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NOTES

HCN Synthesis from NH_3 and CH_4 on Pt at Atmospheric Pressure

The synthesis of hydrocyanic acid from ammonia and methane on platinum catalysts

$$NH_3 + CH_4 \rightarrow HCN + 3H_2 \qquad \Delta H = 240 \text{ kJ/mole} \quad (1)$$

is an important petrochemical reaction, since it constitutes the first step in the manufacture of methyl metaacrylate. Two synthesis processes are used commercially (*1*). In the Andrussow process, air is added to the reactor feed to generate the heat required by the reaction by burning a portion of the reactants. In the Degussa process this heat is provided by transfer through the walls of the reactor (*2*). To our knowledge, no kinetic information about either process is available in the literature. A report on the production of a bench-scale reactor using the Degussa process has been published (*3*). However, uncertainties in the temperature and concentration distributions in that high-conversion reactor make it difficult to obtain reaction rates from production data.

We have measured reaction rates for the synthesis of HCN from NH_3 and CH_4 at atmospheric pressure on Pt wires. The reaction was carried out in a 1-liter Pyrex reactor operated batchwise to avoid producing large quantities of highly toxic HCN. Natural gas (97% methane) was purified as described earlier (*4*). Refrigeration grade (anhydrous) NH_3 passed through a bed of NaOH pellets before entering the reaction chamber. Catalysts were 0.0127-cm-diameter wires of 99.99% purity. A 9-cm length of wire was welded to massive stainless-steel leads and kept straight and horizontal along a diameter of a 1000-cm^3 flask. Before each run, the catalyst was heated at 1300 K in air for about 0.5 h to remove carbon contaminants. Temperatures were measured from the wire electrical resistance while a regulated power supply maintained specified temperatures constant to within a few degrees. Small (10 cm^3) gas samples were drawn at intervals and analyzed for HCN using a spectroscopic technique based in the conversion of cyanide into cyanogen bromide (*5*). Reaction rates were calculated from the slope of plots of HCN concentration versus time. Conversions were kept below 10% so that initial rates were measured.

Figure 1 shows the measured rate of HCN production, *r*, for NH_3/CH_4 mixtures at 1 atm containing 50, 60, and 70% NH_3 and catalytic wire temperatures varying between 1200 and 1500 K. Ammonia contents lower than 50% or temperatures below 1200 K resulted in the rapid formation of a black deposit on the catalyst with the consequent loss of activity. Data shown in Fig. 1 were obtained on several wires cut from the same spool. All data were fit with the expression

$$r = A \exp(-E/RT) f(C) \qquad (2)$$

with parameters shown in Table 1. The observed rates, although rather high, are below the onset of mass transfer resistances. Previous measurements of the rates of NH_3 (*6*) and CH_4 (*4*) decomposition carried out in experimental systems similar to the one used in the present work indicate that mass transfer resistances become important only for reaction rates greater than 10^{20} molecules/cm^2 s. The form of the concentration-dependent term, $f(C)$, could not be deter-

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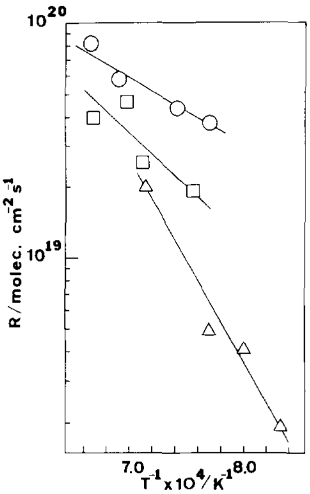

FIG. 1. Reaction rates for HCN synthesis from NH_3 and CH_4 at 1 atm total pressure on a 0.0127-cm-diameter platinum wire. Triangles, circles, and squares denote initial gas-phase mixtures containing 50, 60, and 70% NH_3, respectively. In all cases the balance was CH_4. Slopes and intercepts of the straight lines give rate parameters $Af(C)$ and E/R shown in Table 1.

mined in our experiments because carbon deposits prevented us from measuring reaction rates with reactant mixtures rich in CH_4. Also, the high activation energy observed when the reactor was fed with a stoichiometric mixture may be due to partial blocking of the surface by carbon at the lower temperatures.

The rate-determining step of a catalytic reaction can be estimated from the preexponential factors. Following Baetzold and Somorjai (*7*) we estimate a pseudo-first-order preexponential factor as

TABLE 1

Parameters for Reaction Rates (Eq. (2)) and Pseudo-First-Order Preexponential Factors Calculated Using Eq. (3)

Initial composition %NH_3	$Af(C)$ (molec./cm^2 s)	E/R (K^{-1})	A_1 (s^{-1})
50	2.84×10^{25}	19,800	1.6×10^{15}
60	6.47×10^{21}	6,700	4.6×10^{12}
70	5.46×10^{22}	10,540	6.3×10^{12}

$$A_1 = \frac{r}{C_{CH_4}} \frac{q_T^3}{q_T^2} \exp(E/RT), \qquad (3)$$

where q_T is the translational partition function for methane. Baetzold and Somorjai found that values of A_1 between 10^7 and 10^{12} s^{-1} can be associated with surface diffusion control, while preexponential factors for first- and second-order surface reactions present values in the 10^{13} and 10^9 s^{-1} ranges, respectively. Pseudo-first-order preexponential factors calculated from Eq. (4) with values of the parameters from our experiments are shown in Table 1. Initial reactant compositions containing more than 50% NH_3 result in values of A_1 in the range 10^{11}–10^{12} s^{-1}, suggesting that the reaction is controlled either by surface diffusion or by a surface reaction with order larger than one.

Reaction rates for HCN synthesis from NH_3 and CH_4 on Pt in a catalytic wall tubular reactor were estimated by Koberstein (*3*) and reported in the form of an "effective" rate constant, k_e, defined as

$$k_e = r/C_{CH_4}, \qquad (4)$$

where C_{CH_4} is the concentration of methane in the reactants. Figure 2 shows a plot of k_e values for temperatures varying between 1150 and 1430 K when an equimolar mixture of NH_3 and CH_4 at atmospheric pressure was fed to the reactor. Our results, shown by the full line in Fig. 2, are in remarkable good agreement with the work reported in Ref. (*3*), in spite that Koberstein's data were obtained at much higher conversions (up to over 90%).

Hasenberg and Schmidt (*8*) measured the rate of HCN formation on clean Pt for NH_3 and CH_4 pressures varying between 6.7 and 1330 Pa. Those authors fit their extensive results with a Langmuir–Hinshelwood bimolecular reaction rate expression

$$r = \frac{5.07 \times 10^{15} \exp(-1950/T) P_{CH_4} P_{NH_3}^{1/2}}{(1 + 0.0038 \exp(2390/T) P_{CH_4}/P_{NH_3}^{1/2})^4}, \qquad (5)$$

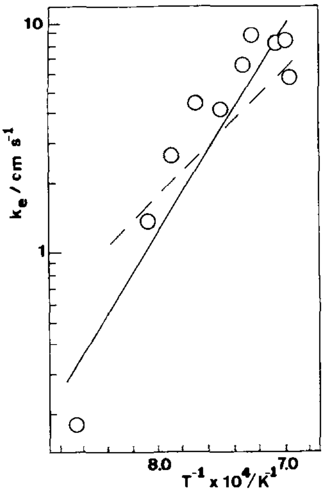

FIG. 2. Reaction rate constant k_e, defined in Eq. (3), measured in a catalytic wall tubular reactor (*3*) (circles), and calculated using Eq. (2) with parameters from Table 1 (full line). Dashed line shows a plot of Eq. (5). In all cases the gas phase was an equimolar mixture of NH_3 and CH_4 at atmospheric pressure.

where the pressures are given in Newtons per square meter. We extrapolated this expression to the reactant partial pressures used in our experiments. When $P_{NH_3} = P_{CH_4} = 0.5$ atm, Eq. (5) closely approximates our results, as shown in Fig. 2.

We conclude that the synthesis of HCN from NH_3 and CH_4 on Pt is a relatively fast reaction probably controlled by surface diffusion or surface reaction. The rate of reaction is strongly affected by the composition of the reactant; concentrations of CH_4 above the stoichiometric result in rapid catalyst deactivation. Reaction rates measured for stiochiometric gas mixtures appear to be reasonably consistent with rates observed in a bench-scale catalytic wall tubular reactor.

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