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NO_2 Reduction with Nitromethane over Ag/Y: A Catalyst with High Activity over a Wide Temperature Range

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Abstract Nitromethane (NM) is a very efficient reductant for converting NO_2 to N_2 over Ag/Y: Between 140 °C and 400 °C, the N_2 yield is close to 100%. This high N_2 yield results from the ability of Ag/Y to effectively catalyze the reaction between NM and NO_2. This high catalytic activity of Ag/Y is minimally affected by surface bound CN^-, NC^-, or acetate, all of which are stable at temperatures below ~300 °C. At $T \geq 400$ °C, there is a reaction path that yields N_2 from NM even in the absence of NO_2. However even at 400 °C, under typical deNO$_x$ conditions, most N_2 molecules are formed as a result of the reaction of NM and NO_2.

Keywords NO_x reduction · deNO$_x$ · Nitromethane · Ag/Y · Zeolite · Catalysis

1 Introduction

Diesel engines are intrinsically more fuel efficient than gasoline powered engines. However, their emissions are more heavily laden with nitrogen oxides than those of a comparable gasoline engine whose exhaust has been treated with a standard three way catalyst. Thus, for society to benefit from the fuel efficiency of diesel engines, nitrogen oxides (NO_x) must be removed from diesel exhaust. One scheme that has recently received considerable attention is NO_x removal using an added reductant over a highly active and selective catalyst. Recent studies have reported results for NO_x removal with acetaldehyde and ethanol as added reductants over zeolite or metal oxide based catalysts [1–3].

There have been several reports that the SCR of NO_x with hydrocarbons involves the production of organic nitro compounds which subsequently react with NO_x to yield N_2 [4–12]. Nitromethane (NM) has been identified as a crucial intermediate in several studies. Blower and Smith studied NM decomposition over metal exchanged Y and X zeolites at 300 °C [3]. They showed that the major products of NM decomposition include NH_3, CO_2, and H_2O, with significant amounts of N_2 and CO. Misono et al. proposed that organic nitro and nitrite compounds are key reaction intermediates in the SCR of NO_x with propene over Pt/SiO$_2$ [4]. Iwamoto and Takeda found that NM is highly efficient as a NO_x reductant over Cu-ZSM-5 [6]. Hayes et al. observed formation of organic nitro compounds from the reaction of propene and NO over Cu-ZSM-5 [7]. Lombardo et al. [9] and Cowan et al. [10] studied NO_x SCR with NM over ZSM-5 zeolites. Lombardo et al. [9] proposed that NM decomposes to NH_3 via a number of steps, including the reaction of NH_3 with NO_2 yielding N_2. Isotopic labeling shows that one of the N atoms in N_2 comes from NM, the other from NO_2. Cowan et al. [10] also observed that NM decomposes to NH_3, which further reacts with NO_2 to give N_2, and that the reaction can be detected below 150 °C. Kameoka et al. [11] studied the adsorption of NM, a possible intermediate in the SCR of NO_x with ethanol on Ag/Al$_2$O$_3$ and Ag/TiO$_2$. They suggest that the efficiency of supported silver catalysts in NO_x reduction with ethanol likely correlates with the nature of the adsorbed NCO species (e.g. its stability and/or reactivity) that are produced from the decomposition of NM. Yamaguchi also studied the decomposition of adsorbed NM on γ-Al$_2$O$_3$ and proposed that a nitrosoaldehyde anion, formed from NM decomposition, is the precursor for NCO^- [14]. Zuzaniuk et al. compared the reactivity of nitromethane and tert-butyl nitrite over γ-Al$_2$O$_3$ [12, 15]. They showed that NM

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decomposes to isocyanate, which reacts to give ammonia, while butyl nitrite decomposes to surface nitrate moieties.

In our previous work we used in-situ infrared spectroscopy to observe gas phase NM during the SCR of NO_2 with acetaldehyde over a BaNa/Y zeolite catalyst [1]. We concluded that NM is produced via two pathways viz. surface acetate + NO_2 and methyl radicals + NO_2. Thus, NM and/or organic nitro compounds can form during SCR of NO_x with hydrocarbons, whereas decomposition of certain organic nitro compounds yields NCO^-, a precursor of ammonia. This suggests that NM can be an efficient NO_x reductant. However, Lombardo et al. report that NO_2 reduction with NM over M-ZSM-5 (M = Co, H, Fe, Cu) catalysts produces less than ~10% N_2 at ~150 °C and ~40% at ~300 °C [9], whereas Cowan et al. report significantly higher yields at ~130 °C over a Co-ZSM-5 catalyst. However, that catalyst deactivated after 120 min at 130 °C, but was stable at 210 °C where the majority of the N_2 yield results from the decomposition of NM [10].

In the present work we report that silver exchanged zeolite Y has very high catalytic activity (~100% NO_2 conversion to N_2) for NO_x reduction with NM at ~150 °C; the Ag/Y catalyst *does not* deactivate over a period of 4 h. This catalyst also retains a high activity over a wide temperature range (150–400 °C). We also report on the effect of adsorbed acetate ions, and adsorbed CN^- containing moieties, which can form from NM during NO_x reduction with NM. These results demonstrate that Ag/Y is a very effective catalyst for NO_2 reduction with NM over a wide temperature range, and that its efficiency for NO_x reduction is not significantly affected by the build up of surface acetate and/or CN^- ions.

2 Experimental

2.1 Catalyst Preparation

Ag/Y was prepared by a threefold wet ion exchange of Na/Y (Si/Al = 2.5, Aldrich) with a 0.1 M $AgNO_3$ solution at ambient temperature. Before each exchange the Ag/Y slurry was stirred for 3 h followed by vacuum filtering. It was then washed thoroughly with doubly de-ionized H_2O, and dried in air. This material was then pretreated as described in Section 2.3. ICP analysis revealed that Na^+ ions were almost completely replaced by Ag^+ ions. H/Y samples were obtained by the same method except that a fivefold wet ion exchange of Na/Y with a 0.1 M NH_4NO_3 solution was employed.

2.2 Infrared Spectroscopy

In-situ FT-IR spectra were recorded in transmission mode using a "home made" IR cell [1], with CaF_2 windows, and a Bio-Rad Excalibur FTS-3000 infrared spectrometer equipped with a HgCdTe (MCT) detector. Unless otherwise stated, each reported spectrum is the result of averaging 70 scans at 4 cm^{-1} resolution under static conditions. Time resolved spectra, which involved different scan conditions, were taken using the "rapid scan" mode of the FTIR.

Typically, a small brush was used to "paint" ~10 mg of sample, in a water slurry, onto the 1.0 × 1.0 cm tungsten grid, held at 353 K. Prior to each experiment the catalyst was heated in vacuum (2×10^{-6} Torr) for 2 h at 703 K and then cooled to the desired temperature. After this treatment, and before the catalyst was exposed to reactants, a spectrum of the catalyst was recorded and used as the "background".

2.3 Catalytic Tests

Catalytic tests were carried out in a continuous-flow tubular fixed-bed micro-reactor. A 200 mg powder sample was packed into the quartz reactor which contained a porous frit. The sample was pretreated in a flow of He and O_2 (v/v = 2, flow rate = 42 mL/min) for 10 h at 500 °C. The reactor was then cooled to the desired temperature and the feed gas was introduced. Its composition was regulated by a five-channel mass flow controller (UNIT Instrument, URS-100). In standard runs, a typical inlet gas composition was 612 ppm NM, 550 ppm NO_2, 7% O_2, and 1% H_2O with helium making up the remainder of the 200 mL/min flow. NM was added by passing the He flow through a NM saturator maintained at 0 °C with an ice-water bath. When desired, acetic acid was added by passing the O_2/He flow through an acetic acid saturator maintained at room temperature. The N_2 concentration in the effluent was analyzed "on-line" with a gas chromatograph (GC) equipped with a thermal conductivity detector (5A column). Before analyzing the effluent, the mixture was allowed to flow through the sample and the system for at least 30 min at the desired temperature. The conversion of NO_2 to N_2 was determined from the formation of N_2. Reported conversion percentages (%) for the heteronuclear reaction of NO_2 to form N_2 are calculated using the formula:

$$NO_2\,\text{conversion to}\,N_2(\%) = ([N_2]/[NO_2]) \times 100\%,$$

$[N_2]$ = ppm concentration of N_2 in the effluent, $[NO_2]$ = ppm concentration of NO_2 in the feed.

3 Results

Results for the conversion of NO_2 to N_2 in the flow reactor, with NM as the reductant, are shown in Fig. 1 (a) and (b).

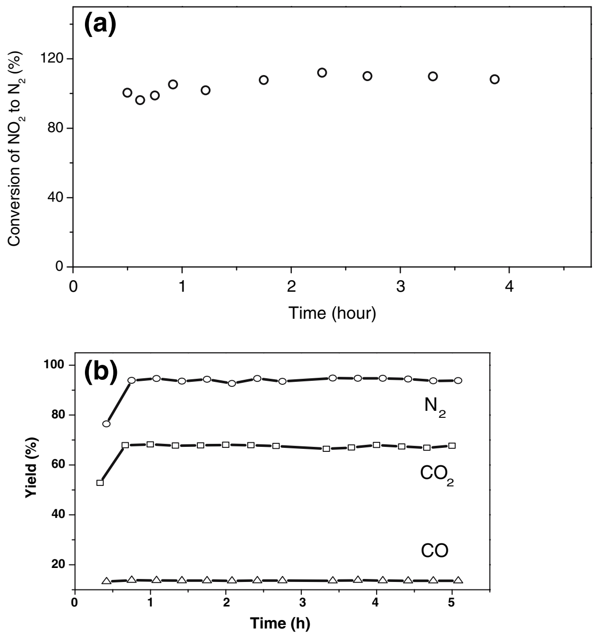

Fig. 1 NO_2 conversion to N_2 over a Ag/Y zeolite catalyst at (**a**) 150 °C and at (**b**) 200 °C with 612 ppm nitromethane, 550 ppm NO_2, 7% O_2, and 1% H_2O in a He flow (flow rate = 200 mL/min)

The fact that the N_2 yield reaches ~100% at 150 °C demonstrates that at low temperature NM is a very efficient reductant for NO_2. Additionally, the catalytic activity does not decrease over the several hours of the run.

When NO_2 was absent from the feed, 256 ppm N_2 were still detected over Ag/Y at 400 °C, (not shown), indicating that a pathway exists for N_2 formation with both N atoms coming from CH_3NO_2. Material balance shows that ~85% of the NM is converted to N_2 at this temperature. When NO_2 was introduced into the feed, a much higher concentration of N_2 (600 ppm) is detected indicating that the majority of the N_2 results from the reaction of NM and NO_2. In contrast, at 300 °C only negligible amounts of N_2 were produced from a NO_2-free feed. No N_2 was detected after the NO_2 flow was terminated at 200 °C. These results demonstrate that below 300 °C, over Ag/Y, the majority of N_2 comes from the reaction of NM with NO_2.

Silver ions in Ag/Y can be reduced at elevated temperature with H^+ becoming the charge compensating cation. To check whether these protons are responsible for the high catalytic activity for NO_2 reduction with NM, we probed HY. Figure 2 shows that NO_2 conversion to N_2 over H/Y is ~60%, demonstrating that at 150 °C H/Y is much less active than Ag/Y. Increasing the temperature to 200 °C did not noticeably enhance the N_2 yield.

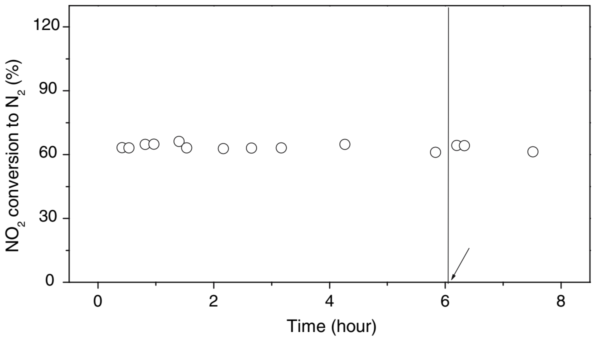

Fig. 2 NO_2 conversion to N_2 over an H/Y zeolite catalyst at 150 °C with 612 ppm nitromethane, 550 ppm NO_2, 7% O_2, and 1% H_2O in a He flow (flow rate = 200 mL/min). After 6 h the temperature of H/Y sample was increased to 200 °C (The time the temperature increase started is marked with an arrow. The ramp rate from 150 °C to 200 °C was 3.3 ° C/min)

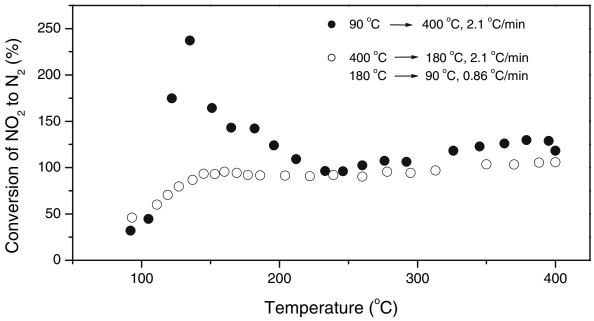

Fig. 3 The temperature dependence of NO_2 conversion to N_2 over a Ag/Y zeolite catalyst with 612 ppm nitromethane, 550 ppm NO_2, 7% O_2, and 1% H_2O in a He flow (flow rate = 200 mL/min). The run started at a Ag/Y temperature of 400 °C. Analysis of the N_2 concentration in the effluent began after allowing the system to stabilize 30 min. The temperature was gradually decreased from 400 °C to 180 °C (ramp rate = 2.1 °C/min) and then from 180 °C to 90 °C (ramp rate = 0.86 °C/min). After reaching 90 °C, the temperature was kept at 90 °C for 10 min and subsequently increased to 400 °C (ramp rate = 2.1 °C/min)

To probe the effect of temperature on the NO_2 conversion, flow experiments were initiated with Ag/Y at 400 °C: the temperature was then slowly decreased to 90 °C (Fig. 3). The N_2 yield remains at ~100% over a wide temperature range down to ~140 °C. When the temperature was slowly increased from 90 °C to 400 °C, the yield of N_2 increased sharply near 140 °C. At this temperature, the apparent conversion of NO_2 to N_2 significantly exceeded 100%, indicating the presence of another source of N atoms. Above 240 °C, the NO_2 conversion is very similar to that observed when the temperature was decreased from 400 °C.

To demonstrate that adsorbed NO_2 and NM provide an additional source of N atoms at low temperature, both of these reactants (NO_2 and NM) were introduced to Ag/Y (Fig. 4) at 90 and 100 °C, respectively. In Fig. 4 (a), broad bands due to surface nitrate are seen at 1,305 and 1,388 cm^{-1}. The strong band centered at 1,616 cm^{-1} is due to gas phase NO_2. The broad and weak band at 2,104 cm^{-1} is likely due to NO^+ [1]. As discussed in prior work, surface nitrate can be produced from either the reaction of $NO_2 + H_2O$

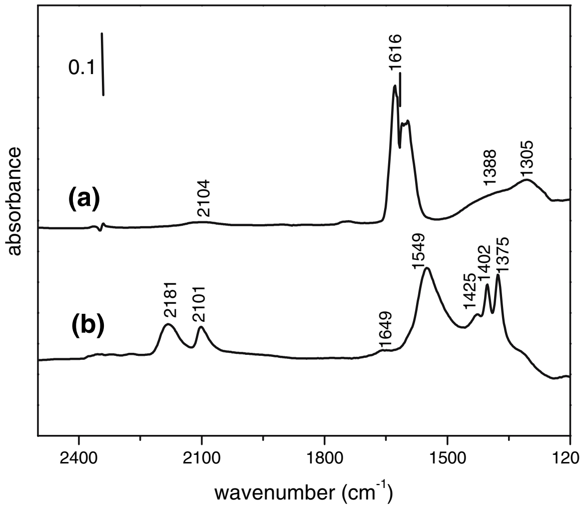

Fig. 4 (a) Ag-Y exposed to 61.2 Torr of a mixture with an NO_2/O_2 ratio = 1/50 at 90 °C, (b) to 1 Torr of nitromethane at 100 °C

$$3NO_2 + H_2O \rightarrow 2NO_3^- + 2H^+ + NO \qquad (1)$$

$$OH + NO_2 \rightarrow NO_3^- + H^+ \qquad (2)$$

or the dissociative adsorption of N_2O_4 produced by dimerization of NO_2 [1]

$$2NO_2 \rightarrow N_2O_4 \rightarrow NO^+ + NO_3^-. \qquad (3)$$

As we showed previously [1], the stability of surface nitrate on this catalyst depends on the history of its formation. Nitrate ions produced by the reaction of NO_2 + H_2O are thermally more stable than those produced from NO_2 alone. In view of the presence of H_2O in these runs, a significant amount of surface nitrate will be produced via both Eqs. 1 and 2. The strong absorption bands at 1,375, 1,402, 1,425, and 1,549 cm^{-1} in Fig. 4 (b), are due to physisorbed NM. The first three bands are bending modes and the last is the $-NO_2$ stretching vibration [1]. The band at 2,181 cm^{-1} is due to isocyanate, $N{=}C{=}O^-$. It is clear that the band at 2,101 cm^{-1} is not NC^- or CN^- for the following reasons: As discussed in Ref. [11], upon exposing Ag/Y to NM, at 200 °C, NC^- is observed at 2,090 cm^{-1} and CN^- at 2,168 cm^{-1}. Whereas neither NC^- nor CN^- reacts with NO_2, the adsorbate causing the band at 2,101 cm^{-1} reacts with NO_2. As discussed in Ref. [2], CN^-, is usually accompanied by NC^-. Therefore, it follows that the band at 2,101 cm^{-1} is unlikely to be due to CN^- and/or NC^-. The species responsible for this band does, however, react with NO_2 [2]. Another obvious possibility would be NCO^-. However experiments with ^{13}C give an isotope shift of 31 cm^{-1}, which is somewhat different from what would be expected for NCO^-. Another possible assignment for this band is fulminate (CNO^-). The assignment of this band deserves further study but is beyond the scope of the present study. We therefore conclude that exposure of Ag/Y to NO_2 and NM at low temperature leads to adsorbed N containing moieties.

The weak band at 1,653 cm^{-1} is likely due to adsorbed H_2O [2]. NM slowly decomposes at 150 °C to reaction products and/or intermediates, such as NH_3, HNCO, and HCN. This decomposition is much more rapid at 300 °C. NO and NO_2 which are expected products of NM decomposition via a radical reaction pathway [1] are *not* detected.

We also note that some data points above ~300 °C slightly exceed 100% yield. Besides experimental error, a possible cause might be the thermal decomposition and reaction of NM to yield N_2 which has been alluded to above.

Figure 5(a) shows spectra recorded after exposure of Ag/Y to a mixture of NM + NO_2 + O_2. In this experiment the Ag/Y was pre-exposed to acetic acid and the cell was subsequently evacuated before the introduction of the gas mixture. During evacuation any weakly adsorbed acetic

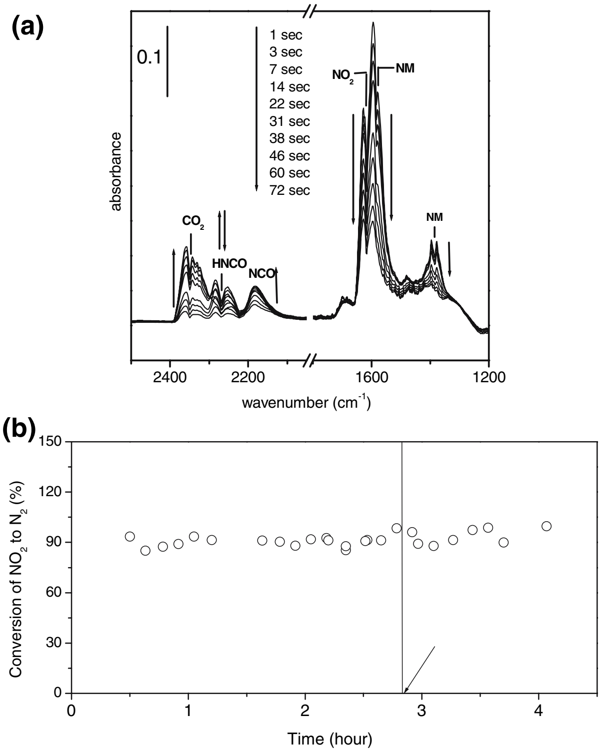

Fig. 5 (**a**) Spectra were taken after Ag-Y was exposed to a mixture of 4 Torr nitromethane + 6 Torr NO_2 + 90 Torr O_2. Before the mixture was introduced the Ag-Y sample was pre-exposed to 2 Torr of acetic acid (AcOH) at 200 °C and subsequently evacuated to remove gas phase and weakly adsorbed acetic acid, (**b**) NO_2 conversion to N_2 over Ag/Y zeolite catalyst at 200 °C with 612 ppm nitromethane, 630 ppm AcOH, 550 ppm NO_2, 7% O_2, and 1% H_2O in a He flow (flow rate = 200 mL/min). After 2.8 h, the AcOH was removed from the feed. (marked with an arrow)

acid will have been removed and there is no observable gas phase acetic acid. The absorption bands due to both gas phase NO_2 and NM decrease in intensity as a function of reaction time and gas phase HNCO and surface NCO^- form. Surface NC^- and CN^- are not visible at 2,088 and 2,168 cm^{-1} because their intensities are too low.

These data (Fig. 5) show that the rate of reaction of NM, in the presence of surface acetate, is *not significantly different* from the rate in the absence of pre-adsorbed acetate (not shown here). The same experiment was performed in the presence of surface CN^- and NC^- which, as discussed in more detail in Ref. [2], are produced on the Ag/Y surface after exposure of the surface to NM at 200 °C. The rate of reaction of NM with NO_2 is, again, not significantly different, indicating that surface CN^- and NC^- do not significantly affect the rate of reaction of NM with NO_2 [2].

Spectra obtained with a feed containing acetic acid are shown in Fig. 5(b). Though the NO_2 conversion to N_2 decreased somewhat at 200 °C, it is still ~90%. Acetic acid was removed from the feed gas after 2.7 h, but no significant change in N_2 yield was detected over a time period of ~1.5 h.

4 Discussion

The Ag/Y catalyst is very active for NO_2 reduction with NM, even at 140 °C. This high activity does not decrease with time on stream over at least 4 h. Clearly, the silver in zeolite Y is responsible for this; Ag-free Y zeolites, such as H/Y, BaNa/Y, and others in Table 1, do not show such activity.

Previously, we found that NM is an intermediate in the NO_x reaction mechanism with oxygenate reductants over BaNa/Y, Ag/Y and Ag/γ-Al_2O_3 [1, 2]. Isotopic labeling experiments on BaNa/Y show that NM, once it is formed, will react with NO_2 to form dinitromethane which decomposes, to HNCO and H_2O [1]. The molecules, NM, dinitromethane and HNCO are expected to be in equilibrium with their chemisorbed anions; the position of these equilibria depends on the nature of the zeolite [1]. HNCO is easily hydrolyzed to NH_3+CO_2; the ammonia will react with HNO_2 to form ammonium nitrite which rapidly decomposes to $N_2 + H_2O$ [16].

This study and our previous results suggest a reaction sequence where nitromethane reacts with NO_2 yielding dinitromethane as a product, followed by dissociation of dinitromethane to produce HNCO. Subsequent chemistry is discussed in the preceding paragraph. Since NM does not rapidly decompose over Ag/Y at 150 °C, NO_2 is crucial in this reaction sequence leading to HNCO. Evidence for this chemistry has been discussed in Ref. [1].

It is possible that formation of HNCO takes place via a formohydroxamic acid, OCH-NHOH, intermediate with a high activation energy for formation of HNCO [17]. Formation of HNCO via this route could thus be the rate limiting step in the decomposition of NM. Formohydroxamic acid will, therefore, not be observed spectroscopically. However, evidence for a formohydroxamic acid intermediate is suggested by isotopic labeling experiments discussed in Ref. [1].

Table 1

Catalyst	Temperature (°C)	Conversion of NO_2 to N_2 (%)	References
Ag/Y[a]	200	100	This work
H/Y[a]	200	60	This work
BaNa-Y[b]	200	42	Unpublished work
Co/ZSM-5[c]	219	75	[10]
Co/ZSM-5[d]	200	20	[9]
HZSM-5[d]	200	15	[9]
Fe-ZSM-5[d]	200	22	[9]

Reaction conditions:

[a] 612 ppm nitromethane, 550 ppm NO_2, 7% O_2, 1% H_2O, flow rate = 200 mL/min, 200 mg sample

[b] 1,000 ppm nitromethane, 500 ppm NO_2, 7% O_2, 2% H_2O, flow rate = 200 mL/min, 200 mg sample

[c] 1,100 ppm nitromethane, 825 ppm NO_2, 2.9% O_2, flow rate = 100 mL/min, 100 mg sample

[d] 2,000 ppm nitromethane, 2000 ppm NO_2, 2.5% O_2, flow rate = 80 mL/min, 50 mg sample

Our data indicate that NM does not significantly decompose below 300 °C. Neither NO nor NO_2 have been detected under our experimental conditions. NH_3, which reacts rapidly with NO_2 in the presence of water, has been detected, but ethane or formaldehyde (or formic acid) have not been detected under the present conditions. Formaldehyde, has been observed when BaNa/Y is exposed to NM at 200 °C [1]. If the decomposition of NM were rapid, NH_3 would be produced at low temperature. This possibility is ruled out by the fact that essentially no NH_3 is formed from NM below 300 °C with Ag/Y, and the rate of decomposition of NM alone is low.

However, the present results show N_2 formation from neat NM above 300 °C. Based on the amount of N_2 produced (~256 ppm) from NM alone at 400 °C, and since it is difficult to envision a pathway for N_2 production from NM in the absence of the formation of NO_2, we propose that approximately 50% of the NM decomposes at 400 °C to CH_3+NO_2:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \tag{4}$$

As suggested by Lombardo et al. [9] NM can decompose to NH_3+CO_2 via a carbamic acid intermediate:

$$CH_3NO_2 \rightarrow NH_2COOH \rightarrow NH_3 + CO_2. \tag{5}$$

NH_3 can also be formed from HNCO that is produced from the reaction of NM on the Ag/Y surface. Consistent with this pathway, NH_3 is observed when NM decomposes. The NO_2 that is produced from reaction (4) and the NH_3 that is produced from (5), (or from HNCO), will rapidly react in the presence of water to ultimately produce N_2 via what can be described as an NH_3 SCR [18]. At these temperatures any ethane or formaldehyde that is produced will react with O_2 and or NO_2 to produce CO_2 and H_2O with methyl peroxide, CH_3OO, and formic acid as plausible intermediates:

$$2CH_3 + 2O_2 \rightarrow 2CH_3OO \rightarrow 2CH_2{=}O + H_2O + 1/2O_2 \quad (6)$$

$$CH_2{=}O + O_2 \rightarrow\rightarrow CHO_2H \quad (7)$$

A surprising observation of the present research is that the N_2 yield is nominally ~240% at ~140 °C when the temperature is ramped up from 90 °C. Obviously, intermediates that lead to N_2 production have been "stored" on the Ag/Y catalyst at low temperature. One possibility is adsorption of HNO_3 at low temperature: This acid can be formed on Ag/Y from NO_2, particularly at low temperature where the reaction rate of NM with NO_2 is low (Fig. 5):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (8)$$

Nitromethane can also be dissociatively adsorbed. Indeed, we observe a strong absorption band at 1,549 cm^{-1} due to adsorbed NM, along with a band due to NCO^-. Upon increasing the temperature these adsorbed moieties react to produce additional N_2. This hypothesis is consistent with the observation that a significant excess of N_2 does not form when the temperature is lowered from 400 °C to 90 °C. Clearly, adsorbed NM and NCO^- do not build up at elevated temperatures. Between 300 °C and 400 °C, the N_2 yield is also higher with ascending than with descending temperature. Thus, some strongly bound surface complexes survive until the Ag/Y temperature reaches 300 °C. This adsorbate is most likely a strongly bound nitrate ion.

The yield of N_2 is minimally affected by adsorbed acetate at 200 °C. Even though such acetate reacts with NO_2 on Ag/Y, the rate of this reaction is relatively slow. Therefore, during the reaction of NM most acetate ions are still bound to the surface. This indicates that NO_2 reduction with NM takes places at sites that are not fully occupied by adsorbed acetate ions. As mentioned above, the N_2 yield does not immediately increase to 100% after the AcOH feed is cut off because the rate of acetate reaction with NO_2 at 150 °C is very low.

Cant et al. studied the decomposition of NM over Co/ZSM-5 in the presence and in the absence of NO_2 at 130 and 219 °C [10]. They found that the rate of NM decomposition is faster in the presence of NO_2 than in its absence, with N_2 and CO_2 as major products. However, in the presence of NO_2 the system deactivated after 2 h of reaction time at 130 °C. At 219 °C, the system did not deactivate in the presence of NO_2. They observed that more N_2 came from NM alone rather than from the reaction of NM + NO_2. The authors suggest that the faster reaction at low temperatures, in the presence of NO_2, is due to reaction of adsorbed NH_3 and HNCO with NO_2. They conclude that adsorbed NH_3 and HNCO poison the surface for the decomposition of NM. Thus, NO_2 effectively "cleans" the surface under their experimental conditions. HNCO does not poison the Ag/Y surface under our experimental conditions because HNCO readily reacts with H_2O on Ag/Y and H_2O is a product of NM decomposition. NH_3 is only weakly adsorbed by Ag/Y, and consequently it is spectroscopically observed in the gas phase, not as an adsorbate.

Cant et al. [10] also reported that cyclic oligomers of HNCO, such as cyanuric acid are produced on Co-ZSM-5 from the decomposition of NM. As reported previously, no cyanuric acid formation has been detected on Ag/Y nor are there any other detectable HNCO oligomers on Ag/Y [2].

5 Conclusions

The result of this work can be summarized as follows: (1) Ag/Y has a high activity for NO_2 reduction with NM even at 140 °C. This activity is maintained up to 400 °C, with ~100% NO_2 conversion to N_2. (2) Ag/Y effectively catalyzes the reaction between NM and NO_2 with the critical step most likely being the production of a dinitromethane intermediate. (3) The catalytic activity of Ag/Y is minimally affected by surface CN^-, NC^-, or acetate, all of which are thermally and chemically stable at low temperatures (below ~300 °C). (4) Ag/Y is a promising catalyst for NO_x reduction with NM.

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