

# The reactions of nitroalkanes over Cu-MFI and Fe-MFI catalysts under hydrocarbon-selective catalytic reduction conditions

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## Abstract

The reactions of 2-nitropropane (2NP) and 2-methyl-2-nitropropane (2M2NP), typical of secondary and tertiary nitroalkanes, respectively, have been investigated over Cu-MFI and Fe-MFI catalysts under conditions relevant to the selective catalytic reduction (SCR) of NO with the use of alkanes. With both catalysts the primary reaction is decomposition to form NO and the alkene, propene from 2NP, and isobutene from 2M2NP. If O<sub>2</sub> is present, then some N<sub>2</sub> is formed by the subsequent SCR reaction between the alkene and NO<sub>x</sub>. Production of N<sub>2</sub> is greater when the feed contains NO, but this is largely due to enhancement of the alkene SCR reaction rather than a direct reaction between the nitroalkane and NO<sub>x</sub>. The alkene also reacts partly through deposition of carbonaceous material, which causes deactivation. In the absence of O<sub>2</sub> propene is also formed, through cracking of the oligomers derived from isobutene produced by 2M2NP decomposition. The reduction of NO/O<sub>2</sub> by propene and isobutene over Fe-MFI proceeds in a manner similar to that of the reduction with propane and isobutane, except for a lower production of HCN. With mixed alkane/alkene feeds, the alkene reacts in preference to the alkane. Overall the data show that secondary and tertiary nitroalkanes are less reactive than primary nitroalkanes over transition-metal zeolites because of the absence of the two α-hydrogens necessary for tautomerism to an aci form and its subsequent dehydration to a reactive isocyanate. Thus secondary and tertiary nitroalkanes are unlikely to be a major source of N<sub>2</sub> during alkane SCR over these catalysts but could play a part through the generation of alkenes that are more reactive than alkanes.

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## 1. Introduction

Many aspects of the selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) over zeolite catalysts can be rationalised on the basis that an initial hydrogen abstraction by a surface NO<sub>x</sub> species produces a radical-like species that combines with NO or NO<sub>2</sub> to produce a nitroso or nitro species [1]. Such intermediates can then undergo facile rearrangements and other processes in which they become compounds with reduced nitrogen centres that are converted to N<sub>2</sub> by reaction with NO<sub>x</sub> molecules [2].

The intermediate reactions that produce the reduced nitrogen centres are most easily envisaged if the nitroso/nitro

species are primary and thus possess two α-hydrogens. Such compounds have tautomeric forms (oxime and *aci*-nitro, respectively) that can readily undergo acid or base-catalysed dehydration. The respective products are a nitrile,



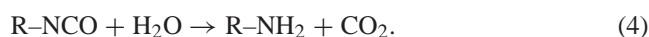
or an N-oxide and then an isocyanate,



Hydrolysis can then produce ammonia and an acid,



or an amine and CO<sub>2</sub>,



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If the nitroso species is a secondary one, then the single  $\alpha$ -hydrogen permits tautomerism to an oxime but not the subsequent dehydration. However, hydrolysis may still take place either directly or after a Beckmann rearrangement in which the R group first migrates to the nitrogen. In the first case the expected hydrolysis products are a ketone and hydroxylamine, in the second, an amine and an acid [3]. If the nitroso compound formed originally has a tertiary structure, then the absence of a  $\alpha$ -hydrogen precludes tautomerism altogether. Likewise, secondary and tertiary nitro compounds cannot react to form isocyanates according to [2]. In these cases further reaction would have to be by some other route.

To our knowledge there are no studies in which the reaction of a nitroso compound has been investigated directly under SCR conditions. However, several investigations have shown that acetone oxime,  $(\text{CH}_3)_2\text{C}=\text{NOH}$ , the tautomer to 2-nitrosopropane, does react in the above ways over Cu-MFI [4–6], H-MFI [5], and Fe-MFI [7]. Both modes of hydrolysis are observable by spectroscopic means, and differences in behaviour are determined by the availability of Brønsted acid sites [7]. The reduced nitrogen species formed by the hydrolysis steps are readily converted to  $\text{N}_2$  by 1:1 reactions with  $\text{NO}_2$  [2,4,5,7].

The clearest evidence for the feasibility of nitro intermediates in HC-SCR is with methane over Co-MFI [8,9]. Unlike SCR with higher hydrocarbons, that reaction operates at temperatures where  $\text{NO}_2$  is a product even under conditions of partial hydrocarbon conversion. Hence formation of  $\text{CH}_3\text{NO}_2$  as an intermediate is not an unreasonable outcome. Experiment shows that nitromethane decomposes to  $\text{NH}_3$  and  $\text{CO}_2$  at temperatures much lower than those required for SCR, with isocyanic acid (HNCO) observable as a gas-phase intermediate as the catalyst deactivates [9]. When NO and  $\text{O}_2$  are present the  $\text{NH}_3$ -SCR reaction is sufficiently fast to take all  $\text{NH}_3$  through to  $\text{N}_2$ . The same basic chemistry is apparent with H-MFI [10], Cu-MFI [10,11], and Fe-MFI [12] and in the reaction of nitroethane over Cu-MFI, where methyl isocyanate becomes observable as the catalyst deactivates [13].

As yet there do not appear to have been any studies of the reaction of a secondary or tertiary nitroalkane over a zeolite-based SCR catalyst under continuous-flow conditions. However, Chen et al. [2] have established that 2-nitropropane, adsorbed on Fe-MFI at 200 °C, gives deposits that produce  $^{14}\text{N}$   $^{15}\text{N}$  on contact with  $^{15}\text{NO}_2$ . In situ infrared measurements showed that the initial deposition formed a number of adsorbed nitrogen-containing species, but the chemistry of the steps was unclear and may not be relevant to SCR conditions that involve higher temperatures and much shorter reaction times. Flow-system studies using Pt/ $\text{Al}_2\text{O}_3$  show that primary, secondary, and tertiary nitropropanes all produce NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CO}_2$  in the presence of water and oxygen, with significant amounts of organic by-products in some cases, but the observed product distribution is probably influenced by the presence of platinum [14].

The aim of the present work was to fill this gap in knowledge by determining the reaction paths of secondary and tertiary nitroalkanes over typical zeolite SCR catalysts when the nitroalkanes are reacted in an inert carrier, in the presence of  $\text{O}_2$ , and in the presence of both  $\text{O}_2$  and NO. The systems examined are the reactions of 2-nitropropane (2NP) and 2-methyl-2-nitropropane (2M2NP) over Cu-MFI and Fe-MFI.

## 2. Experimental

The Fe-MFI used was part of a batch prepared by Kögel et al. [15,16] with a solid-state ion-exchange method that has been described in detail previously. The Fe/Al ratio was 0.75, nominally 150% overexchanged based on  $\text{FeCl}_2$ . Cu-MFI was prepared by the exchange of Na-MFI (Si/Al = 11.9; Tosoh Inc.) with copper acetate followed by drying at 110 °C and calcination in air at 500 °C. The exchange level was 80% (3.2 wt% Cu). Activity testing was carried out on 100-mg samples with particle sizes of 300 to 600  $\mu\text{m}$ . These were contained in a 4-mm id Pyrex U-tube reactor and pre-treated in 10%  $\text{O}_2/\text{He}$  to 480 °C before reaction. The feed mixture, with a total flow rate of 100  $\text{cm}^3/\text{min}$ , was made up with the use of a set of electronic flow meters (Brooks models 5850TR or 5850E) and standard gas mixtures (BOC, Australia). 2-Nitropropane (Ajax Chemicals Ltd.) was supplied by diverting He at a rate of 20  $\text{cm}^3/\text{min}$  through a saturator held at 0 °C, giving a concentration of 900 ppm in the feed based on the vapour pressure. 2-Methyl-2-nitropropane (Aldrich Inc.) was introduced by diverting He at a rate of 5  $\text{cm}^3/\text{min}$  through the liquid, which was maintained at 30 °C (above the melting point of 25 °C). The concentration in feed was estimated to be  $\sim 1000$  ppm, based on vapour pressure data for other nitroalkanes with similar boiling points (since exact data were not available for 2M2NP).

The exit stream from the reactor was analysed by a combination of gas chromatographic and on-line FTIR measurements in a manner similar to that described previously [9]. In essence, a sample of the stream was periodically passed through a micro gas chromatograph (MTI Instruments, model M200) with a 5A molecular sieve column (for analysis of  $\text{N}_2$ ,  $\text{O}_2$ , CO, isobutene, and isobutane) and a Poraplot U column (for analysis of propene,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , HCN, and  $\text{C}_2\text{N}_2$ ). It was then passed through a 16-cm-pathlength infrared cell in a box kept at 90 °C. Spectra, each comprising 64 scans at 0.25  $\text{cm}^{-1}$  resolution, were processed to obtain concentrations based on Beer–Lambert plots for individual lines for the NO,  $\text{NO}_2$ , HCN, 2-nitropropane (at 1556  $\text{cm}^{-1}$ ), and 2-methyl-2-nitropropane (at 1563  $\text{cm}^{-1}$ ). Calibrations were cross-checked by analysis of feeds on by-pass in comparison with the sum of the CO and  $\text{CO}_2$  produced by complete oxidation to carbon oxides over the catalyst.

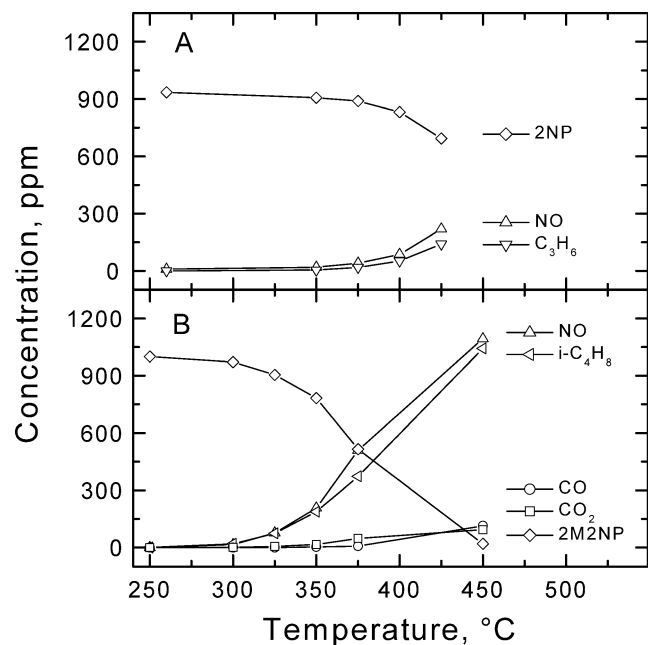


Fig. 1. Concentrations as a function of temperature for the decomposition of nitroalkanes in an empty reactor. (A) 950 ppm 2-nitropropane in helium, (B) 950 ppm 2-methyl-2-nitropropane in helium.

### 3. Results

#### 3.1. Homogeneous decomposition

The results for empty reactor tests using 2-nitropropane (2NP) and 2-methyl-2-nitropropane (2M2NP) on their own are shown in Fig. 1. The products were largely NO (NO<sub>2</sub> was not detectable), the alkene, and water (which could not be measured accurately). According to the literature [17], homogeneous decomposition of nitroalkanes higher than nitromethane occurs unimolecularly by two mechanisms, a higher temperature one in which the C–N bond is broken directly, for example, for 2NP,



and a lower temperature one in which HONO is eliminated via a five-centred mechanism,



The rate constants given recently by Zhang and Bauer [18] indicate a crossover temperature of  $\sim 540^\circ\text{C}$  for 2NP. The dominant nitrogen oxide seen in both regimes is NO, because NO<sub>2</sub> undergoes a rapid reaction (much faster than its direct decomposition) with derived by decomposition of the isopropyl radical



while HONO undergoes decomposition to the same products

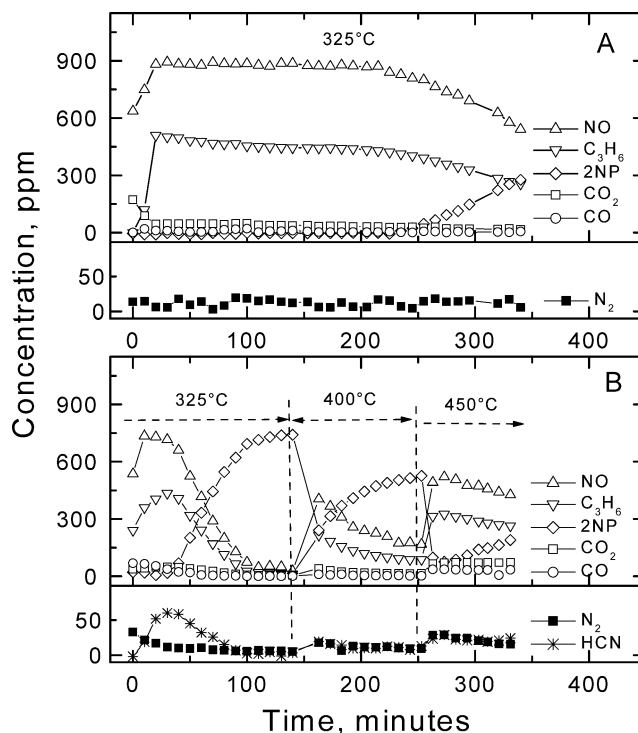


Fig. 2. Exit gas composition as a function of time during the decomposition of 950 ppm 2-nitropropane in helium. (A) over 100 mg Cu-MFI at 325 °C, (B) over 100 mg Fe-MFI at 325 °C and then 400 °C and 450 °C.

The excess oxygen in OH versus water is balanced stoichiometrically by the formation of some CO and CO<sub>2</sub>, as is apparent for 2M2NP at high conversions in Fig. 1B. Notably, N<sub>2</sub> was not detectable. Decomposition of higher nitroalkanes is known to be prone to wall contributions that are likely to be present to some extent in the reactor used here. The conversions measured for 2NP were higher than expected from the flow system data reported by Wilde [19], which in turn are higher than those expected from the rate constants given by Zhang and Bauer [18]. The higher reaction rate of 2M2NP compared with 2NP is in accord with the literature and is caused by an increase in the barrier to internal rotation [17].

#### 3.2. Catalytic reactions of 2NP

It was not possible to determine a steady-state product distribution for the catalytic decomposition of 2NP in helium alone as a function of temperature over either Cu-MFI or Fe-MFI because of the presence of continuous deactivation at partial conversion. Fig. 2 shows the behaviour for 950 ppm of 2NP at 325 °C. Decomposition was more extensive than when an empty reactor was used at the same temperature, with both catalysts giving complete conversion initially. The principal products were again NO and C<sub>3</sub>H<sub>6</sub>, but the yield of alkene was only one-half that of NO. Thus the basic reaction appeared to be the same, but with a considerable fraction of the alkene deposited on the catalyst as carbonaceous matter. This accumulation caused slow deac-

tivation, with the eventual breakthrough of unreacted 2NP. This took 200 min with Cu-MFI (Fig. 2A) but less than 50 min with Fe-MFI (Fig. 2B). Deactivation was nearly total after 120 min in the latter system and continued when the temperature was subsequently raised to 400 and then 450 °C.

The faster deactivation of Fe-MFI is likely to arise through differences in the concentration of Brønsted acid sites. The Fe-MFI was made from H-MFI, and the solid-state method used does not give complete replacement of protons. The Cu-MFI was made from Na-MFI by aqueous exchange, and the concentration of Brønsted acid sites should be lower. A higher concentration of acid sites would favour pore mouth blocking, and hence faster deactivation, through increased alkene oligomerisation. This is discussed in more detail later in connection with the data for 2-methyl-2-nitropropane.

It is clear from Fig. 2 that HC-SCR reactions between  $\text{NO}_x$  and propene were very small during decomposition. Production of  $\text{N}_2$  was at most 30 ppm with Fe-MFI and not consistently detectable with Cu-MFI. However, the distribution of the small amounts of carbon oxides seen does correspond to the HC-SCR reactions over the two catalysts, with  $\text{CO}_2$  predominant over Cu-MFI and  $\text{CO}$  predominant over Fe-MFI at the lowest temperature.

Formation of carbon oxides and  $\text{N}_2$  was considerably greater when 2NP was reacted in the presence of 3%  $\text{O}_2$ , as illustrated in Fig. 3 for reaction at 300 °C. A large fraction of the propene was oxidised to carbon oxides in the initial stages, but the carbon mole balances were still incomplete, with deposition of carbonaceous matter causing deactivation and the eventual emergence of propene, followed some time later by 2NP. The HC-SCR reaction to produce  $\text{N}_2$  was significant initially, especially with Fe-MFI, but it declined to low values when the propene concentration stabilised,  $\sim 20$  ppm with Cu-MFI and 50 ppm with Fe-MFI. Reaction over Fe-MFI also produced some HCN, which is also a characteristic of HC-SCR [20,21]. Clearly, the presence of  $\text{O}_2$  introduced additional SCR, but it remained slow compared with 2NP decomposition and did not prevent deactivation.

The course of the reaction of 950 ppm of 2NP in the presence of both  $\text{NO}$  and  $\text{O}_2$  over Cu-MFI at 300 °C (Fig. 4A) was similar to that in  $\text{O}_2$ . The  $\text{NO}$  produced by decomposition supplemented that in the feed, so that the  $\text{NO}$  concentration in the outlet stream was much greater than that in the inlet stream. Production of  $\text{N}_2$  was still low, with a maximum of 175 ppm when propene appeared after 30 min of reaction and 60 ppm when 2NP emerged. Thus, although the combination of  $\text{NO}$  and  $\text{O}_2$  enhances SCR relative to  $\text{O}_2$  alone, it does not prevent deactivation through the accumulation of deposits arising from propene.

The presence of  $\text{NO}$  and  $\text{O}_2$  changed the reaction of 2NP over Fe-MFI (Fig. 4B) to a greater extent than it did over Cu-MFI (Fig. 4A). Deactivation of Fe-MFI was much less than in  $\text{O}_2$  alone (Fig. 3B), and although the emergence of 2NP was delayed only slightly, its concentration increased

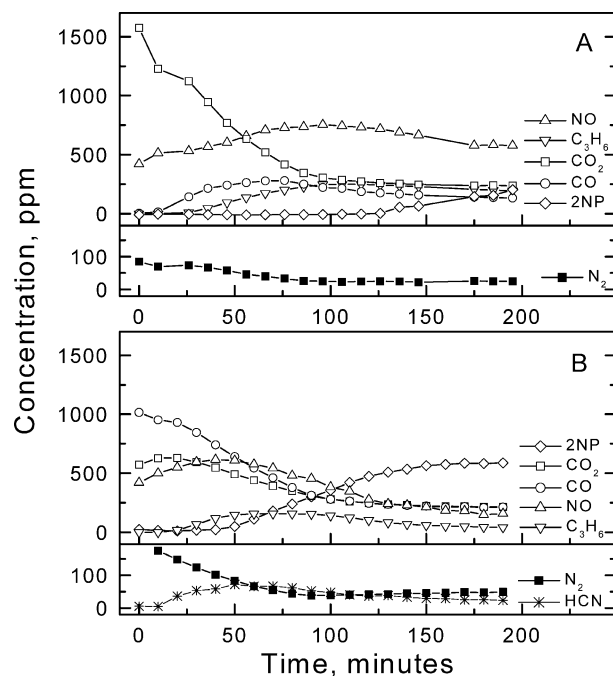


Fig. 3. Exit gas composition as a function of time during the reaction of 950 ppm 2-nitropropane in 3%  $\text{O}_2$  at 300 °C. (A) over 100 mg Cu-MFI, (B) over 100 mg Fe-MFI.

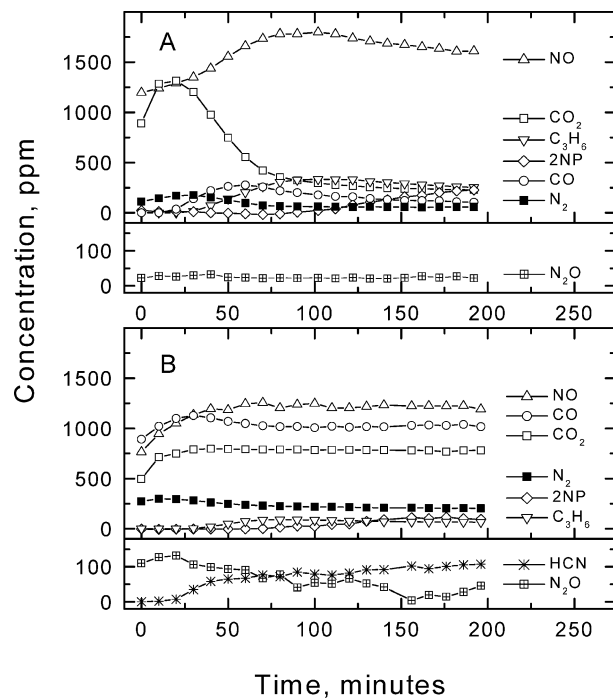


Fig. 4. Exit gas composition as a function of time during the reaction of 950 ppm 2-nitropropane in 1000 ppm  $\text{NO}/3\% \text{O}_2$  at 300 °C. (A) over 100 mg Cu-MFI, (B) over 100 mg Fe-MFI.

much less steeply and eventually levelled out. Likewise, the concentrations of  $\text{CO}$ ,  $\text{CO}_2$ , propene, and  $\text{N}_2$  were nearly constant after 70 min, at which time the mole balances were complete within experimental error. The concentration of  $\text{N}_2$  made was then 220 ppm out of the  $\sim 870$  ppm of 2NP con-



Table 1  
Product distribution and molar efficiency ( $E_{C_3}$ ) during reactions of 2-nitropropane

Catalyst	Feed	Temp. (°C)	Exit gas composition (ppm)					$E_{C_3}^a$
			2NP	NO	C <sub>3</sub> H <sub>6</sub>	N <sub>2</sub> /N <sub>2</sub> O	CO/CO <sub>2</sub>	
Cu-MFI	2NP + O <sub>2</sub> <sup>b</sup>	350	< 10	350	< 10	240/36	< 10/2700	0.60
	2NP + NO + O <sub>2</sub> <sup>c</sup>	350	< 20	940	< 10	410/70	< 20/2520	1.14
Fe-MFI	2NP + O <sub>2</sub> <sup>b</sup>	325	90	380	25	190/25	1310/870	0.59
	2NP + NO + O <sub>2</sub> <sup>c</sup>	325	20	930	< 10	340/34	1500/1000	0.90

<sup>a</sup> Defined as moles of N in N<sub>2</sub> made per mole C<sub>3</sub> used and calculated as:  $E_{C_3} = 2(\text{ppm N}_2 + \text{ppm N}_2\text{O}) / \frac{1}{3}(\text{ppm CO} + \text{ppm CO}_2)$ .

<sup>b</sup> Using 950 ppm 2NP and 3% O<sub>2</sub>.

<sup>c</sup> Using 950 ppm 2NP, 1000 ppm NO and 3% O<sub>2</sub>.

verted. Thus SCR reactions in general were more significant than they were with Cu-MFI (Fig. 4A). However, decomposition was still the principal reaction, since the concentration of NO in the product stream still exceeded that in the feed.

It is clear from Figs. 2–4 that 2NP underwent catalytic decomposition faster than it was converted to N<sub>2</sub>. It also appears more likely that the N<sub>2</sub> that is seen arises through SCR between NO/O<sub>2</sub> and propene rather than reaction of NO/O<sub>2</sub> with 2NP, but this is hard to establish unequivocally. Some inferences can be drawn from a consideration of the product distribution during reactions commenced at higher temperatures where hydrocarbon conversions were almost complete, 350 °C for Cu-MFI and 325 °C for Fe-MFI. Under such conditions the efficiency of conversion of NO to N<sub>2</sub> formation during propene SCR ( $E_{C_3}$ ) with an equimolar feed is typically about 1.0 for Cu-MFI [22] and 0.8 for Fe-MFI [23] on the basis of moles of N in N<sub>2</sub> made per mole of organic used. On the other hand, the expected ratio for an efficient 1:1 SCR reaction between 2NP itself and NO/O<sub>2</sub> would be 2. As may be seen from Table 1,  $E_{C_3}$  was approximately 0.6 for the reaction of 2NP in O<sub>2</sub> alone and approximately 1 with NO present as well, which is more consistent with propene SCR rather than a direct 2NP-plus-NO<sub>x</sub> reaction. The higher value for  $E_{C_3}$  with NO in the feed is explainable in terms of the increased NO/propene ratio.

### 3.3. Catalytic reactions of 2-methyl-2-nitropropane

As with 2NP, the decomposition of 2M2NP alone in helium was initially complete over both catalysts at 325 °C (Fig. 5), but a steady state was reached after approximately 100 min, when the products were largely NO and isobutene. However, the reaction also yielded propene in large amounts initially, especially with Fe-MFI, where the concentration of propene exceeded that of isobutene for the first 50 min. The propene probably arose through acid-catalysed reactions on residual Brønsted acid sites. H-MFI, like H-ferrierite, is an active catalyst for the skeletal isomerisation of *n*-butenes to isobutene, which proceeds, at least in part, by a dimerisation/cracking mechanism through carbenium ion intermediates [24]. However, the selectivity for the reaction is rather poor, since isomerisation of C<sub>8</sub> intermediates leads to additional cracking pathways that facilitate the formation of propene, which can be the largest single product with some

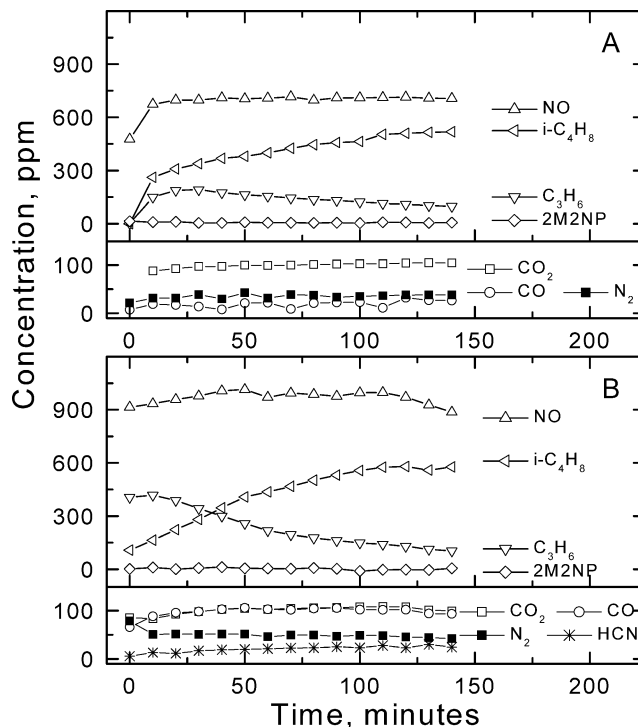


Fig. 5. Exit gas composition as a function of time during the decomposition of 950 ppm 2-methyl-2-nitropropane in helium. (A) over 100 mg Cu-MFI at 325 °C, (B) over 100 mg Fe-MFI at 330 °C.

catalysts at 300 °C [25]. Since isobutene and *n*-butenes are near equally favoured at equilibrium at this temperature, there is no reason why the same processes cannot occur starting from the branched isomer, formed here by the decomposition of the nitroalkane. In principle, C<sub>8</sub> carbenium ion intermediates may also crack to form pentenes, but the amounts produced during the isomerisation of *n*-butenes over H-MFI are much less than that of propene [25]. No peaks attributable to branched pentenes were observed during 2M2NP decomposition over Cu-MFI or Fe-MFI, but analysis for *n*-pentenes was not possible with the gas chromatography system in use here.

The decline in propene formation with time evident in Fig. 5 can be attributed to the accumulation of higher oligomers, including aromatic material as characterised by Andy et al. [26] for the skeletal isomerisation of *n*-butene over H-ferrierite, which has higher selectivity than H-MFI

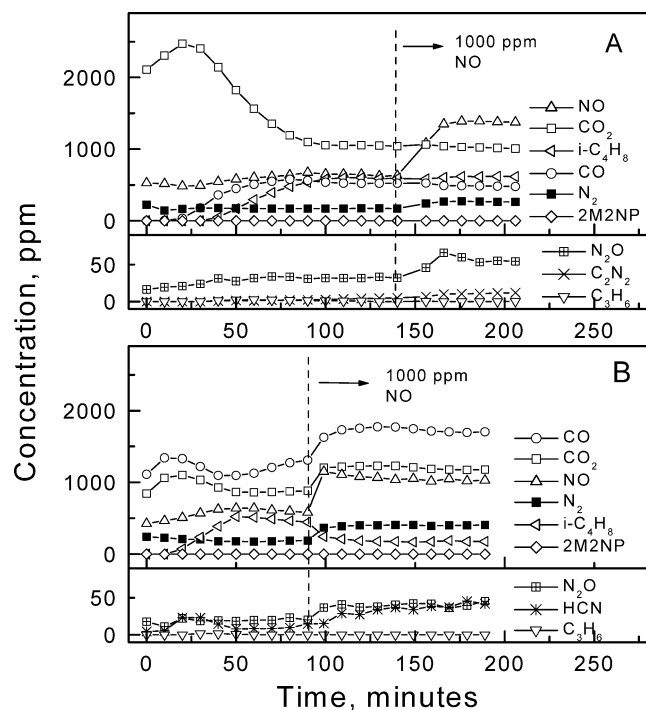


Fig. 6. Exit gas composition as a function of time during the reaction of 950 ppm 2-methyl-2-nitropropane in 3% O<sub>2</sub>/He with 1000 ppm NO added subsequently. (A) over 100 mg Cu-MFI at 315 °C, (B) over 100 mg Fe-MFI at 315 °C.

but otherwise behaves similarly. However, the compositions of the deposits appeared to differ between the two catalysts studied here. With Cu-MFI both carbon and nitrogen balances were low by substantial amounts (~25%), indicating the present of both elements in deposits. With Fe-MFI the only large deficit was that of carbon, so the deposits were predominantly carbonaceous. It is apparent from a comparison of Figs. 2B and 5B that Fe-MFI deactivated faster during the decomposition of 2NP than during that of 2M2NP. The deficit in the carbon balance was also greater with 2NP. It appears that propene oligomerises to nonvolatile material faster than does isobutene, causing greater pore blockage.

Production of propene was totally quenched over both catalysts when 2M2NP was reacted in 3% O<sub>2</sub> (Fig. 6). Carbon oxides and NO were the principal products initially, and the carbon mole balance was then low, indicating deposition. However, this process slowed as isobutene emerged, and deposition was not detectable in the steady state reached after 100 min with Cu-MFI and 50 min with Fe-MFI. Both catalysts then gave approximately 500 ppm NO and 200 ppm N<sub>2</sub>, and the concentration of isobutene approached 500 ppm. Thus decomposition is the major reaction, with subsequent SCR processes using NO<sub>x</sub> derived in this way as a likely source of N<sub>2</sub> and carbon oxides.

With Cu-MFI (Fig. 6A), the addition of NO after 140 min of exposure to 2M2NP in O<sub>2</sub> caused a small increase in N<sub>2</sub> production but little change in the concentrations of CO, CO<sub>2</sub>, and isobutene, consistent with a small increase in isobutene SCR at the expense of alkene oxidation. With

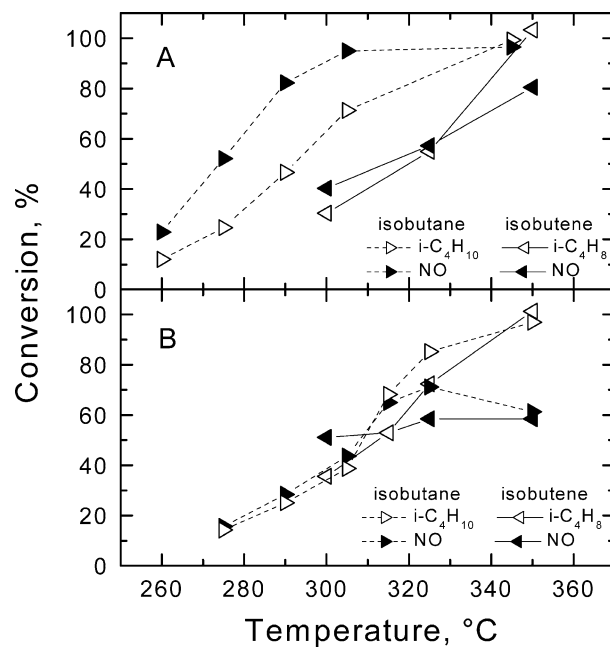


Fig. 7. Temperature dependence of isobutane-SCR and of isobutene-SCR using 1000 ppm hydrocarbon, 1000 ppm NO and 3% O<sub>2</sub>. (A) over 100 mg Cu-MFI, (B) over 100 mg Fe-MFI.

Fe-MFI (Fig. 6B), the inclusion of NO increased the concentration of N<sub>2</sub> to a larger extent, with a corresponding increase in the production of carbon oxides at the expense of isobutene. One possible interpretation could be that the higher NO concentration increased isobutene SCR through the utilisation of more isobutene. Even so, it remains apparent that decomposition of 2M2NP to give NO was at least as fast as all of the processes that produce N<sub>2</sub>, since the NO concentration in the product stream exceeded that in the feed, especially with Cu-MFI. It is noteworthy that the minor CN-containing products evident during the reactions of 2M2NP in NO/O<sub>2</sub>, trace concentrations of C<sub>2</sub>N<sub>2</sub> for Cu-MFI, and high amounts of HCN for Fe-MFI match those seen during isobutane SCR over the same catalysts [11,27].

In the case of 2NP, arguments based on molar efficiency indicated that N<sub>2</sub> was made through alkene SCR rather than a 1:1 SCR reaction between 2NP and NO<sub>x</sub>. This appears to be the case with 2M2NP as well, but the evidence is not quite so clear cut, because the efficiency of SCR with isobutene, based on data presented in Fig. 7, is higher than SCR with propene. Table 2 provides a comparison of product distribution and molar efficiencies for isobutene SCR and the reactions of 2M2NP in O<sub>2</sub>, in NO/O<sub>2</sub>, and in NO<sub>2</sub>/O<sub>2</sub> for Cu-MFI. The expected efficiency for a 1:1 SCR reaction between 2M2NP and NO<sub>x</sub> as defined here is 2. The observed value for the reaction of 2M2NP in O<sub>2</sub> alone is ~1.1 at 315 °C, falling to ~0.7 at 350 °C when isobutene is no longer a product. As may be seen, these values are close to those for isobutene SCR under similar conditions, and the ratios of CO to CO<sub>2</sub> and of N<sub>2</sub>O to N<sub>2</sub> are also similar. Thus it seems likely that most of the N<sub>2</sub> made during the reaction of 2M2NP in O<sub>2</sub> is derived by isobutene SCR rather

Table 2  
Product distributions and molar efficiencies ( $E_{C_4}$ ) during isobutene-SCR and reactions of 2-methyl-2-nitropropane (2M2NP) over Cu-MFI

Feed	Temp. (°C)	Exit gas composition (ppm)					$E_{C_4}^a$
		NO	C <sub>4</sub> H <sub>8</sub>	N <sub>2</sub> /N <sub>2</sub> O	CO/CO <sub>2</sub>	C <sub>2</sub> N <sub>2</sub> /NO <sub>2</sub>	
C <sub>4</sub> H <sub>8</sub> + NO + O <sub>2</sub> <sup>b</sup>	325	440	510	220/70	870/1320	6/nil	1.04
	350	210	nil	310/90	145/3990	nil/4	0.78
2M2NP + O <sub>2</sub> <sup>c</sup>	315	640	590	170/32	530/1050	4/4	1.02
	350	340	nil	270/71	190/3470	nil/5	0.75
2M2NP + NO + O <sub>2</sub> <sup>d</sup>	315	1390	630	260/55	470/990	12/6	1.70
2M2NP + NO <sub>2</sub> + O <sub>2</sub> <sup>e</sup>	315	1530	500	320/54	620/1260	19/9	1.59

<sup>a</sup> Defined as moles NO reduced per mole C<sub>4</sub> used and calculated as:  $E_{C_4} = 2(\text{ppm N}_2 + \text{ppm N}_2\text{O}) / \frac{1}{4}(\text{ppm CO} + \text{ppm CO}_2)$ .

<sup>b</sup> Using 1000 ppm C<sub>4</sub>H<sub>8</sub>, 1000 ppm NO and 3% O<sub>2</sub>/He.

<sup>c</sup> Using 950 ppm 2M2NP and 3% O<sub>2</sub>/He.

<sup>d</sup> Using 950 ppm 2M2NP, 1000 ppm NO and 3% O<sub>2</sub>/He.

<sup>e</sup> Using 950 ppm 2M2NP, 850 ppm NO<sub>2</sub> and 3% O<sub>2</sub>/He.

Table 3  
Product distributions and molar efficiencies ( $E_{C_4}$ ) during isobutene-SCR and Reactions of 2-methyl-2-nitropropane (2M2NP) over Fe-MFI

Feed	Temp. (°C)	Exit gas composition (ppm)					$E_{C_4}^a$
		NO	C <sub>4</sub> H <sub>8</sub>	N <sub>2</sub> /N <sub>2</sub> O	CO/CO <sub>2</sub>	HCN/NO <sub>2</sub>	
C <sub>4</sub> H <sub>8</sub> + NO + O <sub>2</sub> <sup>b</sup>	325	480	280	250/37	1780/1110	13/6	0.79
	350	480	nil	250/39	2420/1630	nil/15	0.58
2M2NP + O <sub>2</sub> <sup>c</sup>	315	610	490	180/20	1200/870	10/3	0.77
	350	410	nil	200/24	1780/1420	nil/66	0.55
2M2NP + NO + O <sub>2</sub> <sup>d</sup>	315	1030	170	400/41	1710/1190	39/5	1.22
2M2NP + NO <sub>2</sub> + O <sub>2</sub> <sup>e</sup>	315	940	60	550/36	2000/1400	39/9	1.38

<sup>a</sup> Defined as moles NO reduced per mole C<sub>4</sub> used and calculated as:  $E_{C_4} = 2(\text{ppm N}_2 + \text{ppm N}_2\text{O}) / \frac{1}{4}(\text{ppm CO} + \text{ppm CO}_2)$ .

<sup>b</sup> Using 1000 ppm C<sub>4</sub>H<sub>8</sub>, 1000 ppm NO and 3% O<sub>2</sub>/He.

<sup>c</sup> Using 950 ppm 2M2NP and 3% O<sub>2</sub>/He.

<sup>d</sup> Using 950 ppm 2M2NP, 1000 ppm NO and 3% O<sub>2</sub>/He.

<sup>e</sup> Using 950 ppm 2M2NP, 850 ppm NO<sub>2</sub> and 3% O<sub>2</sub>/He.

than through a reaction between 2M2NP itself and the NO produced by 2M2NP decomposition. However, the efficiencies for the reactions of 2M2NP in NO/O<sub>2</sub> and NO<sub>2</sub>/O<sub>2</sub> are both > 1.5. The higher values could be a consequence of an improvement in the efficiency of isobutene SCR as a result of the higher NO<sub>x</sub>/isobutene ratio. However, they are sufficiently close to 2 that a contribution from a direct reaction cannot be ruled out.

A primary contribution from isobutene SCR is more certain with Fe-MFI (Table 3). The efficiency and the product distribution for 2M2NP in O<sub>2</sub> match those for isobutene SCR very closely. The efficiencies for 2M2NP in NO/O<sub>2</sub> and NO<sub>2</sub>/O<sub>2</sub> are higher, but they are still well below 2, and kinetic measurements of isobutene SCR over the Fe-MFI used here show that the order in NO is considerably higher for the production of N<sub>2</sub> than of carbon oxides [28]. If the same were true for isobutene SCR, then the efficiency should increase substantially when NO is available from the feed and not just through 2M2NP decomposition.

### 3.4. Alkene SCR versus alkane SCR

The above data indicate that if 2NP and 2M2NP were formed during HC-SCR, then their principal reaction would

not be directly with NO/O<sub>2</sub> to form N<sub>2</sub>. They are more likely to contribute through a sequence such as



However, this is reasonable only if isobutene SCR is much faster than alkane SCR, since alkenes are very minor products of the latter reaction. Fig. 7 compares the temperature dependencies of isobutane SCR and isobutene SCR for the present catalysts under noncompetitive conditions. It is apparent that the two hydrocarbons react at similar rates over Fe-MFI, but isobutane is considerably more reactive than isobutene over Cu-MFI, opposite to the above requirement. However, tests under competitive conditions reveal a different picture, as shown in Fig. 8 for SCR with a mixture of 800 ppm isobutane and 200 ppm isobutene. The reaction of isobutene is complete throughout over both catalysts, even though some isobutane remains unconverted from the start and its concentration grows substantially with time. Thus isobutene reacts in preference to isobutane under competitive conditions. Hence it appears possible that 2M2NP and, by extension, secondary and tertiary nitrocompounds in general, could contribute to N<sub>2</sub> formation during HC-SCR via the above indirect sequence.

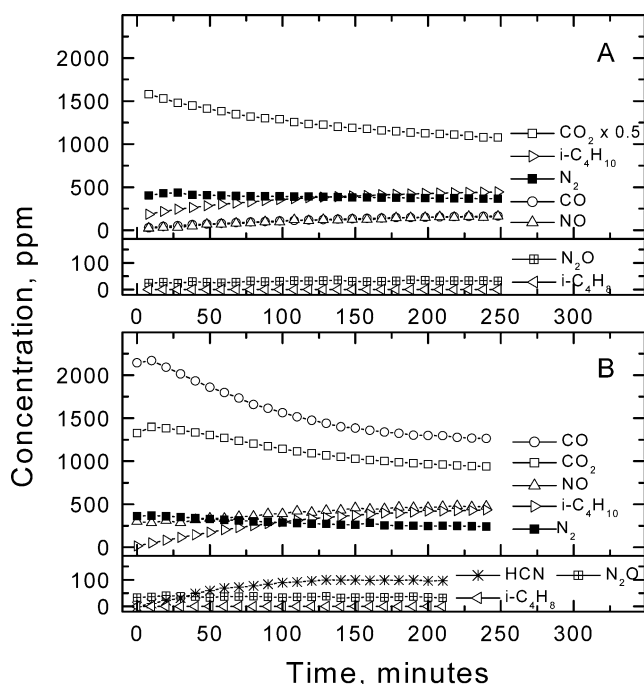
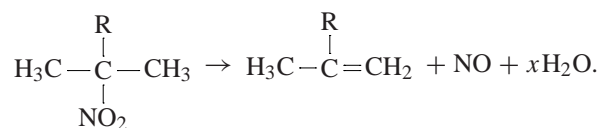


Fig. 8. Exit gas composition as a function of time during the SCR reaction of a mixture of 800 ppm isobutane and 200 ppm isobutene in 1000 ppm NO/3% O<sub>2</sub>/He. (A) 100 mg of Cu-MFI at 325 °C, (B) 100 mg Fe-MFI at 315 °C.

#### 4. Discussion

The possibility that nitro- and nitrosoalkanes are intermediates in the HC-SCR arises because surface NO<sub>x</sub> species are reactive towards saturated hydrocarbons [29]. If hydrogen abstraction leads to species that are like alkyl radicals, then they should combine readily with one electron species, NO or NO<sub>2</sub>. On the grounds of CH bond strength, one would expect radicals to be formed in the order tertiary > secondary > primary, but the geometry of motion of alkanes in narrow zeolite channels and/or a higher number of methyl hydrogens may lessen the bias against primary attack. The ratio of formation, nitroso- versus nitro-, should be influenced by the relative abundance of NO versus NO<sub>2</sub>. NO is dominant when the hydrocarbon conversion is incomplete, but NO<sub>2</sub> is also present at complete conversion.

The present work shows that 2-nitropropane and 2-methyl-2-nitropropane, representative secondary and tertiary nitroalkanes, react in similar ways over Cu-MFI and Fe-MFI. In an inert carrier there is decomposition to the corresponding alkenes and NO (Figs. 2 and 5):



This equation is unbalanced and the additional H ( $x = 1$ ) or missing O ( $x = 0.5$ ) is likely to arise from or be lost to the carbonaceous matter produced by deposition of some of

the alkene. When the feed contains O<sub>2</sub>, some of the NO and alkene undergoes an SCR reaction to form N<sub>2</sub> (Figs. 3 and 6). With NO included as well, the concentration of NO in the outlet stream exceeds that in the input stream. More N<sub>2</sub> is produced, but this can still be explained largely in terms of an SCR reaction between NO<sub>x</sub> and the alkene rather than the nitroalkane and NO<sub>x</sub>.

Thus one conclusion we come to here is that secondary and tertiary nitroalkanes are rather unlikely to be direct intermediates in the SCR reaction of the parent alkane, propane or isobutane, over Cu-MFI or Fe-MFI in the sense that they are directly converted to N<sub>2</sub>. We suggest this despite the fact that Chen et al. [2] have provided good experimental evidence that 2NP, adsorbed on Fe-MFI at 200 °C, reacts readily with NO<sub>2</sub> to produce N<sub>2</sub> in a largely 1:1 fashion. In the present experiments, as is generally true during SCR using higher hydrocarbons at partial conversion, the concentration of NO<sub>2</sub> is low, which may restrict the extent of this reaction. However, a second conclusion is that secondary or tertiary nitroalkanes could still be indirect sources of N<sub>2</sub> in alkane SCR, through the creation of alkenes that react in preference to the starting alkane, as illustrated in Fig. 8. The alkenes are also a probable source of deactivation during alkane SCR under conditions of partial conversion.

The behaviour observed here for secondary and tertiary nitroalkanes is quite unlike that of small primary nitroalkanes. Nitroethane, for example, is readily converted to N<sub>2</sub> over Cu-MFI under SCR conditions with methyl isocyanate as an intermediate and without detectable decomposition to ethylene and NO [13]. (Nitromethane reacts similarly over many transition-metal zeolites [9–12], but that is not so relevant here, since its decomposition cannot yield an alkene directly.) The reason for the different behaviour of primary alkanes is obvious. They possess two hydrogens  $\alpha$  to the NO<sub>2</sub> group that allow the formation of the *aci*-nitro form and its subsequent dehydration per Eq. (2). If there are one or no  $\alpha$ -hydrogens, as in secondary and tertiary nitroalkanes, respectively, then the second or both of these steps are impossible and decomposition to an olefin and NO<sub>x</sub> becomes the default mode.

The demonstration that secondary and tertiary nitroalkanes are unlikely to be direct sources of N<sub>2</sub> during HC-SCR carries implications for the possible involvement of nitrosoalkanes as well, since C–NO bonds are weaker than C–NO<sub>2</sub> bonds. In the gas phase 2-methyl-2-nitrosopropane, the direct analogue to 2M2NP, decomposes rapidly according to



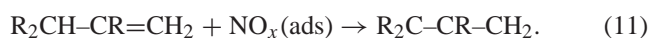
with a half-life of  $\sim 0.5$  sec at 300 °C based on the measurements of Choo et al. [30]. Lifetimes of this order may be sufficient to permit tautomerism and reactions of primary nitrosoalkanes and hence allow the oxime  $\rightarrow$  nitrile  $\rightarrow$  amine route, reactions (1) and (3), under SCR conditions, but this is precluded with secondary or tertiary nitrosoalkanes, and



decomposition seems highly likely, given the behaviour of nitroalkanes.

The mechanism by which zeolites facilitate the decomposition of secondary and tertiary nitroalkanes and, by extension, nitrosoalkanes to NO and alkenes is unclear. One possibility is that it proceeds as in the gas phase, with the strong electric fields within cages enhancing molecular decomposition, reaction (6), and/or direct cleavage of the polar C–NO<sub>2</sub> bond, reaction (5). The alkyl radical formed in the latter case could then give the alkene by loss of hydrogen to the zeolite. This is likely to be a facile process based on the behaviour of C<sub>4</sub>H<sub>9</sub> radicals formed in the gas-phase decomposition of 2-methyl-2-nitrosopropane [30]. The principal products are a 1:1 mixture of isobutene and isobutane through disproportionation with some 2,2,3,3,-tetramethylbutane formed through dimerisation. The formation of isobutene is wall-catalysed, with C<sub>4</sub>H<sub>9</sub> losing H, which is then added to another C<sub>4</sub>H<sub>9</sub> to form isobutane. Loss of hydrogen, and its subsequent oxidation, should be more efficient under SCR conditions, given the transport constraints present in zeolite channels.

The present results suggest that one facet of the alkane SCR reaction could be the formation of more reactive alkenes, as favoured in a recent study of propane SCR over Cu-MFI and H-MFI [31]. The chemistry of the subsequent alkene SCR is easily envisaged. Abstraction of a hydrogen from a carbon adjacent to the double bond should be more favourable than abstraction from an alkane, given the greater stability of the allyl radical that is produced:



The nitroso- or nitroalkenes that could then form by NO<sub>x</sub> addition are necessarily primary, with the two α-hydrogens required for tautomerism and dehydration to an unsaturated nitrile or an isocyanate (i.e., acrylonitrile and allylisocyanate in the case of propene). These compounds are highly reactive and should readily produce N<sub>2</sub>, either through deposit formation and reaction with NO<sub>2</sub>, as shown by Chen et al. [2], or through hydrolysis to ammonia and NH<sub>3</sub>-SCR, as envisaged by Gerlach et al. [32,33], who observed acrylonitrile as a trace product of the propene + NO<sub>2</sub> reaction over H-mordenite. Acrylonitrile has also been observed during propane SCR and, to a larger extent, during propene SCR over H-MFI [31]. Likewise, methacrylonitrile has been seen during isobutane SCR over Fe-MFI [34].

## 5. Conclusions

The primary reactions of 2-nitropropane and 2-methyl-2-nitropropane over Cu-MFI and Fe-MFI are decomposition to NO and the corresponding alkenes, propene and isobutene, respectively. If O<sub>2</sub> is present in the feed, then N<sub>2</sub> can be produced subsequently by an SCR reaction between the NO and the alkene. If the feed contains NO as well, then production

of N<sub>2</sub> is increased, but this can be explained largely by enhancement of the alkene SCR reaction rather than a direct reaction between the nitroalkane and NO/O<sub>2</sub>. Some of the alkene produced by nitroalkane decomposition is converted to carbonaceous deposits that cause catalyst deactivation. Under inert conditions oligomers derived from isobutene produced by decomposition of 2-methyl-2-nitropropane undergo disproportionation to form propene, but this secondary reaction is quenched when O<sub>2</sub> or NO/O<sub>2</sub> is present. The behaviour of the test secondary and tertiary nitroalkanes is quite different from that of primary nitroalkanes, where the presence of two α-hydrogens allows tautomer formation followed by dehydration to a reactive isocyanate. The overall conclusion is that if secondary and tertiary nitroalkanes are formed during alkane-SCR, they are unlikely to be direct sources of N<sub>2</sub>. However, they could still play a role through the production of alkenes, which undergo the SCR reaction to N<sub>2</sub> in preference to the parent alkane.

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