ELSEVIER

Catalysis Today 54 (1999) 473–482

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The reactions of possible intermediates in the selective catalytic reduction of nitrogen oxides by hydrocarbons

N.W. Cant *, A.D. Cowan, I.O.Y. Liu, A. Satsuma[1]

School of Chemistry, Macquarie University, Macquarie, NSW 2109, Australia

---

Abstract

The reactions of formamide and nitromethane, two possible intermediates in the selective catalytic reduction of nitrogen oxides by methane, have been studied over Co-ZSM5, H-ZSM5 and Cu-ZSM5. Formamide, a possible surrogate for nitrosomethane, reacts completely below 250°C over Co-ZSM5 with formation of NH_3 and CO by one route and HCN and H_2O by another. Inclusion of NO causes partial conversion of NH_3 to N_2 at 300°C. H-ZSM5 behaves similarly but with a higher conversion of NH_3 in the presence of NO. Cu-ZSM5 gives CO_2 and N_2 alone, apparently because of its high oxidation activity. The reaction of nitromethane over H-ZSM5 is similar to that previously established for Co-ZSM5 with NH_3 and CO_2 as the initial products and subsequent N_2 formation by the NH_3-SCR reaction. Again N_2 formation is more extensive with H-ZSM5 than Co-ZSM5 when NO is present while Cu-ZSM5 gives only CO_2 and N_2. Deactivation is characteristic of the reaction of nitromethane over all three zeolites at temperatures below ≈280°C with eventual breakthrough of isocyanic acid (HNCO) as a product. In situ FTIR measurements with H-ZSM5 indicate that deactivation is due to reactions of HNCO to form deposits of s-triazine compounds which can be removed by NO_2. The overall conclusion is that nitromethane and formamide, and by inference nitrosomethane, react in ways which are consistent with the possibility that species of these types could be intermediates in the methane-SCR reaction over zeolite catalysts. Distinction between them is possible only with catalysts of low oxidation capability when CO formation is consistent with the involvement of nitrosomethane and CO_2 formation with that of nitromethane.

Keywords: SCR of nitrogen oxides; Formamide; Nitromethane; Hydrogen cyanide; Co-ZSM5; H-ZSM5

---

1. Introduction

The mechanism of the selective catalytic reduction of nitrogen oxides using methane (CH_4-SCR) has been a subject of considerable interest since its discovery with Co-ZSM5 as the catalyst [1,2]. There is now some agreement concerning the initial stages of the reaction. The existence of a strong deuterium kinetic isotope effect indicates that the slow step is abstraction of hydrogen by a surface site [3] and FTIR studies show that adsorbed NO_2 provides that site [4–6]. The subsequent fate of a methyl species which could arise through such an abstraction is difficult to track but combination with NO to produce nitrosomethane (CH_3NO), or with NO_2 to form nitromethane (CH_3NO_2) are two possibilities [7–9].

Recent work has firmly established that the latter is sufficiently reactive to be an intermediate [10–15]. It decomposes to CO_2 and NH_3 below 300°C on Co-ZSM5 and the ammonia-SCR reaction is sufficiently fast at 360°C, the onset temperature for CH_4-SCR, to convert all NH_3 to nitrogen [15]. A

---

* Corresponding author. Tel.: +61-2-9850-8285,
fax: +61-2-9850-8313
E-mail address: noel.cant@mq.edu.au (N.W. Cant)

[1] Permanent address: Department of Applied Chemistry, Nagoya University, Nagoya 464-8603, Japan.

PII: S0920-5861(99)00210-2

curious feature of the reaction of nitromethane over Co-ZSM5 is that conversion drops precipitously after some hours on stream below 280°C due to the formation of deposits, probably derived from the isocyanic acid (HNCO) which eventually breaks through and becomes the major nitrogen-containing product [15]. Recent in situ FTIR measurements indicate that the deposits comprise one or more s-triazine compounds such as melamine [16].

The reaction of CH_3NO has not been investigated but the reaction scheme of Lobree et al. [17] proposes that it is converted to N_2 via a Co-CN species, the generation and reactions of which were established by in situ FTIR measurements. In practice it is not possible to investigate the reactions of CH_3NO itself since its tautomer, formaldoxime (CH_2=NOH), is thermodynamically more stable. Further rapid conversion to yet more stable formamide (NH_2-CHO) by a Beckmann rearrangement also seems likely give the work of Beutel et al. [18] indicating that acetone oxime undergoes such a reaction on Cu-ZSM5 at temperatures below 100°C.

The purpose of the present work was twofold. Firstly, as a possible surrogate for nitrosomethane, we have investigated the reactions of formamide over Co-ZSM5 and, to a lesser extent, Cu-ZSM5 and H-ZSM5. The reaction of HCN, derived from formamide, has also been examined. Secondly, we have extended investigations of the reactions of nitromethane in O_2 to include a comparison between the above zeolites in the presence and absence of NO and in situ FTIR measurements of the formation and reactions of deposits with H-ZSM5. The data enables an evaluation of the circumstances under which it may be possible to decide which, if either, of nitrosomethane or nitromethane are feasible intermediates in CH_4-SCR.

2. Experimental

Reactions involving nitromethane were carried out as described in detail previously [15]. The reactant flow was established with a set of mass flow controllers with one supplying helium through a saturator containing nitromethane at 0°C. Formamide was introduced in the same way using a purpose-built saturator which allowed operation at 83 ± 1°C. This stream could also used to generate HCN as required by passing it through a Pyrex tube with a volume of $\approx 6\,cm^3$ heated to 495°C where decomposition of formamide to HCN was near complete. Water, residual formamide and traces of by-product HNCO were then removed by passage through a drierite trap at room temperature. The standard test conditions were 100 mg of catalyst in a Pyrex *U*-tube reactor with $100\,cm^3$ (STP)/min total flow.

The exit stream was analysed by a combination of gas chromatography and on-line FTIR measurements both of which allowed measurements every 2 min [15]. Formamide was analysed by FTIR with calibration using a feed stream passed through an empty reactor. The infrared cell and all tubing carrying formamide or the exit gas were heated to ≈100°C to prevent condensation of formamide and formation of solid deposits through secondary reactions. In situ FTIR measurements of H-ZSM5 were carried out as described previously [16] on ≈70 mg pressed discs contained in a small volume, flow-through cell in conjunction with a different analysis system which allowed analyses for CO_2, CO, N_2, NO and NO_2 but not NH_3 or HNCO. A total of 64 scans at $2\,cm^{-1}$ resolution was accumulated for each spectrum.

The Co-ZSM5 (Si/Al = 11.2, 110% exchange) was a gift from Dr J.N. Armor of Air Products Inc. The H-ZSM5 was prepared by complete exchange of Na-ZSM5 (Tosoh, Si/Al = 11.9) with ammonium acetate and Cu-ZSM5 by exchange with copper acetate followed by calcination at 500°C. In the case of Cu-ZSM5 the replacement was limited to a single exchange of 80% in order to minimise the introduction of Brønsted acidity. Additional pretreatments and regenerations were carried out in the reactor using either 3% O_2/He at 380°C (with Co-ZSM5) or 10% O_2/He at 450°C (Cu-ZSM5 and H-ZSM5) in the standard reactor system but limited to 280°C with the infrared cell.

3. Results and discussion

3.1. Reactions of formamide

Initial tests with formamide were carried out without NO in the feed in order to avoid secondary

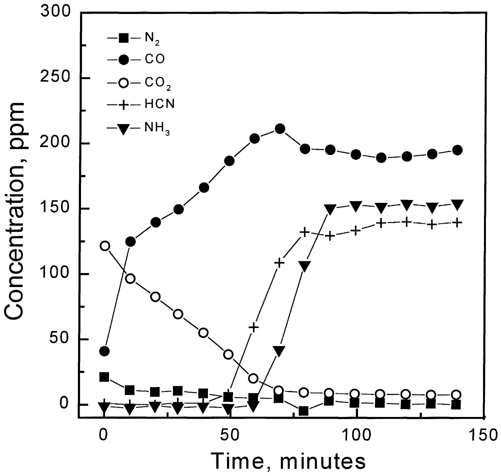


Fig. 1. Product distribution as a function of time-on-stream for the reaction of ≈300 ppm formamide in the presence of 2.9% O_2 over 100 mg of Co-ZSM5 at 250°C with a total flow rate of 100 cm^3(STP)/min.

reactions involving it. Fig. 1 shows the result of a time-on-stream test with ≈300 ppm formamide and 2.9% O_2 over Co-ZSM5 at 250°C. Conversion of formamide is complete throughout. By comparison the CH_4-SCR reaction does not commence until ca. 350°C [1–3]. After an initial period in which CO_2 dominates the system reaches a steady state in which the products are CO, NH_3 and HCN in similar amounts. Water was also observed but the amount could not be quantified accurately. Thus, the two reactions are

$$NH_2\text{-}CHO \rightarrow HCN + H_2O \tag{1}$$

and

$$NH_2\text{-}CHO \rightarrow NH_3 + CO \tag{2}$$

Since reaction (2) is thermodynamically much more favourable than (1), formation of HCN is kinetically controlled.

Similar tests at higher temperatures showed less HCN. Fig. 2 shows the results for reaction at 360°C. Again CO_2 is dominant initially with CO and NH_3 taking over in the steady state. The amounts of HCN are less than those of both N_2 and NO which are likely to be produced by the oxidation of ammonia for which Co-ZSM5 gives considerable conversions at this temperature [15]. However, as shown later, some may also arise directly or indirectly from HCN.

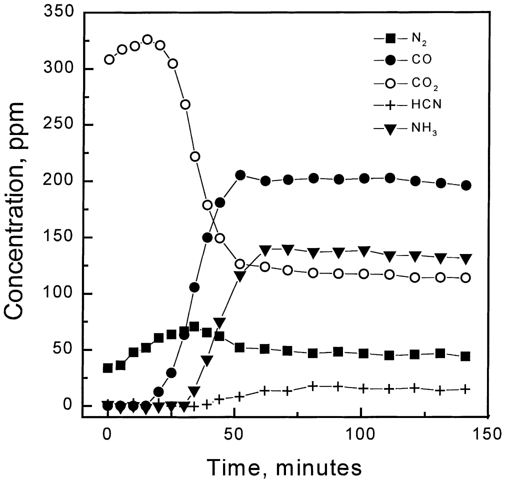


Fig. 2. Product distribution as a function of time-on-stream for the reaction of ≈300 ppm formamide in the presence of 2.9% O_2 over 100 mg of Co-ZSM5 at 360°C with a total flow rate of 100 cm^3(STP)/min.

The effect of NO on the reactions of formamide in the presence of O_2 was investigated at 300°C, the steady state results being as shown in Table 1. In the absence of NO the relative amounts of CO, NH_3 and HCN are intermediate between those in Figs. 1 and 2 and N_2 is almost undetectable indicating that NH_3 oxidation is minimal. Introduction of NO results in conversion of ≈60% of the NH_3 to N_2, presumably by the NH_3-SCR reaction

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{3}$$

This is as expected given that this reaction is faster than ammonia oxidation over Co-ZSM5 [15]. The concentration of HCN is also reduced slightly but it is not possible to decide if it has been converted to CO or CO_2.

Table 1 includes the results of similar experiments with H-ZSM5 and Cu-ZSM5. The data for H-ZSM5 in the absence of NO are similar to those for Co-ZSM5. However, the introduction of NO has a much greater effect with both NH_3 and HCN eliminated almost completely. The implication is that H-ZSM5 is a better catalyst than Co-ZSM5 for NH_3-SCR and is also able to convert HCN to CO_2 by reaction with NO in some way. Both aspects require follow up since there is no evidence in the literature to support either proposition and they are contrary to normal expectation. The results for Cu-ZSM5 are different again since even in

Table 1
Product concentrations for the reaction of ≈300 ppm formamide in 2.9% O_2 at 300°C in the presence and absence of 1000 ppm NO[a]

Catalyst	Feed mixture	Steady-state concentrations (ppm)[b]				
		CO	CO_2	NH_3	HCN	N_2
Co-ZSM5	NH_2CHO/O_2	220	30	180	80	<10
	$NH_2CHO/O_2/NO$	230	30	70	60	160
H-ZSM5	NH_2CHO/O_2	220	20	180	50	<10
	$NH_2CHO/O_2/NO$	150	100	< 10	<10	250
Cu-ZSM5	NH_2CHO/O_2	<10	290	< 10	< 10	130

[a] Using ≈100 mg catalyst with a flow rate of 100 cm^3(STP)/min.
[b] The times on stream needed to reach steady state were in the range 90–180 min.

the absence of NO the only products were CO_2 and N_2. It would appear that Cu-ZSM5 is an extremely effective catalyst for the oxidation of NH_3, and/or HCN and CO, but again this interpretation does require experimental confirmation.

3.2. Reactions of HCN over Co-ZSM5

Fig. 3 shows a time-on-stream plot for the reaction of ≈300 ppm HCN with O_2 in the absence of NO over Co-ZSM5 at 360°C. As with formamide, CO_2 is the dominant product initially with emergence of HCN delayed by 30 min. At this point the conversion of HCN is ≈40%. The major pathway seems to be oxidation to CO_2 i.e.

$$4HCN + 5O_2 \rightarrow 4CO_2 + 2N_2 + 2H_2O \quad (4)$$

Further reaction of the water to produce NH_3 and CO

$$HCN + H_2O \rightarrow NH_3 + CO \quad (5)$$

is probably the reason for the increasing HCN conversion at longer times. Reaction (5) is thermodynamically very favourable ($K_p \approx 6000$ at 360°C).

The results of similar tests of the reaction of HCN and O_2 in the presence of 1000 ppm NO are shown in Fig. 4. The conversion is close to 100%

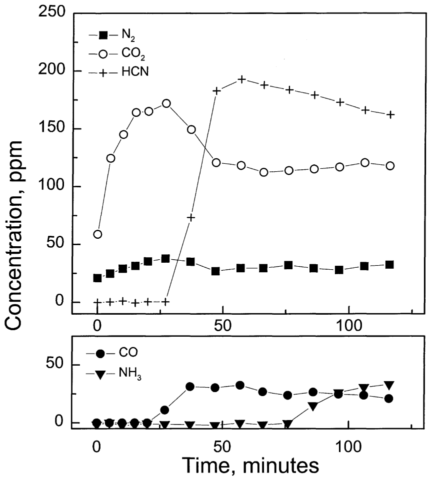


Fig. 3. Product distribution as a function of time-on-stream for the reaction of ≈300 ppm HCN in the presence of 2.9% O_2 over 100 mg of Co-ZSM5 at 360°C with a total flow rate of 100 cm^3(STP)/min.

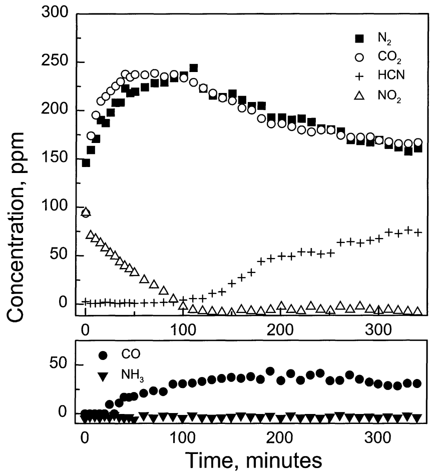


Fig. 4. Product distribution as a function of time-on-stream for the reaction of ≈300 ppm HCN in the presence of 2.9% O_2 and 1000 ppm NO over 100 mg of Co-ZSM5 at 360°C with a total flow rate of 100 cm^3(STP)/min.

for times from 40 min to 2 h and then declines slowly. The initial products are almost entirely CO_2 and N_2, now in near equal amounts, indicating that the latter contains one N from HCN and one from NO. A noteworthy feature is that NO_2 is an initial product but falls to zero at about the same time that conversion starts to decline and HCN emerges. This would suggest that the HCN/NO/O_2 reaction uses NO_2 i.e.

$$4HCN + 4NO_2 + O_2 \rightarrow 4CO_2 + 4N_2 + 2H_2O \qquad (6)$$

The decline in NO_2 formation, and hence HCN conversion, can be attributed to the generation of water which is known to inhibit NO oxidation.

Both reactions of HCN over Co-ZSM5 were much more stable if the feed contained some water. Table 2 compares the exit gas concentrations observed using the dry feed with those obtained when 1800 ppm of water was added. When reacting HCN/O_2 the effect of water is simply to enhance HCN conversion by hydrolysis to CO and NH_3, reaction (5), with little effect on the oxidation reaction (4). The same enhancement by water also occurs when NO is present. Carbon monoxide production is higher as a result of HCN hydrolysis but co-product NH_3 is not seen since it is converted to N_2 by the NH_3-SCR reaction (3).

On the basis of the above results the reaction of formamide over Co-ZSM5 can be summarised by the following scheme.

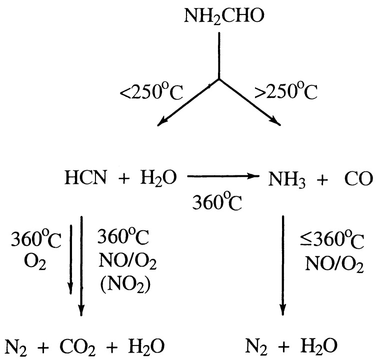


Table 2
Exit gas concentrations for the reaction of ≈300 ppm HCN and 2.9% O_2 with and without NO over Co-ZSM5 at 360°C in the presence and absence of 1800 ppm H_2O

Reactants	H_2O (ppm)	Concentrations (ppm)				
		HCN	CO	CO_2	NH_3	N_2
HCN + O_2	nil[a]	160	20	115	33	32
	1800[b]	75	85	130	115	25
HCN + O_2 + NO	nil[c]	75	30	160	<10	160
	1800[d]	35	120	140	≈15	220

[a] As per Fig. 3 after 100 min.
[b] After 90 min on stream.
[c] As per Fig. 4 after 300 min.
[d] After 210 min on stream.

Dehydration to HCN is favoured below 250°C and decomposition to NH_3 and CO at higher temperatures. Hydrolysis of HCN to NH_3 and CO can also be significant at 360°C. Nitrogen is made most effectively by the NH_3-SCR reaction but can also be generated by a reaction between HCN and NO/O_2 (probably with prior oxidation to NO_2). Thus, formamide can be converted to N_2 (via NH_3-SCR) at temperatures well below those required for CH_4-SCR, ≈350°C [1–3], and hence it is a feasible intermediate in that reaction. The only possible argument against such a conclusion is the apparent moderate activity of Co-ZSM5 for removal of the co-product, CO, since there are no reports that CH_4-SCR over Co-ZSM5 yields other that CO_2. However, such an argument would be premature without measurements of the rate of CO oxidation concurrent with CH_4-SCR under appropriate conditions. In addition, the argument against nitrosomethane relies on the assumption that its oxime tautomer undergoes the Beckmann rearrangement to formamide. However, if the transformation halted at the oxime, then it is conceivable that the latter would undergo dehydration to HCN [19], and hence give N_2 via reactions (4) and (6), without yielding NH_3 and the telltale CO because of the unfavourable framework arrangement.

The present results do not provide any direct information as to how the catalyst brings about the chemistry in the first part of the above scheme. Lobree et al. [17] have suggested a set of reactions on Co^{2+} cations whereby a CH_3NO species could yield N_2 via Co-CN. However, there are standard transformations in the organic chemistry of amides which can readily account for the formation of HCN, NH_3 and CO. Thus, amides are easily converted to nitriles through β-elimination from the enol-form using dehydrating agents [20] i.e.

$$NH_2CHO \rightleftharpoons NH = CHOH \rightarrow HCN + H_2O \quad (7)$$

Water so formed could then facilitate deammination of formamide via acid- or base-catalysed hydrolysis [21] with the former more likely here i.e.

$$NH_2CHO + H^+ \rightarrow NH_2C^+HOH \quad (8a)$$

$$NH_2C^+HOH + H_2O \rightarrow NH_4^+ + HCOOH \quad (8b)$$

Decomposition of NH_4^+ then liberates ammonia and returns the Brønsted site while decarbonylation of the formic acid, another well known reaction [22], gives CO and recycles the water. It seems feasible that these processes could occur using only the acidity of the aluminosilicate framework. H-ZSM5 is certain to contain the Brønsted sites required while the initial formation of dimethyl ether in the Mobil methanol-to-gasoline process on H-ZSM5 attests to its dehydrating power [23]. It is also common for highly metal-exchanged zeolites prepared by aqueous ion-exchange to contain some protonic sites [24]. Conversion of HCN to NH_3 and CO, reaction (5), would be expected to proceed with the amide as an intermediate.

It may be possible to identify the likely reaction sites by further investigation but the important point in connection with the CH_4-SCR reaction is simply that formamide, and by inference nitrosomethane, is very reactive over the zeolites tested and can be a source of CO and HCN.

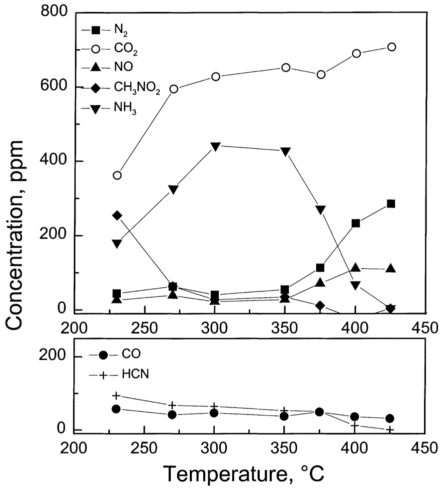


Fig. 5. Temperature dependence of the reaction of ≈1000 ppm CH_3NO_2 and 3% O_2 over 100 mg of H-ZSM5 with a total flow rate of 100 cm^3/min.

3.3. *Reactions of nitromethane over H-ZSM5 and Cu-ZSM5*

The aim here was to establish the extent to which the reactions of CH_3NO_2 over these two zeolites resembled that already established for Co-ZSM5 [15], and hence allow a comparison with the reactions of formamide over all three catalysts. Fig. 5 shows the temperature dependence of the reaction of nitromethane in the presence of O_2 over H-ZSM5. The pattern is very similar to that with Co-ZSM5 [15]. Nitromethane is almost completely converted by 280°C with NH_3 and CO_2 as the dominant products. The concentration of NH_3 falls, due to oxidation to N_2 and some NO, above 350°C which is a little above that needed with Co-ZSM5. Also as with Co-ZSM5, small amounts of HCN and CO are seen with the former favoured at lower temperature and the latter at higher temperature. Several possible explanations for the origin of these by-products were considered previously [15], but in view of the present results for formamide the most probable one is loss of an oxygen from nitromethane to form CH_3NO, or a derivative, which then reacts in accordance with the scheme given previously.

Unlike Co-ZSM5 and H-ZSM5, the reaction of nitromethane in oxygen over Cu-ZSM5 yielded largely CO_2 and N_2 with very little NH_3 or other products. Table 3 provides a comparison between the three zeolites for reaction at 300°C with and without NO

Table 3
Reaction of ≈1000 ppm nitromethane in 3% oxygen with and without NO at ≈300°C

Catalyst	Oxidant	Product concentrations (ppm)[a]				
		CO	CO_2	NH_3	HCN	N_2
Co-ZSM5	O_2	20	670	580	140	100
	O_2 + NO	30	690	580	75	160
H-ZSM5	O_2	45	630	630	65	50
	O_2 + NO	45	630	330	50	200
Cu-ZSM5	O_2	<10	930	20	<10	370
	O_2 + NO	<10	1020	15	<10	860[b]

[a] In the pseudo-steady state reached after 60–120 min of exposure.

[b] Approximately 60 ppm of N_2O was also formed.

present. Co-ZSM5 and H-ZSM5 behave similarly with O_2 alone, but the inclusion of NO results in the removal of much more NH_3 with H-ZSM5 than with Co-ZSM5 as with the corresponding reaction of formamide (Table 1). However, with Cu-ZSM5 both reactions of nitromethane give N_2 and CO_2 almost exclusively. Their ratio is much higher when NO is included as expected with the NH_3-SCR reaction replacing ammonia oxidation. The pattern in Table 3 for reaction with NO present conforms to that observed by Lombardo et al. [14]. Only Co-ZSM5 gives substantial amounts of ammonia at 300°C.

We have previously established that deactivation sets in, and the product distribution changes, after some hours on stream when nitromethane is reacted at 280°C and below over both Co-ZSM5 [15] and Cu-ZSM5 [25]. In a test with H-ZSM5 no deactivation was observable in 6 h when reacting nitromethane in the presence of both NO and O_2 at 280°C but it did occur at lower temperatures especially in the absence of NO. Fig. 6 shows the behaviour at 230°C. Deactivation with parallel reductions in the concentrations of CO_2 and NH_3 commences after ≈100 min and, as with Co-ZSM5 and Cu-ZSM5, it is accompanied by the appearance of another product, isocyanic acid (HNCO). This gradually increases in concentration approaching that of NH_3 after 6 h on stream.

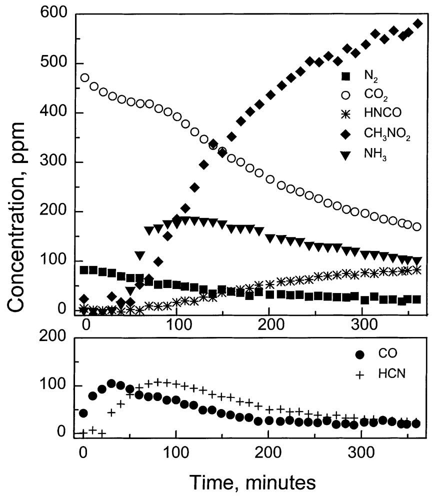
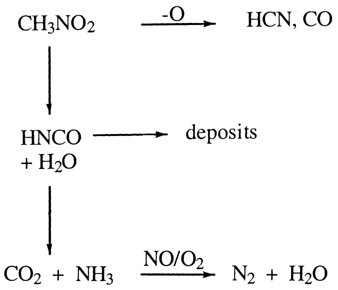


Fig. 6. Product distribution as a function of time-on-stream for the reaction of ≈1000 ppm CH_3NO_2 in the presence of 2.9% O_2 and 1000 ppm NO over 100 mg of H-ZSM5 at 230°C with a total flow rate of 100 cm^3(STP)/min.

The reactions of CH_3NO_2 on the three catalysts can then be summarised according to the following scheme.



The major pathway is an initial decomposition to NH_3 and CO_2, almost certainly via hydrolysis of HNCO, with the latter also giving rise to deactivating deposits [15]. Nitrogen is produced from ammonia by NH_3-SCR as in the formamide system. Formation of the minor products HCN and CO starts after removal of an oxygen from nitromethane and then resembles the chemistry acting with formamide.

The question as to whether nitrosomethane or nitromethane is more likely to be an intermediate in CH_4-SCR can be summarised as follows. Both undergo rapid transformations which result in the formation of N_2 at temperatures well below the onset temperature for the CH_4-SCR reaction over the catalysts studied here. For a catalyst with low oxidation power a high preponderance of CO_2 alone would be consistent with nitromethane being an intermediate while significant amounts of CO would favour the hypothesis that nitrosomethane might be involved. No distinction is possible with a catalyst with high oxidation power (as Cu-ZSM5 in particular seems to be) since CO_2 alone will be seen in both cases. However, measurements of the oxidation of CO (and HCN) concurrently with CH_4-SCR are needed to firm up the actual interpretation for any given catalyst. One important point is that both potential intermediates are predicted to produce N_2 largely via ammonia and this step, unlike the preceding chemistry, is likely to require the exchangeable cation. Hence if they, or surface species related to them, are true intermediates then the initial part of CH_4-SCR can be viewed as simply a front-end to NH_3-SCR.

3.4. In situ FTIR measurements of deposits formed from nitromethane

Deactivation like that seen in Fig. 6 persisted at rather higher temperatures in reactions over H-ZSM5 discs probably because of the smaller catalyst mass and the different flow geometry in the infrared cell. Figs. 7 and 8 detail the progress of one such reaction at 280°C which was followed by flushing with helium and exposure to NO_2/He. Analyses for CH_3NO_2 and NH_3 were not possible with the system used in this part of the work but the CO_2 analyses in Fig. 7 indicate an initial conversion of ca. 75% declining to ≈35% after 210 min. A spectrum recorded after 10 min (Fig. 8) shows the development of a broad band at 1433 cm^{-1}, which can be assigned to NH_4^+ ions, and weaker peaks at 1723 and 1663 cm^{-1}. The NH_4^+ band disappears between 15 and 20 min during which time the 1723 and 1663 cm^{-1} bands grow strongly with the latter going off-scale. Thereafter, the latter band continues to grow in width while the 1723 cm^{-1} band reaches a maximum intensity after 30 min and then gradually disappears. Similar experiments with a disc comprising H-ZSM5 diluted with SiO_2 showed the same behaviour except that the most intense band remained on-scale with a peak wavenumber of ≈1667 cm^{-1} and substantial tailing on the low wavenumber side. It seems highly likely that it is the build-up of the species responsible for the strong absorption at this position which causes deactivation.

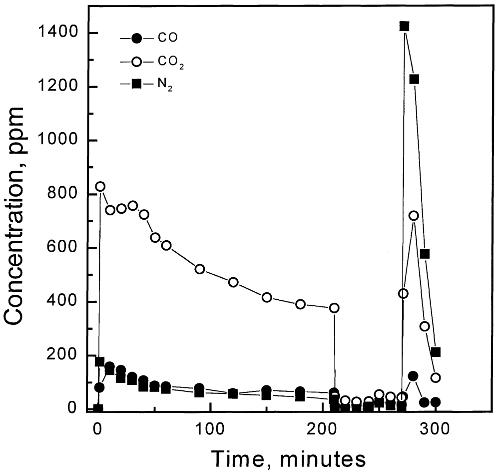


Fig. 7. Product distribution as a function of time-on-stream for the reaction of ≈1000 ppm CH_3NO_2 in the presence of 2.9% O_2 over a 70 mg disc of H-ZSM5 at 280°C with a total flow rate of 100 cm^3(STP)/min followed by flushing with helium and exposure to 1700 ppm NO_2 in helium.

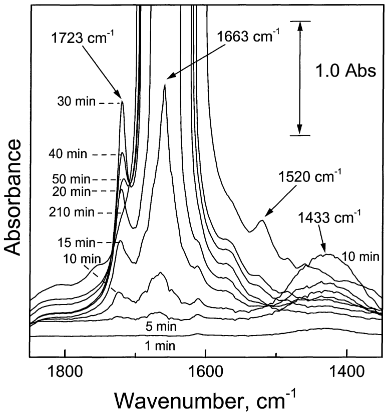
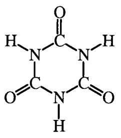
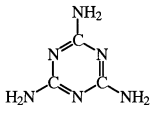
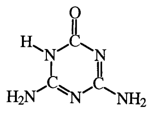


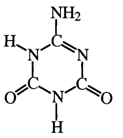
Fig. 8. FTIR spectra of H-ZSM5 disc during exposure to ≈1000 ppm CH_3NO_2 and 2.9% O_2 at 280°C as per Fig. 7.

Our previous work with Co-ZSM5 showed the same sudden growth in the intensity of a band at 1662 cm^{-1} [16] but the band at 1433 cm^{-1} due to NH_4^+ was absent and that at 1723 cm^{-1}, while present, was much less intense. As discussed previously [16] the 1723 cm^{-1} band is probably due to cyanuric acid, the cyclic trimer of HNCO, while the one at 1663 cm^{-1} is caused by another s-triazine compound, melamine and/or derivatives of it such as the two intermediate compounds, ammeline and ammelide.


cyanuric acid


melamine


ammeline


ammelide

All have a size which approaches that of the channels in the ZSM-5 structure. Oligomers such as melam (a linear dimer) and melem (a fused ring trimer) may also contribute. All are very stable compounds with melting points above 300°C and resistant to hydrolysis at similar temperatures when adsorbed on alumina [26]. Melamine is made commercially by the vapour phase reaction of HNCO and excess NH_3 in the presence of an oxide or phosphate catalyst [27] with ammeline and ammelide as possible impurities.

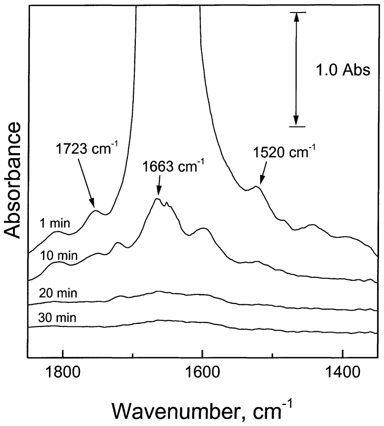


Fig. 9. FTIR spectra of H-ZSM5 disc during NO_2 oxidation of deposits formed by exposure to ≈1000 ppm CH_3NO_2 and 2.9% O_2 at 280°C as per Fig. 7.

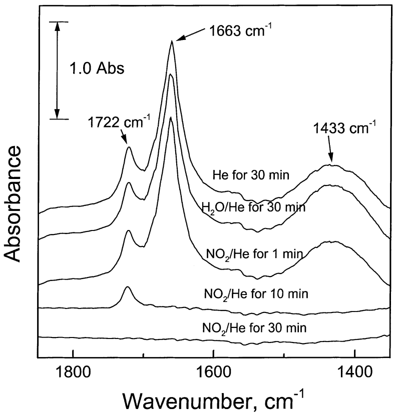


Fig. 10. FTIR spectra of H-ZSM5 disc after exposure to ≈1000 ppm nitromethane in 3% O_2 for 18 min and subsequent flushing with helium alone, 2400 ppm H_2O in helium and then 1700 ppm NO_2 in helium.

More of the latter might be expected with the present system where NH_3 can be sub-stoichiometric. The match between the spectra of such compounds and Fig. 9 is not totally convincing. While all possess very strong bands between 1720 and 1600 cm^{-1}, with a steady progression to lower wavenumber as C=O groups are successively replaced by NH_2 ones, their room temperature solid state spectra also show complex splitting not evident in Fig. 8 [28–30]. The difference may be because the 1663 cm^{-1} band is actually a composite of several overlapping bands, or because the deposits comprise isolated molecules tightly constrained within zeolite channels and hence free of intermolecular interactions. Gaseous melamine shows only one band (at 1598 cm^{-1}) in the region [31].

The species responsible for the 1663 cm^{-1} band was stable in He, H_2O, O_2 and NO/O_2 at 280°C. However, it was readily and completely removed by exposure to NO_2 as illustrated by the spectra of Fig. 9 and this treatment restored the activity of the H-ZSM5. The products of the reaction with NO_2 (see Fig. 7) were N_2 (≈114 μmol), CO_2 (≈56 μmol) and CO (≈8 μmol). Assuming that the nitrogen is derived half from the deposit and half from NO_2, as in the recent work of Chen et al. [32] on the reaction of NO_2 with deposits formed during isobutane-SCR over Fe-ZSM5, then the N to C ratio in the deposit is ≈1.8 (i.e. in between that in ammeline and melamine). The amount of aluminium in the H-ZSM5 disc was ≈90 μmol which implies approximately five s-triazine molecules per exchangeable site.

Experiments were also carried out to determine which of the three species deposited on H-ZSM5 (i.e. NH_4^+, cyanuric acid and the melamine-type compounds) were removed most rapidly by NO_2. This was done by flowing nitromethane/O_2/He for 18 min, after which time peaks due to all three species were evident in the spectrum, flushing with He and H_2O/He and then exposing to NO_2/He. Spectra recorded at the various stages are shown in Fig. 10. It is evident that ammonium ions (i.e. the 1433 cm^{-1} band) and the melamine-type compounds (the 1663 cm^{-1} band) are removed by NO_2 before cyanuric acid (the 1723 cm^{-1} band). This is not unreasonable since the latter contains ring nitrogens only whereas the former also contains aliphatic ones with hydrogen attached and these are likely to be more reactive.

At this time it is impossible to decide if the s-triazine deposits are simply spectator side products in the reaction of nitromethane, as implied by the scheme given earlier, or intermediates through which a significant fraction of the NH_3 passes on its way to N_2. It might be possible to resolve this through FTIR measurements at temperatures above 300°C where deactivation is not apparent but this was impossible with the cell available here.

4. Conclusions

Formamide is fully converted to HCN, H_2O, NH_3 and CO on Co-ZSM5 and H-ZSM5 at temperatures below 250°C. Further reactions, principally NH_3-SCR, then give N_2 above 300°C but some CO remains even at 360°C. Nitromethane is converted to NH_3 and CO_2 via HNCO on Co-ZSM5 and H-ZSM5 below 300°C, again with subsequent conversion of NH_3 to N_2. Both reactions give almost entirely N_2 and CO_2 over Cu-ZSM5, probably because its oxidation activity is higher. All three zeolites eventually undergo deactivation during the reaction of nitromethane at temperatures below 280°C and this is due to the deposition of s-triazine compounds formed from HNCO and NH_3. They are readily removed by NO_2 with formation of N_2 and CO_2. Since all this chemistry can occur at temperatures below that required for CH_4-SCR over these catalysts nitrosomethane and nitromethane, or similar surface species, are possible intermediates in the CH_4-SCR reaction on the zeolites studied here. Formation of CO is intrinsically characteristic of nitrosomethane, and CO_2 of nitromethane, but any distinction between the two becomes impossible for catalysts active for CO oxidation.

Acknowledgements

This work has been supported by grants from the Australian Research Council. We are indebted to Dr. John Armor for his gift of the sample of Co-ZSM5 made originally by Dr. Yu-jin Li.

References

[1] Y. Li, J.N. Armor, Appl. Catal. B 1 (1992) L31.
[2] Y. Li, J.N. Armor, Appl. Catal. B 2 (1993) 239.
[3] A.D. Cowan, R. Dümpelmann, N.W. Cant, J. Catal. 151 (1995) 356.
[4] Y. Li, T.L. Slager, J.N. Armor, J. Catal. 150 (1994) 388.
[5] B.J. Adelman, T. Beutel, G.-D. Lei, W.M.H. Sachtler, J. Catal. 158 (1996) 327.
[6] A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell, Stud. Surf. Sci. Catal. 101 (1996) 661.
[7] D.B. Lukyanov, G. Sill, J.L. d'Itri, W.K. Hall, J. Catal. 153 (1995) 265.
[8] D.B. Lukyanov, J.L. d'Itri, G. Sill, W.K. Hall, Stud. Surf. Sci. Catal. 101 (1996) 651.
[9] D.B. Lukyanov, E.A. Lombardo, G.A. Sill, J.L. d'Itri, W.K. Hall, J. Catal. 163 (1996) 447.
[10] C. Yokoyama, M. Misono, J. Catal. 150 (1994) 9.
[11] H. Yasuda, T. Miyamoto, M. Misono, ACS Symp. Ser. 587 (1995) 110.
[12] N.W. Hayes, R.W. Joyner, E.S. Shpiro, Appl. Catal. B 8 (1996) 343.
[13] N.W. Cant, A.D. Cowan, A. Doughty, B.S. Haynes, P.F. Nelson, Catal. Lett. 46 (1997) 207.
[14] E.A. Lombardo, G.A. Sill, J.L. d'Itri, W.K. Hall, J. Catal. 173 (1998) 440.
[15] A.D. Cowan, N.W. Cant, B.H. Haynes, P.F. Nelson, J. Catal. 176 (1998) 329.
[16] A. Satsuma, A.D. Cowan, N.W. Cant, D.L. Trimm, J. Catal. 181 (1999) 165.
[17] L.J. Lobree, A.W. Aylor, J.A. Reimer, A.T. Bell, J. Catal. 169 (1997) 188.
[18] T. Beutel, B. Adelman, W.M.H. Sachtler, Catal. Lett. 37 (1996) 125.
[19] J. March, Advanced Organic Chemistry, third ed., Wiley, New York, 1985, p. 930.
[20] J. March, Advanced Organic Chemistry, third ed., Wiley, New York, 1985, p. 932.
[21] J. March, Advanced Organic Chemistry, third ed., Wiley, New York, 1985, pp. 338–341.
[22] J. March, Advanced Organic Chemistry, third ed., Wiley, New York, 1985, p. 341.
[23] C.D. Chang, A.J. Silvestri, J. Catal. 47 (1977) 249.
[24] J. Connerton, R.W. Joyner, M.B. Padley, J. Chem. Soc. Faraday Trans. 91 (1995) 1841.
[25] N.W. Cant, D.C. Chambers, A.D. Cowan, I.O.Y. Liu, A. Satsuma, in press.
[26] Z. Zhan, M. Müllner, J.A. Lercher, Catal. Today 27 (1996) 167.
[27] A. Schmidt, Hydrocarbon Proc. 45 (1966) 146.
[28] W.M. Padgett, W.F. Hamner, J. Am. Chem. Soc. 80 (1958) 803.
[29] W.J. Jones, W.J. Orville-Thomas, Trans. Faraday Soc. 55 (1959) 203.
[30] R.J. Meier, J.R. Maple, M.-J. Hwang, A.T. Hagler, J. Phys. Chem. 99 (1995) 5445.
[31] Y.-L. Wang, A.M. Mebel, C.-J. Wu, Y.-T. Chen, C.-E. Lin, J.-C. Jiang, J. Chem. Soc. Faraday Trans. 93 (1997) 3445.
[32] H.-Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, J. Catal. 180 (1998) 171.