

# Impact of Hydrothermal Aging on the Formation and Decomposition of Ammonium Nitrate on a Cu/Zeolite SCR Catalyst

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## ABSTRACT

Low-temperature ( $T \leq 200^\circ\text{C}$ )  $\text{NO}_x$  conversion is receiving increasing research attention due to continued potential reductions in regulated  $\text{NO}_x$  emissions from diesel engines. At these temperatures, ammonium salts (e.g., ammonium nitrate, ammonium (bi)sulfate, etc.) can form as a result of interactions between  $\text{NH}_3$  and  $\text{NO}_x$  or  $\text{SO}_x$ , respectively. The formation of these salts can reduce the availability of  $\text{NH}_3$  for  $\text{NO}_x$  conversion, block active catalyst sites, and result in the formation of  $\text{N}_2\text{O}$ , a regulated Greenhouse Gas (GHG). In this study, we investigate the effect of hydrothermal aging on the formation and decomposition of ammonium nitrate on a state-of-the-art Cu/zeolite selective catalytic reduction (SCR) catalyst. Reactor-based constant-temperature ammonium nitrate formation, temperature programmed oxidation (TPO), and NO titration experiments are used to characterize the effect of hydrothermal aging from 600 to  $950^\circ\text{C}$ .  $\text{N}_2$  adsorption (BET) surface area and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) experiments are also conducted in order to correlate the morphological effects of hydrothermal aging with concomitant changes in ammonium nitrate chemistry. The insights provided herein support the diesel aftertreatment communities' ongoing efforts to understand low-temperature chemical processes such as ammonium salt formation and their impact on emissions.

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## INTRODUCTION

Significant reductions in emissions of oxides of nitrogen ( $\text{NO}_x$ ) from diesel engines have been achieved, first through engine and combustion improvements and later through the integration of the diesel aftertreatment system. Recently, the California Air Resources Board (CARB) has published an optional  $\text{NO}_x$  emission standard up to 90 percent lower than the U.S. Environmental Protection Agency's (EPA) 2010 requirement [1]. This new optional standard (0.02 g/bhp·hr) would necessitate significant reductions in  $\text{NO}_x$  from current diesel engines and aftertreatment systems. One potential improvement and active research area is that of  $\text{NO}_x$  conversion at low engine-out exhaust temperatures ( $T \leq 200^\circ\text{C}$ ) by diesel aftertreatment systems.

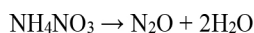
While there are many significant barriers to achieving meaningful improvements in low temperature  $\text{NO}_x$  conversion, one challenge is the potential formation and decomposition of ammonium salts (e.g., ammonium nitrate [AN]) under conditions where both  $\text{NO}_2$  and  $\text{NH}_3$  are present. Equation 1 shows the primary reaction responsible for low temperature AN formation in diesel exhaust systems. Hillard et al. and Pipho et al. have shown that 10 to 30% of the total  $\text{NO}_x$  in exhaust from compression ignition diesel engines is in the form of  $\text{NO}_2$  [2, 3, 4]. Finesso et al. reported a positive correlation between engine-out  $\text{NO}_2/\text{NO}_x$  ratio and intake oxygen concentration [4]. In other words, low exhaust gas recirculation (EGR) rate conditions generally lead to a higher  $\text{NO}_2$

fraction. However, unlike  $\text{NO}_2$ ,  $\text{NH}_3$  is not present in nascent, engine-out diesel exhaust.  $\text{NH}_3$  is introduced in the form of diesel exhaust fluid (DEF), an aqueous urea solution consisting of 32.5 weight percent urea, in diesel engines equipped with a selective catalytic reduction catalyst required to meet stringent worldwide  $\text{NO}_x$  standards such as the U.S. EPA's 2010  $\text{NO}_x$  standard of 0.2 g/bhp·hr.  $\text{NH}_3$  may be either gas-phase resulting from the thermolysis and hydrolysis of DEF or the introduction of gas-phase  $\text{NH}_3$  as has been proposed [5], or a significant amount of  $\text{NH}_3$  may be pre-stored on the catalyst surface [6, 7].

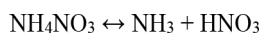
Multiple studies have investigated the formation and decomposition of ammonium nitrate [8, 9, 10]. As is widely acknowledged, AN formation can occur at low temperatures in chemical reactors containing both  $\text{NH}_3$  and  $\text{NO}_2$  through the reaction shown in Equation 1, below. Saunders and Feick et al. reported that the thermal decomposition of AN proceeds through either exothermic, irreversible decomposition to  $\text{N}_2\text{O}$  (Equation 2) or endothermic, reversible dissociation to  $\text{NH}_3$  and nitric acid ( $\text{HNO}_3$ ) (Equation 3) [8, 9]. Saunders et al. found that the irreversible decomposition of pure AN occurs primarily through the  $\text{N}_2\text{O}$  route shown in Equation 2, with trace amounts of nitric oxide, nitrogen dioxide, ammonia, and nitric acid also formed [8]. Figure 1 from Rosser et al. shows the rate of  $\text{N}_2\text{O}$  formation resulting from AN decomposition. Increasing water concentration reduces the rate of  $\text{N}_2\text{O}$  formation (i.e., AN decomposition), while higher temperatures accelerate its formation [10].



(1)



(2)

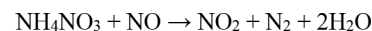


(3)

## EXPERIMENTAL

### Reactor Test Protocol

In this study, the impact of hydrothermal aging on the low-temperature formation and decomposition of AN is evaluated. Aging is conducted at 700, 800, 900, and 950°C for 2 hours at each temperature. For all experiments, AN is formed at either 100 or 125°C for 30 min in a gas mixture consisting of 100 parts per million by volume (ppmv)  $\text{NO}_2$  and 100 ppmv  $\text{NH}_3$  in the baseline gas mixture which consist of 6.5 volume percent (vol.%)  $\text{H}_2\text{O}$ , 10 vol.%  $\text{O}_2$ , 7 vol.%  $\text{CO}_2$ , and balance Ar. Formed AN is then characterized and quantified with TPO and NO titration experiments, respectively. For TPO experiments, the catalyst temperature is increased to 600°C at a rate of 5°C/min in the baseline gas mixture. NO titration experiments are conducted for 3 hr at 125°C following a 30 min AN formation at the same temperature. For these experiments, 100 ppmv NO is added to the baseline gas mixture, and the amount of AN present is calculated based on NO consumption and the stoichiometry in Equation 4, as proposed by Tronconi et al. [12]. A temperature of 125°C was selected for NO titration experiments because the reaction between  $\text{NH}_4\text{NO}_3$  and NO (Eq. 4) is too slow at 100°C to permit accurate measurement.



(4)

### Catalyst Details

This study was carried out on a state-of-the-art small-pore Cu/zeolite SCR catalyst. The active catalyst washcoat is coated onto a 300 cells per square inch (CPSI) cordierite substrate. The catalyst was degreened at 600°C for 2 hours prior to testing in a gas flow consisting of 6.5 vol.%  $\text{H}_2\text{O}$ , 10 vol.%  $\text{O}_2$ , 7 vol.%  $\text{CO}_2$ , and balance Ar. This work focuses on the SCR catalyst, since this catalyst is the most probable location for AN formation due to its high level of  $\text{NH}_3$  storage and the co-location of significant concentrations of  $\text{NO}_2$  and  $\text{NH}_3$ .

### Instrumentation

A catalyst core-reactor was used for experimental work in this study. A schematic of the system is presented in Figure 2, and the reactor system has been described in detail previously [7]. Briefly, the core-reactor consists of MKS™ mass flow controllers for gas metering, a Bronkhorst™ vapor delivery system for introduction of  $\text{H}_2\text{O}$ , a Lindberg™ Blue M tube furnace for reactor temperature control, and a MKS 2030 HS Fourier transform infrared (FTIR) spectrometer for gas analysis. All lines are heated to approximately 190°C to eliminate condensation of water vapor. In addition, all FTIR calibrations were derived for gas-phase measurement at 191°C. The quartz reactor tubes used in this study are 22 inches in length and have inner and outer diameters of 7 and 9.5 mm, respectively.

Catalyst core samples had a length of 1 inch and a diameter of 0.25 inches. Two type K thermocouples (0.02 inch diameter) were inserted into both ends of the core sample for temperature measurement. All gases used in this study were provided by Airgas. Pure gases Ar,  $\text{CO}_2$ , and  $\text{O}_2$  were Ultra High Purity grade (99.999%).

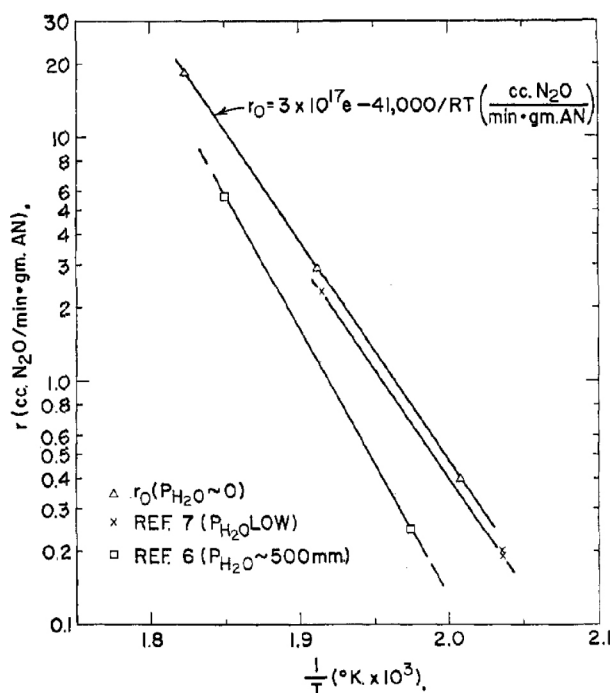


Figure 1. Specific ammonium nitrate reaction rate as a function of temperature and water vapor partial pressure [10].

More recently, Colombo et al. and Tronconi et al. have investigated the role of AN formation and decomposition on selective catalytic reduction (SCR) catalysts, a technology widely used to reduce  $\text{NO}_x$  emissions from diesel engines [11, 12]. In fact, Colombo et al. have published mechanisms and rate expressions explaining the relevant AN chemistry in their mathematical model summarizing cold start effects over zeolite-based SCR catalysts [11]. Furthermore, Tronconi et al. have reported that AN oxidizes NO to  $\text{NO}_2$  at low temperatures ( $100 < T < 250^\circ\text{C}$ ), and that this NO oxidation by AN can enhance the standard SCR reaction, known as “Enhanced SCR” [12].

The present work is focused on understanding the impact of hydrothermal aging on the ammonium nitrate formation and decomposition mechanisms over a state-of-the-art Cu/zeolite SCR catalyst. A reactor-based method is first developed to simulate the real-world formation of AN. AN decomposition is then studied with constant-temperature NO titration and temperature programmed oxidation (TPO) experiments.  $\text{N}_2$  adsorption (BET) surface area and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) experiments are also conducted to correlate the morphological effects of hydrothermal aging with concomitant changes in ammonium nitrate chemistry.

while two component mixtures ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NH}_3$ ) in Ar were National Institute of Standards and Technology (NIST) traceable Primary Standards.

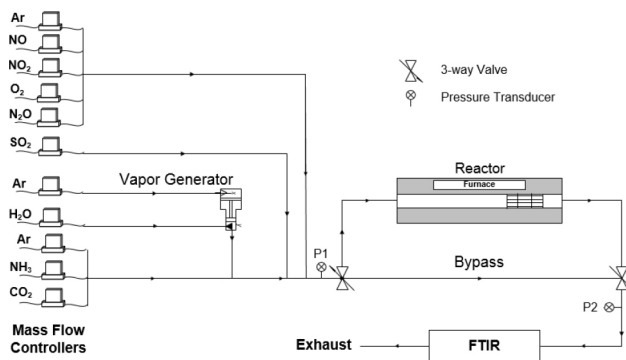


Figure 2. Schematic of catalyst core-reactor

BET surface area was measured with a Micromeritics TriStar II 3020 physisorption analyzer [13]. Ultra High Purity grade (99.999%)  $\text{N}_2$  was used as the sorbate molecule, and the samples were prepared by degassing under vacuum at  $350^\circ\text{C}$  for two hours. The BET equation was then used to calculate the surface area based on an adsorption isotherm constructed from an 11 point  $\text{N}_2$  physisorption experiment performed at  $-196^\circ\text{C}$ .

The DRIFTS reactor, utilized to collect IR spectra of samples after AN formation at  $125^\circ\text{C}$  for 30 min, consists of a Harrick Praying Mantis attachment coupled to a Fisher Scientific Nicolet iS50 FTIR spectrometer with a liquid nitrogen cooled MCT detector. All spectra are presented in absorbance units and are an average of 72 scans taken at a resolution of  $2\text{ cm}^{-1}$ . Spectra are recorded in air at room temperature and are background corrected.

## RESULTS AND DISCUSSION

### AN Formation and Thermal Decomposition

Before aging evaluations, a TPO was conducted on the degreened catalyst after the  $100^\circ\text{C}$ -30min AN formation and is shown in Figure 3.  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{NH}_3$  are all released as the temperature increases from 100 to  $600^\circ\text{C}$  with no apparent  $\text{NO}$  release.  $\text{NH}_3$  release occurs over a broad temperature range from approximately 150 to  $425^\circ\text{C}$ , whereas  $\text{NO}_2$  and  $\text{N}_2\text{O}$  release occur between 200 and  $325^\circ\text{C}$ .  $\text{NH}_3$  release is significantly higher than the release of either  $\text{NO}_2$  or  $\text{N}_2\text{O}$ . The  $\text{NH}_3$  release can be ascribed to both the decomposition of AN (see Equation 3), and the well documented, reversible  $\text{NH}_3$  storage reaction shown in Equation 5. There are three  $\text{NH}_3$  release peaks at approximately 250, 300, and  $370^\circ\text{C}$ , as shown by deconvolution, for clarity. The low- and high-temperature  $\text{NH}_3$  release peaks at 250 and  $370^\circ\text{C}$  can be attributed to the desorption of stored  $\text{NH}_3$  from weak and strong acid sites likely associated with Cu and zeolite Brønsted acid sites, respectively [14]. The release of  $\text{NH}_3$  at approximately  $300^\circ\text{C}$  is due to AN thermal decomposition. In contrast,  $\text{NO}_2$  and  $\text{N}_2\text{O}$  each have a single release peak at approximately  $300^\circ\text{C}$ . The release of both  $\text{NO}_2$  and  $\text{N}_2\text{O}$  can be attributed to the thermal decomposition of AN (see Equations 2 and 3, respectively). Though not a direct product of AN decomposition,  $\text{NO}_2$  likely results from the thermal

decomposition of  $\text{HNO}_3$  as shown in Equation 6 [15]. From Figure 3, the thermal decomposition of AN (i.e., the evolution of  $\text{N}_2\text{O}$ ) begins at approximately  $210^\circ\text{C}$  and accelerates as the temperature increases up to  $300^\circ\text{C}$ . This is in agreement with the findings of Saunders et al. who found that AN decomposes slowly at  $200^\circ\text{C}$  but that the rate of decomposition accelerates significantly at higher temperatures up to  $260^\circ\text{C}$  [8].

Multiple control experiments were conducted to better understand the results in Figure 3. To confirm that the  $\text{NO}_2$  release is not due to the reversible storage of  $\text{NO}_2$ , a control experiment was conducted in which only  $\text{NO}_2$  and baseline gases were introduced at  $100^\circ\text{C}$  for 30 min.  $\text{NO}_2$  release was observed in the subsequent TPO experiment with a peak temperature at  $350^\circ\text{C}$ ,  $50^\circ\text{C}$  higher than the  $\text{NO}_2$  release in Figure 3. In addition, no  $\text{N}_2\text{O}$  was released during the control experiment, further confirming that the co-presence of  $\text{NO}_2$  and  $\text{NH}_3$  is required for AN formation. Two additional control experiments were conducted to better understand real-world formation of AN. First,  $\text{NO}$  was substituted for  $\text{NO}_2$  in the  $100^\circ\text{C}$ -30min AN formation experiment. In this case, there was no evidence of AN formation. Finally, since  $\text{NH}_3$  is not currently introduced into exhaust aftertreatment systems when exhaust temperatures are approximately  $100^\circ\text{C}$ , an AN formation experiment was conducted in which  $\text{NH}_3$  was pre-stored by feeding 100 ppmv  $\text{NH}_3$  in baseline gas at  $100^\circ\text{C}$  for 30 min and then 100 ppmv  $\text{NO}_2$  was introduced for another 30 min. The TPO performed after this staggered AN formation experiment was qualitatively similar to the results in Figure 3, indicating that  $\text{NO}_2$  can react with pre-stored  $\text{NH}_3$  to form AN.

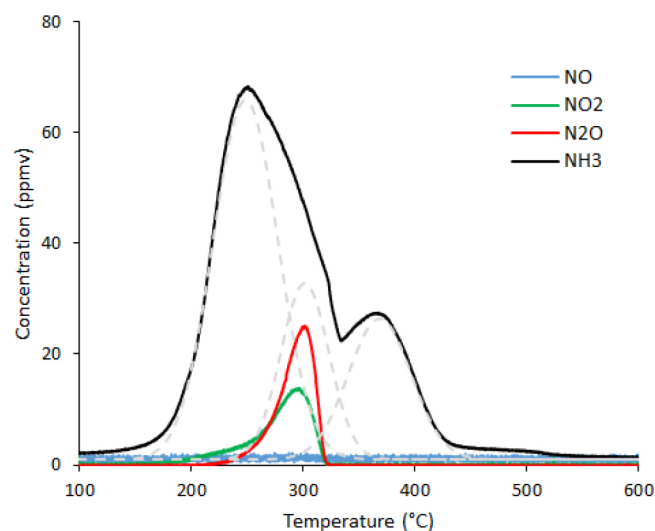
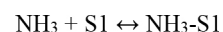


Figure 3. Thermal decomposition of ammonium nitrate formed on the degreened Cu/zeolite catalyst.  $\text{NH}_3$  deconvolution is presented for clarity. Preceded by AN formation with 100 ppmv  $\text{NO}_2$ , 100 ppmv  $\text{NH}_3$ , and baseline gases at  $100^\circ\text{C}$  for 30 min. Dashed, light gray lines show the three  $\text{NH}_3$  release peaks after deconvolution.



(5)

