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An overview of the mechanisms of NO_x reduction with oxygenates over zeolite and γ-Al_2O_3 catalysts

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Abstract

The selective reduction of NO_x with added oxygenates over BaNa/Y and Ag/Y zeolites and Ag/γ-Al_2O_3 takes place via complex reaction pathways with a number of common crucial intermediates. Acetate ions are formed by the oxidation of acetaldehyde over these catalysts. These acetate ions react with NO_2 to form nitromethane which decomposes to HNCO via a dinitro-C_1 intermediate. HNCO hydrolyzes to form NH_3 which can react with HONO to form ammonium nitrite. This NH_4NO_2 efficiently decomposes to N_2 and H_2O at 100 °C, and at even lower temperatures in an acidic environment. The neutral surface species are expected to be in equilibrium with their ions. The rate-limiting step in these reaction sequences is the reaction of acetate ions to form nitromethane. When nitromethane is directly added to a NO_x stream over Ag/Y, ~100% conversion of NO_x to N_2 is achieved at temperatures as low as 140 °C. In such schemes, NO acts as a reductant of nitrate ions, ammonium nitrate and nitric acid. The benefits of isotopically labeled compounds in the elucidation of such reaction mechanisms and for providing insights into reaction dynamics are also discussed.

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1. Introduction

In industrialized countries, regulations limit emissions of toxic nitrogen oxides, carbon monoxide and unconverted hydrocarbons from automotive internal combustion engines. Worldwide, the introduction of catalytic converters, which detoxify the tail gas from gasoline-fired internal combustion engines, has markedly improved the quality of air in cities. Recent legislation in Europe and the U.S. places more stringent regulations on the emissions from vehicles powered by *diesel* engines. This remediation will require novel catalysts, since the traditional ‘‘*three way catalyst*’’ used for internal combustion (or ‘‘Otto’’) engines is unable to efficiently clean the tail gas from diesel engines. Diesel emissions contain several percent of O_2, but almost no reducing gas; moreover, the temperature of diesel emissions is much lower (~200 °C) than that of the tail gas from Otto engines. The requirements for the catalytic abatement of nitrogen oxides from diesel emissions, therefore, differ significantly from those for Otto engines in two important respects:

(1) the catalyst has to be *more active* and
(2) A *reductant* has to be provided.

Moreover, a catalyst for ‘‘cleaning’’ diesel tail gas also has to be *highly selective*, directing the added reducing agent(s) towards NO_x (present as a few hundred ppm) rather than O_2 (present as several %). The catalyst must also be active in the presence of water vapor, and direct NO_x reduction to the desired products: N_2 and H_2O. The reduction of NO_x is known to include a number of steps. With many catalysts of practical interest the final step is the formation of N_2 by decomposition of ammonium nitrite [1–3]:

$$NH_4NO_2 \Rightarrow N_2 + 2H_2O \tag{1}$$

Decomposition of NH_4NO_2 occurs efficiently at 100 °C, and at even lower temperature in an acidic environment [3]. Formation of ammonium nitrite takes place in the presence of ammonia

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which acts as a reductant. Three basic strategies have been described to provide this reductant:

(a) Ammonia injection (e.g. by decomposing urea present in a urea/water slurry) into the tail gas.
(b) Reduction of NO_x that has been trapped on an oxide surface as nitrates, to ammonia by intermittent exposure to a reducing gas.
(c) Injection of a convenient reductant in combination with a selective catalyst that will reduce ~50% of the NO_x to NH_3. This ammonia then acts as a reductant for the remaining NO_x.

While the present paper focuses on issues and data directly related to strategy (c), it also provides data that are of relevance to strategies (a) and (b).

In previous publications we and others have shown why zeolite-based catalysts, such as BaNa/Y, are promising for NO_x reduction [1,4]. Though information on the molecular level details of the mechanisms for the selective catalytic reduction of NO_x is still sparse, the amount of information in this area in the literature is growing; both in terms of the systems considered and the extent of mechanistic detail [1–11].

For example, we have shown that NO_x reduction over BaNa/Y, can take place via two *parallel* routes, one involving free radicals, the other ionic adsorbates in equilibrium with the neutral parent molecules. With acetaldehyde as the primary reductant, the reaction intermediates include *nitromethane, dinitro-methane, formo-hydroxamic acid, isocyanic acid, ammonia, and ammonium nitrite* [1]. Previously published studies have focused on the reaction mechanism for individual systems. Specifically, we have studied the reaction mechanisms that are operative for NO_x reduction over Ag/γ-Al_2O_3, BaNa/Y and Ag/Y zeolites [1,6,7].

The present paper takes a broader view of the operative mechanistic issues than prior publications on the aforementioned systems. The present work focuses on comparisons between the mechanisms and kinetics that are operative in these different systems. Such comparisons serve to highlight similarities and differences of the deNOx chemistry. A comparison of data from these systems allows identification of the rate-limiting step for deNOx chemistry. Once the rate-limiting step is identified an intermediate formed subsequent to this step, nitromethane, is an obvious choice as a reductant. The efficacy of nitromethane as a reductant has been validated by direct testing—nitromethane is an excellent low temperature NO_x reductant, with an efficiency approaching 100% at temperatures as low as 140 °C. We also discuss results on the ability of NO to reduce a variety of relatively undesirable nitrates in NO_x streams to more chemically reactive, and thus more desirable, nitrites.

2. Experimental

The apparatus and experimental approach have been described in detail in recent publications [1,7]. Briefly, catalyst samples were studied by transmission mode infrared spectroscopy using a homemade static cell. Some experiments employed time resolved IR spectroscopy in a rapid scan mode. Since the zeolite and alumina samples are highly scattering powders, a very thin sample was used for transmission spectroscopy. However, it is extremely difficult to form a pellet of such material that is simultaneously self-supporting and thin enough for transmission IR studies. Our samples are prepared by ‘‘painting’’ a thin layer of sample from a slurry onto a heated tungsten wire grid clamped between two nickel jaws. The temperature controlled grid, which is highly transmissive, acts as a ‘‘scaffold’’ to support the very thin film of catalyst and allow for transmission IR studies. The catalytic activity of the samples was also probed with a temperature controlled micro flow reactor which is described in more detail in references [1,5,8].

3. Basic catalytic chemistry

Many strategies for low temperature NO_x abatement have in common that NO_x is converted to ammonium nitrite; a compound that was shown by Millon, 160 years ago [12], to readily and efficiently decompose to N_2 and H_2O at low temperature. In 1931, Abel et al. [13] showed that in the presence of a mineral acid, decomposition of ammonium nitrite even takes place at room temperature. As strong acids will liberate nitrite anions from ammonium nitrite, Abel et al. describe the observed kinetics at 25 °C by Eq. (2).

$$d(N_2)/dt = k[NH_4{}^+][NO_2{}^-][HNO_2] \quad (2)$$

Since mineral acids will protonate ammonium nitrite, it is plausible that reaction (1) actually proceeds in two steps with protonated nitrosamine $[H_2NNOH]^+$ being an intermediate. As Abel et al. studied aqueous solutions, we determined the temperature dependence of the decomposition of ammonium nitrite (reaction (1)) for solids by impregnating quartz powder or an active BaNa/Y catalyst with ammonium nitrite and recording the temperature-programmed decomposition of ammonium nitrite on either support [2]. Our data show that on these supports (in the absence of a strong acid), decomposition to $N_2 + H_2O$ takes place near 100 °C. To examine the effect of solid acids, we studied physical mixtures that consisted of the acid zeolite, HY with ammonium nitrite covered BaNa/Y powder [3]. We found that after 13 h at 25 °C, >80% of the NH_4NO_2 decomposed to $N_2 + H_2O$. This shows that surface diffusion of acid protons and/or ammonium nitrite suffices to enable the solid acid-catalyzed reaction (1) to occur at low temperature [3].

Thus, production and decomposition of ammonium nitrite add up to a potential route to N_2 formation. One strategy for production of ammonium nitrite is the addition of ammonia to a NO_x stream. Our prior data demonstrate that one N atom in the N_2 produced in such a scheme comes from NH_3 and the other from NO_x [14]. *In situ* conversion of nitrogen oxides with ammonia is optimized when NO, NO_2 and NH_3 are present in a 1:1:2 ratio enabling the stoichiometric reaction [5]:

$$NO + NO_2 + 2NH_3 + H_2O = 2NH_4NO_2. \quad (3)$$

Water is always present in diesel exhaust, but, in general, an exhaust gas flow interacting with a catalyst will not have the stoichiometry of reaction (3). Additional reactions therefore become important to convert the actual exhaust gas into the optimum mixture for reaction (3). For example, in practical applications some NO, which is normally in excess, may have to be converted to NO_2.

As using aqueous urea to feed ammonia into exhaust streams (a proposed scheme for on-board NH_3 production) has some drawbacks for motor vehicles, the present paper focuses on catalysts which are able to produce the ammonia required for reaction (3) *in situ* from NO_x and an appropriate reductant. In a diesel-fueled vehicle this reductant could be injected into the gas emitted by the engine. The desirability of an equimolar ratio of NO:NO_2 and the role of NO in the overall reaction mechanism, which until recently was not widely appreciated [5], will be discussed in Section 4.

An important issue in NO_x SCR is the nature of the species formed on the catalyst upon exposure to a NO_x stream. Decomposition and/or reaction products can potentially block catalytically active sites. Our data [5] show that, in particular, nitrates are potential "catalyst poisons", but they can be efficiently reduced to nitrites by NO:

$$[NO_3{}^-]_{ads} + NO_{gas} \rightarrow [NO_2{}^-]_{ads} + NO_{2,gas} \tag{4}$$

For the catalysis under investigation, this is crucial, because chemisorbed $NO_3{}^-$ ions, which can be produced from dissociative chemisorption of N_2O_4 (reaction (5)), could block the surface sites required to catalyze reaction (1).

$$N_2O_4 \rightarrow NO_3{}^- + NO^+ \tag{5}$$

N_2O_4 is formed via dimerization of NO_2. The formation of $NO_3{}^-$ upon exposure of a BaNa/Y zeolite to NO_2 is shown in Fig. 1. It also takes place on Ag/Y and Ag/γ-Al_2O_3 [6,7]. The counter ion in reaction (5), NO^+, has also been observed on BaNa/Y [1] and studied previously on related zeolites [15]. Subsequent to production by (4), $NO_2{}^-$ can combine with NH_3 and H^+ that is present to yield NH_4NO_2. Thus, reaction (4) converts a potential "*catalyst poison*" into a desired reaction intermediate. Below we will present data of relevance to these and other reactions of NO.

4. NO as a reducing agent

Ammonia has been shown to be an efficient reductant for NO_x. In fact, in the systems we have studied, the added organic reductant provides a pathway for the *in situ* production of ammonia. As discussed below and elsewhere [5], both HONO and HNO_3 are expected to be present in realistic NO_x systems, which will contain water. Reaction of nitrous acid with NH_3 leads to the formation of thermally labile ammonium nitrite, whereas reaction of NH_3 with nitric acid leads to the formation of thermally more stable ammonium nitrate.

In prior work, we found that NO is an efficient reductant for nitric acid and surface nitrates [5]. Our studies of the reduction of NO_x with ammonia led to the reaction mechanism summarized in Scheme 1 (reproduced with permission from Ref. [5]). This mechanism contains two major branches. In the branch on the left, NO^+, produced in reaction (5), reacts with water to form HONO. Data showing that NO^+ and $NO_3{}^-$ ions form on a BaNa/Y zeolite surface simply by exposure of that surface to NO_2 are shown in Fig. 1. NO^+ is quite stable in the absence of water: at 200 °C the NO^+ absorption has been observed for up to 3 h [1]. However, NO^+ rapidly reacts with water to form HONO and H^+, thus acting as a source for nitrous acid. This reaction also produces OH groups whose infrared absorption bands can be seen in Fig. 1. The HONO that is formed can then react with NH_3 to give NH_4NO_2. The chemistry detailed in reaction (1) then prevails. The right hand branch of the scheme is more complex and deals principally with the fate of $NO_3{}^-$, which can react with a proton to form nitric acid (HNO_3), which can then react with ammonia to form ammonium nitrate.

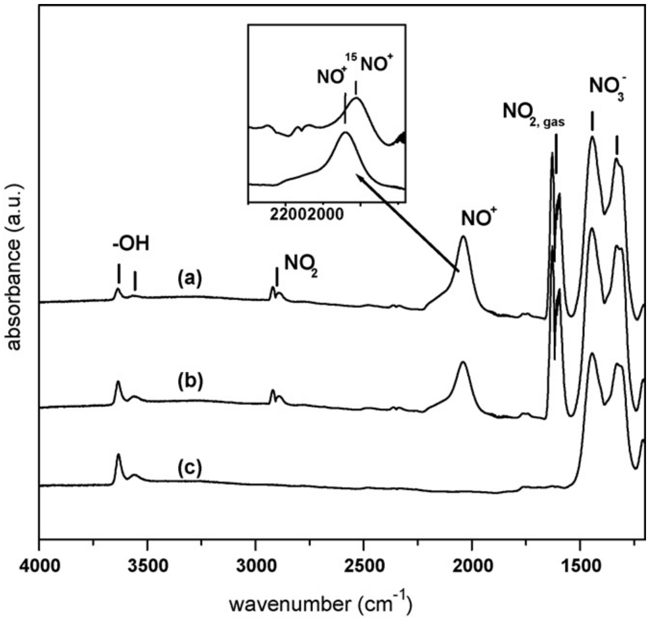
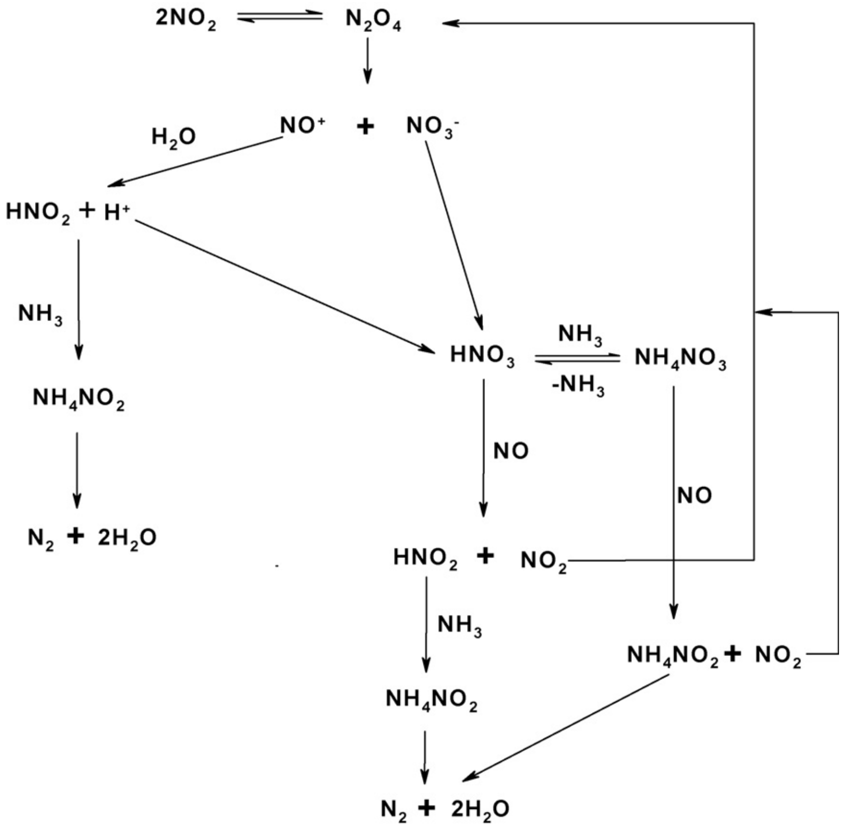


Fig. 1. Infrared spectra taken after BaNa/Y was exposed to NO_2 (introduced as a mixture of NO + O_2) at 200 °C. (a) after 1 min, (b) after 3 min, (c) after 9 min and subsequent to evacuation of IR cell. The insert is an expansion of the region in which the absorption due to NO^+ is observed. The top trace is a spectrum taken exposure of Ba/Y was exposed to a mixture of $^{15}NO + O_2$ at 200 °C.

As indicated in Scheme 1, our data demonstrate that NO reduces HNO_3 to HONO [5] which can then react with NH_3, thus providing another reaction path to NH_4NO_2. Similarly, NO reduces surface nitrates to surface nitrites which are generally more thermally labile and thus less likely to act as a "poison" for the operative catalysts [5]. Finally, we have recently shown that NO can also efficiently reduce ammonium nitrate under acidic conditions [16]. The chemical nature of the catalyst surface affects the efficiency of and temperature at which this acid catalyzed reaction takes place. Unsupported solid NH_4NO_3 is not appreciably reduced by contact with NO below its melting point of 170 °C, but when NH_4NO_3 is supported on an even mildly acidic material, such as BaNa/Y, H–Y, or quartz, reduction of NH_4NO_3 by NO is easily detectable at ~100 °C. Data showing a comparison of the



Scheme 1. This Scheme is reproduced by permission from: Journal of Catalysis 231, Y.H. Yeom, J. Henao, M.J. Li, W.M.H. Sachtler and E. Weitz "The role of NO in the mechanism of NO_x reduction with ammonia over a BaNa-Y catalyst", 181–193, copyright 2005, Elsevier Inc.

temperature dependence of the reduction of ammonium nitrate on BaNa/Y versus neat ammonium nitrate is shown in Fig. 2. It is clear that the presence of BaNa/Y lowers the temperature at which reduction takes place. The mechanism involved in the reduction of NH_4NO_3 by NO is treated in more detail in Ref. [16], which includes a discussion of the role of acid sites in the reduction of ammonium nitrate. However, the proposed mechanism can be summarized as follows: NH_4NO_3 is in dissociative equilibrium with NH_3 and HNO_3 [9,17,18]. Brønsted and Lewis acid sites reversibly bind NH_3 to form NH_4^+ (or NH_3A^+) [16]; thereby "freeing up" HNO_3 to be reduced by NO to HNO_2 [5,9] thus providing an indirect path, via the equilibrium indicated in Scheme 1, for NH_4NO_3 to be reduced by NO at 100 °C in the presence of acids. Finally, the reversible binding of NH_3 to acid sites allows NH_3 to leave and recombine with HNO_2 to form NH_4NO_2, which readily decomposes to N_2 and H_2O at ~100 °C [3]. Thus, we conclude that below its melting point the dominant mechanism for NH_4NO_3 reduction by NO is via the equilibrium, shown in Scheme 1, between NH_4NO_3 and HNO_3. However, above the melting point, we cannot exclude direct reduction of NH_4NO_3 by NO. This direct reduction channel is shown in Scheme 1.

As discussed in Ref. [5], the optimal NO:NO_2:NH_3 ratio of 1:1:2 for the deNOx chemistry with ammonia is consistent with the role of NO as a reductant. Deviation from the 1:1, NO:NO_2 ratio results in less efficient NO_x reduction. Thus, NO is an efficient and important reductant in deNOx chemistry. Its reductive ability acts to "channel" the reaction mechanism depicted in Scheme 1 along branches that lead to more efficient production of N_2 instead of potential catalyst "poisons".

5. *In situ* production of ammonia from NO_x and the SCR mechanism

5.1. The SCR mechanism

Since, as indicated above, ammonia is an efficient and selective reductant for NO_x, one strategy for NO_x SCR is the *in-*

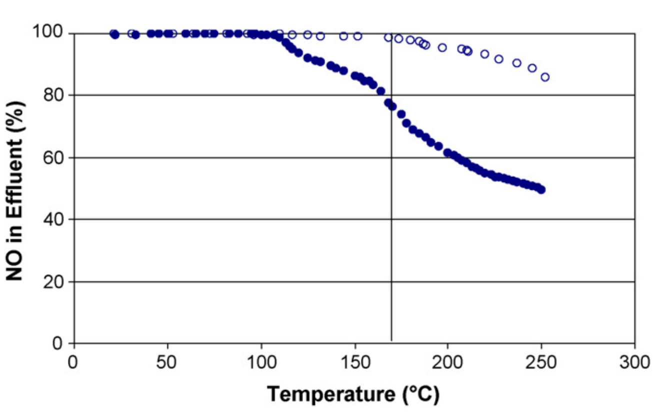


Fig. 2. Depletion of NO when NO is flowed over 0.2 g ground NH_4NO_3 (open circles) and 0.2 g ground NH_4NO_3 physically mixed with 0.15 g BaNa–Y (filled circles). The melting point of NH_4NO_3 (170 °C) is designated by a vertical line. Flow rate is 16.8 cm^3/min of a mixture of 2% NO in He.

situ production of ammonia by reduction with an appropriate organic molecule. Previously we had shown that over a BaNa/Y, Ag/Y and Ag/γ-Al_2O_3 catalysts acetaldehyde is readily oxidized to acetate ions, which are subsequently converted to nitromethane [1,6,7]. These data imply that a di-substituted C_1 intermediate is formed in this reaction network. We have explained the acceleration of the rate of reaction of nitromethane in the presence of NO_2 [1,8] in terms of the sequence:

$$CH_3COO^-{}_{(ads)} \rightleftarrows [CH_2{=}CO_2{}^-{}_{(ads)}] + H \qquad (6)$$

This hydrogen atom abstraction could be facilitated by interaction of surface acetate with NO_2, which would be followed by

$$[CH_2 = CO_{2(ads)}{}^-] + NO_2 \rightleftarrows [O_2N{-}CH_2{-}CO_2{}^-] \qquad (7)$$

and then by

$$[O_2N{-}CH_2{-}CO_2{}^-] \rightarrow CO_2 + [O_2N{-}CH_2{}^-] \qquad (8)$$

followed by

$$[O_2N{-}CH_2{}^-] + H^+ \rightarrow CH_3NO_2, \qquad (9)$$

where $CH_2{=}CO_2{}^-$, $O_2N{-}CH_2{}^-$ and $O_2N{-}CH_2{-}CO_2{}^-$ are proposed intermediates.

Nitromethane can also be formed along a parallel route from acetaldehyde and NO_2, initiated by formation of an acetyl radical:

$$CH_3CHO + {}^{\bullet}NO_2 \rightarrow HONO + {}^{\bullet}CH_3CO$$

$$^{\bullet}CH_3CO + {}^{\bullet}NO_2 \rightarrow CO + CH_3NO_2$$

Evidence for a second parallel channel involving radical intermediates comes from a comparison of the chemistry that takes place with acetaldehyde and acetic acid as reductants [1].

Acetic acid forms surface acetate on contact with a variety of surfaces including BaNa/Y. The subsequent chemistry attributed to the ionic channel on BaNa/Y is identical with acetaldehyde and acetic acid as reductants. As expected, significant carbon dioxide formation is observed with acetic acid. Timing of the formation and isotopic labeling indicate that there are two primary steps for CO_2 formation: (1) the displacement of CO_2 by reaction of surface acetate with NO_2, as shown in reaction (8), and (2) the formation of CO_2 on hydrolysis of HNCO, which is accompanied by ammonia formation via the reaction:

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad (10)$$

As discussed below, and in reaction (11), HNCO is a product of the reaction of nitromethane and NO_2.

With acetaldehyde as the reductant (but not with acetic acid) other products, including a significant amount of CO and methanol are observed. We have also shown that CO is not significantly oxidized to CO_2 over BaNa/Y under reaction conditions [1]. Fig. 3 presents data showing the formation of CO and methanol over BaNa/Y with acetaldehyde as a reductant. Formaldehyde is also a likely product. These products are attributed to the parallel radical reaction channel. A plausible mechanism that is consistent with formation of methanol along with considerable CO formation is shown in Scheme 2. This mechanism also leads to the formation of nitromethane. Based on the observation of significant CO there is evidence for a parallel radical pathway with Ag/Y and Ag/Al_2O_3 as catalysts with acetaldehyde or ethanol as a reductant [6,7].

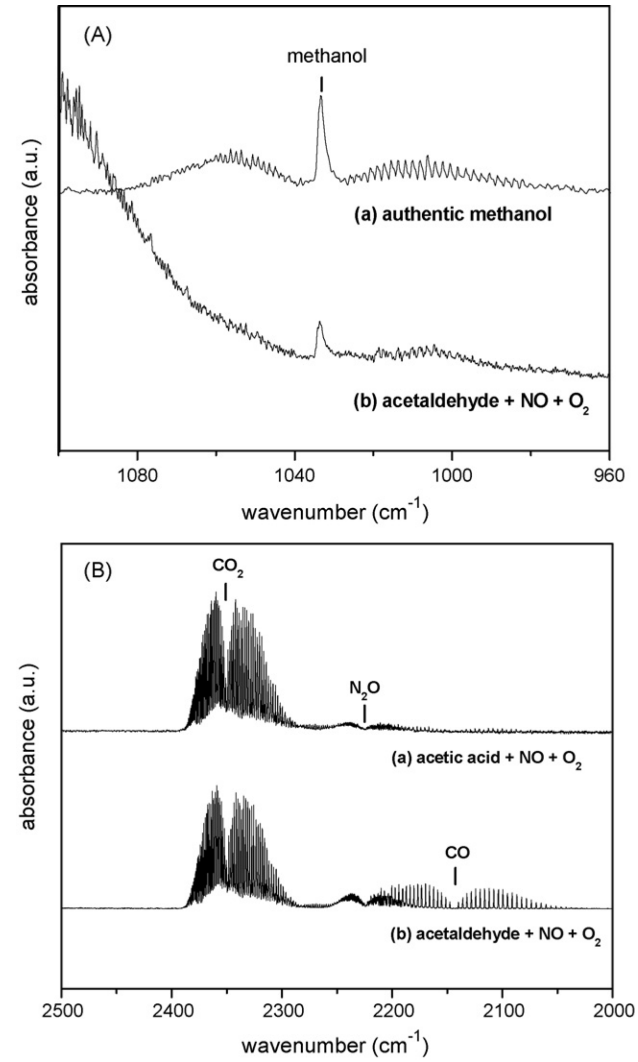
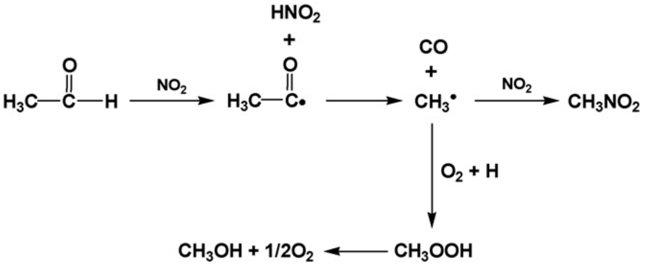


Fig. 3. Panel A: (a) The spectrum was taken after introduction of gas phase methanol into a IR cell. (b) Gas phase spectrum was obtained after BaNa/Y was exposed to a mixture of acetaldehyde + NO + O_2 at 270 °C. Panel B: (a) A gas phase spectrum was recorded after BaNa/Y was exposed to acetic acid + NO + O_2 at 200 °C. (b) A gas phase spectrum was recorded after BaNa/Y was exposed to acetaldehyde + NO + O_2 at 200 °C.

Nitromethane, once formed by either the ionic or radical pathways in any of the aforementioned systems, can then react with NO_2:

$$CH_3NO_2 + NO_2 \rightarrow HNCO + H_2O + NO_2 \qquad (11)$$

As evidenced by the results of experiments using $^{15}NO_2$, this reaction is not simply a NO_2 displacement reaction; rather NO_2 accelerates the reaction of nitromethane leading to formation of HNCO [1,8]. Though nitromethane can decompose on surfaces yielding HNCO under the conditions that have been studied, this reaction is slow relative to the reaction (11) with NO_2



Scheme 2.

concentrations that are representative of meaningful deNOx conditions. Evidence has been presented that reaction (11) proceeds through a symmetric dinitromethane intermediate: $(NO_2)CH_2(NO_2)$, which is likely in equilibrium with its aci anion, with the equilibrium constant dependent on the nature of the catalyst, as the nature of the catalyst affects the ion-catalyst stabilization energy [1].

In the absence of NO_2, nitromethane isomerizes to formo-hydroxamic acid, HCO–N(H)OH. Formo-hydroxamic acid loses water and becomes isocyanic acid:

$$CH_3NO_2 \rightarrow HCO{-}N(H)OH \rightarrow HNCO + H_2O \qquad (12)$$

HNCO can be readily hydrolyzed:

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad (13)$$

The combination of reactions (11) and (13) or (12) and (13) thus produces the ammonia required for reaction (3). Under actual NO_x reduction conditions, the majority of NH_3 must be formed via reactions (11) and (13) rather than reactions (12) and (13). Formation of ammonia allows for reaction with HONO to form ammonium nitrite, which as discussed above provides an efficient low temperature route to N_2.

Adding up reactions (12) and (13) shows that in the overall process nitromethane is efficiently converted to $NH_3 + CO_2$:

$$CH_3NO_2 \rightarrow NH_3 + CO_2 \qquad (14)$$

Combining this with Eqs. (1) and (2) shows that over some catalysts NO_x is efficiently reduced by nitromethane:

$$2CH_3NO_2 + NO + NO_2 \rightarrow 2CO_2 + 2N_2 + 3H_2O \qquad (15)$$

As alluded to above, a pathway that is qualitatively very similar can be followed when ethanol is used as an added reductant over either Ag/γ-Al_2O_3 or Ag/Y zeolite [6,7]. As shown in reaction (16), ethanol can be converted to acetaldehyde by oxidation with O_2.

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O \qquad (16)$$

Once acetaldehyde is formed, the subsequent chemistry follows that seen when acetaldehyde is added as a reductant [7]. However, there is an important difference with ethanol. Ethanol can be oxidized by either O_2 as shown above, or by NO_2. When oxidation by NO_2 is dominant, as we have shown is the case for Ag/γ-Al_2O_3 at temperatures below 300 °C, ethyl nitrite is formed as an intermediate. Ethyl nitrite can dissociate to give acetaldehyde as a product, with the following reaction mechanism proposed in the literature [19].

$$C_2H_5ONO \rightarrow C_2H_5O + NO$$

$$C_2H_5O + NO \rightarrow HNO + CH_3CHO$$

$$2HNO \rightarrow N_2O + H_2O$$

$$C_2H_5O + NOH \rightarrow C_2H_5OH + NO.$$

Ethyl nitrite can also dissociate to give N_2O—an undesirable greenhouse gas which sequesters N_2. Thus, as shown in Fig. 4, it is not surprising that ethyl nitrite is not as efficient a reductant for NO_x as acetaldehyde. Therefore, a key to efficient use of ethanol as a reductant is to identify a system in which ethanol is oxidized to acetaldehyde at low temperature. This can be accomplished with Ag/Y zeolite at ~320 °C. At this temperature ethanol leads to NO_x reduction approaching 80% [6].

In this paper, for simplicity, we have typically written reactions for neutral species unless we intend to emphasize the role of the ionic pathway. However despite differences between the catalytic systems we have studied, *in each of these cases nitromethane and/or its aci-anion is a crucial intermediate* [1,6,7].

Materials that are able to catalyze reaction (8) at a low temperature obviously hold important potential as deNOx catalysts. These considerations lead to a novel perspective and two resulting scenarios for NO_x abatement:

- *Scenario 1*: Nitromethane is produced *in situ* from NO_2 and an added reductant, such as acetaldehyde or ethanol.
- *Scenario 2*: Nitromethane is provided from an external source.

In previous papers we have shown that Scenario 1 described the chemistry of some promising catalyst systems. For example, acetaldehyde is easily oxidized to acetate ions by NO_2 over BaNa/Y catalysts:

$$CH_3CHO_{ads} + NO_2 \rightarrow [CH_3COO]_{ads}^{-} + H_{ads}^{+} + NO \qquad (17)$$

The acetate ions react with the free radical $^{\bullet}NO_2$, forming the acetate radical ion, $[^{\bullet}H_2C{=}CO_2]^{-}$, which reacts with

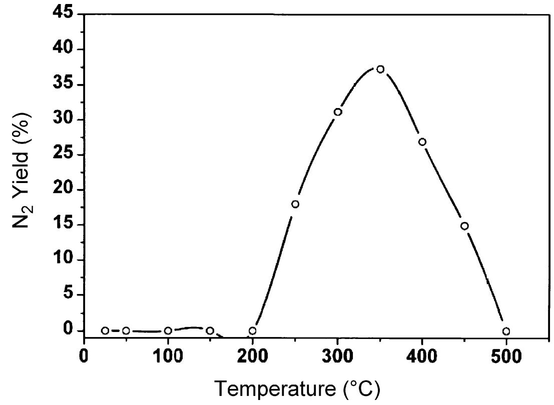


Fig. 4. The N_2 yield as a function of temperature over 0.2 g Ag/γ-Al_2O_3. The mixture contained: 1100 ppm ethyl nitrite, 500 ppm NO_2, 7% O_2, 2% H_2O at a GHSV of 18,000 h^{-1}. The N_2 yield is calculated based on the amount of NO_2 initially present.

another $^{\bullet}NO_2$ molecule forming the ion $[O_2C–CH_2–NO_2]^-$. This intermediate rapidly loses CO_2, becoming the aci ion of nitromethane. This chemistry can be summarized as follows:

$$[CH_3COO]_{ads}^- + 2NO_2 \rightarrow [CH_2NOO]_{ads}^- + HONO + CO_2 \quad (18)$$

This catalysis, producing nitromethane from acetate ions at the catalyst surface and impinging NO_2 molecules, appears quite demanding. Therefore, we report below the results of experiments in which nitromethane was fed directly to the NO_x containing mixture.

If for a given catalyst the *in situ* formation of nitromethane from acetaldehyde is the rate-limiting step, it follows that the formation of N_2 from nitromethane that is directly fed into a NO_x stream will be much faster and observable at a lower temperature. Flow reactor studies support this conclusion. Virtually 100% NO_x reduction can be achieved with nitromethane as an added reductant at temperatures as low as 150 °C over a Ag/Y zeolite catalyst [8]. Interestingly, the NO_x reduction yield is *not* significantly affected when the surface of the zeolite is pre-exposed to an acetate precursor, such as acetic acid, or when the surface sites are occupied by CN^- or NC^- [8]. In contrast, on BaNa/Y, a high coverage of surface acetate inhibits NO_x reduction [1].

Though still speculative and needing further study, these results suggest intriguing and important mechanistic conclusions regarding the microscopic details of the reaction of nitromethane with NO_2 relative to the reaction of NO_2 with surface acetate. The reaction of surface acetate with NO_2 becomes less efficient as the coverage of acetate ions increases, implying that surface sites necessary for the reaction of NO_2 with acetate can be occupied by acetate [1]. This suggests a Langmuir–Hinshelwood mechanism for the reaction of acetate with NO_2. However, surface acetate does not significantly affect the yield of N_2 when nitromethane is the added reductant [8]. This result suggests that the reaction of nitromethane with NO_2 takes place on a different set of sites than is used by strongly bound acetate ions in their reaction with NO_2. Further, since acetate ions appear to block NO_2 adsorption, these results taken together suggest that the reaction of NO_2 with nitromethane takes place via an Eley-Rideal mechanism. Hopefully, further studies will examine these conclusion which if confirmed will provide an even more detailed microscopic view of the overall reaction processes. These results also bring up the question as to whether nitromethane formed in the reaction of acetate with NO_2 migrates to other surface sites or whether there are multiple types of sites on which nitromethane can react. This is another issue for clarification in future studies.

5.2. Rate-limiting step(s)

Efficient NO_x reduction with acetaldehyde to N_2 over BaNa/Y requires a temperature near 200 °C and even higher temperatures over Ag/Y and Ag/γ-Al_2O_3 [6,7]. However, as discussed above and in Refs. [7,8], NO_x reduction to N_2 proceeds with a high rate and a high nitrogen yield at 140 °C, *when nitromethane is used as the primary reductant*. Interestingly, the temperature at which NO_x reduction is initiated in the systems delineated above qualitatively correlates

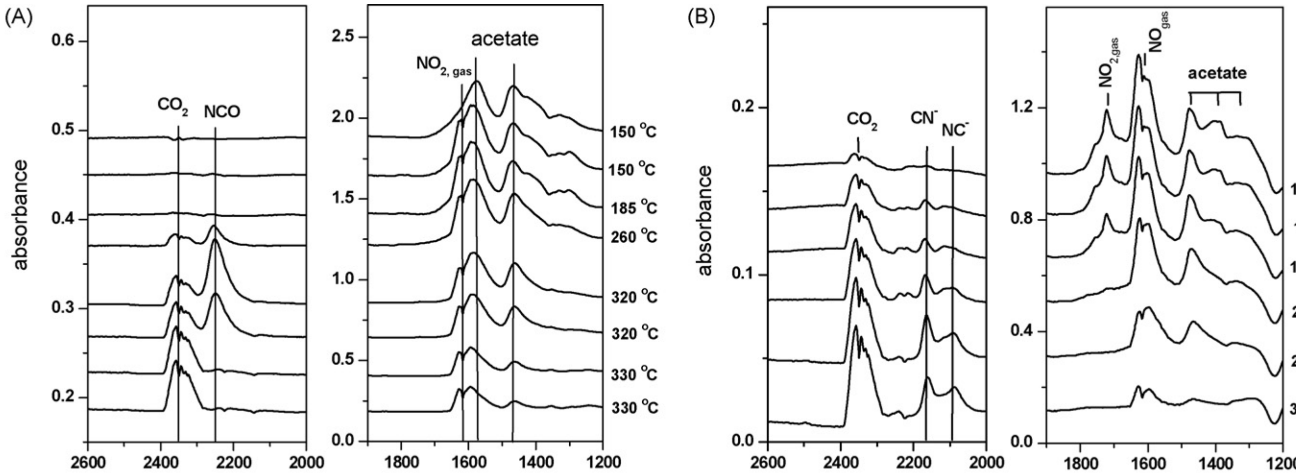


Fig. 5. The reactions of surface acetate on Ag/γ-Al_2O_3 and Ag/Y as a function of temperature. (Panel A) Ag/γ-Al_2O_3 was exposed to acetic acid and the gas phase acetic acid was then removed by evacuation. The top spectrum in was recorded after evacuation at 150 °C. After evacuation of the acetic acid, 4.9 Torr NO_2 + 60 Torr O_2 was introduced at 150 °C, and a spectrum was recorded at 150 °C. After recording the spectrum 150 °C the temperature was increased and spectra at the indicated temperatures were sequentially recorded. (Panel B) Ag/Y was pre-exposed to acetic acid and subsequently evacuated before the introduction of 5.9 Torr of NO_2 (not shown here). From top to bottom, the elapsed time for the first three traces is: 1, 2, and 3.5 min (all at 150 °C). The temperature was then increased from 150 to 320 °C. The spectra, which were recorded sequentially are labeled by the temperature at which they were taken. This figure is reprinted from the Journal of Catalysis, (2006) 238 100 by Y.H. Yeom, M.J. Li, W.M.H. Sachtler and E. Weitz, entitled "A study of the mechanism for NO_x reduction with ethanol on γ-alumina supported silver", Figure 10, page 106, copyright 2006 with permission from Elsevier Limited and from the Journal of Catalysis (2007) 246 413 by Y.H. Yeom, M.J. Li, W.M.H. Sachtler and E. Weitz, entitled, "Low – temperature NO_x reduction with ethanol over Ag/Y: A comparison with Ag/g-Al_2O_3 and BaNa/Y", Figure 12 page 423, copyright 2007 with permission from Elsevier Limited.

with the temperature at which the reaction of surface acetate and NO_2 becomes efficient. For example, NO_x is efficiently reduced to N_2 at 200 °C over BaNa/Y (~90%) or Ag/Y (~60%) while no NO_x is reduced over Ag/γ-Al_2O_3 at the same temperature. This is shown in Fig. 5 for Ag/Y and Ag/γ-Al_2O_3 (not shown for BaNa/Y). As can be seen in the Fig. 5, N-containing intermediates start to form at ~150 °C over Ag–Y and at ~260 °C over Ag/γ-Al_2O_3. Reactivity of surface acetate and detailed assignments of absorption bands has been discussed in Refs. [6,7]. The combination of these results leads to the key point: There is efficient NO_x reduction at temperatures that correlate with the reactivity of acetate with NO_2, in a reaction that leads to nitromethane formation and there is very efficient (near 100%) for NO_x reduction with nitromethane of Ag/Y at a temperature significantly below that where acetate reacts with NO_2. In combination these results strongly suggests that *formation* of nitromethane is the rate-limiting step in NO_x reduction over the catalysts in which nitromethane is produced via *in situ* reactions of added oxygenates [8].

5.3. Isotopic labeling

One of the paramount issues in applications of transient spectroscopy for the elucidation of reaction mechanisms is the identification of reaction intermediates. Often infrared is the spectroscopy of choice for such studies due to the chemical specificity of the IR absorption region (i.e. the fingerprint region). However, chemically similar species typically absorb in the same infrared region. In such cases, use of isotopically labeled compounds and the attendant shifts in the positions of infrared absorptions in these compounds can provide information that is critical to the successful identification of an intermediate. We have extensively employed isotopic labeling to allow us to identify intermediates in NO_x SCR. For example, the isotopic shift on ^{15}N substitution in NO^+ (see Fig. 1) is in good agreement with literature values [1,20,21].

Isotopic labeling can also play an important role in the determination of reaction dynamics and reaction mechanisms. As an illustration, we have employed isotopically labeled acetic acid to probe the mechanism of NO_x SCR over BaNa/Y zeolite [1]. As alluded to above, the published mechanism for this process indicates that CO_2 should be generated in two steps [1]: one is the replacement by NO_2 of the carboxylic acid group bound to a Ba leading to the aci-anion of nitromethane (Eq. (19)),

$$CH_2COO^- + NO_2 \rightarrow CH_2NO_2^- + CO_2 \qquad (19)$$

The other step leading to (the second) CO_2 is the hydrolysis of either HNCO, NCO or NCO^- (Eq. (13) shows this for HNCO) which in turn is produced via the decomposition of dinitromethane and/or its aci anion. Eq. (20) below is shown for the neutral pathway for production of NCO.

$$CH_2(NO_2)_2 \rightarrow H_2O + NO_2 + NCO \qquad (20)$$

As alluded to in Section 5.1, the fact that there are two CO_2 producing steps is confirmed by isotopic labeling [1]. Upon labeling one of the carbons in acetic acid, we observe that one CO_2 being formed contains the label of the carboxylic acid carbon and the other contains the label of the methyl carbon. Labeling of the NO_2, which is allowed to react with unlabeled nitromethane, provides additional mechanistic information. The observation that the resulting HNCO (see Eq. (11)) found in the presence of a 1:1 mixture of $^{15}NO_2$ and $^{14}NO_2$ is ~1:1 $H^{14}NCO$ and $H^{15}NCO$, strongly suggests a symmetric intermediate such as dinitromethane [1]. Finally, prior experiments using ^{15}N demonstrated that one N in the N_2 resulting from NH_3 SCR of NO_x came from the NO_x and one came from NH_3 [14]. These results implicate an intermediate that contains two N atoms and readily dissociates to N_2: as discussed in Section 3, ammonium nitrite fits these criteria.

6. Conclusions

A comparison of the mechanisms for the selective catalytic reduction of NO_x with acetaldehyde or ethanol over different catalysts (BaNa/Y, Ag/Y and Ag-γAl_2O_3) allows for the elucidation of similarities and differences in the mechanisms. The mechanisms for NO_x reduction in these systems proceed by a route that is qualitatively similar and involves the formation of surface acetate ions which react with NO_2 to form nitromethane. This crucial intermediate then reacts with NO_2 to form dinitromethane, which rapidly decomposes to give HNCO. It is well known that HNCO readily hydrolyzes to give NH_3, which can react with another HONO molecule to form ammonium nitrite. This ammonium nitrite then decomposes at low temperature (≤100 °C) to cleanly give N_2 and H_2O. Further, NO is an efficient reductant for converting nitric acid, surface nitrates and ammonium nitrate to the respective nitrite. In each case, the result of the reduction reaction is to produce a mechanistically more desirable species that favors the production of thermally labile ammonium nitrite or surface nitrites as opposed to more thermally stable ammonium nitrate or surface nitrates. There is also strong evidence for a parallel pathway for formation of nitromethane in some systems that is initiated by the formation of acetyl radicals. Evidence for this pathway comes from a comparison of the chemistry that takes place with acetic acid versus acetaldehyde as the reductant. With acetic acid there is only evidence for formation of surface acetate and reactions of NO_2 with acetate and subsequent intermediates. However, acetyl radicals that can form as a result of H atom abstracted by NO_2 from acetaldehyde can readily decompose to methyl radicals with CO as a co-product. They can also react to yield products that are not observed with acetic acid as the reductant. The observation of a much higher CO/CO_2 ratio and additional reaction products serves as a signature of this radical pathway.

One major difference among the systems that we have studied is the temperature at which deNOx chemistry takes place. This temperature can be correlated with the temperature at which acetate reacts with NO_2 to form nitromethane, thus identifying this reaction as the rate-limiting step in the reaction mechanism. It follows that direct addition of nitromethane should lead to lower temperature SCR of NO_x. Indeed, N_2 yields of ~100% have been obtained at temperatures as low as 140 °C. Further, the reaction of nitromethane is relatively insensitive to the presence of surface acetate or CN^- and NC^-. These observations allow for some interesting speculations on the molecular level mechanistic details of the reactions of acetate and nitromethane with NO_2.

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