

## Effect of Water Vapour in the Catalytic Destruction of Cyanogen Chloride

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The effect of water vapour on the catalytic destruction of cyanogen chloride (CNCl) over a commercial Pt/ $\alpha$ -alumina catalyst is to increase the overall conversion of CNCl, apparently by hydrolysis, providing a reaction path parallel to oxidation; the presence of water vapour also lowers the apparent activation energy for CNCl destruction, and the selectivity for CO formation is negligible in the presence of water vapour.

Catalytic oxidation is widely used to control low levels of organic compounds in air. It has been applied to industrial emissions,<sup>1</sup> volatile organic compounds<sup>2-4</sup> and military life-support systems.<sup>5</sup> For military applications, systems based on catalytic oxidation have certain advantages over carbon-based adsorbents, including longer mission life in hot and humid environments,<sup>6</sup> and the potential to control a wide range of chemical compounds.

In addition to the wide range of chemicals that a catalytic oxidation system must destroy, there are important differences between military use and conventional end-of-pipe environmental control systems. These include the extremely high levels of conversion required and deactivation. The US Army has initiated a programme to develop mathematical models of the catalytic oxidation of organic compounds containing heteroatoms. Work by Rossin and coworkers has examined the catalytic oxidation of diethyl sulfide,<sup>7</sup> di(*n*-propyl) sulfide<sup>8</sup> and chloroacetonitrile.<sup>9</sup> Also of interest is cyanogen chloride, CNCl, which is the subject of the present study.

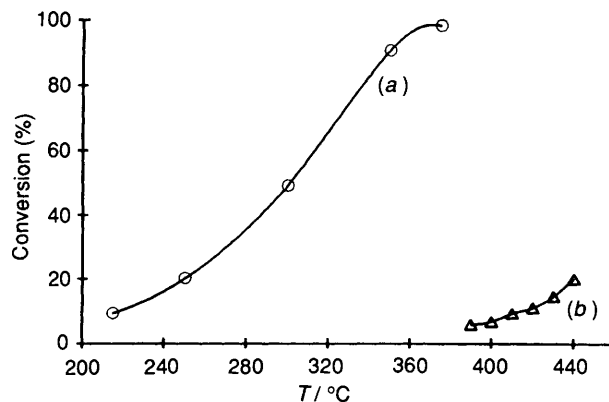
Little has been reported on the catalytic oxidation of cyanogen chloride. Lester and Marinangeli<sup>5</sup> examined its oxidation over a 'high Pt/chemically modified alumina' and Pt/titania catalyst, at 250, 150 and 75 °C at 5% relative humidity with 30 ppm CNCl in the inlet gas, and also at 90% relative humidity at 250 °C. For both catalysts oxidation was complete in 2 h at 250 and 150 °C, but not at 75 °C, at which temperature the alumina-supported catalyst was much less effective than that supported on titania. It was suggested that

both hydrolysis and oxidation could account for the destruction of the cyanogen chloride, but no systematic study was carried out. Subsequent patent literature<sup>10</sup> suggests that catalytic hydrolysis is an important mechanism for halocarbon destruction on this type of catalyst.

A systematic study of the role of hydrolysis on the catalyst activity and selectivity during CNCl destruction is presented here. A fixed bed laboratory scale quartz reactor (7 mm i.d.) was used, with a commercial 2.15% Pt/ $\alpha$ -alumina catalyst (60-80 mesh; 210  $\mu$ m average particle size; Engelhard Corporation, Iselin, NJ). The Brunauer-Emmett-Teller (BET) surface area of the catalyst was around 5 m<sup>2</sup> g<sup>-1</sup>. N<sub>2</sub> containing 2% CNCl was mixed with appropriate amounts of O<sub>2</sub> and CNCl-free N<sub>2</sub> to provide the desired gas composition. The oxygen concentration was 21% in all experiments, and both dry and humid feed streams were investigated. The humidified stream was prepared by passing CNCl-free N<sub>2</sub> through a water bubbler before mixing with the feed stream. A Hewlett Packard Model 5890 gas chromatograph equipped with TCD and FID was used to analyse CNCl, CO and CO<sub>2</sub>.

The oxidation of CNCl was negligible in the absence of catalyst (1.5% at 425 °C in dry stream, flow rate 100 cm<sup>3</sup> min<sup>-1</sup>; 3.6% at 400 °C, flow rate 200 cm<sup>3</sup> min<sup>-1</sup>, in humid stream, dew point 4 °C). The higher CNCl conversion in the humid stream suggests that the presence of water vapour aids CNCl destruction.

Fig. 1 shows the effect of temperature and humidity on CNCl conversion. The activity for CNCl oxidation in the dry stream was very low (20% conversion at 440 °C). The



**Fig. 1** Effect of temperature and humidity on catalytic conversion of cyanogen chloride over a platinum/ $\alpha$ -alumina catalyst. (a) 5200 ppm CNCl, 7800 ppm  $\text{H}_2\text{O}$ ,  $1.7 \times 10^5 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ ; (b) 5300 ppm CNCl,  $0.46 \times 10^{-5} \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ , dry stream.

conversion decreased with decrease in temperature to 5.8% at 390 °C. The addition of 7800 ppm water vapour to the feed stream resulted in a considerable increase in CNCl conversion: 9.3% at 215 °C to 98% at 375 °C. The conversion increased steadily with temperature at low temperatures, but levelled off above 360 °C. Higher CNCl conversion in the humid stream was observed even though the space velocity for the tests with the humid stream was roughly four times that with the dry stream. The presence of water vapour also changed the selectivity for oxidation products. While only  $\text{CO}_2$  was formed in the humid feed stream, both  $\text{CO}$  and  $\text{CO}_2$  were formed in the dry feed stream, with a selectivity for  $\text{CO}$  as high as 60%.

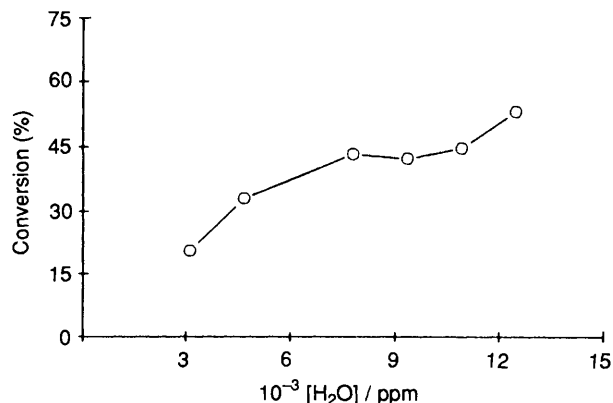
The water vapour also reduced the apparent activation energy for CNCl oxidation, which was  $23 \text{ kcal mol}^{-1}$  between 390 and 440 °C in the dry stream but only  $12 \text{ kcal mol}^{-2}$  between 185 and 215 °C in the humid stream ( $1 \text{ cal} = 4.184 \text{ J}$ ). A lower temperature range was used for the humid stream to maintain differential conditions (CNCl conversion <15%).

The reduction in the apparent activation energy in the humid stream by a factor of two suggests the presence of internal diffusion resistance, but the experiments were run under conditions that were free from internal and external diffusion resistance, as confirmed by conducting the oxidation in the humid stream with a smaller catalyst particle size, 114  $\mu\text{m}$ . CNCl conversion and the apparent activation energies were the same for both catalyst particle sizes. If the reaction was limited by internal diffusion resistance, the conversion would increase with decrease in particle size. Also, the activation energy of an internal diffusion controlled process is half that of a kinetically controlled process. The reaction could be pore-diffusion-controlled even at the smaller particle size (114  $\mu\text{m}$ ), but Weisz and Prater's intraparticle transport criteria<sup>11</sup> shows that the reaction is well within the intrinsic kinetic control regime.

The absence of external diffusion resistance was confirmed by conducting the CNCl destruction in a humid stream at different flow rates, but constant space velocity. The conversion and apparent activation energies did not change when the total gas flow was increased from 100 to 200  $\text{cm}^3 \text{ min}^{-1}$  at constant space velocity. If the reaction was limited by external diffusion resistance, the conversion would increase with increasing flow rate, at constant space velocity. Furthermore, the apparent activation energy for an external diffusion-controlled process would be close to zero. Thus, the reaction is free from internal and external diffusion resistances under these experimental conditions.

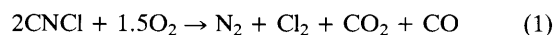
The effect of water vapour concentration on CNCl conversion was also examined (Fig. 2). The conversion increased from 20.5% at 3120 ppm  $\text{H}_2\text{O}$  (0 °C dew point) to 52.9% at 12 480 ppm  $\text{H}_2\text{O}$  (11 °C dew point).

Thus, the addition of water vapour to the feed results in



**Fig. 2** Effect of water vapour concentration on catalytic conversion of cyanogen chloride over a platinum/ $\alpha$ -alumina catalyst. 300 °C, 5200 ppm CNCl,  $1.66 \times 10^5 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ .

considerable differences in catalyst performance for CNCl destruction, leading to different activities, selectivities and apparent activation energies for CNCl destruction in humid than in dry streams. Reactions (1) and (2) may explain this.



In a dry stream, the CNCl is oxidized to  $\text{N}_2$ ,  $\text{Cl}_2$  and  $\text{CO}_x$  [reaction (1)]. The ratio of  $\text{CO}$  to  $\text{CO}_2$  depends on the catalyst activity. However, the presence of water vapour in the feed favours the hydrolysis of CNCl to ammonium chloride (or  $\text{NH}_3 + \text{HCl}$  and  $\text{CO}_2$ ). The presence of  $\text{HCl}$  and  $\text{Cl}_2$  in the effluent stream was confirmed by Dräger tube analysis. The oxidation of  $\text{NH}_3$  to produce nitric oxide, the first step in the industrial production of nitric acid from ammonia, might be expected to occur, but this requires temperatures of 810 to 850 °C at 1 atm pressure for conversions of 97–98% over a platinum gauze catalyst.<sup>12</sup> Because the temperatures in this study are much lower, this reaction is not expected to be significantly rapid.

Thus, we have shown that the water vapour hydrolyses CNCl to  $\text{NH}_4\text{Cl}$  ( $\text{NH}_3 + \text{HCl}$ ),  $\text{CO}_2$  and  $\text{HCl}$  in parallel with the direct catalytic oxidation reaction. The CNCl conversion increases almost linearly with the water vapour concentration in the range 3120 to 12 480 ppm.

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