JOURNAL OF CATALYSIS 62, 167–172 (1980)

The Importance of Ammonia Pressure in the Kinetics of Ammonia Synthesis over Supported Ru

The synthesis of ammonia over ruthenium-based catalysts has been extensively studied by Ozaki and co-workers (*1–6*). In particular, it was suggested that the synthesis rate over celite- (90% silica) and γ-alumina-supported ruthenium is independent of the ammonia partial pressure in the reactor effluent for fractions of equilibrium conversion less than approximately 25%. (It should be noted here that values of the equilibrium ammonia partial pressure at the total pressure and temperature range studied by Ozaki *et al.* vary from approximately 200 to 2200 Pa.) In the above studies, the synthesis rate was measured using a recirculation reactor system in which the ammonia produced was trapped out of the gas phase after each passage of the reactant mixture through the catalyst bed. Yet, in these studies the reactor effluent ammonia partial pressure was not directly determined, and the independence of the synthesis rate on the ammonia pressure was inferred by measuring the rate at different flow rates through the reactor. The present note, therefore, reexamines the ammonia dependence of the synthesis rate over supported (but unpromoted) ruthenium using data collected with a flow reactor coupled with effluent ammonia determination.

Silica gel (Davison, Grade 952) and γ-alumina powder (Davison, SMR-7) were impregnated to ca. 1.0–1.3 wt% ruthenium loading by incipient wetness using an aqueous solution of $RuCl_3 \cdot 3H_2O$ (Alfa Division, Ventron). Following this impregnation, the samples were dried overnight in air at 380 K, and then a portion, 1.5 g in the case of the silica-supported sample and 2.2 g in the case of the alumina-supported sample, was loaded into a flow reactor for hydrogen reduction (at 700 K for ca. 50 h) and subsequent ammonia synthesis studies at atmospheric pressure (0.1 MPa). The flow reactor and accompanying glass gas-handling/purification system are shown in Fig. 1. The reactor itself was fabricated from fritted Vycor tubes of 20-mm nominal diameter. Catalyst bed heights were maintained approximately constant at 15 mm, and the catalyst bed temperature was measured by means of a thermocouple well projecting into the bed. Flow rate was regulated by a needle valve and measured by timing the travel of a soap bubble through a graduated buret. Volumetric flow rates during synthesis were varied from 1.2 to 3.8 $cm^3\ s^{-1}$. The hydrogen (Chemetron, 99.8%) used for catalyst reduction and the 3 : 1 $H_2 : N_2$ synthesis gas mixture (Matheson, prepurified, certified standard) were each further purified by flowing through a Deoxo gas purifier (Engelhard Industries) followed by a packed bed of 13X molecular sieves (Davison, 4- to 8-mesh beads) immersed in a dry ice/acetone slush bath. Prior to use, the molecular sieves were regenerated in flowing helium at temperatures of 570 to 620 K. The ammonia produced at steady-state conditions was measured by two independent methods. One method consisted of bubbling the reactor effluent through a gas scrubber and determining the aqueous ammonia concentration by standard titration techniques (*7*). The other technique was to flow the reactor effluent through an infrared gas cell and measure the ammonia absorbance at 966.5 cm^{-1} with a grating infrared spectrophotometer (Perkin–Elmer Model 407). Both methods were calibrated and periodically checked for accuracy using a standard calibration gas of 146 ppm by volume ammonia in nitrogen (Matheson, certified standard).

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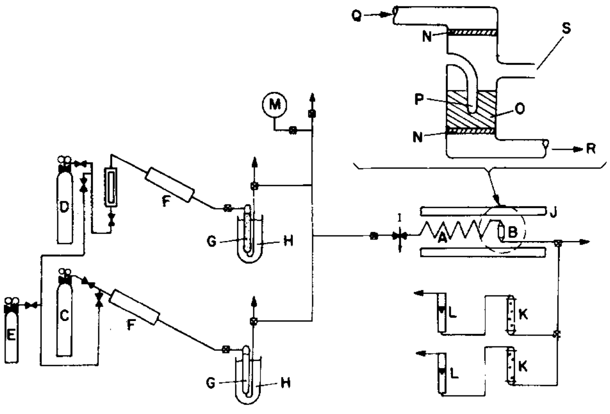

FIG. 1. Reactor system for ammonia synthesis studies; (A) Gas preheating coil, (B) catalytic reactor, (C) $H_2 : N_2$ gas mixture, (D) hydrogen, (E) helium, (F) Deoxo purifier, (G) 13X molecular sieve trap, (H) dry ice/acetone slush bath, (I) needle valve, (J) furnace, (K) gas scrubber, (L) bubble flowmeter, (M) pressure gauge. Reactor detail: (N) Vycor frit, (O) catalyst bed, (P) thermocouple well, (Q) inlet, (R) outlet, (S) unsealed sample port.

For the conditions used in the present study, the equilibrium ammonia partial pressure varies from 318 Pa (at 691 K) to 1910 Pa (at 574 K). The maximum fraction of equilibrium conversion obtained in this study was 15%, and it is therefore possible to neglect the effect of the reverse reaction to within a negligible 2% error (*8*, *9*). Indeed, typical fractions of equilibrium conversion were of the order of 10%, and as such the measured synthesis kinetics should be comparable to those observed by Ozaki *et al.* The influence of back-diffusion could be neglected in view of the fact that the ratio of the bed height to the catalyst support grain size was approximately 300 (*9*, *10*). This permits the reactor to be adequately modeled as a plug-flow reactor. With regard to the criteria presented by Mears (*11*, *12*) for freedom from transport limitations, calculations indicated that the reactor would be free from intraparticle, interparticle, and interphase transport limitations. A diagnostic test of the type described by Koros and Nowak (*13*) was conducted using $RuCl_3/SiO_2$ with the result that mass transfer limitations were not present.

The relation between the partial pressure of ammonia in the reactor effluent and the reciprocal of the volumetric flow rate (v_0) is shown in Figs. 2 and 3 for each of the catalysts. Because the overall ammonia synthesis rate, r', is determined from the product of the ammonia partial pressure in

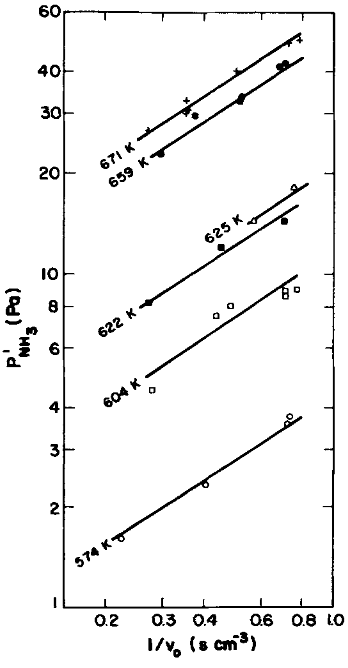

FIG. 2. Effluent ammonia partial pressure dependence on reciprocal volumetric flow rate (0.098 MPa, 298 K) for $RuCl_3/SiO_2$.

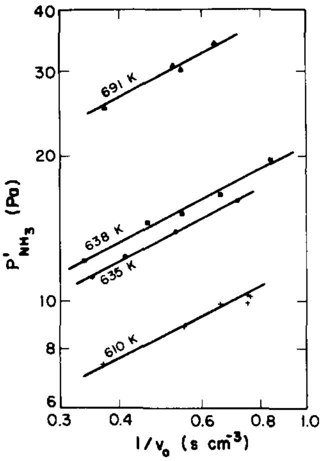

FIG. 3. Effluent ammonia partial pressure dependence on reciprocal volumetric flow rate (0.098 MPa, 298 K) for $RuCl_3/\gamma\text{-}Al_2O_3$.

the reactor effluent and the volumetric flow rate measured at the system outlet conditions (0.098 MPa, 298 K), it is apparent that

$$P'_{NH_3} \propto r' \cdot \left(\frac{1}{v_0}\right).$$

If r' were, in fact, independent of the ammonia partial pressure, then logarithmic plots such as those in Figs. 2 and 3 should exhibit lines of slope equal to unity. Obviously, such is not the case for these particular catalysts, for which slopes of 0.64 and 0.50 have been determined for the $RuCl_3/SiO_2$ and $RuCl_3/\gamma\text{-}Al_2O_3$ catalysts, respectively.

The nature of the synthesis rate dependence on the ammonia partial pressure is illustrated in Figs. 4 and 5. Here the dependence of the ammonia synthesis rate, expressed as the turnover frequency N (NH_3 molecules produced in one second per surface Ru atom), is depicted as a function of the partial pressure of ammonia in the reactor effluent. The ruthenium surface areas needed for turnover frequency calculations were determined using hydrogen adsorption, as described by Dalla Betta (*14*), and the corresponding ruthenium dispersions for the silica- and alumina-supported catalysts are given in the upper half of Table 1. Again, if the ammonia synthesis rate were truly independent of ammonia partial pressure, then the anticipated slope of the lines in Figs. 4 and 5 would be zero. In fact, the measured slopes are −0.56 for the $RuCl_3/SiO_2$ catalyst and −1.0 for the $RuCl_3/\gamma\text{-}Al_2O_3$ catalyst, indicating an inhibiting effect of ammonia on the overall synthesis rate.

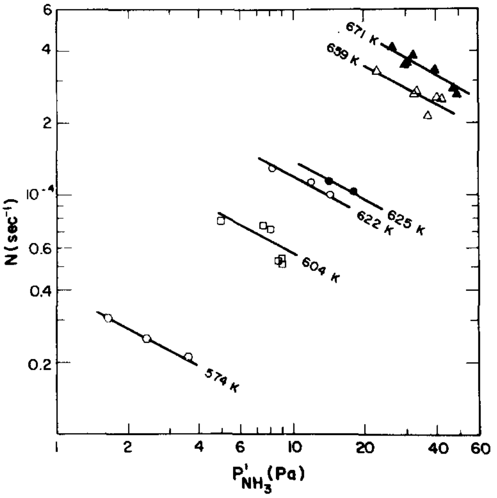

FIG. 4. Turnover frequency versus effluent ammonia partial pressure for $RuCl_3/SiO_2$.

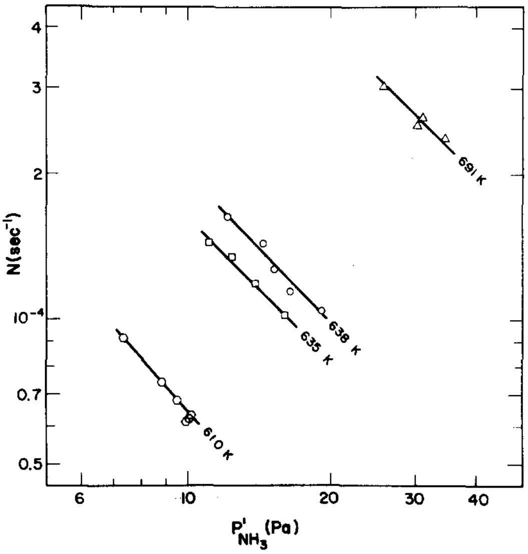

FIG. 5. Turnover frequency versus effluent ammonia partial pressure for $RuCl_3/\gamma\text{-}Al_2O_3$.

TABLE 1

Kinetic Parameters for Ruthenium Catalysts

Catalyst	Dispersion (%)	E_A (*kJ/mol*)	E_{CF} (*kJ/mol*)	m'	N ($s^{-1} \times 10^4$) at 673 K	P'_{NH_3} (Pa) for rate N
$RuCl_3/SiO_2$	46	134 ± 4	88 ± 4	0.28	12	4.2
$RuCl_3/\gamma\text{-}Al_2O_3$	37	100 ± 4	54 ± 4	0.50	1.0	46
$RuCl_3$/celite[a]	3[b]	—	94	—	1.7[b]	4.2[c]
Ru/Al_2O_3[a] (commercial)	27[b]	—	59	—	5.0[b]	46[c]

[a] Data from Aika *et al.* (*2*).

[b] Based on CO adsorption with an assumed stoichiometry of CO : Ru = 2.

[c] Calculated from flow rate and specific synthesis rate data at 79 kPa total pressure.

It is convenient to use the following expression for the overall rate of ammonia production, r', in terms of the ammonia partial pressure in the reactor effluent, P'_{NH_3}, an apparent rate constant k', and an apparent ammonia reaction order $-2m'$ (where the factor of 2 is retained for consistency with accepted ammonia synthesis kinetics over iron (*8*)):

$$r' = \frac{k'}{(P'_{NH_3})^{2m'}}.$$

(It may be noted that the total pressure as well as the hydrogen and nitrogen partial pressures were always held constant, and as such, they can be incorporated into k'.) In terms of this expression, the slopes in Figs. 2 and 3 are equal to $(2m' + 1)^{-1}$, and those slopes in Figs. 4 and 5 are equal to $-2m'$. The values of m' determined from these plots are given in the upper half of Table 1. In accord with the previous work (*2*), Arrhenius plots at a constant flow rate (1.3 $cm^3\ s^{-1}$ in this case) are shown in Fig. 6. In Table 1, the corresponding activation energies, E_{CF}, are presented and can be compared with those values reported by Ozaki *et al.* For both the silica- and alumina-supported catalysts, the constant flow rate activation energies are within 7% of the reported values. Furthermore, the turnover frequencies obtained in these two studies are quite compatible at the same partial pressures of ammonia (see Table 1). Thus, the results of the present study are in good agreement with those of Ozaki *et al.* with respect to turnover frequency and apparent activation energy at constant flow rate. However, the dependence of the synthesis rate on the ammonia partial pressure observed in the present study requires that apparent activation energy values such as these reflect *both* the temperature dependence of the rate parameters and the variation of the effluent ammonia partial pressure between experiments conducted at different temperatures but at the same flow rate. As a different approach to the apparent temperature dependence of the ammonia synthesis rate, Arrhenius plots at a constant ammonia partial pressure of 15 Pa are shown in Fig. 6, and the derived apparent activation energies (E_A) are also given in the upper half of Table 1. These values are independent of the constant ammonia partial pressure chosen for the construction of the Arrhenius plots. However, it should be mentioned that extrapolation of the data shown in Figs. 4 and 5 is required for such a treatment of the temperature dependence of the synthesis rate. The significance of such activation energy values will be described shortly.

The detailed rate expression for the synthesis of ammonia over supported ruthenium cannot yet be ascertained from the above data. It may be anticipated, for ex-

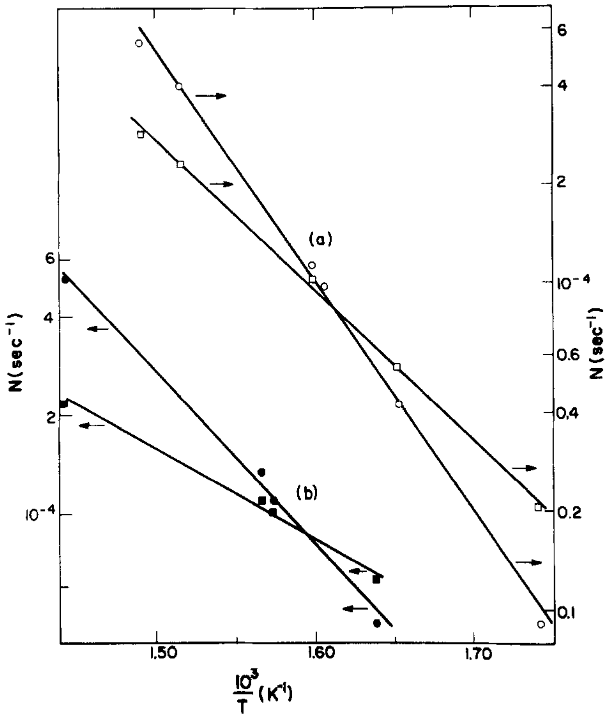

FIG. 6. Arrhenius plots for supported ruthenium catalysts: (a) $RuCl_3/SiO_2$ at constant ammonia pressure of 15 Pa (○) and at constant flow rate of 1.3 cm^3 s^{-1} (□). (b) $RuCl_3/\gamma\text{-}Al_2O_3$ at constant ammonia pressure of 15 Pa (●) and at constant flow rate of 1.3 cm^3 s^{-1} (■).

ample, that a general expression of the following form may be useful (*8*):

$$r = \frac{kF(P_{H_2},P_{N_2})}{[1 + KG(P_{H_2},P_{N_2}) \cdot P_{NH_3}]^{2m}},$$

where r is the synthesis rate at a given temperature and partial pressures of H_2, N_2, and NH_3; $F(P_{H_2},P_{N_2})$ and $G(P_{H_2},P_{N_2})$ are functions of the hydrogen and nitrogen pressures; m is an exponent with a value between 0 and 1; and k and K are rate and equilibrium constants, respectively. For a plug-flow reactor, the experimentally accessible overall synthesis rate, r', and effluent ammonia partial pressure, P'_{NH_3}, would be related by the expression

$$r' = (2m + 1)kF(P_{H_2},P_{N_2}) \frac{KG(P_{H_2},P_{N_2}) \cdot P'_{NH_3}}{[1 + KG(P_{H_2},P_{N_2}) \cdot P'_{NH_3}]^{2m+1} - 1}.$$

It was noted earlier that a simple expression of the form

$$r' = \frac{k'}{(P_{NH_3})^{2m'}}$$

was adequate to fit the experimental kinetic data with m' being constant for a given catalyst. It may be tentatively suggested that this implies that the term $KG(P_{H_2},P_{N_2}) \cdot P'_{NH_3}$ is significantly greater than unity for our experimental conditions. Indeed, if this term is substantially much greater than one, then the apparent activation energy at constant ammonia partial pressure (E_A) assumes the physical significance

$$E_A = E - 2m\Delta H,$$

where E and ΔH are activation energy and heat of adsorption terms that reflect the temperature dependence of k and K, respectively.

In summary, our studies of unpromoted ruthenium supported on silica gel and γ-alumina have yielded ammonia synthesis turnover frequencies and apparent activation energies at constant flow rate that are in good agreement with the results of Ozaki *et al.* However, the present study has also shown that the rate of ammonia synthesis does indeed exhibit an ammonia dependence in the same range of ammonia pressures studied previously by Ozaki *et al.* Correspondingly, apparent activation energies calculated at constant ammonia pressure are greater than those determined at constant flow rate. Although the detailed form of the synthesis rate expression is not yet known, the importance of the ammonia partial pressure in the reaction kinetics over supported ruthenium must be considered.

ACKNOWLEDGMENTS

We would like to thank Ralph Butz for his technical assistance and Carl R. F. Lund for his aid in determining the Ru surface areas. For their financial support of this study, we would like to thank Haldor Topsøe A/S. Finally, acknowledgement is made to the National Science Foundation for providing a Graduate Fellowship to one of us (W.K.S.).

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Received June 11, 1979