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RHENIUM - AN AMMONIA SYNTHESIS CATALYST

N.D. Spencer and G.A. Somorjai

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RHENIUM - AN AMMONIA SYNTHESIS CATALYST

N.D. Spencer* and G.A. Somorjai
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemistry,
University of California, Berkeley, CA 94720

ABSTRACT

Polycrystalline rhenium has been studied as a catalyst for the synthesis of ammonia from its elements. It appears to have an initial activity which is nearly an order of magnitude greater than that of the most active crystal plane of iron (Fe(111)) at the reactant pressures (20 atm.) temperatures studied (603-713 K). It displays an activation energy for ammonia synthesis of 16.2 kcal mole^{-1}, which is appreciably lower than that of iron(111) (19.4 kcal mole^{-1}) under identical experimental conditions. Rhenium appears to become reversibly poisoned by the presence of 1-2 torr of product (ammonia), although exposure to water or pre-sulfidation appears to have little effect on the catalytic activity (in marked contrast to the behavior of iron under similar conditions).

*Present Address: W.R. Grace and Co., Washington Research Center,
7379 Route 32, Columbia, MD 21044

While rhenium, when dispersed with platinum, is used extensively as an industrial reforming catalyst, the ability of this element to catalyze the synthesis of ammonia from nitrogen and hydrogen has not been explored under well-defined conditions.[1,2] In this letter we describe our investigations of the catalytic activity of clean rhenium for ammonia synthesis. We also compare the behavior of rhenium under synthesis conditions with that of iron--the principal component of the industrial ammonia synthesis catalyst used at present.

The high pressure-low pressure apparatus used for these studies has been described in detail elsewhere.[3,4] It consists of a stainless steel UHV chamber containing an Auger spectrometer, quadrupole mass spectrometer and argon sputter-ion cleaning facilities. In addition, a high-pressure cell could be placed around the catalyst sample and connected to an external circulation loop, enabling catalytic reactions to be run in situ and monitored at pressures of up to 20 atmospheres. Ammonia was detected by means 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. The catalyst sample consisted of a 6 mm x 6 mm square polycrystalline rhenium foil (99.97%, 0.025 mm thickness, Alfa Division, Ventron Corporation) which was cleaned by repeated argon ion bombardment (500 V, 1.5×10^{-5} Acm^{-2}) and annealing at 1000°C. The principal contaminant in the foil was found to be carbon.

Over the temperature range studied (603-713 K), rhenium displayed an initial catalytic activity which was nearly an order of magnitude higher than that of the most active plane of iron (Fe(111)[4]). At 673 K, the maximum turnover rate was approximately 3.3×10^{-8} moles NH_3 cm^{-2} s^{-1}. The synthesis activity decreased as the background pressure of ammonia rose above ~ 1-2 torr (Figure 1): this is in contrast to the behavior of iron. The fall-off in catalytic activity of the rhenium is apparently due to "product poisoning" of the catalyst surface

by the synthesized ammonia. This could be prevented by trapping the product periodically in a cooled section of the circulation loop, after which the rhenium was able to synthesize ammonia at the initial rate. This procedure could be repeated many times, with little diminution of the initial catalytic activity.

By plotting the logarithm of the maximum activity (i.e., the slope of the straight-line section of the synthesis curve) vs. reciprocal temperature, we obtained a straight line, whose slope yielded an activation energy of 16.2 kcal $mole^{-1}$. In Figure 2, this line is plotted with comparable data obtained for the most active iron crystal face (Fe(111)[4]). If similar surface coverages during reaction are assumed, the pre-exponential factors for the rhenium- and iron(111)-catalyzed synthesis appear to be the same. The similar activation energies also suggest, but do not prove, that the mechanisms for ammonia synthesis on iron and rhenium catalysts are related.

Iron catalysts are poisoned by the presence of surface sulfur or by the introduction of water with the reactant gas mixture.[4]. However, surface sulfur or water in the reactant feed had little effect on the activity of the rhenium catalyst used in these experiments.

The higher turnover rate over rhenium appears to be the result of the somewhat lower activation energy for the dissociation of dinitrogen on rhenium than on iron. The most likely explanation of the product poisoning is that a high coverage of intermediates such as NH or NH_2 is blocking catalytic surface sites, and that their concentration is in equilibrium with that of the gas phase ammonia. Thus, when the gaseous ammonia concentration is reduced by condensation, the surface site-blocking species' concentration is concommitantly reduced. The decomposition of ammonia by rhenium has been studied by others[5,6] who have postulated that NH_2 or NH species may be involved in the rate-limiting step of the decomposition reaction. If this is the case, then it would account

for the apparent equilibrium relationship between gas phase ammonia and the site-blocking adsorbed species.

The greater poison resistance of rhenium to water and sulfur, as compared to that of iron, may be explained in terms of the relative reactivity of the two elements. While iron reacts with water to produce iron oxides, even at room temperature, rhenium is resistant to attack by water at temperatures and pressures well in excess of those used in the present study. Although surface sulfur is known to react rapidly with iron to produce sulfides which are inactive as ammonia catalysts, the rate of the rhenium-sulfur reaction to produce a chemisorbed sulfur layer or rhenium sulfide is uncertain, 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 that either the rhenium-sulfur species is as effective at ammonia synthesis as rhenium itself, or that the active sites for ammonia synthesis on rhenium are distinct from those which adsorb sulfur. Since the sample used in the present investigation was polycrystalline, it is conceivable that some crystal faces are active in ammonia synthesis and unable to adsorb sulfur, while others sulfide rapidly, but are unable to catalyze ammonia synthesis.

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FIGURE CAPTIONS

Figure 1: Evolution of Ammonia during synthesis reaction on rhenium catalyst.

Figure 2: Arrhenius plots for polycrystalline rhenium and Fe(111) ammonia catalysts.

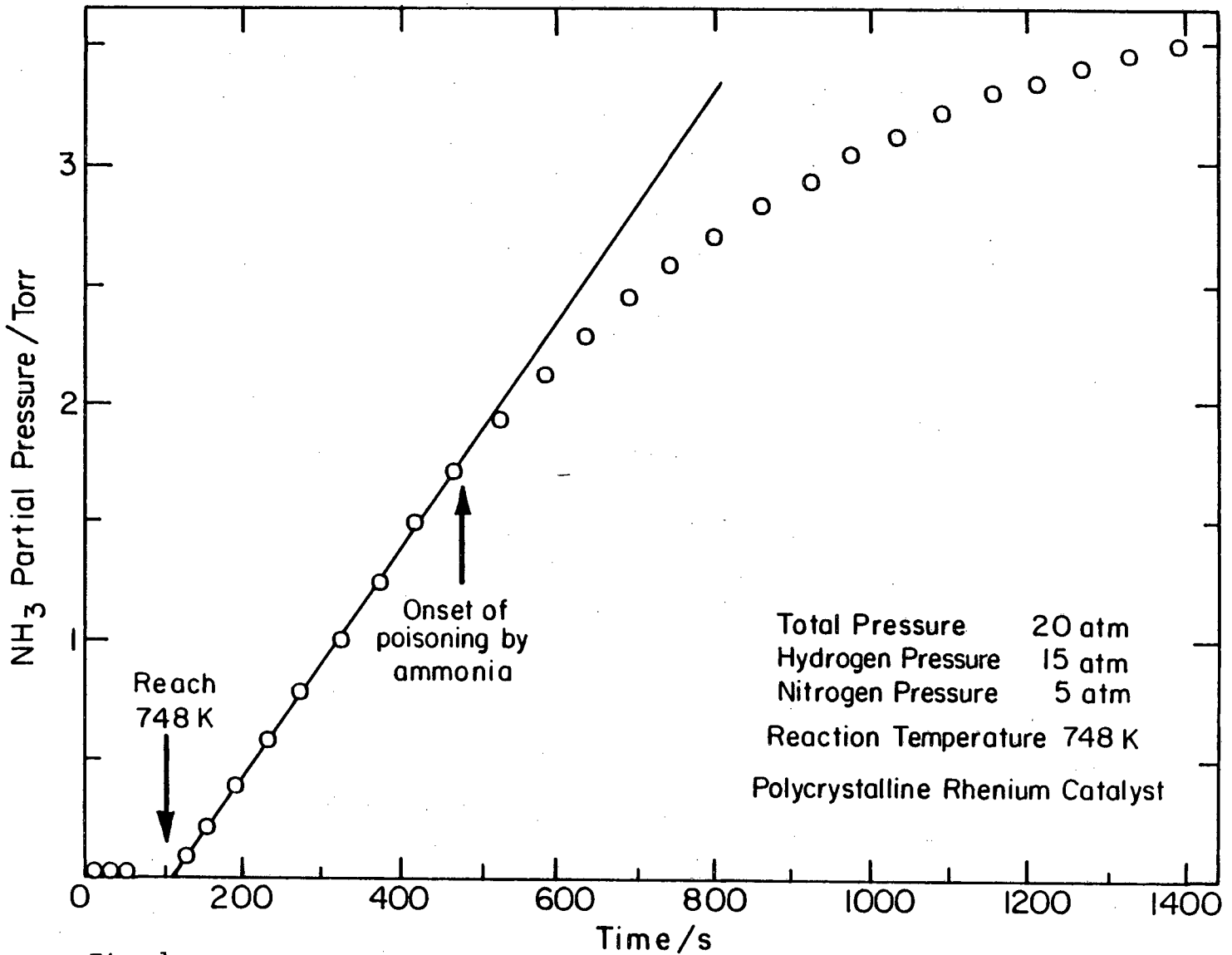

Fig. 1

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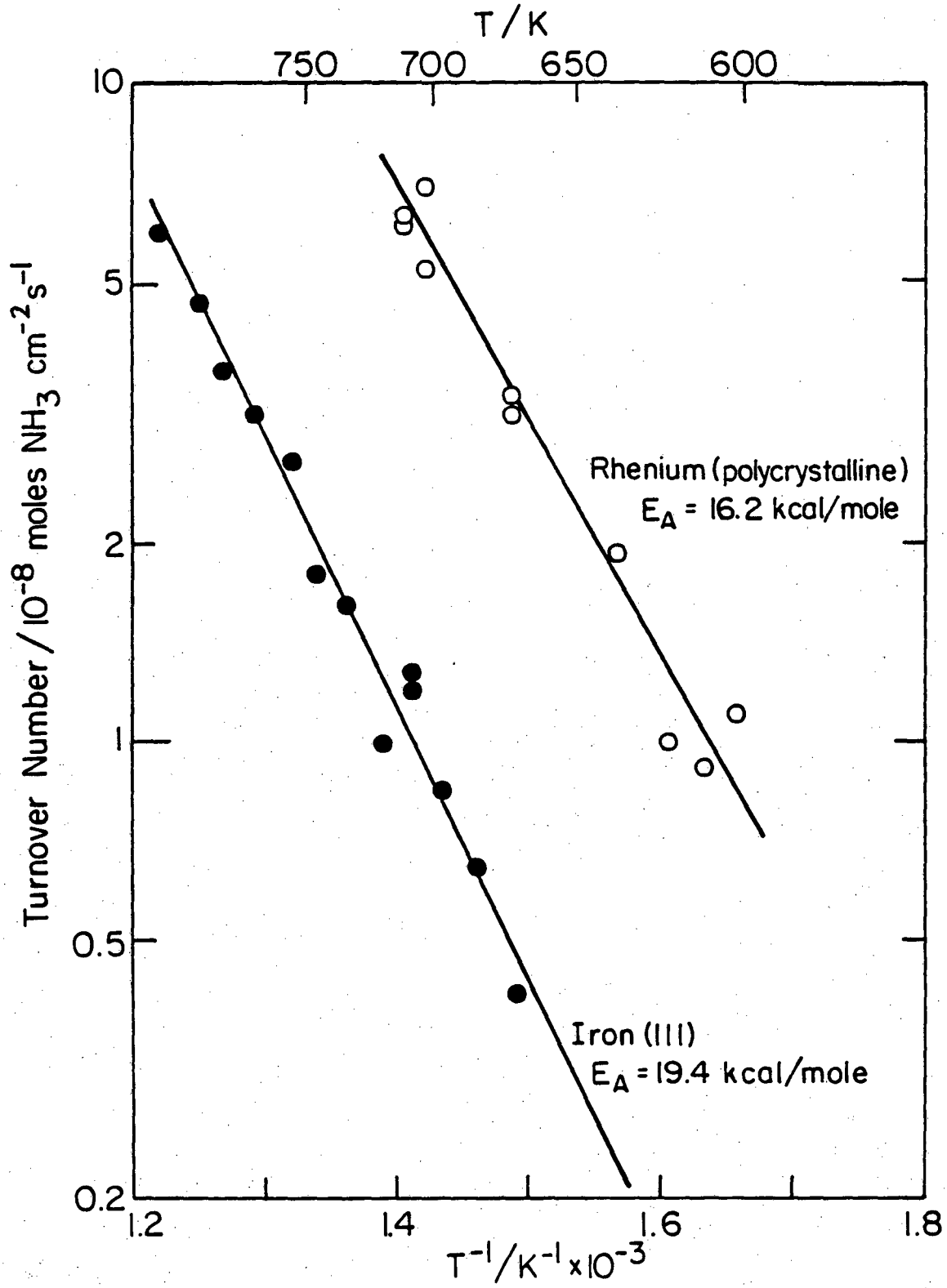

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Fig. 2

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