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The formation of HCN during the reduction of NO by isobutane over Fe-MFI made by solid-state ion exchange

Irene O.Y. Liu [a], Noel W. Cant [a,*], Markus Kögel [b] and Thomas Turek [b]
[a] *Department of Chemistry, Macquarie University, Sydney, NSW 2109, Australia*
E-mail: noel.cant@mq.edu.au
[b] *Institut für Chemische Verfahrenstechnik, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany*

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FTIR analysis of the gaseous products of the selective catalytic reduction of NO by isobutane over a Fe-MFI catalyst made by solid-state ion exchange shows, for the first time, that HCN can be a substantial product. Under dry conditions the amounts formed can exceed that of N_2 for temperatures up to 280 °C and NO conversions of 25% with a maximum HCN concentration of $\sim$150 ppm formed at 315 °C. However, introduction of 0.7% water causes the subsequent conversion of about one-half the HCN to N_2, probably through hydrolysis to NH_3 and the NH_3-SCR reaction which is very rapid on Fe-MFI. The steps through which HCN forms remain to be established.

Keywords: hydrogen cyanide, NO reduction, isobutane, Fe-MFI

1. Introduction

The reports by Feng and Hall [1,2] that Fe-MFI made by a unique exchange process is a water- and SO_2-tolerant catalyst for the reduction of NO_x by isobutane has generated a lot of interest. Subsequent investigations have shown that the preparation is not easily reproduced [3] but somewhat similar performance has since been claimed for catalysts made by vapour-phase ion exchange [4–7]. However their effectiveness does seem to be hydrocarbon dependent, with isobutane and n-butane giving considerably better NO_x conversion than propane [6,7]. Fe-MFI catalysts made by a simpler ball milling and calcination procedure are also capable of similar performance with propane and are highly effective for the reduction of N_2O in the presence of NO [8,9].

The mechanism of NO_x reduction over Fe-MFI has been investigated in detail by Chen et al. [10], who concluded that nitrogen was formed by the reaction of NO_2 with deposits containing C, N, O and H. There is now good evidence that a variety of possible intermediate compounds containing carbon, nitrogen and oxygen can indeed be readily converted to N_2 over hydrocarbon-SCR catalysts. These include oximes [11,12], nitroalkanes [13–17], isocyanates [18,19], N oxides [20] and amides [21]. In some cases the conversion appears to proceed via ammonia with the NH_3-SCR reaction forming the nitrogen–nitrogen bond:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Baiker et al. [22–25] have also established that relevant small molecules, HCN, HNCO and NH_3 can be formed in trace amounts during HC-SCR using ethylene and propylene over Cu-MFI. Cyanogen has been reported for Ce-MFI [13]. In the case of Fe-MFI, Sachtler et al. [7] detected traces of HCN when reacting isobutane/NO/O_2 but only in large trapped samples and without quantification. However, we know of no reports of a system in which the amounts of such intermediate or by-product compounds have approached or exceeded that of N_2 itself during HC-SCR. The present work establishes that this can occur during reduction of NO by isobutane over Fe-MFI made by solid-state ion exchange.

2. Experimental

The Fe-MFI samples used here were from a batch, the preparation of which has been described in detail previously [8,9]. In essence, a starting NH_4-MFI (Si/Al ratio of 11.4, AlSi-Penta Zeolithe Gmbh, Germany) was ball milled for an hour with $FeCl_2{\cdot}4H_2O$ in a ratio giving Fe/Al $= 0.75$. It was then heated to 550 °C and maintained there for 6 h. After cooling it was washed with water and dried overnight at 110 °C. Samples were pressed, crushed and sieved to give 300–600 μm particles which were pretreated in 3% O_2/He at 450 °C in the Pyrex U-tube reactor prior to reaction. The standard test conditions employed 1000 ppm isobutane, 1000 ppm NO, 0.7% H_2O (if present) and 3% O_2 in a helium carrier with a total flow rate of 100 cm^3(STP)/min over a 100 mg sample of Fe-MFI (GHSV $\approx$ 30000 h^{-1}). The inlet and product streams were analysed by a combination of gas chromatography (for isobutane, CO, CO_2, N_2, N_2O and HCN) and on-line FTIR (for HCN, NO, NO_2, NH_3 and HNCO) in a manner similar to that described previously [17]. The FTIR method for HCN was absolute,

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[*] To whom correspondence should be addressed.

making use of the HITRAN data base to generate a set of synthetic spectra from which the relationship between the absorbance of the Q-branch at 712.1 cm^{-1} and concentration was constructed. This provided a detection limit of ∼10 ppm. The chromatographic method for HCN was capable of detecting 20 ppm but the accuracy was limited by peak tailing and the need to assume a sensitivity factor since no calibration mixture was available. The two methods for HCN correlated quite well but the gas chromatograph values were consistently lower (by up to 30%) because of the difficulties with integration and, possibly, an inappropriate choice for its sensitivity factor (that of CO).

3. Results and discussion

The performance of the Fe-MFI made by solid-state ion exchange for the isobutane/NO/O_2 reaction, dry and in the presence of 0.7% H_2O, is shown in figure 1. Removal of NO reaches a maximum value of ∼70% at a temperature of 315 °C. This performance is similar to that of catalysts made by vapour-phase ion exchange [4], but considerably inferior to the "good" preparations described by Hall et al. [3]. As with the former preparations water enhances NO removal slightly at temperatures below the maximum in NO conversion but retards it slightly at higher temperatures. With all three catalysts NO conversion exceeds that of isobutane at low temperature indicating that more than one NO molecule can be removed per molecule of i-C_4H_{10} reacted.

The corresponding distribution of carbon oxides is shown in figure 2. Again, as found by Chen et al. [4], the amounts of carbon monoxide and carbon dioxide are comparable at temperatures below that giving maximum NO conversion but CO_2 becomes dominant above this temperature. Figure 2 includes the distribution found during the reaction of i-C_4H_{10} with O_2 alone. The rate is lower than when NO is present but there is still a maximum in CO production with CO_2 dominant at the highest temperature. Hence it seems that CO formation is characteristic of how isobutane is oxidised over Fe-MFI and not brought about solely because NO is present.

The only nitrogen-containing product quantified in previous studies of the present system has been N_2 [1,2,4–6]. It was therefore surprising to find that substantial amounts of HCN were formed over the present catalyst under some conditions. As shown in figure 3, HCN formation exceeds that of N_2 at low temperature under dry conditions reaching a maximum value of ∼150 ppm at 315 °C but falling steeply at higher temperatures. Neither N_2O nor NH_3 exceeded the detection limit of about 10 ppm. Although inclusion of water enhances both N_2 and HCN formation at the lowest temperature (possibly due to suppression of the formation of carbonaceous residues) it reduces the maximum amount of HCN to ∼100 ppm at 290 °C and helps the removal of HCN at higher temperatures.

There are two possible explanations for the observation of HCN here but not in previous work – either the present catalyst is intrinsically different or the conditions and analytical methods used previously resulted in its escaping detection. The former possibility seems rather unlikely given the similarity between the data in figures 1 and 2 and that of both Chen et al. [4] and that for the "poor" catalyst of Hall et al. [3]. The operating conditions in the various experiments were not the same (1000 ppm each of i-C_4H_{10}

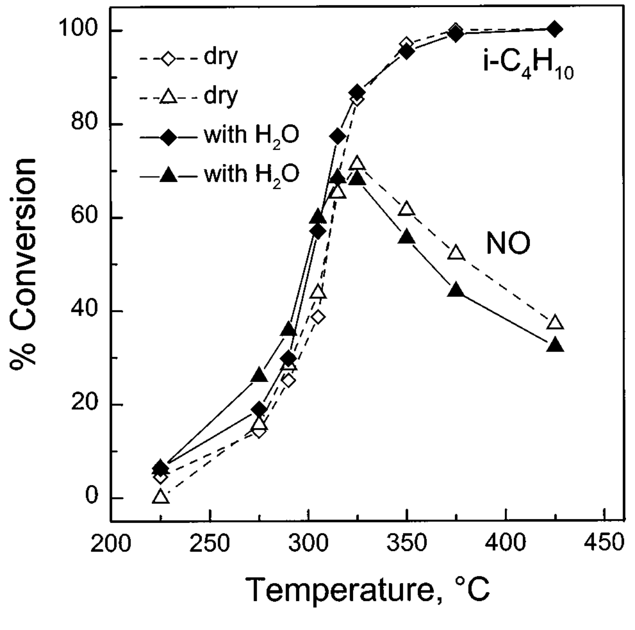


Figure 1. Isobutane and NO conversions as a function of temperature during the i-C_4H_{10}/NO/O_2 reaction of Fe-MFI made by solid-state ion exchange under the standard test conditions (1000 ppm isobutane, 1000 ppm NO, 3% O_2 with GHSV of ∼30000 h^{-1}) in the presence and absence of 0.7% water.

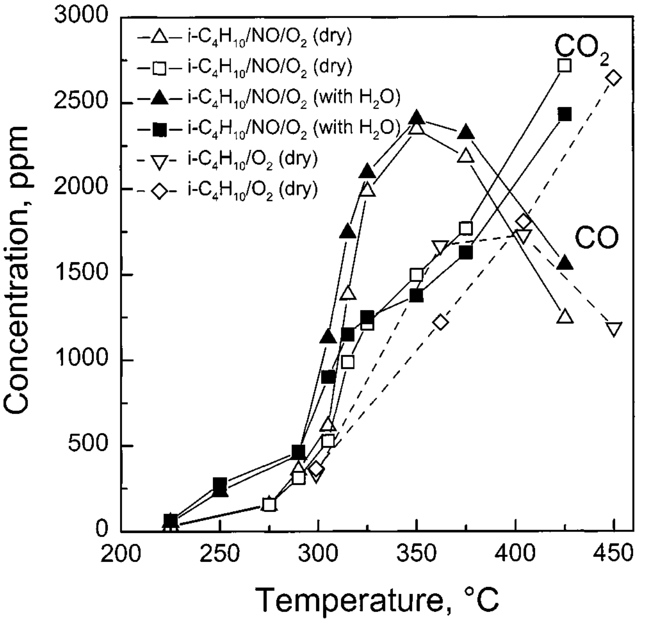


Figure 2. Formation of CO and CO_2 from the i-C_4H_{10}/NO/O_2 reaction over Fe-MFI in the experiments shown in figure 1 and during the reaction of i-C_4H_{10} with O_2 alone under the same conditions.

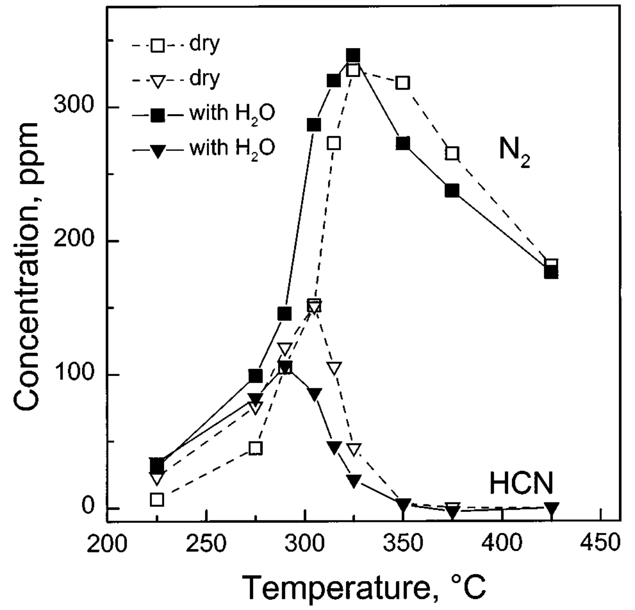


Figure 3. Formation of HCN and N_2 from the i-C_4H_{10}/NO/O_2 reaction over Fe-MFI in the experiments shown in figure 1.

and NO and a GHSV of 30000 h^{-1} here versus 2000 ppm of each reactant and a GHSV of 42000 h^{-1} previously) and this may contribute to a difference. One other possibility is that the time allowed for equilibration was varied. To test this, the approach to equilibrium was followed for an experiment with the catalyst at 315 °C (figure 4). The dominant nitrogen-containing product is N_2 initially but this passes through a maximum after 30 min before declining slowly to a near steady state after 200 min. HCN is just measurable (by the FTIR method) from the beginning but approximately 100 min are required to reach two-thirds of the final concentration. If only 30 min was allowed for stabilisation, as in the experiments of Chen et al. [4], and/or if experiments were carried out with steadily increasing temperatures, then HCN concentrations present could be so low as to escape detection unless the analytical method was very sensitive. It may be noted here that some of the previous work was carried out with 10 or 20% water present. Under these conditions, little HCN would be expected since, as shown in figure 4, even 0.7% water was sufficient to induce conversion of about one-half the HCN to N_2.

The formation of HCN is very significant in mechanistic terms, since the existence of a maximum temperature for its formation (figure 3), and the subsequent fall at higher temperatures with formation of N_2, implies that it is an intermediate in the overall conversion from NO to N_2. One feasible route for this conversion is via hydrolysis and NH_3-SCR:

$$HCN + H_2O \rightarrow NH_3 + CO$$
$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

In previous work we have shown that the first reaction can occur on Co-MFI [21] while recent reports [26,27], confirmed for the present catalyst, demonstrated that Fe-MFI is extraordinarily active for NH_3-SCR. This high activity explains the absence of detectable ammonia. Some HCN may also be removed by a direct reaction with NO_2, but further work is needed to establish its significance.

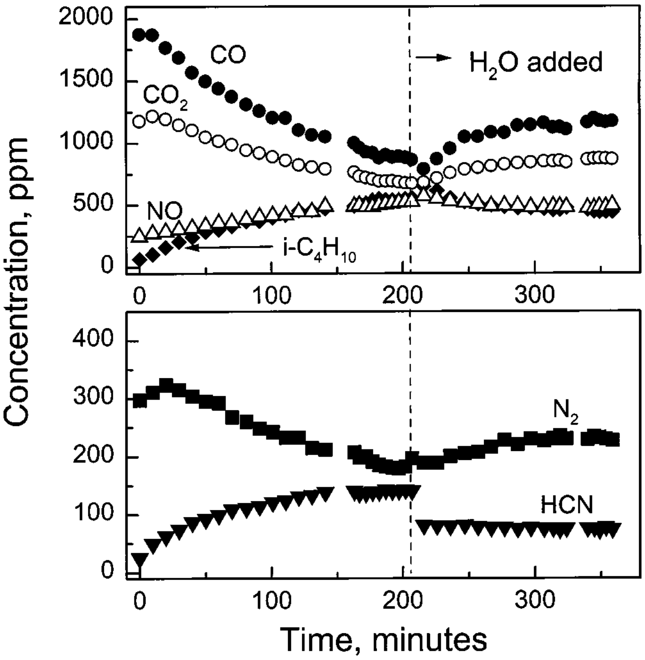
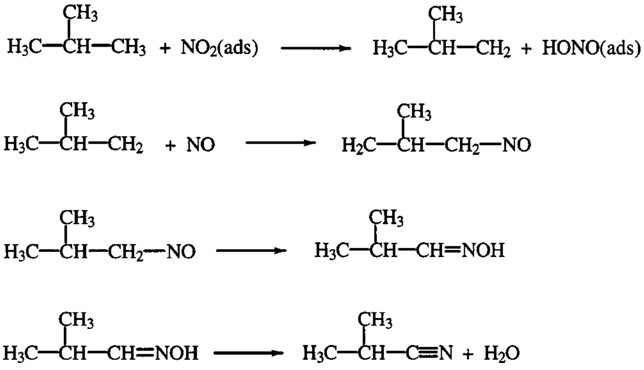


Figure 4. Concentration of products as a function of time on stream for the i-C_4H_{10}/NO/O_2 reaction over Fe-MFI at 315 °C under the standard test conditions.

The route by which HCN is formed is a matter of speculation but one possibility is an extension to the abstraction-nitroso-oxime sequence first postulated by Beutel et al. [11], i.e.,



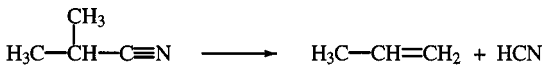
$$H_3C-\overset{CH_3}{\overset{|}{C}}H-CH_3 + NO_2(ads) \longrightarrow H_3C-\overset{CH_3}{\overset{|}{C}}H-CH_2 + HONO(ads)$$

$$H_3C-\overset{CH_3}{\overset{|}{C}}H-CH_2 + NO \longrightarrow H_2C-\overset{CH_3}{\overset{|}{C}}H-CH_2-NO$$

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

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

Dehydration of an oxime to make a nitrile (isobutyronitrile here) is a standard acid-catalyzed reaction [28]. Hydrogen cyanide could then be formed by elimination from isobutyronitrile:



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

This seems feasible given the results of Obuchi et al. [20] showing that tertiary-butyl cyanide, $(CH_3)_3CCN$, can decompose to HCN and isobutene over alumina even though it lacks a tertiary hydrogen adjacent to the cyanide group.

Direct formation of HCN and propene by an internal dehydration of the oxime may also be possible, given that a six-membered ring could be formed. An particular feature of such a scheme is that formation of HCN is accompanied by production of a reactive second hydrocarbon molecule, propene, which is then available to reduce another NO molecule. This is consistent with NO conversions exceeding isobutane conversions at low temperature without the need to assume that an intact four-carbon chain is attacked twice by NO_x species.

Objections can be raised to the above model on bond-strength grounds in that one would normally expect hydrogen abstraction from the CH group of isobutane in preference to that from a methyl one. However, work with Cu-MFI [19] shows that the isobutane/NO/O_2 reaction, unlike the methane/NO/O_2 system, does not exhibit a pronounced deuterium kinetic isotope effect indicating that the abstraction step is probably not rate limiting in higher hydrocarbon systems. If formation of the NO_2 abstraction site, through NO oxidation, is the slow step instead, then abstraction from one of the three methyl groups of isobutane could well be favoured on purely statistical grounds. In any case the nitroso compound formed after abstraction from the CH group of isobutane would have a tertiary structure for which no oxime tautomer is possible. The above chemistry would then be impossible and a completely different pathway, perhaps via the deposits containing C, N and O believed important by Chen et al. [10], would be required for its degradation.

4. Conclusions

Fe-MFI made by solid-state ion exchange has similar performance for the isobutane/NO/O_2 reaction as that prepared by vapour-phase exchange. Hydrogen cyanide is a significant product at temperatures below those giving maximum NO removal and HCN appears to be a major intermediate for N_2 formation under those conditions. The conversion of HCN to N_2 could proceed through hydrolysis to NH_3 followed by the NH_3-SCR reaction, but further work is required to establish the steps which lead to the formation of HCN itself.

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