Formation of HNCO during Catalytic Reduction of NO_x with Olefins over Cu/ZSM-5

Frank Radtke, René A. Koeppel and Alfons Baiker*

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

Gaseous cyanic acid (HNCO) is formed in the temperature range 513–666 K during the selective catalytic reduction of NO_x with olefins (ethene, propene) over Cu/ZSM-5 under dry conditions, whereas with ammonia no HNCO is observed in the presence of water in the same temperature range; other by-products are hydrogen cyanide, formaldehyde, ethene (with propene as reducing agent), methane and 2-methylpent-1-ene.

The problem of large NO_x emissions originating from human activities has fostered studies aiming at the removal of these harmful gases from exhausts.[1,2] The selective catalytic reduction by NH_3 is still the most efficient technique for the removal of NO_x from the exhausts of stationary combustion sources. However, the use of NH_3 as a reducing agent is not suitable for applications in mobile combustion sources, such as lean burn engines. This has initiated the search for catalysts which will reduce NO_x in the presence of hydrocarbons. There is currently considerable interest in the use of copper and cobalt containing zeolite catalysts for this reaction.[3] Recently, Yokoyama and Misono[4] found a loss in the nitrogen, carbon and oxygen balances for the selective catalytic reduction of NO_x with propene over Ce/ZSM-5. The ratio of N : C : O in the loss was approximately 1 : 1 : 1 and the authors proposed that this 'undetected' component could be HNCO. Hayes *et al.*[5] reported the formation of aliphatic cyanide species for the same reaction using Cu/ZSM-5. Here we report the identification of HNCO and further by-products during the selective catalytic reduction of NO_x by olefins over a Cu/ZSM-5 catalyst. The presence of water in the exhaust gas is shown to influence strongly the formation of HNCO and other undesired products.

The Cu/ZSM-5 catalyst was prepared by a standard ion-exchange method[6] from Na/ZSM-5 (Si : Al = 22 : 1; Chemie Uetikon). The copper loading of the catalyst, as determined by atomic adsorption spectroscopy, was 2.60 *%m/m*. With this catalyst, the copper is assumed to exist as isolated ions or in small clusters dispersed throughout the bulk of the zeolite. BET surface area measurements of the precursor Na/ZSM-5 and the ion-exchanged catalyst indicated that the ion exchange did not lead to a significant change of the surface area, which amounted to 373 $m^2 g^{-1}$ for both samples. Catalytic tests were conducted using the simulated exhaust gas compositions presented in Table 1. Before measuring the catalytic activity, the catalyst (250 mg, 42–80 mesh) was pretreated at 873 K with 5% O_2 in nitrogen (150 ml min^{-1}) for 2 h and then cooled to 473 K in nitrogen. The temperature dependence of the catalytic behaviour was measured by raising the temperature in steps of 50 K from 473 to 873 K. At each temperature step, two absorbance spectra were recorded, using an FTIR spectrometer (Bruker IFS 66) with a heatable gas cell (100 ml volume gas cell; Infrared Analysis Inc.) and an MCT detector for gas analysis at the reactor inlet and outlet, respectively. A U-tube quartz glass reactor (i.d. 6 mm) was used and the total flow of simulated exhaust gas was 150 ml min^{-1} (W/F = 0.1 g s ml^{-1}).

Results of the catalytic behaviour of the Cu/ZSM-5 catalyst employed in this study have been reported earlier.[6] Regarding the formation of gaseous products other than CO_2, H_2O and N_2, an unknown compound was detected in the temperature range 513–666 K in the absence of water (feeds 1–4), possessing two characteristic bands at 2250 and 2283 cm^{-1} [Fig. 1(*a*) and (*b*)]. Maximal intensities of these bands were reached at 666 K with both reductants, but with ethene the intensity was considerably smaller. With 10% water in the feed (feeds 1w–4w), the bands disappeared and ammonia was formed in the same temperature range, with concentrations of up to 8 ppm at 666 K (feed 3w). The position of the bands and the concomitant disappearance of the unknown compound with the appearance of ammonia in the presence of water led us to conclude that the unknown component could be cyanic acid or an alkyl isocyanate. Alkyl isocyanates possess characteristic bands around 2250 cm^{-1}.[7] Furthermore, isocyanates have been reported to decompose rapidly to primary amines in the presence of water.[8] Consequently, in our experiments under wet conditions, ammonia

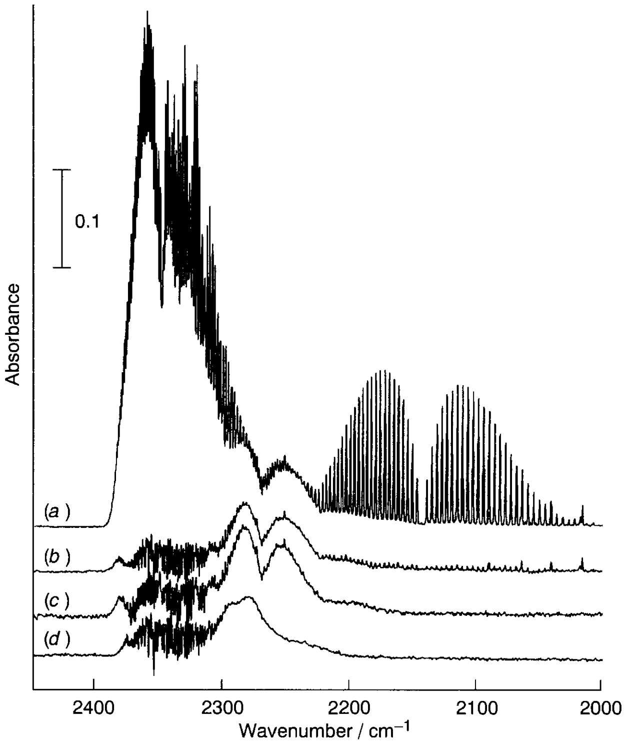

Fig. 1 (*a*) Spectrum of the effluent gas recorded at 665 K over Cu/ZSM-5 with feed 3; (*b*) spectrum (*a*) after subtraction of the spectra of carbon dioxide, carbon monoxide and nitrous oxide; (*c*) reference spectrum of cyanic acid; (*d*) reference spectrum of ethyl isocyanate.

Table 1 Simulated exhaust compositions (feed gas mixtures) employed in catalytic studies; balance nitrogen

Feed[a]	NO/ppm	NO_2/ppm	C_2H_4/ppm	C_3H_6/ppm	O_2 (%)	H_2O (%)
1 (1w)	980(940)	0	0	910(860)	2.0 (2.0)	0 (10)
2 (2w)	920(940)	0	1290(1260)	0	2.0 (2.0)	0 (10)
3 (3w)	0	970(940)	0	910(860)	1.9 (2.0)	0 (10)
4 (4w)	0	980(950)	1450(1270)	0	1.9 (2.0)	0 (10)

[a] Values in parentheses correspond to feeds containing 10% water, which are denoted with **w**.

Table 2 Selective catalytic reduction of NO$_x$ by olefins (ethene, propene) over Cu/ZSM-5. Temperature ranges (in K), where various products are observed under 'dry' and 'wet' conditions

Feed[a]	Cyanic acid	Ammonia	Hydrogen cyanide	Formaldehyde	Ethene	Methane
1	513–662	—	513–614	563–662	513–662	—
1w	—	663	614–663	563–663	614–712	712–856
2	669	—	469–669	569–669	—	669–717
2w	—	—	563–663	563–663	—	714–811
3	515–666	—	468–612	565–665	612–712	—
3w	—	566–666	470–666	470–666	566–666	666–857
4	665	—	512–665	469–665	—	—
4w	—	—	569–669	569–714	—	714–856

[a] Feed compositions are specified in Table 1.

could be formed by the hydrolysis of cyanic acid, whereas under dry conditions cyanic acid could be stable and detectable in the gas phase.

To prove this hypothesis, HNCO was prepared by thermal depolymerization of cyanuric acid according to a technique similar to that described by Herzberg and Reid.[9] HNCO was trapped in liquid nitrogen and the resulting liquid was decanted into an empty U-tube reactor, also cooled with liquid nitrogen, which was then connected to the apparatus. Absorbance spectra were recorded by passing nitrogen through the cooled reactor. The resulting spectrum [Fig. 1(*c*)] shows the same characteristic features as Fig. 1(*b*) with the minimum between the two bands centred at 2271 cm^{-1}. Herzberg and Reid[9] observed a minimum between the P and R maximum at 2274 cm^{-1} for gaseous HNCO. To compare the characteristic spectra of alkyl isocyanates and cyanic acid, the spectrum of ethyl isocyanate [Fig. 1(*d*)] was recorded. The result clearly shows that the detected bands of the unidentified component can be assigned to cyanic acid.

The maximal concentration of HNCO observed with propene (feed 3) was *ca.* 15 ppm, while up to 8 ppm ammonia were found with feed 3w under wet conditions. This finding indicates that the presence of water has only a slight influence on the sites active for the formation of surface bound NCO species, which under dry conditions desorb as HNCO, whereas ammonia is formed through hydrolysis under wet conditions.

Although bands were found from HNCO under dry conditions using ethene (feeds 2 and 4), no ammonia was detected using wet conditions (feeds 2w and 4w). This may be due to the higher detection limit for ammonia (8 ppm) when ethene is used.

In addition to the formation of cyanic acid and ammonia, other by-products such as hydrogen cyanide, formaldehyde, ethene (feeds 1/1w and 3/3w) and methane were identified in different temperature ranges, as listed in Table 2. With feeds 1 and 3 at low temperatures, Cu/ZSM-5 also catalyses alkylation reactions, producing a 2-methylalk-1-ene, (most probably 2-methylpent-1-ene, resulting from two propene molecules).[10] Raising the temperature favoured cracking reactions and ethene, formaldehyde, hydrogen cyanide[6] and cyanic acid were produced, together with the desired N_2, CO_2 and H_2O. Around 666 K, concentrations of formaldehyde (not quantified), ethene (92 ppm) and cyanic acid (15 ppm) reached their maxima, accompanied by the formation of significant amounts of further unidentified oxidation products. Morrow and Cody[11] claimed that HCN and C_2N_2 chemisorbed on silica as SiNC and SiCN can be converted to SiNCO after heating in oxygen. These findings allow us to suppose similar routes of formation for HNCO and HCN.

The present study adds another component to the understanding of the complex mechanism of the reduction of NO$_x$ by hydrocarbons, which is a prerequisite for the design of efficient catalysts for this reaction. The identification of surface and gas phase species is at the origin of this endeavour.

We thank Dr G. Kaefer from Asea Brown Boveri for his help in the quantitative analysis of HNCO. Financial support of this work by the Nationaler Energie-Forschungs-Fonds is gratefully acknowledged.

Received, 29th November 1994; Com. 4/07299E

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