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An acid catalyzed step in the catalytic reduction of NO_x to N_2

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Contact of adsorbed ammonium nitrite, NH_4NO_2, with HCl vapor or a solid acid such as the zeolite HY, significantly lowers the temperature of its decomposition to $N_2 + H_2O$. Protonated NH_4NO_2 decomposes at room temperature. The decomposition of ammonium nitrite is one of the steps in the catalytic reduction of NO_x with ammonia or other reductants.

KEY WORDS: NO_x reduction; ammonium nitrite decomposition; Ba/Y; zeolite catalysts.

1. Introduction

Previous work revealed that the catalytic reduction of toxic nitrogen oxides, NO_x, to environmentally benign nitrogen is a multi-step reaction, for which the mechanistic route depends on the reductant and the catalyst [1–8]. A common feature of this chemistry, that appears valid for all well-studied systems, is the final reaction in this sequence [9]; ammonium nitrite, NH_4NO_2, always appears to be formed, which swiftly decomposes to nitrogen and water:

$$NH_4NO_2 = 2N_2 + 2H_2O \qquad (1)$$

This reaction was first reported in 1847 by Millon [10] for aqueous solutions of ammonium nitrite. There are indications that (1) actually consists of two elementary steps, *viz* formation of nitroso-amine, ON–NH_2, followed by its decomposition. In a previous paper we demonstrated by temperature-programmed decomposition (TPD) that solid ammonium nitrite readily decomposes near 100 °C to $N_2 + H_2O$ in the absence of a catalyst. The TPD profiles were almost identical for NH_4NO_2 deposited on quartz powder or a Ba, Na/Y zeolite, while only the latter material is known to be an effective catalysts for NO_x reduction with acetaldehyde.

Under the conditions of NO_x abatement in the tailpipe of a diesel engine, nitrate ions are known to be primary adsorbates. However, ammonium nitrate does not decompose at the temperatures where ammonium nitrite does; the decomposition of the nitrate requires a higher temperature than that of the tailpipe of many diesel-driven vehicles. The nitrate ions thus have the potential to block the active sites of the catalyst [11]. At higher temperature when ammonium nitrate does decompose, the major N-containing product is nitrous oxide, N_2O, a greenhouse gas. For these reasons it is mandatory for any vehicular NO_x abatement catalyst that nitrate ions on its surface have to be swiftly reduced chemically, preferentially to nitrite ions. Indeed, as we have shown in a recent paper, reduction of nitrates with NO to nitrites is catalyzed by zeolite-based materials, such as BaNa/Y [12].

Subsequent to Millon's 1847 paper several groups studied the decomposition of ammonium nitrite in aqueous solution. However, reproducibility of the results was poor until Abel *et al.* [13] reported in 1931 that *in the presence of an added acid* well reproducible straight lines are obtained for the yield of N_2 as a function of time. This acid-catalyzed NH_4NO_2 decomposition took place at significantly lower temperature than in the absence of an acid. Even at 25 °C perfectly linear $p(N_2) = f(t)$ plots were obtained by these authors. This finding indicates that strong Brønsted acids interacting with NH_4NO_2 lower the activation energy of reaction (1), possibly by forming a short lived complex. In view of the application of this chemistry in modern De-NO_x catalysis over heterogeneous catalysts, it is of interest to know whether the decomposition of ammonium nitrite is also catalyzed by the Brønsted acid sites of a solid on which the nitrite is supported. Answering that question is the objective of the present work.

2. Experimental

Ammonium nitrite supported on Ba,Na/Y or quartz, was prepared by impregnating the support with an aqueous solution of 3.5 M NH_4NO_2, followed by drying at room temperature, as described in [11]. In the absence of acid sites, the rate of decomposition is known to be negligible at room temperature for both

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ammonium nitrate and nitrite. The resulting solid was subsequently exposed at room temperature to HCl vapor with $P_{HCl} = 190$ Torr. In a different run, quartz covered with deposited NH_4NO_2 was physically mixed with the zeolite HY; this mixture was ground to ensure intimate contact of the two solids. Before every run, the system was purged with Ar at room temperature until no gas other than Ar was detected in the effluent. Temperature-programmed decomposition of supported NH_4NO_2 or its mixtures was carried out in a flow reactor under an Ar flow of 40 ml/min at room temperature. The exit gas was analyzed by on-line gas chromatography or computer-interfaced mass spectrometry (Gas Analyzer, Dycor M200 Quadrupole). In those runs where the catalyst had been in contact with HCl vapor or solid H/Y at room temperature inside a closed vessel, the first peak after starting the TPD program shows the gas which has accumulated during this contact time.

3. Results

Figure 1 shows the evolution of N_2 in a TPD run of NH_4NO_2/BaNa/Y (a Y-zeolite with Ba and Na ions) that had been exposed to HCl vapor for 3 h at room temperature. It took ~2 min to displace the gas which had been in contact with solid; a large N_2 peak appearing at that time thus represents the N_2 accumulated during the 3 h period during which the solid had been exposed to HCl vapor. After 20 min the TPD program was started. The peak at ~100 °C is found at the same position as with genuine NH_4NO_2/BaNa/Y that had never been exposed to HCl, as shown in our previous paper [11].

Apparently, interaction with HCl has created novel complexes enabling ammonium nitrite to decompose at a significantly lower temperature. This conversion is incomplete after 3 h at room temperature. The experiment was, therefore, repeated using a longer exposure time for the solid to HCl. Figure 2 shows the result after exposure to HCl for 13 h. In this case the high temperature peak characteristic of the decomposition of the original ammonium nitrite has disappeared: all ammonium nitrite has decomposed at room temperature while NH_4NO_2 /BaNa/Y was exposed to HCl vapor. As a different duration of exposure to HCl vapor is the only difference between the runs depicted in these two figures, we conclude that the solid state reaction of ammonium nitrite clusters with HCl is a slow process at room temperature, as might be expected.

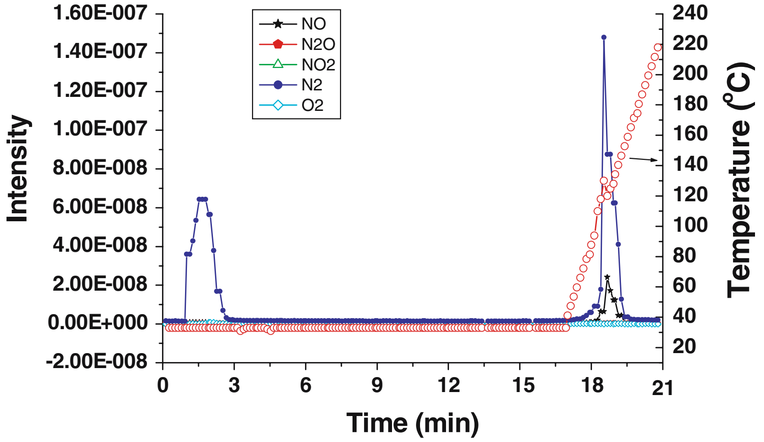
In order to ascertain that interaction with a strong Brønsted acid is the cause of the significant decrease of the activation energy of ammonium nitrite decomposition to $N_2 + H_2O$, an experiment was designed using a physical mixture of two solids:

(1) HY zeolite
(2) NH_4NO_2 deposited on quartz powder, dried for 12 h at 25 °C The mixture was kept under Ar for 13 h, followed by the TPD run shown in figure 3. Clearly, the majority of the NH_4NO_2 decomposes at low temperature. A minority decomposing at much higher temperature could be due to isolated NH_4NO_2.

4. Discussion

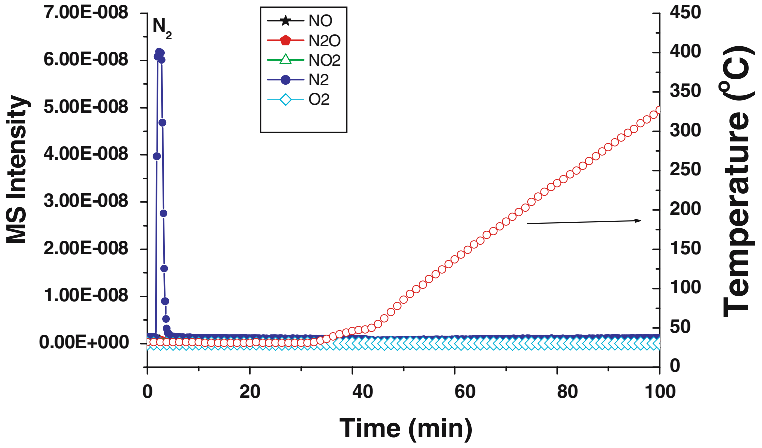
The results of this study show that HCl and HY are both able to provide the protons which react with ammonium nitrite. The proton will presumably be added to one of the O atoms i.e.

$$NH_4NO_2 + H^+ \Rightarrow [NH_4NOOH]^+ \qquad (2)$$



- **Purging NH_4NO_2 sample with Ar**
- **Introducing HCl vapor to reactor at RT**
- **Close all valves, and leave NH_4NO_2 in reactor 3 h under HCl vapor**

Figure 1. Decomposition of NH_4NO_2/Ba, Na/Y under HCl vapor after 3 h.



- **Purging NH_4NO_2 sample with Ar**
- **Introducing HCl vapor to reactor at RT**
- **Close all valves, and leave NH_4NO_2 overnight (13 h) under HCl vapor**

Figure 2. Decomposition of NH_4NO_2/Ba, Na/Y under HCl vapor after 13 h.

An isomer of this intermediate will have the structure $[HON(OH)NH_3]^+$. Either isomer will release H_2O, forming $[HON–NH_2]^+$, a protonated nitroso-amine, which can easily decompose. This leads to the catalytic cycle:

$$H_3O^+ + NH_4NO_2 \Rightarrow \{[NH_4NOOH]^+ \leftrightarrows (HO)_2NNH_3]^+\} + H_2O \qquad (3a)$$

$$\{[NH_4NOOH]^+ \leftrightarrows HON(OH)NH3]^+\} \Rightarrow [HON - NH_2]^+ + H_2O. \qquad (3b)$$

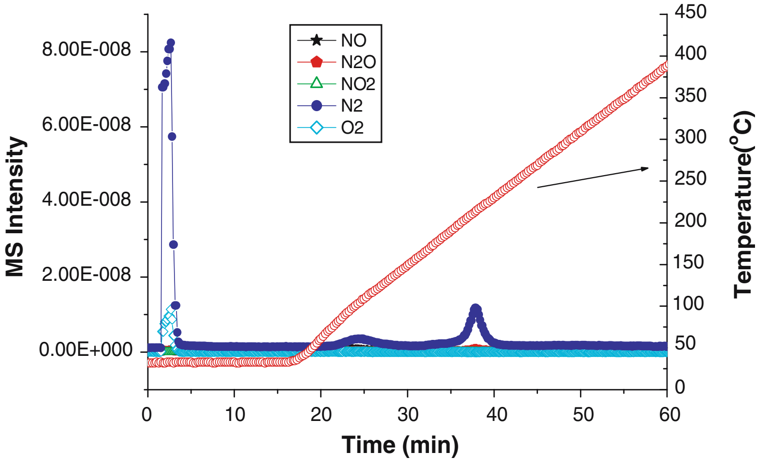
$$[HON - NH_2]^+ \Rightarrow N_2 + H_3O^+ \qquad (3c)$$

This adds up to

$$NH_4NO_2 \Rightarrow N_2 + 2H_2O \qquad (3d)$$

The present data do not permit us to decide which of the two steps, formation or decomposition of the nitroso-amine, is rate limiting. In step (3b) one of the N–H bonds in the ammonium ion is broken, facilitating formation of a chemical bond between the two N atoms.

These results demonstrate that the basic chemistry proposed in [13] by Abel *et al.* remains valid also in the absence of an aqueous phase. Diffusion is, of course, slower in solids and over solid surfaces than in a liquid phase; a physical mixture of one solid carrying the Brønsted sites and another solid carrying the ammonium nitrite requires hours at room temperature for the



- **Purging mixture of NH_4NO_2/SiO_2 and HY with Ar**
- **Close all valves, and leave mixture sample of NH_4NO_2/SiO_2 and HY overnight**

Figure 3. Decomposition of NH4NO2/Quartz mixture with HY.

Brønsted acid catalyzed decomposition of the ammonium nitrite to become effective. However, with some modern catalysts designed for NO_x reduction in the tail pipe of automotive vehicles both reaction partners are present on the same zeolite. Surface diffusion over a distance of a few nanometers is typically fast. If a hydrocarbon or an "oxygenate" is used as the primary reductant, the formation of ammonia by reaction of such primary reductant with NO_x becomes rate limiting for automotive NO_x abatement at 200 °C.

5. Conclusion

The results show that Brønsted acid sites catalyze the decomposition of ammonium nitrite even in the absence of a liquid phase. This reaction is known to be part of the reaction network of catalytic NO_x reduction with ammonia or any reductant, capable of converting part of the NO_x to NH_3.

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