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Reduction over zeolite-based catalysts of nitrogen oxides in emissions containing excess oxygen
Unraveling the reaction mechanism

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Abstract

Reduction of NO_x to N_2 over zeolite-based catalysts is a multi-step reaction for which transition metal (TM) ions are helpful but not indispensable. The present state of understanding the mechanism is reviewed for the catalyzed NO_x reduction with ammonia or alkanes; reduction with acetaldehyde is also sketched, but will be described in detail in a separate paper. A decisive step is the interaction of two reaction intermediates containing N atoms in different oxidation states. A favorable reaction path uses an organic molecule to reduce part of the NO_x to ammonia, this product then reacts with $NO + NO_2$ to give N_2. Isotopic labeling shows that each N_2 molecule has one N atom from the NH_3 intermediate, the other from NO_x. N_2 is formed at room temperature, if an 1:1 mixture of NO and NO_2 is in contact with an Fe/MFI catalyst covered with NH_3. During NO_x reduction with CH_4 over Pd/zeolite catalysts, H/D exchange of methane has been observed, indicating that methane is dissociatively adsorbed on Pd^0 clusters that are present in the steady-state of surface oxidation and reduction steps.

BaNaY catalysts, containing negligible impurities of TM elements, catalyze NO_x reduction with acetaldehyde at 200 °C. In the prevailing mechanism acetaldehyde is transformed via acetate ions and nitromethane to isocyanic acid, which is hydrolyzed to NH_3. Again, N_2 is ultimately produced from NH_3 and N_2O_3 via ammonium nitrite.

Keywords: Reduction; Zeolite-based catalysts; Transition metal ions

1. Introduction

Legislation in all industrialized countries limits the permitted level of toxic nitrogen oxides, NO and NO_2, for which we shall further use the collective term NO_x in gaseous emissions from cars, trucks and stationary engines. Formation of NO from N_2 and O_2 is thermodynamically favorable at high temperatures as used in modern IC engines. NO_x is therefore, present in the emissions from all engines exposing gases containing nitrogen and oxygen to high temperature. For the clean-up of the tail gas of passenger cars, an important breakthrough was achieved in the 1970s by the invention of the *Three Way Catalyst*, which reduces the level of unburned hydrocarbons, carbon monoxide and NO_x by >99% in emissions from conventional gasoline fueled cars. This catalyst requires a stoichiometric air/fuel intake ratio, because it is unable to reduce NO_x in a gas containing significant amounts of O_2. The *Three Way Catalyst* is therefore, not suited to abate NO_x in the emissions from those vehicles which use energy efficient *lean-burn* gasoline or *diesel* engines, that run on an excess of air.

This presents the catalysis community with the challenging task of designing an entirely different class of highly selective catalysts that are able to induce chemical reaction of a potential reductant with NO_x present at ppm levels, while reaction of the same reductant with the more abundant O_2

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should be strongly restrained. Such catalysts should be very active, because the contact time with the gas in the tailpipe will be very short and in some driving modes the temperature of diesel emissions is rather low. The ideal catalyst should also have a wide window of operation temperatures, including cold start and driving modes that produce very hot exhausts. Moreover, it should tolerate a considerable dose of poisons and remain active during the entire life of the vehicle.

The catalyst that meets all these demands does not exist as yet. Research in a number of laboratories has, however, led to results supporting the conclusion that reduction of NO_x in the emissions of diesel or lean-burn gasoline engines can be achieved by certain catalysts. This task is easier for stationary engines, as in power plants, where the options for the reductant are wider than for automotive vehicles. The most efficient reductant is ammonia. Catalysts recommended for selective catalytic reduction (SCR) of NO_x with ammonia in stationary sources include supported V_2O_5 [1,2], V_2O_5-WO_3-TiO_2 [3], MnO_x/Al_2O_3 [4], MnO_x/NaY [5], Cr_2O_3 [6], and $NiSO_4/Al_2O_3$ [7]. For obvious reasons, the use of liquid ammonia is not an option for cars and trucks. In a variant of the SCR strategy, an aqueous solution of urea is used and decomposed on board of the vehicle. Some problems inherent to this strategy are the need for a dense network of delivery stations where the driver can purchase the urea supply, the difficulty of enforcing such laws, and the danger that some ammonia will slip through the converter and be oxidized to more NO_x.

These considerations directed interest on non-ammonia reductants and catalysts that catalyze the selective reduction for NO_x in the presence of a large excess of oxygen. One class of materials of promising potential in such NO_x reduction is a group of zeolite-based catalysts. The present paper gives an overview of the state-of-the-art of this field with emphasis on the mechanistic understanding of the chemistry. As it turns out that alkanes and acetaldehyde first convert part of the NO_x to ammonia, this paper presents mechanistic evidence grouped in different sections for different reductants.

*First reports by Held and coworkers [8,9] and Iwamoto and Hamada [10,11] indicated that some zeolite-based catalysts are able to selectively catalyze the reduction of NO_x with on-board hydrocarbons. A catalyst called Cu/ZSM-5, consisting of copper ions in the cavities of a zeolite with MFI structure, displayed a remarkable capability to catalyze the reduction of NO_x to N_2 with simple hydrocarbons and in the presence of a large excess of O_2. It actually turned out that oxygen was necessary because the pathway of NO reduction was found to start with its partial oxidation to NO_2 [12]. The world-wide effort exploring NO reduction over zeolite-based catalyst, such as Cu/ZSM-5 provided important mechanistic insights. In 1995 Poignant et al. showed by means of IR spectroscopy that (part of) the NO_x is reduced to ammonia, and that isocyanates, RNCO, are intermediates in this reaction [13]. Cu/ZSM-5 does not catalyze reduction of NO_x with methane, but materials containing Co or Pd ions inside the cavities of certain zeolites were found highly active for this reaction [14,15]. Cant et al. proposed that over Co/FER catalysts HNCO is formed during reaction of nitromethane [16–18]. Likewise, Ukisu et al. concluded that with Al_2O_3-supported Cu catalysts isocyanates are decisive intermediates in NO_x reduction with hydrocarbons [19]. Research on Cu/ZSM-5 revealed the importance of dinuclear oxygen-bridged oxo-ions, $[Cu–O–Cu]^{2+}$ [20]. Reduction of Cu^{2+} to Cu^{+} and re-oxidation of the latter ion was monitored by FT-IR exploiting Sárkány’s discovery that Cu^{2+} and Cu^{+} ions exert different effects on the zeolite lattice vibrations [21,22]. Beutel et al. observed that ${}^{15}NO_3{}^{-}$ ions ligated to Cu^{2+} exchange their ${}^{15}NO_2$ moiety with physisorbed ${}^{14}NO_2$ or ${}^{14}NO$ [23]. It was also observed that an interconversion of nitrogen oxides is catalyzed, including the reaction:

$$NO_2 + N_2O = 3NO \qquad (1)$$

Interest in the Cu/ZSM-5 catalyst almost evaporated, however, when it became evident that water vapor was deleterious for the catalytic activity of this material. Water is, of course, a major component of the emissions from all internal combustion engines using hydrocarbon fuels. In this situation, most car manufacturers apparently lost hope for finding a satisfactory zeolite-based catalyst within the time frame imposed by pending legislation. Adsorbents were developed that act as “NO_x traps”, and computerized systems have been designed that periodically interrupt the lean-burn operation by short pulses with a high fuel/air ratio in order to reduce the trapped NO_x.

Meanwhile some academic groups continued basic research on zeolite-based catalysts. As the rate of the catalyzed oxidation of NO to NO_2 at low temperature was considered too low, the use of a non-thermal plasma was considered and explored [24–27]. Fundamental research on catalytic reduction of NO_x and non-thermal plasma reactors continued in some laboratories, because researchers believed that the long-term potential of such strategies can only be assessed if one understands their *modus operandi*. Novel techniques were developed to prepare zeolite-based catalysts. For instance, the chemical vapor deposition (CVD) technique was used to sublime $FeCl_3$ into the acid form of a zeolite, such as HMFI. (The MFI lattice is often called ZSM-5 after its first code name by Socony Mobil.) This led to catalysts with much higher Fe loading than can be achieved by conventional ion exchange from an aqueous solution [28]. After replacing the Cl ligands by OH groups and applying certain thermal treatments, active and selective catalysts have been obtained. They maintain their activity in feeds containing high concentrations of water vapor. Modern catalyst characterization methods revealed that such catalysts contain a variety of sites including metal ions, dinuclear oxo-ions, and oxidic nano-particles. Crucial reaction steps in the reduction of NO_x with isobutane over such Fe/MFI catalysts have been identified by isotopic labeling. Co/FER and Co/MFI catalysts that are active in the NO_x reduction with methane, were characterized and it was found that the position of the Co ions in the cavities is important for the catalytic performance [29,30]. A group at Pacific Northwest National Laboratory reported that acetaldehyde, which is formed from hydrocarbons in a non-thermal plasma, reduces NO_x to N_2 over BaY and NaY catalysts at relatively low temperature [31]. Studies at Northwestern University of the mechanism of this novel catalyst system confirmed that catalytic NO_x reduction is indeed possible without transition metals. It revealed a novel reaction mechanism involving at least six steps with rather exotic intermediates (vide infra). Important insights have been obtained by using FT-IR spectroscopy and isotopic labeling. While this research is still in progress, the present paper will give an overview of the mechanistic concepts emerging from this work. The text will be structured using the catalysts with which these results have been obtained: viz. Fe/MFI, Pd/MFI, Co/MFI and BaNaY.

2. NO_x reduction with isobutane over Fe/MFI

In zeolites the number of exchangeable ions is limited by the charge balance. The negative charge is essentially given by the number of Al-centered tetrahedra in the framework, each of these tetrahedra contributing one electron. For three-fold positive ions such as Ga^{3+}, Rh^{3+} or Fe^{3+}, this limits the number of ions which can be positioned inside the zeolite cavities by conventional ion exchange to one-third of the number of Al-centered tetrahedra. It has, however, been shown that this limitation can be circumvented by providing metal ions carrying charge-compensating ligands. This is achieved by decomposing the vapor of a volatile chloride onto the H-form of the zeolite [28,32,33] or by grinding a mixture of the solids $FeCl_3$ and HMFI [34]. The reaction of $FeCl_3$ with an the acidic proton is given by:

$$FeCl_3 + H^+_{zeol} \Rightarrow HCl + [FeCl_2]^+_{zeol} \qquad (2)$$

Only one of the three positive charges of Fe^{3+} has to be compensated by the zeolite framework, the other two are compensated by Cl^- ligands. The maximum ratio of Fe atoms to Al-centered zeolite tetrahedra Fe/Al becomes = 1 with this technique, instead of 1/3 with conventional ion exchange from aqueous solutions. The Cl^- ligands can be replaced by OH^- groups and upon calcination water is released. A variety of oxo-ions and/or oxide particles can be formed in this way. Conditions have been found where dinuclear Fe ions with one oxygen bridge, $[HO–Fe–O–Fe–OH]^{2+}$, prevail. The identification of this structure has been described in a number of papers [35–39], this will not be repeated here. In typical tests, 0.2 g catalyst is exposed to a flow of 0.2% NO, 3% O_2, 0.2% i-C_4H_{10} at a flow rate of 280 ml/min. As shown in Fig. 1, the N_2-yield increases with temperature reaching a maximum of roughly 80% at 350 °C, followed by a decrease. Basically, two parallel reactions are catalyzed, one in which the hydrocarbon reacts with NO_x and one in which it reacts with O_2. As the former reaction has a lower activation energy, it prevails at lower temperature, but at higher temperature the hydrocarbon is depleted by its reaction with the oxygen that is initially present in 15-fold excess over the NO. Adding water to the feed has little effect on the maximum N_2 yield, but it changes the composition of the co-products CO and CO_2. The fact that the CO/CO_2 ratio is increased by H_2O excludes significant contribution of the “water gas shift” catalysis and suggests that a carbonaceous deposit on the catalyst is volatilized by interaction with water vapor.

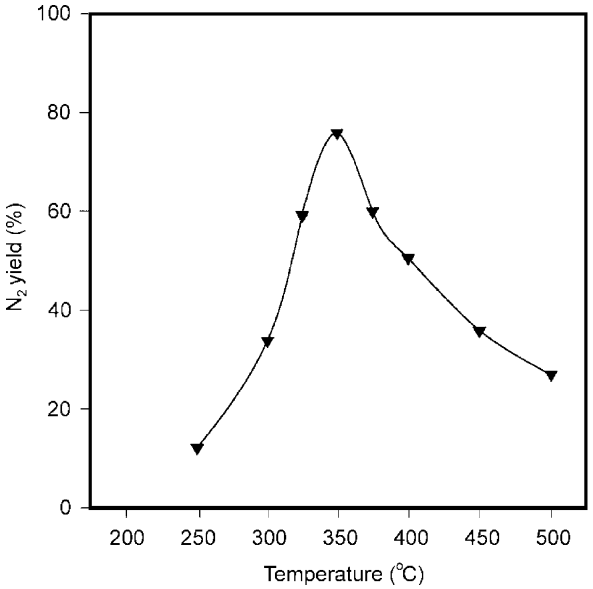

Fig. 1. N_2 yield over Fe/MFI with *iso*-C_4H_{10}. Feed: 0.2% NO, 3% O_2, 0.2% *iso*-C_4H_{10}, flow rate: 280 ml/min. (Curve with inverted triangles in Fig. 2, J. Catal. 180, 171 (1998) 363). (Reproduced from J. Catal. 180, 171 (1998) with permission.)

As with Cu/MFI, only negligible NO_x reduction takes place in the absence of O_2. Again, NO has to be oxidized, at least in part, to NO_2. This is considered a general aspect of NO_x reduction over catalysts of this type. Tünter et al. [40] showed in 1986 for a non-zeolite catalyst that maximum reduction is achieved with a ratio of $NO/NO_2 = 1/1$. This suggests that the gas phase equilibrium between NO, NO_2 and N_2O_3 is established and nitrite ions are formed on the catalyst [41]. The presence of nitro groups, nitrate [42]and nitrite [43] ions on Fe/MFI has been confirmed by IR spectroscopy.

Temperature programmed oxidation of used catalysts confirms the hypothesis that a deposit is formed on the catalyst, as we mentioned above in the context of the CO/CO_2 ratio and its response to the water content of the feed. Chen et al. showed that this deposit plays a very positive role as a reaction intermediate [44]. Upon exposing the catalyst covered with this deposit to a flow of $NO + O_2$ but no reducing molecule, it appeared that N_2 was released. This surprising observation could still be rationalized in two ways: either the deposit worked as a reductant for NO_x or it exposed groups

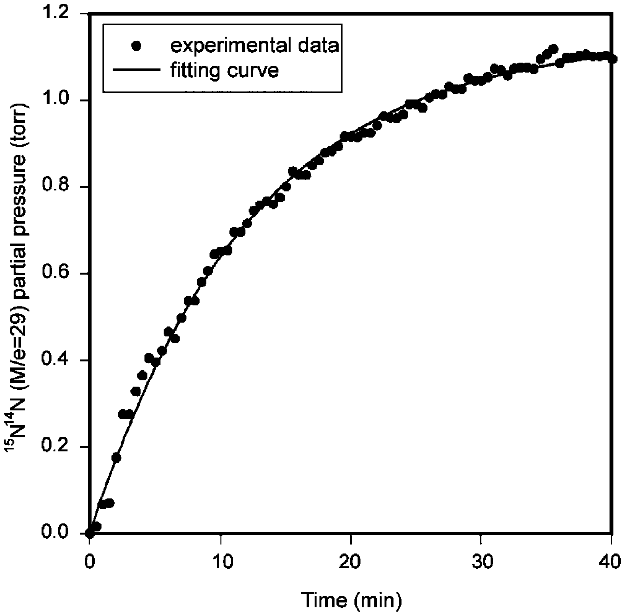

Fig. 2. $^{14}N^{15}N$ formation upon exposure to $^{15}N_2 + O_2$ of a Fe/MFI, catalyst, covered with a ^{14}N deposit that had been formed during previous $^{14}NO_x$ reduction with C_4H_{10}. (Reproduced from J. Catal. 186, 91 (1999) with permission.)

that contained a reactive form of nitrogen. To discriminate between these possibilities an experiment was carried out with labeled nitrogen isotopes. For this purpose, a catalyst was first contacted with a feed of ^{14}NO, O_2 and C_4H_{10} at the reaction temperature of 350 °C. After sufficient deposit was formed on the catalyst, the gas was replaced by a mixture of ^{15}NO, O_2 and He; this mixture was circulated over the catalyst. Again N_2 was formed and its mass spectrometric analysis showed that it consisted almost exclusively of the heteronuclear isotopomer $^{14}N^{15}N$. (see Fig. 2). This result clearly shows that the two N atoms in each N_2 molecule have a different history: one came from NO_x, the other atom had spent part of its life in the reduced deposit at the catalyst surface.

Quantitative analysis of the reaction kinetics with deposits formed from a variety of sources revealed [45] that the formation of the reactive N atom groups in the deposit depends on the nature of the original reductant. As Langmuir–Hinshelwood kinetics was found to be applicable, the rate constants were determined for a number of model compounds, which were deposited on the same catalyst, including amines, ammonia, nitriles, and ethyl isocyanate. All of these reacted with NO + O_2 to form N_2 These model compounds were compared with deposits from NO_x reduction tests with propane, butane or isobutane. The rate constants are compiled in Table 1. In the same table the ratio of homonuclear $^{15}N_2$ to heteronuclear $^{14}N^{15}N$ has also been included upon using ^{15}NO in the feed and deposits containing ^{14}N only. As seen in Table 1, the highest rate constants were found for ammonia, ethylamine and ethyl isocyanate. For the other model compounds the measured rate constants were lower than those obtained with the deposits from the catalytic test runs. As the isocyanate is easily hydrated to amine+CO_2 these kinetic data support the conclusion that the reactive groups in the deposit are amine groups or adsorbed ammonia molecules. The isotope distribution shows that with ammonia and ethylamine 100% of the N_2 is heteronuclear, one N atom stemming from the surface compound, the other from NO_x. The data thus support the conclusion that a crucial task of the catalyst is to convert part of the NO_x to ammonia or an amine. The reaction of these molecules with impinging NO_x results in the formation of N_2.

Table 1
k values and $^{15}N_2/^{15}N^{14}N$ ratios for different deposits and model compounds

Deposit formed by	*k* (min^{-1})	$^{15}N_2/^{15}N^{14}N$
$NO_y + C_3H_8$	0.085	0.05
$NO_y + n\text{-}C_4H_{10}$	0.083	0.15
$NO_y + i\text{-}C_4H_{10}$	0.073	0.15
NH_3	0.163	0
$C_2H_5NH_2$	0.175	0
CH_3CN	0.066	0
$CH_2{=}C(CH_3)\text{–}CN$	0.035	0.27
C_2H_5NCO	0.099	0.33
$(CH_3)_2CHNO_2$	0.045	0.15

In these tests the interaction between deposit and impinging molecule took place on a Fe/MFI catalysts. However, in a blank test of ethyl amine interacting with NO + O_2, it was found that formation of N_2 is quite fast, even at rather low temperature. The catalyst thus is mainly required to produce the amine groups or ammonia molecules, but their subsequent interaction with NO_x is facile and non-catalytic. Indeed, it is well-known that $N_2O_3 + H_2O$ easily reacts with ammonia to ammonium nitrite, that decomposes to N_2+H_2O at or below 100 °C without a catalyst. Likewise, primary amines are known to interact with NO_2 forming diazo- (or diazonium-) compounds that easily decompose by releasing N_2 [46,47].

Ammonia formation by reducing NO_x with organic molecules over a Cu/MFI catalyst has been reported by Poignant et al. [48,49]. Liu et al. [50] detected HCN as a major product of NO_x reduction with isobutane over Fe/MFI. In the presence of water vapor HCN is converted to NH_3 and CO_2. All these results link NO_x reduction with organic molecules to the chemistry of NO_x reduction with ammonia which will, therefore, be inspected in the next section.

3. NO_x reduction with ammonia over Fe/MFI

The formation of ammonia or amines from a hydrocarbon reacting with NO or NO_2 may be expected to have a considerable activation energy. It is therefore, instructive to compare NO_x reduction with hydrocarbons or ammonia over the same catalyst. In the absence of a transition metal, the oxidation of part of the NO to NO_2 will become rate limiting [51]. Over Fe/MFI, that does expose oxidation sites, formation of N_2 is much faster with ammonia than with a hydrocarbon so that a much higher space velocity has to be chosen ($3.6 \times 10^5\ s^{-1}$) to compare both feeds [40,52]. With a dry feed NO_x reduction upto 90% has been achieved below 300 °C. The unconverted NO_x consists exclusively of NO, because the NO_2 is quantitatively consumed. In the presence of O_2, the consumption ratio of the three reactants NO, O_2 and NH_3 is equal to 4:1:4, in accordance with the stoichiometry of an ammonium nitrite intermediate:

$$4NO + O_2 + 4NH_3 + 2H_2O = 4NH_4NO_2 \quad (3)$$

The gas phase equilibria $NO + NO_2 \rightarrow N_2O_3$ and $N_2O_3 + H_2O \rightarrow 2HONO$ will remain established. It has been known for more than a century that ammonium nitrite readily decomposes at low temperature [53]. The formation of ammonium nitrite thus opens a favorable reaction path for the formation of N_2:

$$NH_4NO_2 = N_2 + 2H_2O \quad (4)$$

When isotopically-labeled molecules are used in the NO_x reduction with ammonia, it is found that all N_2 molecules consist of one N atom stemming from NH_3 and one from NO, as expected for processes such as (4). To test the kinetics over a Fe/MFI catalyst an NO_x mixture was prepared with a ratio of $NO/NO_2 = 1/1$, so that the gas phase equilibrium

$$NO + NO_2 = N_2O_3 \quad (5)$$

will yield the highest possible concentration of N_2O_3, the obvious precursor of ammonium nitrite and no NO or NO_2 would be left after a reaction consuming these molecules in a 1:1 ratio. This was verified by circulating an equimolar mixture of $^{15}NO + ^{15}NO_2$ over an Fe/MFI catalyst covered with pre-adsorbed $^{15}NH_3$. The result of this test is shown in Fig. 3. Clearly, N_2O_3 is rapidly reduced even at room temperature and resulted in N_2 consisting for 100% of the heteronuclear molecule $^{14}N^{15}N$. This result confirms ammonium nitrite as the crucial reaction intermediate. It follows that reduction of each NO_2 molecule entails simultaneous consumption of one NO molecule, the $NO_2/NO = 1/1$ mixture is ideal for NO_x reduction with ammonia at low temperature.

Unlike NO and NO_2, the N_2O_3 molecule has no unpaired electrons. It has been detected at room temperature at the surface of Fe/MFI by its IR bands at 1876 and 1297 cm^{-1} which are shifted by co-adsorbed ammonia to 1865 and 1300 cm^{-1}, respectively [54,55]. The nitrite ion has been identified by the band at 1320 cm^{-1} [43]. The reaction path via ammonium nitrite is not limited to Fe/MFI or zeolite-based catalysts. The finding of Tünter et al. [40] that the highest rate of NO_x reduction with ammonia is achieved for a NO_x feed with a 1:1 ratio of NO:NO_2 was confirmed by Madia et al. for V_2O_5-TiO_2 catalysts [56]. Likewise, Blakeman et al. [57] showed that over a non-zeolite catalyst the reduction of $NO + NO_2$ mixtures with NH_3 is clearly superior to pure NO or NO_2. It is interesting that Stevenson and Vartuli reported that SCR of NO_2 with NH_3 can be achieved over an HMFI catalyst, this result suggests that NO_2 is reduced to NO by NH_3 without a transition metal [58].

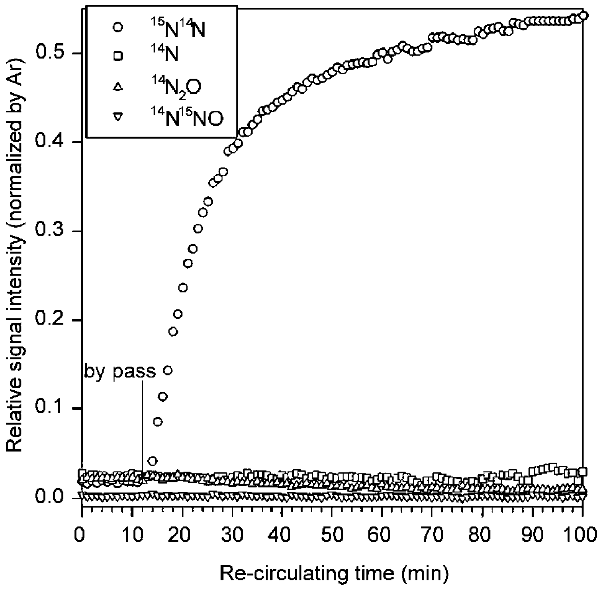

Fig. 3. Time dependence of the partial pressure of $^{14}N^{15}N$ upon circulating a gas mixture of 20 Torr ^{15}NO, 20 Torr Ar, 5 Torr O_2, 100 Torr He at room temperature over Fe/MFI covered with adsorbed $^{14}NH_3$. (Reproduced from J. Catal. 201, 89 (2001) with permission.)

Summarizing, the main conclusions from the experiments described in this and the previous chapter, is that for the catalytic NO_x reduction with organic molecules, part of the NO must be oxidized to the 3+ state as in N_2O_3 or HONO, and part must be reduced to the oxidation state 3− in NH_3 or an amine. One can imagine that ammonium nitrite will be formed, its decomposition is known to take place at 100 °C in the absence of a catalyst. If one writes the release of water in two steps nitrosoamine, $ONNH_2$, becomes a hypothetical intermediate [59,60]. Using the formal oxidation states of nitrogen, the formation of N_2 molecules can be summarized by

$$N^{3+} + N^{3-} = N_2^{o}. \quad (6)$$

With NH_3 as the reductant, the ideal and most economic stoichiometry for the selective catalytic reduction (SCR) is

$$2NH_3 + 2NO + \tfrac{1}{2}O_2 = 2N_2 + 3H_2O. \quad (7)$$

Higher NO_2/NO ratios result in formation of ammonium nitrate, besides nitrite, the nitrate is, of course, known to decompose to N_2O+H_2O. Indeed, Koebel et al. reports N_2O formation over some catalysts for feeds containing an excess of NO_2 over NO [61]. When hydrocarbons are used to reduce a feed of NO and O_2, the ideal and most economic scenario is for the catalyst to achieve two tasks: (1) reduction of 50% of the NO to NH_3 and (2) oxidation of 25% of the NO to NO_2. Note, however, that additional NO_2 may be reduced to NO in the process of converting NO_2 with an organic reductant to NH_3, as has been found with acetaldehyde.

4. NO_x reduction with methane over Pd/MFI or Co/MFI

Among the zeolite-based catalysts that are active with hydrocarbons, one sub-group also works with methane as the sole reductant. Some of these have cobalt and/or palladium in their cavities [62], others consist of zeolite-supported gallium [63–66], indium [67,68] or silver [69]. In the context of the present paper, Co/FER and Co/MFI catalysts are of interest because they are amenable to certain physical methods to identify adsorption complexes for which other materials, including Cu/ZSM-5 and Fe/MFI are less suitable. This chapter will, therefore, focus on Co/MFI and Pd/MFI.

The Co^{2+} ion has seven *d* electrons, distributed over five orbitals. Two configurations are:

(1) The "*high spin*" state with four paired electrons, occupying two orbitals, and three unpaired electrons each in a different orbital.
(2) The "*low spin*" state with six paired electrons occupying three orbitals and one unpaired electron in a different orbital.

Which of these states is preferred energetically depends on the ligands to the Co^{2+} ion. With ammonia the Co^{2+} tetra-ammine ion is stable in the *low spin* configuration. If a zeolite with Co^{2+} ions in its cavities is exposed to ammonia, the Co^{2+} ions are present in that configuration, as evidenced by a sharp ESR signal. When such material is exposed to O_2 at 77 K, the signal disappears completely, showing that all Co^{2+} ions have lost their unpaired electron and become diamagnetic Co^{3+} ions [70]. The electron donated by the Co^{2+} ion is captured by the adsorbed O_2 molecules, which thus become superoxide ions, O_2^-. Inspection of the ESR signal of this species shows that there are eight wobbles superimposed to the signal. This *super hyper fine structure* reflects the interaction of the unpaired electron at the superoxide ion with the nuclear spin of 7/2 on the cobalt nucleus. This shows that the O_2^- ion is directly ligated to the Co^{3+} ions. ESR data indicating formation of O_2^- ions from O_2 have also been reported for Fe/MFI [71] and V/MFI-22 [72].

Superoxide ions have been implicated by Lobree et al. in the formation of nitrate ions on transition metal/zeolites [73]. Gao et al. [54] report for Fe/MFI that formation of nitrate ions from $NO+O_2$ depends on the order how these gases are contacted with the catalyst. The IR band of the nitrate ion was easily observed upon first exposing the catalyst to O_2, followed by exposure to NO, but hardly when the inverse sequence was used. Clearly, admitting O_2 first will favor the formation of superoxide ions that react subsequently with an impinging NO molecule:

$$O_2^- + NO \Rightarrow NO_3^- \tag{8}$$

If the NO is adsorbed first, it will occupy the ligand positions at the metal ion so that subsequent admission to O_2 will not result in ready formation of superoxide or nitrate ions along this route. The superoxide route is accessible also to other catalysts exposing transition metal ions. In addition to this chemistry, the formation of peroxide ions has been observed by UV Raman spectroscopy on Fe/MFI [74]and Co/MFI [75].

The efficiency of Co ions to act as active sites also depends on their positions in the zeolite cavities, as shown by Wichterlová and coworkers [76]. Catalysts can therefore, be improved by shifting Co ions from their original positions to places of highest efficiency. In some cases, this can be achieved by simple hydrothermal treatments [77].

As mentioned, Co/MFI and Pd/MFI catalyze the reduction of NO_x with CH_4, whereas Fe/MFI is inactive for NO_x reduction with methane. As this might qualify the former materials as catalysts for the cleaning of the emission from power plants, it is of interest to find the cause of this remarkable difference between otherwise rather similar catalysts. A possible clue came from TPR data of these catalysts. This method showed that in Fe/MFI catalysts the redox couple is Fe^{3+}/Fe^{2+} [78]. With Cu/MFI the couple Cu^{2+}/Cu^+ is responsible for the oxidation of NO to NO_2 [79]. However, analysis of the TPR data of Co/MFI shows that Co^{2+} is reduced to Co^0; no Co^{3+} or Co^+ appears to be operative [80,81]. In this respect, Co is similar to Pd, where the relevant redox couple is obviously Pd^{2+}/Pd^0. This finding led to the question, whether the metallic state of Co^0 or Pd^0 is responsible for the propensity of these elements to activate methane. It is well-known that methane is dissociatively chemisorbed at the surface of a transition metal such as Pd^0 or Co^0 [82].

When considering this hypothesis, keep in mind that the oxidation state of surface atoms in the steady-state of a catalytic reaction inside a flow reactor is given by the *dynamic* equilibrium of reaction steps in which surface atoms are reduced and re-oxidized by interaction with gas molecules. This dynamic equilibrium can differ from the *thermodynamic* equilibrium to which Gibbs' phase law applies. Reduced and oxidized states can coexist as solid (nano-) particles, although some of them would not be stable in the equilibrium defined by the phase law.

Although, many physical methods exist which permit the identification of metallic particles, it is not easy to apply them to the steady-state of a dynamic reaction inside a microflow reactor. The relatively high concentration of O_2 and the high oxidizing power of NO_2 will keep the steady-state concentration of Pd^0 nano-particles low. Fortunately, chemical and catalytic methods exist that are capable of detecting the presence of Pd_n^0 clusters. One of them is based on the propensity of transition metals to catalyze the H/D exchange in hydrocarbons including methane. An attempt was therefore made to detect the presence of Pd^0 clusters by adding some D_2 to the feed of NO, O_2 and CH_4. It was expected that most of this D_2 would be oxidized to D_2O, but if part of it would show up as deuteromethanes CH_3D, CH_2D_2 and/or CHD_3, this would be evidence, that indeed some Pd_n^0 clusters were present in the steady-state. The work is described in more detail in [83], the relevant result is depicted in Fig. 4. In the same paper it was also demonstrated that no H/D ex-

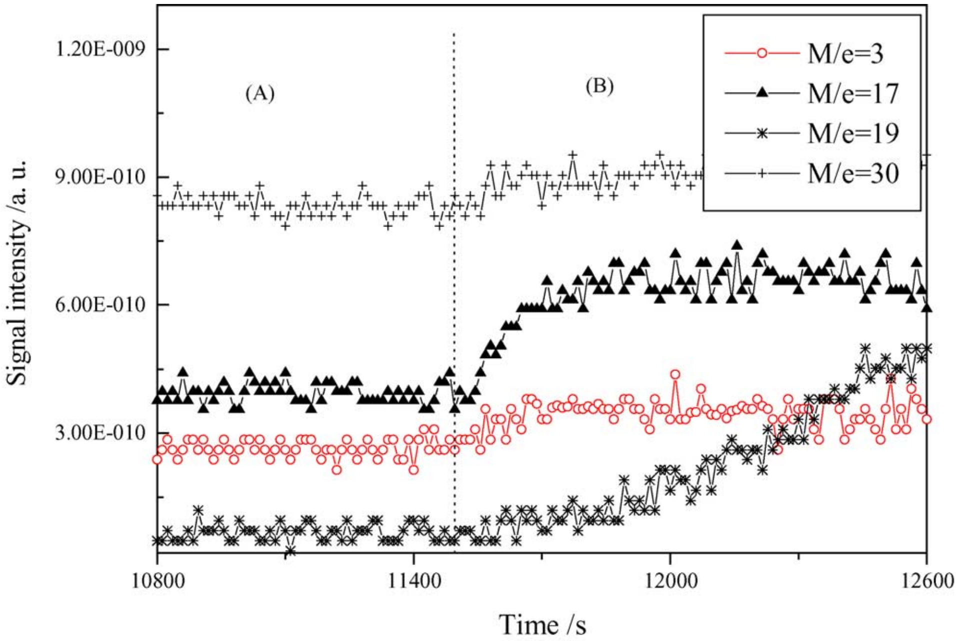

Fig. 4. Effect of introducing 1000 ppm of D_2 (at time B) into NO-CH_4-O_2 feed after steady-state was obtained at 400 °C and GHSV = 90,000 h^{-1} over a Pd/MFI catalyst. NO: 1000 ppm, CH_4: 2000 ppm, O_2: 2%, $P = 1$ atm. (Reproduced from J. Catal. 204, 314 (2001) with permission.)

change can be observed those zeolite-based catalysts that do not catalyze NO_x reduction with methane [84]. These results indicate that $Pd_n{}^0$ particles are a likely cause of the ability of Pd/zeolite catalysts to activate methane.

5. NO_x reduction with acetaldehyde over BaNaY

Most catalytic oxidation and reduction processes in the chemical industry make use of the propensity of transition metal elements to change their oxidation state rather easily. The so called *Mars-van Krevelen mechanism* describes the underlying chemistry [85]. It is quite remarkable that the reduction of NO_x with acetaldehyde over Ba,NaY catalysts does not follow this route. Though, traces of Fe are present in all commercial Y zeolites, the inactivity of these catalysts for the oxidation of CO to CO_2 at a temperature which suffices to reduce NO_x to N_2, suggests that any Fe traces inside the zeolite framework do not play an active part in the conversion of NO_x over BaNaY, unless the material has been subjected to the severe conditions which destroys part of the zeolite lattice. If part of the Na^+ ions in NaY are exchanged against Ba^{2+} ions the activity of the catalysts is markedly increased, which justifies the assumption that the Ba^{2+} ions play an important role.

Reactions which is efficiently catalyzed by Ba,NaY are the aldol condensation:

$$2CH_3CHO \Rightarrow CH_3CH(OH)CH_2CHO \tag{9}$$

and the dehydration of aldol to crotonaldehyde:

$$CH_3CH(OH)CH_2CHO \Rightarrow CH_3CH = CHCHO + H_2O \tag{10}$$

However, this reaction is not responsible for the reduction of NO_x over these catalysts. On the contrary, crotonaldehyde easily polymerizes in the pores of the zeolite and blocks the active sites for the desired reaction. In the presence of water vapor the equilibrium (10) is shifted to the left. This is a likely explanation, why for these catalysts water has a positive effect on NO_x reduction, even though it competes with ammonia for the same sites. Wen et al. showed that at 200 °C the conversion of NO_x is quite weak in the absence, but strong in the presence of water vapor [86]. Another relevant finding is that also with BaNaY catalysts N_2 is formed with low activation energy from ammonium nitrite, whereas a much higher temperature is required to decompose ammonium nitrate. In one favorable reaction path over BaNaY, part of the NO_x has to be reduced to ammonia, which reacts subsequently with $NO + NO_2$ to $N_2 + H_2O$ in basically the same way as shown above for other zeolite-based catalysts.

The mechanism of NO_x reduction to NH_3 over a Y zeolite having Na^+ and Ba^{2+} ions in its cages, has been the subject of recent research at Northwestern University; the results have been published [87]. The high electric field inside cavities of the Y zeolite strongly favors formation of charged moieties. This is evident from the heterolytic dissociation of N_2O_4, the dimer of NO_2, on BaNaY. FT-IR reveals predominant chemisorption as $NO^+ + NO_3{}^-$. The nitrate ions are ligated to Ba^{2+} ions, their positive 2+ charge is thus dissipated into two 1+ charges:

$$Ba^{2+} + N_2O_4\,(\text{gas}) \Rightarrow [Ba\text{–}NO_3]^+ + NO^+ \tag{11}$$

This process will lower the Coulomb energy of the system by enabling each of the two carriers of a positive charge to find a location near the locus of the negative charge which, in a zeolite, is the fixed position of an immobile Al-centered tetrahedron.

Upon exposing BaNaY inside an FT-IR cell at 200 °C to a gas mixture of acetaldehyde, nitric oxide and oxygen, initial chemisorption is followed by a chemical reaction. The acetaldehyde bands gradually disappear, while new bands emerge. Acetaldehyde is oxidized to acetic acid, evidenced by bands at 1392, 1551, 1628 and 1689 cm^{-1}. Simultaneously bands of gaseous formaldehyde become visible. If the NO that is formed by

$$CH_3(C{=}O)H + NO_2 \rightarrow CH_3(C{=}O)OH + NO \qquad (12)$$

is re-oxidized to NO_2 in an excess of O_2, this cycle will be repeated until all acetaldehyde is oxidized to acetic acid which is chemisorbed dissociatively as an acetate ion and a proton. A following step is the replacement of the carboxylate group by NO_2, i.e. the aci form of nitromethane, CH_3NO_2, is formed.

Earlier Cant [88] proposed that nitromethane could be an important intermediate in NO_x reduction with methane over Co/MFI catalysts, because nitromethane can be dehydrated to isocyanic acid, HNCO, which can be converted further to ammonia. Zazaniuk et al. [89] and Hu et al. [90], have shown that nitromethane isomerizes in the gas phase, first to its aci-form, then to formohydroxamic acid which easily loses water and forms HNCO. This is an essential chemistry in the cascade of NO_2 reduction to NH_3. In addition, the FT-IR work with BaNaY shows that on this zeolite the reaction path is more complicated, as it was found that the rate of HNCO formation is strongly enhanced by NO_2. Analysis of this observation by FT-IR shows that NO_2 reacts with the aci-anion of nitromethane, forming the anion $O_2NCH_2NO_2{}^-$. At 200 °C this anion decomposes possibly to the fulminate anion, CNO^-

$$O_2NCH_2NO_2{}^- \Rightarrow NO_2 + H_2O + CNO^- \qquad (13)$$

which isomerizes to the cyanate ion, NCO^- and reacts with a proton to form isocyanic acid, HNCO. As mentioned above, Poignant et al. had suggested in 1995 that isocyanates are likely intermediates in NO_2 reduction. Over the BaNaY catalyst HNCO formation is followed by its hydrolysis:

$$HNCO + H_2O = NH_3 + CO_2 \qquad (14)$$

This multi-step process is completed by the uncatalyzed reaction of the ammonia with $N_2O_3 + H_2O$ to ammonium nitrite and its decomposition to $N_2 + H_2O$. The reaction cascade from acetaldehyde to ammonia is summarized by:

$$\begin{aligned} CH_3CHO &\Rightarrow CH_3COO^- \Rightarrow CH_2NO_2{}^- \Rightarrow O_2NCH_2NO_2{}^- \\ &\Rightarrow NCO^- \Rightarrow HNCO \Rightarrow NH_3 \qquad (15) \end{aligned}$$

Although, each of these steps is well documented by spectroscopic data, there still is a problem: summation of the steps, as written, leads to an overall process in which both carbon atoms of acetaldehyde end up as CO_2, but gas analysis shows formation of considerable amounts of CO. This is tentatively attributed to a second parallel path starting with H abstraction from acetaldehyde, aldol or croton aldehyde. If indeed acetyl radicals are formed, they can decompose to CO and a methyl radical. This hypothesis is now under investigation.

6. Conclusion

Transition metal ions inside zeolite cavities are instrumental, but not indispensable for the catalytic reduction of NO_x to N_2. The reaction mechanism depends on the catalyst and the reductant. An element of commonality for NO_x reduction over a variety of catalysts is that N_2 is produced by chemical interaction of one group containing nitrogen in an oxidation state N^{3+} with another group with nitrogen in a N^{3-} state. The prototype for this chemistry is the formation and decomposition of ammonium nitrite. To obtain such groups, part of NO must be oxidized to NO_2 and the catalyst has to provide a path for the reduction of 50% of the NO_x to ammonia or an amine. Over catalysts such as Fe/MFI, Co/MFI or Pd/MFI the transition metals in the catalyst play a crucial role in this reduction to NH_3. In the case of Co/MFI and Pd/MFI there are indications that small amounts of Pd^0 or Co^0 exist in the dynamic equilibrium and promote dissociative chemisorption of methane.

With catalysts such as BaNaY which do not contain a transition metal, a reaction path exists which converts acetaldehyde and NO_2 to nitromethane. This intermediate is transformed to isocyanic acid via a reaction using the aci-form of nitromethane and an anion with two nitro groups attached to the same carbon atom. Hydrolysis of isocyanic acid leads to ammonia and CO_2. The ammonia reduces NO_x, for instance by forming ammonium nitrite which decomposes to N_2. The total process of NO_x conversion to N_2 has a high rate at temperatures as low as 200 °C.

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