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Low activation energy pathway for the catalyzed reduction of nitrogen oxides to N_2 by ammonia

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A low activation energy pathway for the catalytic reduction of nitrogen oxides to N_2, with reductants other than ammonia, consists of two sets of reaction steps. In the first set, part of the NO_x is reduced to NH_3; in the second set ammonium nitrite, NH_4NO_2 is formed from this NH_3 and $NO + NO_2$. The NH_4NO_2 thus formed decomposes at ~100 °C to $N_2 + H_2O$, even on an inert support, whereas ammonium nitrate, NH_4NO_3, which is also formed from NH_3 and $NO_2 + O_2$, (or HNO_3), decomposes only at 312 °C yielding mainly N_2O. Upon applying Redhead's equations for a first order desorption to the decomposition of ammonium nitrite, an activation energiy of 22.4 is calculated which is consistent with literature data. For the reaction path *via* ammonium nitrite a consumption ratio of 1/1 for NO and NO_2 is predicted and confirmed experimentally by injecting NO into a mixture of $NH_3 + NO_2$ flowing over a BaNa/Y catalyst. This leads to a yield increase of one N_2 molecule per added molecule of NO. Little N_2 is produced from $NH_3 + NO$ in the absence of NO_2.

KEY WORDS: NO_x reduction; NO/NO_2 ratio; ammonium nitrite; Ba/Y–zeolite catalyst.

1. Introduction

In 1847, E. Millon reported that an aqueous solution of ammonium nitrite, NH_4NO_2, decomposes into nitrogen and water below 100 °C [1]. In 1849, B.P. Corenwinder showed that for this reaction it is not necessary to prepare crystalline ammonium nitrite; an aqueous solution containing ammonium ions and nitrite ions easily releases N_2 molecules [2]. Conceptually, a combination of this old chemistry with the known reactions:

$$NO + NO_2 = N_2O_3 \tag{1}$$

$$N_2O_3 + H_2O + 2NH_3 = 2NH_4N_2 \tag{2}$$

provides a simple, low activation energy pathway for the reduction of nitrogen oxides with ammonia to nitrogen and water:

$$NO + NO_2 + 2NH_3 + H_2O \Longrightarrow 2N_2 + 4H_2O \tag{3}$$

An identifying criterion for this path is that the oxides NO and NO_2 are consumed in a ratio of 1:1, Statements in the modem literature that maximum activity of NO_x reduction is achieved over a variety of oxide catalysts when the NO_x consists of a 1 : 1 mixture of these two nitrogen oxides are, therefore, consistent with, albeit not conclusive for, this reaction path. In this respect, the following observations appear of interest:

Kato *et al.* reported that for an iron–titanium oxide catalyst, the rate of NO_x reduction with ammonia is higher when the reaction mixture contained an equimolar mixture of NO and NO_2 than for either of NO or only NO_2 [3]. Likewise, Tünter *et al.* reported that over a V_2O_5–WO_3–TiO_2 catalyst, the highest SCR rate is achieved with an equimolar $NO + NO_2$ mixture [4]. Koebel et al. found that the SCR performance over V_2O_5-WO_3/TiO_2 is highest with a 1/1 mixture of NO and NO_2 [5]. More recently, Sun *et al.* [6] used isotopic labeling of the nitrogen. With ^{14} NH_3 and an equimolar ^{15}NO + $^{15}N0_2$ mixture they find 100% NO_x reduction over an Fe/MFI catalyst at low temperature. The N_2 consists entirely of the heteronuc1ear isotopomer proving that in (3) one N atom in each N_2 molecule is from NH_3 the other from NO_x.

The existence of a low activation energy pathway that operates even in the absence of a catalyst suggests that two crucial tasks of an efficient heterogeneous catalyst for NO_x abatement in emissions from internal combustion engines are: (1) to bring the NO/NO_2 ratio in emissions containing O_2 and potential reductants towards the required 1/1 ratio, (2) to convert non-ammonia reductants with part of the NO_x to ammonia or an amine.

Regarding the second point, it should be mentioned that Poignant *et al.* found that propene and nitrogen oxides are converted to ammonia over a Cu/MFI catalyst [7]. Chen *et al.* showed that a feed containing nitrogen oxides and iso-butane produces N_2 over Fe/MFI in two major steps: first a deposit is formed exposing–NH_2 groups, in the second step these groups react with NO + O_2 to form N_2 [8]. Isotopic labeling showed that in the N_2 molecules one atom stems from the–NH_2 groups of the deposit, the other from NO_x.

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More recently, we studied the reduction of NO_x with acetaldehyde over BaNa/Y [9,10]. The results strongly suggest that this catalyst converts part of the NO_x to ammonia; while the subsequent formation of N_2 is achieved, either partly or entirely, by reaction (3).

The primary objective of the work described in the present paper is to test this hypothesis. For this purpose the decomposition rates of supported ammonium nitrite and ammonium nitrate are compared and the products are analyzed. We also compare the thermal decomposition of ammonium nitrite on BaNa/Y with that on quartz as the prototype for an inert material with low surface area. In a crucial experiment, we measured how much additional N_2 is produced upon adding NO to a reaction mixture of NO_2 with excess NH_3 in its steady state over a NaBa/Y catalyst. This extra N_2 formation due to NO addition is compared with the N_2 production from NO with excess NH_3 in the absence of O_2 or NO_2.

In the reaction network leading to ammonia production from NO_2 and acetaldehyde over BaNa/Y, NO is formed. The role of NO in the reduction of nitric acid and surface nitrates is being explored in another study of our group (Yeom *et al.*, in preparation).

2. Experimental

2.1. Catalyst preparation

The zeolite-based catalysts were obtained by a threefold ion exchange of Na–Y (Si/Al = 2.5, Aldrich) with an aqueous 0.1 M $Ba(NO_3)_2$ solution at ambient temperature. For every exchange, the slurry was stirred for 48 h prior to being vacuum filtered, washed thoroughly with doubly deionized H_2O, and dried in air. Elemental analysis *via* inductively coupled plasma spectroscopy (ICP) gave the following unit cell composition $Ba_{9.6}Na_{33.8}Al_{53}Si_{139}O_{384} \cdot xH_2O$. Even though this zeolite acts functionally as a BaY [11], we will refer to it as a BaNa/Y, because it contains more Na^+ than Ba^{2+}.

2.2. Catalytic tests

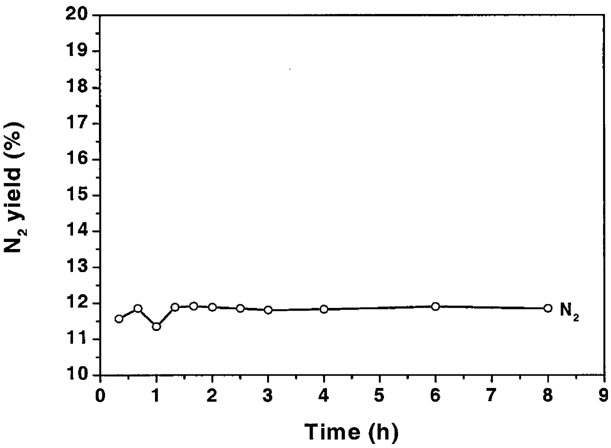
Catalytic tests were carried out in a fixed bed microflow reactor, described in more detail in Refs. [9,10]. Briefly, 0.2 g of the powdered BaNa/Y catalyst was packed into the quartz reactor. Control experiments were performed with 0.2 g of quartz powder substituting for the BaNa/Y. The composition of the feed gas was regulated by mass-flow controllers (UNIT Instrument, URS-100). Experiments with equimolar amounts of NO and NO_2 were conducted with an NO–NO_2–NH_3 feed which was measured upstream after by-passing the catalyst, to contain approximately 500 ppm NO, 500 ppm NO_2, 2000 ppm NH_3 and 1.0% H_2O with ultra-high purity He as the diluent. The total flow rate was 200 mL/min (GHSV : 60000 h^{-1}). H_2O was introduced into the reaction system by bubbling He through a H_2O saturator. The composition of the effluent could be analyzed "on-line" by a GC equipped with a thermal conductivity detector (TCD) (5A column for N_2 and CO, Porapak Q for CO_2). A cold trap was employed between the reactor and the GC to protect the column from H_2O.

2.3. Temperature programmed decomposition

NH_4NO_3, supported on BaNa/Y and NH_4NO_2 supported on BaNa/Y or quartz, were prepared by impregnating the support with an aqueous solution of 3.5 M NH_4NO_3 or NH_4NO_2, followed by drying overnight at room temperature. Temperature-programmed decomposition of supported NH_4NO_3 or NH_4NO_2 was carried out in a flow reactor under an Ar flow of 40 ml/min with a temperature ramp of 8 °C/min from room temperature to 55 °C. Before every run, the system was purged with Ar at room temperature until no gases other than Ar were detected in the effluent. When desired, computer-interfaced mass spectrometry (Gas Analyzer, Dycor M200 Quadrupole) was employed to analyze the effluent. As the fragment $m/e = 30$ is common to NO and NO_2, the latter molecule was analyzed from the signal $m/e = 46$.

3. Results

As shown in figure 1, conversion is very low for NO over BaNa/Y at 200 °C in the absence of O_2 or NO_2. In contrast, as shown in figure 2, 100% yield of N_2 is achieved with an equimolar NO + NO_2 mixture over BaNa/Y in the presence of excess NH_3 and water. Over NaY at 200 °C the N_2 yield is ~98%. The yield difference between BaNa/Y and Na/Y is small, but reproducible. High yields could also be obtained in the absence of water. Figure 3 shows the yield of N_2 when NH_3 is oxidized with O_2 in the absence of nitric oxides. It demonstrates that the presence of NO_x is necessary to attain high conversion of ammonia.



NO: 1000 ppm, NH_3: 2500 ppm, H_2O: 1.0% , 200 ml/min

Figure 1. NO reduction with NH_3 in the absence of O_2 over BaNa/Y at 200 °C.

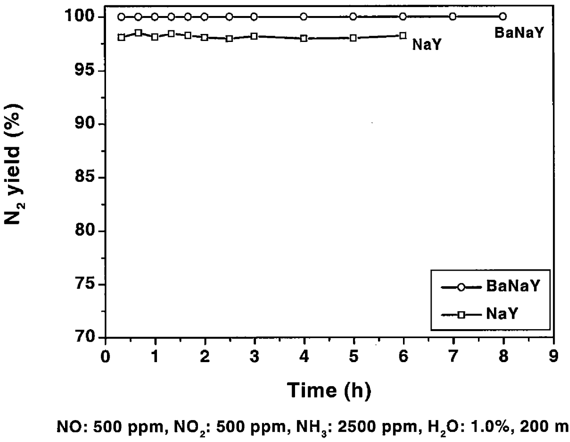


Figure 2. Reduction with NH_3 of NO_x with NO/NO_2 = 1 in the presence of H_2O over (–○–) BaNa/Y or (–□–) NaY at 200 °C.

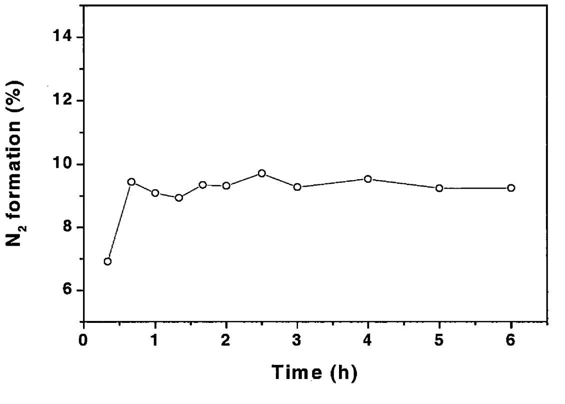


Figure 3. NH_3 oxidation with O_2 over BaNa/Y at 200 °C.

The importance of having both NO and NO_2 in the same feed is illustrated by a test in which NO was added to a feed containing pure NO_2 mixed with excess NH_3 after a steady state has been reached over BaNa/Y. As shown in figure 4, ~75% of the NO_2 is converted to N_2 prior to injecting NO. Upon adding NO, the conversion of NO_x to N_2 increases dramatically. No induction period is observed. Quantitative evaluation of these data shows that the number of additional N_2 molecules formed as a result of adding NO is equal to the number of NO molecules added, and thus to the maximum number of moles of N_2O_3 that can be formed.

Temperature programmed decomposition studies were performed with NH_4NO_2 and NH_4NO_3 over BaNa/Y and quartz in an Ar carrier gas. As seen in figure 5a, a large amount of N_2 is produced at 96 °C from the decomposition of ammonium nitrite. In contrast, figure 5c shows that with ammonium nitrate, decomposition peaks at ~312 °C. In this case, N_2O is the dominant product, N_2 and NO are minor products. Figure 5b shows the decomposition of NH_4NO_2 depos-

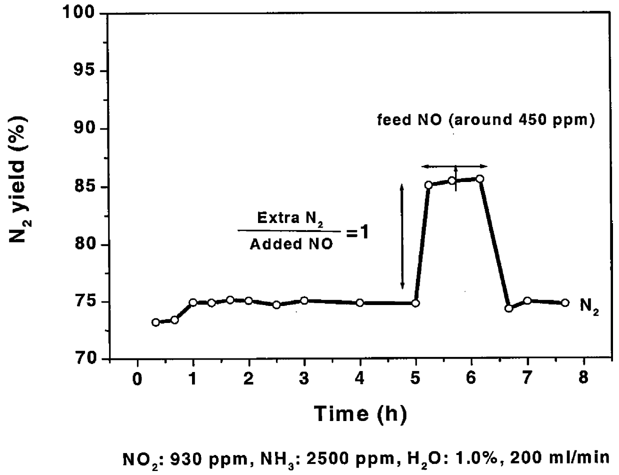


Figure 4. NO_2 reduction with NH_3 over BaNa/Y at 200 °C; effect of adding NO.

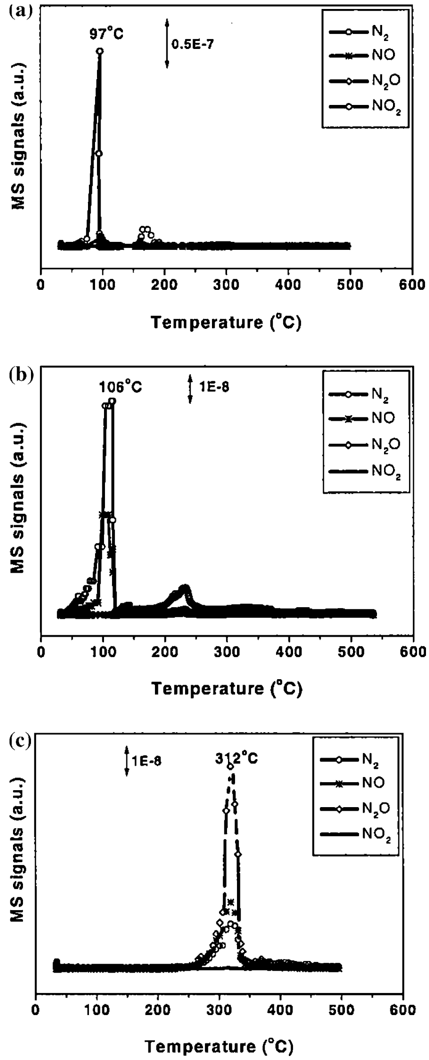


Figure 5. Temperature programmed decomposition of NH_4NO_2 and NH_4NO_3. (a) Decomposition of NH_4NO_2 over BaNa/Y; (b) Decomposition of NH_4NO_2 over quartz; (c) Decomposition of NH_4NO_3 over BaNa/Y.

ited on quartz. Comparison shows that the decomposition temperature of NH_4NO_2 is nearly the same when the nitrite is deposited on BaNa/Y or quartz. No catalyst is necessary for this decomposition in agreement with the findings of Millon [1] and Corenwinder [2].

4. Discussion

The data in figure 5 show that thermal decomposition of ammonium nitrite readily leads to formation of N_2 in catalytic runs carried out at or above 100 °C. This decomposition does not require a catalyst; within experimental error the decomposition rate is equal on catalytically inert quartz with low surface area and a Y zeolite with a surface area near 10^3 m^2/g. In contrast, ammonium nitrate decomposes only at 312 °C, giving mainly N_2O. Redhead showed [12] that for first order desorption the activation energy can be derived from the peak position by using

$$E/\mathrm{RT_p} = \ln(\upsilon T_\mathrm{p}/\beta) - 3.64 \tag{4}$$

with $\upsilon_1 = \mathrm{kT/h} = 10^{13}\ \mathrm{s}^{-1}$; β stands for the temperature ramp in $T = T_0 + \beta t$. In the present case $\beta = 8$ K/s. Using equation (4) an activation energy of 22.38 kcal/mol is calculated from the peak temperatures for the decompositions of ammonium nitrite. This value is in fair agreement with the number of 20 kcal/mol calculated from the temperature dependence of the thermal decomposition rate of an aqueous solution of ammonium nitrite reported by Kolarov *et al.* [13].

Clearly, in catalytic test runs that are typically carried out at 200 °C, the decomposition of the nitrate will be kinetically irrelevant. If adsorbed nitrate ions are not removed from the catalyst by chemical interaction with an appropriate reductant, they will poison the catalyst.

In previous work with Fe/MFI catalysts our group had shown that the highest rate of NO_x reduction to N_2 is achieved for NO_x mixtures with a NO/NO_2 ratio of 1/1, i.e. the stoichiometry of N_2O_3. Similar results were reported by others for non-zeolite based catalysts, as mentioned above. With Fe/MFI it was found that isotopically labeled $^{15}NO_x$ reacts with ^{14} NH_3; giving 100% of the isotopomer $^{14}N^{15}N$, implying an intermediate incorporating one NO or NO_2 molecule and one ammonia molecule [6]. These and other data from the literature suggest that a key step in the reduction of NO_x to N_2 is the formation of ammonium nitrite. As mentioned, it has been known for more than 150 years that ammonium nitrite readily decomposes to produce water and dinitrogen at modest temperatures [1,2]. The TPD data in figures 5a, b show that this decomposition takes place at essentially the same temperature, ~100 °C, over quartz and over BaNa/Y zeolite. They also confirm that the primary gas phase product is N_2. Thus, efficient production of NH_4NO_2 in a stream of NO_x will lead to efficient production of N_2 in the final step in the NO_x reduction process.

Nitrous acid, HONO, reacts, of course, with NH_3 to form ammonium nitrite. HONO is expected in NO_x streams since it is part of a complex set of equilibria involving NO, NO_2, H_2O and HNO_3. The data in figure 4 confirm that adding NO to a gas containing NO_2 and excess of ammonia increases the N_2 yield by the potential number of N_2O_3 molecules that can form after this injection. This number will be maximum in a 1 : 1 mixture, which leads to complete conversion to N_2 over BaNa/Y and to 98% yield over NaY.

If ammonia is used as the reductant, the ammonium nitrite can easily form *via* gas phase equilibria. A different situation exists when ammonia has to be produced *in situ* from a different reductant and part of the NO_x. With BaNa/Y there is evidence that nitrosyl ions will react with water to form HONO [10]. The possibility that NO will reduce nitrate ions to nitrite ions is being investigated as part of another study in our group (Yeom *et al.*, in preparation).

The data in figure 4 also permit a qualitative comparison of the rate constants of three competing processes:

Let k_1 be the rate constant for the production of N_2 *via* ammonium nitrite

Let k_2 be the rate constant for reduction of NO_2 to N_2 without involvement of NO

Let k_3 be the rate constant for NO_2 reduction to NO with ammonia

It then follows that k_2 and k_3 cannot both be very small, because there was significant N_2 production (75% yield of N_2) before NO was injected.

It also follows that neither k_2 nor k_3 can be $\gg k_1$, because in that case NO injection would have had little effect.

A scenario consistent with the data assumes that before NO injection, the k_3 reaction converted some 37% of the NO_2 to NO; this enabled 75% of the NO_x to be converted to N_2 *via* the k_1 route. The k_3 and the k_1 reactions are successive steps, while the k_2 process is a parallel path with little kinetic significance. Our estimate is thus:

$$k_1 > k_3 > k_2.$$

The speed, by which the system responds to the NO injection, precludes a long induction period. We estimate that with our equipment and the gas flow rate used, a plug flow would travel from injection point to sampling valve in less than 2 min. As the first sampling was done 15 min after injection, the gas flow could not lead to measured delays. The small positive slope of the line in figure 4 after NO injection could indicate that sites deep inside the nano-pores of the zeolite contribute with some delay to the gas phase composition behind the catalyst.

The high rate of N_2 formation in spite of the unfavorable position of the equilibrium (1) seems to indicate that collisions of NO and NO_2 molecules in the gas phase are quite often followed by the energetically downhill reaction sequence leading *via* N_2O_3 to HONO, NH_4NO_2 and ultimately to N_2. An important conclusion from the present study is the identification of uncatalyzed steps in the complex reaction network of NO_x reduction with acetaldehyde over BaNa/Y catalysts. Clearly, the formation of ammonium nitrite from NO + NO_2 + NH_3 + H_2O and its decomposition to N_2 + $2H_2O$ have low activation energies even in the absence of a catalyst. Reaction paths *via* NH_4NO_2 are likely to be used over a variety of catalysts. Long *et al.* conclude that over an Fe–Mn based oxide catalyst the reduction of NO with NH_3 to N_2 is likely to proceed *via* ammonium nitrite [14]. For the SCR over a vanadia–titania catalyst Madia *et al.* reported that the reaction is much faster with a feed having an NO//NO_2 = 1/1 ratio than with pure NO_2 [15]. In comparison to a feed gas containing NO + O_2 in a 4/1 ratio the reduction with ammonia below 250 °C was found to be ten times faster for the NO//NO_2 = 1/1 feed. This indicates that even over that catalyst the oxidation of some 50% of the NO to NO_2 is slower than the formation of N_2 from NH_3 and the NO/NO_2 = 1/1 mixture.

Understanding the important role played by uncatalyzed steps in the kinetic network enables the catalytic community to better define the requirements for an efficient de-NOx catalyst. From the present study we conclude that essential chemical prerequisites are:

(1) to bring NO_x feeds closer to the NO/NO_2 = 1/1 ratio.
(2) to convert non-ammonia reductants to ammonia or amines by reaction with part of the NO_x.
(3) to ascertain that the rates of desired reactions of this network compete favorably with the undesired oxidation of NH_3 with O_2 to more NO_x or an excessive reduction of NO_2 with NH_3 to NO, or combustion of organic reductants.
(4) to convert strongly bound adsorbates, that are not removed thermally, to volatile entities; in particular NO_3^- ions have to be reduced chemically to NO_2^- ions.
(5) to make the rates of all steps compatible with the contact time in the tail pipe.

5. Conclusions

The results show that a path of low activation energy exists for the catalytic reduction of NO_x with ammonia. It passes through an ammonium nitrite intermediate. Even when deposited on an inert solid, this nitrite decomposes swiftly at ~100 °C to N_2 + H_2O. In contrast, ammonium nitrate decomposes only at ~312 °C with N_2O being a dominant product. Effective NO_x reduction with ammonia requires an equimolar NO + NO_2 mixture in accordance with the stoichiometry of ammonium nitrite formation. Feeds with low NO_2 ratios therefore, require an oxidation catalyst. Injection of NO to an NH_3 + NO_2 mixture increases the N_2 yield by one N_2 molecule per added NO, though mixtures of NH_3 + NO yield only little N_2.

Acknowledgments

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