ammonia synthesis as metallic rhenium, or that the active sites for ammonia synthesis are distinct from those which adsorb sulfur. The polycrystalline nature of the sample used in the present study may also be important, since it is conceivable that some crystal faces are active in ammonia synthesis and unable to adsorb sulfur in our reaction conditions while others sulfide rapidly, but do not catalyze ammonia synthesis readily. It is known that iron reacts with surface sulfur to produce a sulfide (*9*), even at room temperature, and the inactivity of sulfur-covered iron in ammonia synthesis is presumably due to the inability of FeS_x to catalyze ammonia synthesis.

Iron reacts with water, even at room temperature, to produce iron oxides. These oxides are not active in ammonia synthesis, and this accounts for the poisoning action of water on iron ammonia catalysts. Rhenium is unaffected by water up to temperatures and pressures well in excess of those used in the present studies. It, therefore, is resistant to poisoning by water present in the ammonia synthesis reactant feed.

It is interesting to compare the results obtained in this investigation with those described by Ozaki *et al.* (*4*). These workers found, in contrast to the present study, that a rhenium catalyst (finely divided rhenium on coconut carbon) was inactive at temperatures up to 400°C (stoichiometric reactant mixture, 600 Torr) unless promoted with metallic potassium. Presumably their detector system was not sensitive enough to register the small amount of ammonia produced by the unpromoted rhenium before product poisoning set in. However, when promoted with metallic potassium, their supported rhenium appeared to catalyze ammonia synthesis with an activation energy of $\sim$16.5 kcal mole^{-1}—very similar to the 16.2 kcal mole^{-1} observed for clean rhenium at low conversions in the present study. The effect of potassium on ammonia synthesis catalysts is an area still in need of much research. However, this comparison suggests that the presence of potassium allows the rhenium catalyst to continue to operate with the same mechanism as observed at low conversion through the product-poisoning barrier, making it a potential contender as a poison-resistant, large-scale, ammonia synthesis catalyst.

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REFERENCES

1. Haber, F., and van Oordt, G., *Z. Anorg. Chem.* **43,** 11 (1904).
2. Mittasch, A., *Adv. Catal.* **2,** 81 (1949).
3. Zenghelis, C., and Stathis, E., *Osterr. Chem. Zeitung.* **40,** 94 (1937).
4. Ozaki, A., Aika, K., and Hori, H., *Bull. Chem. Soc. Japan* **44,** 3216 (1971).
5. Spencer, N. D., Schoonmaker, R. C., and Somorjai, G. A., *J. Catal.* **74,** 129 (1982).
6. Blakely, D. W., Kozak, E., Sexton, B. A., and Somorjai, G. A., *J. Vac. Sci. Technol.* **13,** 1091 (1976).
7. Fukuda, Y., Honda, F., and Rabalais, J. W., *Surface Sci.* **99,** 289 (1980).
8. Gasser, R. P. H., and Green, D. P., *Surface Sci.* **82,** L582 (1979).
9. Margot, E., Oudar, J., and Benard, J., *C. R.* (*Paris*) **C270,** 1261 (1970).