The Formation of Methyl Isocyanate during the Reaction of Nitroethane over Cu-MFI under Hydrocarbon-Selective Catalytic Reduction Conditions

Irene O. Y. Liu,* Noel W. Cant,*,1 Brian S. Haynes,† and Peter F. Nelson‡

* Department of Chemistry, Macquarie University, New South Wales 2109, Australia; † Department of Chemical Engineering, University of Sydney, New South Wales 2006, Australia; and ‡ CSIRO Division of Energy Technology, PO Box 136, North Ryde, New South Wales 1670, Australia

Received April 17, 2001; revised July 9, 2001; accepted July 16, 2001

The reaction of nitroethane with NO in the presence of O_2 has been investigated over Cu-MFI. For short periods on-line, conversion is complete above 250°C with CO₂ and N₂ as the products. However, at temperatures below 330°C accumulation of deposits leads to deactivation with the appearance of isocyanates and CO. FTIR gas analysis confirms the formation of toxic methyl isocyanate (CH₃NCO), with yields approaching 25% along with smaller amounts of isocyanic acid (HNCO). Nitromethane reacts similarly but deactivation to give HNCO alone is an order of magnitude slower. Emergence of HNCO is accompanied by significant amounts of HCN and NH₃. Nitroethane reacts in O₂ alone in a manner similar to that in NO/O_2 but with less than half the initial N_2 yield. Deactivation is faster and small amounts of HCN and NH₃ appear concurrently with CH₃NCO and HNCO. In the nitroethane system, HNCO, HCN, and NH₃ arise from decomposition of deposited material as demonstrated by the temperature-programmed decomposition in helium. The main reaction pathway with the two nitrocompounds appears to be rearrangement followed by dehydration to the corresponding isocyanate and hydrolysis to amine (or ammonia), with the latter steps proceeding on Brønsted acid sites. Nitrogen is then formed by reaction with NO/O2 on the transition metal as in the ammonia-selective catalytic reaction which is fast over Cu-MFI. A parallel route to N₂ involves reaction of NO₂ with deposited material but this can occur only as long as the catalyst retains activity for the oxidation of NO. Otherwise deactivation ensues with appearance of isocyanate. Selective catalytic reduction of NO using ethane over Cu-MFI in excess O₂ yields some NO₂ in which case the various reactions involving nitroethane would be sufficiently fast for it to be an intermediate in this system. © 2001 Academic Press

Key Words: Cu-MFI; methyl isocyanate; nitroethane; hydrocarbon-selective catalytic reduction.

INTRODUCTION

There have been many suggestions, starting with Yokoyama and Misono in 1994 (1, 2), that nitro and/or nitroso-like compounds are key intermediates in the selective catalytic reduction (SCR) of nitrogen oxides using hydrocarbons. Subsequent work has established that nitrogen can indeed be formed when such compounds, or derivatives of them, are adsorbed on Cu-MFI (3–5), H-MFI (4), H-mordenite (6, 7), and Fe-MFI (8) and reacted with nitrogen oxides, especially NO₂. The full chemistry is yet to be resolved but facets of sequences such as nitroso \rightarrow oxime tautomer \rightarrow amide (by the Beckmann rearrangement) \rightarrow acid plus nitrile \rightarrow amine (or ammonia) \rightarrow N₂ have all been established, principally by spectroscopic means.

The situation is somewhat simpler for the steady-state reaction of possible intermediates in the methane-SCR system. Nitrosomethane (CH₃NO) and its oxime tautomer $(CH_2=NOH)$ are not easily studied but the Beckmann rearrangement product, formamide (NH₂CHO), has been shown to react completely at temperatures as low as 200°C (9). With Co-MFI and H-MFI, the low-temperature products are HCN and H₂O, while NH₃ and CO become dominant by 300°C. Some of the NH₃ and HCN is converted to N_2 if NO is added (9) and both conversions are complete if NO₂ is used instead (10). However, considerable CO remains even at 360°C (9). Cu-MFI is much more active, with complete conversion of formamide to N₂ and CO₂ at 300°C in O₂ alone (9). Nonetheless the sequence NH₂CHO \rightarrow $HCN + H_2O \rightarrow NH_3 + CO \rightarrow N_2 + CO_2$ can still be inferred from the way the catalyst deactivates at lower temperature (10).

Parallels exist in the reactions of nitromethane (11–13). Co-MFI gives complete conversion to NH₃ and CO₂ at 300°C (12). Conversion of NH₃ to N₂ is complete by 360°C when the feed includes O₂ or NO/O₂. Deactivation is apparent at temperatures below ~290°C, with isocyanic acid (HNCO) eventually taking over as the major nitrogencontaining product. Since HNCO is readily hydrolyzed, the sequence appears to be CH₃NO₂ \rightarrow HNCO + H₂O \rightarrow NH₃ + CO₂ followed by NH₃ + NO_x, with each step sufficiently fast to be feasible at the onset temperature for the CH₄-SCR reaction. As with the reactions of formamide,



 $^{^1}$ To whom correspondence should be addressed. Fax: 61 2 9850 8313. E-mail: noel.cant@mq.edu.au.

Cu-MFI is more active still, with complete conversion of nitromethane at 300°C, but the intermediate steps can still be recognized during the course of prolonged reaction at lower temperatures (14).

On the basis of the above, it appears that N₂ can arise via NH_3 in both C_1 systems, through intermediate formation of cyanide in the nitroso (amide) path but isocyanate in the nitro path. The aim of the present work was to establish the corresponding reaction characteristics for nitroethane with Cu-MFI chosen as the catalyst because of its higher oxidation activity and superior SCR performance with larger molecules even though it is ineffective with methane. There have been no previous determinations of the products of the reaction of higher nitrocompounds under steady-state conditions. However Szanyi and Paffett (15) have reported the observation of bands assignable to adsorbed acetonitrile when nitroethane is adsorbed on Cu-MFI at 400 K, and Chen et al. (8) have shown that 2-nitropropane deposited on Fe-MFI is readily converted to nitrogen (largely ¹⁴N¹⁵N) by reaction with ¹⁵NO₂ at 200°C. HNCO and HCN are also known minor products of the C₂H₄/NO/O₂ SCR reaction over Cu-MFI (16-19).

EXPERIMENTAL

Cu-MFI was prepared by exchange of Na-MFI (Si/Al =11.9, Tosoh Inc.) with copper acetate followed by drying at 110°C and calcination in air at 500°C. The exchange level was 80% (3.2 wt% Cu). Activity testing was carried out on 100-mg samples of 300- to 600- μ m particle size, contained in a 4-mm-i.d. Pyrex U-tube reactor and pretreated in 10%O₂/He to 480°C before reaction. The gas mixture, with a total flow rate of 100 cm³/min, was made up using a set of electronic flowmeters (Brooks Model 5850TR or 5850E) and standard gas mixtures (BOC, Australia). Nitroethane (Fluka AG) was supplied by passing a separate stream of He through a saturator held at a temperature such that the nitroethane concentration in the reactant mixture was \sim 750 ppm as determined by complete oxidation and analysis of the CO₂ produced. Nitromethane was provided similarly to a concentration of 1000 ppm.

The exit stream from the reactor was analyzed by a combination of gas chromatographic and on-line FTIR measurements in a manner similar to that described previously (12). In essence, the stream was periodically sampled into a micro-gas chromatograph (MTI Instruments, Model M200) with molecular sieve and Poraplot U columns for analysis of N₂, O₂, N₂O, and CO₂ (detection limits <5 ppm) and then made to flow through a 16-cm-pathlength infrared cell in heated box held at 90°C. Spectra, each comprising 64 scans at 0.25 cm⁻¹ resolution, were processed to obtain concentrations based on Beer–Lambert plots for individual lines of NO, NO₂, and HCN. HNCO was determined from its peak at 2284 cm⁻¹ using the relationship ppm = $3364 \times$ absorbance at 90°C, as established in previous work (14), and CH₃NCO from its peak at 2308 cm⁻¹ using the corresponding relationship ppm = $3990 \times absorbance$ at 90°C, calculated from spectra of an authentic sample measured for us by Infrared Analysis, Inc., Anaheim, California.

RESULTS

Figure 1 shows the exit gas composition for the reaction of a $C_2H_5NO_2/NO/O_2$ stream over Cu-MFI with points obtained in random order, allowing approximately 1 h at each temperature. The principal products at all temperatures are CO_2 and N_2 . Small amounts of CO are evident below 300°C with some NO_2 , formed by oxidation of residual NO, above 325°C. On the time scale used here no nitroethane emerged at any temperature. However, although the carbon and nitrogen balances were complete within experimental error above 350°C there was an increasingly larger deficit at lower temperatures. Thus, deposited material was being built up.

If the reaction was allowed to run for some hours below \sim 330°C then peaks due to other products eventually became apparent in the infrared spectra of the product stream as shown in Fig. 2. Spectrum a corresponds to that obtained after 4 h for a reaction started at 285°C with subtraction of the contribution due to CO₂. It shows two relatively broad bands at 2284 and 2308 cm⁻¹, with weaker ones near 2340 and 2266 cm⁻¹. Superimposed fine structure is evident below 2300 cm⁻¹ which clearly corresponds to that of isocyanic acid (HNCO), spectrum b. The fine structure in (a) can be removed by subtracting an appropriate multiple of



FIG. 1. Exit gas composition and atom balances as a function of temperature for the reaction of 750 ppm $C_2H_5NO_2$ with 1000 ppm NO in 3% O_2 /He over 100 mg of Cu-MFI with a flow rate of 100 cm³/min. Data for \sim 1 h of reaction at each temperature.



FIG. 2. Infrared spectra in isocyanate region after correction for CO₂: (a) product gas from $C_2H_5NO_2/NO/O_2$ mixture after 4 h of reaction over Cu-MFI under conditions of Fig. 1; (b) spectrum of HNCO as determined in Ref. (14); (c) spectrum a after subtraction of contribution from HNCO; (d) spectrum of authentic sample of methyl isocyanate.

(b), which gives spectrum c, a close match to that of an authentic sample of methyl isocyanate, spectrum d. The concentrations of CH_3NCO and HNCO, calculated using the calibration factors given earlier, are 200 and 65 ppm, respectively.

It should be noted that methyl isocyanate is the extremely toxic substance (TLV = 0.02 ppm) that was responsible for the disaster in Bhopal, India, in 1984. The flow system used here was fitted with an alarm system set up to provide a warning signal if the difference between the flow being vented and the inlet one exceeded 1%, as this would indicate a leak.

Figure 3 shows how the product distribution changed with time during the experiment described above in relation to Fig. 2. Carbon dioxide and nitrogen are the only significant products for the first 50 min (apart from the rapidly falling amounts of NO₂ seen in the first few analyses). Both decline thereafter as small amounts of CO appear followed by CH₃NCO, HNCO, and, finally, unreacted nitroethane. The carbon balance is 60 to 80% throughout, with the nitrogen balance higher (since more than half of it is initially present in NO). Traces (<20 ppm) of N₂O, NH₃, and HCN are just measurable under some conditions.

The results of an equivalent experiment with nitromethane (CH₃NO₂) at almost the same temperature are shown in Fig. 4. As before, CO₂ and N₂ are the principal initial products. However, deactivation is much slower, \sim 17 times relative to nitroethane, and also \sim 10 times slower than nitromethane at the lower temperature of 250° C (14). Isocyanate, now HNCO alone, does not appear until 1800 min (30 h) of reaction. (This required operation unattended overnight and a change in feed saturation is responsible for the step change apparent in CO₂ and N₂ production between 500 and 1500 min.) The concentrations of minor products are also different with the smaller nitroparaffin. Notably, NO₂ and N₂O are present in significant amounts from the beginning but NO₂ has declined to zero by the time deactivation starts. In addition, ammonia and hydrogen cyanide emerge at the same time as HNCO.

The data in Figs. 3 and 4 require that N_2 is derived from NO as well as the nitroparaffin, indeed almost equally in both cases. This is a significant contributor to the overall chemistry which is rather different when NO is absent. As shown in Fig. 5 for reaction at 288°C, the initial production of CO₂ is similar when using $C_2H_5NO_2$ with O_2/He alone, but the concentration of N_2 is lower by a factor of 2 since it can now arise only from the nitrocompound. Deactivation commences somewhat earlier and the concentrations of NH_3 and HCN that emerge at the same time as CH_3NCO and HNCO are considerably greater than when NO is present as well (Fig. 3). Concentrations of the two



FIG. 3. Exit gas composition and atom balances as a function of time during the reaction of 750 ppm $C_2H_5NO_2$ with 1000 ppm NO in 3% O_2 /He over 100 mg of Cu-MFI at 285°C with a flow rate of 100 cm³/min.

1000

500

C

200

100

0

100

0

0

HCN

NH₃ HNCO

× CH_NCC

Concentration, ppm

FIG. 4. Exit gas composition and atom balances as a function of time during the reaction of 1000 ppm CH_3NO_2 with 1000 ppm NO in 3% O_2/He over 100 mg of Cu-MFI at 290°C with a flow rate of 100 cm³/min.

isocyanates both pass through shallow maxima and show small stepwise drops when 1200 ppm of water is subsequently introduced. These drops are correlated with a rise in production of CO₂, as expected for isocyanate hydrolysis. In the case of HNCO the other expected product is NH₃, and a small increase in the concentration of the latter is again discernible. The hydrolysis product expected for methyl isocyanate is methylamine. Tests with methylamine showed that it, like ammonia, was very reactive under SCR conditions at 275°C (Table 1). However, the re-

FIG. 5. Exit gas composition and atom balances as a function of time during the reaction of 750 ppm $C_2H_5NO_2$ in 3% O_2 /He over 100 mg of Cu-MFI at 288°C with a flow rate of 100 cm³/min (1200 ppm water introduced where indicated).

Time, minutes

200

300

N.C

100

1.0

0.8

0.6

0.4

0.2

0.0

CO

action of methylamine was accompanied by a mass balance deficit due to adsorption which would have been sufficient to make its observation difficult under the conditions of the experiment illustrated in Fig. 5 given a relatively high detection limit by FTIR (\sim 70 ppm here for its strongest band at 780 cm⁻¹).

The data in Fig. 5 show that hydrolysis of product methyl isocyanate is less than 30% when 1200 ppm water is added at 288°C. Combustion processes typically produce 10% or more water which would certainly result in greater

 TABLE 1

 Reactions in O2/He over Cu-MFI

Feed (all in O ₂ /He)	Temperature (°C)	Conversion (%)	Product concentration (ppm)			
			$\overline{CO_2}$	N_2	N ₂ O	NO ₂
800 ppm NH ₃ + 1000 ppm NO ^a	275	>95		1100	50	50
400 ppm $CH_3NH_2 + 1000$ ppm NO^a	275	>95	220^{b}	350 ^c	20	50
1000 ppm NO ^b	275	${\sim}40$	_	_	_	400
800 ppm NH ₃ ^{<i>a</i>}	275	\sim 80	_	270	<20	<20
360 ppm HCN + 1000 ppm NO ^a	270	>95	400	380	—	25

^a In 3% O₂/He, using 100 mg of Cu-MFI with a total flow rate of 100 cm³/min.

^{*b*} In 5% O_2 /He, using 140 mg of Cu-MFI with a total flow rate of 100 cm³/min.

^c Forty percent deficit in carbon and 20% in nitrogen, possibly due to disproportionation and adsorption of di- and trimethylamines.





FIG. 6. Exit gas composition and atom balances as a function of time during the reaction of 750 ppm $C_2H_5NO_2$ in 3% O_2/He over 100 mg of Cu-MFI at 328°C with a flow rate of 100 cm³/min.

hydrolysis. Only further experimentation, beyond the scope of the present work, can establish if hydrolysis would then be complete.

Deactivation was also apparent, but slower, when nitroethane was reacted in O₂/He alone at a higher temperature. At 328°C, as shown in Fig. 6, deactivation did not commence until 170 min of reaction but then followed a course similar to that in Fig. 5, with NH₃ and HCN emerging together with CH₃NCO and HNCO. After 280 min, when the accumulated mass balance deficits in carbon and nitrogen were, very approximately, 3600 and 2200 μ mol/g, respectively, the sample was heated in He alone at $\sim 10^{\circ}$ C/min. As may be seen from Fig. 7, decomposition commenced at \sim 350°C. Hydrogen cyanide was generated in the largest amount with a peak concentration of \sim 380 ppm at \sim 470°C. Other products include CO₂ and NH₃, with peak concentrations at 420 and 450°C, respectively, plus HNCO, which exhibits a peak at 380°C and is formed continuously at the hold temperature of 480°C.

Following the experiment illustrated by Fig. 7, the sample was subjected to temperature-programmed oxidation after first being cooled to 330°C in helium. As shown in Fig. 8, CO_2 and N_2 are formed immediately on admission of oxygen with peak yields of both at ~430°C. Small amounts of N_2O and CO are evident at lower temperature. The cumu-



FIG. 7. Composition of gas evolved during temperature-programmed decomposition in 100 cm³/min He of deposits formed on Cu-MFI by $C_2H_5NO_2/O_2$ reaction as per Fig. 6.

lative amounts of C and N liberated during the combined decomposition/oxidation of Figs. 7 and 8 were 2600 and 1400 μ mol/g, respectively, in reasonable agreement with those estimated from the mass balance deficits in Fig. 6,



FIG. 8. Composition of gas formed during temperature-programmed oxidation in 100 cm³/min 3% O₂/He of material remaining after decomposition of deposits from $C_2H_5NO_2/O_2$ reaction as per Fig. 7.



FIG. 9. Exit gas composition and atom balances as a function of temperature during the reaction of 1000 ppm C_2H_6 with 1000 ppm NO in 3% O_2 /He over 100 mg of Cu-MFI with a flow rate of 100 cm³/min.

bearing in mind the considerable errors inherent in the latter.

The results of an SCR experiment carried out over the Cu-MFI catalyst with an ethane/NO/O₂ mixture are shown in Fig. 9. The maximum yield of reduced products occurs at 365° C, with formation of 185 ppm of N₂ and 25 ppm of N₂O, a net removal of 40% which is similar to the maximum observed by Burch and Scire (20). The total conversion of NO is higher at 430°C but NO₂ then constitutes a significant fraction of the products. Some NO₂ is also evident at the two lowest temperatures. Carbon monoxide is always negligible compared with CO₂ and both C and N mass balances are always within experimental error.

DISCUSSION

The data in Figs. 3 and 4 demonstrate that nitroethane and nitromethane react similarly over Cu-MFI under SCR conditions. At temperatures near 290°C, each yields CO_2 and N_2 initially but deactivation due to deposited material results in the eventual appearance of isocyanates. The simplest interpretation is that the reaction is sequential,

nitroparaffin \rightarrow isocyanate \rightarrow N₂ + CO₂,

with the deposited material having a larger effect on the rate of the second step than the first so the intermediate eventually becomes detectable.

The conversion of nitroparaffin to isocyanate is likely to occur through dehydration of its *aci*-form on Brønsted acid sites, i.e., with R = H or CH_3 :

$$\begin{array}{l} \text{R-CH}_2\text{-NO}_2 \ \rightleftharpoons \ \text{R-CH} = \text{NOOH} \\ \\ \rightarrow \ \text{R-CNO} \ [+H_2\text{O}] \rightarrow \text{R-NCO}. \end{array}$$

The work of Obuchi et al. (21) shows that isomerization of N-oxides (R-CNO) to isocyanates (R-NCO) is facile, with substantial conversion at 100°C on alumina for example. There are two possible routes from the isocyanate to N_2 . One is through hydrolysis to R-NH₂ (or ammonia) followed by an SCR reaction, the other by deposition of the isocyanate and reaction with NO2. Hydrolysis is far from complete when water is added with a greatly deactivated catalyst (Fig. 5) but this would not preclude its occurrence at a faster rate prior to deactivation. Hydrolyses of isocyanates, both acid- and base-catalyzed, are well-known reactions (22, p. 807), and tests show that the process is fast at 300°C on both acidic and basic oxides (23, 24). Only silica is relatively inactive. As shown in the work of Connerton et al. (25), Cu-MFI contains similar numbers of Brønsted acid sites whether it is made from H-MFI or, as here, from Na-MFI.

The NH₃-SCR reaction is also fast on Cu-MFI (26). As shown in Table 1, both NH₃-SCR and the corresponding reaction with methylamine are near complete at 275° C with the present catalyst. Thus the sequence

$$\begin{aligned} & \text{R-NCO} + \text{H}_2\text{O} \rightarrow \text{R-NH}_2 + \text{CO}_2 \\ & \text{R-NH}_2 + \text{NO} + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}[+\text{CO}_2], \end{aligned}$$

with the first proceeding on Brønsted acid sites and the second requiring the transition metal, appears feasible until prevented by a buildup of deposited material.

The alternative path to N₂, the reaction of deposited material with NO₂, has been shown to occur at 200°C for a variety of compounds, including isocyanates, adsorbed on Fe-MFI (8). As may be seen from Table 1, Cu-MFI has considerable activity for the oxidation of NO to NO₂ at 275°C and some NO₂ is formed from residual NO in the reactions with NH₃, CH₃NH₂, and HCN. This is also true during the initial stages of the reaction of nitromethane (Fig. 4) but the NO₂ declines to zero by the time deactivation commences. With nitroethane, NO₂ is observable only at the very beginning of reaction and deactivation starts much earlier. One possible implication is that NO₂ can slow deactivation by reacting with material being deposited. This would be less effective with nitroethane since its extra carbon will increase the amount of NO₂ required for complete oxidation. It is also significant here that although Co-MFI deactivates faster than Cu-MFI during the reaction of nitromethane in NO/O_2 , there is no deactivation if NO_2/O_2 is used instead (12). Complete reaction is possible at 200°C in the latter system. Overall it appears that NO₂ is capable of generating N₂ by reaction with deposited material. However, this cannot be the sole route to N2 since nitroethane reacts in a similar way in O₂ alone (Figs. 5 and 6) where neither NO₂ nor NO is present. The probable route to N_2 in that system is hydrolysis followed by ammonia oxidation which is also quite fast at 270°C (Table 1).

In situ infrared measurements during the course of the nitromethane/NO/O₂ reaction over Co-MFI and H-MFI indicate that the deposited material comprises highly stable *s*-triazine compounds related to melamine ($C_3H_6N_6$) and cyanuric acid ($C_3H_3N_3O_3$) (9, 14, 27). This is understandable since melamine itself is made commercially by combination of isocyanic acid and ammonia using alumina or solid phosphate catalysts (28). The deposits formed during the reaction of nitromethane over Cu-MFI appear to have the same structure (29). The larger size of trimers of methyl isocyanate may restrict equivalent trimerization reactions within the cavities of MFI, but they would still be possible on external surfaces, leading to blockage of pore entrances. Isocyanates can also add to ammonia, amines, and amides to form stable ureas (22, p. 823).

The reactions of nitromethane and nitroethane differ in the distribution of minor products as deactivation proceeds. Nitromethane gives rise to much more ammonia which is understandable since it is an expected hydrolysis product with HNCO compared with methylamine in the C₂ system. Nitromethane also produces more HCN, the expected dehydration product of formaldoxime (CH₂=NOH) or formamide (NH₂-CHO). This suggests that some nitromethane is reacting with loss of oxygen,

$$CH_3NO_2 \rightarrow CH_3NO \rightarrow CH_2=NOH \rightarrow HCN + H_2O$$
,

and, if the Beckmann rearrangement were to proceed,

$$CH_2 = NOH \rightarrow NH_2 - CHO \rightarrow HCN + H_2O.$$

Formamide reacts readily in O_2 /He over Cu-MFI at 250°C and the reaction exhibits slow deactivation during which time HCN can be observed (10). However, the concentrations of HCN formed are much smaller than those of NH_3 and CO which arise through hydrolysis:

$$NH_2$$
-CHO + $H_2O \rightarrow NH_3$ + HCOOH
 $\rightarrow NH_3$ + CO + H_2O .

Since the HCN/CO ratio is high, not low, during the reaction of nitromethane it appears that the HCN observed in this system arises from the oxime not the amide. This is understandable since Beckmann rearrangements do not usually proceed with movement of a hydrogen (22, p. 1008), as is required to convert CH_2 =NOH to NH_2 -CHO.

On the other hand, the Beckmann rearrangement of the corresponding C_2 -oxime from nitroethane should be faster since it can proceed with shift of a methyl rather than hydrogen:

$$CH_3CH = NOH \rightarrow CH_3NH - CHO.$$

In this case the expected hydrolysis products are CO and methylamine:

$$CH_3NH$$
- $CHO \rightarrow CH_3NH_2 + CO.$

This can explain why nitroethane produces considerably more CO than nitromethane. The coproduct methylamine was not seen but that is understandable given its reactivity and uptake (Table 1) coupled with a high detection limit here. If the C_2 -oxime were to undergo dehydration rather than rearrangement then the expected product is acetonitrile:

$$CH_3CH = NOH \rightarrow CH_3CN + H_2O.$$

This was not seen in the present work although the conversion of adsorbed nitroethane to adsorbed acetonitrile has been observed to proceed on Cu-MFI at a lower temperature (127° C) (15).

It should be noted here that the dehydration, hydrolysis, and rearrangement reactions mentioned above are all wellknown proton-catalyzed reactions (22), and hence can proceed on small numbers of Brønsted sites remaining when the metal sites necessary to convert reduced nitrogen compounds to N_2 itself have been deactivated.

Unlike the above, there is no standard chemistry that can explain the small amounts of HNCO, and even smaller amounts of HCN, produced in the largely deactivated state when nitroethane is reacted in NO/O2 or O2 alone (Figs. 3, 5, and 6). They probably arise through direct decomposition of deposited material since both are generated when the deactivated catalyst is heated in He alone (Fig. 7). HNCO appears initially at a considerably lower temperature than does HCN, consistent with the larger amount of the former produced while deactivation is proceeding. The HCN/HNCO ratio is lower during reaction in NO/O₂ (Fig. 3) than in O_2 alone (Fig. 4) because the HCN itself reacts readily with NO/O2 to give N2 on Cu-MFI (Table 1), whereas it undergoes deactivation with formation of cyanogen (C_2N_2) when reacted with O_2 alone (30). It appears likely that the small amounts of HCN and HNCO seen during the C₂H₄/NO/O₂ reaction on Cu-MFI in other studies (16-19) also arise by decomposition of deposits.

The question as to whether it is feasible for nitroethane to be a major intermediate in N_2 formation in the SCR reaction using ethane over Cu-MFI can now be considered. As shown in Fig. 9, that reaction converts 300 ppm of NO at 296°C with formation of 60 ppm of N_2 , 20 ppm of N_2O , and 65 ppm of NO₂. If the 120 ppm of NO that has been reduced to N_2 were converted to nitroethane first then, based on Figs. 1 and 3, complete reaction to N_2 and CO₂ would be expected initially. Any deposits formed would tend to be removed by reaction with the NO₂ also present so deactivation should be slow if present at all. Hence it is feasible, although not proved, for nitroethane to be a major intermediate in the ethane/NO/O₂ reaction. It could be formed within cavities by an initial hydrogen abstraction followed by addition of NO_2 to the resulting radical.

It is significant that NO_2 formation during the SCR reaction at 296°C is much less than that with NO/O_2 alone at a lower temperature (Table 1). Furthermore, the NO_2 concentration first declines with temperature above 300°C during SCR to a minimum near 365°C where ethane consumption is complete. The implication is that NO_2 is being consumed by a reaction involving ethane that has a higher activation energy than NO oxidation. Thus NO_2 does appear to be a key reactant in this system in agreement with current views concerning hydrocarbon-SCR reactions over transition metal zeolites.

CONCLUSIONS

Nitroethane reacts readily in NO/O₂ over Cu-MFI with initial conversion to CO₂ and N₂. Deactivation due to deposited material occurs below 330°C with the eventual emergence of isocyanates, principally CH₃NCO by dehydration, but with some HNCO, by deposit decomposition, as well. Nitromethane reacts in a similar way but deactivation is much slower. While HNCO is then the only isocyanate formed, significant amounts of HCN and NH₃ are also seen. With both systems nitrogen can arise either by hydrolysis of isocyanate to amine (or ammonia) on Brønsted sites and subsequent SCR reactions involving transition metal ions or through reaction of NO₂ with deposits. The rates of these processes are sufficiently fast for nitroethane to be feasible as an intermediate during the selective catalytic reduction of NO by ethane on Cu-MFI.

ACKNOWLEDGMENTS

This work has been supported by grants from the Australian Research Grants Committee. We are grateful to Mr. A. Asano for provision of the starting zeolite sample.

REFERENCES

- 1. Yokoyama, C., and Misono, M., J. Catal. 150, 9 (1994).
- 2. Yokoyama, C., and Misono, M., Catal. Today 22, 59 (1994).

- Beutel, T., Adelman, B., and Sachtler, W. M. H., Catal. Lett. 37, 125 (1996).
- 4. Wu, J., and Larsen, S. C., J. Catal. 182, 244 (1999).
- Rebrov, E. V., Simakov, A. V., Sazonova, N. N., and Stoyanov, E. S., *Catal. Lett.* 64, 129 (2000).
- Gerlach, T., Schütze, F.-W., and Baerns, M., J. Catal. 185, 131 (1999).
- 7. Gerlach, T., and Baerns, M., Chem. Eng. Sci. 54, 4379 (1999).
- Chen, H.-Y., Voskoboinikov, T., and Sachtler, W. M. H., J. Catal. 186, 91 (1999).
- Cant, N. W., Cowan, A. D., Liu, I. O. Y., and Satsuma, A., *Catal. Today* 54, 473 (1999).
- 10. Liu, I. O. Y., unpublished results.
- Cant, N. W., Cowan, A. D., Doughty, A., Haynes, B. S., and Nelson, P. F., *Catal. Lett.* 46, 207 (1997).
- Cowan, A. D., Cant, N. W., Haynes, B. H., and Nelson, P. F., *J. Catal.* 176, 329 (1998).
- Lombardo, E. A., Sill, G. A., d'Itri, J. L., and Hall, W. K., J. Catal. 173, 440 (1998).
- 14. Cant, N. W., Chambers, D. C., Cowan, A. D., Liu, I. O. Y., and Satsuma, A., *Top. Catal.* **10**, 13 (2000).
- Szanyi, J., and Paffett, M. T., J. Chem. Soc. Faraday Trans. 92, 5165 (1996).
- Radtke, F., Koeppel, R. A., and Baiker, A., *Appl. Catal. A* 107, L125 (1994).
- Radtke, F., Koeppel, R. A., and Baiker, A., *Environ. Sci. Technol.* 29, 2703 (1995).
- Radtke, F., Koeppel, R. A., and Baiker, A., J. Chem. Soc. Chem. Commun., 427 (1995).
- Radtke, F., Koeppel, R. A., and Baiker, A., *Catal. Today* 26, 159 (1995).
- 20. Burch, R., and Scire, S., Appl. Catal. B 3, 295 (1994).
- Obuchi, A., Wögerbauer, C., Köppel, R. A., and Baiker, A., *Appl. Catal. B* 19, 9 (1998).
- March, J., "Advanced Organic Chemistry," p. 807. Wiley, New York, 1985.
- Dümpelmann, R., Cant, N. W., and Trimm, D. L., J. Catal. 162, 96 (1996).
- 24. Chambers, D. C., Angove, D. E., and Cant, N. W., J. Catal. in press.
- Connerton, J., Joyner, R. W., and Padley, M. B., *J. Chem. Soc. Faraday Trans.* 91, 1841 (1995).
- Sullivan, J. A., Cunningham, J., Morris, M. A., and Keneavey, K., *Appl. Catal. B* 7, 137 (1995).
- Satsuma, A., Cowan, A. D., Cant, N. W., and Trimm, D. L., *J. Catal.* 181, 165 (1999).
- 28. Schmidt, A., Hydrocarbon Proc. 45, 146 (1966).
- Beloshapkin, S. A., Paukshtis, E. A., and Sadykov, V. A., *J. Mol. Catal.* A 158, 355 (2000).
- 30. Liu, I. O. Y., and Cant, N. W., J. Catal. 195, 352 (2000).