

Reduction of NH_4NO_3 by NO: Acid Catalyzed Reduction May Prevent Catalyst Deactivation in Low Temperature DeNOx

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Introduction

The Environmental Protection Agency has mandated a 90% decrease in NOx emission standards for on-road diesel vehicles starting in 2007 [1]. As such, low temperature DeNOx catalysis (200°C) is desirable for diesel vehicular exhaust treatments. An important problem is that NH_4NO_3 , which is thermally stable below 250°C, can form in these reaction networks in the presence of NH_3 and potentially deactivate catalysts by blocking catalytically active sites [2-4]. A crucial question is, therefore, whether other gas molecules present in low temperature DeNOx systems can chemically reduce NH_4NO_3 to less thermally stable species. One possible candidate for the reductant is NO. The present study focuses on the ability of NO to reduce NH_4NO_3 to NH_4NO_2 . The product of reduction, NH_4NO_2 , is well known to be thermally unstable above ~100°C and readily decomposes to N_2 and H_2O . We have investigated the effects of different substrates on this reaction.

Materials and Methods

NH_4NO_3 was ground and physically mixed with the powders of various substrates: quartz, trimethylated quartz, Na-Y zeolite, and H-Y zeolite. Following mixing, samples were exposed to either a He flow or a NO flow, in He carrier gas, in a U-shaped quartz flow reactor. The effluent was monitored by either FTIR or GC during controlled heating of the reactor in a cylindrical oven. Temperature programmed desorption experiments with NH_3 as an adsorbate are planned for the various substrates to determine the relative concentrations of Brønsted acid sites.

Results and Discussion

The reaction of NH_4NO_3 with NO at 100°C on quartz yielded N_2 as a final product with NO_2 as the coproduct, consistent with a mechanism that involves an NH_4NO_2 intermediate. In FTIR experiments, NO depletion in the effluent was taken as indicative of the reduction of NH_4NO_3 by NO.

In contrast to methods such as wet impregnation, the physical mixing method of sample preparation preserved the separation of ground NH_4NO_3 and substrate powders, allowing them to remain as discrete but interspersed particles. This mitigated chemical dissociation of the bulk of NH_4NO_3 on substrate powders during sample preparation. Based on depletion of NO in the effluent, neat NH_4NO_3 as well as NH_4NO_3 physically mixed with trimethylated quartz were both reduced by NO only above NH_4NO_3 's melting point (170°C). Whereas physical mixing of NH_4NO_3 with substrates containing exposed Brønsted acid sites facilitated the reduction of NH_4NO_3 by NO at $\leq 100^\circ\text{C}$. Our data show a qualitative correlation between the extent of reaction at a given temperature and the acidity of the substrate (Figure 1). A possible mechanism for the acid catalyzed reduction of NH_4NO_3 by NO will be presented.

Significance

Neat NH_4NO_3 can be reduced by NO above its melting point (170°C), while when physically mixed with acidic substrates NH_4NO_3 can be reduced by NO below 100°C. These temperatures could impact the lower limits for efficient low temperature NOx reduction, and may point towards the desirability of incorporating acidic supports in low temperature DeNOx catalysts.

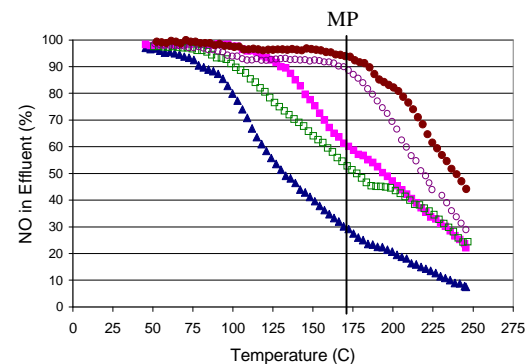


Figure 1. NO depletion during temperature programmed reaction with neat NH_4NO_3 and NH_4NO_3 physically mixed with four different substrates: NH_4NO_3 – No substrate (filled circles), trimethylated quartz (open circles), Na-Y zeolite (filled squares), quartz (open squares), H-Y (filled triangles). The melting point of NH_4NO_3 (MP) is marked with a vertical line for comparison.

References

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