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Mechanistic studies of the selective reduction of NO_x over Cu/ZSM-5 and related systems

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Abstract

The selective catalytic reduction of NO by hydrocarbons in the presence of a large excess of oxygen is one of the greatest challenges facing catalytic chemists today. The first catalyst reported to show substantial promise for this reaction was ion-exchanged Cu/ZSM-5, and this has since become the 'bench-mark' lean NO_x catalyst. A large number of studies have been performed on this catalyst system, and the characteristic features of the reaction over this material are fairly well defined. These characteristic features are collected together and analysed within this review article. In addition, a number of investigators have attempted to determine the reaction mechanism over this catalyst. These studies are discussed in detail, and the evidence both for and against each of the mechanistic proposals is assessed. Mechanistic studies performed on related catalyst systems are also reviewed herein, and are discussed with respect to the work carried out on Cu/ZSM-5.

Keywords: Nitrogen oxides; Copper–ZSM-5; Mechanistic studies; Selective reduction

1. Introduction

When car exhaust catalysts were first introduced in the mid 70's, their task was relatively simple by today's standards. The engines of the time produced a gas stream which was net reducing in stoichiometry (i.e., the engines ran slightly rich), so air pumps were added to the vehicles to generate a net oxidising environment over the catalyst. The catalysts were then required to oxidise the CO and hydrocarbon (HC) pollutants into CO_2 and H_2O which, under oxidising conditions, is reasonably straightforward. These early catalysts comprised Pt and Pd on an Al_2O_3 support. The next major stage in autocatalyst development came at the beginning of the 1980's, when the simultaneous removal of CO, HC, and NO_x became possible using the three-way catalysts (TWC's) which are still in use today. The demands on the emissions system and the catalyst were increased, because the reduction of NO_x was required alongside the oxidation of CO and HC. The systems were changed to incorporate an oxygen sensor which ensured that the gas stream passing over the catalyst had approximately equal concentrations of oxidants and reductants. Rh was added to the catalyst because its efficiency at NO reduction substantially exceeds that of both Pt and Pd, and ceria (CeO_2) was incorporated into the formulations because of its oxygen storage capacity [1] (amongst other things) which helps the catalyst to cope with the oscillations of the gas stream about the stoichiometric point. The typical TWC is based upon a $Pt/Rh/CeO_2/Al_2O_3$ formulation.

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The next major change in operating stoichiometry for the car exhaust catalyst will require the simultaneous removal of CO, HC and NO_x *under net oxidising conditions.* Many car companies are currently working towards the development of lean-burn engines, which will present a strongly oxidising gas feed to the autocatalyst. These engines will be more fuel efficient than current gasoline engines, and will therefore produce lower CO_2 emissions. While the large scale introduction of lean-burn gasoline engines is certainly a few years away, there is already an application for the successful lean NO_x catalyst within the diesel engine area. The exhaust stream from these engines is strongly oxidising, and this, coupled with the ever-tightening legislation applicable to the exhaust from motor vehicles, means that the need for a lean NO_x catalyst for the diesel application is just around the corner.

The other potential application of lean NO_x catalysts is to remove NO_x from the effluent of stationary sources, such as power plants. The current technology employs NH_3 as the reductant over catalysts based upon V_2O_5 on titania. There are undoubtedly a number of problems associated with this technology, such as ammonia 'slip', high equipment costs, and the requirement to transport ammonia through populated areas to the location of the plant, but this SCR (selective catalytic reduction) approach is capable of achieving very high NO_x conversions under highly oxidising conditions. Indeed, the substantial difference in the relative selectivities exhibited by hydrocarbons (low) and ammonia (very high) towards NO removal under these conditions means that very large improvements in performance will be required before hydrocarbons can compete effectively with ammonia within this application. Nevertheless, methane is potentially an attractive alternative to ammonia because of its plentiful supply and low(-ish) cost, and also because many sites (e.g., natural gas-fuelled power stations and industrial boilers) will already have a plentiful supply of CH_4 on site. This possibility is discussed elsewhere in this volume [2], but, for the reasons outlined above, it is commonly believed that the most immediate widespread application of lean NO_x catalysts will be within the automotive industry. Consequently, this is the application considered in this review article.

The *reduction* of substantial quantities of NO under strongly *oxidising* conditions in a vehicle exhaust is undoubtedly an extremely ambitious target, and was long thought to be impossible. But, as has been the case in many other areas of science, the initial breakthrough sparked off intense research activity in the topic. The breakthrough in lean NO_x catalysis occurred at more or less the same time in Germany and Japan. In Germany, Held et al. [3] reported NO_x conversions of up to 66% under lean conditions over catalysts based upon zeolites ion-exchanged with various metals. Cu/mordenite was the best system reported in their study, but Cu/ZSM-5, which has since become the bench-mark lean NO_x catalyst, was also studied. Independently, Iwamoto also reported that the selective catalytic reduction of NO could be achieved over ion-exchanged Cu/ZSM-5 under oxidising conditions [4]. These ground-breaking reports led to an enormous increase in the research activity in the lean NO_x area, and act as the starting point for this review.

Many of the research papers that have been published since the original discovery have been aimed at obtaining an understanding of the mechanism by which the lean NO_x reaction occurs over Cu/ZSM-5. As will be seen, the mechanistic area is a controversial one, and there is still widespread disagreement regarding the actual reaction sequence. This review outlines the principal features of the reaction over Cu/ZSM-5 and discusses the mechanistic conclusions that different authors have reached from these observations. The more limited mechanistic studies over other zeolite-based catalyst systems are also discussed. And finally, the major conclusions which can be drawn from the studies to date will be collected together, and the possible direction of future research in this area will be outlined.

2. Mechanistic studies over Cu/ZSM-5

2.1. Characteristic features of the lean NO_x reaction over Cu/ZSM-5 catalysts

Fig. 1 shows typical data for the performance of a Cu/ZSM-5 catalyst under conditions similar to those encountered on a lean burn vehicle [5]. The gas mixture used in this study comprised 300 ppm NO, 300 ppm CO, 800 ppm C_3H_6, 5% O_2, 10% H_2O, 13% CO_2 in N_2. The mass hourly flow rate used was 120 l/h/g, which is again representative of conditions within the automotive application. Qualitatively similar results have been obtained by many other workers, and clearly demonstrate that NO conversions of the order of 40% or so can be obtained under lean burn exhaust gas conditions using a Cu/ZSM-5 catalyst. Having shown that the catalyst system has promise under realistic conditions, we can now move on to consider the general features of the reaction, which any successful mechanism must be able to account for.

There are a number of observations which have been independently reported by several authors in the open literature, and these can be considered to be general properties of the Cu/ZSM-5 catalyst system within the lean NO_x reaction. The first, and perhaps the most important of these, is that it is hydrocarbon species which perform the NO_x reduction. This is true both in realistic lean burn gas feeds [6–8] and (obviously) in model HC/NO/O_2 mixtures (e.g., [9]). During light-off tests, the hydrocarbon oxidation trace and the NO reduction trace are always highly correlated, i.e., the hydrocarbon oxidation and NO reduction occur simultaneously. Neither CO nor H_2 are effective at reducing NO in the presence of excess oxygen over Cu/ZSM-5, because these species react preferentially with the oxygen [6,7]. In this context, it is interesting to note that Cu/ZSM-5 actually generates CO during the lean NO_x reaction [5,7,8]. This CO is generated via the partial combustion of the hydrocarbon, since it is also observed in simple HC/O_2 feeds [6]. Furthermore, the CO formation is not merely a transient effect; it has also been observed during steady state kinetics studies [9]. However, this CO is not responsible for the NO conversion in this system.

At an early stage in the development of the Cu/ZSM-5 lean NO_x catalyst, Iwamoto divided potential NO reductants into two categories: those which are effective as reductants, which he named ‘selective’ (e.g., C_3H_6, C_2H_4, C_3H_8, etc) and those which are not, which he termed ‘non-selective’ (H_2, CO, CH_4 and C_2H_6) [10]. While this nomenclature is certainly not valid for related catalysts comprising other metals ion-exchanged into the ZSM-5 framework (see e.g., [2]), it is still broadly valid for the Cu/ZSM-5 system. In addi-

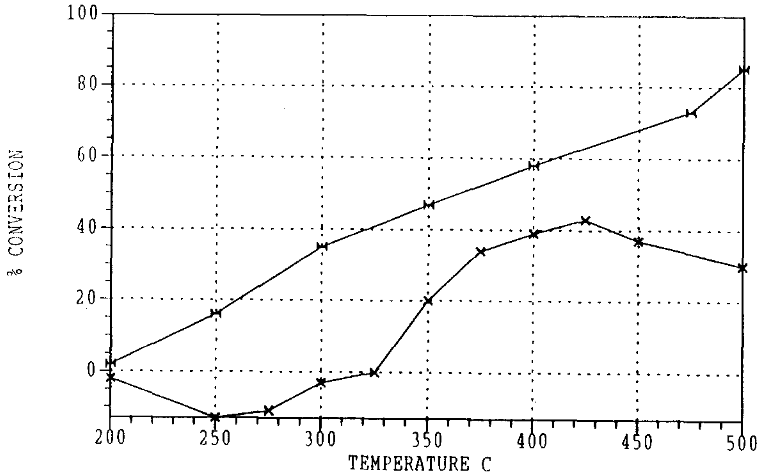


Fig. 1. The NO (X) and C_3H_6 (H) conversion profiles obtained over Cu/ZSM-5 during temperature programmed reaction under a realistic full gas mix. (For details of the conditions, see text). Taken from Ref. [5].

tion, while both alkenes and alkanes appear in the 'selective' category, all studies performed under realistic conditions find that a given alkene produces higher NO conversion than the corresponding alkane (e.g., propene is more effective than propane [7]).

Another characteristic feature of the lean NO_x reaction over Cu/ZSM-5 is the behaviour of the NO conversion as a function of temperature. As Fig. 1 shows, the NO conversion peaks at a certain temperature (425°C in this case) and then decreases. These observations are not caused by the (permanent) deactivation of the catalyst, since the behaviour is reversible (provided that the maximum temperature that the catalyst is exposed to is not too high — see later). This characteristic behaviour has also been observed during studies of the direct NO decomposition reaction over this catalyst [11], where it has been attributed to a decrease in the surface coverage of the proposed gem-dinitrosyl $Cu(NO)_2$ reaction intermediate with increasing temperature [12,13]. During the lean NO_x reaction itself, this behaviour may also be a consequence of similar adsorption/desorption effects, or it may be related to the more rapid oxidation of the hydrocarbon at higher temperatures. These possibilities are discussed later. For fresh catalysts, the temperature at which the peak NO conversion occurs is dependent on a number of factors, including the nature of the hydrocarbon reductant, the concentration of the hydrocarbon, the space velocity, and the exact specification of the catalyst (Cu loading, method of preparation etc.) [7,9,14,15].

The peak NO conversion over Cu/ZSM-5 increases as the concentration of the hydrocarbon reductant is increased [7,8,10]. Indeed, steady state kinetic analysis of the model $C_3H_6/NO/O_2$ system reveals a near first order dependence of NO conversion on C_3H_6 partial pressure [9]. These observations are not too surprising, since it is clear that it is the hydrocarbon which effects the reduction of the NO under lean burn conditions. What is more surprising, however, is that the reaction is very strongly promoted by oxygen [10]. As Fig. 2 shows, the initial addition of O_2 into the gas feed has a dramatic effect on the NO conversion performance of the catalyst. The NO conversion then levels out, before decreasing slowly as the O_2 concentration is further increased. Despite this moderate inhibition at high oxygen concentrations, Iwamoto and Hamada point out that the catalytic activity at 10% O_2 is still 60 times greater than that without oxygen [10]. These observations were made using a model $C_3H_6/NO/O_2$ gas feed and a reasonably low space velocity. However, using more realistic gas feeds and much higher space velocities, other authors have made the same observations [6,8]. In this context, it is also interesting to note that partially oxygenated hydrocarbon species are also capable of reducing NO under strongly oxidising conditions [6]. In addition, such partially oxygenated species perform NO conversion in the *absence* of gas phase molecular oxygen — something which propene (for example) is virtually incapable of doing.

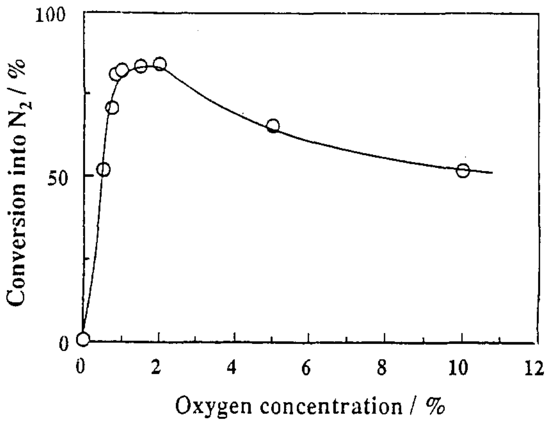


Fig. 2. The effect of oxygen concentration on the conversion of NO into N_2 over Cu/ZSM-5. ($W/F=0.3$ g s cm^{-3}, temperature = 573 K, $P_{NO}=1000$ ppm, $P_{C_3H_6}=1000$ ppm). Taken from Ref. [36].

Another parameter which has considerable impact on the NO conversion performance of the Cu/ZSM-5 catalyst is the Cu loading within the sample. For example, Iwamoto and co-workers have shown that the lean NO_x efficiency of catalysts comprising Cu ion-exchanged into the ZSM-5 structure increases as the exchange level rises to ca. 100–120% [14]. As more Cu is incorporated into the formulation, the efficiency gradually drops. Kharas observed a similar trend, but reports the optimum Cu content as being in the 150–200%

range [7]. If one uses Na/ZSM-5 as the catalyst precursor, then the ion-exchange level is calculated assuming that one copper(II) ion can be exchanged for two sodium(I) ions. The nature of the Cu species formed within these excessively ion-exchanged Cu/ZSM-5 catalysts is discussed elsewhere [17]. For the purposes of this article it is merely pertinent to note that catalysts with Cu contents in excess of that required for 100% ion-exchange are generally accepted as being the most active within the lean NO_x application.

The impact on the catalyst reactivity of various potential 'poisoning' species has also been characterised. The effect of adding SO_2, one of the traditional poisons within automotive catalysis (especially for base metal catalysts), has been investigated in several studies. The catalytic efficiency of Cu/ZSM-5 for the lean NO_x reaction is slightly decreased by the introduction of 300 ppm SO_2 [16]. The catalyst gradually recovers its activity after the flow of SO_2 is stopped, indicating that SO_2 does not cause permanent deactivation under these conditions. This concentration of SO_2 is extremely high when one considers that the typical level of SO_2 present in a vehicle exhaust is of the order of 20 ppm. Kharas investigated the impact of SO_2 at the 20 ppm level using a full simulated lean burn gas feed at a space velocity of around 120 000 h^{-1} and found that the addition of this level of SO_2 had essentially no effect under these conditions [7]. Monroe et al. reported a slight decrease in NO conversion efficiency when 5 ppm SO_2 was added to a realistic gas feed at a space velocity of 45 000 h^{-1} [8]. They found that increasing the SO_2 concentration to 20 ppm had no additional detrimental effect on the NO conversion. The observation of only minor or zero inhibition of NO conversion by SO_2 is the opposite to the observations made during studies of the NO decomposition reaction [16]. In this case, the activity of the Cu/ZSM-5 catalyst was completely removed by the addition of 220 ppm of SO_2. The decomposition activity could only be restored by heating the catalyst to 700°C under He.

Remaining with the 'poisoning' theme, it is clear that water vapour is an extremely important gas phase component when studying the Cu/ZSM-5 catalyst. In addition to durability issues raised by the presence of steam (see later), the NO conversion is decreased by the addition of H_2O into the gas phase [14]. When the experiment is carried out using 3.9% H_2O in a C_3H_6/$NO/O_2/SO_2$ gas feed at a temperature of 500°C this deactivation is completely reversible (Fig. 3), at least for exposure times of up to 90 min. However, when the same experiment is performed using higher concentrations of water vapour, some irreversible deactivation is observed [14]. The factors leading to irreversible deactivation of the Cu/ZSM-5 material are further discussed below.

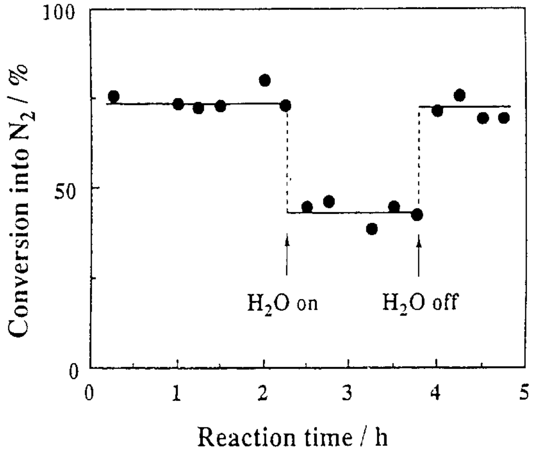


Fig. 3. Effect of the introduction of water vapour on the conversion of NO into N_2 over Cu/ZSM-5. ($W/F = 0.1$ g s cm^{-3}, temperature = 773 K, $P_{NO} = 600$ ppm, $P_{C_3H_6} = 940$ ppm, $P_{O2} = 1.5\%$, $P_{SO_2} = 250$ ppm, $P_{H_2O} = 3.9\%$). Taken from Ref. [36].

This section would not be complete without a final note on the deactivation characteristics of Cu/ZSM-5. Whilst these are dealt with in detail elsewhere in this edition [18], the deactivation processes may tell us something about the reaction mechanism, so the general features which have been reported regarding the durability of Cu/ZSM-5 catalysts are outlined here. Ultimately, of course, high activity *on its own* is not enough to make a material successful in the world of automotive catalysis; the catalyst must also be extremely durable under operating conditions, and be able to survive excursions to elevated temperatures. The effect of thermal ageing under reducing, oxidising, and cycled feeds was investigated by Monroe et al. [8]. They found that the NO conversion was decreased from its fresh value of 41% to 8% following a 4-h ageing at 800°C in 5% H_2/N_2, to 14% following a 4-h ageing at 800°C in 5% O_2/N_2, and to 9% following a 4-h ageing at 800°C in a feed which was switched between 5% H_2/N_2 and 5% O_2/N_2 every 10 s. It is clear that Cu/ZSM-5 can be rapidly deactivated by thermal ageing. Kharas et al. found that subjecting Cu/ZSM-5 to one hour's lean NO_x catalysis at 600°C induced a dramatic increase in the operating temperature of the catalyst, without significantly affecting the peak NO conversion value [19]. They demonstrated that this was not merely a thermal effect, since calcining the catalyst in air at 600°C for 6 h did not lead to any noticeable increase in operating temperature. It is important to note that the gas feed under which they performed the catalysis contained 10% H_2O — a level typical of the automotive application. They observed further progressive increases in the temperature at which peak NO conversion was observed following an hour's catalysis at temperatures of 700, 750, and 800°C. In each of the latter three cases the peak NO activity was lower than that of the fresh catalyst. However, there is also evidence that the deactivation of the Cu/ZSM-5 material can be induced at significantly lower temperatures. For example, Ansell et al. reported that the activity of a Cu/ZSM-5 monolith sample fell from 60% to 17% over the course of 70 h at 485°C under a simulated lean burn gas feed (containing 10% H_2O) flowing at a GHSV of 30 000 h^{-1} [20]. Furthermore, workers at Ford have demonstrated that Cu/ZSM-5 deactivates rapidly if the catalyst is treated in a feed containing 10% H_2O in air at 410°C [21]. This deactivation is not observed if the catalyst is treated in dry air at the same temperature. The mechanistic implications of these observations will be discussed later, but it is clear that dramatic improvements in the hydrothermal stability of the Cu/ZSM-5 material are necessary if it is ever going to be used within the automotive catalysis application.

2.2. *Mechanistic studies of the lean NO_x reaction over Cu/ZSM-5 catalysts*

2.2.1. *Introduction*

Several different schemes have been proposed for the mechanism of the lean NO_x reaction over Cu/ZSM-5. They can be broken down into four major groups with some overlap between the groups. The first of these proposes that the mechanism follows the NO decomposition pathway, with the role of the hydrocarbon being to reduce the Cu^{II} species back to the active Cu^{I} state following the NO decomposition step. The second is that some partially oxidised hydrocarbon species reacts preferentially with the NO. The third proposes that an organonitrogen species forms on the Cu sites and subsequently decomposes to give N_2, CO_2, and H_2O. And finally, it has been proposed that the reaction is an example of bifunctional catalysis, with the hydrocarbon species being activated by the zeolite, and the NO being activated (usually as NO_2) by the Cu sites. These four possibilities are discussed in detail below.

2.2.2. *NO decomposition*

This proposal is based upon the known NO decomposition capability of Cu/ZSM-5 (see e.g. [22]). Within the NO decomposition reaction, the NO conversion passes through a maximum as the temperature is increased; this same observation is made during studies of the lean NO_x reaction using hydrocarbons as reductants (see Fig. 1). The NO decomposition reaction over Cu/ZSM-5 is believed to proceed over isolated Cu^+ sites via the initial formation of the mononitrosyl [13,23]. This species is converted into a $Cu(NO)_2$ gem-dinitrosyl species by the addition of a second NO molecule, and this dinitrosyl rearranges and decomposes to release N_2O with concomitant oxidation of the Cu^+ site to the Cu^{2+} oxidation state. The N_2O is reduced to N_2 during a subsequent interaction with a Cu^+ site, while the oxidised Cu^{2+} site undergoes reduction back to the active Cu^+ form via the desorption of oxygen. The relatively low desorption temperature of oxygen from Cu/ZSM-5 (ca. 400–450°C) has been reported by several authors [5,24], and this spontaneous Cu^{2+}-to-Cu^{+} reduction has been followed at 500°C using ESR [23]. It is this low temperature desorption of oxygen which is believed to give rise to the low temperature NO decomposition activity of Cu/ZSM-5, since oxygen has long been recognised as an inhibitor of the NO decomposition reaction. Indeed, the NO decomposition step is extremely facile over Cu/ZSM-5 catalysts provided they contain a reasonable concentration of Cu^{+} sites. For example, NO decomposition will proceed at room temperature over partially-reduced (i.e., Cu^{+}-containing) Cu/ZSM-5, but stops when all of the Cu^{+} sites have been oxidised to Cu^{2+} by this step of the reaction [5,25]. It is the reductive regeneration of the catalyst (i.e., the Cu^{2+} to Cu^{+} reduction) which requires the elevated temperature. The fact that the NO conversion rises to a maximum and then decreases as the temperature is progressively increased can be rationalised in terms of the anticipated steady state concentration of the gem-dinitrosyl $Cu^{+}(NO)_2$ reaction intermediate, which will decrease as the temperature rises [23]. These observations suggest that lowering the temperature at which the blocking oxygen species is removed from the catalyst might increase the activity of the material, since lower temperatures will enable a higher equilibrium concentration of the gem-dinitrosyl intermediate species to be established.

Most studies of the NO decomposition reaction have been performed using streams containing NO concentrations well in excess of those typical of automotive catalysis, and using very low space velocities. Indeed, very low NO conversions are obtained (in the absence of a reductant) under conditions of excess oxygen, low NO concentration, and realistically high space velocity [26].

So, when the reduction of the (inactive) Cu^{2+} to the (active) Cu^{+} sites is required to occur 'spontaneously', via the desorption of oxygen, the steady state rates observed are too low to be useful within the automotive catalysis industry. However, it is clear that the addition of reductant species to the gas feed could substantially accelerate this Cu^{2+}-to-Cu^{+} transformation, and a mechanism based upon this possibility has been advanced by Burch and Millington [27]. They propose that the NO decomposition reaction occurs over Cu^{+} sites, and that the hydrocarbon reductant is responsible for maintaining a reasonable concentration of the active Cu^{+} sites during the course of the reaction. In this context it is interesting to note that both CO [10] and H_2 [28] are capable of reducing NO over Cu/ZSM-5 in the *absence* of O_2 (presumably via such a redox mechanism).

This elegant mechanistic proposal is capable of explaining many of the characteristic features of the lean NO_x reaction. For example, the temperature dependence of the reaction (see Fig. 1) can be explained by considering that the equilibrium concentration of the intermediate $Cu^{+}(NO)_2$ gem-dinitrosyl species will decrease with increasing temperature, by analogy with the NO decomposition reaction. Obviously, the depletion of the hydrocarbon reductant as a function of catalyst bed length at high HC conversions (i.e., high temperatures) will also act to decrease the integral NO conversion. At low HC conversions, the whole length of the bed will have access to useable concentrations of reductant, while at high conversions there will be far less useable HC towards the back of the bed than at the front. This will be particularly accentuated once the HC conversion reaches 100%, since additional temperature increases will mean that sites located towards the back of the catalyst bed will see no HC reductant at all.

However, the performance of the Cu/ZSM-5 catalyst as a function of temperature also supports this reaction mechanism in a more subtle way. Most authors agree that alkenes give rise to higher peak NO conversions that do the corresponding alkanes. For example, propene is a more effective reductant than is propane under most conditions [7]. (Other authors have claimed that propane is more effective than propene [29], but their experiments were not performed in the presence of a large excess of oxygen). It is also the case that propane is converted at higher reaction temperature than is propene under lean NO_x conditions (see e.g., [7]). Clearly, if the NO decomposition-based mechanism is correct, then reduction of the Cu^{2+} to Cu^+ at lower temperatures should help to increase the reaction rate by increasing the steady state concentration of the intermediate $Cu^+(NO)_2$ species. So these observations certainly suggest that the NO chemistry over Cu/ZSM-5 is partially governed by a temperature-dependent equilibrium, which is (at least) partly responsible for the shape of the NO conversion profile as a function of temperature. Of course, these observations are completely consistent with the NO decomposition-based mechanistic proposal.

The addition of water vapour to lean NO_x gas streams results in a (reversible) decrease in the observed NO conversion [14]. Within the NO decomposition literature there are conflicting reports about the effect of H_2O addition on NO removal. In an early review paper, Iwamoto claims that the catalytic performance is not affected by the addition of water vapour to the NO decomposition feed stream [22]. However, he contradicts himself in a later paper, in which he states that H_2O does inhibit the decomposition reaction [30]; he also points out that this inhibition is reversible. Li and Hall have also investigated the effect of water vapour [31], and they report that its addition reversibly inhibits the NO decomposition reaction. The balance of opinion, therefore, is that the direct decomposition reaction is reversibly inhibited by H_2O addition, which represents another parallel with the lean NO_x reaction.

One argument which has been used to attempt to refute this NO decomposition-based mechanistic proposal is that both CO and H_2 are far less effective than propene for NO reduction in the presence of excess oxygen [6,14,32]. Even in experiments in which each molecule of C_3H_6 is replaced by six molecules of CO, the NO conversion is substantially greater in the propene-containing feed [14]. This seems surprising if the only role of the reductant species is to transform inactive Cu^{2+} sites into active Cu^+ sites. However, as Burch and Millington point out [27], the reducing power of a single C_3H_6 molecule is extremely high, particularly when it is within a confined space — each molecule is capable of reacting with 4.5 oxygen molecules. In contrast, each CO molecule can only react with 0.5 molecules of O_2. Therefore, when an oxidised Cu^{2+} site is reduced to Cu^+ by a CO molecule, it is very likely that it will be subsequently reoxidised by oxygen, because the CO does not possess *concerted* reducing power. Propene, on the other hand, is capable of the initial reduction of the oxidised Cu^{2+} site, and is also capable of removing subsequent incoming oxygen molecules to protect the Cu^+ site thereby maintaining it as Cu^+ for a greater period of time. This will obviously increase the probability of NO reduction over the reduced site. This 'concerted reducing power' hypothesis is further supported by the observation that methanol is not capable of effecting lean NO_x reduction [6], since the reducing power of a methanol molecule is low with respect to that of propene. Other (larger) partially oxidised hydrocarbons are active for NO reduction under lean conditions [6], which also supports the theory. This apparent dependence of NO conversion efficiency on the reducing power of the reductant species is further illustrated by Fig. 4 [27], which shows the rate of N_2 formation from NO as a function of the number (n) of oxygen molecules required to balance the reaction:

$$C_xH_yO_z + nO_2 = CO + (x-1)CO_2 + (y/2)H_2O$$

Burch and Millington [27] defined 'n' as the quantity of oxygen required to oxidise the reducing agent almost completely, while still leaving some reducing power (i.e., 'n' is a measure of the concerted reducing power of a molecule). Note that they explicitly state that the equation is balanced with CO merely to demonstrate that some residual reducing power exists; they do not mean to imply that the actual reducing species is CO. It is clear from Fig. 4 that reducing agents with low 'n' coefficients are not effective lean NO_x reductants, while those with higher 'n' coefficients are.

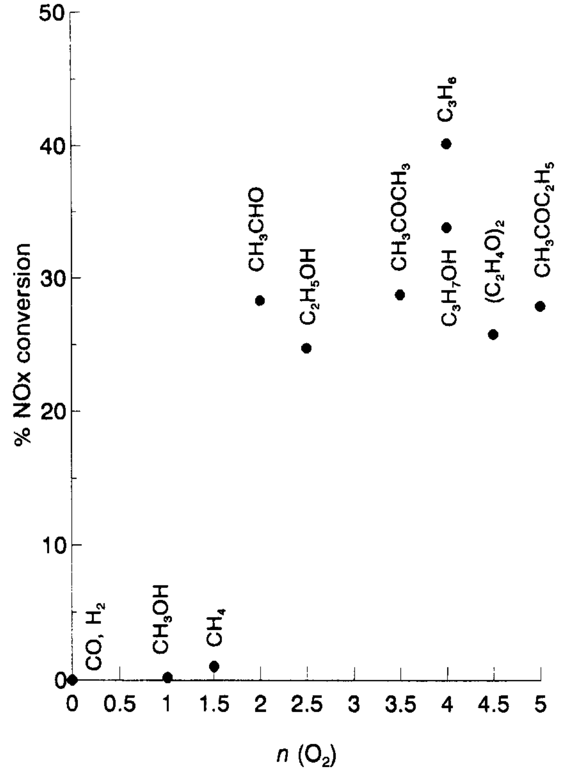


Fig. 4. Conversion of NO as a function of the reducing power of various compounds. Taken from Ref. [27] — for full experimental details see Ref. [6].

Therefore, within this mechanism, the role of the zeolite is to provide the correct chemical and physical environment for the Cu species. The limited accessibility of the Cu sites within the zeolite channels is proposed to play a major factor in the efficiency of the Cu/ZSM-5 catalyst for the lean NO_x reaction.

Another observation which has been frequently used to counter this mechanistic proposal (see e.g., [14]) is the dramatic oxygen-induced promotion of the NO reduction rate [10]. It is certainly to be expected that the presence of excess gas phase oxygen will lead to a decrease in the steady state concentration of the NO decomposition-active Cu^+ sites, and it is known that the addition of gas phase oxygen under direct NO decomposition conditions (i.e., in the absence of reductant) inhibits the NO decomposition rate [23]. Whether Cu^+ sites actually exist within Cu/ZSM-5 under conditions of excess oxygen has been questioned, and electron spectroscopy has revealed that the Cu^{2+} state predominates following exposure to a 1:1:6 C_3H_6:NO:O_2 (i.e., slightly lean) gas feed at 360°C [33]. More convincingly, Petunchi and Hall used EPR to demonstrate that under realistically lean conditions (i-butane:NO:O_2 = 1:1:40) the lean NO_x reaction proceeds with virtually no reduction of the Cu^{2+} sites to Cu^+ [34]. However, the results from the in situ XANES/EXAFS study of Liu and Robota [35] indicate that significant concentrations of Cu^+ can be sustained within the Cu/ZSM-5 catalyst under lean NO_x conditions. These experiments were performed during a temperature ramp from room temperature to 600°C at a rate of 5°C/min. Therefore, it is possible that their data were complicated by transient effects associated with the build up of adsorbed hydrocarbon species within the zeolite at low temperatures and the gradual subsequent release of these species as the temperature was increased. Such effects will lead to the generation of strongly locally reducing environments, as the hydrocarbon species desorb; the overall effect is then to increase the number of Cu^+ species observed to a level well in excess of the Cu^+ concentration under steady state conditions within the selected gas feed. The high propene concentration (3200 ppm) and the low ramp rate will have accentuated this effect. The precipitous decrease in normalised Cu^+ concentration from 0.9 to 0.28 which was observed on increasing the temperature from 369 to 433°C also supports this hypothesis. It is very likely that significant hysteresis would have been observed had the measurements also been made as the temperature was decreased. Therefore, while their observations clearly demonstrate that Cu^+ species can be generated under lean NO_x conditions, the Cu^+ concentrations derived during these measurements are probably significantly higher than those which will pertain under steady state operating conditions (where the Cu/ZSM-5 catalyst is still extremely active).

Nevertheless, the fact that substantial quantities of CO are released from the catalyst during lean NO_x catalysis is certainly consistent with the view that a time-averaged 'local' reducing environment can be sustained around the Cu sites within the zeolite. The CO release tends only to be observed during studies conducted at reasonably high space velocities [36], in which the contact time for CO generated within the reaction is rather short. At longer contact times the CO will be predominantly oxidised to CO_2.

The presence of Cu^+ species within the zeolite under lean NO_x conditions is also suggested by the observation of acrolein formation under certain conditions. Ansell et al. reported that acrolein is formed by Cu/ZSM-5 at low temperature under a lean C_3H_6/O_2 gas feed [5]. It is known that cuprous oxide is active and selective for the generation of acrolein [37,38], implying that Cu^+ sites can be formed in the zeolite under lean conditions. However, as the discussion above suggests, it is most likely that the majority of the Cu will be present as Cu^{2+} under the strongly oxidising conditions which characterise the lean NO_x operating regime.

In order to explain the oxygen promotion effect, Burch and Millington have proposed that the excess of oxygen prevents the (deactivating) over-reduction of the Cu sites to Cu^0 [27]. Other workers have indeed reported that Cu^0 species can be formed when sub-stoichiometric concentrations of oxygen are present [32,34]. It has also been proposed that the oxygen prevents the build-up of site blocking carbonaceous deposits on the Cu sites [29].

A more serious problem for the proponents of the NO decomposition-based mechanism concerns the respective responses of the direct NO decomposition and the lean NO_x reactions to the introduction of SO_2. The direct decomposition reaction is completely poisoned by the addition of SO_2 [16], while the lean NO_x reaction undergoes a slight and reversible deactivation [16]. It is extremely difficult to reconcile these observations within the NO decomposition-based lean NO_x mechanistic hypothesis. Whilst it is possible that the hydrocarbon, or some partially-oxidised derivative of the hydrocarbon, scavenges the SO_2 in some way, it is difficult to see exactly how this could occur.

The NO decomposition reaction and the lean NO_x reaction also exhibit different dependencies on the Cu ion exchange level of the catalyst. Within the lean NO_x reaction, Iwamoto and Mizuno demonstrated that the catalyst efficiency at 250°C increases steadily as the exchange level is increased from 0 to 100% under their conditions [14]. They also showed that further increases in Cu level led to a decrease in the catalytic performance. However, under NO decomposition conditions no conversion is seen at 450°C until the Cu exchange level increases above 50% [30]. Furthermore, the catalyst efficiency continues to increase as the exchange level is increased from 100 to 150%; this is the opposite of the case for the lean NO_x reaction.

It has also been pointed out [39] that a redox cation is not essential for the lean NO_x reaction to proceed, since H/ZSM-5 is also active for the reaction. Interestingly, H/ZSM-5 is completely inactive for the direct NO decomposition reaction. This has also been put forward as evidence that the lean NO_x reaction over Cu/ZSM-5 does not occur via NO decomposition. Of course, it is possible that the reaction proceeds via different mechanisms over the two catalysts.

In conclusion, therefore, it is apparent that a number of observations are completely consistent with the NO decomposition-based mechanistic proposal. However, there are certainly several disparities between the characteristics of Cu/ZSM-5 within the direct NO decomposition reaction and its characteristics within the lean NO_x reaction. Some of these are extremely difficult to reconcile.

2.2.3. Partially oxidised hydrocarbon species reacts preferentially with NO

This hypothesis, which has been put forward by a large number of authors (see e.g., [6,14,26]), proposes that the oxygen reacts with the hydrocarbon reductant to generate a partially oxidised hydrocarbon species which is highly selective towards reaction with NO. This theory was originally put forward to account for the known oxygen-induced promotion of the lean NO_x reaction [10], but can obviously also explain the inability of CO and molecular H_2 to effect substantial NO conversion under extremely lean conditions [6,14,32]. In addition, the feasibility of the formation of partially oxidised species in a strongly oxidising environment over Cu/ZSM-5 is supported by the observed net generation of CO during lean NO_x catalysis [5,7,8]. Furthermore, acrolein (C_3H_4O) formation has been observed over Cu/ZSM-5 at low temperatures using a lean C_3H_6/O_2 gas feed [5]. Cuprous oxide (Cu_2O) is known to be active (and selective) for the generation of acrolein from C_3H_6/O_2 feeds [36,37], which supports the notion that Cu^+ sites can be generated within the zeolite under these conditions (as discussed above). It has also been reported that water vapour inhibits the generation of acrolein over Cu-based catalysts [37], which is consistent with the known water vapour-induced inhibition of the lean NO_x reaction [14]. The decrease in NO conversion at high temperatures can also be explained within this mechanism in terms of severe total oxidation of the intermediate or the raw hydrocarbon by O_2 at these temperatures.

Within this mechanism, the principal role of the zeolite is to provide the correct environment for the Cu sites, to ensure that they are not capable of over-oxidising the partially oxidised species through to CO_2 and H_2O. The generation of a local reducing environment around the Cu sites within the confines of the channel structure of the zeolite is certainly feasible. As outlined in Section 2.2.2, the propene species can actually protect the Cu sites from oxidation via its concerted reducing ability. The Cu sites are then responsible for activating the hydrocarbon (and converting it into the partially oxidised species), and activating/adsorbing the NO ready for reaction with this species.

The first real test of this hypothesis was conducted by Montreuil and Shelef [6], who reasoned that if this were indeed the correct mechanism, then one might expect some partially oxidised hydrocarbon compounds to be significantly more effective within the lean NO_x reaction than alkanes and alkenes. This was not found to be the case. The partially oxidised species investigated were methanol, ethanol, propanol, acetaldehyde, acetone, methyl ethyl ketone, 1,4-dioxane with propene being used as a standard. Propene was found to be significantly the most active of these species under their test conditions (482°C under a gas feed simulating that from a lean burn engine). The performance of propanol was close to that of propene (34% versus 39%), with most of the other compounds giving conversions in the 25–30% range. The exception to this was methanol, which was almost completely inactive for the selective reduction under their conditions. One possible explanation of methanol's observed inactivity within this study is that it undergoes preferential oxidation by O_2 at substantially lower temperatures than does (say) ethanol. This would then mean that there would be significantly more ethanol than methanol available at the selected reaction temperature of 482°C.

However, this explanation is ruled out by the later results of Hamada et al. [40], who showed that over a broad temperature range (200–500°C) ethanol gave substantial NO conversion, while methanol gave none. This massive disparity between the relative efficiencies of methanol and ethanol presents difficulties for the partially oxidised hydrocarbon intermediate mechanism. When this is combined with the fact that none of the partially oxidised hydrocarbon compounds were more effective than propene under lean NO_x conditions, this mechanistic hypothesis begins to look less compelling.

In addition, the results of Montreuil and Shelef [6] imply that any partially oxidised hydrocarbon intermediate is extremely unlikely to be a gas phase component which adsorbs on the surface and subsequently reacts with NO with high reaction probability. This is supported by the knowledge that most workers use gas chromatographs (GCs) to follow hydrocarbon conversion during the reaction and no one has reported the gas phase release of any partially oxidised hydrocarbon component during these experiments. The exception to this is the observation of acrolein release during the temporal analysis of products (TAP) study of Ansell et al. [5]. These results were, however, obtained under conditions of low pressure, low temperature (ca. 160°C) and low space velocity, which may help to rationalise these observations. If it is instead proposed that the intermediate is some partially oxidised $C_xH_yO_z$ fragment adsorbed on (say) the acidic sites of the zeolite, then this mechanism starts to resemble the one discussed in Section 2.2.5 below.

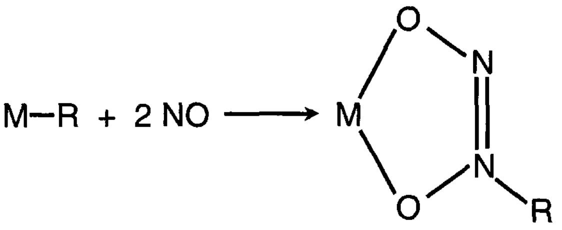
Another major issue which such a mechanism needs to address is how the nitrogen–nitrogen bond forms within such a scheme. As has been seen in Section 2.2.2 above, the NO decomposition-based mechanistic hypothesis has the N–N bond formation step built into it. It is more difficult to see how dinitrogen can be formed via the interaction of NO with a $C_xH_yO_z$ species, and this important aspect of the reaction has received little attention from the proponents of the partially oxidised hydrocarbon intermediate mechanism. Of course, this does not prove that the reaction does not proceed via this mechanism, but it does make the reaction sequence more difficult to visualise.

2.2.4. Organonitrogen or isocyanate intermediate

The possible intermediacy of isocyanate species within the lean NO_x reaction over Cu-based catalysts has been proposed by Ukisu et al. [41,42]. As is almost invariably the case with reaction schemes involving isocyanate intermediates, their evidence comes from infra-red (IR) spectroscopy. Arguably the greatest problem facing advocates of the IR technique is how to distinguish between spectral features due to true reaction intermediates and those due to spectator species. Indeed, the formation of isocyanate species on a Cu–Cs/Al_2O_3 catalyst exposed to a mixture of C_3H_6/NO/O_2 under approximately stoichiometric conditions is not particularly surprising. No convincing evidence that this isocyanate species is an important intermediate in the lean NO_x reaction was presented by these authors.

Iwamoto has also proposed that surface NCO species, formed from the reaction between some unspecified hydrocarbon-derived intermediate and NO, are crucial intermediates in the lean NO_x reaction [43]. Once again, this proposal was based largely upon IR data.

Kharas used reasoning derived from the field of organometallic/inorganic chemistry to suggest that the reaction proceeds via the intermediacy of organonitrogen species [7]. He proposed that Cu-alkyl species are formed via oxidative activation, and that these intermediates add NO via insertion to form *N*-nitroso-*N*-alkylhydroxylamate species on the Cu sites:



It is suggested that such an intermediate might decompose to generate N_2, N_2O, CO_2 and H_2O. The oxygen-induced promotion of the lean NO_x activity sits happily within this mechanism, since the initial activation of the hydrocarbon proceeds by the interaction of the hydrocarbon with the oxidised Cu surface. This interaction leads to the abstraction of a hydrogen atom from the hydrocarbon molecule with concomitant generation of an alkyl (or allyl) species. This proposal also considers the importance of the N–N bond formation step, and can be used to explain the relatively poor performance of CO and molecular H_2 for the reaction. However, no experimental evidence in direct support of the mechanism was provided in the paper. In addition, the double insertion of NO molecules in this manner appears to be unlikely, especially since the NO molecule usually bonds to Cu via the N atom. Indeed, in their recent in situ XANES/EXAFS investigation of the Cu/ZSM-5 catalyst system, Liu and Robota established that any hydrocarbon complexes formed between the Cu centre and hydrocarbon reductant do not have oxygen in close proximity to the Cu [35]. Nevertheless, evidence for a related intermediate has since been reported by Hayes et al. using IR spectroscopy [44]. They identified the organonitrogen intermediate as a nitrile, and elegantly demonstrated that it decomposes selectively to dinitrogen when exposed to oxygen. However, their data do suggest that the rate of decomposition of the intermediate to N_2 when exposed to O_2 may not be rapid enough for this species to be the intermediate, since a significant delay was observed between introducing the O_2 and observing the peak of the N_2 release profile.

2.2.5. *Bifunctional catalysis*

This proposal is based around the hypothesis that the hydrocarbon species is activated by the zeolite, while the NO is activated by the Cu sites. Note that in all of the other mechanistic theories considered thus far, all of the chemistry is assumed to be occurring on the Cu sites, with the special role of the zeolite being to fix the Cu in an appropriate physical and/or chemical state. However, since the acidic characteristics of zeolites are well known, the bifunctional catalysis proposal is certainly feasible.

Indeed, a large number of the features of the lean NO_x reaction can be explained by assuming that the hydrocarbon is activated by the surface acidity of the zeolite. For example, the known ineffectiveness of CO and molecular H_2 for the reaction [6,7,14] is accounted for within this mechanism. So too is the fact that alkenes are more reactive than alkanes, by analogy with the known relative ease of cracking of alkenes and alkanes. The extremely poor performance of methanol [6,40] and methane [10] within the reaction is also consistent, since primary carbenium ions are not particularly stable. The observation that partially oxidised hydrocarbon compounds are active for NO reduction under oxidising conditions [6] can also be incorporated into such a model, since the ZSM-5 zeolite can form carbocations from a wide range of organic compounds.

The importance of support acidity is also implicated by a number of studies on non-zeolite systems. For example, alumina-based catalysts are generally far more active than silica-based materials [45]. In addition, Hamada et al. have shown that the selective reduction occurs over other, non-metallised solid acid catalysts, such as H-form zeolites [46] and sulphated forms of TiO_2 and ZrO_2 [47]. Furthermore, Obuchi et al. [48] have used ESR to show that carbonaceous radicals are formed on a γ-alumina catalyst during the course of the lean NO_x reaction when propene is used as the reductant. They also showed that similar deposits were formed when methyl tert-butyl ether (MTBE) was used. A good correlation was established between carbon deposit density and lean NO_x performance.

Therefore, it is clear that the acidity of the zeolite may have a role to play in the activation of the hydrocarbon species within the lean NO_x reaction. However, it is well-known (see e.g., [7,14]) that the most active Cu/ZSM-5 catalysts are those which have been 'over-exchanged' with Cu, i.e., those which contain Cu levels in excess of that required to give 100% exchange based on the number of exchangeable cations. (In the two cases quoted (i.e., Ref. 7 and 14), the peak performance was observed at exchange levels in the 100–200% range). Obviously, one would expect the Bronsted acidity of the zeolite to fall as the Cu was exchanged in, and one might expect that over-exchanged samples of Cu/ZSM-5 would contain virtually no acidic sites. This latter assumption is challenged by the results of Hall and co-workers [39], who demonstrated that an over-exchanged sample of Cu/ZSM-5 was extremely effective at cracking i-butane at temperatures of relevance to the lean NO_x reaction (350–400°C). Indeed, their results were in fairly good agreement with the known performance of H/ZSM-5 for i-butane cracking at higher temperature [49]. These results clearly show that over-exchanged Cu/ZSM-5 is an effective catalyst for Bronsted acid catalysis reactions.

The relationship between the Cu loading and the acidity of the Cu/ZSM-5 material has been studied in detail by Parrillo et al. [50]. They used a combination of temperature programmed desorption (TPD) and thermogravimetric analysis (TGA) to demonstrate that the concentration of Bronsted acid sites does indeed decrease as Cu is exchanged into the sample. However, they found that substantial concentrations of Bronsted acid sites were still present in their 130% Cu ion-exchanged sample. They interpreted these results by suggesting that a fraction of the Cu is not associated with the Al sites within the zeolite. Whatever the reason, it is clear that so-called 'over-exchanged' Cu/ZSM-5 samples do contain significant concentrations of Bronsted acid sites. It is also interesting to note that Parrillo et al. observed the formation of Bronsted acid sites during the Cu ion exchange of a Na/ZSM-5 sample. They point out that fairly high Na concentrations are required to obtain Na/ZSM-5 samples with no Bronsted acid sites [51], and propose that there is an equilibrium between protons in the (solvent) water and Na cations during ion-exchange.

Centi et al. [52] have recently proposed that Bronsted acidity is not a key requirement for activity in Cu/ZSM-5 catalysts. They studied the performance of Cu/ZSM-5 and Cu-ion-exchanged boralite, in which the group IIIa element within the zeolite structure is boron rather than the more usual aluminium, and found that the catalytic performance of the two materials was fairly similar. They point out that the substitution of Al with B in MFI-type zeolites leads to the formation of weaker Bronsted acid sites, and conclude that Bronsted acidity is not essential for activity in these systems. However, they also found that the non-metallised boralite had comparable lean NO_x performance to the non-metallised ZSM-5 sample. This observation clearly demonstrates that the ability of the boralite to activate hydrocarbons into a form suitable for reaction with NO_x under lean conditions is similar to that of the ZSM-5 material. They also point out that the boralite materials possess strong Lewis acid sites. Therefore, taken together, their results are completely consistent with a model in which the activation of hydrocarbon species occurs on the acidic sites of the support material (whether boralite or conventional ZSM-5).

Therefore, there is evidence suggesting that the hydrocarbon species is activated by the acidic sites on the zeolite. Most of the workers who have advocated this bifunctional model believe that the NO is activated by the Cu sites, and that it is converted to NO_2 (see e.g., [5,39]). This allows the mechanism to explain the strong oxygen-induced enhancement of the lean NO_x reaction rate [10], and is consistent with the thermodynamics of the system, since the equilibrium strongly favours NO_2 in the presence of both NO and O_2 at temperatures below about 530°C. Another attractive feature of the NO_2-based hypothesis is that it does not rely on the generation of partially reduced Cu^+ sites within the zeolite, unlike the NO decomposition-based proposals (see Section 2.2.2). As has already been seen, the available evidence suggests that the majority of the Cu sites will be present in the Cu^{2+} state under lean NO_x conditions [33,34].

The ability of Cu/ZSM-5 to catalyse the NO to NO_2 conversion is well known (see e.g., [53]), and it is very interesting to note that this reaction parallels the lean NO_x reaction in a number of key respects. First of all, the reaction rate increases as the temperature rises above about 200°C, it peaks at around 400°C or so, before falling away as a consequence of thermodynamic equilibrium [53]. (Note that the temperature dependence quoted above was obtained using a very high flow rate and very low catalyst contact time; the exact temperatures will be strongly dependent on the contact time used). This trend is similar to that observed for the lean NO_x reaction [5,53]. In addition, the activity of Cu/ZSM-5 within the NO to NO_2 reaction is greater than that of both H/ZSM-5 and Cu/Al_2O_3 [52], which parallels the performance of these three materials within the lean NO_x reaction. Finally, over Cu/ZSM-5 the NO to NO_2 reaction is suppressed by water vapour [53], as is the lean NO_x reaction. Indeed, the relative suppression of the activity by water vapour is reasonably similar for the two reactions.

Petunchi and Hall tested the feasibility of the NO_2 intermediate hypothesis by comparing the relative performance of mixtures of i-butane/NO/O_2 and i-butane/NO_2/O_2 [54]. They found that the NO_x conversion occurred at slightly lower temperatures when NO_2 was used, and that the hydrocarbon conversion followed this same trend (i.e., occurring at a slightly lower temperature with NO_2). From these data they concluded that it is feasible that NO_2 plays a critical role in the reaction mechanism over Cu/ZSM-5. They also proposed that the promoting role of the oxygen is associated with its ability to oxidise NO to NO_2, to keep the catalyst free of site blocking carbonaceous species, and to maintain the Cu sites in a 'nearly completely oxidised state'.

However, in very similar experiments involving ethene instead of i-butane, Iwamoto and Mizuno [14] reached the opposite conclusion, i.e., that the respective reductions of NO and NO_2 proceed via different mechanisms. They found that the NO_x conversion occurred at a significantly lower temperature when NO_2 was the species to be reduced than when NO was being reduced (200 versus 250°C), and that the ethene conversion followed the same trend (i.e., occurring at significantly higher temperature when NO was used). Iwamoto and Mizuno interpreted their results as evidence that NO_2 was *not* an intermediate in the lean NO_x reaction. The major difference between the work of Iwamoto and that of Hall was the hydrocarbon reductant used. This, in addition to the difference in space velocity, resulted in the NO_x conversions occurring at significantly different temperatures in the two sets of experiments. For example, in the work of Petunchi and Hall [54] the NO_x conversions (in both the NO and NO_2 experiments) were only just starting to take off at a temperature of 200°C, while the NO_2-to-N_2 conversion actually peaked at this temperature in the experiments of Iwamoto and Mizuno [14]. Therefore, the results of the two groups can be partially reconciled by observing that the NO_x conversion temperatures were significantly different in the two cases, since it is possible that the ethene/NO/O_2 experiment of Iwamoto and Mizuno was performed under conditions in which the conversion of NO to NO_2 was rate limiting (because of the low temperature). In this case one would not expect identical results to be obtained using NO and NO_2, even if the underlying mechanism of NO conversion required the intermediacy of NO_2. This 'reconciliation' hypothesis is further supported by the results of Chajar et al. [55], who studied the propane/NO/O_2 and propane/NO_2/O_2 reactions over Cu/ZSM-5. They were working at 350°C (because propane is reasonably difficult to activate) and found that the behaviour of NO and NO_2 was identical in the two feeds under these conditions. The observations of Iwamoto and Mizuno represent possibly the strongest evidence reported to date against the NO_2 hypothesis but, as is clear from the discussion above, there is a substantial body of data which supports the possible intermediacy of NO_2 in the lean NO_x reaction.

Hence, there is reasonable evidence that the zeolite may be activating the hydrocarbon species, and the Cu may be oxidising the NO to NO_2. Is it possible to link these observations together to construct a feasible mechanistic proposal? The work of Yamashita et al. [56] suggests that it is. They studied the rate at which NO was converted to N_2 over a coal char (i.e., carbon) material, and found, not surprisingly, that this rate was greatly accelerated when Cu (or Ni or Ca) was added to the system. However, they further found that the rate of NO_x conversion was remarkably promoted at 300°C by the addition of excess O_2 to the gas feed (1000 ppm NO, 5% O_2 in He), which correlates with the lean NO_x experience. It is extremely unlikely that this promotion is associated with an increase in (say) the rate of the NO decomposition reaction over the Cu sites, since oxygen is known to inhibit this reaction [23]. It should also be stressed that there was no gas phase reductant present during the course of these experiments. Bearing these factors in mind, the results are consistent with a mechanism in which the Cu sites oxidise the NO to NO_2 using the excess O_2, with this NO_2 then reacting with the carbon support. Indeed, the carbon support was consumed to a considerable extent at 300°C under these conditions. This result is consistent with the work of Cooper and Thoss [57], who showed that the combustion rate of (carbonaceous) diesel particulate was greatly increased by adding air to NO to generate NO_2. NO_2 has a much higher reactivity

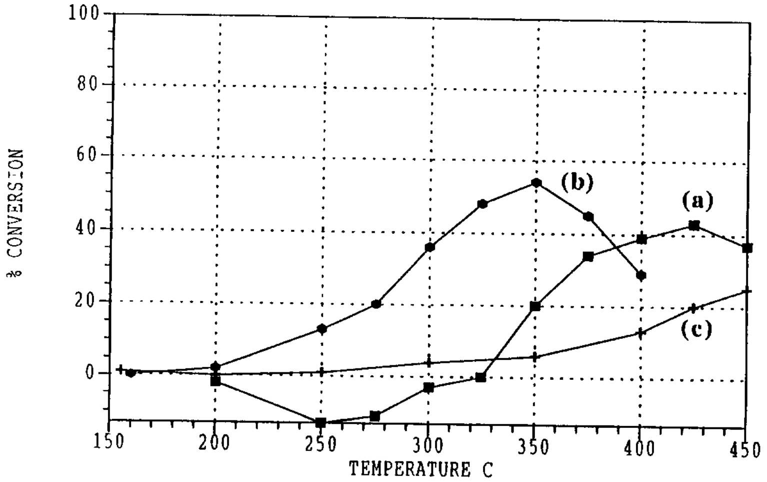


Fig. 5. NO_x conversion profiles obtained over: (a) fresh Cu/ZSM-5 under a full gas mix; (b) pre-coked Cu/ZSM-5 under a full gas mix minus propene (i.e., effective components NO $+O_2$); (c) pre-coked Cu/ZSM-5 under a full gas mix minus propene and oxygen (i.e., effective component NO). Taken from Ref. [5].

towards such carbon-based particulates than either NO or O_2.

This mechanistic hypothesis is also supported by the work of Ansell et al. [5], who pre-treated their Cu/ZSM-5 catalyst under a simulated lean burn full gas mix (both with and without oxygen, in separate experiments) at 160°C for 30 min. They then heated the sample under N_2 to 400°C to desorb any weakly-held hydrocarbon species, but showed, using temperature programmed oxidation (TPO) that this pretreated catalyst retained a substantial quantity of carbon-containing material, presumably associated with zeolitic sites. As a consequence of this they termed the pretreated catalyst 'pre-coked'. This sample was then heated from 160 to 450°C under a simulated full gas mix *minus hydrocarbon* (i.e., the effective components within the gas feed were NO and O_2). Under these conditions (Fig. 5) they found that substantial NO_x conversion occurred at significantly lower temperatures than was observed when heating the untreated Cu/ZSM-5 catalyst under the full gas mix (i.e., with hydrocarbon). Therefore, the species generated by the low temperature pretreatment and subsequent desorption is/are extremely reactive for NO_x conversion when exposed to a gas feed containing both NO and O_2. When the pre-treated sample was exposed to the full gas mix *minus hydrocarbon and oxygen* (i.e., when the effective component was NO) very little activity was observed. These observations are consistent with the oxygen-induced promotion of the lean NO_x reaction, and suggest that this promotion is associated with the transformation of poorly reactive NO into highly reactive NO_2. Obviously, questions remain about the nature of the hydrocarbon-derived species deposited on the catalyst, and of whether these species form rapidly enough under actual reaction conditions to be involved in the reaction steps. Nevertheless, the fact that these species are extremely reactive for NO_x reduction in the presence of both NO and O_2 is a highly significant result.

The highly active, pre-treated sample generated in the work of Ansell et al. was termed 'pre-coked' by the authors, which leads us into a discussion of the nature of the hydrocarbon species which is activated by the acidic zeolite surface. Some workers have reported carbon balances in excess of 98% [58,59], leading them to suggest that significant carbon deposition is not occurring under lean NO_x conditions. Shelef et al., on the other hand, report that the use of propylene as the lean NO_x reductant leads to a 'copiously sooted surface' under their conditions [53], while they find propane to be a clean reductant. Burch and Millington performed switching experiments and carefully examined the catalytic behaviour during the first few minutes of reaction [27]. They found that the conversion of NO to N_2 reaches a steady state activity in a very short period of time, and interpreted this as evidence that carbon deposition is not responsible for the reactivity of Cu/ZSM-5. d'Itri and Sachtler have also reported that the deposition of coke is detrimental to lean NO_x activity, and have shown that the rate of removal of 'carbonaceous deposits' by O_2 is substantial at temperatures exceeding 350-400°C [29]. A similar temperature dependence of coke removal has also been reported by Ansell et al. [5]. These results clearly demonstrate that there will not be a high steady state concentration of coke at the working temperature of the Cu/ZSM-5 catalyst under realistic operating conditions (where the catalyst would need to be operated at 350–500°C to obtain high NO_x conversions). However, it is clear from the preceding discussion that the activation of hydrocarbons as carbocation/carbenium ions on the acidic sites of the zeolite is feasible. It should also be noted that the necessity to locate the Cu sites close to Bronsted acid sites is implicit within this mechanism.

As has already been seen, this bifunctional mechanism is capable of accounting for several of the general observations reported for the lean NO_x reaction over Cu/ZSM-5 (and over a number of other catalysts). For example, within this mechanism the temperature dependence of the NO_x conversion trace is accounted for in two ways. First of all, the NO to NO_2 equilibrium is known to be temperature dependent (see e.g., [53]), with its dependence paralleling that of the lean NO_x reaction. Secondly, as the temperature is increased the excess of oxygen will rapidly start to consume the activated hydrocarbon species, and will compete effectively with the NO_2 (which is present in much lower concentrations) for these species. The selective nature of high (i.e., $> C_1$) hydrocarbons over CO, H_2 and C_1 hydrocarbons can also be rationalised, as outlined above. The promoting role of oxygen is accounted for by the necessity of NO_2 formation, and even the H_2O inhibition can be explained by the ability of water vapour to inhibit the NO oxidation reaction [53]. Recall that one of the major arguments against the NO decomposition-based mechanism is the fact that the NO decomposition reaction is completely poisoned by SO_2, whereas the lean NO_x reaction is merely inhibited. It is feasible to suggest that the NO oxidation reaction will be merely inhibited by SO_2, but this hypothesis, which would certainly strengthen the argument for the NO_2 intermediate, awaits experimental investigation.

There is potentially a significant overlap between this bifunctional mechanism and the partially oxidised hydrocarbon intermediate hypothesis (see Section 2.2.3), if one proposes that the partially oxidised, activated $C_xH_yO_z$ species reside on the zeolite surface. As has been discussed in Section 2.2.3, one of the conceptual problems with the partially oxidised intermediate proposal is that it leaves open the issue of how the nitrogen–nitrogen bond forms to generate dinitrogen. A similar criticism can be laid at the door of the bifunctional catalysis theory. However, the strong evidence which points towards the intermediacy of NO_2, together with the proven ability of hydrocarbons to convert NO_2 to N_2 under lean NO_x conditions, reveals that such pairing of the nitrogens can occur from NO_2. In addition, the fact that non-metallised H/ZSM-5 is able to effect lean NO_x reduction demonstrates that nitrogen pairing does occur in the absence of metal-mediated redox chemistry. It is relevant to note that the available evidence suggests that the lean NO_x reaction proceeds via the intermediacy of NO_2 over the H/ZSM-5 catalyst (see Section 4 below).

3. Deactivation of the Cu/ZSM-5 catalyst

Whilst the deactivation of the catalyst is discussed in detail elsewhere [18], it is possible that information regarding the mode of deactivation could help to discriminate between the various mechanistic hypotheses presented above. Therefore, the major conclusions of the deactivation studies performed to date are briefly considered here.

As discussed in Section 2.1, the major obstacle to be overcome if Cu/ZSM-5 is to be commercialised is its lack of durability. Prolonged exposure to temperatures of the order of 800°C leads to substantial catalyst deactivation [7,8]. However, the catalyst also undergoes rapid deactivation at much lower temperatures (400–500°C) [20,21]. These latter observations are more serious, since this temperature range represents the optimum operating condition for the Cu/ZSM-5 catalyst under realistic conditions (see e.g., Fig. 1).

Grinsted et al. [21] studied the deactivation process and demonstrated that at 410°C the deactivation due to ageing in dry air was virtually absent. However, when the catalyst was aged at 410°C in wet air, its activity fell rapidly. They used magic angle spinning nuclear magnetic resonance (MASNMR) to probe for any changes in the amount of tetrahedrally coordinated Al induced by the ageing process, and thereby to characterise the extent of dealumination associated with the ageing. They found that the amount of tetrahedrally coordinated Al was essentially unchanged by ageing in dry air, but that it was decreased substantially by ageing in wet air. They also performed XRD analyses of their samples, and demonstrated that there was no significant loss in the crystallinity of the zeolite following these low temperature ageing treatments. From their XRD traces it also appears that substantial sintering of Cu species was *not* observed under these conditions, but the scaling of their XRD traces makes it impossible to state that no sintering occurred. They concluded that dealumination of the zeolite is facile at mild temperatures under wet conditions, and that this appears to correlate with the decrease in catalyst performance following this treatment.

Kharas et al. have investigated the deactivation process following more demanding catalyst pretreatments, involving exposure to lean burn gas feeds at temperatures of between 600 and 800°C [19]. They find that such treatments lead to substantial deactivation, in broad agreement with the study of Grinsted et al. [21]. Kharas et al. found that substantial losses of pore volume accompanied the deactivation; such pore blockage is often attributed to dealumination. However, Kharas et al. concluded that dealumination was not the primary deactivation mode under their conditions, and proposed instead that the sintering of the active Cu species into large, relatively inactive phases such as CuO was responsible for the deactivation. Their XRD data clearly show that formation of bulk CuO did occur during the high temperature treatments — a result backed up by their EXAFS analyses. They proposed that the pore volume losses were induced by the sintering of the Cu entities. Their model involved the growth of CuO species inside the zeolite channel structure. As the size of these CuO crystallites exceed the channel dimensions of the zeolite, further sintering requires the local destruction of the zeolite, leading to the observed losses in micropore volume.

Unfortunately, Kharas et al. [19] reached their conclusion about the absence of dealumination without *directly* investigating the extent of dealumination within the Cu/ZSM-5 material. They did not study the MASNMR spectrum of this catalyst because the presence of paramagnetic Cu^{2+} species leads to peak shifting and broadening in NMR, which can significantly complicate the analysis in certain cases. Instead of studying Cu/ZSM-5, they looked at Zn/ZSM-5 (Zn^{2+} is diamagnetic, and does not present the same problems as Cu^{2+}), and found that very little dealumination occurred in this catalyst following hydrothermal ageing at 800°C. They also found that their reference H/ZSM-5 sample suffered considerable dealumination following this treatment, and proposed that Cu^{2+} should suppress this dealumination, by analogy with Zn^{2+}. Other workers have, indeed, observed that the introduction of Cu into H/ZSM-5 inhibits the dealumination [21,34]. It should be noted that the MASNMR results of Grinsted et al. [21] were obtained on Cu/ZSM-5 samples, and, while some peak broadening was observed, it was not substantial, and did not (apparently) lead to problems with the analysis of the data.

Furthermore, the results of Petunchi and Hall [34] are in qualitative agreement with the conclusions reached by Grinsted et al. [21]. They studied the extent of dealumination in a number of Cu/ZSM-5 samples following treatment in a lean i-butane/NO/O_2 gas stream at various temperatures. Note that water vapour was not included in the mix, but that the catalyst would obviously be exposed to steam generated via the combustion of the hydrocarbon. They reported low levels of dealumination following treatments at 350 and 450°C, and substantial dealumination after treatment at 600°C.

Taken together, these results indicate that dealumination can occur within Cu/ZSM-5 under relatively mild conditions. It is also clear that substantial sintering of the Cu species can occur at higher temperatures. However, since the bulk of the evidence suggests that under mild conditions the deactivation of the catalyst is principally associated with the dealumination of the zeolite, the successful mechanism must certainly be consistent with these observations. The bifunctional mechanism is obviously consistent with these results, since dealumination is synonymous with the loss of Bronsted acid sites. However, dealumination will also destroy the geometric integrity of the ion-exchanged Cu sites, which means that the mechanistic hypotheses which revolve around the Cu sites alone are also consistent with this behaviour. Unfortunately, therefore, the deactivation studies do not allow discrimination between the various mechanistic theories. However, they clearly reveal that Cu/ZSM-5 deactivates substantially, even under relatively mild conditions, and indicate that dramatic increases in hydrothermal stability are required before the Cu/ZSM-5 catalyst can be used within the automotive application.

4. Mechanistic studies over other zeolite-based systems

A large number of studies have been carried out on other (i.e., non Cu/ZSM-5) zeolite-based systems (see e.g., [60–63]), but very few of these can realistically be referred to as 'mechanistic studies', since their primary purpose is to report the discovery of a new catalyst (or catalysts) capable of effecting the lean NO_x reaction. An exception to this is the work of Inui et al. [64] who studied the lean NO_x reactivity of a series of metallosilicates. They investigated the effect of changing the character of the metal species incorporated into the metallosilicate, from metals whose oxides are not easily reducible (e.g., Al, Ga), through those whose oxides are partially reducible (e.g., Fe, Mn) to those whose oxides are easily reducible (e.g., Cu). The resulting silicate catalysts were in the protonated form (e.g., H-Fe-silicate), with the different metallosilicates having different acidities. For example, H-Fe-silicate is fairly acidic (but weaker than H/ZSM-5), H-Mn-silicate is weakly acidic and H-Cu-silicate has virtually no acidity. Using cetane as the reductant they found that H-Fe-silicate was the most selective for the NO reduction reaction, and concluded that both the acidity and the redox characteristic of the catalyst are important for the reaction over these catalysts (H-Fe-silicate is acidic and also possesses reasonable redox capabilities). On the basis of their results they proposed a mechanism very similar to that put forward by Burch and Millington [27], in which the hydrocarbon removes oxygen from the metal sites and the NO subsequently decomposes over these reduced species.

Perhaps the mechanistic study of greatest relevance to the Cu/ZSM-5 studies reviewed above was the one carried out over H/ZSM-5 by Sasaki et al. [65]. They studied the propane/NO/O_2 and propane/NO_2/O_2 reactions over H/ZSM-5 at very low space velocity, and found that the conversion of NO_x to N_2 was virtually identical in the two cases. This parallels the behaviour of these two gas feeds over the Cu/ZSM-5 catalyst [55]. Sasaki et al. also studied the propane/O_2 reaction, and found that the rate of removal of propane is much higher when NO or NO_2 are added to the propane/O_2 gas feed. They interpreted their observations as evidence that the reaction proceeds via the initial formation of NO_2 from NO, and that this NO_2 reacts with propane, which is presumably activated by the acidic sites on the zeolite.

The other ZSM-5-based catalyst system which has been receiving a great deal of attention recently is Pt/ZSM-5 (see e.g., [66–68]). Once again, however, none of these studies can realistically be referred to as mechanistic investigations, since their aims were largely to report the discovery of a new lean NO_x catalyst, and to detail the characteristic features of the reaction over this catalyst. These studies have demonstrated that Pt operates at significantly lower temperatures than does Cu, as a result of its greater propensity to oxidise hydrocarbons. They also show that hydrocarbons are the active reductants [67,68], and that H_2O hardly inhibits Pt/ZSM-5 [67], which contrasts with the stronger inhibition of water vapour over Cu/ZSM-5 [14]. In common with Cu/ZSM-5, however, it appears that the durability of the Pt/ZSM-5 catalyst is poor [68]. In their comprehensive study of the characteristics of the Pt/ZSM-5 material, Kharas et al. showed that the catalyst undergoes severe deactivation when aged for brief periods of time (10–20 h) at 700°C [68]. At 800°C the deactivation is even more pronounced. Their TEM analysis of the aged, deactivated catalyst indicated that the Pt particles had been covered by siliceous films, derived from the silica within the zeolite, and that the deactivation was due to loss of accessible Pt surface area. It should be noted that there is evidence that the lean NO_x reaction over Pt-based catalysts occurs via NO decomposition followed by re-reduction of the active Pt sites by the HC species [69].

5. Conclusions and possible future directions

It is clear from the contents of this review article that the mechanism of the lean NO_x reaction over Cu/ZSM-5 has still not been unambiguously determined. It is perhaps fair to say that the bulk of the evidence currently points towards the involvement of NO_2 as a reaction intermediate, which possibly reacts with hydrocarbon species activated on the acidic sites of the zeolite. However, there is also a substantial body of evidence which points towards the mechanism pivoting around the coupling of two NO species adsorbed on Cu sites, with the hydrocarbon being responsible for maintaining as many as possible of the Cu sites in the (NO decomposition-active) Cu^+ state. One of the major objectives for the advocates of this mechanistic hypothesis is to explain the very different responses of the direct NO decomposition and lean NO_x reactions to the presence of SO_2, as described in Section 2.2.2. Alternatively, all of the important chemistry may occur over the Cu sites, as proposed within the NO decomposition-based mechanism, but the reaction may proceed via the formation of an organonitrogen intermediate.

It is, in fact, possible that the true mechanism incorporates elements of a number of hypotheses. For example, perhaps the activated hydrocarbon species on the zeolite keeps adjacent Cu sites clean to allow the relevant NO_x chemistry to proceed over these sites. It is also possible that the N–N bond is formed via the reaction between an NO and an NO_2 species, or between two NO_2 species, adsorbed on the Cu sites, since inorganic chemistry teaches that both the dimerisation of NO_2 to N_2O_4 and the coupling of NO_2 with NO are more likely than the coupling of two NO molecules (see e.g., [70]). In this context, it is interesting to note that adsorbed NO_2 species have been observed during IR studies of the direct NO decomposition reaction over Cu/ZSM-5 [13,71], despite the fact that the prevailing conditions (high temperature, much lower oxygen concentration) are far less favourable for the formation of NO_2. Indeed, it is possible that the NO decomposition reaction itself proceeds via the intermediacy of NO_2 [13,71], which would bring together elements of the bifunctional hypothesis (particularly the importance of NO_2) with elements of the NO decomposition theory (particularly the need for Cu sites to bring about N–N bond formation).

In summary, there is still work to do in order to build up a *complete* understanding of the lean NO_x

reaction mechanism over Cu/ZSM-5. However, it is clear that substantial improvements in the thermal and hydrothermal durability stability are necessary before Cu/ZSM-5 can be used commercially within the autocatalyst application. The development of related catalysts with the required durability, and comparable or superior activity, is a major challenge for future research in this area.

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