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Hysteresis during High-Pressure Ammonia Synthesis

While investigating the kinetics of ammonia synthesis over a triply promoted commercial iron catalyst, we unexpectedly observed rate hysteresis during temperature cycles. The catalyst was triply promoted (Al_2O_3–CaO–K_2O) KM-I supplied by Haldor–Topsøe. Kinetic measurements were done in a 3-in. Berty CSTR (Autoclave Engineers) on 8- to 10-mesh (2.0–2.4 mm) catalyst particles. High-purity hydrogen and nitrogen (Matheson) were further purified after mixing to contain less than 0.1 ppm O_2 and less than 0.5 ppm H_2O. The catalyst was carefully reduced according to the procedure recommended by Nielsen (*1*). Constant activity for several days was observed prior to taking the data reported below. The rate of ammonia synthesis was monitored periodically by gas chromatographic analysis of the reactor effluent. The maximum ramp rate of 20°C/h was chosen to ensure that several turnovers per site occurred during the time required to change the temperature by 1°C.[1]

The results are shown in Fig. 1. These data were obtained by measuring the initial up-ramp after cooling the reactor from 480 to 200°C and holding at 200°C for several hours. Higher rates of ammonia synthesis were observed during the subsequent down-ramps. The upper curves in the figure represent the steady-state activity of the catalyst at the conditions noted. This was verified by observing constant activity during long hold periods at 280, 300, and 400°C during the down-ramp. The constant activity observed during a long hold time at 280°C also shows that these results were not an artifact caused by reversible poisoning or surface oxidation by sub-ppm levels of O_2 or H_2O. We would expect the activity to decrease over time if poisoning were a factor since iron is not easily reduced at 280°C (*5*). Also, it is known (*1*) that the activity of triply promoted iron will decline over time in the presence of poisons; we noted no detectable decline in activity during these measurements.

The hysteresis is reproducible provided the catalyst is maintained for several hours under conditions essentially free of ammonia, e.g., under conditions where the rate of ammonia synthesis is very low. For instance, after holding the catalyst at 200°C overnight, conditions under which no detectable ammonia was produced, we observed identical hysteresis during the subsequent up-ramp and down-ramp. At 200°C ammonia synthesis was occurring but at a very low rate, below the detection limit of the gas chromatograph. The important point is that the hysteresis can be reproduced only after holding for an extended period of time at low temperature. On the other hand, if one holds the catalyst at 200°C only briefly (<1 h), one observes activity coincident with the steady-state down-ramp curve during the subsequent up-ramp. We also noted that at very slow initial up-ramps, e.g., 3°C/h, the rate of ammonia synthesis follows the upper curves in Fig. 1 during the subsequent up-ramp.

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[1] The exposed iron surface area for KM-I is 0.6 m^2/g (*1*) or about 1.6 m^2/cm^3. A C_7 site, as suggested by Boudart *et al.* (*2*) and Dumesic *et al.* (*3–4*), requires at least three surface iron atoms; therefore there are less than 4×10^{18} sites/cm^3. A 0.1% ammonia concentration or change in concentration at 15,000 v/v/h corresponds to about 10^{17} molecules/s or 1.8×10^{19} molecules per degree change in temperature at 20°/h.

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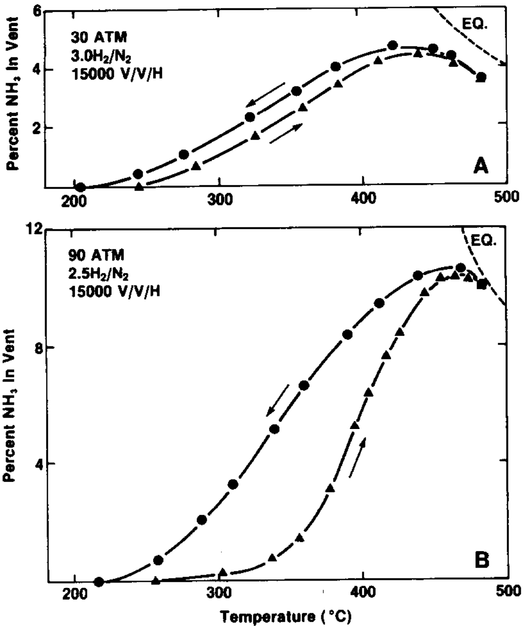

FIG. 1. Ammonia synthesis rate (as vol% ammonia in vent) versus temperature. (A) Initial up-ramp at 20°C/h from 200 to 340°C and 10°C/h to 480°C. Down-ramp results were independent of down-ramp rate for rates less than 20°C/h. Below 420°C the observed rates were less than 30% of equilibrium. (B) Initial up-ramp at 20°C/h from 200 to 320°C and 10°C/h to 480°C. Down-ramp results were independent of down-ramp rate for rates less than 20°C/h.

We speculate that the hysteresis occurs as a consequence of two kinetic phenomena. During the initial up-ramp the catalyst is slowly changing and an increasing number of intrinsically more active sites are formed. Simultaneously, the activity of all the sites increases with increasing temperature due to the activation energy of the reaction. At up-ramp rates in the range of 10 to 20°C/h, the rate of change lags and the catalyst is less active than it is during the subsequent down-ramp where the number of sites is at steady state under the given conditions.

There is evidence that the activity of pure iron for ammonia synthesis varies with the exposed crystallographic plane and that promoted iron catalysts reconstruct during ammonia synthesis. Brill and co-workers (*6, 7*) have shown that the catalytic activity of iron for ammonia synthesis at atmospheric pressure is highest on the Fe(111) crystal face. Recent work at 20 atm (1 atm = 101.3 kN m^{-2}) confirmed this result and showed that the catalytic activity increased as the exposed crystal surface became less densely packed, i.e., Fe(111) > Fe(100) > Fe(110) (*8*). Dumesic *et al.* (*2–4*) reported that ammonia induces the surface of small polycrystalline iron particles supported on magnesium oxide to reconstruct to a more open structure with a higher concentration of exposed C_7 sites. After reconstruction the catalytic activity increased; therefore, they concluded that these were the sites active for ammonia synthesis. Amariglio and Rambeau suggest that the ammonia synthesis reaction itself causes the formation of "special configurations" at the surface of pure iron, carbon-supported iron, and triply promoted iron during ammonia synthesis at atmospheric pressure (*9*). Ertl states (*10, 11*) that atomic nitrogen causes reconstruction of the Fe(111) and Fe(110) surfaces leading to complex surface structures, "surface nitrides," which are probably related to the structure of Fe_4N. The work of Amariglio and Rambeau lead Emmett (*9*) to suggest that evidence of reconstruction be sought at high-pressure commercial conditions.

The data presented here are consistent with the notion that the surface of a fully reduced, polycrystalline, triply promoted iron ammonia catalyst reconstructs at high pressure and high temperature yielding a catalyst with higher activity. One interpretation of our results is that ammonia promotes and hydrogen inhibits reconstruction. Furthermore, under these conditions, the time scale of the reconstruction is on the order of many minutes to hours and is reversible.

Since the hysteresis can be reproduced only after holding for an extended period of time at low temperature where ammonia synthesis proceeds at very low rates, we speculate that the surface slowly converts to its original low activity form under these conditions and that the ammonia synthesis activity that remains occurs at the sites of lower intrinsic activity characteristic of unreconstructed iron. This is evidence that the regeneration of the original surface is a slow process. Therefore, during short hold times at 200°C the catalyst did not change sufficiently to affect the rate of ammonia synthesis during the subsequent up-ramp. Though we cannot rule out with absolute certainty that the hysteresis was caused by reversible poisoning by water or oxygen, we believe that these results indicate that poisoning is very unlikely. If water or oxygen at the sub-ppm level were oxidizing the surface and if the low rates during the initial up-ramp or during up-ramps after long low-temperature hold periods were caused by reduction of oxidized iron to catalytically active metallic iron, then it becomes very difficult to explain the constant activity observed during long hold periods at 280°C. We would expect oxidation to occur very readily at 280°C and cause reduced rates of ammonia synthesis. Therefore, we propose that these results are consistent with reversible reconstruction of the catalyst surface on a time scale of hours.

A comparison of the initial up-ramps at 90 and 30 atm suggests that reconstruction is inhibited at higher total pressure. For example, at 300°C and 30 atm, one observes about 0.8% ammonia compared to only 0.2% ammonia at 300°C and 90 atm. Since the partial pressure of ammonia is higher at 30 atm where the rate of ammonia synthesis is higher, it is not likely that ammonia inhibits reconstruction. Also, our results at high pressures are consistent with ammonia- or nitrogen-promoted reconstruction as proposed by Amariglio and Rambeau (*9*) and Ertl (*10, 11*) for ammonia synthesis at low pressures. Thus it is likely that the observed inhibition is caused by hydrogen.

In summary we have presented evidence that the surface of a fully reduced triply promoted iron catalyst can exist in two different states above 30 atm total pressure. Our results suggest that one state is favored at high hydrogen pressure in the absence of ammonia and is relatively inactive for ammonia synthesis while the second reconstructed state is very active for ammonia synthesis. While these states cannot be observed directly at high pressure, they are consistent with lower-pressure reactor studies and with surface science studies at very low pressures.

REFERENCES

1. Nielsen, A., "An investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," 3rd ed. Gjellerups Forlag, 1968.
2. Boudart, M., Delbouille, A., Dumesic, J. A., Khammouma, S., and Topsøe, H., *J. Catal.* **37**, 486 (1975).
3. Dumesic, J. A., Topsøe, H., Khammouma, S., and Boudart, M., *J. Catal.* **37**, 503 (1975).
4. Dumesic, J. A., Topsøe, H., and Boudart, M., *J. Catal.* **37**, 513 (1975).
5. Richard, M. A., Soled, S. L., Fiato, R. A., and DeRites, B. A., *Mater. Res. Bull.* **18**, 829 (1983).
6. Brill, R., and Kurzidim, J., *Colloq. Int. C.N.R.S.* **187**, 99 (1969).
7. Brill, R., Richter, E. L., and Ruch, E., *Angew. Chem. Int. Ed. Engl.* **6**, 882 (1967).
8. Spencer, N. D., Schoonmaker, R. C., and Somorjai, G. A., *J. Catal.* **74**, 129 (1982).
9. Amariglio, H., and Rambeau, G., "Proceedings, 6th International Congress on Catalysis, London, July 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 1113. The Chemical Society, London, 1977.
10. Ertl, G., *CRC Crit. Rev. Solid State Mater. Sci.* **10**(4), 349 (1982).
11. Ertl, G., *J. Vac. Sci. Technol. A* **1**, 1247 (1983).

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