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The Possible Role of Nitromethane in the SCR of NO_x with CH_4 over M-ZSM5 (M = Co, H, Fe, Cu)

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The reactions of nitromethane with NO_2 or NO in the presence of excess O_2 have been studied and the results compared over four catalysts: Co-, H-, Fe-, and CuZSM-5. Data were collected at a series of temperatures for the selective catalytic reduction of NO with CH_4 (SCR) for the former two catalysts for comparison. Product composition data were obtained both chromatographically and by IR analysis of the exit gases. The data showed that, whereas the light-off temperatures were lower when CH_3NO_2 was substituted for CH_4, they passed through peak conversion to N_2 at the same temperature and then fell off rapidly at higher temperatures in the way typical for SCR reactions. The reaction of CH_3NO_2 with O_2 alone produced results similar to those for the SCR reaction, but with roughly 50% of the peak conversion to N_2. The activity of CuZSM-5 in these reactions was much greater than for the other three catalysts. The IR data showed the presence of HCN, NH_3, and HNCO in various low concentrations below 400°C. N_2 and N_2O were obtained by GC. These data differed over the four catalysts. All of these compounds have been suggested in the literature as possible intermediates in the formation of N_2 and their behavior in these experiments was not inconsistent with these ideas. These results suggested, however, that one single pathway to N_2 formation does not exist; several optional mechanisms may function as suggested by the earlier literature. When $^{15}N^{18}O + O_2$ was substituted for the unlabeled molecule, the predominant N_2 product was $^{15}N^{14}N$, suggesting that one N-atom is supplied by each of the two reacting molecules, CH_3NO_2 and NO_2. © 1998 Academic Press

INTRODUCTION

In 1994 Witzel *et al.* (1) argued that reduction of NO to N_2 and combustion of hydrocarbons to $CO_2 + H_2$ were coupled reactions and suggested that a complex, free radical network is involved in the selective catalytic reduction (SCR) of NO with hydrocarbons in the presence of excess O_2. At about the same time Misono and co-workers (2) and Li *et al.* (3) proposed that alkyl nitrates may be key intermediates in the SCR of NO_x with propene (2) over CuZSM-5 and with methane (3) over CoZSM-5. Cant and co-workers (4) found a primary kinetic isotope effect of ∼2.0 for the reaction of CH_4 versus CD_4 with NO and O_2 over CoZSM-5. This result demonstrated that the breaking of a C–H versus C–D bond is the rate-determining step in this reaction, suggesting methyl radicals as the primary product. A distinct parallel with the methane-coupling reaction, modified by the presence of the stable free radicals, NO_x, was apparent. The methyl radicals can combine with NO or NO_2 to form CH_3NO_2 as observed (5). This compound reacts in some way yet to be defined forming the N–N bond (2). Bell and co-workers (6) have postulated the formation of CH_3NO that is then converted to adsorbed nitrile which further reacts with NO_2 to produce N_2. Other pathways have been suggested.

Sachtler (7) and Baiker (8) and their co-workers in considering the reaction using propane or propene suggested that the acetone oxime or allyl oxime might be intermediates for NO_x reduction over CuZSM-5. Lunsford and co-workers (9) studied the reaction of CH_4 with NO in the presence of excess O_2 over Sr/La_2O_3 using a mass spectrometer. They suggested that CH_3NO was a likely intermediate at temperatures above 550°C.

We have made careful kinetic measurements (10–12) of the reactions between CH_4 and nitrogen oxides, both with and without O_2 over Co- and HZSM-5. Our data is consistent with the formation of methyl radicals and the possible role of carbon–nitrogen–oxygen complexes as reactive intermediates in these reactions.

In the present work, the reactions of CH_3NO_2 over Co-, H-, Fe-, and CuZSM-5 with NO or O_2 and with NO in the presence of excess oxygen have been studied and compared with the results for the SCR reaction. $^{15}N^{18}O$ was used with these catalysts to trace the origin of the N atoms in the N_2 product.

EXPERIMENTAL

Catalysts

Co-, Cu-, H-, and FeZSM-5 used in these studies have been characterized in detail and reported elsewhere

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(1, 10–13). They are identified here as CoZSM-5-11-98, CoZSM-5-11-70, CuZSM-5-11-103, HZSM-5-11-100, and FeZSM-5-19-183, where the cationic form comes first while the Si/Al ratio and percentage exchange follow the zeolite type. The Co-, Cu-, and NH_4- forms were made using conventional procedures. The Fe form was prepared by ion exchange of the Na form with FeC_2O_4 in the absence of oxygen, following a procedure developed in our laboratory (13). The H- form was prepared by ramping NH_4ZSM-5-11-100 in flowing 10% O_2/He at a rate of 4°/min from 25 to 450°C and maintaining this temperature overnight.

Reaction Studies

The U-tube quartz reactor contained 50 mg of catalyst held between two quartz wool plugs. The catalysts were dehydrated in flowing O_2 as the temperature was raised (4°C/min) from 25 to 500°C and held there overnight before cooling in pure He to the selected temperature (at this point no O_2 could be detected by GC in the He stream).

The gases, NO (1%) in He, NO_2 (1%) in He, O_2 (10%) in He and pure He, were metered by electronic mass flow controllers and the liquid (nitromethane) was fed using a saturator containing the liquid at 0°C.[3] All the experiments were run at $\text{GHSV} = 42{,}000\ \text{h}^{-1}$ unless otherwise indicated. This space velocity was chosen to make these experiments comparable with earlier studies of the SCR reaction mechanism over similar catalysts (10–13). The reacting gases were analyzed both by FTIR and by two gas chromatographs. The outlet of the reactor first passed through a conventional gas cell (15-cm path length with KBr windows) installed inside the chamber of a Mattson Research Series II Instrument. Heating tape was used to maintain the temperature of the lines and the cell at about 80°C. After leaving the cell, the gas flowed through a sampling valve connected to a Hayesep Q column ($1/8'' \times 6'$) thermostated at 130°C where nitromethane was determined. From there gases were passed through a dry ice cooled trap and through a second sampling valve connected to an Alltech CTR concentric dual column held at 25°C for determination of N_2, N_2O, CO, and CO_2.

Tracer Experiments

These experiments were carried out in the same reaction system but $^{15}N^{18}O$ was substituted for $^{14}N^{16}O$. The reactor outlet gases after flowing through the GC sampling valve were fed to a quadrupole mass spectrometer through a capillary injector (GC-MS type) operated in the differential mode to determine the isotopic distribution in the reaction products.

RESULTS

Homogeneous Reactions

In order to ascertain possible contributions from homogeneous gas phase reactions the reactant mixtures were fed to the same reactor (vol. = 0.6 ml) containing no catalyst.

Table 1 shows the reactant mixtures explored and the results obtained. Essentially no reaction occurred at temperatures below 430°C under the conditions used. No N_2 was ever detected in the course of these experiments up to $T = 730$°C. This same behavior has been found for the SCR reaction using CH_4 as the reducing gas (10). When the reactor was filled with 50 mg of either silica gel or the parent NaZSM-5 no significant change in behavior occurred.

Heterogeneous Reactions

The results obtained using all four catalysts can be compared, one with another, in Figs. 1, 2, 3, and 4. Figure 1 contains the nitromethane reaction results as a function of temperature for (a) Co-; (b) H-; (c) Fe-; and (d) CuZSM-5, as determined by chromatography. Figure 2 presents both IR and GC data for these same catalysts for the $CH_3NO_2 + NO + O_2$ mixture. These results may be compared with those obtained when CH_3NO_2 was reacted with O_2 alone in Fig. 3. The mass spectroscopy results are contained in Fig. 4. In all these experiments the reaction conditions were the same for all catalysts except that the weight of CuZSM-5 was reduced by a factor of five because of its unexpected high activity in the nitromethane reactions. This effectively increased its space velocity to $210{,}000\ \text{h}^{-1}$. In this case, the catalyst was thoroughly mixed with 40 mg of the inactive parent NaZSM-5-11-100 to maintain the reaction volume constant.

TABLE 1

Homogeneous Reactions of Nitromethane (NM) in Empty Reactor[a]

Reactant mixture	Light-off temperature (°C)	Main products[b]	Coke
NM(2000 ppm)/He	500	NO + traces of (CO + CO_2)	Yes
NM(2000 ppm) + O_2(2.5%)/He	450	$CO_2 + H_2O$	No
NM(2000 ppm) + NO(2000 ppm) + O_2(2.5%)/He	430	$CO_2 + H_2O + NO_x$	No
NM(2000 ppm) + NO_2(2000 ppm) + O_2(2.5%)/He	430	$CO_2 + H_2O + NO_x$	No

[a] Reactor size 0.6 cm^3; total flow rate 80 cc/min.

[b] NO can only be detected in the absence of O_2. No N_2 was detected in any of these experiments even at reaction temperatures is high as 730°C. No effort was made to identify two other small peaks shown at low retention time on the chromatograms.

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[3] CH_3NO_2 is a liquid having physical properties similar to H_2O. It is toxic and appropriate precautions must be used to avoid contamination of the laboratory air.

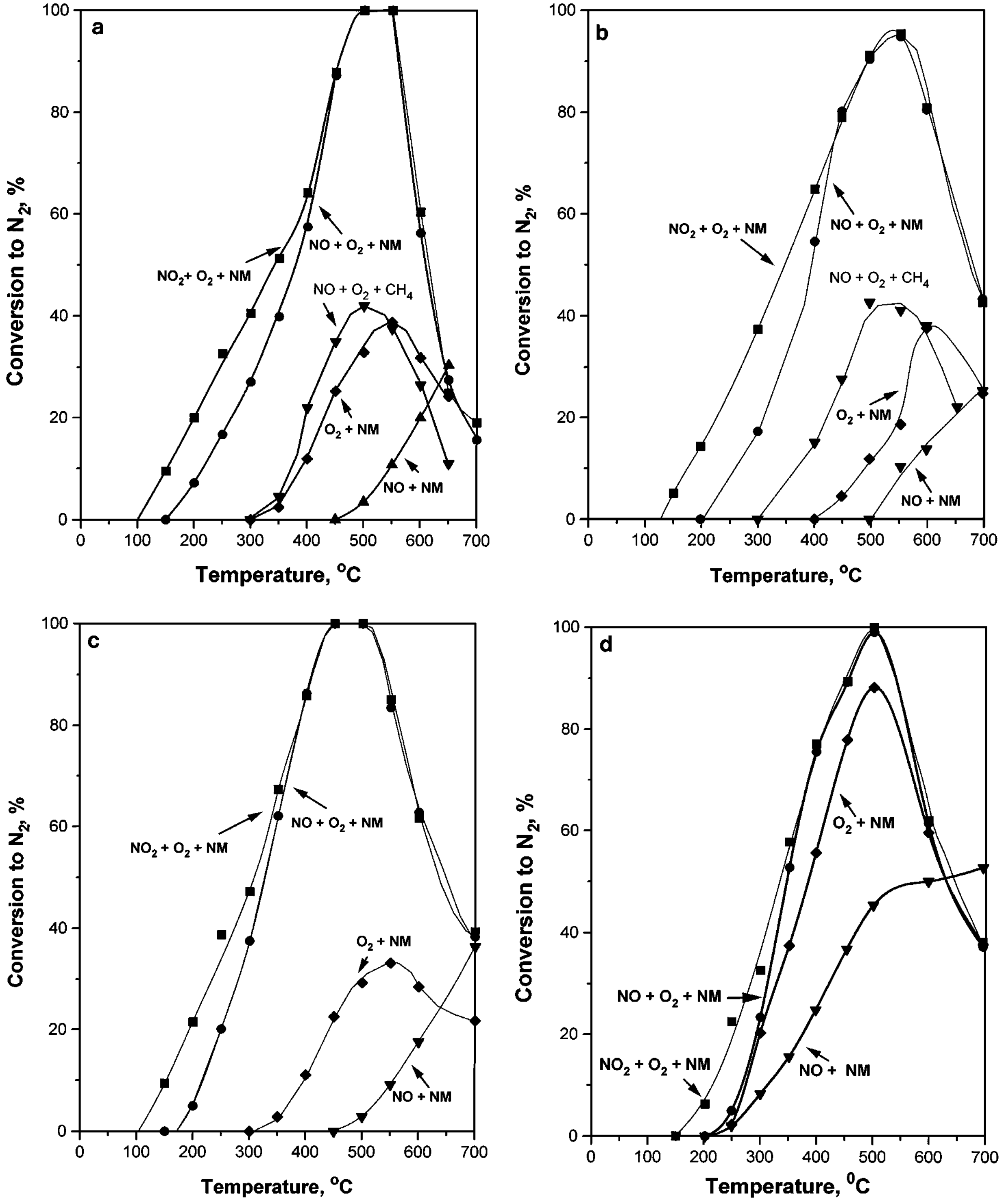


FIG. 1. Nitromethane reactions over several zeolite catalysts: (a) CoZSM-5; (b) HZSM-5; (c) FeZSM-5; and (d) CuZSM-5; GC was used for product analyses. The feed contained 2000 ppm of nitromethane or CH_4, 2000 ppm of NO_x, 2.5% O_2, and He to 1 atm. The flow rate was 80 mL/min and 50 mg of the zeolite catlayst was used except for CuZSM-5 (see text).

Nitromethane Reactions

The percentage conversion to N_2 as a function of temperature is shown for CoZSM-5 in Fig. 1a for several different reaction mixtures. The results were normalized by calculating the maximum amount of N_2 that could be stoichiometrically produced from each reacting mixture. For comparison the N_2 production (given on the same basis) from the reaction between methane and either NO or NO_2 in excess O_2 is also shown (data from Ref. (11)).

All kinetics data reported herein were obtained with decreasing temperatures from 500°C downward. After reaching the lowest temperature, the data point at 500°C was redetermined to agreement within 5%. From hereon the temperature was increased up to 700°C. In early experiments it was found that conversion values $>$100% were obtained when the experiments were initiated at low temperature and points taken as the temperature was increased. This was traced to capillary condensation of CH_3NO_2 in the pore system, *vide infra*.

The light-off temperature was about 200°C lower for nitromethane than for $CH_4 + NO_x$. This was to be expected since Cant and co-workers (4) have shown that the breakage of the C–H bond in methane is the rate limiting step in the SCR reaction. The maximum conversion to N_2 was much lower in the CH_4 reaction than in the reactions of CH_3NO_2 with NO_x, despite the fact that the reductant/oxidant ratio is higher in the former than in the latter. NO_2 appeared to be somewhat more effective than NO at $T < T_{\max}$. Using NO in the absence of O_2 sharply increased the light-off temperature over Co-, H-, and FeZSM-5 (Figs. 1a–c) in much the same way as was observed with methane (9).

In drawing similarities and differences among the four catalyst systems the following should be noted. Overall the behavior was much the same. However, Fe- and Cu-zeolites are not catalysts for the SCR reaction using CH_4. Hence, these comparisons cannot be made. CoZSM-5 was somewhat more active in SCR than HZSM-5, but otherwise it was similar. CuZSM-5 was exceedingly more active than any of the other catalysts in reactions with CH_3NO_2. The space velocity had to be increased to over 200,000 h^{-1} to obtain comparable results. This suggests that it is a much more active oxidation catalyst and that it is for this reason that CH_4 cannot be used in the SCR reducing mixture. Note the low light-off temperature of the $NO + CH_3NO_2$ mixture (Fig. 1d). This behavior is very different than that obtained with the other three catalysts.

The gas phase infrared spectra of the exhaust reactor gases showed the presence of other compounds not detected by the GC system (Fig. 2). These data are plotted somewhat differently than those of Fig. 1. To minimize confusion, data for $T > 500$°C have been omitted although the behavior was the same as those given in Fig. 1. Note that 2000 ppm of N_2 and CO_2 correspond to 100% conversion. This technique was first applied by Baiker and co-workers (8) and more recently by Cant *et al.* (14) with considerable success. The IR technique allowed the quantification of HCN, HNCO, and NH_3 (Fig. 2).

Shown in Fig. 3 is the conversion to N_2 when CH_3NO_2 is reacted with O_2. These data were quantified by both GC and FTIR. In many respects they resemble closely those of Fig. 2, but differed significantly in one way: the evolution of N_2 began only after the concentration of N_2O, NH_3, and HCN approached zero, except for CuZSM-5. Above 600°C the product stream contained mainly CO_x, H_2O, N_2, NO, and excess O_2 (Fig. 1). Note that under these conditions NO_2 has almost completely dissociated into NO and O_2, as required by thermodynamics.

The data of Fig. 2a follow similar trends as those reported by Cant and co-workers (14). N_2O, HCN, and NH_3 were all formed, but converted to N_2 below 375°C. The same three compounds were formed from CH_3NO_2 in comparable amounts in O_2 alone, i.e., when NO was omitted from the feed stream (Fig. 3). HCN and NH_3 passed through maxima at about 275 and 325°C, respectively, before disappearing at ∼350°C, as reported by Cant and co-workers (14); moreover, as reported by them, the evolution of N_2 in the presence of O_2 alone began as the HCN and NH_3 abruptly dropped to zero near 375°C. On addition of NO, however, formation of N_2 began at the light-off temperature (Fig. 2a). Also in this case the amount of N_2 produced at 450°C was several times larger than in its absence.

Figures 3a, 3b, 3c, and 3d differ somewhat in detail. Over the CoZSM-5, HCN appears first near 250°C, followed by NH_3 and N_2O near 275°C. The N_2 evolution starts as these compounds drop to zero near 380°C. On the other hand, the evolution of CO_2 begins at about 250°C and by 450°C accounts for more than half the carbon in the feed. With HZSM-5 (Fig. 3b), however, N_2O was the only other nitrogen-containing species observed; it appeared in small amounts up to 400°C. N_2 was formed above 400°C as the N_2O disappeared. These results suggest that N_2O is also an intermediate in N_2 formation. Note that with HZSM-5 combustion to produce CO_x is slow (Fig. 3b).

Over FeZSM-5 (Fig. 3c), HCN was formed in the absence of NH_3, although small amounts of N_2O did appear and passed through a shallow maximum around 250°C. Over CuZSM-5 (3d) only N_2, CO_2, and small amounts of N_2O were detected, whereas in the companion experiment in Fig. 2d, HCN, HNCO, and N_2O were all present. The most significant difference between these two sets of experiments was that N_2 formation generally started at, or close to, the light-off temperature for all products with NO present, whereas in the experiments in Fig. 3, the evolution started as the intermediate species dropped to zero as observed by Cant (14).

It was observed in these kinetic experiments that the conversion values recorded with decreasing temperatures

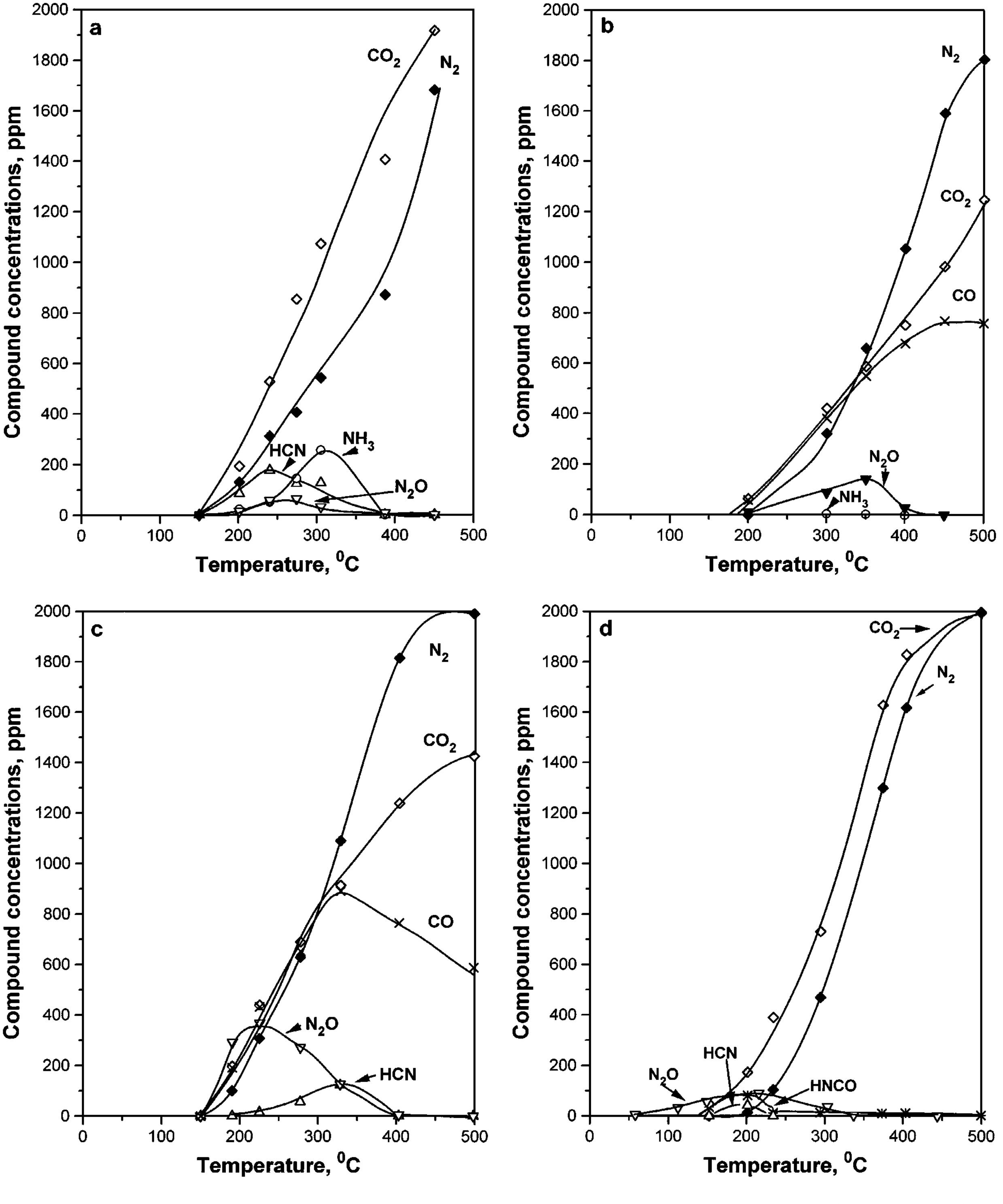


FIG. 2. Nitromethane reactions over Co-, H-, Fe-, and CuZSM-5 catalysts (a, b, c, d) using IR spectroscopy and GC for analysis. The feed mixture was nitromethane, 2000 ppm; NO, 2000 ppm; and O_2, 2.5%. The reaction conditions were the same as those described for Fig. 1.

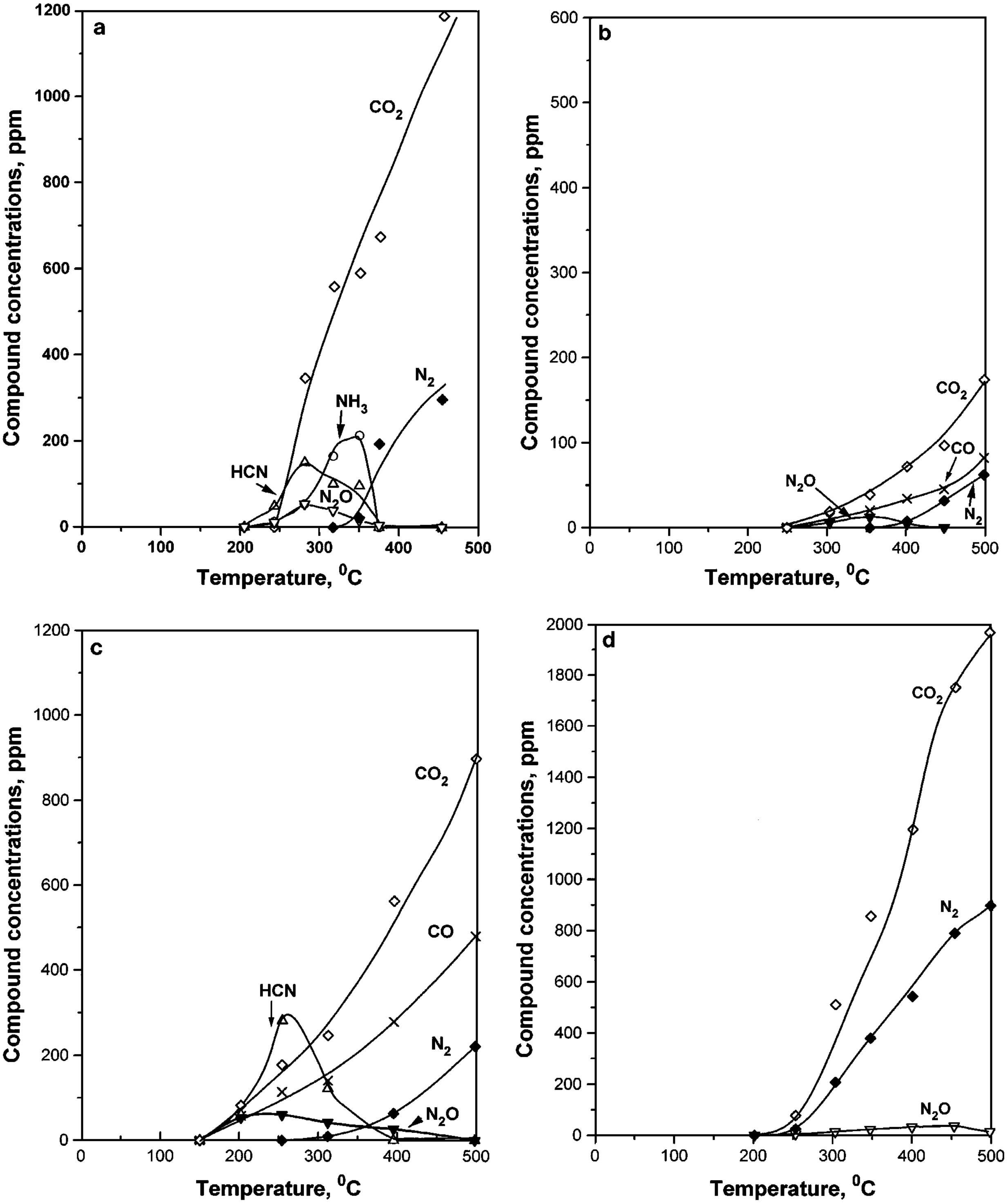


FIG. 3. Nitromethane reactions with O_2 over Co-, H-, Fe-, and CuZSM-5 catalysts (a, b, c, d); nitromethane, 2000 ppm, and O_2, 2.5% were used as feed. IR spectroscopy and GC were used for analysis. The catalysts and reaction conditions were the same as those described for Fig. 1.

(starting at ∼400°C) were lower than those obtained with increasing T. This phenomenon was clarified as follows. After experiments with ternary reacting mixtures carried out starting at 500°C, on lowering the temperatures stepwise to 100°C, the catalyst accumulated unreacted CH_3NO_2. Then on retracing the steps upward, more products were produced than possible at the feed rate of CH_3NO_2 used. This reacted when the temperature was ramped upward at 100°C per minute to 500°C. These results will be reported in detail in a following paper.

Tracer Studies

The origin of the N atoms that combine to form the N_2 molecule was investigated. Nitromethane was reacted with $^{15}N^{18}O$ in the presence of excess O_2 and the results for CoZSM-5 are shown in Fig. 4a. The predominant nitrogen molecule formed was $^{15}N^{14}N$ (m/e = 29), suggesting that one N atom came from CH_3NO_2 and the other from $^{15}N^{18}O$. No $^{30}N_2$ was detected while $^{28}N_2$ could not be measured due to the intrinsic background of the mass spectrometer, but it could be estimated that $^{28}N_2$, if formed, never amounted to more than 10% of the total. Note that $^{16}O^{18}O$ (m/e = 34) molecules were detected at $T > 300$°C with CuZSM-5, but only at higher temperatures with Co- and FeZSM-5.

Relatively large peaks at m/e = 30 and 33 appeared at 25°C when the reactor was bypassed. In Figs. 4a–c, these peaks decreased and passed through a minimum at about 500°C, where all of the nitrogen in the feed was converted to N_2 and the m/e = 29 peak passed through a maximum. The m/e = 33 peak shows the relative concentration of uncreacted $^{15}N^{18}O$ tracer remaining as conversion to N_2 decreased at temperatures above 500°C, where this conversion dropped as the NO_2 supply became scarce; the m/e = 34 concentration increased concomitantly.

The signal at m/e = 30 could arise from two sources. It is the main fragmentation peak from CH_3NO_2 (NO) and it could also be attributed to $^{15}N^{15}N$. Since no N_2 was present in the feed (reactor bypassed), however, this peak must arise from the NO formed by fragmentation of CH_3NO_2 in the mass spectrometer. Also note that this peak (m/e = 30) passed through a minimum as all the nitrogen in the feed was converted to N_2, demonstrating that very little $^{15}N^{15}N$ is formed and, consequently, that $^{14}N^{14}N$ is also minimal. At $T > 500$°C, the conversion to N_2 decreased sharply due to conversion of the NO_2 in the feed to $NO + \frac{1}{2}O_2$. Thus the m/e = 33 peak rose sharply while additional NO (m/e = 30) was produced by thermal decomposition of CH_3NO_2. At these temperatures GC indicates no CH_3NO_2 remains. Thus at $T > 550$°C, both $^{15}N^{18}O$ and $^{14}N^{16}O$ were present in nearly equimolar amounts. Also, $^{15}N^{16}O$ (m/e = 31) appears in this temperature region where $^{18}O^{16}O$ (m/e = 34) became an important product. These interpretations were confirmed by IR spectra of the effluent gases.

Qualitatively, the results in Fig. 4 were similar for Co-, H-, and FeZSM-5. In both cases the m/e = 29 peak passed through a maximum together with that for the formation of N_2. Identical interpretations may be made for the remaining assignments. Some significant differences were obvious, however, with the exceedingly active CuZSM-5 (Fig. 4d). The m/e = 30 peak did not pass through a minimum as the conversion to N_2 reached its maximum. Instead this peak increased monotonically with temperature. This might be attributed to NO decomposition involving two ^{15}NO molecules yielding $^{15}N_2$. Also note the minimal recovery of the $^{15}N^{18}O$ (m/e = 33) at $T > 500$°C and the greatly enhanced $^{16}O^{18}O$ peak (m/e = 34) in this range, suggesting that exchange between $^{15}N^{18}O$ and lattice oxygen occurred as observed previously (15).

At temperatures ≥550°C, severe coking was observed with the HZSM-5 catalyst. This led to a decrease in the conversions with time on stream. After removing the carbonaceous residues with 10% O_2 in He at 500°C, the catalyst recovered ca 80–90% of its original activity. The extent of this recovery, however, depended on both maximum temperature reached and time on stream. To avoid uncertainties due to coking, a new aliquot of HZSM-5 was used after runs in which coking was observed.

DISCUSSION

The catalytic reactions of nitromethane over the solids studied is entirely consistent with the radical mechanism we have proposed previously (12) for the selective catalytic reduction of NO_x with methane. The proposed mechanism may be briefly reiterated as follows:

$$CH_4(g) + NO_2(ads) \rightarrow CH_3\cdot(g) + NO(ads) + HO\cdot(g) \quad [1]$$

$$HO\cdot(g) + CH_4 \rightarrow CH_3\cdot(g) + H_2O \quad [2]$$

$$\begin{aligned} CH_3\cdot(g) + NO_x &\rightarrow CH_3NO_2 \text{ and } CH_3NO \\ &\rightarrow N_2 \text{ path (plus } CO_2 \text{ and } H_2O) \end{aligned} \quad [3]$$

$$CH_3\cdot(g) + O_2 \rightarrow CH_3OO\cdot \rightarrow CO_2 + H_2O \text{ path.} \quad [4]$$

This chemistry explains the decrease in selectivity to N_2 with increasing temperature and conversion. Missing, however, are the final steps of Eqs. [3] and [4] which lead to the formation of N_2, CO_2, and H_2O.

It has been demonstrated by Cant and co-workers (4) that the rate-determining step is the breaking of the CH bond in methane; i.e. reaction [1] in our scheme. As shown by the data of Fig. 1, when CH_3NO_2 is reacted with NO in excess oxygen, the light-off temperatures were about 150°C lower than for the SCR reaction using $CH_4 + NO_x$ in excess O_2. Nevertheless, the maximum conversions occurred at about the same temperature. Since the concentration of NO_2 in the reaction stream becomes equilibrium limited at higher temperatures, the fall in conversion to N_2 above

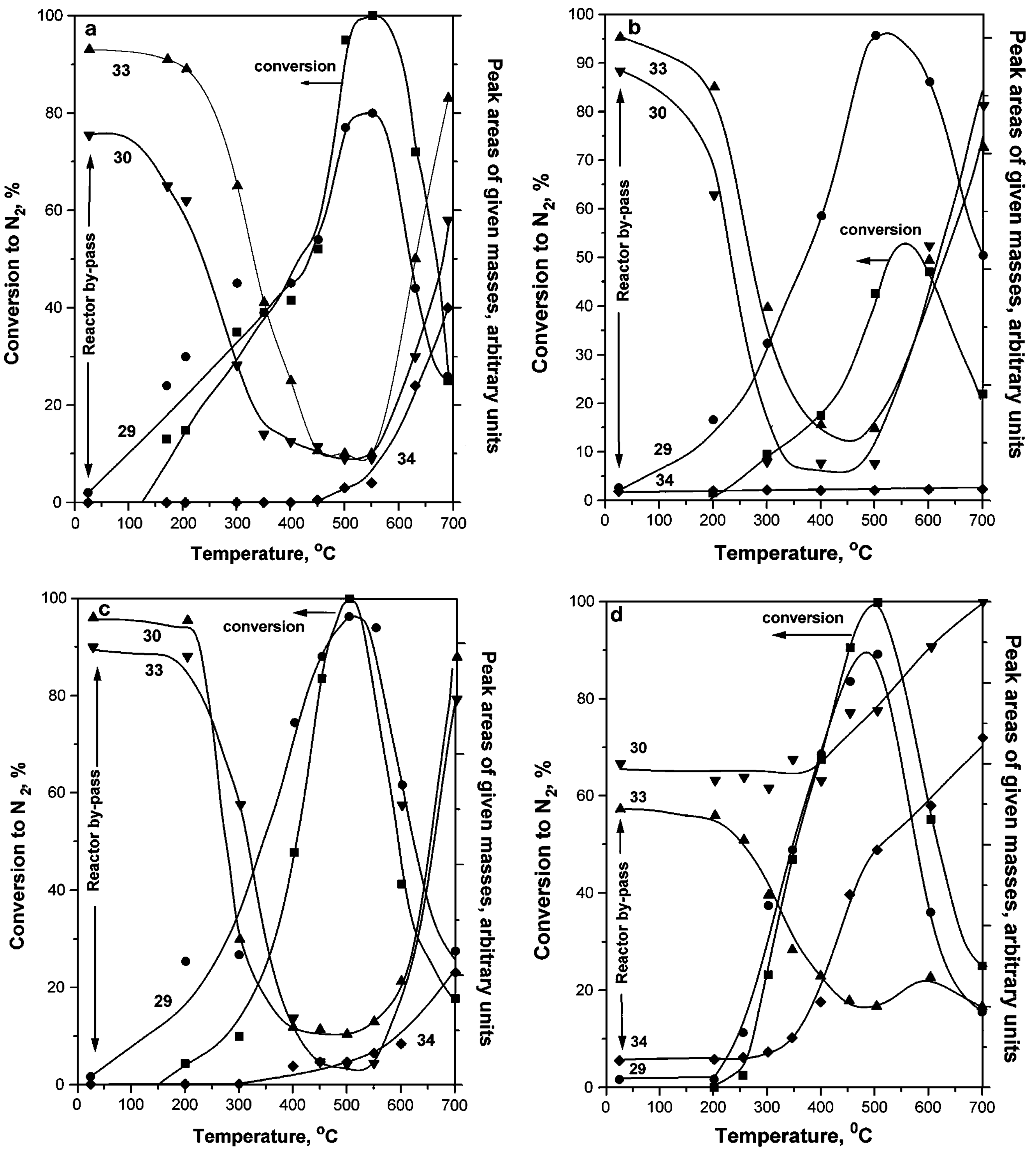
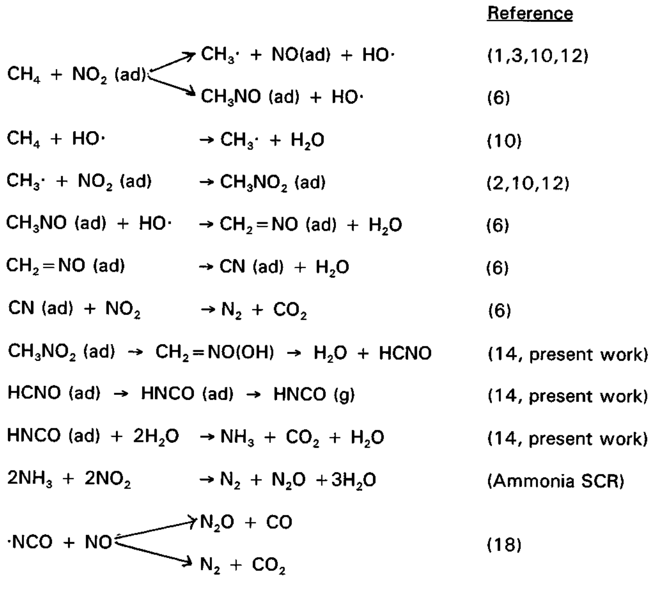


FIG. 4. Tracer results from reaction of nitromethane, 2000 ppm; $^{15}N^{18}O$, 2000 ppm, and O_2, 2.5% over these same zeolite catalysts. For convenience, m/e = 28 is not shown because of strong interference from CO; m/e = 29 corresponds to $^{15}N^{14}N$; m/e = 30 is from NO formed by decomposition of nitromethane; m/e = 33 corresponds to unreacted $^{15}N^{18}O$; and m/e = 34 is from $^{18}O^{16}O$ produced by exchange of $^{15}N^{18}O$ with oxygen.

500°C suggests that NO is not nearly as effective in the reaction as NO_2. This is supported by the generally high temperatures required for the reaction of CH_3NO_2 with NO shown in Fig. 1. These observations are consistent with the prediction that the reaction between CH_4 and NO_2 is the rate-limiting step for both the formation of N_2 and combustion to CO_2 and H_2O. Note that neither FeZSM-5 nor CuZSM-5 are active for the SCR reaction using CH_4, but once the initiation step is overcome by starting with nitromethane, the reaction over FeZSM-5 proceeds at about the same rate as with CoZSM-5 and it is much faster over CuZSM-5.

Another common feature of the catalysts studied is that NO_2 is consistently a little more active than NO (in excess oxygen) at the low temperature side, suggesting that NO_2 preferentially reacts with nitromethane to produce nitrogen. The catalysts assayed have rather low activity to oxidize NO to NO_2 at temperatures below 350°C at the space velocity used here (16). The much lower reactivity of NO with nitromethane in the absence of oxygen (Figs. 1a–c) confirms this point. Most significant, however, is the coincidence of the maxima for SCR with that for N_2 formation from CH_3NO_2. Clearly some common chemistry is taking place in the formation of N_2 using either CH_4 or CH_3NO_2.

How nitromethane reacts with O_2 and NO_x to yield N_2, N_2O, CO_2, and H_2O may be via the secondary products observed by FTIR (Figs. 2 and 3) acting as intermediates. This idea is supported by reports from the literature showing that sorbed CN, NCO, oximes, NH_3, and N_2O may all be converted to N_2. These data are summarized in Scheme 1. Cant and co-workers (14) have very recently reported that nitromethane reacting with $O_2 + NO_x$ over Co-ZSM-5 yielded NH_3, HCN, HNCO, N_2, and CO_2 under varying reaction conditions. These observations have been confirmed in the present work. The space velocities and reactant concentrations were close to those used in the CH_4 SCR reaction and therefore also to the conditions used in this work. They limited their study to reactions catalyzed by CoZSM-5 and at temperatures below 500°C. They showed that oxidation of CH_3NO_2 with O_2 alone produced nearly stoichiometric amounts of CO_2 and NH_3. This, together with the fact that formation of N_2 commenced at about 380°C, where the NH_3 abruptly disappeared from the gas phase, led them to speculate that in the final steps of the SCR reaction NH_3 was used to produce N_2.



SCHEME 1

Ying and co-workers (5) have recently observed the formation of CH_3NO_2 and its accumulation on the surface of CoZSM-5 using DRIFT. As shown in Scheme 1, all the species observed by IR, or shown to be formed on the catalyst surface, may be reacted in the ambient feed stream to N_2, CO_2, and H_2O. In particular, the reaction of NH_3 and NO_2 to $N_2 + H_2O$ has been known for many years and it has been shown (17) that $^{15}N^{14}N$ (m/e = 29) is the principal nitrogen product formed. (In view of these facts it is tempting to suggest that the formation of N_2 in this reaction system does not occur by a single mechanism but that several pathways are available, depending on the catalyst used and the reaction conditions.) Note that over CoZSM-5 HCN, NH_3 and N_2O are all produced below 400°C, whereas only N_2O was detected over HZSM-5. Over FeZSM-5 only N_2O and HCN were formed while CuZSM-5 yielded N_2, HCN, and HNCO. If these compounds are indeed intermediate products, the amount detected in the out-gas is a balance between the rate of formation and the rate of consumption. Moreover, as the temperature was raised above 400°C, these products fell below the limit of detectability as they were consumed to form N_2. This is particularly clear in the results of Cant *et al.* (14), where the amount of these minor products fell suddenly to zero at about 380°C and was accompanied by the appearance of an equivalent amount of N_2.

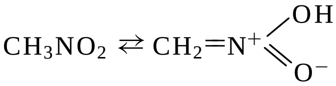
Earlier we had pointed out (1) that the formation of both N_2 and N_2O would be anticipated from known chemistry (18) if the ·NCO radical were produced. In the present work HCN, NH_3, HNCO, and N_2O were all observed in varying amounts, depending upon the catalyst. Note that N_2O already has formed the N–N bond and that it can be readily decomposed to $N_2 + \frac{1}{2}O_2$. It was present over every catalyst tested in amounts comparable with the other species mentioned above. It seems reasonable to suggest, therefore, that more than one pathway to N_2 exists.

When FeZSM-5 was the catalyst, aside from N_2O, HCN was the only secondary compound detected by IR in the gas phase under steady state conditions; NH_3 was detected, however, under nonsteady state conditions. Similarly, over HZSM-5 in the steady state no secondary products other than N_2O appeared in the gas phase, although under transient conditions NH_3 appeared. These experiments will be described in a following paper. In brief, Co- and FeZSM-5 produced both NH_3 and HCN in quite different proportions, while HZSM-5 formed detectable NH_3 only under nonsteady state conditions.

At first sight, the hypothetical stoichiometric reaction

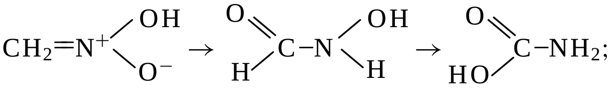
$$CH_3NO_2 \rightarrow NH_3 + CO_2 \qquad [5]$$

appears most unlikely. Nevertheless, this overall result was observed (14). It appears to the present authors that the most likely explanation is by transformation of the nitromethane to carbamic acid, via aci-nitromethane, i.e.,



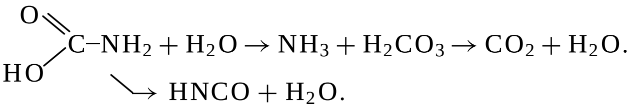
$$CH_3NO_2 \rightleftarrows CH_2{=}N^+\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown O^-} \qquad [6]$$

followed by rearrangement into carbamic acid



$$CH_2{=}N^+\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown O^-} \rightarrow \genfrac{}{}{0pt}{}{O\diagdown\!\!\diagdown}{H\diagup}C{-}N\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown H} \rightarrow \genfrac{}{}{0pt}{}{O\diagdown\!\!\diagdown}{HO\diagup}C{-}NH_2; \qquad [7]$$

then



$$\genfrac{}{}{0pt}{}{O\diagdown\!\!\diagdown}{HO\diagup}C{-}NH_2 + H_2O \rightarrow NH_3 + H_2CO_3 \rightarrow CO_2 + H_2O. \qquad [8]$$

$$\hookrightarrow HNCO + H_2O. \qquad [9]$$

This chemistry finds partial support in a previous work of Blower and Smith (19). These authors studied the decomposition of nitromethane over metal ion-exchanged X and Y zeolites, although at much higher concentrations and lower space velocities than those used in SCR systems. They observed the formation of a carbamate double salt on cooling the outlet stream. Hence, it seems likely that the catalyzed decomposition of nitromethane may involve the transient formation of unstable carbamic acid, yielding products as outlined. Cant and co-workers (14) have made similar speculations.

Also note that during SCR of NO_x with hydrocarbons over zeolites, the following compounds have been detected in small amounts: HCN by Misono (2) and Baiker (8); NH_3 by Cant (14) and by Baiker (8); and HNCO by Baiker (8).

The source of the HCN is not clear. With hydrocarbons larger than CH_4, it has been suggested (8) that it may be formed by trans-elimination from the oxime forming concomitantly an aldehyde. This is obviously not possible using CH_3NO_2. The suggestion in Scheme 1 that CH_3NO is formed along with CH_3NO_2 (5) appears to offer the most plausible explanation.

This set of reactions and the different nature and/or proportions of secondary products mentioned in the literature are symptomatic of radical reaction mechanisms as suggested previously (1). Of course, the oxidation of NH_3 by O_2 and by NO_2 to N_2 are well known. Note that the latter reaction would produce the $^{15}N^{14}N$ found in our tracer experiments. These show (Figs. 4a–d) that for nitromethane the two N atoms come from each of the two sources. This was invariably the same over all four catalysts, although some of the N_2 formed over CuZSM-5 may have involved NO decomposition and/or exchange to produce some $^{15}N_2$. Evidently this feature is introduced during the reactions of CH_3NO_2 with $^{15}NO_2$.

A secondary process was observed at $T > 450°C$ on CoZSM-5 (Fig. 4a) and at $T \geq 400°C$ on FeZSM-5 (Fig. 1c), namely the appearance of a signal at $m/e = 34$. This corresponds to $^{18}O^{16}O$ appearing in the gas phase as it is released by the catalyst. This could result from a higher oxygen mobility in these catalysts at these higher temperatures. This exchange process was not observed on HZSM-5 up to 700°C, a fact that is consistent with the higher selectivity to N_2 observed with this catalyst.

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