

Ammonia Decomposition over 430-SS Etched Metal Catalysts

INTRODUCTION

Iron-based catalysts have been frequently studied for ammonia decomposition mainly to gain insight into the mechanism of ammonia synthesis. Recent works related to ammonia decomposition studies include ammonia decomposition over well-defined iron single crystals (1-4) and ammonia decomposition over polycrystalline iron wires (5). In the work of Ertl and Huber (1), a mechanism and a resultant reaction rate model are presented which explain the observed kinetics of zero-order behavior with partial pressure of ammonia at low temperatures and first-order behavior at high temperatures. McCabe (6) went further to properly define the rate constants in the reaction model presented by Ertl and applied it to his data for ammonia decomposition over nickel wires. Similar kinetics have also been reported by Tsai and Weinberg (7) for the steady-state decomposition of ammonia on Ru (001).

The work presented below examines an iron-chromium material (430 stainless-steel, 430-SS) whose surface is activated. The activation process patented by Baldi and Damiano (8-11) involves diffusion coating aluminum into the surface of a metal such as 430-SS. The surface is then "etched" with an alkali or acid solution in which aluminum is removed and a very rough "activated" surface remains. The resultant material is called an "etched metal catalyst." Etched metal catalysts have been reported active for the selective catalytic reduction of nitric oxide by ammonia (12-14). These catalysts showed surface areas of 1 to 10 m²/g compared to a few square centimeters for bare inactivated

wires. Because etched metal catalysts showed such a high activity for the selective reduction of NO by NH₃ and are composed of iron it was felt that further investigation of these catalysts for activity in other reactions related to ammonia was warranted.

EXPERIMENTAL

The experiments were carried out by flowing ammonia in a helium carrier at atmospheric pressure across a quartz tube (2.14 cm in diameter) holding a coiled wire mesh of activated catalyst. The catalyst was a coiled 430-SS 23 wire mesh (of about seven wraps) of about 1 cm in length and weighed between 2.5 and 3.5 g. A typical activity evaluation involved passing a stream composed of 5% ammonia and 5% nitrogen in a helium carrier flowing at 3.4 liters/min across the catalyst. Outlet nitrogen mole fractions were measured by a gas chromatograph as a function of temperature. Ammonia decomposition to nitrogen as function of temperature was calculated by the equation

$$\% \text{ NH}_3 \text{ decomposed to N}_2 = \frac{y_{\text{N}_2 \text{ prod.}} - y_{\text{N}_2 \text{ feed}}}{y_{\text{NH}_3 \text{ feed}}(0.5 - y_{\text{N}_2 \text{ prod.}})} * 100, \quad (1)$$

where y_i is the mole fraction of species i , subscript "feed" represents the feed mole fraction of the respective gas to the catalyst, and subscript "prod." represents the product mole fraction after flowing across the catalyst.

For the kinetic studies discussed below, no nitrogen was present in the carrier gas. Attempts were made to keep percentage decomposition below 20% by adjusting flow

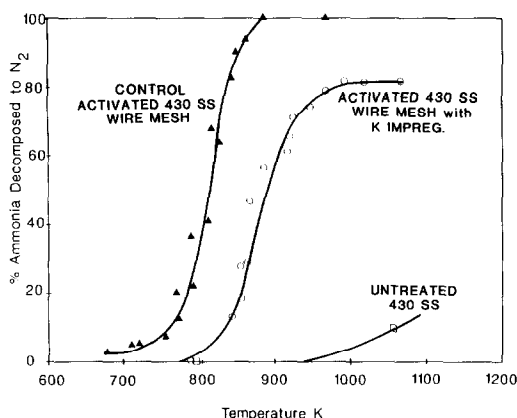


FIG. 1. Activity comparison for ammonia decomposition of two activated 430-SS etched metal catalysts and an unactivated 430-SS wire mesh.

rates. Thus, rates could be calculated directly by assuming a differential reactor by the equation

$$r_{\text{NH}_3} = Q_{\text{NH}_3} (273\text{K}/T_m) * N_a * X_{\text{NH}_3} / (22,400 * A), \quad (2)$$

where r_{NH_3} is the rate of ammonia decomposition in molecules per second per square meter, Q_{NH_3} is the ammonia flowrate in cubic centimeters per second, T_m is the temperature at which the ammonia flow rate is measured (K), N_a is Avogadro's number 6.022×10^{23} molecules/g mole, X_{NH_3} is the fractional decomposition of NH_3 , A is the area of the wires taken as cylinders $4 * W / \rho * D$, W is the weight of the catalyst in grams, ρ is the density of the wire material taken as 7.6×10^6 g/m³, and D is the wire diameter = 0.000432 m.

Ammonia decomposition rates were found for ammonia partial pressures of 150, 300, 750, and 1500 Pa (0.15, 0.30, 0.75, 1.5% ammonia in helium). Analysis of nitrogen and ammonia was done by an Antek Model 310 LP gas chromatograph using a Porapak QS column. An UTI mass spectrometer was used quantitatively to confirm the presence of H_2 as a reaction product.

For this study, two 430 stainless-steel wire meshes were activated by diffusion coating with aluminum and were subse-

quently leached with NaOH to create a very rough surface. The control, which had no further treatments, had a surface area of 1.33 m²/g as measured by a Quantachrome Model MS-8 single-point BET. The other etched metal catalyst, potassium promoted, was further processed by adding potassium to the surface through an impregnation process. The impregnation process involved dipping the coil into 10 wt% of potassium nitrate in water. The coil was dried at 378 K and then calcinated in air for 2 h at 811 K. This catalyst measured a surface area of 0.65 m²/g. Further details about etched metal catalyst morphology can be found in (12).

RESULTS AND DISCUSSION

The first series of evaluations involved activity and stability comparisons of the two etched metal catalysts for ammonia decomposition. Figure 1 shows an activity comparison for three coils for percentage ammonia decomposed to nitrogen for a feed of 5% ammonia and 5% nitrogen in helium flowing across the catalysts at a space velocity of 80,000/h. In this work, space velocity is defined as the total volume occupied by the coil (including the macrovoids between wraps) in the quartz reactor divided by the gas flow rate adjusted to STP conditions. The control, a 430-SS wire mesh diffusion coated with aluminum followed by leaching in NaOH, showed the best activity. Full ammonia decomposition was observed at 840 K under the conditions investigated.

The first evaluation of the potassium-impregnated activated 430-SS catalyst showed its activity to be below that of the control (see Fig. 1). The difference in activity may be attributed in part to too much potassium on the surface based on the impregnating solution used.

Also shown in Fig. 1 are results for ammonia decomposition over an untreated 430-SS wire mesh. Comparison of these results with the results for activated 430-SS demonstrates the improvement in activity

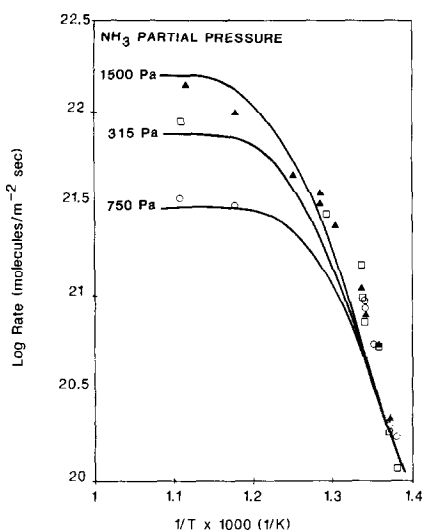


FIG. 2. Kinetic study of ammonia decomposition over a 430-SS etched metal catalyst. Effect of ammonia partial pressure.

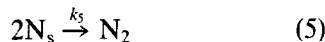
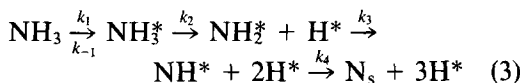
because of surface enhancement and activation. Note that the untreated wire mesh did not show activity until 950 K and reached a maximum of 13% decomposition at 1090 K, the highest temperature investigated.

Repeated evaluations on the potassium-impregnated catalyst showed its activity to increase compared to the first evaluation. The second evaluation showed 100% conversion by 900 K. After further evaluations, the catalyst's activity settled to a constant level of about 85% conversion at 900 K. The explanation for the initial rise followed by a slight decay is as follows. At first, there was too much potassium on the surface which hampered activity. As the surface potassium left the surface, a maximum in activity was observed as the promotional effects of a small amount of surface potassium enhanced the reaction rate. Finally, as all of the surface potassium eroded away, the potassium-impregnated catalyst surface became more like the control surface. Evidence of surface changes were seen in the micrographs taken before and after testing. The pre-testing micrographs showed a rough surface, while the post-testing micro-

graphs still showed a rough surface but it was smoother than that of the pre-testing micrographs. Further evidence of surface potassium erosion was that potassium-promoted catalyst lost 3% of its weight during the testing sequence.

Kinetic Study

Figure 2 shows an example of results for kinetic studies done for the two catalysts. The results show a transition from zero-order kinetics to first-order kinetics as temperature increases. A mechanism and resultant model presented by Ertl and Huber (1) assist in understanding results shown here. Their mechanism is



and the resultant model, as modified by McCabe to account for active site concentrations, is

$$r_{\text{NH}_3} = \frac{[k_1 k_2 P_{\text{NH}_3} / (k_{-1} + k_2)]}{1 + [(k_1 k_2 P_{\text{NH}_3}) / n_0 k_5 (k_{-1} + k_2)]} \quad (6)$$

Parameter explanations for this model and estimates for data shown in Fig. 2 are presented in Table 1. The solid curves shown in Fig. 2 represent Eq. (6) with the parameters shown in Table 1 for the activated 430-SS. Also shown in Table 1 are the parameters found for the potassium-impregnated catalyst.

The advantage of this mechanism and resultant model over a Langmuir-Hinshelwood (L-H) kinetic model with ammonia adsorption as rate controlling is that it predicts activation energy which is closer to the surface nitride decomposition than that to the heat of adsorption of ammonia. For instance, the heat of adsorption of ammonia on iron is reported in the range 55 kJ/mole (3).

TABLE I
Rate Parameter Explanation and Estimates for NH₃ Decomposition over 430-SS Etched Metal Catalysts

Parameter	Function form (explanation)	Parameter values		
			Activated 430-SS Fig. 1	Activated 430-SS plus potassium impregnation
k_{-1}	$k_{-1}^{\circ} \exp(-E_{-1}/RT)$ (desorption rate constant for ammonia)	k_{-1}°	$1 \times 10^{13} \text{ s}^{-1}$	$1 \times 10^{13} \text{ s}^{-1}$
		E_{-1}	79.5	79.5
k_1	$S^{\circ}(2\pi MRT_g)^{-1/2}N_a$ (rate constant for adsorption of ammonia)	S°	0.000513	0.000316
k_2	$k_2^{\circ} \exp(-E_2/RT)$ (rate constant for ammonia decomposition to NH ₂)	k_2°	$1 \times 10^{13} \text{ s}^{-1}$	$1 \times 10^{13} \text{ s}^{-1}$
		E_2	56.5	56.5
k_3	$k_3^{\circ} \exp(-E_3/RT)$ (rate of nitrogen formation from surface nitride)	k_3°	$8.004 \times 10^{18} \text{ s}^{-1}$	$1.128 \times 10^{14} \text{ s}^{-1}$
		E_3	248.1	196.3
n_0	(active site surface concentration sites/m ²)	n_0	0.15×10^{20}	0.15×10^{20}

Note. E_i [=] kJ/g mole; $M = 17$ kg/kg mole; $R = 8,314$ kg m²/(s kg mole K) or 8.314 J/g mole K; $N_a = 6.022 \times 10^{26}$ (molecules/kg mole).

The activation energies found for the surface nitride decomposition for the two catalysts were 248 and 196 kJ/mole for the control and potassium-promoted catalysts, respectively. It should be noted that the other parameters related to the NH₂ species and adsorbed ammonia species were estimated from numbers presented by McCabe for nickel. A major difference in this work compared to McCabe's and Ertl's was the conditions under which the experiments were conducted. In this work, the total pressure was atmospheric (101.3 kPa) and ammonia partial pressures ranged from 150 to 1600 Pa. Ertl's data for ammonia decomposition over iron were at a P_{NH_3} of 7×10^{-4} Pa and McCabe's for decomposition over nickel ranged from 5 to 133 Pa.

CONCLUSIONS

430-SS wire meshes which have been diffusion coated with aluminum which is sub-

sequently etched away have been found to be quite active for ammonia decomposition. The kinetics follow a zero-order behavior at low temperatures and change to first-order kinetics in partial pressure of ammonia as temperature rises. The transition occurs at around 800 K. The results support a mechanism developed by Ertl and Huber (1) in which rate of ammonia decomposition is related to the decomposition of a surface nitride. Because these materials are composed of wire mesh and because they are of relatively low cost, they should be considered good commercial catalysts for any system requiring ammonia decomposition.

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REFERENCES

1. Ertl, G., and Huber, M., *J. Catal.* **61**, 537 (1980).
2. Ertl, G., Grunze, M., and Weiss, M., *J. Vac. Sci. Technol.* **13**, 314 (1976).
3. Grunze, M., Bozso, F., Ertl, G., and Weiss, M., *Appl. Surf. Sci.* **1**, 241 (1978).
4. Weiss, M., Ertl, G., and Nitschke, F., *Appl. Surf. Sci.* **2**, 614 (1979).
5. Loffler, D. G., and Schmidt, L. D., *J. Catal.* **44**, 244 (1976).
6. McCabe, R. W., *J. Catal.* **79**, 445 (1983).
7. Tsai, W., and Weinberg, W. H., *J. Phys. Chem.* **9**, 5302 (1987).
8. Baldi, A. L., and Damiano, V. V., U.S. Patent 4,154,705 (1979).
9. Baldi, A. L., and Damiano, V. V., U.S. Patent 4,292,208 (1981).
10. Baldi, A. L., and Damiano, V. V., U.S. Patent 4,041,196 (1977).
11. Baldi, A. L., and Damiano, V. V., U.S. Patent 3,867,184 (1975).
12. Willey, R. J., Conner, W. C., and Eldridge, J. W., *J. Catal.* **92**, 136 (1985).
13. Willey, R. J., Eldridge, J. W., and Kittrell, J. R., *IEC Prod. Res. Dev.* **24**, 226 (1985).
14. Willey, R. J., Ph.D. dissertation, University of Massachusetts, Amherst, MA, 1984.

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