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The Synthesis of HCN in a Solid Electrolyte Cell

Two synthesis processes account for most of the HCN produced today. The first is based on the classical technology developed by Andrussow according to which methane, ammonia, and air react over platinum based catalysts at 950–1050°C:

$$CH_4 + NH_3 + \tfrac{3}{2} O_2 \rightarrow HCN + 3\,H_2O \qquad \Delta H^\circ = -113 \text{ Kcal/mol.} \quad (1)$$

The second method is the strongly endothermic Degussa process according to which CH_4 and NH_3 react in absence of air, at 1100–1150°C:

$$CH_4 + NH_3 \rightarrow HCN + 3\,H_2 \qquad \Delta H^\circ = +60 \text{ Kcal/mol.} \quad (2)$$

The Andrussow process offers the big advantage of being energy sufficient, that is, the reaction is carried out adiabatically at the desired temperature. Thus, despite the low HCN content (≈8%) in the off-gas stream, the larger number of by-products, and the large recovery equipment to accommodate the gas volume, it is the dominant route to HCN today (*1*).

The energy requirement of the HCN system, as well as the role of oxygen in the overall reaction scheme, led to the interest in running this reaction in an O^{2-} conducting solid electrolyte cell reactor. In this process, the anode of the cell is exposed to a CH_4–NH_3 mixture and the cathode is exposed to air. Oxygen of the air is transported in the form of O^{2-} through the solid electrolyte wall and reaches the anode where it reacts with the fuel to produce HCN. Simultaneously part of the reaction free energy is converted to electricity. The feasibility of this process has already been demonstrated (*2*). In the present communication the kinetics of the HCN synthesis in an yttria stabilized zirconia (YSZ) cell are presented. The role of O^{2-} is compared to that of gaseous oxygen under reaction conditions.

The reactor cell configuration is shown in Fig. 1. It consisted of an YSZ tube of 16-mm ID, 19.5-mm OD, open at both ends and enclosed in a 22-mm ID, 25-mm OD quartz tube. The CH_4–NH_3 mixture was flowing in the annulus between the YSZ and the quartz tube. The anode (catalyst) was prepared by applying Engelhard A3786 Pt ink on the outside surface of the YSZ tube, followed by air drying at 90°C for 1 h and calcining for ½ h at 850°C with a temperature increase rate of 200°C/h. The procedure was repeated three times to achieve an electrode resistance of less than 0.30 Ohms. The catalyst ring on the YSZ surface was about 1 cm long. A similar Pt film, but 3–4 times longer, was deposited on the inside surface of the YSZ and served as a cathode. The cell was located in a furnace (length of heating elements ≈ 18 cm) where the temperature was controlled within 2–3°C. Reactants and products were analyzed by on-line gas chromatography. Currents were imposed by means of an externally connected galvanostat. Additional information on the experimental apparatus can be found elsewhere (*2, 3*).

A freshly made catalyst was inactive to HCN formation upon exposure to CH_4–NH_3 mixtures. It takes 60–80 h exposure to a 20.5% CH_4–8% NH_3, balance He mixture in order for the rates of HCN and N_2 production to reach a steady state value (*3*). After this initial activation period the Pt film maintained its reactivity for more than 1000 h of open-circuit operation. Scanning electron microscopy showed that this activation period is associated with structural rearrangements of the anodic electrode, resulting in a skeleton-type porous film with average pore size of 2–3 μm (*3*).

The reaction of HCN synthesis was studied at temperatures 750–1000°C and atmo-

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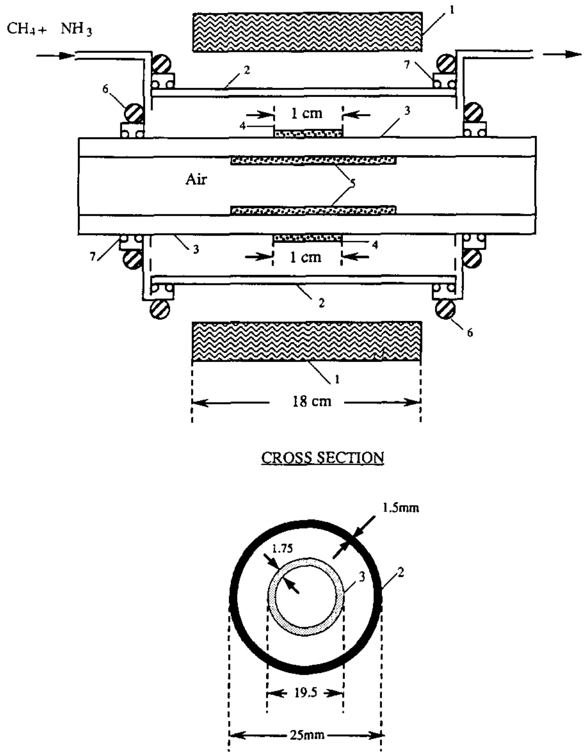

FIG. 1. Reactor cell configuration: (1) Heating element, (2) Quartz tube, (3) Zirconia tube, (4) Pt catalyst-anode, (5) Pt-cathode, (6) Cooling coils, (7) O-rings.

spheric total pressure. In addition to unreacted CH_4 or NH_3, the compounds identified in the effluent stream were HCN, CO, H_2, H_2O, CO_2, N_2, and N_2O. Oxygen was totally consumed in all catalytic experiments.

The contribution of noncatalytic gas-phase reactions was first investigated by using a reactor identical to that shown in Fig. 1 but without depositing catalyst on the outside YSZ surface. The effective reactor volume was 12 cm^3. At 760°C, reaction rates in the "blank" reactor did not exceed 15% of the global (catalytic plus noncatalytic) rate. No HCN or CO were found at this temperature in the "blank" reactor. At 960°C, HCN and CO did form noncatalytically, accounting typically for about 5% of their corresponding global rates. The noncatalytic consumption of ammonia typically accounted for about 30% of the global rate at 960°C. In presence of oxygen, only trace amounts of HCN were detected at 960°C.

The reaction kinetics on platinum were studied under both open-circuit and closed-circuit operation. Under open-circuit (zero current) oxygen was introduced in the gas phase together with CH_4 and NH_3. Figure 2 shows the rate of HCN formation as a function of the product of the partial pressures of the reactants in presence and in absence of oxygen. It can be seen that neither electrochemical nor gaseous oxygen affect significantly the HCN rate, which is essentially determined by the partial pressures of CH_4 and NH_3 in the reactor. As such, the outlet partial pressures of either reactant were taken, since it was shown that the mixing characteristics of the cell resemble those of a CSTR (*3*). Hydrogen cyanide follows a first order dependence with respect to both reactants. The data in presence of oxygen

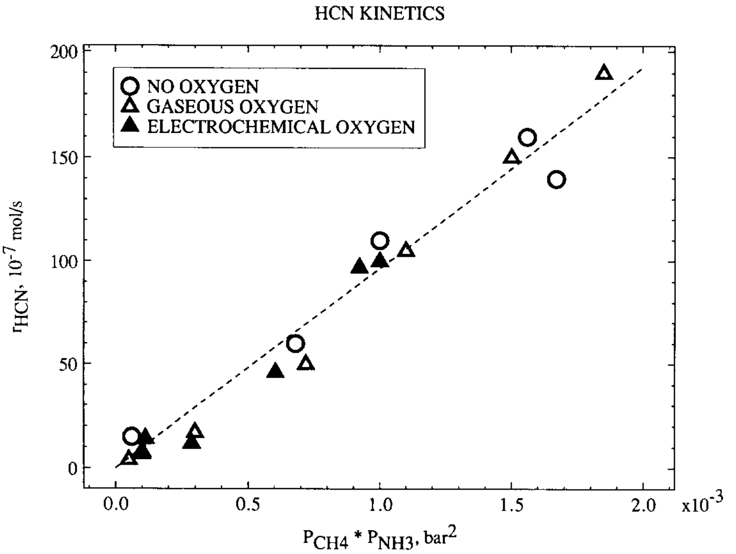

FIG. 2. Kinetics of HCN synthesis in the cell reactor in absence and in presence of gaseous or electrochemical oxygen; open symbols: gaseous oxygen, filled symbols: electrochemical oxygen; G_{O2i} = 26 × 10^{-7} mol/s.

(either electrochemical or gaseous) in Fig. 2 correspond to an oxygen inlet of about 2.6 × 10^{-6} mol/s of O_2. This value corresponds to a current density of 160 mA/cm^2 for the case of electrochemical oxygen. Higher electrochemical oxygen inlets were limited by the thickness of the employed electrolyte (1.8 mm). Data for intermediate values of current density fall very close to the line of Fig. 2 and are not shown for clarity. In all runs, essentially ohmic resistance polarization was observed with the electrolyte resistance dominating (*3*), in agreement with other studies with comparable electrolyte thickness (*4*).

Carbon monoxide and water were the primary oxidation products in both cases (gaseous or electrochemical oxygen) and this is shown in Fig. 3. Carbon dioxide was observed only at high O_2 and at rates one order of magnitude less than those of CO. There was no NO detected in any experiment and only in rare occasions (low CH_4/NH_3 ratios, high O_2) N_2O was formed. Figure 3 shows that insignificant differences are observed between open- and closed-circuit rates for all CH_4/NH_3 ratios above 0.1. In fact, under these conditions, carbon monoxide is, generally, favored over water which starts being produced only at higher oxygen inlets. Maximum water rates correspond to only about 30% of the carbon monoxide rates under these conditions. Water is enhanced at low CH_4/NH_3 ratios (high NH_3 contents) where its rate becomes comparable to the CO rate. In addition, a slight difference between gaseous and electrochemical oxygen is manifested under these conditions and high oxygen inlets, where it seems that electrochemical oxygen enhances H_2O in the expense of CO to a greater extent than gaseous oxygen does. This is shown more clearly in Fig. 4 where the rates of CO and H_2O are plotted as a function of the NH_3/CH_4 inlet ratio. The data correspond to an oxygen inlet of 2.6 × 10^{-6} mol/s and were taken from Fig. 3. Finally, oxygen did not affect significantly the nitrogen formation rate either under open- or closed-circuit conditions at this temperature (960°C).

Several investigators have studied the reaction of HCN synthesis in presence and in

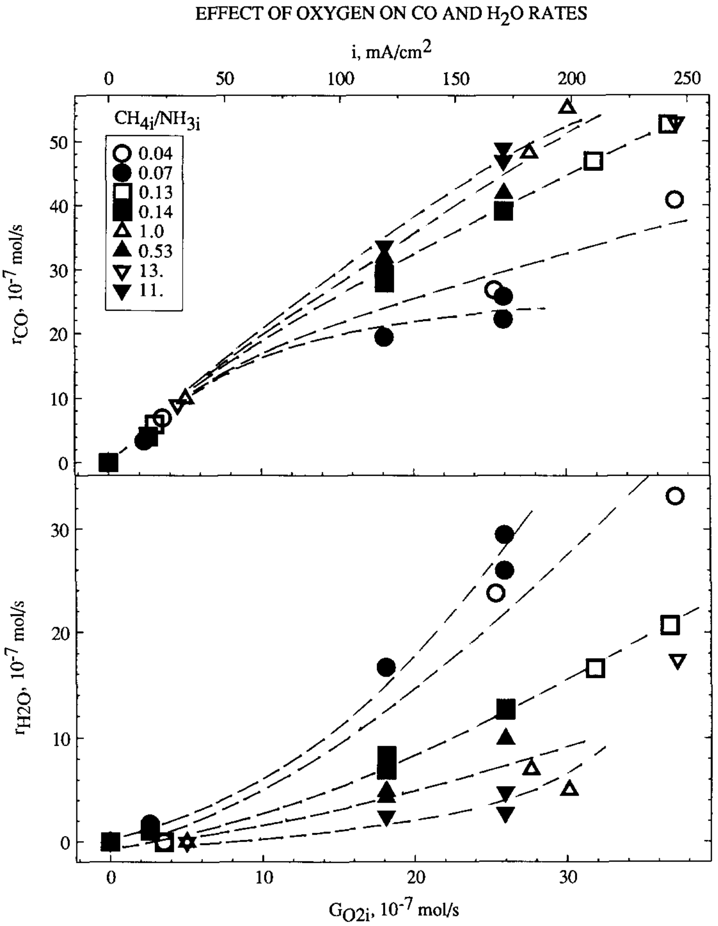

FIG. 3. Effect of gaseous or electrochemical oxygen on the formation rates of CO and H_2O open symbols: gaseous oxygen, filled symbols: electrochemical oxygen.

absence of oxygen (*5–10*). The most thorough study was done recently by Hasenberg and Schmidt (*8–10*) on Pt and Rh catalysts. The two catalysts exhibited similar behavior. It is suggested that HCN is formed by the interaction of carbon containing species CH_x with nitrogen containing species NH_y, while nitrogen is formed by the interaction of two NH_y species. Depending on the extent of carbon adsorption and on its own surface coverage, oxygen can either enhance or decrease the HCN production rate (*10*). Waletzko and Schmidt (*1*) prepared a model that simulated the performance of industrial reactors using kinetic data for 13 unimolecular and bimolecular reactions. Despite the complexity of the problem and the many sources of experimental data used, the model predictions are in very good agreement with either the Degussa or Andrussow reactors.

The present kinetic observations seem to be in agreement with the kinetic model derived by Hasenberg and Schmidt in Ref. (*8*, *9*). Specifically, the rate dependence on CH_4 and NH_3 is the same as in Refs. (*8*, *9*) assuming insignificant reactant inhibition for the present experiments. Furthermore, for most of the experimental conditions examined the apparent temperature dependence of the

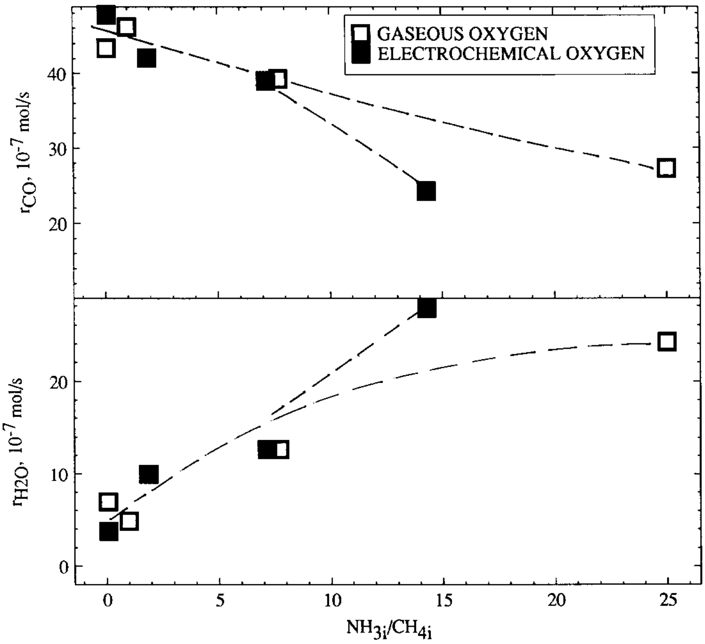

FIG. 4. Effect of gaseous composition on the formation rates of CO and H_2O for $G_{O2i} = 26 \times 10^{-7}$ mol/s; open symbols: gaseous oxygen, filled symbols: electrochemical oxygen.

HCN formation rate was found to be within 10% of that implied by the model of the above references.

The fact that CO is favored over H_2O (Fig. 3) indicates that under most conditions, the coverage of carbon species is higher than that of nitrogen species, in agreement with the observations of Hasenberg and Schmidt (*10*). The only differences found in the present study are the relatively lower selectivities (selectivity defined as moles of HCN produced/mole of NH_3 consumed) and the absence of NO in the effluent stream. To a large extent, these differences can be explained if one takes into account that the YSZ cell operated (*3*) at high conversions (conversions of CH_4 and NH_3 were typically 25–30% and 55–65%, respectively). In a high conversion reactor, NO may be formed but quickly undergo reactions with carbon or oxygen containing species to form CO, HCN, or N_2 so that it is not detected at measurable amounts in the off-gas stream. In addition, noncatalytic gas phase reactions, which are much less selective to HCN, contributed significantly in the overall conversion of NH_3, especially at temperatures higher than 800°C (*3*).

Finally, as Figs. 2 and 3 indicate, gaseous oxygen and electrochemical oxygen appear to affect rates in the same manner for a wide range of CH_4/NH_3 ratios. A slight difference exists only for very low CH_4/NH_3 ratios (<0.07) where electrochemical oxygen seems to favor H_2O in expense of CO, while the opposite is true for gaseous oxygen. A possible explanation can be found in the homogeneous reactions that O_2 can undergo as opposed to O^{2-}, which is consumed on the surface and does not appear in the gas phase. Thus, it was found (*3*) that under these conditions, gaseous oxygen is significantly consumed through noncatalytic reaction with NH_3. Both NH_3 and O_2, however, regulate the extent of carbon layer on the Pt surface. Therefore, it seems that relatively higher carbon coverages are maintained when gaseous oxygen is used and CO is slightly favored over H_2O. This is evident only at higher oxygen inlets where noncatalytic reactions are enhanced to a larger extent (*3*).

In summary, the present study showed that the HCN synthesis can be carried out in an oxygen ion conducting solid electrolyte cell with oxygen electrochemically introduced into the reacting mixture. In the present study the O^{2-} flux was limited by the resistance of the solid electrolyte. Higher fluxes can be attained by decreasing the YSZ wall thickness (*2*). Hence, the construction of thin-wall (40 μm) zirconia cells will be a crucial forward step in the development of a reactor that could combine advantages of both the Andrussow and Degussa processes.

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REFERENCES

1. Waletzko, N., and Schmidt, L. D., *AIChE J.* **34,** 1146 (1988).
2. Kiratzis, N., and Stoukides, M., *J. Electrochem. Soc.* **134,** 1925 (1987).
3. Kiratzis, N. E., Ph.D. Thesis, Tufts University (1990).
4. Farr, R. D., and Vayenas, C. G., *J. Electrochem. Soc.* **127,** 1478 (1980).
5. Pan, B. Y. K., *J. Catal.* **21,** 27 (1971).
6. Pan, B. Y. K., and Roth, R. G., *Ind. Eng. Chem. Proc. Des. Dev.* **7,** 53 (1968).
7. Koberstein, E., *Ind. Eng. Chem. Proc. Des. Dev.* **12,** 44 (1973).
8. Hasenberg, D., and Schmidt, L. D., *J. Catal.* **91,** 116 (1985).
9. Hasenberg, D., and Schmidt, L. D., *J. Catal.* **97,** 156 (1986).
10. Hasenberg, D., and Schmidt, L. D., *J. Catal.* **104,** 441 (1987).

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