Selective Catalytic Reduction of NO$_x$ with N-Free Reductants

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I. Introduction

Oxides of nitrogen, the ubiquitous byproducts of high-temperature combustion,[1] are unwanted pollutants in the atmosphere.[2] Their removal from the burnt gases is required in most advanced societies in stationary installations, power plants or factories, and in mobile sources—automotive vehicles. The main means for their removal is catalytic "unfixing" back to dinitrogen at temperatures <800 °C where the oxides of nitrogen are thermodynamically unstable yet kinetically extremely stable in the absence of suitable catalysts.[3,4] The catalytic decomposition to elements without a reductant was deemed for a long time much too slow to be of practical use,[5] so recourse is made to catalytic reduction. In vehicles the regulations demand an almost total removal of the products of incomplete combustion, CO and unburnt hydrocarbons. These molecules serve as the on-site reductants for the nitrogen oxides. When the composition of the exhaust flowing over the catalyst is maintained by modern electronic controls as close to stoichiometry as possible[6] all the noxious pollut-

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ants are removed. In stationary sources the combustion is carried out with a large excess of air so the reductant, introduced to the flue gases, has to be able to *selectively* reduce the oxides of nitrogen. The amount of reductant needed to reduce both the small concentrations of NO$_x$, a few hundred parts per million (ppm), and the large quantities of oxygen, several percent, is prohibitive hence the need for *selective catalytic reduction* (SCR) where, optimally, the reductant is oxidized by the oxides of nitrogen without being burned by the oxygen.

Notwithstanding the large thermodynamic driving force in the reduction of the nitrogen oxides, on most heterogeneous catalysts the common reductants are preferentially consumed by catalytic combustion with oxygen, if the latter is present in excess. This has to do with the demanding process of pairing the nitrogens into dinitrogen molecules. Only under certain conditions, usually at temperatures <400 °C and when the reductant is a molecule containing its own nitrogen atom, can the selective catalytic reduction be readily accomplished. Large-scale SCR installations have been constructed in Japan and Europe to clean power plant effluents from oxides of nitrogen using ammonia as a selective reductant.[4] Several proposals have been made to use other N-containing reductants, urea or cyanuric acid, etc., but owing to its availability and ease of use, NH$_3$ is used in practice.

The use of NH$_3$ in the SCR of NO$_x$ in stationary plants has drawbacks compared to the more common

reductants, CH_4, CO, H_2, C_3H_8, etc., if a selective catalyst could be found. Chief among the drawbacks are cost and "slip" of unreacted NH_3 which is environmentally objectionable. Historically, the need to treat industrial NO_x containing effluents arose 70 years ago in connection with nitric acid plant tail gases which were discarded as acrid, brown plumes. In the 1950s such visible insults to the environment were outlawed. In the search for selective processes various reductants including methane, refinery off-gas (a mixture of light hydrocarbons), kerosene vapors, and hydrogen were explored[7] over noble metal catalysts. While at low temperatures some selectivity for NO_x reduction vs O_2 consumption was observed, the use of NH_3 as the selective reductant was preferred. The catalysts of choice for low-temperature (<300 °C) SCR with NH_3 are noble metal catalysts and for medium temperature range (<425 °C) the vanadia/titania catalysts, but it was known for some time that, even when using an N-containing reductant, zeolitic catalysts are usable at somewhat higher temperatures.[8]

There is also an important incentive in automotive use for a catalyst capable of selectively reducing NO_x. The presently employed stoichiometric carburetion in internal combustion Otto (spark-ignited) engines, where the amount of air admitted to the engine is dosed exactly to convert the fuel to CO_2 and water, precludes the more thermodynamically efficient "lean-burn" (LB) engines which promise a 10% gain in fuel efficiency.[9] The LB internal combustion Otto engine, operating close to the misfire region, is inherently more efficient than the same engine operating at stoichiometry. This is due to (a) lower pumping losses, (b) a higher ratio of the specific heat of the burnt gas at constant pressure to the same property at constant volume, (c) reduced heat loss to the walls of the combustion chamber. The operating air/fuel ratio (A/F) of an LB engine is in the 21–23 range as opposed to 14.7 for stoichiometric operation. The operation is extended to the higher A/F by improved turbulence and spark advance. A stable catalyst for a "lean-burn" engine would allow the realization of this potential.[10]

The catalysts for SCR with hydrocarbons may find their first automotive use in vehicles powered by compression-ignited diesel engines. The high fuel efficiency of diesel engines derives, in large measure, from the very lean carburetion. One of the impediments to a wider adoption of diesel engines is the difficulty of simultaneously meeting both particulate and NO_x emissions standards. The explanation of this nexus is beyond the scope of this review but the SCR process using zeolitic catalysts is being explored as one possible solution.

In a recent contribution from Iwamoto's group,[11] there are listed more than 50 catalysts, reported in the course of 1991–1992, that promote selectively the reduction of nitric oxide in the presence of excess oxygen, by a variety of hydrocarbons. All this fever-ish activity has been spurred on by the renewed realization[12–14] that copper-exchanged zeolite ZSM-5 is active for this process. There exists a precedent of a 1981 patent issued to the Union Carbide Corp.[15] for a "process which involves intimately contacting

a gas stream containing NO_x, CO and hydrocarbons with a catalyst bed made of copper metal or copper ions and a high-silica zeolite". The patent was aimed at replacing the automotive three-way catalysts. The patent lists copper-exchanged ZSM-5, ZSM-8, ZSM-11, ZSM-12, and other zeolites with a $SiO_2/Al_2O_3 > 20$. Using dry inlet gases containing 7000 ppm NO, 1.4% CO, 4640 ppm C_3H_6 and 5% O_2 in He, high conversions of the NO (~90%) were attained at 350 °C and a space velocity of 13000 h^{-1}. This mixture corresponds roughly to a 2-fold stoichiometric excess of oxidant. At the time samples of these materials were also tested under more realistic conditions but were found to be lacking in durability.[16]

The Cu-ZSM-5 catalyst (vide infra) still remains the one most actively studied. The same catalyst is also active in the decomposition of nitric oxide into dioxygen and dinitrogen although this process is much slower than the selective reduction. The mechanism of the decomposition is conceptually simpler because it involves only one reactant, but even here different schemes have been advanced.[17–19] Numerous attempts to sketch out a possible reaction course for the selective reduction have been made for the SCR process on this catalyst, but a truly coherent description has proven to be elusive. When the behavior of the other catalysts is considered and the various deactivation phenomena are pondered the picture is even less clear. This review is an attempt to take stock as of the beginning of 1994. It is possible, but by no means certain, that the practical implementation will precede the understanding by a long time as is always the case with catalytic processes.

Since the references contain a wide assortment of catalysts, reductants, and conditions, the review is not all inclusive. The empirical data are considered first, followed by results of examination by physical methods, and finally, mechanisms. The review contains also a short chapter on the decomposition of NO to elements on a Cu-ZSM-5 zeolite catalyst. There are some commonalities to the two processes but also sharp differences. In the decomposition the Cu-ZSM-5 appears, so far, to be unique, while the multitude of catalysts pertains to the SCR.

II. The Cu-ZSM-5 Catalyst

For our purposes it is sufficient to define the general zeolite material, i.e. our primary catalyst support, as a crystalline alumosilicate having a unit cell $M_{(x/n)}[(AlO_2)_x(SiO_2)_y] \cdot H_2O$, where M is a metal cation with a positive charge that can be exchanged into the zeolite. This is a narrow definition and the reader is referred to the following sources of ever-increasing detail.[20–22] The spatial structures are built up of oxygen ion tetrahedra with either Si^{4+} or Al^{3+} at the center. Charge neutrality demands an additional positive charge for every Al^{3+} in the lattice. This charge is provided by protons or other positive ions either metallic or nonmetallic.

The simple alumosilicate composition may crystallize in an almost infinite variety of three-dimensional structures having channels and passages of molecular dimensions (or larger).[22] The zeolites are char-
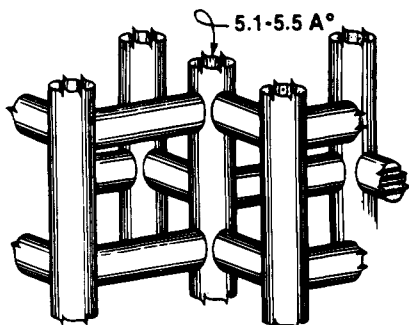
Figure 1. Channel system in ZSM-5.[26]

acterized in commerce by their Si/Al atomic ratio (y/x in the above formula) or, more commonly, by the SiO_2/Al_2O_3 molar ratio. This ratio determines the amount of protons, ammonium ions, or metal ions that can be exchanged into the zeolite. As this ratio increases, the loading of exchanged ions decreases.

The ZSM series of zeolites derives its name from the laboratory where they were discovered (Zeolite Socony Mobil). There are 20 or so well-characterized members of this family[23] of which the most used and studied is ZSM-5. The ZSM-5 and ZSM-11 zeolites are end members of the Pentasil series. In the overall notation of zeolites[22] ZSM-5 is classified under the MFI-type code. All these names (ZSM, Pentasil, MFI) are used interchangeably.

The ZSM-5 structure is well understood.[24,25] The three-dimensional depiction of ZSM-5 is shown on Figure 1.[26] The oxygen tetrahedra in ZSM-5 are linked into five-membered rings. In turn, these link together into two kinds of intersecting channels: a straight one with elliptical mouths (5.1 × 5.7 Å) and a "zigzag" channel with nearly circular openings of 5.5 Å. The openings are ten-membered. The channel intersections create cavities of ~9 Å in diameter. The catalytically active, strong acid sites are thought to be located in these cavities.[27]

Straight chain paraffins and olefins have access to the channels; branched hydrocarbons with a cross section up to that of neopentane can also move into the channels. This structure is the foremost representative of the medium-pore zeolites devoid of large size supercages accessed by smaller size windows. The structure is stable over a very wide range of SiO_2/Al_2O_3 ratios (10 → 60000). In the H-form of this zeolite the protons are Bronsted acid sites of high and uniform strength. The concentration of the protons is directly related to the concentration of the tetrahedral Al ions in the framework.[28]

The external surface also contains acid sites as it is often enriched in Al as compared to the bulk of the crystal. To a large degree the catalytic properties of zeolites are associated with the acidity of their surfaces. While noncrystalline alumosilicates also exhibit surface acidity, the protons in zeolites are located at spatially defined sites. The hydrophilic character of the material decreases and the thermal (and hydrothermal) stability increases with the increase of the SiO_2/Al_2O_3 ratio. ZSM-5 is used mostly in the high-silica varieties and the ensuing relatively low hydrophilicity is of considerable importance in the SCR applications.

The as-synthesized, commercial ZSM-5 is in the Na form. Exchange of multivalent transition metal ions into the ZSM-5 can be accomplished directly from this precursor using nitrate or acetate solutions under well-specified conditions. To avoid the effects of residual Na, the Na form is exchanged first for the NH$_4$ form which yields HZSM-5 upon heating. This form is then used for the exchange of the multivalent transition metal ions. When exchanged with copper solutions, the cupric ions occupy well-defined sites within the structure of the ZSM-5 zeolite. By examining the ESR spectra of freshly exchanged, hydrated Cu-ZSM-5, Anderson and Kevan[29] located the Cu^{2+} ion at the channel intersection, i.e. the big cavity. Dehydration at 400 °C produces a copper species which is recessed and inaccessible. The adsorption of other polar molecules draws back the cupric ions into the main channels.

If the cupric ion is the one to be exchanged, say from a nitrate solution, and we denote generically the zeolitic "anion" as Z, the exchange reaction with the protonic form can be written formally as

$$Cu^{2+}(NO_3^-)_2 + 2H^+Z^- \leftrightarrow 2HNO_3 + Cu^{2+}Z^-_2 \quad (1)$$
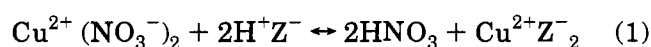
The neutralization of two immobile monovalent "anions" by a single divalent cation is only possible if the former are sufficiently close, as might be the case in zeolites with a low SiO_2/Al_2O_3 ratio. In high-Si zeolites this is impossible and the second positive charge of the cupric ion has to be satisfied by a negative charge extraneous to that associated with the tetrahedrally coordinated Al^{3+}. Such negative charges can be extralattice oxygens or hydroxyl ions.[30,31] This simple consideration is not entirely trivial because the literature has adopted the stoichiometry of reaction 1, i.e. 1 Cu^{2+} per 2 H$^+$, as the formal "limit". Every ion inserted beyond this limit is, erroneously, considered to be "overexchanged". In fact, most of the samples designated as "overexchanged" are simply highly exchanged. If the loading exceeds 200% of the *nominal* exchange the excess copper is certainly present as the oxide. If the ion is of higher valence than 2 and if it will exchange into a high-Si zeolite, it will replace only one monovalent "anionic" site, with the other charges being satisfied extraneously to the zeolitic lattice.

The most important, and often overlooked, consequence is the misleading counting of the ions being exchanged out of the sample. If, for instance, a high-Si H-ZSM-5 is "100%" exchanged with Cu^{2+} ions, it should, according to this accounting, have lost all its Bronsted acid sites. In actuality, in high-Si$_2$/Al$_2O_3$ zeolites, the number of remaining acid sites will be still commensurate with that of the cupric ions.

III. Catalytic Decomposition of NO to Elements

The catalytic decomposition of nitric oxide to elements is a rare example of a chemical reaction which is strongly favored thermodynamically at temperatures below 1000 K[32] but which proceeds very slowly on the myriad of catalysts explored over the last century.[33] Therefore, the finding of Iwamoto and co-workers[34,35] that it does take place at an appreciable

rate over Cu-exchanged zeolites, in particular over Cu-ZSM-5, caused considerable scientific and industrial interest. Recently, Iwamoto and Hamada[17] have again summarized their work. While the reaction is faster than on previously studied heterogeneous catalysts it is conceded that the "new" decomposition catalysts do not have sufficient activity for practical implementation, notwithstanding that they begin to decompose nitric oxide at temperatures below those of the "old", conventional decomposition catalysts. There is little indication as well that the needed improvement in activity by 1−2 orders of magnitude can be achieved, because the usual means of temperature increase is not feasible: with the increase of the temperature above 600 °C the rate of the reaction decreases. The study of the decomposition on Cu-ZSM-5 is nevertheless worthwhile because it may indicate ways how to devise more active catalysts.

These are the main features of catalytic NO decomposition on Cu-ZSM-5: the reaction is a true decomposition and under controlled conditions a good material balance is achieved.[36,37] The decomposition passes through a reversible maximum with rising temperature, at 500−600 °C. The reaction order in NO is 1.0−1.2[37] and it may change with NO concentration. Oxygen inhibits the reaction but the inhibition decreases with temperature.[37] Excess Cu loading in zeolite (i.e. more than one Cu ion inserted per 2 Na^+ ions, or protons) enhances the activity. The specific decomposition rate per exchanged copper ion decreases with the increase of the aluminum content of the zeolite structure. Sulfur compounds in the gas phase suppress the decomposition activity.

The mechanism proposed to account for these observations is a cyclical process:[38,39] a pair of cupric ions loses a doubly charged oxygen ion upon heating, which is considered the activation step and a pair of cuprous ions is formed due to the electrons the doubly charged oxygen ion left behind. The pair of cuprous ions adsorbs a pair of NO molecules. The adsorption is such that the cuprous ions reduce the nitric oxide molecules to produce an adsorbed pair of anions. The pair of anions decomposes into a molecule of dioxygen and a molecule of dinitrogen, restoring the pair of the cuprous adsorption sites. The cuprous ions are not poisoned by the oxygen, either formed by the decomposition or present originally in the gas stream, because they are deemed to be stable in the zeolite at the elevated temperatures of the process. Neither is the cuprous ion easily reduced to the metal.

The stable activity is also due, according to Iwamoto,[39] to the absence of copper particle growth within the ZSM-5 structure under the conditions of use. The supporting evidence is adduced from IR spectra of NO chemisorption on Cu-ZSM-5 at room temperature and EPR spectra. The IR spectrum[38,40] shows a large band assigned to NO^+ (nitrosonium) at 1906 cm^{-1}, and smaller bands, NO^- (nitrosyl) at 1813 and a doublet due to a negative pair of nitrosyls $(NO)^-_2$ at 1827 and 1734 cm^{-1}. The negatively charged bands are less stable and decrease with time at room temperature. The dominant band at 1906 cm^{-1} grows at their expense. The negatively charged species are said to be adsorbed on Cu^+ since their

formation required treatment at high temperatures and is blocked out by CO, known to adsorb preferentially on cuprous ion sites. Because the room temperature decay in the IR absorbance peaks, ascribed to negatively charged adsorbed nitrosyls, was fit to a second-order plot, it was concluded that this process (at room temperature) is the basis for the mechanism given above (at reaction temperature).[40]

Hall and co-workers have elaborated on this mechanisms in several publications[19,30,31,37] taking O_2 desorption from Cu-ZSM-5 as evidence of spontaneous reduction at reaction temperatures. They ascribe the vast difference in activity between Cu-ZSM-5 and Cu-Y zeolites to the differences in the desorption of oxygen. From XPS measurements Sepulveda-Escribano et al.,[41] deduced that the cuprous ions are stabilized to a higher extent in Cu-ZSM-5 than in Cu-Y, after high-temperature calcination and therefore the former is more active. The difference between the activity of catalysts based on the MFI type of zeolites and the other zeolites is also apparent in SCR (vide infra).

A mechanism which does not require a surface redox process was also proposed.[18] Since the decomposition of nitric oxide requires pairing of the molecules, it is plausible that the adsorbed geminal dinitrosyls are important. But the evidence presented is not compelling that they adsorb on the cuprous ions and are negatively charged upon chemisorption. Pairing of nitrogens by the interaction of two NO molecules, each one adsorbed on a different copper site does not seem probable because in high-silica zeolites the copper ions are spaced too far apart.

In studies of NO chemisorption on copper-on-alumina, it was established that nitric oxide chemisorbs overwhelmingly on cupric ions forming the surface $(NO)^+$ nitrosonium ion.[42] Moreover, IR studies of NO chemisorption on transition metal ions show that the assignment of the absorption peak of a negatively charged surface nitrosyl should be in the frequency range below 1700 cm^{-1}. The review of Kung and Kung[43] gives only three examples of such low absorption peak frequency in 70 recorded IR spectra of chemisorbed NO and only these are assigned to negatively charged species. Such assignments also agree with organometallic nitrosyls in solution, where IR peaks of NO^+ are shifted upward of NO in the gas and the IR peaks of NO^- very far downward.[44]

The reason for the low absorption peak frequency of negatively charged (anionic) surface nitrosyls is straightforward. The donated electron goes into the available antibonding orbital (π^*2p_x) of the NO molecule. This results in a weakened nitrogen to oxygen bond, i.e. a vibrator with a less stiff spring. The formation of this anion is (in most cases) a thermodynamically uphill process and the anionic surface species is unlikely to be stable at the catalyst operating temperatures. Whether negatively charged, adsorbed nitrosyls exist at all, even at room temperature, has been questioned.[44]

Conversely, the donating of the electron located in the antibonding orbital of the NO molecule is favored,

but requires an accepting orbital in the chemisorption site. Therefore, NO adsorbs prevalently on Cu^{2+} (d^9) ions and not on Cu$^+$ (d^{10}) ions. For which reason solutions of *cupric* ions are used to absorb nitric oxide present in gas streams.[45] Hence, it is more plausible that the antisymmetric and symmetric vibrations of the *gem*-dinitrosyl on Cu-ZSM-5 observed at 1827 and 1734 cm^{-1} are associated with neutral surface species chemisorbed coordinatively through their lone pairs. References 43 and 46 afford a summary of *gem*-dinitrosyls on several ionic adsorbents, including zeolites, showing that their IR absorption peaks all appear in the frequency range consistent with an assignment to a nonionized surface species. There are over 30 examples listed.

The nonredox mechanism[18] posits that the decomposition of nitric oxide does not require the oxyreduction of the surface which prevails when both oxidizing species and reducing species from the gas phase alternately donate and remove an oxygen ion from the surface. It assumes that cupric (Cu^{2+}) ions are the active sites. More precisely, only those cupric ions which adsorb the *gem*-dinitrosyls. The pair of nitrosyls adsorbed in a proximity of molecular dimensions on a single site rearranges itself so as to desorb as the thermodynamically favored O$_2$ and N$_2$ molecules.[47,48]

The reversible course of the NO decomposition on Cu-ZSM-5 going over a maximum with rising temperature is most likely associated with the temperature sensitive adsorption equilibrium:

$$Cu^{2+}{:}NO + NO_g \rightleftharpoons Cu^{2+} \ (\textit{gem}\text{-dinitrosyl}) \quad (2)$$
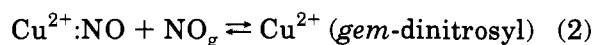
which shifts to the left at higher temperatures. As noted, both mono- and dinitrosyls, with IR absorption peaks in the same range, coexist.

The difference in these two views of NO decomposition over Cu-ZSM-5 is simply put as follows: if the isolated copper ion in the high Si/Al structure can be spontaneously reduced by heating in a highly oxidizing atmosphere (NO, O$_2$, NO$_2$) to the Cu$^+$ state, the redox mechanism is plausible and if not, the pairing of the nitrogens is not dependent on the change in the oxidation state of the copper. The arguments in favor of the redox mechanism[19] essentially make the same point.

Recently Valyon and Hall[30] revised their view to make it consonant with the absence of a redox process in the decomposition. With the increased realization of the importance of NO$_2$ in the surface processes leading to dinitrogen they introduced a surface NO oxidation step by an oxygen atom held at the active copper site. The NO$_2$ formed on this site interacts with another gas NO molecule. The surface complex, consisting now of 3 O's and 2 N's, releases N$_2$ and O$_2$ restoring the original oxygen at the copper site. Moreover, the algebraic treatment of these steps yields the empirical rate expression determined by Li and Hall[36]

$$r = kP_{NO}/(1 + KP_{O_2}^{1/2}) \quad (3)$$

In the last few years the question of the spontaneous thermal reduction of the cupric ions in Cu-ZSM-5 has

been explored by several techniques, again with conflicting results. We postpone discussion of this to section V because it has implications for the mechanism of the SCR as well.

Recently, other aspects of catalytic decomposition formerly considered as settled have been questioned. Moretti[49] analyzed published rate data showing that the specific rate per Cu ion, i.e. the turnover number, increases with the number of aluminums per unit cell of the zeolite, exactly opposite to the observations of Iwamoto. Since the density of exchangeable Cu ions is directly proportional to the Al^{3+} in the framework he suggested that the active sites are actually pairs of Cu ions rather than the isolated single ions proposed in the previous schemes. The findings of Campa et al.,[50] are directionally consonant with this view. They found that the last portion of the exchanged Cu ions, 80–100%, has a specific activity in decomposition higher by orders of magnitude than the ions at low exchange level. They also found the "overexchanged" portion of the Cu ions to be completely inactive.

Water vapor suppresses, reversibly, the NO decomposition activity of Cu-ZSM-5[39] and its mere presence in concentrations typical of combustion effluents negates practical application. The presence of SO$_2$ completely poisons the activity requiring regeneration at higher temperatures.[39]

IV. SCR: Experimental Observations

A. Oxidic and Metallic Catalysts

Although the main development direction in the SCR of NO$_x$ with N-free reductants is related to zeolitic catalysts many investigations, particularly in Japan, have been devoted to nonzeolitic catalysts.[51–57] For the most part these were screening runs where a few hundred ppm of NO and of a short hydrocarbon each were passed over the catalyst at a low space velocity, in the presence of a large excess O$_2$. Some of these catalysts showed the desired selectivity at temperatures >773 K. The more active catalysts were those on *acidic* supports, alumina, silica–alumina, zirconia, etc., containing small amounts of transition metals such as Cu or Co. There are no data available for realistic space velocities in the presence of water.

The SCR results for nonzeolitic, supported noble metal catalysts, Pt, Ir, Ru, Pt/Ir/Pd[58–62] pertain to the low-temperature regime (<300 °C). The reductant is a mixture of CO and H$_2$ or a hydrocarbon. Considerable levels of SCR were attained[58] at very high space velocities of 400000 h^{-1} but such low temperature behavior, in particular in the presence of H$_2$ as a reductant, is not new.[3]

B. Zeolitic Catalysts

1. Cu-ZSM-5

As noted, this catalyst has been the one most intensively investigated.[12–14,63–78] Various experimental conditions and different catalyst specimens were employed by different investigators. Neverthe-

less the common observations can be broadly generalized. The main experimental features of SCR over Cu-ZSM-5 are as follows: The reaction rate goes through a maximum with temperature in the 450–550 °C range, the temperature of highest nitric oxide conversion being dependent on the nature of the catalyst, the type and concentration of the hydrocarbon, time on stream, and space velocity. In certain instances the conversion reaches a plateau with rising temperature. Conversions of practical interest can be achieved in steam-containing streams with *non-deactivated* catalysts. Carbon monoxide is one of the reaction products. The activity is quite resistant to sulfur, present as SO_2 in the gas stream. The selective NO reduction is activated by oxygen or, alternatively, by an oxygen-containing moiety in the reductant molecule. Hydrogen and CO are inactive in the selective NO reduction as are small paraffins (C1,C2). Olefins and oxygenated hydrocarbons are more active than paraffins (in most cases). Fast oxidation of the hydrocarbon reductant suppresses the desired selectivity. The deactivation can be divided into reversible and irreversible phenomena: both the instantaneous suppressing effects of the addition of H_2O to the stream and the accumulation of deposits are reversible. The catalyst deactivates irreversibly on stream if a certain temperature is exceeded. The irreversible deactivation is accelerated by the increase of water vapor content of the gas stream and higher operating temperatures.

It is worth noting that the reaction course with rising temperature is similar to the behavior of Cu-ZSM-5 in NO decomposition but in other respects SCR and the decomposition reaction differ sharply. The acidity of the ZSM-5 makes itself apparent by the formation of copious, and visible, amounts of carbonaceous deposits, in particular when olefinic reductants are used.

2. Other Zeolitic Catalysts

Several ions exchanged into ZSM-5, besides copper, have been studied for their SCR activity. To begin with, H-ZSM-5 (and H-mordenite or H-ferrierite) show activity at low gas throughputs under dry conditions. This was observed using propylene or propane over H-ZSM-5,[79,80] over a H-ZSM-type silicate[81,82] where the Al^{3+} has been replaced by Fe^{3+}. This silicate was also active when using a prototypical diesel fuel, cetane, as the reductant.[83] Even CH_4 is an active reductant under these conditions.[84] However, in the only reported instance of actual testing with actual lean-burn automotive exhaust H-ZSM-5 was completely inactive.[85]

The isomorphous substitution of trivalent ions such as Fe^{3+} or Ga^{3+} for the Al^{3+} in ZSM-5 is well known and the substituted ZSM-5 retains acidity and the ability for the activation of hydrocarbons.[86,87] Hence, the process may not require an exchanged transition metal ion, which is of considerable mechanistic importance. This is confirmed by the fact that the exchange (and/or impregnation) of the valence invariant Ga^{3+} or In^{3+} ion into ZSM or ferrierite gives very active and selective catalysts when using either reactive C_2H_4 or C_3H_6 as reductants[88–90] or the

relatively inert CH_4.[91] There is a dearth of information on the effect of H_2O but, apparently, it virtually suppresses the SCR. Ga-ZSM-5 has attracted attention because it is commercially used in the transformation of lower alkanes to aromatics[92] and has been thoroughly characterized.[93,94] The exchange of Ga^{3+} into high-silica ZSM-5 is not simple and the ionic species being exchanged are $Ga(OH)_2^+$ or GaO^+ ions i.e. one proton for one Ga^{3+} ion. The aromatization of hydrocarbons is not very sensitive, similarly to the SCR, to the exact locus of the Ga in the zeolite.

Exchanging Ce and Pr ions, both multivalent rare earths, into ZSM-5 gives catalyst more active and selective, under dry conditions, than the corresponding Cu catalysts.[95,96]

It is not necessary to enumerate all the Edisonian attempts to replace copper in ZSM-5 by other transition metal ions. But two examples are worth noting to stress the widely different behavior. When the active center is a noble metal the combustion of the reductant is fast, the SCR activity is shifted to low temperatures and methane becomes an active reductant.[97,98] The replacement of the Cu^{2+} by Co^{2+} in ZSM-5 also activates CH_4 as a reductant[99,100] but the process is, again, very susceptible to deactivation by water.[101] As is often the case in a rapidly evolving field, attempts at the rationalization of the empirical observations have spawned several mechanistic suggestions.

C. Reductants

Several schemes envisage, in vehicular applications, external dosing of the reductant upstream of the SCR catalyst to assure the required extent of NO_x removal. In stationary sources applications the cost and availability of the reductant is important.

The reductants studied in SCR investigations range all the way from CH_4 to molecules present in diesel fuel, such as cetane, and diesel fuel itself. In between these extremes, the studies encompassed paraffins and olefins of varying sizes with C_3 and C_4 hydrocarbons being used for the most part. Oxygenated organic water-soluble molecules were also studied.[64]

Witzel *et al.*[102] have carried out comparative reactivity studies using several reductants on the same samples of Cu- or Co-exchanged ZSM-5. A central objective of their work was related to size exclusion, since only molecules below a cross section of ~5.5 Å can freely diffuse into the intersectional cavities of the ZSM-5 framework where both the protonic and metal-exchanged sites are believed to be situated. On ZSM-5 exchanged with transition metals they have found similar partitioning of the reductant, i.e. selectivity between the NO and oxygen, independent of the hydrocarbon size. This holds even for those hydrocarbons that should have been excluded from the internal channels. It means that the activation and fragmentation of the larger reductant molecules take place on the external surfaces of the crystallites. Neononane, $C(C_2H_5)_4$, is less reactive. A similar observation was also made for *m*-xylene.[103]

D. Practical Considerations

1. Throughputs

The effluent streams from combustion are very voluminous and dilute in NO$_x$. To keep the volume of the catalyst used for treatment within affordable limits the rates at which the treated gases are passed over the catalyst must be high. In particular, this is so in automotive use where space is at a premium. Under normal operating conditions, 3000–100000 volumes of gas, corresponding to ambient temperature and pressure conditions, are contacted with 1 volume of catalyst per hour. This is denoted in chemical engineering practice as a space velocity (SV) of $(3-10) \times 10^4$. Since only 10% of the volume of a typical monolithic catalyst are occupied by the catalytically active "washcoat", the rest being the monolith itself and the void channels, the SV when compared to the laboratory tests using powdered samples is even higher by 1 order of magnitude. The throughputs in the treatment of stationary effluents are ~10-fold lower[4] but still far larger than those used in most laboratory investigations. When evaluating the utilitarian claims based on laboratory results these differences must be considered.

2. Selectivity

It is important to define the selectivity of the SCR process since there are several selectivities involved. There is the selectivity in the N-containing products between N$_2$ (complete reduction) and N$_2$O (incomplete reduction) and selectivity in the C-containing products between CO$_2$ (complete oxidation) and CO (incomplete oxidation). These are of some importance but not as important as the partitioning of the hydrocarbon reductant between the useful reaction, SCR, and the combustion by the excess oxygen. In any case, data on CO and N$_2$O formation are very scant. The definition of selectivity in the partitioning of the reductant hydrocarbon between the useful reduction of the NO and the parasitic combustion by oxygen is the ratio of the useful to the total HC consumption. This selectivity determines the cost of the reductant if added to the system or whether there is enough of it to accomplish the SCR if it is present in the stream as is the case in engine exhaust.

The balanced complete reduction of NO by HC's (ignoring some CO formation) is

$$a\text{NO} + \text{C}_m\text{H}_n = m\text{CO}_2 + (a/2)\text{N}_2 + (n/2)\text{H}_2\text{O} \quad (4)$$
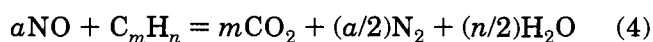
where $a = 2m + n/2$. The coefficient a (at 100% selectivity) is 4 for CH$_4$, 5 for C$_2$H$_2$, 9 for C$_3$H$_6$, 10 for C$_3$H$_8$, and so on. When one molecule of NO is reduced in the process for one molecule propane used, the selectivity is only 10%. Here it has to be pointed out that the formal stoichiometry of the above equation is not the one that prevails in practice. If every NO molecule has to be preoxidized to NO$_2$ in order to be subsequently reduced to N$_2$, as it presently appears, only 2 NO$_2$ molecules can be reduced by a methane molecule and only 5 by propane, etc.

The selectivities vary widely with conditions and catalyst type. Often they are not reported directly and in many cases cannot even be calculated from the published information. Often conversion of O$_2$ is not given and has to be estimated by difference from the total conversion of the hydrocarbon which is also rarely reported. Usually experimental reactant ratios are chosen so that the amount of the reductant stoichiometrically exceeds that of the NO several-fold; in turn, the amount of oxygen exceeds that needed to completely oxidize the hydrocarbon by up to an order of magnitude or more. The ratio of the fractional conversions of NO and O$_2$ is an incorrect measure of selectivity because the very large excess of oxygen tends to obscure the "partitioning" results by making the fractional consumption of the oxygen small and the NO selectivity seemingly high. In most instances, with rising oxygen content the ratio of NO and O$_2$ conversions rises but the partitioning of the reductant shifts in favor of the oxygen, i.e. more of the reductant is being burned up. A catalyst with low selectivity will be of little use for stationary sources because the large excess of needed reductant will make it noncompetitive with current installations which use NH$_3$. In mobile sources (i.e. lean-burn engine exhaust) the minimum acceptable selectivity will be determined by the engine-out concentrations of NO and HC's.

The selectivity reported for a Cu-ZSM-5-type catalyst operating under lean-burn conditions in an actual engine exhaust where the gas stream contained 180 ppm NO, 6300 ppm HC (as C$_1$), and ~7.5% oxygen[14] is very low. At a conversion of 16% for NO and 43.5% for the HC, at a temperature of 783 K, it is only 0.0035. In a different patent,[63] issued to the same company, the selectivity is higher, 0.16, even though the catalyst is Cu-Y zeolite. But in the latter instance the data are from a simulated exhaust with $T = 673$ K, NO = 1000 ppm, and the HC = 600 ppm as C$_3$. A selectivity of 0.18 may be obtained for a Cu-ZSM-5 sample when the temperature is lowered by 150 degrees to 523 K and the propene is cut ~4-fold.[95] The relatively low space velocity of ~9000 affords a conversion of 20% of the 1000 ppm NO at the inlet. In the early patent[15] with a Cu-ZSM-5 catalyst the inlet gas contained: He, 92.81%; O$_2$, 4.64%; CO, 1.39%; NO, 0.696%; and C$_3$H$_6$, 0.464%. At 623 K and 13000 h^{-1} space velocity all of the CO and propene were oxidized. Concurrently, 56% of the NO was reduced to nitrogen with a selectivity of 0.095. The stoichiometric ratio of the oxidants to the reductants was only slightly higher than 2. On other supports copper is not as selective as in Cu-ZSM-5.[64]

The acidic supports, H-ZSM-5, alumina or silica–alumina,[79] although not very active, have selectivities between 0.13 and 0.25. As the HC/NO ratio increases the NO conversion increases but the oxidation of the HC by the oxygen excess rises even faster. Among other cations exchanged into ZSM-5, Ce-ZSM-5 has an activity and selectivity which slightly surpasses that of Cu-ZSM-5,[95] 0.28. The reaction was run at 623 K, 9000 h^{-1}, and 2.0% O$_2$, 1000 ppm NO, 166 ppm C$_3$H$_6$ in He. One notes that the excess of propene over NO was lower than in most other examples.

Very high selectivities were reported on the Ga-exchanged zeolites using CH$_4$,[91] C$_2$H$_4$,[84] or C$_3$H$_6$,[88]

under dry conditions. On the basis of the reduction of NO_2 the selectivities were as high as 0.9. The most obvious reason is that while valence-invariant Ga ions activate the hydrocarbons they are not very active in catalyzing combustion by oxygen.

3. Durability

As is the case in most heterogeneous catalytic processes, the SCR process is susceptible to chemical, thermal, and combined deactivation. To begin with there is the reversible mode of deactivation with rising temperature. In the decomposition reaction this was ascribed[18] to an adsorption equilibrium between the gem-dinitrosyl and a single nitrosyl on the isolated square-planar Cu^{2+} sites with the equilibrium shifting to the single configuration at higher temperatures (eq 3). In SCR there may be other reasons as well (vide infra).

Steam is unavoidable in combustion gases. Different SCR catalysts respond differently in their initial activity to the presence of water vapor in the gas stream. While the fresh activity of Cu-ZSM-5 the $NO-O_2$-propene system is only moderately affected by ~10% steam in the gas this amount of steam in the $NO-O_2$-methane system over Co-ZSM-5 wipes out much of the initial activity.[101] The suppression of fresh activity by a short exposure to steam is, in most cases, reversible. SO_2 present in the gas stream at the level of $10-100$ ppm also suppresses the fresh activity of several catalysts but Cu-ZSM-5 is relatively resistant.[104] This deactivation is also reversible on certain catalysts.

The Cu-zeolite catalysts deactivate irreversibly on stream if a certain temperature is exceeded.[105,106] The irreversible deactivation is accelerated by the increase of water vapor content of the gas stream and shifts to lower temperatures or shorter times on stream. Several deactivation modes have been suggested: at the high end of the temperature range (>650 °C) structural collapse of the zeolite and out-migration of the active component followed by its agglomeration; at lower temperatures (~500 °C) dealumination, removal of the tetrahedrally coordinated Al^{3+} ions from the zeolite lattice,[107] has been suspected. It is straightforward to distinguish between collapse of the structure and dealumination by the use of X-ray diffraction to follow the crystallinity and of magic-angle spinning nuclear magnetic resonance to follow the characteristic signature of the tetrahedral aluminum.[108,109] Dealumination is synonymous with the loss of the isolated Cu ions because the latter exchange for the protons which neutralize the excess negative charge associated with Al^{3+}. These exchanged transition metal ions will tend to out-migrate to the exterior of the zeolitic crystallites forming an agglomerated copper oxide. In Cu-ZSM-5 a part of the activity is irreversibly destroyed by dealumination while another part is quite resistant.[108] When the reductant is a reactive olefin the formation of carbonaceous deposits can be very rapid, in particular under dry conditions, so as to impede the access of the gaseous reactants to the surface.[69] Inadvertent exposure to strongly reducing conditions, as might occur in automotive use, will induce the reduction and irreversible migration of the exchanged metal ions out of the framework, in particular of Cu.[68]
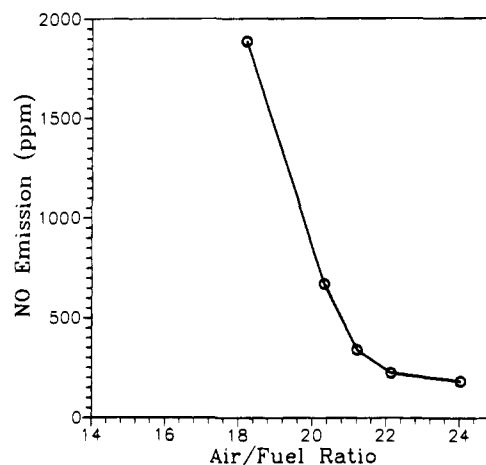

Figure 2. Effect of air/fuel ratio on engine-out hydrocarbon emissions. Operating conditions: 1500 rpm, indicator mean effective pressure 3.75 bar, optimum (MBT) spark timing, no exhaust gas recirculation, $T_{coolant}$ 88.2 °C.

Notwithstanding the paramount importance to application, the understanding of deactivation is rudimentary at the present time, at least in the open literature. One must make the catalyst operative in large excess of steam for very long service periods. The aim, common to all heterogeneous catalysts, is to stabilize the catalytically active centers without impairing the activity. Introduction of certain ions into the structure of the ZSM-5 can be used to inhibit dealumination by steam[110,111] but such efforts are, in the main, proprietary.

The equally important reversible deactivation by steam may be related to the effect of the polar water molecules on certain acidic centers in the catalyst and to the intermediacy of nitrogen dioxide (NO_2) (vide infra).

4. System Issues

With the rise in the air/fuel ratio in the automotive engine intake from the stoichiometric value to the region of LB operation, the exhaust concentration of NO steadily decreases (Figure 2). At LB operation conditions only a modest conversion suffices to bring the vehicle into compliance with the recently legislated stringent standards. The behavior of the HC emissions, the required reductant, is more complex in this A/F range. Lean of stoichiometric A/F the HC content of the engine exhaust decreases to a range of $1000-2000$ ppm (expressed as C_1) but then rapidly rises when the LB operation approaches the misfire limits (Figure 3).

The above gives rise to what may be best described as the nitric oxide removal "window" of a catalyst for LB operation. The rich side bound of this window will be determined by the desirable gain in engine efficiency and by the rising exhaust NO content; the lean side bound will be dictated by the misfire limit of a particular engine and the desired level of HC which is needed for the attainment of a certain predetermined level of NO conversion. It is expected that an oxidation catalyst designed to scavenge the excess HC and CO will be placed downstream of the LB catalyst. An LB catalyst "window" is shown, schematically, on Figure 4.[112] It can be assumed that this window will be wider on the A/F scale than the
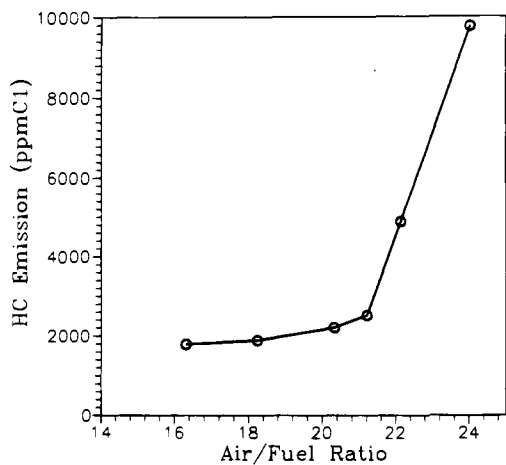
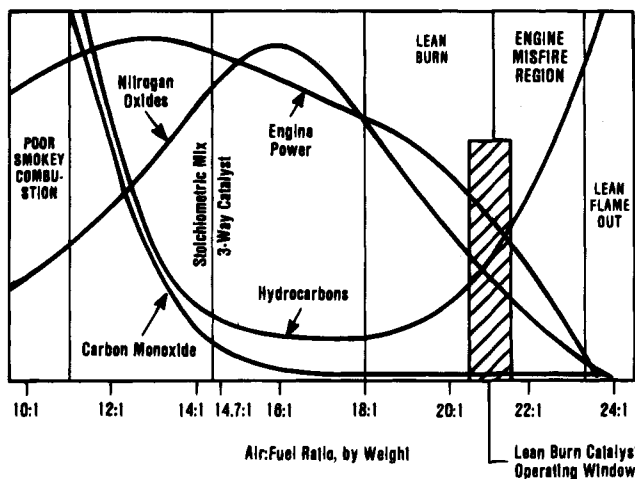**Figure 3.** Effect of air/fuel ratio on engine-out nitric oxide emissions. Conditions as in Figure 1.

Figure 4. Changes in emissions and engine power of internal combustion spark-ignited engines, showing three-way and lean-burn operating "windows", with air/fuel ratio. (Adapted from ref 112).

present TWC window. Its position on the same scale will vary somewhat for different engines. The control system will probably avail itself of lean oxygen sensors and misfire sensors. Apart from the required activity the most important issue will be the long-term durability of the catalyst itself. One has to be aware that the whole system may be quite complex. Lean combustion cannot be maintained during power enrichment and an active oxidation catalyst is a must for cold starts. The copper-exchanged zeolitic catalyst itself may be harmed by the reducing conditions. Hence, a parallel three-way catalyst may be required. This, in turn, will require a valving system. The use of the selective reduction of NO by hydrocarbons in diesel engine powered vehicles will, most likely, require external injection of the reductant in considerable excess, because the natural HC emissions of diesels are low.

V. Characterization of the Catalysts

Several surface characterization methods have been applied to zeolitic SCR catalysts and in particular to Cu-ZSM-5. Among these are Fourier-transform infrared (FTIR) spectroscopy of the adsorbed species,[40,113-117] electron-spin resonance (ESR)

spectroscopy of exchanged ions (in particular Cu^{2+}) and of carbonaceous deposits,[29,39,85,115,118-127] magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) to probe dealumination,[108,109] X-ray photoelectron spectroscopy (XPS),[41,128-130] X-ray absorption near-edge structure (XANES),[131,132] temperature-programmed desorption (TPD) of adsorbed species,[133,134] photoluminescence,[135] and other methods.

It must be borne in mind that for the most part surface studies are carried out at room temperature or *in vacuo*, depending on the method. This is done either separately from the catalytic studies or on specimens taken out from the catalytic reactor. Often the characterization is done at very low temperatures or *in vacuo*. Extrapolation of such results to a detailed mechanism requires the augmentation of the observations by conjecture. The relation of adsorbed species, as identified by FTIR for example, to the active surface sites is often tenuous, because there is seldom sufficient information to distinguish between "spectator" and reactive species. Even when the observation is carried out *in situ*[124-127,131,132] it usually registers only a part of the relevant information, the state of the copper ions by ESR, for example, but no information about the equally important acidic sites. For this reason only the more significant results are discussed below.

The main objective of the characterization of Cu-ZSM-5 by surface studies was to determine the coordination and oxidation state of the copper ions and their interaction with the gaseous reactants.

The notion of spontaneous thermal reduction of the cupric ions can be traced, conceptually, to the early ESR work on Cu-mordenite[136] where a reduction of the cupric ions by water at 300 °C was reported. The interconversion between the oxidation states of copper ions *in vacuo* was also reported.[137] Schoonheydt[138] affirms that H-mordenite is more stable than Cu^{2+}-mordenite and, in parallel to the electrochemical series, copper is the most easily reducible among the transition metal ions exchanged into zeolites. Iwamoto et al.[39] using a ZSM-5 with a SiO$_2$/Al$_2$O$_3$ ratio of 23 "overexchanged" to 116% has observed that after vacuum treatment at high temperature the ESR Cu^{2+} signal has decreased and the sample adsorbed CO which commonly adsorbs only on cuprous ions. This was interpreted as a spontaneous thermal reduction of the cupric ions even under strongly oxidizing conditions of the NO decomposition reaction and served as the basis for the redox mechanism of the latter (*vide supra*). Other workers[30,133] have taken the desorption of oxygen during high-temperature treatment as evidence for the spontaneous thermal reduction. The strongest evidence for the spontaneous thermal reduction was provided by *in situ* XANES study[131] of a Cu-ZSM-5 sample, "overexchanged" to 164%, at temperatures up to 600 °C. It was determined that at 500 °C, in a stream of 1% NO in N$_2$, the fraction of cupric ions is about 25%.

The evidence contradicting the spontaneous reduction is mainly related to Cu-ZSM-5 samples where care was taken to assure that the ions are *isolated*. This was deemed necessary for the unambiguous

interpretation of the ESR spectra which become very complex when there is formation of ion clusters and extra lattice aggregates. The extensive characterization work was done by ESR.[118,119] When a ZSM-5 zeolite of the H or Na form with a Si/Al ratio of 36 is exchanged by cupric ions to the extent of 20%, the product, dehydroxylated at 500 °C, contains two differently coordinated isolated Cu^{2+} ions and virtually no clustered cupric ions. Both kinds of Cu^{2+} ions are coordinatively unsaturated: one in a square-pyramidal (S-PY) and the other in a square-planar (S-PL) configuration. Both S-PL and S-PY cupric ions are in the main channels and accessible.[123] Takeshima[14] located the 4-coordinated S-PL sites in the large cavities and the 5-coordinated S-PY sites in the five-membered rings of the ZSM-5 structure. The isolated cupric ions in ZSM-5 are resistant to reduction and the desorption of the oxygen upon heating from isolated cupric ions in Cu-ZSM-5 has been shown not to be associated with their reduction.[118] These ions are coordinatively unsaturated and therefore adsorb at room temperature even nonpolar molecules such as xenon and hexane.[123] This tendency to adsorb virtually any gaseous species also explains the observation that evacuated CuH-ZSM-5 adsorbs CO. Furthermore, owing to their structure the isolated Cu^{2+} ions are also resistant to reduction by CO below 400 °C but easily reduced by H_2. Reduction by CO requires the demanding abstraction of an O^{2-} anion from the zeolite lattice, while upon reduction of the cupric ion by hydrogen (and also by hydrocarbons) protons can easily substitute the positive charge to maintain neutrality. As noted, in high-silica zeolites the distance between Al ions is large, therefore it is unlikely that one Cu^{2+} cation compensates directly two lattice charges and one of the charges is compensated by the cupric ion is an "out-of-lattice" OH^-. If the Cu-ZSM-5 was precalcined, to remove traces of organic residue, no reduction of the cupric ions upon heating in vacuo to 450 °C was observed.[119]

Recently, these conclusions were directly reconfirmed by direct *in situ* ESR studies of the isolated Cu^{2+} ions at temperatures up to 500 °C, in a stream of gas with a varying composition.[124–127] After ascertaining that the ESR signal is associated with all the cupric ions and using internal markers to account for the signal changes due to the rise in temperature it was established that there is no spontaneous reduction of the cupric ions.[124] The formation of adsorption complexes with NO changes the coordination of the cupric ions and NO_2 forms strong adsorption complexes at ambient conditions.[125] Methane reduces the cupric ions at 500 °C but not when excess oxygen is present.[126] Carbon monoxide forms activated adsorption complexes with the cupric ions, which is not the case on other adsorbents, below 300 °C without reduction.[126] Propene easily reduces the Cu^{2+} ions at ambient temperature but in excess oxidant, as is the case in SCR, virtually all the ions are in the cupric state; ethanol is a much less active reductant of the copper.[127] The main conclusion is that not only is there an absence of spontaneous thermal reduction in the CuH-ZSM-5 with well isolated copper ions but even in the presence of strong

reductants at high temperature and in excess oxygen these ions are not reduced. Giamello *et al.*[115] studied, by ESR and IR, CuH-ZSM-5 with isolated Cu^{2+} ions and deduced that cupric ions are reduced to cuprous *in vacuo* at high temperature like in "overexchanged" zeolites, but the cuprous ions are unstable in NO at ambient conditions. Complete bridging of the "gap" between these results and those pertaining to the heavily "overexchanged" specimens will require a detailed parallel study under similar conditions. Some measurements in this vein were made by ESR on a series of differently loaded Cu-ZSM-5 samples[85] which did not extend, however, all the way to low-loaded specimens assuring ion isolation. These data indicate that the spontaneous thermal reduction commences only when the nominal exchange level approaches 100%.

XPS examination of the copper exchanged into the ZSM-5 is hampered by the X-ray beam induced reduction[128–130] in the course of the examination and only cooling to −100 °C allows the acquisition of unambiguous XPS results. The important information acquired by XPS is that in samples of low Cu loading there is no reduction due to dehydration.[129] Even in "overexchanged" specimens a large proportion of the ions are isolated (or in small clusters) and while the interconversion between the various oxidation states is facile with the change in the redox potential of the gas, under conditions relevant to SCR the copper is predominantly in the cupric state.[130] The dilute exchanged sample is resistant to severe oxyreduction treatments and did not show any outmigration of Cu from the framework below 500 °C.[129] On the other hand, impregnated samples easily form large metallic aggregates upon reduction.[130]

The cumulative results of ESR and XPS can be best summarized as follows: the *isolated* copper ions copper ions in ZSM-5 are easily reducible by X-ray beams, heating *in vacuo*, hydrogen, hydrocarbons, etc. but not under the strongly oxidizing conditions which prevail in SCR or, still more so, catalytic decomposition.

The information on the IR spectroscopy of nitric oxides and other molecules is extensive. The most complete set of peak assignments was given by Valyon and Hall[117] (Table 1). In all IR studies prominent peaks were registered at <1600 cm^{-1}, the part of the spectrum associated with surface nitrito and nitrato complexes.

TPD of isopropylamine coupled with thermogravimetric analysis has been employed[134] to study the exchange of copper into H-ZSM-5. The exchange of Cu ions decreases Bronsted acid sites, roughly one for one, with the sum of both equal to the amount of Al^{3+} ions. This is the most direct evidence that defining the formal limits of exchangeability by the equivalence of the ions is incorrect. The exchanged copper sites do adsorb isopropylamine and propene. Some copper not associated with the aluminum sites was present in all the samples. The work of Yokota *et al.*[103] where the acid sites and exchanged copper sites were discriminated by NH_3 adsorption shows that there is always residual Bronsted acidity even when the extent of "overexchange" exceeds 200%.

Table 1. IR Absorption Peaks and Their Tentative Assignment for Surface Species Formed from NO on Cu Zeolites^a (Reprinted from ref 117. Copyright 1993 American Chemical Society)

freq, cm^{-1}		adsorbed	
CuZSM-5-26-166	CuY-2.5-80	species	note and assignments
	1902–1891	NO	on isolated Cu^{2+} moved to accessible position;
1895	1912–1907		on Cu^{2+} carrying extralattice oxygen;
1905	1951–1946		on accessible isolated Cu^{2+}
1825	1825 (asym)	$(NO)_2$	dinitrosyl or $(NO)_2$ dimer on Cu^+
1730	1732 (sym)		dinitrosyl or $(NO)_2$ dimer on Cu^+
1807–1815	1796–1802	NO	mononitrosyl on Cu^+
2230–2240		N_2O	only at low temperature; weak band
2120–2140		?	strong band under reaction conditions; forms as NO is being reduced (catalyst oxidized); may result from a reaction of other NO molecules with the deposited O, but it is not obtained from NO_2
1619–1630		NO_2	asymmetric NO_2 stretching;
1300–1340			symmetric NO_2 stretching; strong bands under reaction conditions; also band at 1305 cm^{-1} has been assigned to N_2O_3
1305	1400	NO_3^-	
1643		ONO?	
additional bands		$O(NO_2)$	no other specific assignment of these bands was attempted
in the 1630–1100-cm^{-1} region		NO_3	

^{a} Peaks were obtained from absorption of NO on CuZSM-5-26-166 and CuY-2.5-80 and samples under different conditions (173 K $< T <$ 773 K, P_{NO} = 0.5–30 Torr, time of adsorption >5 min).

VI. Surface Chemistry

A. Importance of the Structure

The effect of molecular sieving as related to the structure of the zeolite is probably of minor importance to the particular usefulness of MFI-type zeolites in SCR which may be simply due to the high proton acidity which in turn assures higher activation rates of the hydrocarbon reductants. Nevertheless, the possibility of the zeolite structure affecting the pairing of the N-containing species should not be overlooked. It was shown that zeolites with a small channel opening have a pronounced enhancing effect on the coupling of paramagnetic NO molecules into diamagnetic dimers.[139] Although MFI was not one of the zeolites examined, a zeolite with a 5 Å channel diameter was far more effective than zeolites with bigger pores. The uniqueness of the MFI zeolites in SCR has not generated, so far, much work to clarify it.

B. Role of Oxygen

In all instances of selective reduction of NO by HC's the reduction does not take place or is sluggish in the absence of excess oxygen. Oxygen in the gas phase or as part of the reductant molecule itself greatly enhances the reaction. The enhancing effect of oxygen is also universally observed in the reduction of NO_x by NH_3. The effect of oxygen on Pt catalysts has been known since 1967.[140] The effect of oxygen in the reduction of NO by NH_3 on zeolites[141,143] is almost the same as in the SCR by HC's and the role of oxygen is also important on the commercial vanadia/titania catalysts.[4]

The effect of oxygen may be due to the activation of one of the reactants, NO or HC, or to the influence on the catalytic sites. All the possibilities have been suggested to be of importance.[66] Among these are (a) oxygen is needed to activate the NO by converting it to NO_2 either in the gas phase or on the surface and empirical evidence is accumulating that this is indeed the case; (b) oxygen activates the hydrocarbon

by forming an oxygenated surface intermediate; there is less evidence for this, but an oxygen-containing molecule does not need gaseous oxygen to initiate its reaction with NO; (c) the oxygen is needed to maintain the proper oxidation state of the metal ion active site, Cu^{2+}, in some views, or a proper Cu^+/Cu^{2+} ratio in other views; (d) oxygen keeps the surface clean by removing the polymeric, carbonaceous deposit which forms in the reaction.

Hamada et al.[79] were the first to suggest the formation of an NO_2 intermediate in SCR over a H-ZSM-5 catalyst and Al_2O_3. In rationalizing the observation that it is easier to reduce NO_2 than NO, the first step in the overall process was taken to be the oxidation of the NO. Under the low flows of their experiment this may occur partly in the gas phase and, in part, heterogeneously over the zeolite. The intermediacy of NO_2 was then proposed on other H form zeolites[82] and on Cu-ZSM-5 as well.[30,65,66,71,77] It was shown that under the high-flow conditions envisaged for implementation, the homogeneous oxidation of the NO to NO_2 is by far too slow and that on Cu-ZSM-5 it is fast on the copper sites.[144] This oxidation is much faster on Cu-ZSM-5 than on H-ZSM-5 or on Cu/Al_2O_3. The activity of NO oxidation parallels the SCR activity and is, similarly, partially suppressed by steam. Figure 5 shows the effect on NO oxidation and on SCR under the same conditions. Under reducing conditions the NO_2 is reduced only back to NO without pairing to dinitrogen. These results strengthen the notion of NO_2 intermediacy. The possible role of NO_2 in the coupling of the nitrogens under oxidizing conditions will be discussed below.

As the evidence mounts that the preponderance of the Cu ions in Cu-ZSM-5 is in the cupric state and that this is due to the prevailing strong oxidizing conditions it is rather self-evident that the excess oxygen is implicated. However, since H-ZSM-5 or Ga-ZSM-5 are also active and require the presence of O_2 but are valence invariant, the role of oxygen in maintaining the higher oxidation state of the copper
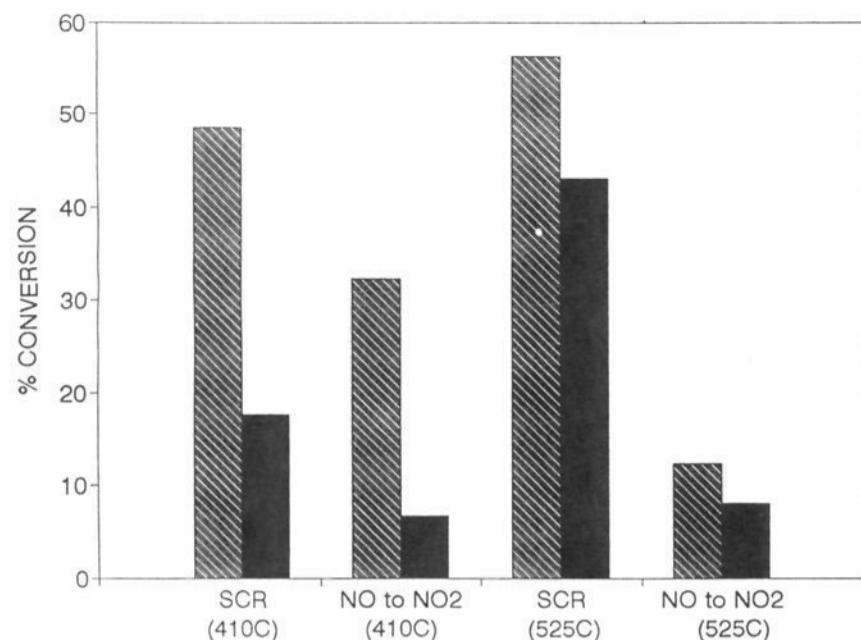
Figure 5. Comparison of the effect of water on SCR and NO + O$_2$ catalytic reaction over Cu-ZSM-5:[144] hatched bars indicate dry data; solid bars, wet data.

ions, however important, appears to be secondary to NO$_2$ intermediacy.

Also, the role of oxygen in the removal of the soot seems to be secondary because oxygen is a must when little or no carbonaceous deposit formation is observed, i.e. when using methane as the reductant. This role of oxygen is again negated by the need for it before any deposit could have formed. It can be of importance if the conditions and the reductant favor rapid formation of massive deposits blocking the access to the zeolite channels.

C. Activation of the Reductant

It is notable that all active catalysts, nonzeolitic and zeolitic, in SCR by hydrocarbons have surface acidity. Surface acid centers chemisorb hydrocarbons and activate them by forming carbonium/carbenium/oxonium ions and this property is the reason for their importance in hydrocarbon processing. Sufficient evidence is at hand to assert that, indeed, the hydrocarbon is catalytically activated by the surface acidity, in a manner analogous to the initiation of catalytic cracking. This is supported by the fact that CO and H$_2$ are inactive reductants and that nonzeolitic surfaces with acidic properties such as alumina or silica–alumina are much more active than nonacidic surfaces, e.g. silica. The activation of alkenes is more facile than that of alkanes in accordance with the observed behavior in cracking reactions. On γ-alumina the formation of carbonaceous deposits, a corollary of cracking, was directly measured during the selective reduction of NO by propene, and was found to correlate with the activity.[145] Carbonaceous deposits were also assigned a role in the reaction over Cu-ZSM-5.[71] Oxygenated HC species also promote reduction of the NO,[64] consistent with the ability of ZSM-5 to form carbocations from a wide range of organic compounds.

C$_1$ species (e.g. methanol and methane) are inactive for the NO reduction on Cu-ZSM-5, in keeping with the low stability of primary carbenium ions. The presence of acid surface sites may be necessary but not sufficient to activate nonreactive HC's, CH$_4$ for example. As noted, on MFI-type zeolites, which contain Co or Ga, methane is quite an active reductant for SCR of NO under dry conditions.

D. Coupling of Nitrogens

The reaction path for the reduction of NO to dinitrogen has to include the pairing of the nitrogens. Indeed, the main kinetic barrier which is to be overcome in the decomposition or SCR of the thermodynamically unstable NO to dinitrogen (defixation) is the coupling of the nitrogens. This task is simplified when the reductant carries its own nitrogen as in ammonia, urea, cyanuric acid, and the formed dinitrogen contains, in the main, one nitrogen atom each from NO and the reductant, as was amply demonstrated in several isotopic studies.[146] There are several conceivable modes of N coupling. In the first place the nitric oxide molecules can pair within the channels or cavities of the zeolite before shedding the oxygen atoms if brought into a close proximity. The pairing can be between two NO's, two NO$_2$'s, or between one of each. The pairing between a molecule striking from the gas and an N-containing surface entity is also conceivable. The N-containing surface species can be an adsorbed moiety or a moiety of the carbonaceous deposit. The cited literature contains suggestions of all of the above. What appears less likely in zeolitic catalysts is the pairing of N atoms by diffusion across the surface after the shedding the oxygens.

The formation of paired entities of nitrogen oxides, in particular in condensed phases at low temperatures is well documented in textbooks of inorganic chemistry[147,148] and the temperature ranges of the thermodynamic stability of such dimers as N$_2$O$_2$, N$_2$O$_3$, and N$_2$O$_4$ are known.[149] The stability of these oxides increases with the number of oxygen atoms in the dimer and the intermediacy of NO$_2$ is conceivably associated with the pairing of these molecules to form the more stable, at a given temperature, surface complexes. This coupling mode would apply equally well to nonzeolitic and zeolitic catalysts. In Cu-ZSM-5 the dinitrosyl complexes, discussed above, provide another N-pairing possibility.

The pairing between a gaseous molecule striking from the gas and an adsorbed N-containing moiety underlies the notion of the isocyanate intermediate. It has been proposed for Cu-Cs/Al$_2$O$_3$[53] and for Cu-ZSM-5.[150] In this context one notes that proven Eley–Rideal surface reactions of this type are rare.

There are data indicating that in the systems under consideration the N-coupling takes place on surfaces to which the nitrogen oxides, in particular the dioxide, stick with a high probability. An incipient film of activated hydrocarbons could, perhaps, be such a surface. It has been shown by Yogo et al.[89] that the carbonaceous deposits formed in the presence of NO + O$_2$ incorporate nitrogen which couples one-to-one with the NO$_x$ in the gas phase. There is direct corroborating evidence for the interaction of NO with the carbonaceous deposits. It was noticed in the course of in situ[127] studies by ESR on Cu-ZSM-5 that the presence of NO or NO$_2$ gas phase radicals quenches the ever-present radicals associated with the carbonaceous deposits.

VII. Mechanism of the SCR

A. Active Sites

Several publications on SCR feature the word "Mechanism" in the title but more often than not they touch only on a single facet of the process. This is because the definition of the active site(s) in the SCR of NO$_x$ with hydrocarbons appears to be more complex than is the case in most heterogeneous catalytic reactions. There are sites on which the NO is activated by oxidation to form NO$_2$; sites, or spaces, where the coupling of nitrogen-containing molecules takes place; sites where the hydrocarbon is activated; sites where the carbon oxides are formed. The same site may be involved in more than one step or there may be a requirement for two different sites in close proximity as in bifunctional catalysis. Further, if the carbonaceous deposits are involved, the latter stages of the process may not be site specific at all. It is logical to consider the mechanism in the order of increasing complexity.

B. Nonzeolitic Oxides

The simplest surfaces on which the SCR by hydrocarbons is observed, albeit at very low rates, are the acidic alumina and silica—alumina. In this case the gas-phase formation of NO$_2$ appears sufficient to account for the observed rate[54] but it is not excluded that the heterogeneous oxidation of NO also takes place. The acidic sites engender the formation of carbonaceous deposits. The carbonaceous deposit, identified by its characteristic ESR line at $g = 2.004$,[145] reduces the NO (NO$_2$) with high selectivity, i.e. it is only slowly gasified by oxygen. The authors noticed that without oxygen in the system the carbonaceous deposits are inactive for NO reduction and assumed that the deposits partially oxidized by oxygen interact with the NO to form an isocyanate-like surface entity which couples selectively with another gas-phase NO molecule. They have shown that charcoal mixed into the alumina is not selective toward NO. It is likely that NO oxidation precedes the reaction with the carbonaceous radicals and the moiety coupling with the second gas molecule differs from a surface isocyanate. The authors have also shown that carbonaceous surface deposits on alumina are involved even when the reductant is the partially oxidized methyl *tert*-butyl ether. It is implied that the coupling of the N-containing species results in the formation of the final products. Viewed from this perspective the oligomerization of the hydrocarbon is not merely a side reaction but a very crucial link in the SCR. Moreover, at least one step in the overall process, the incorporation of the nitrogen into the carbonaceous deposit, is a reaction between *radicals*.

C. Zeolites without Metal Ions

Going from nonzeolitic oxides to zeolites, in particular MFI or ferrierites, the principal difference is in the acid strength of the surface and the availability of channel pores of molecular dimensions. Both differences are likely to enhance the oxidation of NO to NO$_2$. Odenbrand *et al.*[141−143] have established that the acid sites in zeolites (mordenites) are active for

NO oxidation and that in the SCR of NO by NH$_3$ over the mordenites this is the rate-limiting step since it is multimolecular and requires the transfer of several electrons. In mordenite, contrary to ZSM-5, the exchange of the protons by copper ions attenuates the oxidation of NO,[143] but in experiments in our laboratory this could not be confirmed.[152] The acid sites responsible for the oxidation of NO are, apparently, not the surface protons (Bronsted acids) which activate the hydrocarbons but those formed upon dehydroxylation (Lewis acids) at the reaction temperature. If so, this circumstance may have relevance to the (reversible) deactivation of the SCR by water and underlie the extreme vulnerability of the H form zeolites. The better activity of MFI-type zeolites is probably related to the favorable structural factors of medium-pore zeolites where the bringing together of the reactants is facilitated.[139]

The pairing of the nitrogens on H-zeolites entails either the formation of N-containing carbonaceous deposits which then react with gas phase NO or the bringing together of a paired surface complex with an activated hydrocarbon fragment (*vide infra*). Yogo *et al.*[82] noted a modest reduction of NO by CH$_4$ at low space velocities over a series of H-zeolites and it is unlikely that methane forms oligomeric carbonaceous deposits.

A subcategory of zeolites without reducible ions, apart from the H-forms, are zeolites containing such ions as Ga^{3+}, mentioned above. Ga-ZSM-5 does not chemisorb NO[91] and in this respect differs from catalysts with reducible ions. Although Co ions easily undergo changes in oxidation state when supported on alumina, their exchange into the ZSM-5, at low loading, firmly stabilizes the divalent state as observed in *in situ* XPS studies[151] but Co-ZSM-5 does chemisorb NO. The peculiarity of these two systems is their ability to strongly activate methane which also requires the presence of Bronsted acid sites.[100] The NO$_2$ intermediacy and very high susceptibility to deactivation by H$_2$O are common for both catalysts. The blockage of NO adsorption on the cobalt ions, given as the reason for the effect of the water in SCR activity, cannot be applied to the Ga-containing zeolites. Further work is needed to elucidate the activation of CH$_4$.

D. Addition of Metal Ions to Oxides

The addition of transition metals, such as Cu, to Al$_2$O$_3$ also increases the SCR activity[54−56] suggesting that copper ions are active in the oxidation of NO. Moreover, the maximum SCR activity enhancement is observed at rather low Cu loadings of 0.3 wt %[55,57] implying that isolated Cu ions are involved in the oxidation of the NO to NO$_2$. It is to be expected that the addition of multivalent transition metal ions may adversely affect selectivity because they are active in the catalytic oxidation of hydrocarbons.

E. Cu-ZSM-5

From the behavior of the relatively simple catalysts one realizes that the detailed course of the SCR may differ from case to case. How is this reflected in Cu-ZSM-5 which has a zeolitic structure, Bronsted and

Lewis acid sites, isolated Cu^{2+} ions in two coordinations and, depending on the copper loading, other surface copper entities? It is a combination, not necessarily additive, of all the previous cases. The cupric ion is the locus of NO adsorption and oxidation to NO_2. The surface Bronsted acid is the HC activator. Such a catalyst falls under the *bifunctional* designation but in this particular case both sites may perform multiple functions. It is likely that more than one surface reaction path is possible in the SCR on Cu-ZSM-5. This is at the bottom of the widely divergent "mechanisms" arrived at by different investigators.

While there is a growing consensus that the formation of NO_2 is a prerequisite, there have been disagreements as to the importance of the carbonaceous deposits as the intermediate reductant on Cu-ZSM-5. Ansell et al.[71] make a strong case for it but Burch and Millington[70] arrive at the opposite conclusion based on reactant switching experiments. The accumulation of deposits with time on stream does not assure prolonged activity once the reductant, propene, is switched off. This might not be a clinching argument against the intermediacy of the oligomeric deposits if the latter have to be constantly nitrated "in real time" by the NO_2 formed on the cupric sites. For the moment one has to accept the intermediacy of the deposits is a distinct possibility. In any case the distinction between single activated hydrocarbons, fragments thereof or oligomers is semantic and depends on the reductant and other reaction conditions. The relative rates of the oligomerization of the surface carbon species and of the overall oxidation to carbon oxides determine how much deposit, if any, is present on the surface under any set of operating conditions. The generalization of Witzel et al.[102] who found the same specific reactivity (per carbon atom) for a wide array of reductants shows that the activation of the reductant is not the limiting step while the oxidation of NO to NO_2 probably is.

Kharas has speculated on a detailed reaction path for SCR on Cu-ZSM-5[77] and in particular on the way a paired entity of surface nitrogen oxides comes into reactive contact with the reductant. He suggests complex multiatomic surface intermediates based on known organometallic antecedents. In an intermediate of this type the anionic hyponitrite moiety is bound to the surface metal ion and to a organic moiety. Presently this scheme remains just a speculation since it has not been examined experimentally. In contrast to the initial steps of the process the various suggestions for the removal of the oxygens from the paired nitrogen oxides are at present not very well substantiated.
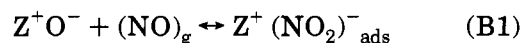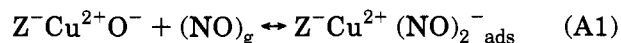
The mechanism is further complicated because the SCR is proceeding parallel to the oxidation of the reductant by the large excess of O_2 and it is not immediately apparent whether the oxidation of the hydrocarbon by dioxygen takes place on the same sites. Contrary to SCR, transition metal ions are required for good hydrocarbon oxidation and one may assume that it may take place on any copper site and that it proceeds by a surface redox mechanism. On acidic surfaces it can proceed by the oxidation of the

carbonaceous residue formed in the cracking of the reductant on acid sites. Excessive loading of the ZSM-5 framework with copper will therefore suppress the desired selectivity for NO reduction. Since the redox reaction can occur on any copper site, including the isolated Cu^{2+}, there is also direct competition for these sites. Formation of small amounts of CO is usually observed when the reaction is carried out at high space velocities notwithstanding the huge excess of oxygen. In one instance[64] for each reacted NO molecule, 3–4 CO molecules were formed but the CO was also formed over Cu-ZSM-5 in the absence of NO during the oxidation of the hydrocarbon by the oxygen. Under similar conditions on alumina-supported copper oxide, CO is absent from the reaction products. Hence, the CO formation is due to that part of the oxidation which takes place on the isolated Cu ions in the zeolite. A portion of this CO is then oxidized to CO_2. The residual CO content depends on the conditions, mainly residence time and temperature. In sum, CO_2 can be formed either directly or through the intermediacy of CO.
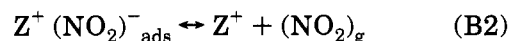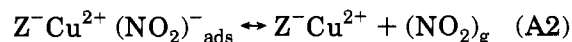
To summarize, the present understanding of the reaction path of the SCR is outlined below. The complete reaction path, the equations designated by the letters "A" and "B", pertains to a Cu-ZSM-5 catalyst, in which the copper ions are largely isolated when a fairly active, representative hydrocarbon reductant, such as propene, is used. The partial reaction path, designated by "B", is that proceeding on metal-free MFI-type zeolites. In sketching out the *admittedly speculative probable* sequence of steps we try to account for the most pertinent experimental observations, anticipating future emendations as more knowledge is gained.

If we denote the zeolite framework by "Z", then under reaction conditions at steady state there are three kinds of active surface sites in Cu-ZSM-5: copper ions mainly in the cupric oxidation state Z^-Cu^{2+} (positively charged), Bronsted acids Z^-H^+ (neutral), and Lewis acids Z^+O^- (negatively charged). One Lewis acid is formed by dehydroxylation of two Bronsted acids.[143] Since in high-silica zeolites the Bronsted acids are relatively far apart the quantity of Lewis acids is small. All three active sites are bonded to the tetrahedral Al^{3+} ions in the zeolite and therefore their sum is limited by the number of the latter. Under the prevailing strongly oxidizing conditions a part of the cupric ions is associated with an oxygen ion as $Z^-Cu^{2+}O^-$ creating a negatively charged site akin to the Lewis acid site.

The NO_x activation starts with the formation of adsorbed nitrite ions on the charged sites:

$$Z^-Cu^{2+}O^- + (NO)_g \leftrightarrow Z^-Cu^{2+}\,(NO)_2{}^-{}_{ads} \quad (A1)$$

$$Z^+O^- + (NO)_g \leftrightarrow Z^+\,(NO_2)^-{}_{ads} \quad (B1)$$

This is followed by gaseous NO_2 formation by desorption:

$$Z^-Cu^{2+}\,(NO_2)^-{}_{ads} \leftrightarrow Z^-Cu^{2+} + (NO_2)_g \quad (A2)$$

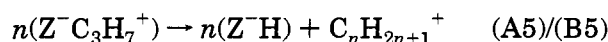$$Z^+\,(NO_2)^-{}_{ads} \leftrightarrow Z^+ + (NO_2)_g \quad (B2)$$

The experimentally observed catalytic oxidation of NO on low-exchange, high-silica Cu-ZSM-5 and H-ZSM-5 mandates the restoration of the oxygen ions onto the cupric ions and of the Lewis acids from gas-phase oxygen, schematically:

$$Z^-Cu^{2+} + \tfrac{1}{2}O_2 \rightarrow Z^-Cu^{2+}O^- \qquad (A3)$$

$$Z^+ + \tfrac{1}{2}O_2 \rightarrow Z^+O^- \qquad (B3)$$
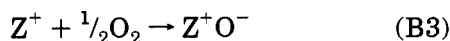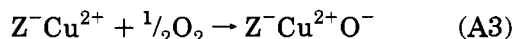
activation of the propene on Bronsted acid sites by the formation of adsorbed carbenium ions:

$$Z^-H^+ + C_3H_6 \rightarrow Z^-C_3H_7^+ \qquad (A4)/(B4)$$
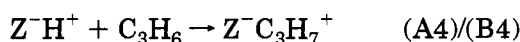
and oligomerization of carbenium ions, schematically:

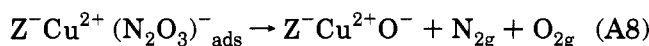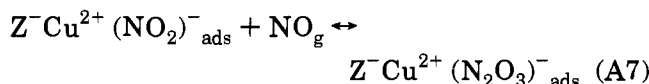$$n(Z^-C_3H_7^+) \rightarrow n(Z^-H) + C_nH_{2n+1}^+ \qquad (A5)/(B5)$$

These surface oligomers contain radicals, and the monomer is also included.

The next step is the formation of nitroxy–carbon species by reaction of the oligomers with NO$_2$ (or to a lesser extent by NO):

$$mNO_2 + C_nH_{2n+1}^+ \rightarrow C_nH_{2n+1}N_mO_{2m} \qquad (A6)/(B6)$$

Here, the pairing between gas-phase radicals (NO$_x$) and surface radicals takes place. Pairing of nitrogens on copper sites follows:

$$Z^-Cu^{2+}(NO_2)^-_{ads} + NO_g \leftrightarrow$$
$$Z^-Cu^{2+}(N_2O_3)^-_{ads} \quad (A7)$$

$$Z^-Cu^{2+}(N_2O_3)^-_{ads} \rightarrow Z^-Cu^{2+}O^- + N_{2g} + O_{2g} \quad (A8)$$

And nitrogens on surface nitroxy-oligomers (gasification of nitroxy-oligomer by NO$_x$) are then paired:

$$(NO_2)_g + C_nH_{2n+1}N_mO_{2m} \rightarrow$$
$$N_2 + CO_2 + H_2O_g \quad (A9)/(B9)$$
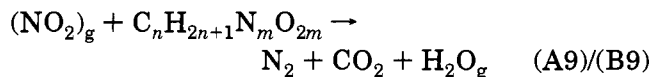
In parallel there is a slow gasification of the oligomer by dioxygen:

$$C_nH_{2n+1}^+ + O_{2g} \rightarrow CO_2 + H_2O \qquad (A10)/(B10)$$
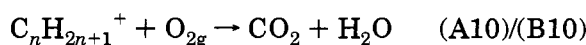
The fast catalytic combustion of the propene on the copper sites in Cu-ZSM-5 probably proceeds by redox mechanism where the copper ions undergo cycling between the cuprous and cupric states. Small amounts of CO are formed on the copper ions. In low-exchange specimens the redox process may be confined to the small proportion of sites with copper ions in close proximity. The suppressing effect of steam on the SCR activity may be ascribed to the blocking (rehydroxylation) of the sites in reactions A1 and B1, inhibiting the rate-determining oxidation of NO to NO$_2$. Reaction A7 is analogous to the pairing of nitrogens in the decomposition[30] and this temperature-

dependent adsorption equilibrium explains the peaking of SCR with temperature.

VIII. Concluding Remarks

Much knowledge has been gained on the SCR of NO$_x$ with N-free reductants but large gaps remain. While scepticism still prevails in many quarters as to implementation because of the enumerated durability problems, progress is being made in this area as well. The implementation may come first in the uses where the conditions are less stressful for the relatively fragile zeolitic catalysts. Among these may be the treatment of stationary effluents where the water vapor content is low or the treatment of diesel engine exhaust gas where the temperatures are low. Ultimately only actual reduction to practice will attest to the real usefulness of the subject of this review.

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