Catalytic Hydrolysis of HCN over H-Ferrierite

Tetsuya Nanba,* Akira Obuchi, Somchai Akaratiwa, Shetian Liu, Junko Uchisawa, and Satoshi Kushiyama
Atmospheric Environmental Protection Department, National Institute for Resources and Environment
16-3 Onogawa, Tsukuba, Ibaraki, 305-8569

(Received May 24, 2000; CL-000503)

The decomposition of HCN over H-ferrierite below 670 K proceeded mainly by hydrolysis to NH_3 and CO. In the presence of NO and NO_2, NH_3 formed further reacted to form N_2 and N_2O.

The selective catalytic reduction of NO*x* with hydrocarbons (HC-SCR) has attracted the attention of many catalyst researchers over the past decade.[1] Although many studies have investigated the reaction steps and the intermediates thought to be involved in this process, the reaction mechanisms are still not fully understood. Several research groups have observed nitrogen-containing by-products such as HCN,[2,3] HNCO,[4] and acrylonitrile[5] and suggested that they may be intermediates in the HC-SCR process. In this study, we focused our interest on HCN and investigated its decomposition behavior over H-ferrierite, which was reported to be a good catalyst for HC-SCR,[6] and the role for N_2 and N_2O formation in HC-SCR.

About 30 mg of H-ferrierite (Tosoh; HSZ-720HOA, SiO_2/Al_2O_3= 17.0) was wash-coated onto a small piece of cylindrical cordierite honeycomb (8 mmϕ, 9 mm length; 400 cell $inch^{-2}$), and the catalytic reactions were carried out under conventional flow reactor conditions with a flow rate of 160 mL min^{-1}.[7] HCN was continuously generated by the reaction between KCN and H_2SO_4 and was added to the reactant gas. HCN concentration was 220–300 ppm. The N_2, N_2O, CO, and CO_2 produced were analyzed with GC, and other gaseous products were analyzed with an FTIR (Nicolet; Magna 560, resolution set at 0.5 cm^{-1}) equipped with a multi-reflection gas cell (Gemini Specialty Optics; Mercury Series, optical path length = 2 m).

Figure 1 shows the decomposition behavior of HCN in the presence of various co-existing gases. NO*x* (= NO + NO_2) conversion in figures 1(c) and 1(d) was defined as (NO*x* inlet concn(ppm) – NO*x* outlet concn (ppm))/(HCN inlet concn (ppm)) × 100. Product yield was defined as (product concn

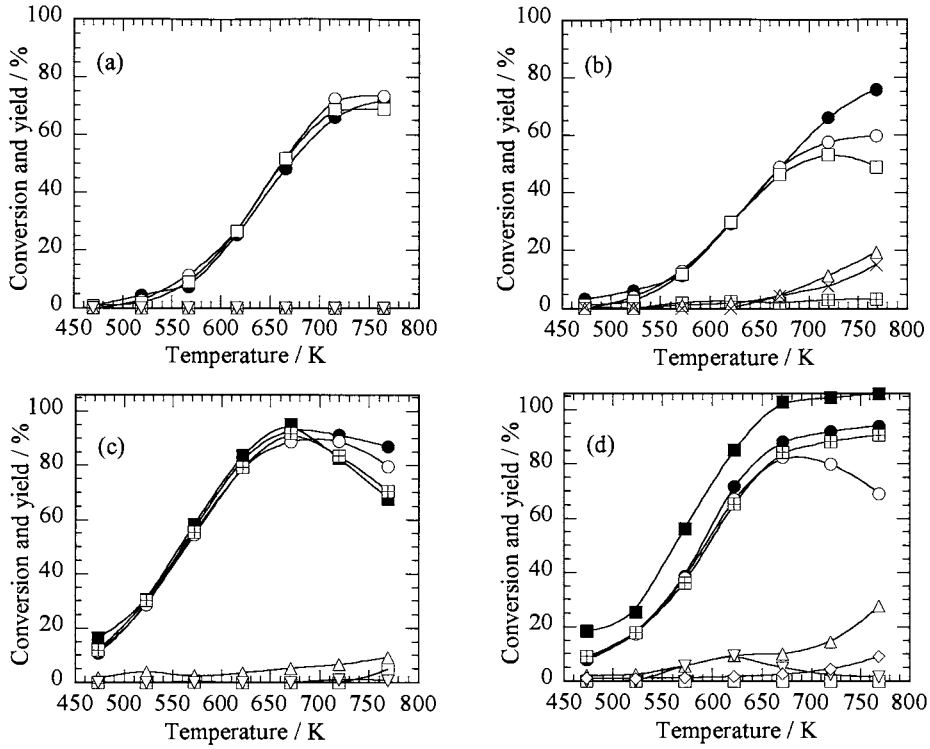

Figure 1. Temperature dependence of HCN decompostion under various feed gases. Feed gas was composed of (a) 220-240 ppm HCN + 2000 ppm H_2O, (b) 230-260 ppm HCN + 2000 ppm H_2O + 5% O_2, (c) 240-280 ppm HCN + 2000 ppm H_2O + 5% O_2 + 1000 ppm NO, and (d) 260-300 ppm HCN + 2000 ppm H_2O + 5% O_2 + 1000 ppm NO_2. Symbols indicate HCN (●) and NOx conversion (■), and yields of CO (○), NH_3 (□), N_2 (⊞), CO_2 (△), N_2O (▽), HNCO (◇), and NO (×).

(ppm))/(HCN inlet concn (ppm)) × 100. As shown in Figure 1(a), HCN decomposed into equivalent amounts of NH_3 and CO in the presence of H_2O vapor. Evidently, hydrolysis occurred according to the reaction:

$$HCN + H_2O \rightarrow NH_3 + CO$$

HCN conversion increased with increasing temperature. Since equivalent amounts of NH_3 and CO were also produced under O_2 + H_2O flow below 670 K (Figure 1(b)), it is clear that HCN was preferentially hydrolyzed under these conditions. Above 670 K, small amounts of NO and CO_2 were detected. Since the decomposition of NH_3 or CO was negligible under similar conditions, we speculate the NO and CO_2 to be formed by the oxidation of HCN. Figures 1(c) and (d) show HCN decomposition behavior in the presence of NO + O_2 + H_2O and NO_2 + O_2 + H_2O, respectively. HCN conversions increased, compared to the results obtained in the absence of NO or NO_2. However, CO yields were almost equal to HCN conversions below 670 K. On the other hand, NH_3 was not formed at all; instead, N_2 was formed in amounts equal to the amount of HCN converted. Moreover, NO*x* conversion in figure 1(c) was very close to N_2 yield. These results strongly suggest that one NO molecule reacts with one NH_3 molecule produced by HCN hydrolysis to give one N_2 molecule. In figure 1(d), NO*x* conversion was apparently higher than HCN conversion and N_2 yield but it was due to the formation of HNO_3 and HNO_2. In the presence of NO_2, HNCO was formed at high temperatures, probably due to the oxidation of HCN by NO_2, and N_2O was formed with the maximum yield at 623 K, presumably as a product of the reaction between NO_2 and NH_3. The increase in the HCN conversion in the presence of NO*x* is discussed below.

Figure 2 shows the selectivities of N_2 and N_2O in the NH_3 + NO + NO_2 + O_2 reaction at 623 K with a varying ratio of NO and NO_2 in the reactant gas (total NO*x* = 1000 ppm). Under all conditions, NH_3 was completely converted into N_2 or N_2O. N_2O formation was observed particularly in the presence of much more NO_2 than NO. It is evident from these results that NH_3 reacts rapidly on H-ferrierite with both NO and NO_2 to produce N_2 and N_2O. Also, it is strongly suggested that self-poisoning by the NH_3 formed was suppressed due to the reaction between NH_3 and NO*x*, so that HCN hydrolysis, occurring most probably on acid sites, was enhanced in the presence of NO*x*.

In conclusion, below 670 K the decomposition of HCN over H-ferrierite proceeds preferentially through hydrolysis, which results in the formation of NH_3 and CO. In the presence of NO or NO_2, the NH_3 formed reacts further with NO*x* to form N_2 and N_2O, with N_2O produced only in the presence of much more NO_2 than NO. We separately performed selective reduction of NO_2 (1000 ppm) with C_2H_4 (1000 ppm) in the presence of O_2 (5%) over the same H-ferrierite, and observed the production of 76, 106, and 51 ppm HCN at 523, 623, and 723 K, respectively. Taking account of the high reactivity toward hydrolysis, HCN observed in the HC-SCR process may not be a simple by-product but may be one of the intermediates toward N_2 and N_2O. The mechanism of HCN formation in HC-SCR is under investigation and will be reported elsewhere.

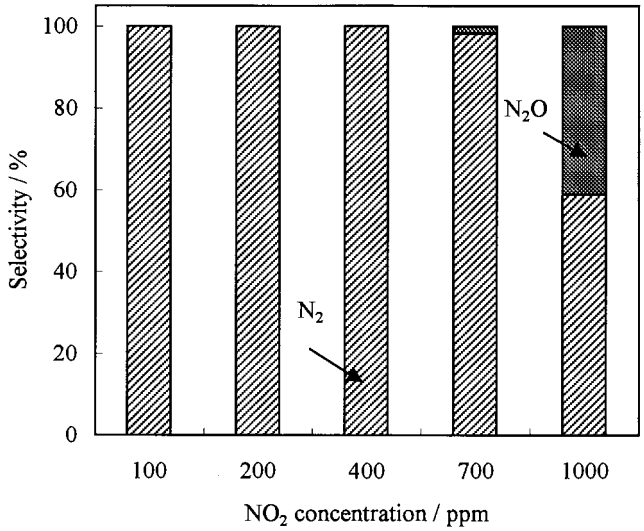

Figure 2. Products of the NH_3 and NOx reaction at 623K. Feed gas was composed of 200 ppm NH_3, 1000 ppm NO+NO_2, and 5% O_2. Total flow rate was 160 ml min^{-1}.

References

1 V. I. Pârvulescu, P. Grange, and B. Delmon, *Catal. Today*, **46**, 233 (1998).
2 F. Radtke, R. A. Koeppel, and A. Baiker., *Appl. Catal., A*, **107**, L125 (1994).
3 I. O.Y. Liu, N. W. Cant, M. Kögel, and T. Turek, *Catal. Lett.*, **63**, 241 (1999).
4 Y. Ukisu, S. Sato, G. Muramatsu, and K. Yoshida, *Catal. Lett.*, **11**, 177 (1991).
5 T. Gerlach, U. Illgen, M. Bartoszek, and M. Baerns, *Appl. Catal., B*, **22**, 269 (1999).
6 K. Yogo, M. Umeno, H, Watanabe, and E, Kikuchi, *Catal. Lett.*, **19**, 131 (1993)
7 A. Obuchi, I. Kaneko, J. Oi-Uchisawa, A. Ohi, A. Ogata, G. R. Bamwenda, and S. Kushiyama, *Appl. Catal., B*, **19**, 127 (1998).