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The mechanism of the selective reduction of nitrogen oxides by hydrocarbons on zeolite catalysts

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Abstract

The mechanism of the selective catalytic reduction (SCR) of nitrogen oxides over 3d transition metal zeolites has been investigated in a variety of ways. The initial step is the abstraction of hydrogen from the hydrocarbon by adsorbed NO_2 species which is rate determining with methane but not with isobutane. The subsequent path appears to involve nitroso and/or nitro compounds. Comparative studies of the reactions of such compounds indicate that nitromethane is more likely to be an intermediate than nitrosomethane during the methane-SCR reaction over Co-MFI although the latter cannot be ruled out entirely. In both cases the predominant route to N_2 is an initial decomposition to carbon oxides and ammonia followed by the NH_3-SCR reaction. The isobutane-SCR reaction over Fe-MFI produces substantial amounts of hydrogen cyanide which disappears only at temperatures where all the hydrocarbon has been consumed. Hydrogen cyanide appears to arise from isobutyronitrile, the expected dehydration product if an initially formed nitroso compound undergoes tautomerism to an oxime. HCN is converted to N_2 largely by reaction with NO_2 which is fast well below 300°C in the absence of isobutane. The corresponding isobutane-SCR reaction over Cu-MFI gives rise to cyanogen (C_2N_2) rather than HCN. The general path is probably the same in the two systems with the difference arising from variation in the relative reactivity of HCN. The copper-containing catalyst is very effective at forming and dimerising adsorbed cyanide groups while the iron catalyst has higher activity for the oxidation of NO to the NO_2 needed to convert adsorbed cyanide to N_2. The difference between the apparent involvement of a nitro route in methane-SCR with Co-MFI, and a nitroso one with isobutane, is similarly explainable. The former reaction proceeds with simultaneous production of NO_2 which can participate in the intermediate chemistry that follows. However, the NO_2 concentration is low during the latter reaction over Cu-MFI and Fe-MFI as long as any hydrocarbon remains. This is due to the blocking of sites for NO oxidation by deposits and the recycling of NO_2 back to NO during hydrocarbon oxidation. Thus only NO is available and the nitroso route prevails. The extent to which this picture applies with other catalysts and other hydrocarbons remains to be established. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The application of Cu-MFI catalysts for the selective reduction of nitrogen oxides in excess oxygen was first reported in the open literature 10 years ago [1,2] although there were earlier reports in patents [3,4]. Under laboratory conditions its performance is impressive. Using isobutane, for example, complete NO_x removal is possible above 300°C with a hydrocarbon/NO_x ratio of unity [5]. Even so, the effective utilisation of the hydrocarbon is quite poor with less than one-tenth used for reduction, if the oxidant is taken as NO, and less than one in five if it is NO_2. The remainder is wasted through combustion.

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The overall removal of NO_x under practical conditions in vehicle tests is low, less that 30%, due to a variety of factors including inhibition by the high steam content, the presence of interactions within hydrocarbon mixtures and a poor temperature match [1]. Even worse, the catalyst deactivates quickly under vehicle conditions [6] and is poisoned by sulphur from fuel.

Despite a great deal of subsequent work a stable catalyst with overall performance better than Cu-MFI is yet to be found. Platinum-based systems can resist sulphur, and are active at low temperature but their effective temperature range is very narrow and undesirable N_2O is produced as well as N_2 [7,8]. Initial reports for a novel Fe-MFI indicated high effectiveness and good resistance to steam and SO_2 [9,10]. Unfortunately, these findings have proven difficult to reproduce [11] although other methods of preparation remain a matter of interest [12].

A somewhat similar story pertains in respect of possible catalysts for the selective reduction of nitrogen oxides using methane in stationary source applications. The performance of the first reported catalyst, Co-MFI, is very good under laboratory conditions but it is inhibited by water [13]. Cobalt-beta zeolite exhibits the best resistance to sulphur poisoning and it may be useable for SCR on natural gas fuelled combustion systems where the SO_2 concentrations are very low [14]. Some progress in improving performance continues to be reported for both oxide and zeolite catalysts but systems suitable for replacement of NH_3-SCR systems on power stations, for example, remain a long way off.

Despite the technological disappointments so far, the area remains one of the considerable scientific interest, especially in respect of the mechanism through which the hydrocarbon facilitates nitrogen–nitrogen bond formation. Four potential mechanisms were identified early on for Cu-MFI catalysts [15]. One suggested that the initial step was NO dissociation, a known reaction on Cu-MFI, with the hydrocarbon acting to remove the deposited oxygen which otherwise strongly inhibits decomposition. A second postulated that the initial step was partial oxidation to produce a C_xH_yO species which achieves reduction in the same way as oxygenates in general. The third proposal was that organonitrogen compounds are formed. This idea has subsequently become intertwined with the fourth idea, that NO is first oxidised to the more effective oxidant, NO_2, followed by production of N_2 through a series of degradations starting from species containing all three of carbon, nitrogen and oxygen. Misono and co-workers [16,17] were the first to speculate that nitroparaffins (i.e. R–NO_2) were intermediates in the latter process while Beutel et al. [18] presented findings indicating that nitroso species (R–NO) were another possibility.

In recent years a variety of evidence has been built up to show that the fourth mechanism is feasible, at least in principle, although full details at the elementary step level on the catalyst surface remain to be established. The amount of literature in this area is too large to be considered in full here. Instead the presentation will selectively consider some of the findings which implicate the involvement of NO_2 and then consider pathways which have been established as generators of N_2. Attention there will focus on the reactions of compounds related to potential intermediates over 3d transition metal zeolites as studied in this laboratory and elsewhere.

2. Experimental aspects

The determination of hydrocarbon and NO_x conversion during HC-SCR is straightforward using standard gas chromatographs and chemiluminescent analysers, respectively. However, kinetic investigations requiring product analysis at low conversions are not necessarily simple since the determination of N_2 and N_2O at <100 ppm (i.e. 20% yield from a 1000 ppm NO feed) is approaching the limit of most conventional chromatographs with standard thermal conductivity detectors. So-called micro-gas chromatographs, with solid state elements that are accurate at parts per million concentrations, are then advantageous. FTIR using flow through gas cells is also very useful for trace analysis. Determination of NO, NO_2, N_2O, CO, CO_2, HCN, HNCO and many hydrocarbons is feasible and the procedure can be made absolute for many small molecules through processing against the HITRAN tabulation of spectral lines [19]. Multiple reflection cells can be used to lengthen the pathlength and improve the detection limit but are not really necessary for parts per million analysis if the resolution is relatively high ($0.25\,cm^{-1}$) and an MCT detector is available to allow accumulation of many scans in a reasonable time.

The catalyst testing described here was carried out in a standard flow system with simultaneous analyses using a micro-gas chromatograph (MTI Instruments Model M200) and FTIR (Mattson Cygnus 100) with a heated 16 cm pathlength cell both on a cycle time of ~2 min. Full details may be found elsewhere [20]. A quadrupole mass spectrometer with multiple ion monitoring (Vacuum Generators SX200 or Balzers Thermostar) was added when feeding deuterated hydrocarbons (in order to follow the approach to isotope equilibrium) and to confirm the identification of cyanogen which exhibits characteristic signals with *m/z* of 26 and 52.

The Co-MFI (Si/Al = 11.2, 4.2 wt.% Co, 91.5% exchanged) was provided by Dr. J. Armor of Air Products and preparation details can be found elsewhere [13,21,22]. Cu-MFI was prepared by exchange of Na-MFI (Tosoh, Si/Al = 11.9) to an exchange level of 80% followed by drying and calcination in air. The Fe-MFI (Si/Al = 11.4, Fe/Al = 0.75) was from a batch prepared by Kögel et al. [23,24] using a solid state ion exchange method. The Fe-ferrierite was prepared similarly from an NH_4^+-exchanged potassium ferrierite (Tosoh, Si/Al = 8.4).

3. Results and discussion

3.1. Evidence for NO_2 involvement

The simplest evidence for the involvement of NO_2 are experiments showing more extensive reaction if it is fed in place of NO, or that NO_2 is formed and consumed under reaction conditions. Fig. 1 shows an example during methane-SCR over Co-MFI. In the absence of methane, NO_2 formation is close to equilibrium above 400°C. With methane present it is well short. The simplest explanation is that the SCR step consumes NO_2 not NO but there are other possibilities.

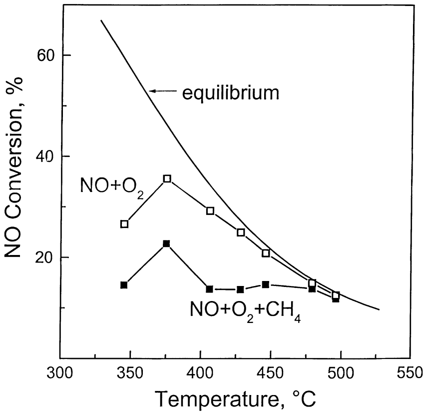


Fig. 1. Conversion of NO to NO_2 as a function of temperature in the presence and absence of methane over 0.36 g Co-MFI using 1640 ppm NO, 1000 ppm CH_4 in 3%O_2/He with total flow rate of 100 cm^3/min.

More convincing evidence for the involvement of NO_2 in hydrocarbon-SCR is the apparent bifunctionality of the reaction with NO oxidation occurring on one type of site and subsequent conversion to N_2 on others. Thus a mechanical mixture of Mn_2O_3 (a good catalyst for oxidising NO to NO_2) and Ce-MFI gives considerably better NO_x removal efficiency with propene than either component alone [25]. The same is true for mixtures of Mn_2O_3 with Sn-MFI (a very poor SCR catalyst on its own). This system also eliminates the inhibition by water which is characteristic of 3d transition metal zeolites, since water does not affect the activity of Mn_2O_3 for NO oxidation. Indeed performance is better in the presence of water which suppresses hydrocarbon combustion. Similarly, the performance of In-MFI, a highly selective but low activity catalyst for methane-SCR, can be improved by the addition of small amounts of noble metals, especially iridium, which provide a NO oxidation function unaffected by water [26]. The concept of bifunctionality has been taken further by Iwamoto et al. [27] who tested two bed systems with the hydrocarbon added between an upstream Pt-MFI catalyst (for NO oxidation) and another metal zeolite downstream. All combinations exhibited improved NO conversion over that of the downstream catalyst alone at low temperatures but improvements at higher temperature were confined to ones with a low activity catalyst downstream (e.g. Zn-MFI). Active ones (e.g. Cu-MFI) then showed no improvement which could be because their activity for the oxidation of NO to NO_2 is already such that the extra NO_2 provided by the upstream bed of Pt-MFI is of no benefit.

Another interesting example is provided by recent work comparing Fe-MFI and Fe-ferrierite for

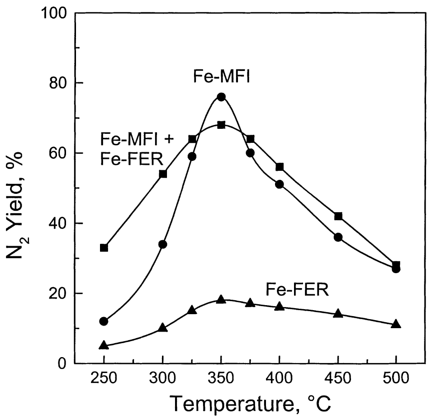


Fig. 2. NO_x conversion as a function of temperature during isobutane-SCR over: (a) 0.2 g Fe-MFI; (b) 0.2 g Fe-ferrierite; (c) mixed bed of 0.1 g Fe-MFI and 0.1 g of ferrierite using 2000 ppm NO, 2000 ppm C_4H_{10} in $3\%O_2$/He with total flow rate of 280 cm^3/min. Constructed from data in Ref. [28].

isobutane-SCR [28]. As may be seen from Fig. 2, the maximum conversion of NO is much lower with Fe-ferrierite (18%) than with Fe-MFI (76%). This was explained in terms of restrictions to the diffusion of isobutane within the smaller pores of ferrierite. Despite this, a 1:1 combination of Fe-ferrierite and Fe-MFI was considerably more active than the same total mass of Fe-MFI at low temperature, with little loss in peak conversion efficiency. Again this is a bi-functional effect. As shown in Fig. 3, Fe-ferrierite is more active than Fe-MFI (and other transition metal zeolites) for NO oxidation [29,30] and hence provides NO_2 which can be utilised for SCR within the larger pores of Fe-MFI. The mixed catalyst also exhibited much slower deactivation than Fe-MFI under conditions of partial isobutane conversion since more NO_2 was available for oxidation of deposited carbonaceous material.

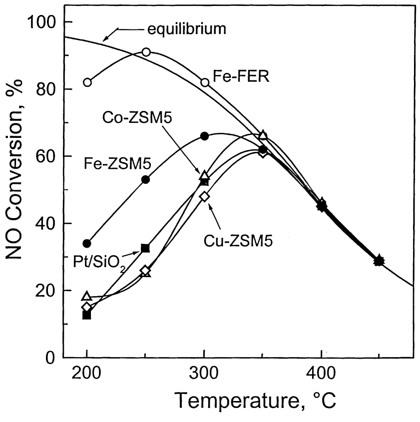


Fig. 3. Comparison of activities for NO oxidation using 0.14 g of catalyst, 1000 ppm NO in $5\%O_2$/He and total flow rate of 100 cm^3/min.

It should be noted here that a high activity for NO oxidation is not without some disadvantage since unreacted nitrogen oxides may contain considerable NO_2 which is less desirable than NO on health and environmental grounds. In practice the NO_2/NO ratio in the product gas is usually well short of equilibrium due to a combination of NO_2 consumption, its back conversion to NO through hydrocarbon oxidation (see later) and the inhibition of NO oxidation by water present.

Further evidence for the involvement of oxidised NO comes from infrared measurements. Exposure of Cu-MFI to NO/O_2 mixtures produces surface nitro and/or nitrate species which are stable to at least 200°C and react readily with propane, forming N_2 [31]. However, they do not react with methane which is consistent with the low effectiveness of Cu-MFI for methane-SCR. On Co-MFI, which is active for methane-SCR, the corresponding species are nitrito-like and will react with both CH_4 and C_3H_8 [31]. Exposure of Fe-MFI to NO/O_2 also leads to nitro/nitrate species, and some NO adsorbed as mononitrosyl as well, but the latter are replaced by the former over time [32]. The nitro/nitrate species form reactive surface deposits in contact with propane at 200°C and to a much greater extent with isobutane as well. These deposits yield nitrogen when exposed to more NO_2. There is also spectral evidence that NO_2 is required for nitrogen generation during the final step in methane-SCR over Co-MFI and Mn-MFI, which is thought to be reaction with surface cyanide groups [33,34].

Thus there is a good reason to believe that an initial oxidation of NO is an essential feature of hydrocarbon-SCR on 3d transition metal zeolites. However, that may not be the case during methane-SCR over Pd-H-MFI where the most recent infrared results suggest that a particular form of strongly adsorbed NO, not NO_2, is the adsorbed species which reacts with the hydrocarbon [35].

Table 1
Kinetic isotope effect for SCR with different hydrocarbons over transition metal zeolite catalysts

Hydrocarbon	Catalyst	Temperature (°C)	Rate (C_nH_{2n+2}) /rate (C_nD_{2n+2})	
			N_2	CO_2
Methane	Co-MFI	375	2.1	2.4
	Co-ferrierite	406	2.1	2.3
	Cu-MFI	375	–	2.3
	Pd/H-MFI[a]	400	1.65	1.56
	Pd/H-MFI[a]	350	1.22	1.10
Isobutane	Co-MFI	346	1.0	1.0
	Cu-MFI	282	1.0	1.0
	Fe-MFI	295	1.0	1.0

[a] Data of Kato et al. [40].

3.2. The rate determining step

In general terms this can be defined as the elementary step, which if alone made faster, would lead to an increase in the overall reaction rate. If this step involves the breaking of a single carbon to hydrogen bond then one can expect the rate to drop by a factor of 2 or more if the hydrogen is replaced by deuterium because of the kinetic isotope effect arising from the difference in zero point energy. Table 1 summarises results for the deuterium kinetic isotope effect for a number of hydrocarbon-SCR systems. The methane-SCR reactions over Co-MFI, Co-ferrierite and Cu-MFI are clearly systems in which the rate determining step involves hydrogen abstraction [36–38]. At the other extreme in Table 1, it is apparent that no kinetic isotope effect is associated with the isobutane-SCR reaction over Cu-MFI or Fe-MFI [37,39]. This should not be taken as implying that no hydrogen abstraction is involved, simply that if present, its rate does not restrict the overall SCR process. Other possible slow steps could be, for example, NO oxidation or decomposition of a surface intermediate. The rate ratios in Table 1 for Pd-H-MFI represent an intermediate case and are unusual in that the KIE value increases with temperature contrary to that expected theoretically. The original interpretation was that NO oxidation was more rate controlling than hydrogen abstraction by adsorbed NO_2 at lower temperatures while the reverse was true at higher temperatures [40]. This may need revision, given the more recent work indicating that adsorbed NO rather than NO_2 is the reaction site [35].

3.3. The reactions of possible intermediates in methane-SCR

The above data suggests that methane-SCR on Co-MFI involves adsorbed NO_2 and the initial breaking of a carbon to hydrogen bond in methane. If so, then it seems reasonable to represent this step as

$$CH_4 + NO_2\,(ads) \rightarrow CH_3 + HONO \qquad (1)$$

As yet there is no definitive proof as to the existence of either product as such with zeolite systems. A search for the generation of gas phase methyl radicals over Co-MFI was unsuccessful [41]. They have been implicated in the $CH_4/NO/O_2$ reaction over Ba/MgO catalysts but are thought to be formed through abstraction by an adsorbed oxygen species and to react further by combination with NO [41]:

$$CH_3 + NO \rightarrow CH_3NO \qquad (2)$$

Combination with NO_2, another one electron species, would also seem to be feasible:

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad (3)$$

Hence nitromethane (CH_3NO_2) and nitrosomethane (CH_3NO) are potential intermediates in methane-SCR.

The reactions of nitromethane over a variety of catalysts has been established recently [20,42,43]. Fig. 4 shows the distribution of the major products as a function of temperature for reaction in the presence of both

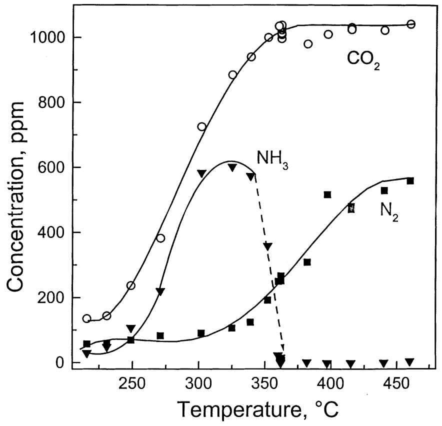


Fig. 4. Distribution of major products as a function of temperature during the reaction of ~1100 ppm CH_3NO_2, 1000 ppm NO in 3%O_2/He over 0.1 g of Co-MFI with total flow rate of 100 cm^3/min.

NO and O_2 over Co-MFI with relatively short equilibration times (~30 min). Reaction is substantial even at 200°C with complete conversion of nitromethane by 300°C. The dominant carbon-containing product is CO_2. Ammonia is the principal nitrogen-containing one below 350°C. Thus the major overall reaction is then decomposition alone:

$$CH_3NO_2 \rightarrow CO_2 + NH_3 \tag{4}$$

Above 350°C the concentration of ammonia falls steeply and is replaced by nitrogen. The change-over is due to the advent of the ammonia-SCR reaction:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{5}$$

It is apparent that reactions (4) and (5) are sufficiently fast that nitromethane is a feasible intermediate in methane-SCR over Co-MFI since, if it was formed at the onset temperature for that reaction (~360°C), then reaction through nitrogen should be complete.

This general picture carries over to other conditions and catalysts. If nitromethane is run over Co-MFI without NO or O_2 then ammonia persists to high temperature. Cu-MFI, which is more active than Co-MFI for NH_3-SCR, gives nitrogen rather than ammonia at all temperatures [43].

At temperatures below 300°C the product distribution with Co-MFI changes with time in a way which provides clues as to the mechanism of the decomposition process. As may be seen from Fig. 5, conversion falls beyond 150 min and a new product, isocyanic acid (HNCO), starts to emerge. It eventually becomes the principal nitrogen-containing product. The deactivation process occurs on a similar time scale if NO is absent, and addition of water to the deactivated catalyst then leads to near complete hydrolysis of HNCO to CO_2 and NH_3 [20]. Thus it appears that HNCO is an intermediate in nitromethane decomposition i.e.,

$$CH_3NO_2 \rightarrow HNCO + H_2O \rightarrow CO_2 + NH_3 \tag{6}$$

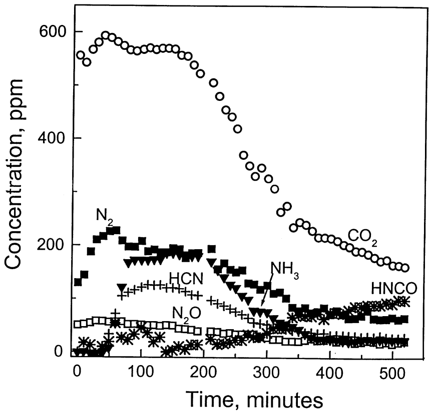
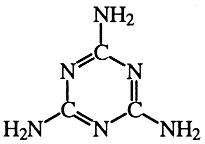


Fig. 5. Product distribution as a function of time during the reaction of ~1100 ppm CH_3NO_2, 1000 ppm NO in 3%O_2/He over 0.1 g of Co-MFI at 250°C with a total flow rate of 100 cm^3/min.

The process appears to proceed through an initial dehydration of aci-nitromethane, CH_2=NO(OH) or its isomers, carbamic acid, NH_2–COOH or formohydroxamic acid, NH(OH)CHO [20,43]. Such reactions are well-known acid–base catalysed processes in organic chemistry [44]. Experiments in which HNCO itself is fed directly also indicate that it can be converted to N_2 through a combination of hydrolysis and NH_3-SCR and possibly by direct reaction with NO_x as well [37,45].

In situ FTIR measurements of Co-MFI under reaction conditions [46] show that deactivation is associated with the deposition of cyclic material with structures like that of melamine ($C_3N_6H_6$)



which are stable to over 300°C. Since melamine is made commercially by combination of isocyanic acid and ammonia on oxide or phosphate catalysts [47] it seems reasonable to represent the deactivation process as follows:

$$3HNCO + 3NH_3 \rightarrow C_3N_6H_6 + 3H_2O \tag{7}$$

Thus deactivation can be attributed to the simultaneous formation of isocyanic acid and ammonia within the zeolite. Their combination to melamine leads to pore blockage. It is interesting to note that Cu-MFI undergoes deactivation in a similar way, but it takes much longer which can be attributed to a lower concentration of ammonia as a result of the higher NH_3-SCR activity of this catalyst. Indeed, little deactivation is observed with Co-MFI itself if the reaction of nitromethane is carried out with NO replaced by NO_2, which reacts

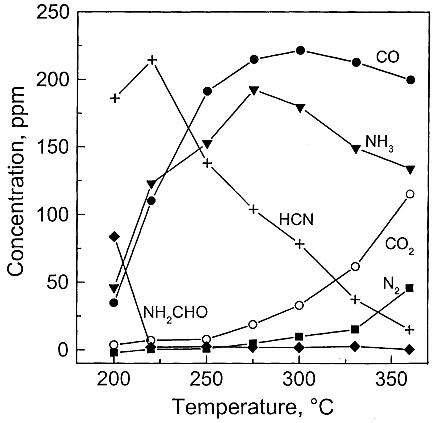


Fig. 6. Product distribution as a function of temperature during the reaction of 320 ppm formamide in 3% O_2/He over 0.1 g of Co-MFI with a total flow rate of 100 cm^3/min.

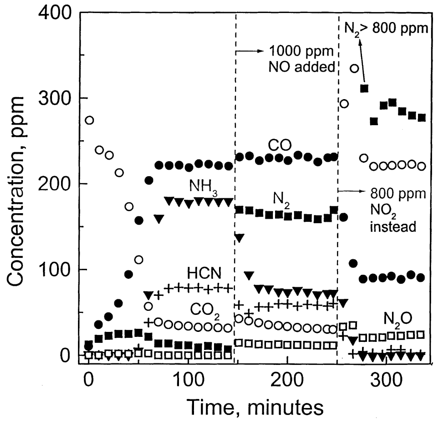


Fig. 7. Effect of NO and NO_2 on the reaction of 320 ppm formamide in 3% O_2/He over 0.1 g of Co-MFI at 300°C with a total flow rate of 100 cm^3/min.

with NH_3 much faster than does NO. There is complete conversion even at 220°C with nitrogen and CO_2 as the only significant products [20].

The possible involvement of the alternative intermediate, nitrosomethane, cannot be investigated directly since spontaneous conversion to its more stable tautomer, formaldoxime (CH_2=NOH) can be expected. Further conversion to formamide (NH_2–CHO) by the Beckmann rearrangement can also be expected since that reaction proceeds readily on zeolites. We have therefore investigated the reactions of formamide as a surrogate for nitrosomethane. The product distribution for a NH_2–CHO/O_2 mixture is shown in Fig. 6. Decomposition is substantial even at 200°C with complete conversion by 225°C. The major product then is HCN arising by dehydration:

$$NH_2\text{–}CHO \rightarrow HCN + H_2O \quad (8)$$

Decarbonylation to form ammonia and carbon monoxide:

$$NH_2\text{–}CHO \rightarrow NH_3 + CO \quad (9)$$

takes over at higher temperature. Both processes are typical of acid-catalysed reactions [44]. Subsequent oxidation, yielding CO_2 and N_2, becomes increasingly important above 300°C.

The corresponding reaction in the presence of NO_x has not been investigated over a full range of temperature but the effect of adding NO or NO_2 to a formamide/O_2 mixture at 300°C is shown in Fig. 7. The inclusion of NO results in the conversion of ~60% of the NH_3 to N_2 by the NH_3-SCR reaction but the HCN formation falls only slightly. Substitution of NO_2, however, induces total conversion of HCN to N_2 and CO_2 and also lowers the CO concentration. The latter effect probably results from the interception of intermediates in the pathway to CO rather than its oxidation once formed. Thus although Co-MFI is not very active for the removal of HCN by oxidation with O_2 at 300°C, with or without NO present, it is certainly very active for the following reaction with NO_2:

$$4HCN + 4NO_2 + O_2 \rightarrow 4CO_2 + 4N_2 + 2H_2O \quad (10)$$

Similar tests at 360°C show that NO alone is then sufficient to induce conversion of all HCN but only as long as the catalyst maintains the ability to generate measurable NO_2 [48]. This ability is slowly lost for a reason which is not understood and HCN then breaks through. It should be noted here that some CO remained unoxidised even at 360°C. This casts some doubt on the possibility that formamide could be an intermediate in CH_4-SCR over Co-MFI since the latter reaction never generates CO. However, this does not totally exclude the possible involvement of a nitrosomethane-like species if the tautomer to which it should be converted rapidly (i.e. formaldoxime), underwent very rapid dehydration, another well-known acid catalysed reaction [44]:

$$CH_2{=}NOH \rightarrow HCN + H_2O \qquad (11)$$

In that case, HCN could be removed by Eq. (10) and CO would not necessarily be a product unlike the situation with formamide in Fig. 6.

It may be noted here that HCN is formed in significant quantities during the initial stages of the reaction of nitromethane over Co-MFI at low temperature (Fig. 5). This may be a consequence of the loss of oxygen to form nitrosomethane, and then HCN, in which case the nitro and nitroso routes are to some extent linked.

3.4. Possible intermediates in SCR with higher hydrocarbons

Unlike the methane-SCR system the reactions of higher hydrocarbons gives rise to side products which can provide clues to the chemistry involved. As first demonstrated by Radtke et al. [49,50], SCR using ethene and propene over Cu-MFI can produce up to 30 ppm of HCN and 15 ppm of HNCO. Water suppresses the formation of both with conversion of HNCO to NH_3. The reaction of propene/NO_2/O_2 mixtures over Ce-MFI also gives rise to trace amounts of HCN while the same reaction over Na-MFI and sodium mordenite can produce cyanogen (C_2N_2) as well [17,51]. The extent to which these cyanide and isocyanate compounds represent the primary intermediates from which most N_2 is formed in these systems, or are simply by-products, is yet to be resolved.

Much larger amounts of hydrogen cyanide are formed during the isobutane-SCR reaction over Fe-MFI [52]. As shown in Fig. 8, the concentration of HCN formed in the steady state at 315°C approaches that of N_2 itself (i.e. one-third of the NO converted). Inclusion of water leads to some conversion of HCN to N_2 probably through hydrolysis:

$$HCN + H_2O \rightarrow NH_3 + CO \qquad (12)$$

followed by the NH_3-SCR reaction which is exceptionally fast on Fe-MFI [53–55]. Similar amounts of HCN are formed if NO_2 is used in place of NO, since as shown in Fig. 9, there is complete conversion of unreacted NO_2 to NO so the reactions are near equivalent. Only above 350°C (not shown), when traces of NO_2 start to be detected in the exit gas, is HCN no longer observable at all.

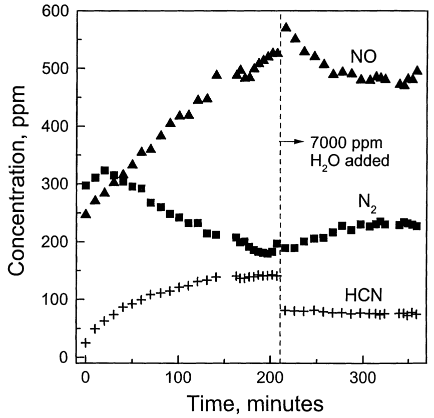


Fig. 8. Effect of 7000 ppm water on product distribution during the reaction of 1000 ppm C_4H_{10}, 1000 ppm NO in 3%O_2/He over 0.1 g of Fe-MFI at 315°C with a total flow rate of 100 cm^3/min.

It may be noted from Figs. 8 and 9 that the two isobutane-SCR reactions over Fe-MFI approach steady concentrations after 100–200 min when first put on stream and respond faster thereafter. This was not the case with Cu-MFI and the product distributions were also different. Hydrogen cyanide was not detectable (limit ≤10 ppm) when using either NO or NO_2. However, as shown in Figs. 10 and 11, cyanogen does become measurable instead after 100 min of

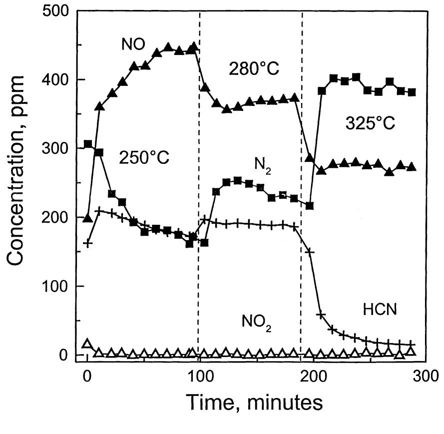


Fig. 9. Product distribution during the reaction of 1000 ppm C_4H_{10}, 1000 ppm NO_2 in 3%O_2/He over 0.1 g of Fe-MFI with a total flow rate of 100 cm^3/min.

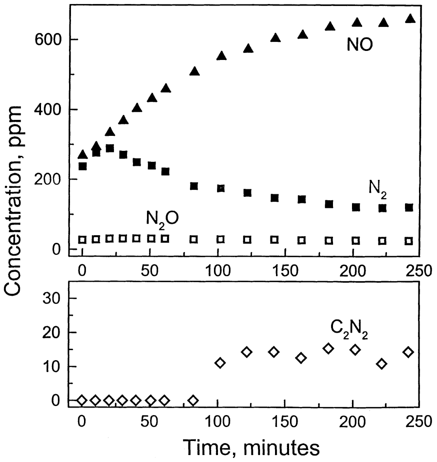


Fig. 10. Product distribution as a function of time during the reaction of 1000 ppm C_4H_{10}, 1000 ppm NO in 3%O_2/He over 0.1 g of Cu-MFI at 275°C with a total flow rate of 100 cm^3/min.

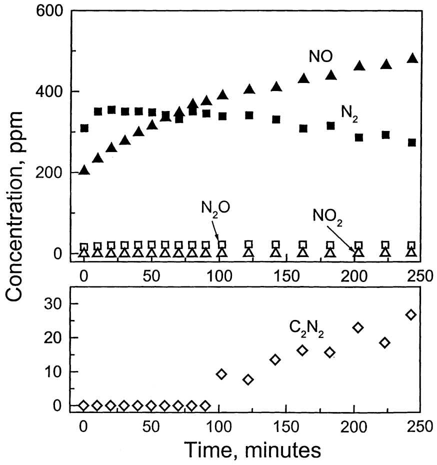
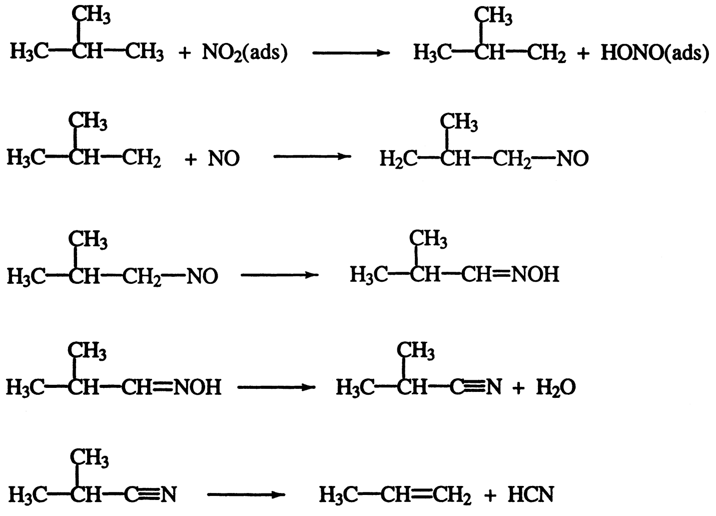


Fig. 11. Product distribution as a function of time during the reaction of 1000 ppm C_4H_{10}, 1000 ppm NO_2 in 3%O_2/He over 0.1 g of Cu-MFI at 275°C with a total flow rate of 100 cm^3/min.

reaction at 275°C using either NO or NO_2. As with Fe-MFI, the NO_x conversion is somewhat higher when using NO_2 than NO and all unreacted NO_2 is converted to NO. However, unlike Fe-MFI, the reactions over Cu-MFI have not reached steady conversion even after 250 min of reaction and this made it difficult to determine cyanogen yield at other temperatures. Reactions commenced above 300°C gave complete isobutane conversion, without formation of cyanogen, for very long periods while operation significantly below 275°C led to rapid deactivation to very low conversion [37].

The data in Figs. 8–11 raise two questions. Firstly, what is the process which gives rise to the cyanide compounds with the both catalysts? Secondly, why is HCN formed with Fe-MFI but C_2N_2 with Cu-MFI? A conceivable route to HCN passing through a nitroso intermediate is as follows (Scheme 1).



$$H_3C-\overset{CH_3}{CH}-CH_3 + NO_2(ads) \longrightarrow H_3C-\overset{CH_3}{CH}-CH_2 + HONO(ads)$$

$$H_3C-\overset{CH_3}{CH}-CH_2 + NO \longrightarrow H_2C-\overset{CH_3}{CH}-CH_2-NO$$

$$H_3C-\overset{CH_3}{CH}-CH_2-NO \longrightarrow H_3C-\overset{CH_3}{CH}-CH=NOH$$

$$H_3C-\overset{CH_3}{CH}-CH=NOH \longrightarrow H_3C-\overset{CH_3}{CH}-C\equiv N + H_2O$$

$$H_3C-\overset{CH_3}{CH}-C\equiv N \longrightarrow H_3C-CH=CH_2 + HCN$$

Scheme 1.

Table 2
Reactions of ≈800 ppm isobutyronitrile on Fe-MFI alone and in the presence of 3%O_2 or 1000 ppm NO/3%O_2

Feed	Temperature (°C)	Conversion (%)	Concentrations (ppm)			
			C_3H_6	HCN	N_2	CO + CO_2
$(CH_3)_2CHC{\equiv}N$ alone	400	65	550	650	Nil	Nil
	350	<10	60	≈30	Nil	Nil
$(CH_3)_2CHC{\equiv}N + O_2$	350	50	25	300	20	900
$(CH_3)_2CHC{\equiv}N + O_2 + NO$	350	100	10	200	670	2600

In this scheme an initially created nitroso compound first converts to its thermodynamically more favoured oxime tautomer which then undergoes dehydration to a nitrile, isobutyronitrile in this case. Hydrogen cyanide could then be formed through elimination. The co-product is propene which can be used in further SCR. A possible objection to the scheme is that the tertiary hydrogen should be preferred in the initial abstraction but this could be offset through geometrical constraints within pores supplemented by the large preponderence of methyl hydrogens (i.e. nine to one).

Table 2 summarises the results of experiments to determine if isobutyronitrile can react as postulated above over Fe-MFI. When reacted alone at 400°C, approximately two-thirds of the nitrile is cleanly converted to HCN and propene in accordance with Scheme 1. The conversion at this temperature may be partially restricted by thermodynamics since estimates using the ASPEN program indicate that the theoretical equilibrium conversion is about 94%. The conversion is much lower at 350°C but HCN and propene are still seen. The presence of O_2 at this temperature increases the conversion to ~50% with most propene oxidised to CO and CO_2 in a ratio (1:2) which is somewhat lower than that during isobutane oxidation [52]. Production of HCN is now much greater (~300 ppm) with a small amount of N_2 formed as well. With NO also present in the feed, nitrile conversion is near complete with approximately 75% ending up as N_2. The nitrogen is probably formed via HCN since, despite the higher conversion, the concentration of HCN is lower than when only O_2 is included. It is highly likely that the large increases in conversion seen when using O_2, and especially with NO/O_2 mixtures, is a consequence of partial removal of site blocking deposits which restrict conversion when the nitrile is fed alone.

The data in Table 2 indicates not only that the previous scheme is a feasible explanation for the observed formation of HCN during the isobutane-SCR reaction over Fe-MFI but also that the catalyst is apparently effective for the conversion of HCN to N_2 when using NO/O_2 mixtures but not O_2 alone. The latter proposition has been tested directly as shown in Fig. 12. In the presence of O_2 alone at 360°C, ~85% of the HCN is oxidised, largely to CO_2 and N_2 in the ratio 2:1 as expected for the overall reaction:

$$4HCN + 5O_2 \rightarrow 4CO_2 + 2N_2 + 2H_2O \qquad (13)$$

At 300°C the conversion falls to ~50%. Some ammonia is then evident, and the CO/CO_2 ratio is also higher, as expected if there is some hydrolysis of HCN according to Eq. (12) using water produced by Eq. (13). This conversion probably passes through a formamide-type intermediate using acid sites. The situation changes dramatically when NO is added.

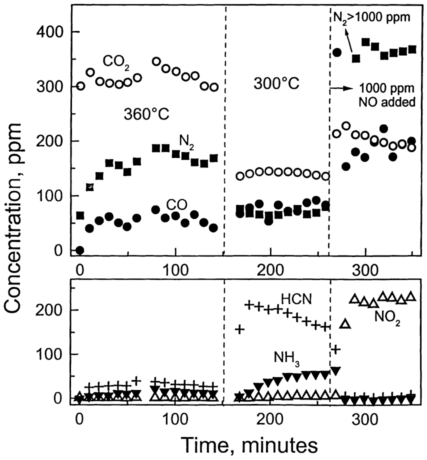


Fig. 12. Effect of 1000 ppm NO on the reaction of 360 ppm HCN in 3%O_2/He over 0.1 g Fe-MFI with total flow rate of 100 cm^3/min.

Hydrogen cyanide is now removed completely and all NH_3 disappears as well, probably through conversion to N_2 via the NH_3-SCR reaction. It is also noteworthy that the exit gas now contains a considerable amount of NO_2 in addition to NO. Further tests with $HCN/NO/O_2$ mixtures showed that conversion of HCN to N_2 still exceeded 90% at 200°C and that some NO_2 was still formed. It seems likely that HCN is being converted by reaction with NO_2, Eq. (10), as was the case with Co-MFI (Fig. 7). A question which arises given this exceptional activity of Fe-MFI for HCN removal is, why then is HCN observed at all during the two isobutane-SCR reactions at a considerably higher temperature (Figs. 8 and 9). The probable explanation is that the concentration of NO_2, which is required for HCN removal, is maintained at a very low level by reaction with isobutane. Once isobutane is fully converted, which occurs at ~350°C, NO_2 can be formed and HCN disappears completely.

The overall conclusion is that isobutyronitrile is a feasible source of the HCN seen during the isobutane-SCR reaction over Fe-MFI. The elimination of HCN from nitriles may well be general since Obuchi et al. [56] have shown that the reaction of 3-methylbutanenitrile over alumina forms isobutene and HCN which will convert to N_2 if NO_2 is also present. If one accepts that the elimination process can also occur with Cu-MFI, although this is yet to be proved, then the question is why should cyanogen be seen rather than HCN during the two isobutane-SCR reactions with this catalyst (Figs. 10 and 11)?

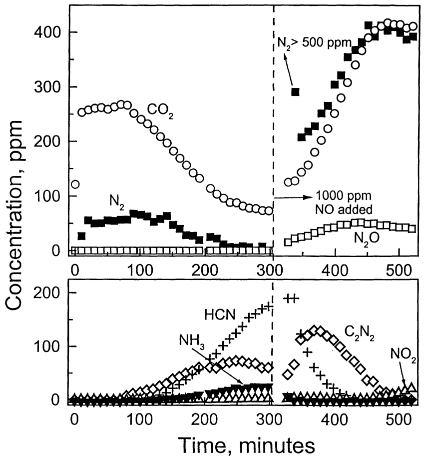


Fig. 13. Effect of 1000 ppm NO on the reaction of 360 ppm HCN in $3\%O_2/He$ over 0.1 g Cu-MFI at 270°C with total flow rate of 100 cm^3/min.

Fig. 13 shows the results of a time-on-stream experiment at 270°C which was commenced with HCN/O_2 and NO added subsequently. Only CO_2 and N_2 are formed initially. At the same time there is a substantial deficit in the atom balances, especially for nitrogen, indicating the accumulation of deposited material. After ~100 min deactivation sets in and cyanogen emerges followed by HCN and, after ~150 min, by small amounts of ammonia. The addition of NO then causes an immediate peak in N_2 formation, probably through an SCR reaction with adsorbed ammonia, after which the catalyst steadily regains activity for HCN removal, initially to form cyanogen but subsequently with complete conversion to CO_2, N_2 and a small amount of N_2O. Some NO_2 then emerges. Tests with $HCN/NO/O_2$ mixtures at 220°C showed a HCN conversion of 90% but with cyanogen as the major steady state product accounting for more than two-thirds of the HCN converted. No NO_2 was detected, again underlining its importance for N_2 formation. The persistence of C_2N_2 at 275°C during the isobutane-SCR reactions, Figs. 10 and 11, but not during the $HCN/NO/O_2$ reaction (Fig. 13), is consistent with the absence of NO_2 during SCR due to back-conversion to NO through hydrocarbon oxidation.

The conclusions from Figs. 12 and 13 then are that Cu-MFI is equally as active as Fe-MFI for the reaction of HCN with NO/O_2 mixtures and that this proceeds by reaction (10) using NO_2 generated by NO oxidation. The difference between the two catalysts is that cyanogen is a significant side or intermediate product with Cu-MFI but not Fe-MFI although it has been observed in trace amounts in trapped products when using propane and *n*-butane over the latter catalyst [57]. The formation of cyanogen with the copper catalyst is not surprising since it is a known product of the reaction of HCN with CuO surfaces [58,59]. The process has been represented as starting with an initial dissociation to yield OH^- and Cu^+CN. A second dissociation then gives another OH^- and $Cu(CN)_2$ which liberates C_2N_2. The net effect is reduction of the surface to cuprous hydroxide which would need to undergo dehydration and reoxidation to complete a catalytic cycle. The overall process may be possible on Cu-MFI through use of extra lattice oxygen.

In simplistic terms the competition to form cyanogen versus N_2 can be represented as follows:

$$\mathrm{HCN} \rightarrow \mathrm{OH\,(ads)} + \mathrm{CN\,(ads)} \tag{14}$$

$$2\mathrm{CN\,(ads)} \rightarrow \mathrm{C_2N_2} \tag{15}$$

$$\mathrm{CN\,(ads)} + \mathrm{NO_2\,(ads)} \rightarrow \mathrm{N_2} + \mathrm{CO_2} \tag{16}$$

The formation of C_2N_2 with Cu-MFI requires that step (16) be relatively slow compared to steps (14) and (15). On the other hand, the absence of C_2N_2 with Fe-MFI would require the reverse, i.e. (16) is fast compared to (14) and (15). This difference is in accordance with other observations. Fe-MFI is considerably more active than Cu-MFI for NO oxidation (Fig. 3) and hence can supply more of the NO_2 required for cyanide removal. However, Cu-MFI appears intrinsically more active for HCN dissociation since it initially gives complete conversion with HCN/O_2 mixtures at 270°C (Fig. 13), and with cyanogen as a product as deactivation sets in, while the corresponding conversion with Fe-MFI is less than 50% at 300°C (Fig. 12).

3.5. The overall process and nitrogen–nitrogen bond formation

The data in Figs. 8 and 9 for the isobutane-SCR reaction over Fe-MFI, and our recent work on the temperature dependence of the reaction [52], show that HCN is a significant intermediate in N_2 formation. Together with the data in Table 2 it is consistent with a nitroso → oxime → nitrile sequence (i.e. Scheme 1). There is a good deal of other evidence for the same process in related systems. This dates back to the work of Beutel et al. [18] on the conversion of acetone oxime to N_2 on Cu-MFI and the more recent NMR studies of Wu and Larsen [60] showing how the oxime converts to ketones, acids, amines, etc. on the same catalyst and on H-MFI as well. In the same vein, Gerlach et al. [61–63] have shown that acrylonitrile is detectable as an intermediate in the reaction of NO_2 with propene on H-mordenite. It arises via an oxime and can convert further to an amide and then ammonia through successive hydrolyses.

A key question then is the step which forms nitrogen. Gerlach et al. [61–63] stress acid-catalysed steps to give ammonia followed by NH_3-SCR with H-mordenite. However, it is also clear that with various MFI zeolites, secondary oximes degrade to other reduced nitrogen species, hydroxlamine, amines and organic nitriles, which can then react 1:1 with NO_x to form N_2 [57,60]. Since these reactions appear to be reasonably fast it is quite likely that their relative importance will vary between catalysts and between hydrocarbons. In the higher hydrocarbon systems studied here, the reaction between adsorbed cyanide groups and NO_2, reaction (16), is more important than the hydrolysis of HCN to ammonia followed by NH_3-SCR although the latter does occur to some extent (Fig. 8 and Ref. [52]). This reflects the dominant role of the transition metal versus the acid function in H-mordenite.

Hence the formation of an initial nitroso species appears quite feasible with higher hydrocarbons. However, the work with nitromethane indicates that a nitro species is feasible, and perhaps more likely, as a starting point during methane-SCR on Co-MFI. This is not unreasonable. This reaction proceeds at higher temperature with co-production of significant amounts of NO_2 (Fig. 1), which is then available to combine with a methyl species if formed. By contrast, NO_2 concentrations are very low during SCR with higher hydrocarbons, due to site blocking and recycling back to NO (Figs. 9 and 11), so the combination of alkyl species with NO is favoured. The situation could change at higher temperature when all hydrocarbons are consumed and NO_2 may form. Higher nitrocompounds adsorbed on Fe-MFI are readily converted to nitrogen by reaction with NO_2 [64]. The catalytic requirement here does not seem to be restrictive since N-oxides (R–CNO), the expected dehydration product of nitroparaffins, isomerise to isocyanates (R–NCO) over alumina below 100°C, and further reaction with NO_2 then yields N_2 with amines, HCN and NH_3 as the reactive intermediates [56].

Overall, the work on the reactions of possible intermediates over SCR catalysts, in these laboratories and elsewhere, has been very informative in showing the pathways that are feasible. Its weaknesses are that feasibility is not proof of involvement, although the intermediacy of HCN in isobutane-SCR over Fe-MFI now comes close to that, and that the connection between the complex chemistry that has been uncovered and the catalyst surface itself is poorly defined. In part this is because the intermediate chemistry is rather fast, probably with few specific catalytic requirements other than weak acid–base properties, and a variety of pathways are possible depending on structure. It is in NO oxidation that the catalyst plays its key role — to create the active NO_x species, and to provide more NO_2 for conversion of reduced nitrogen species to N_2. The task for the future is to establish the relative importance of the various paths in individual systems and to better define the elementary steps on the surface of each catalyst.

4. Conclusions

The chemistry of the selective catalytic reduction of nitrogen oxides by hydrocarbons over 3d transition metal zeolites is very complex. It appears that NO must first be oxidised to NO_2 to provide a site which can abstract hydrogen from the hydrocarbon. The same, or a second, NO_x molecule then produces a nitroso or nitro intermediate, which through a series of rearrangement and degradation steps, generates a reduced nitrogen centre. Conversion to N_2 then requires another NO_2 molecule. Hydrogen abstraction by an adsorbed NO_x species is the rate determining step using methane over Co-MFI and a nitro route appears marginally favoured over a nitroso one. Combination of NO_x with ammonia or, less easily, with cyanide can yield the final nitrogen product. With isobutane over Fe-MFI and Cu-MFI, oxidation of NO is limiting, not because this step is intrinsically slow but because active sites are blocked by adsorbed material and NO_2 is recycled to NO through hydrocarbon oxidation. Hydrogen cyanide is a significant product with Fe-MFI and may arise from isobutyronitrile which is consistent with a nitroso starting species. A reaction between adsorbed cyanide and NO_2 is the dominant source of nitrogen. The same chemistry seems to apply during the corresponding SCR reaction over Cu-MFI but cyanogen rather than HCN becomes the observable intermediate due to differences in relative rates. Details of the nitrogen–nitrogen bond forming step are less well established with other catalysts and hydrocarbons.

Acknowledgements

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