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The Catalytic Chemistry of Nitromethane over Co-ZSM5 and Other Catalysts in Connection with the Methane-NO_x SCR Reaction

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The reaction of nitromethane over Co-ZSM5 has been studied with the aim of establishing the paths by which it can be converted to N_2 under the conditions of the methane-SCR reaction over this type of catalyst. When reacted alone it readily decomposes above 250°C to give CO_2 and NH_3 but the latter is further converted to N_2 at temperatures above 360°C if NO and O_2 are also present. The reaction of ammonia with NO and O_2 is sufficiently fast to account for all N_2 formed. The nitromethane reaction systems are stable above 300°C but below that deactivation sets in after a few hours with isocyanic acid (HNCO) eventually becoming the major nitrogen-containing product. If water is then added to the feed the HNCO is largely hydrolysed to NH_3 and CO_2 and conversion stabilises. Reaction in the presence of water at higher temperature restores the original activity. It is believed that HNCO is the initial decomposition product of nitromethane and deactivation under dry conditions is due to its deposition, possibly as a polymer such as cyanuric acid. Nitromethane also decomposes to CO_2 and NH_3 over alumina, H-ZSM5, and Na-ZSM5 but only the latter shows deactivation. There is even some conversion over silica but with HNCO observable from the beginning and produced in larger amounts than NH_3 below 340°C. Experiments with deuterated nitromethane show that the reaction over Co-ZSM5 has only a small kinetic isotope effect. However, there is rapid H/D exchange between methyl groups and water, most likely via the hydroxyl groups of aci-nitromethane, the enol tautomer of nitromethane. Hydrogen cyanide is a significant minor product over all three zeolite systems at temperatures around 300°C. With Co-ZSM5 its concentration tracks that of ammonia during the course of deactivation and the subsequent enhancement of HNCO hydrolysis when water is added. Nitromethane reacts much faster with NO_2 than with NO and O_2 over all three zeolites with complete conversion at ≈220°C to give almost entirely N_2 and CO_2 with Co-ZSM5 and Na-ZSM5 but with CO and N_2O formed as well over H-ZSM5. NO_2 may act by removal of strongly adsorbed decomposition products (NH_3 or HNCO) since the reaction of NH_3 with NO_2 is very fast with Co-ZSM5 and gives N_2 as the dominant product. The overall findings can be explained in terms of a scheme involving dehydration/hydrolysis reactions, largely on the aluminosilicate surface, followed by conversion of nitrogen-containing species to N_2 on the transition metal. A reaction scheme which can explain the observations has been developed and its implications with respect to the possible involvement of nitrocompounds in the corresponding SCR reactions of higher hydrocarbons over other catalysts is discussed.

Key Words: **nitromethane; Co-ZSM5; selective catalytic reduction; NO_x reduction.**

INTRODUCTION

The selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons in the presence of oxygen is of great current interest (1, 2). The reaction using higher hydrocarbons is potentially applicable to diesel engines and to lean burn petrol engines while that with methane to NO_x control on power stations and other fixed sources. The most studied catalysts with methane are cobalt exchanged ZSM5, ferrierite, and mordenite (3–6). With the first two catalysts there is a large deuterium kinetic isotope effect with the reaction of CH_4 proceeding at twice the rate of CD_4 (7, 8). Thus the rate-determining step is hydrogen abstraction. There is also infrared evidence to suggest that the abstraction site is adsorbed NO_2 (9–11) formed by oxidation of NO which has led to some agreement (9, 12–15) that the initial steps are

$$2NO + O_2 \rightarrow 2NO_2$$

$$CH_4 + NO_2(ads) \rightarrow CH_3 + HONO \quad (\text{or } OH + NO)$$

with the second rate determining. Aylor *et al.* (11, 16) have suggested that the second step on Co-ZSM5 is an insertion yielding adsorbed CH_3NO (which gives adsorbed cyanide and then N_2 by reaction with NO or NO_2), but it is unclear if that process would exhibit a kinetic isotope effect of the magnitude observed. The more usual proposal (9, 12–15) has been that a methyl species combines directly with adsorbed NO_2 yielding CH_3NO_2, nitromethane.

There have been several tests of the reactivity of nitromethane in connection with suggestions that the SCR reaction with higher hydrocarbons also proceeds with nitrocompounds as intermediates (17–20). This proposal seems to have been first put forward by Misono *et al.* (17) who

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showed that N_2 could be produced by the reaction of NO_2 with nitromethane adsorbed on Ce-ZSM5 at 150°C. It was subsequently found (18) that the oxidation of nitromethane over a variety of catalysts yielded N_2 and N_2O in a ratio that paralleled that seen during SCR with propene over the same catalysts, thus implying that the same type of adsorbed deposits were involved. This led to the suggestion that adsorbed nitrocompounds were formed during SCR and converted to isocyanic acid (HNCO) and cyanide species from which N_2 was formed. Subsequent work by Takeda and Iwamoto (21) has shown that HNCO adsorbed on Cu-ZSM5 can indeed react in that way. However, they also noted that the course of this reaction was different when water was present and raised the possibility that the adsorbed isocyanate was then converted to ammonia from which N_2 was derived by reaction with NO, NO_2, and O_2. This is in line with our observations that HNCO can yield NH_3 over Cu-ZSM5 (22) under continuous flow conditions and suggestions by Poignant *et al.* (23, 24) that adsorbed NH_3 participates in propane-SCR. In recent tests Hayes *et al.* (20) have also shown that nitromethane reacts readily over Cu-ZSM5 with N_2 as a product but they advance a route involving reductive elimination via a diazo intermediate.

The above ideas concerning the chemistry of nitromethane during hydrocarbon SCR need to be set against the most extensive study of its reaction over zeolites, that of Blower and Smith (25), under quite different conditions. They passed undiluted nitromethane over seventeen different metal exchanged X and Y zeolites at 300°C and found near complete decomposition in all cases. All materials (including Na-Y) gave a solid product, reported as a mixture of NH_4HCO_3 and $NH_4NH_2CO_2$, probably formed by the reaction of NH_3 and CO_2 in the low temperature trapping system, plus some CO, CO_2, N_2, and water. Thus it appears that zeolite frameworks in general can decompose nitromethane. In recent work (26) we have shown that this is indeed the case with Co-ZSM5 when nitromethane is fed diluted with helium alone. However, if O_2, or NO and O_2, are also present then all NH_3 is converted to N_2 above 360°C. This establishes one way in which methane-SCR could proceed through nitromethane. Lombardo *et al.* (27) have since confirmed these findings for Co-ZSM5 and shown that the same basic pathway exists with Cu-ZSM5, Fe-ZSM5, and H-ZSM5, although there are distinct differences in activity and product distribution.

The aim of the present work was to investigate the chemistry of the conversion of nitromethane over Co-ZSM5 in greater detail and to extend the study of the reaction to other catalysts and with NO_2 present as well. Some of the pathways found are related to those proposed for the decomposition of nitromethane adsorbed on alumina in a publication by Yamaguchi (28) which appeared subsequent to the completion of this work.

EXPERIMENTAL

Catalytic testing was carried out on 100 mg samples in a flow system using procedures which have been outlined previously (26). The reaction mixture (100 cm^3/min) was made by blending five streams controlled by electronic mass flowmeters. The NO, NO_2, and O_2 supplies were 1% standard mixtures in helium with the O_2 introduced closest to the reactor which limited upstream homogeneous oxidation of NO to NO_2 to <2% conversion. Two of the five streams could be diverted through four separate saturators containing H_2O (or D_2O) and CH_3NO_2 (or CD_3NO_2). The temperature of the saturators, and the flows through them, were set so as to give nominal concentrations of 1100 ppm for nitromethane and 2400 ppm for water. Mass balance calculations under conditions of total conversion indicated that the real concentration of nitromethane was probably somewhat less due to some inefficiency in saturation but within 10% of the nominal value.

The outlet of the reactor was sampled into a high speed micro gas chromatograph (MTI model M200) and also passed through a 16-cm pathlength infrared cell with all tubing between the reactor and the cell, and the cell itself, heated to $105 \pm 5°C$ using a combination of nichrome wire and heating tape. The gas chromatograph provided parallel analyses for O_2, N_2, CH_4, and CO (on a molecular sieve 5A column) and CO_2, N_2O, and C_2 hydrocarbons (on a Poraplot U column) with a detection limit of <3 ppm. The latter column also exhibited peaks for HCN and H_2O but only approximate concentrations could be obtained due to peak tailing and the absence of exact standards. The chromatograph was normally set up to analyse repeatedly with a cycle time of 2 min. Infrared spectra were recorded with a Mattson Cygnus 100 FTIR spectrometer equipped with an MCT detector set to repeatedly accumulate, display and save spectra after 64 scans at 0.25 cm^{-1} resolution on a cycle time of 2 min. The saved spectra were batch-processed at the end of each experiment to give concentrations. The species analysed and the spectral lines used for each were as follows: NO (1900.0 cm^{-1}), NO_2 (1630.3 cm^{-1}), NH_3 (average of 1007.5 and 992.8 cm^{-1}), CH_3NO_2 (1573.15 cm^{-1}), HNCO (average of 2274.6, 2279.3, and 2271.0 cm^{-1}) and HCN (712.25 cm^{-1}). Calibration for the first three was based on measurements against standard mixtures and that for the two nitromethanes against the concentrations provided by the saturators on bypass. HCN was determined by fitting against a series of synthetic spectra generated using the program MALT (29) which processes the HITRAN database (30), a procedure which should be accurate to better than 10%. HNCO was also determined by FTIR using an extinction coefficient estimated in previous work (31).

The procedure for the deuterium labelling experiments was the same, except that part of the exit stream from the infrared cell was sampled at 30 cm^3/min into a quadrupole mass spectrometer (Vacuum Generators Model 300SX) with a secondary electron multiplier and multiple ion monitoring. The system was set to repetitively acquire signals with m/z of 60 to 64 on a cycle time of 10 s. The relative amounts of the four nitromethanes were then calculated from the intensities of the signals after allowance for fragmentation, natural abundance ^{13}C and CHD_2NO_2 in the starting deutero material. The deuteronitromethane (>99% D) was from Stohler Isotope Chemicals and the D_2O (>99% D) from the Australia Nuclear Science and Technology Organisation.

The Co-ZSM5 (Si/Al ratio 11.2, 4.2 wt% Co, 110% exchange) and Co-ferrierite (Si/Al ratio 8, 91.5% exchange) catalysts were provided by Dr. J. Armor of Air Products and Chemicals. Further details of their preparation can be found elsewhere (4–6). The Na-ZSM5 (Si/Al = 11.9, 4.0% Na_2O) was a gift from Tosoh Corp. Analysis by proton induced X-ray emission showed that the only significant impurities in it were iron (≈0.013 wt%) and titanium(≈0.016 wt%). The corresponding hydrogen form was prepared by two exchanges with a solution of ammonium acetate followed by drying at 110°C and overnight calcination in air at 500°C. Samples suitable for activity tests were prepared by pressing the zeolite powders at 250 MPa (2500 kg/cm^2) for 1 min followed by crushing and sieving of the resultant discs to give a 300–600 μm particle fraction. The silica gel was Davison grade 62 (285 m^2/g, 160 to 180 μm) and the alumina Norton type SA-6173 γ-Al_2O_3 (200 m^2/g) crushed and sieved to 106 to 180 μm. All activity testing was carried out with 100 mg samples contained in a 4-mm ID Pyrex U-tube reactor pretreated overnight by drying under helium at 110°C and then heating to 500°C (at 5°C/min) in 10% O_2/He. After being held at that temperature for a minimum of 1 h the samples were cooled to reaction temperature in flowing helium.

RESULTS

Basic Reactions of Nitromethane over Co-ZSM5

Figure 1 shows the temperature dependence of the reaction of nitromethane over Co-ZSM5 on its own, with O_2 and with NO and O_2 together in terms of residual CH_3NO_2 and production of CO_2. The extent of reaction is similar for the three feeds and significant at 220°C which is approximately 130°C lower than required for the methane-NO_x SCR reaction over the same catalyst (4, 7). Above 320°C the carbon mass balance was complete within experimental error with carbon dioxide accounting for >90% of the carbon-containing products. Carbon monoxide was always small (35 ppm maximum at 270°C) but there were significant amounts of other minor products below 300°C as explained later.

The distribution between the major nitrogen-containing products under the same conditions is illustrated in Fig. 2. Ammonia is the principal product at temperatures below 340°C with all three feeds. Thus the net reaction in this temperature regime is largely decomposition,

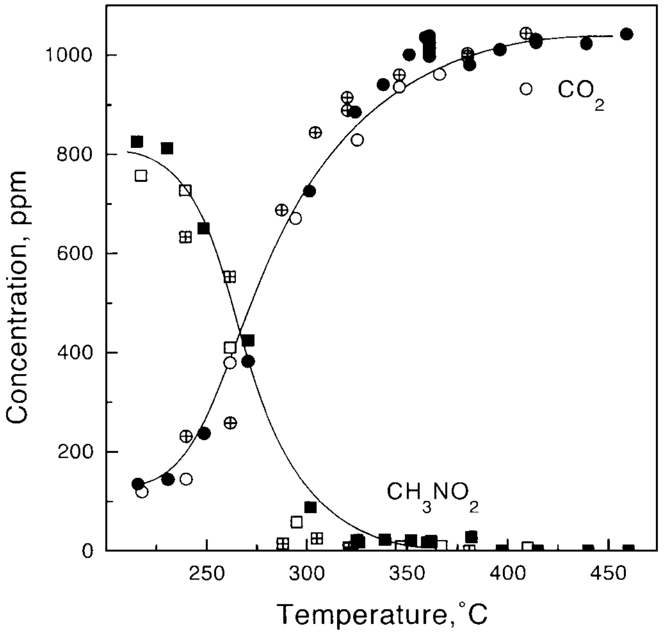


FIG. 1. CH_3NO_2 and CO_2 concentrations as a function of temperature during the reaction of 1100 ppm nitromethane over Co-ZSM5 with and without NO and O_2. Open symbols: CH_3NO_2 alone; crossed symbols: CH_3NO_2 with 2.9% O_2; solid symbols: CH_3NO_2 with 1000 ppm NO and 2.9% O_2.

$$CH_3NO_2 \rightarrow NH_3 + CO_2, \quad [1]$$

unassisted by O_2 or NO. In the absence of O_2 ammonia remains the dominant nitrogen-containing product at higher temperatures. In the presence of O_2, the concentration of ammonia declines steeply above 340°C and nitrogen becomes the chief nitrogen-containing product. These results are similar to those reported earlier (26), but the extent of N_2 formation using O_2 as compared to NO + O_2 is better defined. It is clear that more N_2 is formed in the latter case.

The results in Figs. 1 and 2 with O_2 present are in close agreement with the data of Lombardo *et al.* (27) but their data with NO present show a substantial enhancement in both the conversion and the yield of N_2. This could be due to differences in catalyst, NO concentration (2000 ppm versus 1000 ppm here) or possibly a greater extent of conversion of NO to NO_2. As shown later and in their work (27), NO_2 is much more effective than NO at converting nitromethane with N_2 as the dominant product under all conditions.

The conclusion that ammonia is being converted to N_2 by oxidation and/or a selective catalytic reduction reaction with NO or NO_2 has been tested experimentally as shown in Fig. 3. The reactions of NH_3 with O_2 and NO + O_2 are somewhat slower than that of nitromethane (dotted line) but much faster than that of methane with NO and O_2. The

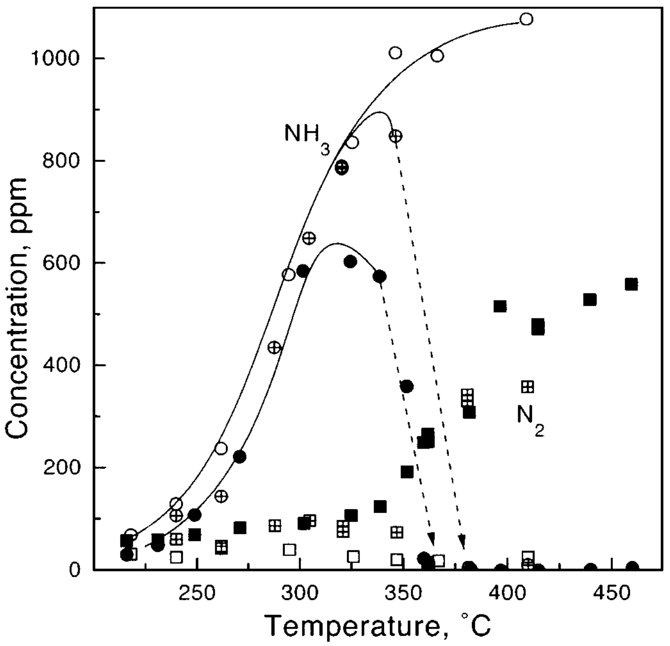


FIG. 2. NH_3 and N_2 concentrations as a function of temperature during the reaction of nitromethane in the experiments of Fig. 1. Open symbols: CH_3NO_2 alone; crossed symbols; CH_3NO_2 with 2.9% O_2; solid symbols: CH_3NO_2 with 1000 ppm NO and 2.9% O_2.

$NH_3/NO/O_2$ reaction (complete at ≈350°C) is slightly faster than the NH_3/O_2 one (complete by ≈380°C). The reaction of NH_3 with NO_2/O_2 is much faster still with complete conversion by 250°C. It may be a marginal contributor to the higher rate of the $NH_3/NO/O_2$ reaction as compared to the NH_3/O_2 one since oxidation of NO to NO_2 is noticeable over Co-ZSM5 at 350°C (8).

Figure 4 shows the product distributions for the three reactions of ammonia. That with O_2 alone (Fig. 4A) yields largely N_2 and NO with the amount of the latter passing through a maximum at ≈350°C. The decline in NO yield above that is probably due to its consumption by the $NH_3/NO/O_2$ reaction. That reaction (Fig. 4B) yields more nitrogen than that with O_2 alone, as expected, given the two sources of nitrogen. However, the NO/NH_3 consumption ratio is less than unity, leading to residual NO, some of which is converted to NO_2 above 350°C. The reaction of NH_3 with NO_2 (Fig. 4C) yields N_2 almost exclusively. It is noteworthy that for all three reactions the amount of nitrous oxide formed is much less than that of N_2 and that the N_2O/N_2 ratio is least with NO_2. This is not because N_2O is formed and then decomposed. Tests with N_2O, alone and in combination with NH_3, showed no reaction at 250°C.

Overall it is clear from Figs. 3 and 4 that ammonia can react with NO, O_2, and NO_2 over Co-ZSM5 in ways which are sufficient to account for the conversion of nitromethane to nitrogen via ammonia. Correspondingly, if any CH_3NO_2 was formed during the reaction of methane with NO and O_2 over Co-ZSM5 above the onset temperature for that reaction (≈350°C) then it would be rapidly converted to nitrogen via ammonia.

It would appear extremely unlikely that a rearrangement as complicated as that required for reaction [1] could take place in one step. Clues as to the processes involved arose from tests in which nitromethane was flowed over the catalyst for long periods at temperatures below 300°C. The measurements of Figs. 1 and 2 were carried out with temperatures chosen in random order allowing 30 to 60 min to reach a quasi-steady state at each temperature. The system was stable for much longer periods at temperatures above 300°C. As may be seen from the data in Fig. 5 for reaction in the presence of O_2 at 325°C, while carbon dioxide emerges almost instantly, that of ammonia is delayed by 40 min due to adsorption, during which time N_2 formation passes through a small maximum. Thereafter the system is stable with >90% conversion of nitromethane. Figure 6 shows the behaviour at 285°C. The reaction was apparently stable for ≈160 min with >90% conversion of CH_3NO_2, largely to CO_2 and NH_3 but with HCN and N_2 as significant minor products. Beyond that the yields of NH_3 and CO_2 started to decline, the concentration of unreacted CH_3NO_2 climbed and a new product, HNCO (isocyanic acid), appeared. Beyond 5 h the latter became the major nitrogen- and carbon-containing product. When 2400 ppm water was

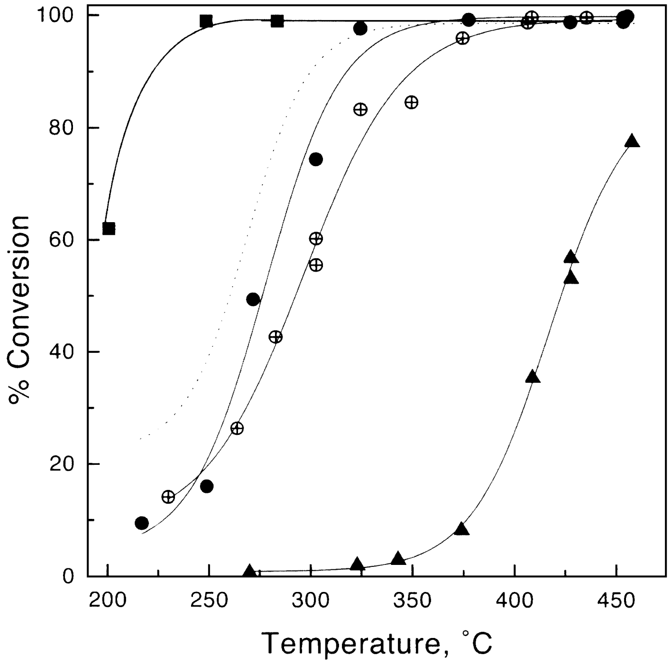


FIG. 3. Reaction of NH_3 with NO, NO_2 or O_2 as a function of temperature in comparison with those of CH_3NO_2 and of CH_4 with NO and O_2. ⊕ 500 ppm NH_3 with 2.9% O_2; ● 500 ppm NH_3 with 500 ppm NO and 2.9% O_2; ■ 500 ppm NH_3 with 500 ppm NO_2 and 2.9% O_2; ▲ 1040 ppm CH_4 with 1640 ppm NO and 2.6% O_2; dotted line 1100 ppm CH_3NO_2 with 1000 ppm NO and 2.9% O_2 as in Fig. 1.

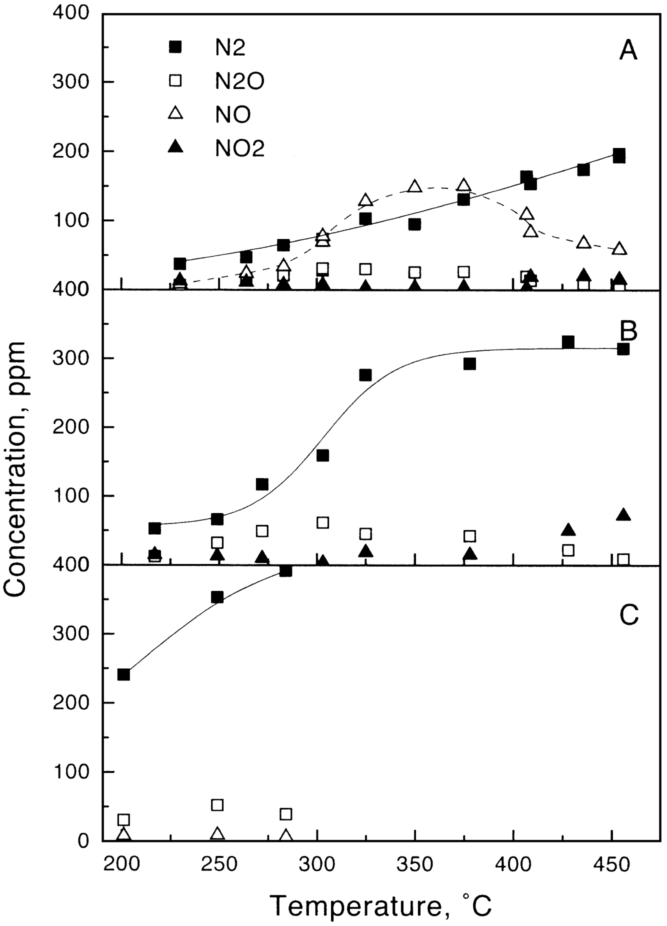


FIG. 4. Concentrations of nitrogen-containing products as a function of temperature during the reaction of ammonia with NO, NO_2, and/or O_2 under the conditions of Fig. 3: A, NH_3 with 2.9% O_2 alone; B, NH_3 with 500 ppm NO and 2.9% O_2; C, 500 ppm NH_3 with 500 ppm NO_2 and 2.9% O_2.

then added the concentration of HNCO fell steeply while those of NH_3 and CO_2 rose correspondingly. There was also a slight drop in the concentration of CH_3NO_2 but its conversion remained well below the starting one. It is clear that gaseous HNCO is hydrolysed in the presence of the added water but a deactivating species, which inhibits the decomposition of nitromethane, is still present on the catalyst.

Figure 7 shows the result of a similar experiment in which the temperature of the catalyst was raised to 360°C after exposure to water and then lowered back to 288°C. Formation of NH_3 and CO_2 exceeded that possible from the nitromethane concentration in the feed when the temperature first reached 360°C. In addition, the conversion of CH_3NO_2 and the yields of NH_3 and CO_2 were restored to their initial values on subsequent cooling to 288°C. Thus, exposure to water at 365°C was sufficient to remove the deactivating species. If water was present from the beginning then, as shown in Fig. 8, the reaction was stable for long periods at 288°C. This experiment included NO in the feed. As expected from Figs. 1 and 2 removal of this NO had no effect on CH_3NO_2 conversion or CO_2 formation, but there was a small increase in NH_3 concentration and a corresponding decrease in N_2 formation due to loss of the

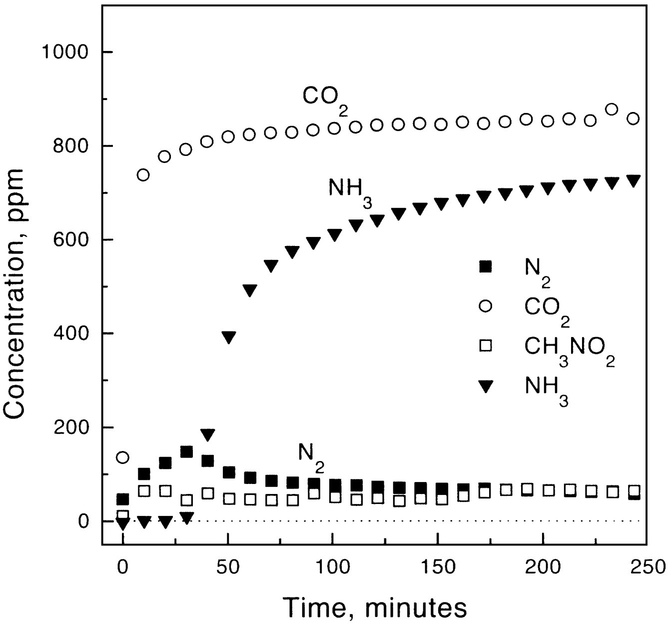


FIG. 5. Product distribution as a function of time on-line during the reaction of 1100 ppm nitromethane with 2.9% O_2 over Co-ZSM5 at 325°C.

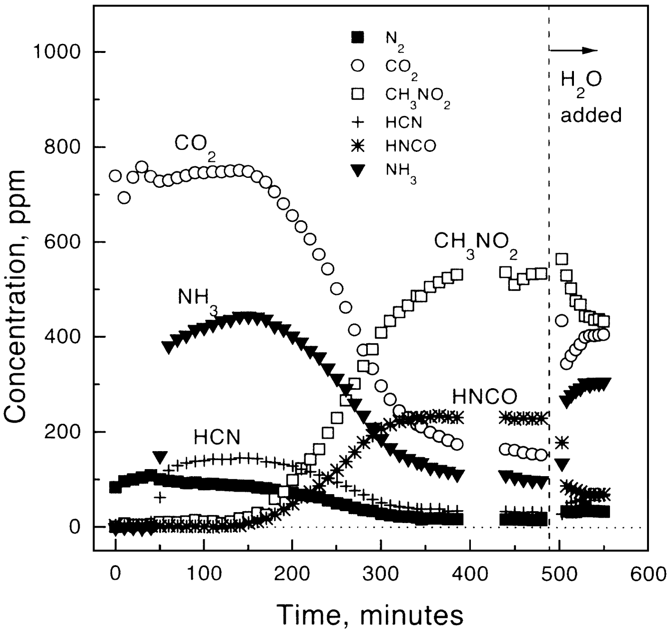


FIG. 6. Product distribution as a function of time on-line during the reaction of 1100 ppm nitromethane with 2.9% O_2 over Co-ZSM5 at 285°C with subsequent addition of 2400 ppm water at 285°C.

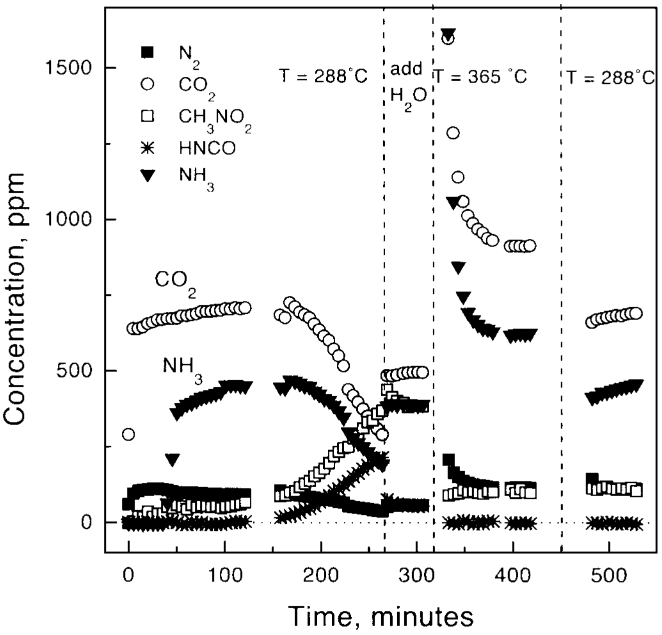


FIG. 7. Product distribution as a function of time on-line during the reaction of 1100 ppm nitromethane with 2.9% O_2 over Co-ZSM5 at 288°C under standard conditions with subsequent exposure to 2400 ppm water at 288°C and heating to 365°C.

$NH_3 + NO$ reaction. However, deletion of water was followed, after a period, by drops in CO_2 and NH_3 formation and breakthrough of HNCO and unreacted nitromethane.

We believe that the decomposition of CH_3NO_2 over Co-ZSM5 under the conditions used here is best explained by the scheme

$$\begin{array}{c} CH_3NO_2 \rightarrow HNCO + H_2O \rightarrow NH_3 + CO_2 \\ \downarrow\uparrow \\ (HNCO)_n \end{array} \qquad [2]$$

Below 300°C some of the HNCO initially generated is deposited, possibly as a polymer such as cyanuric acid ($n = 3$) which has a decomposition temperature of >300°C. This progressively blocks sites and poisons the activity for hydrolysis to NH_3 and CO_2. Added water increases the rate of hydrolysis and, if the temperature is sufficient for depolymerisation, the initial activity is restored.

The balance between polymerisation, depolymerisation, and hydrolysis is a delicate one. At temperatures below about 260°C slow continuous deactivation was observed even when the feed contained 2400 ppm water. The rates of hydrolysis and/or depolymerisation were then insufficient to prevent polymer buildup. A further factor which probably operates under dry conditions is separation of the H_2O and HNCO formed through CH_3NO_2 decomposition. If the water is carried through faster than HNCO then there will be an excess of the latter at the front of the catalyst bed and polymerisation, followed by progressive loss of decomposition activity, will proceed as seen in Fig. 6 for reaction at 288°C. The time required for deactivation was very temperature and catalyst dependent. Co-ferrierite behaved quite similarly to Co-ZSM-5 in respect of nitromethane decomposition but did not show deactivation and the transition to HNCO formation until after more than 12 h of reaction at 285°C.

Behaviour of Other Catalysts

Experiments with silica and alumina catalysts reinforced the above picture. It has been shown previously that HNCO can be formed in considerable yield by the reaction of H_2, NO, and CO over Pt/SiO_2 at temperatures from 230 to 300°C (31, 32). Thus SiO_2 must be a poor catalyst for hydrolysis of isocyanic acid. Figure 9 shows the behaviour of silica for the reaction of nitromethane in the presence of O_2. The activity is considerably less than that of Co-ZSM5 but conversions are still substantial above 300°C. Isocyanic acid is formed in larger amounts than NH_3 or CO_2 at 288 and 334°C. Thus silica, renowned for its general catalytic inertness, can decompose nitromethane at a rate faster than the hydrolysis of the initial reaction product, HNCO. However, although nitromethane decomposition is apparently a facile process it does require a catalyst. As we have shown previously the homogeneous decomposition does not commence until ≈400°C (26) and does not give CO_2 and NH_3 as products.

Our previous work with HNCO also established that alumina is a very good hydrolysis catalyst (32). Isocyanic acid

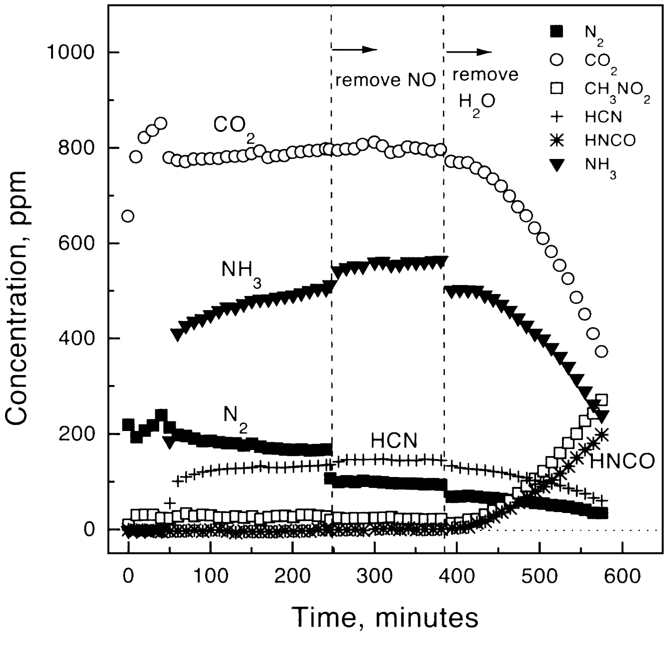


FIG. 8. Effect of removing NO and then H_2O during a reaction commenced with 1100 ppm nitromethane, 1000 ppm NO, 2400 ppm H_2O, and 2.9% O_2 over Co-ZSM5 at 285°C.

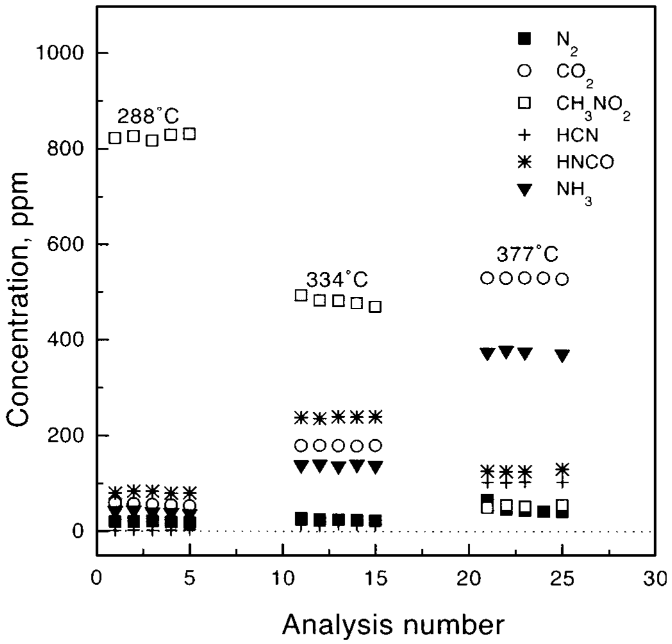


FIG. 9. Temperature dependence of the reaction of 1100 ppm nitromethane and 2.9% O_2 over SiO_2.

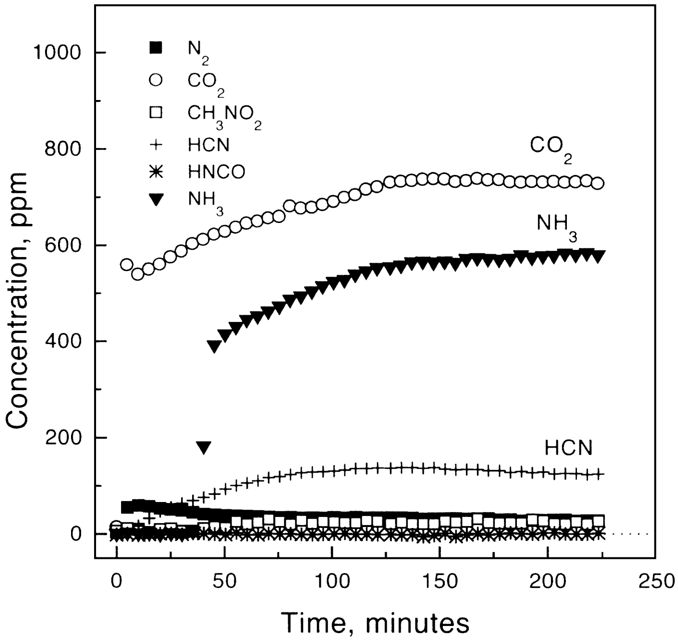


FIG. 11. Product distribution as a function of time on stream during the reaction of 1100 ppm nitromethane and 2.9% O_2 over H-ZSM5 at 290°C.

formed over Pt/SiO_2 is completely hydrolysed by Al_2O_3 placed downstream and Pt/Al_2O_3 gives NH_3 and CO_2 without trace of HNCO. Figure 10 shows the behaviour of alumina for the reaction of nitromethane and O_2 at 288°C. The system is stable with complete conversion to NH_3 and CO_2 even in the absence of water. H-ZSM5 (Fig. 11) was also stable although ammonia was slow to emerge presumably due to strong adsorption and HCN formation is noticeable. Na-ZSM5, on the other hand, exhibited less holdup of ammonia but substantial deactivation although without a noticeable concurrent breakthrough of HNCO (Fig. 12). There was, however, a shortfall in the nitrogen and carbon mass balances throughout, even when water was introduced. The most likely explanation is that HNCO is formed and accumulated more rapidly than with Co-ZSM5 because Na-ZSM5 lacks activity for HNCO hydrolysis.

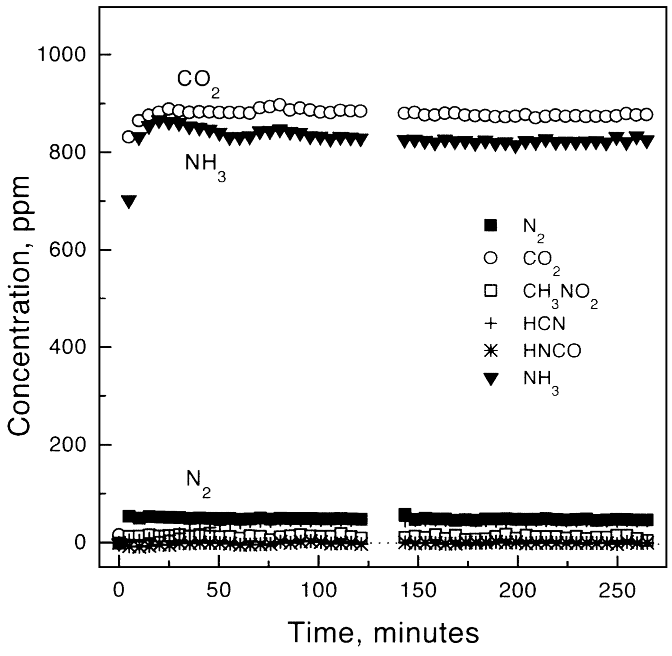


FIG. 10. Product distribution as a function of time on stream during the reaction of 1100 ppm nitromethane and 2.9% O_2 over Al_2O_3 at 286°C.

Thus the ability of Co-ZSM5 to convert nitromethane to ammonia is by no means unique. However, activity for the subsequent conversion of the ammonia to nitrogen is not so universal. While alumina, H-ZSM and Na-ZSM5 can make ammonia effectively there was only minor conversion to nitrogen below 400°C. It should be noted here that the Na-ZSM5 tested used by Lombardo *et al.* (27) was reported to be inactive for the reaction of nitromethane. There is no obvious reason for this difference from the present results. The impurity content of the Na-ZSM5 used here seems too low to account for it and its sodium content was very close to that expected from the Si/Al ratio.

HNCO Formation

A possible route for the conversion of nitromethane to HNCO is dehydration of its enol (aci-nitro) form, $CH_2{=}N(O)OH$, in a manner akin to that of the conversion of ethanol to ethylene for which alumina is an excellent catalyst. Experiments with deuterium containing feeds

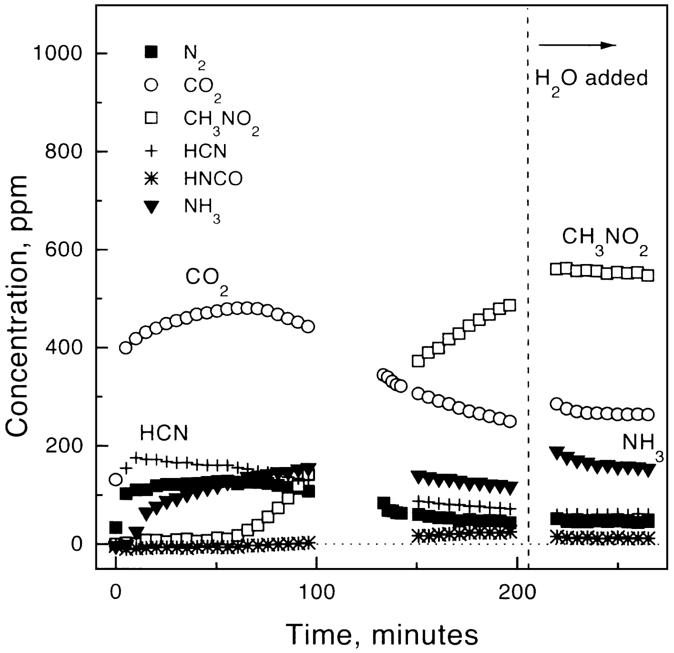


FIG. 12. Product distribution as a function of time on stream during the reaction of 1100 ppm nitromethane and 2.9% O_2 over Na-ZSM5 at 285°C.

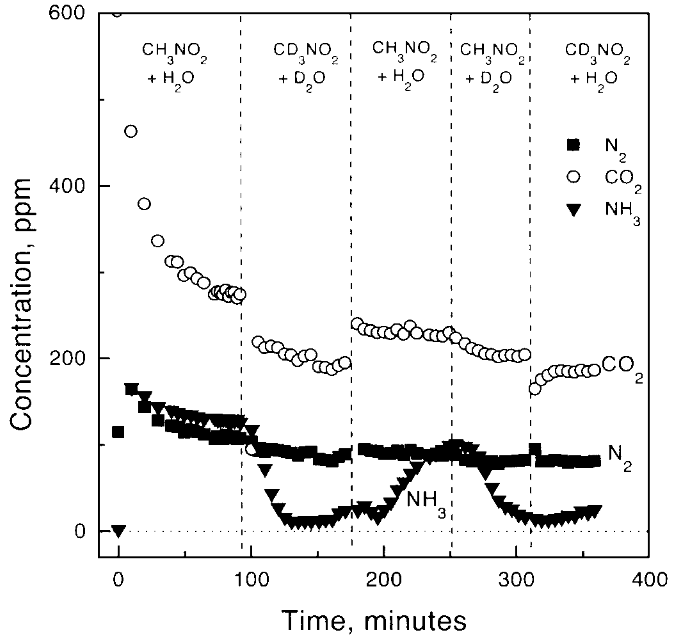


FIG. 13. Concentrations of N_2, NH_3, and CO_2 as a function of time during the reaction of mixtures of deuterium containing nitromethane (1100 ppm) and water (2400 ppm) with NO (1000 ppm) and O_2 (2.6%) over Co-ZSM5 at 255°C.

were carried out to explore enol formation and to test the possibility that the reaction of nitromethane might exhibit a kinetic isotope effect. In order to calculate meaningful relative rates for CD_3NO_2 versus CH_3NO_2 using the differential reactor approximation it was necessary to operate at low to moderate conversions. With Co-ZSM5 this required the use of temperatures below 260°C where some continuous deactivation was unavoidable even with water present. Figure 13 shows the behaviour at 255°C with water, NO and O_2 all present. The reaction was commenced with CH_3NO_2/H_2O, switched to CD_3NO_2/D_2O once the initial steep drop in activity was over and then back to CH_3NO_2/H_2O. Subsequent switches were made to mixed feeds, CH_3NO_2/D_2O and CD_3NO_2/H_2O. As may be seen, each switch was followed quickly by small changes to the concentrations of CO_2 and N_2 and much larger slower adjustments of NH_3. It was not possible to calibrate the FTIR for NH_2D, NHD_2, and ND_3. However, peaks due to each could be seen in spectra recorded in the changeover period and ND_3 was present in the greatest amount when the product distribution from the CD_3NO_2/D_2O mixture had stabilised.

The product stream was also monitored by mass spectrometry to determine the deuterium distributions in unreacted nitromethane. Figure 14 shows the concentrations of each during the interchanges between CH_3NO_2/H_2O and CD_3NO_2/D_2O, scaled so that the combined nitromethane concentration matched that expected from the nitromethane conversion. Each changeover is followed by transient formation of the D_1 and D_2 mixed species, CH_2DNO_2 and CHD_2NO_2. This implies rapid H/D exchange and the presence of a substantial pool of adsorbed nitromethane (and of water if it, too, contributes to the exchange). Analyses showed the presence of the mixed

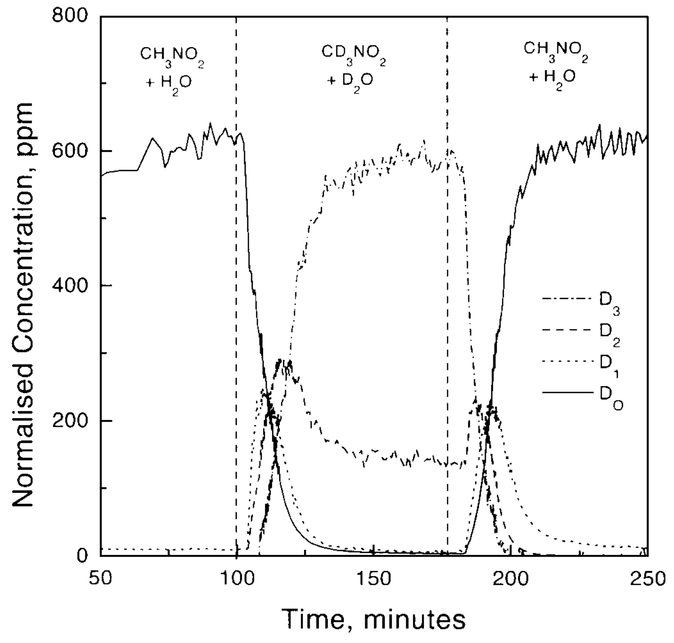


FIG. 14. Concentrations of CH_3NO_2 (D_0), CH_2DNO_2 (D_1), CHD_2NO_2 (D_2), and CD_3NO_2 (D_3) following interchanges between mixtures of CH_3NO_2/H_2O and CD_3NO_2/D_2O over Co-ZSM5 at 255°C during the experiments of Fig. 13.

TABLE 1

Product Concentrations and Deuterium Distribution for Reactions of Labelled Nitromethane/Water Mixtures over Co-ZSM5 at 255°C[a]

	Product concentration, ppm		Deuterium distribution in nitromethane, %			
Mixture used	CO_2	N_2	D_0	D_1	D_2	D_3
$CH_3NO_2 + H_2O$	270	105	>98	<2	0	0
$CD_3NO_2 + D_2O$	195	90	1	1	18	80
$CH_3NO_2 + H_2O$	230	90	98	2	0	0
$CH_3NO_2 + D_2O$	204	81	20	32	32	15
$CD_3NO_2 + H_2O$	185	80	21	32	29	17

[a] 1100 ppm nitromethane, 2400 ppm water, 1000 ppm NO, 2.9% O_2.

species in the steady state when feeding both CH_3NO_2/D_2O and CD_3NO_2/H_2O over the catalyst (although none was observed on bypass), so the H/D exchange is indeed between water and nitromethane.

The results of the labelling experiments are summarised in Table 1. After allowance for the continuous deactivation throughout the experiment, it appears that the ratio, rate (CH_3NO_2)/rate (CD_3NO_2), is 1.1 to 1.2 for CO_2 production and 1.0 to 1.1 for N_2. These values are not sufficiently different from unity to carry mechanistic significance, bearing in mind that the primary kinetic isotope effect associated with the detachment of H versus D in a rate-determining step would be approximately 4 at the temperature used (33). In respect of the amount of deuterium in unreacted nitromethane, it is clear that the two mixed feeds gave rise to similar distributions. Thus there was extensive exchange, as might be expected, if the nitro to aci-nitro interconversion was rapidly reversible. While the exchange was certainly substantial it may not be fully at equilibrium. In that situation one would expect more deuterium in the nitromethane when feeding 1100 ppm CH_3NO_2/2400 ppm D_2O (a D/H ratio of $\approx 3:2$ in the feed) than when feeding CD_3NO_2/H_2O (D/H of $\approx 2:3$), rather than near equality as observed.

Minor Products

As may be seen from Fig. 6, HCN is a significant minor product of the reaction of nitromethane over Co-ZSM5 at 285°C and first appears when NH_3 breaks through. It was present in much smaller amounts in the experiment of Fig. 5 at 325°C (<55 ppm) and below the detection limit of 10 ppm above 380°C. The linkage between HCN and NH_3 was most clearly seen in experiments in which water was introduced while the catalyst was in its initial deactivation phase and then subsequently removed. Figure 15 shows the distribution of nitrogen-containing products in one such experiment at 288°C. Hydrogen cyanide appears at the same time as ammonia and, allowing for the difference in scale, is present at approximately one-third the concentration during both the initial period of stability and the subsequent deactivation. Introduction of water leads to loss of most HNCO and sharp rises in the concentration of HCN and NH_3. Both decline steeply when water is removed and HNCO reappears as a result.

Hydrogen cyanide was also detected when using other catalysts as shown in Figs. 10 to 12, but concentrations, both absolute and relative to ammonia, varied substantially. Table 2 shows a comparison of product distributions after 1 to 2 h on stream with a dry feed. With silica, which produces more HNCO than ammonia, HCN was below the detection limit at both 288 and 335°C. The concentration of HCN was also low with alumina, even though this catalyst produced the most ammonia. However, H-ZSM5, which resembles alumina in terms of stability and NH_3 formation, gave as much HCN as Co-ZSM5 while Na-ZSM5, which deactivates (Fig. 12), formed more HCN than NH_3 at the point of comparison. Thus while HCN is a significant product, with the zeolite-based catalysts, and tracks ammonia with Co-ZSM5, it seems more likely that the latter relationship reflects kinetics and adsorbed species rather than

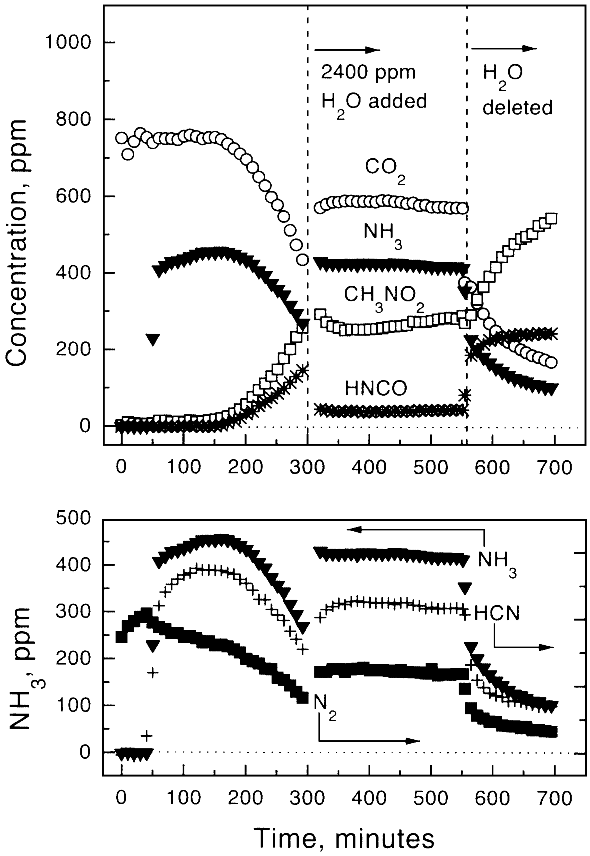


FIG. 15. Relationship between HCN and NH_3 following the addition and deletion of 2400 ppm water during the reaction of 1100 ppm nitromethane over Co-ZSM5 at 293°C.

TABLE 2

Exit Gas Composition for Reaction of Nitromethane in the Presence of Oxygen[a]

Catalyst	T°C	Stability	Concentration, ppm						
			CH_3NO_2	CO_2	NH_3	N_2	HNCO	HCN	CO
Co-ZSM5	285	Unstable	<20	750	435	90	<20	140	30
Na-ZSM5	285	Unstable	<20	480	140	125	<20	150	30
H-ZSM5	290	Stable	<40	730	575	30	<10	130	80
Al_2O_3	286	Stable	<20	880	840	50	<10	40	23
SiO_2	288	Stable	825	55	40	20	80	<10	<10
SiO_2	335	Stable	480	180	140	<25	240	<20	<10

[a] 1100 ppm CH_3NO_2 and 2.9% O_2 after 1 to 2 h on-stream.

thermodynamic equilibrium. One other difference between the catalysts, also pointed out by Lombardo *et al.* (27) is that H-ZSM5 produces more CO than the rest.

Reactions of Nitromethane with NO_2

As illustrated by Figs. 1 to 3 the reaction of CH_3NO_2 over Co-ZSM5, either alone or in combination with NO/O_2, becomes insignificant below 200°C. However, nitromethane does react readily with NO_2 at much lower temperatures. Figure 16 shows the result of one experiment at 138°C with O_2 also present. The initial conversion of nitromethane exceeded 90% with CO_2 and N_2 as the major products. Ammonia was barely detectable while the N_2O/N_2 ratio was small as with the reaction of NH_3 with NO_2 (Fig. 4C). The amount of carbon monoxide formed relative to that of carbon dioxide was higher than in experiments with NO and O_2. The system was stable for ≈120 min before it deactivated steadily to 15% conversion. In an experiment at 219°C there was no deactivation with >95% conversion of CH_3NO_2 and 75% conversion of NO_2. Similar results were obtained using CH_3NO_2 and NO_2 alone so the reaction does not require the presence of O_2. Approximate mass balance calculations indicated that more nitrogen was derived from CH_3NO_2 (≈60%) than NO_2 (≈40%) and that the stoichiometry to the major products is approximately

$$8CH_3NO_2 + 6NO_2 \rightarrow 7N_2 + 8CO_2 + 12H_2O. \quad [3]$$

This facile reaction of nitromethane with NO_2 was not confined to Co-ZSM5. Our samples of Na-ZSM5, H-ZSM5, and alumina were also stable above 220°C and exhibited near complete conversion of nitromethane although the product distributions differed (Table 3). Na-ZSM5 behaved similarly to Co-ZSM5 but with larger amounts of N_2O and HCN. H-ZSM5 was considerably different. The amount of CO produced exceeded that of CO_2 while N_2O approached that of N_2. Unlike the other zeolites it also yielded significant concentrations of NO at the steady state but almost no HCN.

DISCUSSION

General Considerations

The present work shows that nitromethane can be readily converted to nitrogen over Co-ZSM5 in two ways. One is by

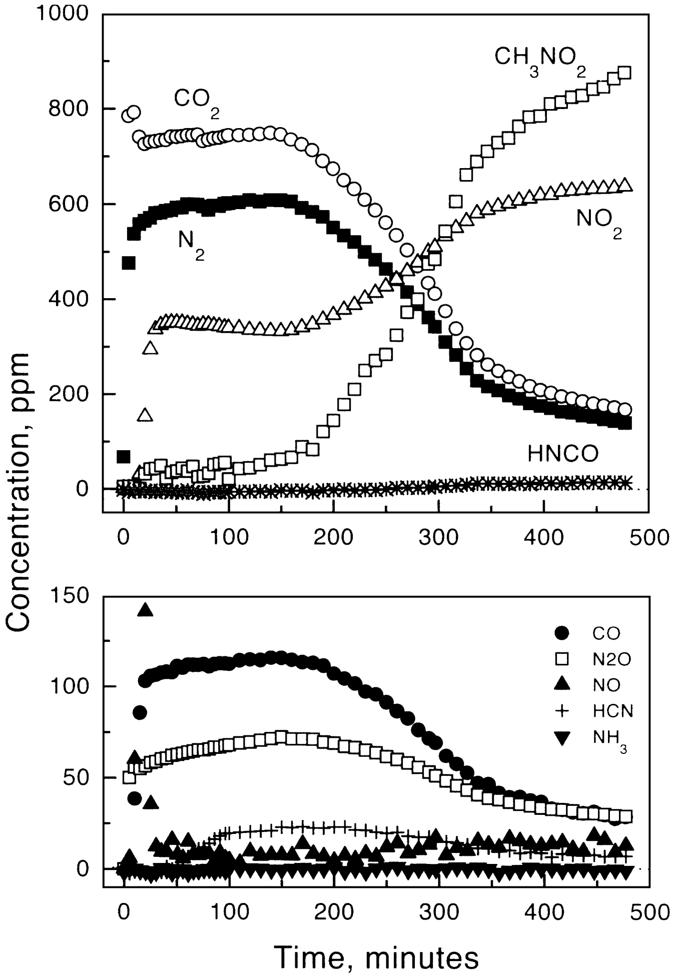


FIG. 16. Product distribution as a function of time during the reaction of 1100 ppm CH_3NO_2 with 825 ppm NO_2 and 2.9% O_2 over Co-ZSM5 at 138°C.

TABLE 3

Exit Gas Composition for Reaction of Nitromethane with NO_2 and O_2[a]

		Concentration, ppm							
Catalyst	T°C	CH_3NO_2	CO_2	CO	N_2	N_2O	NO	HCN	NH_3
Co-ZSM5	219	<30	860	125	770	44	34	<20	<40
Na-ZSM5	211	<20	816	135	700	105	45	46	<40
H-ZSM5	239	<15	420	550	440	365	190	<20	<20
Al_2O_3	324	<15	850	70	560	95	68	32	<80

[a] 1100 ppm CH_3NO_2, 825 ppm NO_2, and 2.9% O_2.

decomposition to ammonia followed by reaction with NO and/or O_2 as exemplified by Fig. 2 and outlined previously (26), i.e.,

$$CH_3NO_2 \rightarrow NH_3 + CO_2 \qquad [4]$$

$$NH_3 + NO\ (+\ O_2) \rightarrow N_2 + H_2O. \qquad [5]$$

The second is through a reaction between CH_3NO_2 and NO_2 (Fig. 16) with the approximate stoichiometry given in Eq. [3]. Of these processes only the conversion of NH_3 to N_2 requires the transition metal. The decomposition of CH_3NO_2, and its reaction with NO_2, also proceeds on alumina, H-ZSM5, and Na-ZSM5 (Figs. 10 to 12 and Table 3), and also Cu-ZSM5 and Fe-ZSM5 (27). Even silica has some activity for the initial decomposition (Fig. 9). Blower and Smith (25) have also shown that many metal-exchanged X and Y zeolites are active for nitromethane decomposition at 300°C. Thus decomposition appears to be a facile reaction for which aluminosilicates in general are active catalysts.

A notable characteristic of the reaction of CH_3NO_2 over Co-ZSM5 (and Na-ZSM5) in the absence of NO_2 is deactivation at temperatures below 300°C. With Co-ZSM5 this deactivation is accompanied by the appearance of HNCO (Figs. 6 to 8) which can be halted by the addition of water which hydrolyses HNCO to NH_3 and CO_2 (Figs. 6, 7, 15). This behaviour, coupled with the observation of HNCO as the major product with silica, but NH_3 and CO_2 with alumina, strongly suggests that HNCO is an intermediate in the conversion of CH_3NO_2. Deactivation can then be attributed to the buildup of deposits (possibly cyanuric acid, the cyclic trimer of HNCO) as given by Eq. [2].

In past work with H_2/NO/CO mixtures over Pt/Al_2O_3 (34) we have shown that the hydrolysis of HNCO to NH_3 and CO_2 occurs via Al-NCO groups and a similar involvement of surface isocyanates seems likely when reacting nitromethane. The ability of γ-Al_2O_3 (and H-ZSM5) to completely hydrolyse HNCO for long periods presumably reflects high concentrations of hydroxyl groups and the availability of surface acid sites. Conversely, the inability of Co-ZSM5 and Na-ZSM5 to sustain complete HNCO hydrolysis for more than an hour or two at <300°C (Figs. 6, 7, 12, and 15) can be attributed to a paucity of hydroxyl groups while the low activity of silica (Fig. 9) arises through catalytic inertness rather than lack of hydroxyl groups.

Conversion of CH_3NO_2 to HNCO

Given the wide range of materials over which nitromethane reacts, it seems that mechanistic explanations for the conversion of HNCO should be sought in terms of the general properties of aluminosilicate surfaces. The data in Fig. 14 and Table 1 reveal that reaction in the presence of D_2O over Co-ZSM5 is accompanied by extensive deuterium exchange into unreacted nitromethane. This can be explained in terms of interconversion between the nitro and aci-nitro forms

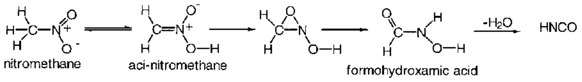
$$CH_3NO_2 \rightleftharpoons CH_2{=}N(O)OH \qquad [6]$$

with exchange of the hydroxyl of the latter. Such exchanges are usually very rapid on oxide surfaces and can occur on acid or base sites. For nitromethane these processes could be written as

$$\begin{aligned} CH_2{=}N(O)OH + D^+ &\rightarrow CH_2{=}N(O)OHD^+ \\ &\rightarrow CH_2{=}N(O)OD + H^+, \\ CH_2{=}N(O)OH + B &\rightarrow CH_2{=}N(O)O^- + BH^+(\rightleftharpoons BD^+) \\ &\rightarrow CH_2{=}N(O)OD, \end{aligned}$$

respectively. In the gas phase the nitro form of nitromethane is more stable than its aci-nitro counterpart by 14 kcal/mole (35). However, theoretical calculations (36) indicate that the difference is reduced to 7 to 8 kcal/mol on MgO and CaO surfaces and that the nitronate (enolate) ion, $CH_2{=}N(O)O^-$, should be more stable than both. The ion has been observed directly on both these oxides by NMR (37) and on alumina by both FTIR and NMR in the recent study of Yamaguchi (28), where it was proposed that O^{2-} ions were the abstracting species. The nitronate ion is not observed when nitromethane is adsorbed on H-ZSM5 (37), but heating to 473 K does give ammonia and carbon dioxide as observed with the three oxides.

By analogy with Brønsted or Lewis acid catalysed dehydration of alcohols on silica-alumina and alumina (38, 39) dehydration of the aci-nitro form could proceed from either the protonated or anionic intermediates above. However, in either case the direct product would be HCNO (fulminic acid) rather than HNCO, as observed. Rapid isomerisation may be possible since HCNO is extremely unstable with respect to polymerisation and isomerisation to HNCO, even as a gas at room temperature and low pressure (40). Blower and Smith (25) have suggested that a cyclic intermediate might be formed, in which case isomerisation prior to dehydration could be formulated as



Passage through a three-membered oxaziridine ring from the aci-nitro form transfers one oxygen from nitrogen to carbon and one hydrogen from carbon to oxygen giving formohydroxamic acid so that subsequent dehydration gives HNCO rather than HCNO. Dehydration of formohydroxamic acid to HNCO should be easier than the corresponding dehydration of aci-nitromethane to HCNO on bond strength grounds given the relative weakness of the carbonyl CH bond.

Standard organic reactions which can also achieve the same conversions are known. Primary nitroparaffins can be converted to hydroxamic acids by reaction with sulfuric acid (41), a variant of the Nef reaction. The hydroxamic acid can be isolated but under the conditions usually used it is hydrolysed to a carboxylic acid and hydroxylamine, i.e.

$$\mathrm{CHO{-}N(R)OH} + \mathrm{H_2O} \rightarrow \mathrm{RCOOH} + \mathrm{NH_2OH}. \quad [7]$$

However, dehydration to an isocyanate might be more probable at higher temperature with a solid catalyst. Such a dehydration is equivalent to the Lossen rearrangement for the conversion of O-acyl derivatives of hydroxamic acid to isocyanates by reaction with base or through heating alone (42):

$$\mathrm{R'{-}CO{-}N(H){-}O{-}CO{-}R} \rightarrow \mathrm{R'NCO} + \mathrm{RCOOH}.$$

It is possible to envisage various experimental tests by which the above possibilities could be distinguished but in their absence the situation must remain speculative.

Formation of HCN and Other Products

The apparent relationship between HCN formation and ammonia (Fig. 15) is interesting. One possible reason is the well-known synthesis of nitriles by thermal decomposition of ammonium carboxylate salts (43) as seen, for example, during the retorting of oil shales which contain ammonium feldspars and organic acids (44). In the present case it would proceed via formamide ($\mathrm{NH_2{-}CHO}$) as

$$\mathrm{NH_4^+} + \mathrm{HCOO^-}\ (\text{or } \mathrm{NH_3} + \mathrm{HCOOH}) \rightleftharpoons \mathrm{NH_2{-}CHO} + \mathrm{H_2O}, \quad [8]$$

$$\mathrm{NH_2{-}CHO} \rightleftharpoons \mathrm{NH{=}CHOH} \rightleftharpoons \mathrm{HCN} + \mathrm{H_2O}. \quad [9]$$

Again the intermediate is an enol. The slow breakthrough the ammonia in, for example, Figs. 5 to 8 and 11, indicates that considerable amounts are adsorbed on Co-ZSM5 and H-ZSM5, quite possibly in the $\mathrm{NH_4^+}$ form. Formation of adsorbed formate from adsorbed nitromethane was detected by both FTIR and NMR in the study of Yamaguchi (28) and several routes to it can be envisaged for Co-ZSM5. One is hydrolysis of formohydroxamic acid in the way referred to above (Eq. [7]). Another would be dissociation of nitromethane to CH_3 and NO_2 with subsequent reaction of the methyl with O_2 or NO_2 to give CH_3O and then formate. Previous modelling has indicated that formation of a methoxy species is the major pathway in the purely homogeneous reaction of $CH_3NO_2/NO/O_2$ mixtures above 450°C (26), but there is no direct experimental evidence for its occurrence in the catalytic systems. Dehydration of adsorbed formic acid or formates would offer an explanation for the formation of carbon monoxide seen with some catalysts. It is noteworthy that H-ZSM5, the most acidic material, also produces the most CO (Table 2).

Aylor *et al.* (11, 16) have proposed that cyanide species are formed from nitrosomethane (CH_3NO) during the methane/NO_x reaction over Co-ZSM5 by reactions on a cobalt site. The present work showing that nitromethane dehydrates very readily on zeolite surfaces raises other possibilities. The enol form of nitrosomethane, formaldoxime ($\mathrm{CH_2{=}NOH}$), is more, not less, stable than the keto form (the reverse of the situation with nitromethane). Oximes are readily dehydrated to give nitriles (45):

$$\mathrm{CH_2{=}NOH} \rightleftharpoons \mathrm{HCN} + \mathrm{H_2O}. \quad [10]$$

However, under acidic conditions oximes can also be converted to amides by the Beckmann rearrangement (46), i.e.,

$$\mathrm{CH_2{=}NOH} \rightarrow \mathrm{NH_2{-}CHO}, \quad [11]$$

from which HCN could be formed as described by Eq. [9]. It seems quite possible that the adsorbed cyanide seen by Aylor *et al.* (11, 16) during methane-SCR could have arisen from the HCN formed in one of these ways, but it would imply that $HCN/NO/O_2$ mixtures should be converted to N_2 over Co-ZSM5. We know of no experimental test for this. It seems unlikely that dehydration of formaldoxime is the source of the HCN seen in the present experiments, however, since that would require reduction of nitromethane, presumably by NH_3, given the observed linkage between the formation of HCN and NH_3.

Reaction of CH_3NO_2 with NO_2

There are few similar clues to the steps involved in the reaction between CH_3NO_2 and NO_2 which exhibits near total conversion to N_2 over Co-ZSM5 at 219°C (Table 3), even though the corresponding reaction with NO and O_2 is minimal under the same conditions (Fig. 1). Na-ZSM5 and H-ZSM5 are also active at similar temperatures (Table 3). One possible explanation is that nitromethane decomposition occurs readily at these temperatures even in the absence of NO_2 but the immediate reaction products, isocyananic acid, and NH_3, are too strongly bound to desorb and hence the reaction sites are poisoned to further reaction. If NO_2 was able to react with these bound products to give N_2 then the reaction would proceed continuously. This seems feasible given that the reaction of NH_3 with NO_2 (Figs. 3 and 4) is fast enough the account for N_2 below 200°C and that Yokoyama and Misono (18) have shown that NO_2 will react with nitromethane adsorbed on Ce-ZSM5 at temperatures as low as 150°C. The slow onset of deactivation over Co-ZSM5 at 138°C even with NO_2 present (Fig. 16) would imply that site blockage and clearance are close to balance at this temperature with blockage eventually taking over. If the above explanation is not correct then one needs to postulate a direct reaction between NO_2 and adsorbed nitromethane or aci-nitromethane but we can find no well-established precedent for the chemistry which might be involved.

Thus a set of reactions consistent with our data for the reactions of nitromethane is

$$CH_3NO_2 \leftrightharpoons CH_2{=}N(O)OH \qquad [6]$$

$$CH_2{=}N(O)OH \rightarrow CHO{-}N(H)OH \quad \text{(formohydroxamic acid)} \qquad [12]$$

$$CHO{-}N(H)OH \rightarrow HNCO + H_2O \qquad [13]$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad [14]$$

$$NH_3 + NO\,(+\,O_2) \rightarrow N_2 + H_2O \qquad [5]$$

$$CHO{-}N(H)OH + H_2O \rightarrow HCOOH + NH_2OH(\rightarrow N_2) \qquad [7]$$

$$NH_3 + HCOOH \rightarrow HCN + 2H_2O \quad (\text{via } NH_2{-}CHO) \qquad [8], [9]$$

$$HCN \quad (\text{or as adsorbed CN}) + NO\,(+\,O_2) \rightarrow N_2 + CO_2 \qquad [15]$$

$$NH_3 + NO_2 \rightarrow N_2 + H_2O \qquad [16]$$

$$HNCO \quad (\text{or as adsorbed NCO}) + NO_2 \rightarrow N_2 + CO_2. \qquad [17]$$

The reactions involving N_2 formation are themselves complex and are shown in nonstoichiometric form. The first five equations describe the conversion of nitromethane to N_2 with NO and O_2 present. They are very similar to those in the scheme of Lombardo *et al.* (27), except that they propose that formohydroxamic acid is converted to HNCO via carbamic acid ($NH_2{-}COOH$). This also seems possible although in conventional chemistry carbamic acids are regarded as intermediates in the hydrolysis of isocyanates to amines rather than in isocyanate formation (47). Equations [7], [8], [9], and [15] are proposed for the formation and removal of HCN. Equations [16] and [17] allow for the high rate of reaction of nitromethane with NO_2.

Implications for Methane and Higher Hydrocarbon-SCR

Two conclusions can be drawn from the present work concerning the mechanism of the methane/NO_x reaction over Co-ZSM5. The first is that nitromethane is converted sufficiently fast to be an intermediate in the process as originally proposed by Li *et al.* (9). The conversion to N_2 could proceed either by decomposition to ammonia and further reaction of the latter with NO and O_2 or through a reaction with NO_2. The latter is certainly a possibility during methane-SCR since significant amounts of NO_2 are present in the exit gas from that process over both Co-ZSM5 and Co-ferrierite (7, 8). However, feasibility is not proof and other methods will be required to assess the actual involvement of CH_3NO_2 versus alternative intermediates such as CH_3NO which could also arise from the original CH_3 species or through reaction of CH_4 with adsorbed NO_2 as proposed by Aylor *et al.* (11, 16). They have presented convincing infrared evidence that the methane-SCR reaction is more likely to proceed via surface cyanide species than isocyanate ones. However, those conclusions were based on tests in which the adsorbed species were reacted with NO/NO_2 in the absence of water and may not be realistic for methane-SCR which gives rise to water which could hydrolyse isocyanates. The second conclusion is that the initial stages of the further conversion of CH_3NO_2, and by inference CH_3NO, do not require the transition metal. Aluminosilicates of many types seem to suffice. However, the transition metal is still needed for subsequent conversion of the species generated by decomposition, NH_3 and HCN, for example, to N_2 if only if NO and O_2 are available for oxidation.

While the above observations can be taken as general support for propositions (17, 18, 20, 48) that SCR using higher hydrocarbons, over Ce-ZSM5 and Cu-ZSM5, for example, may also involve nitrocompounds, the ideas may not be fully transferable to those systems for two reasons: One is the temperature difference. With Cu-ZSM5 it is possible to achieve substantial NO_x conversions using propene, or a reactive paraffin such as isobutane, at temperatures below 300°C, whereas 400°C or more would be necessary for the same extent of reaction with methane over Co-ZSM5. The lower temperature may be insufficient to drive some of the degradation chemistry of nitro or nitroso compounds unless NO_2 is present. A possible difficulty here is that the SCR reaction with isobutane does not exhibit a deuterium kinetic isotope effect (22), implying that hydrogen abstraction is not the rate-limiting step, from which it might be inferred that generation of the abstraction site (adsorbed NO_2) is slow. This indicates that NO_2 concentrations are likely to be low and this is the case experimentally (22, 49).

The second difficulty relates to the hydrocarbon structure. This can be explained with reference to the ideas of Adelman *et al.* (50, 51) concerning SCR using propane. They propose that the initial abstraction (by an adsorbed nitro group) is from the 2-position generating a secondary propyl radical which combines with NO to form 2-nitrosopropane with subsequent enolisation to its oxime

$$CH_3CHCH_3 + NO \rightarrow (CH_3)_2C(H)NO \rightarrow (CH_3)_2C{=}NOH.$$

This oxime lacks an α-hydrogen and cannot easily dehydrate to a nitrile which closes off one path available with CH_3NO (that to give HCN, reaction [10]), although it could be hydrolysed to acetone and hydroxylamine (52). It can also undergo the Beckmann rearrangement to N-methylacetamide (46),

$$(CH_3)_2C{=}NOH \rightarrow CH_3C(O){-}N(H)CH_3,$$

as was seen by Adelman *et al.* (51) in the absence of NO. Again this cannot be dehydrated to the nitrile but it can hydrolyse (to methylamine and acetic acid as per the reverse of Eq. [8]). Isobutane could not start down either of these routes if the initial hydrogen abstraction was from the central carbon since the resultant tertiary nitroso structure cannot undergo enolisation to an oxime. Similar considerations apply in respect the conversion of nitrocompounds. Isocyanates cannot be formed from ones with a secondary or tertiary structure. In these cases further reaction of nitroso or nitro intermediates seemingly requires intervention of more NO or NO_2. Of course one might argue that the initial abstraction is from an end carbon (on steric grounds and because primary radicals are thermodynamically favoured over secondary or tertiary ones) in which case there are no restrictions on nitrile or isocyanate formation. Similar considerations apply with olefins as in the proposal of Radtke *et al.* (53) that propene reacts via the allyl radical.

If it is accepted that the initial steps in higher hydrocarbon-SCR involve formation of a nitro (or nitroso) species then two fundamentally different modes for the subsequent conversion to N_2 can be envisaged. One is through decomposition/dehydration/hydrolysis etc. to give isocyanates, oximes, amines, hydroxylamines, nitriles, etc., as discussed above and in the literature (53), followed by conversion of these degradation products to nitrogen by reaction with NO, NO_2, and O_2. There are established precedents for the last step, both catalytically, through SCR using NH_3 (54, 55) and the conversion of nitriles to N_2 (56), and also in the gas phase, as in the reaction of NCO with NO etc. (57, 58). Radkte *et al.* (53, 59–62) have established the conditions under which unreacted fragments are observed as trace products over different catalysts. The alternative possible path is via further attack on the initial nitrogen-containing species by another nitrogen containing species with formation of a N–N bond, either directly or subsequently from within the species formed. It would seem that such a route may be required if the nitro (or nitroso) species formed initially is a tertiary one. There are no good guides in organic chemistry as to how formation of N_2 might occur in this way but there are several ideas that have been developed in the recent SCR literature. In the scheme of Adelman *et al.* (50) for the reaction of propane, a secondary oxime forms a N–N bond by reaction with NO and this is eliminated as N_2O which is further converted to N_2. Hayes *et al.* (20) suggest that a nitro compound is first reduced to a hydroxylamine which then combines with R-NO to give a diazo compound which eliminates nitrogen. Kharas *et al.* (63), through analogy with organometallic models, proposed insertion of 2 NO on an alkyl species at a copper centre to form a coordinated N-nitroso-N-alkylhydroxylamate species which decomposed to N_2, CO_2, etc. Some of these proposals specifically involve intervention of a transition metal site which the present results indicate may not be absolutely essential for nitrogen formation during the reaction of NO_2 with nitromethane (although they might still be needed for the conversion of NO to NO_2). It may be possible to distinguish between some of the above possibilities through further work with compounds having structures similar to potential intermediates but definitive results and linkage to sites on the catalyst surfaces could well be quite elusive given the speed with which many of the reactions are likely to proceed.

CONCLUSIONS

The conclusion from the present work is that nitromethane reacts readily over Co-ZSM5 at temperatures well below that required for the methane-NO_x SCR reaction. Above ≈220°C decomposition gives NH_3 which can react further to give nitrogen. The corresponding reaction of CH_3NO_2 with NO_2 commences below 150°C. It is possible to formulate a plausible reaction scheme for many of the steps involved, but those involving NO_2 are obscure. Further work will be required to show if the processes seen are applicable with other hydrocarbon-NO_x SCR catalyst systems and to evaluate their significance relative to other possible pathways, via initial formation of CH_3NO for example.

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