Urea-SCR for NOx Diesel Emission Control: The influence of urea and its decomposition products on the SCR activity of zeolites

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Introduction

Diesel engines are an attractive alternative to gasoline internal combustion engines because they operate with high compression ratios making them 20-25% more fuel efficient. However, due to the combustion of diesel with excess air gaseous emissions such as NO_x cannot be abated by using the 3-way catalyst strategy of gasoline engines [1]. NO_x causes ground level ozone (smog), induces the formation of toxic chemicals as well as acid rain, and is therefore regulated in the U.S. by the EPA. As NO_x standards are becoming more stringent for motor vehicles, the need for NO_x abatement technology is growing.

In power plants and stationary sources, selective catalytic reduction (SCR) is already used to reduce NO_x with NH_3. For diesel vehicles it is proposed to use an aqueous urea solution as the NH_3 source because it is non-toxic and can be much more easily and safely transported [2]. After the injection of the urea solution into the hot diesel exhaust, urea ideally decomposes into NH_3 and CO_2. However, alternative urea decomposition products could poison the SCR catalyst [2]. Hence, the investigation of the urea decomposition in the absence and presence of catalysts is inevitable to understand catalyst deactivation mechanisms and its prevention.

Therefore, we studied the decomposition of urea with and without zeolitic catalysts in the temperature range between 20 and 500°C by simultaneous thermogravimetric (TG) and differential thermoanalysis (DTA). The evolved reaction gases were detected by GC/MS, and the intermediate products at specific temperatures were analyzed by FTIR.

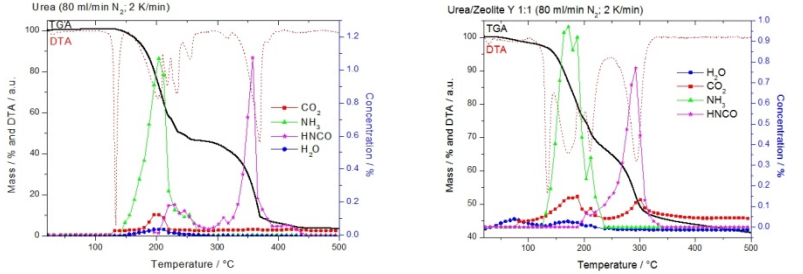
To simulate the influence of the injection of liquid urea into the exhaust stream, we also run measurements in a flow-through reactor with an integrated steam generator that allowed the injection of steam or aqueous urea solution to study the NO_x conversion activity of zeolitic catalysts before and after aging of the samples in water- and urea-containing atmospheres.

Materials and Methods

TGA was done with a TG-DTA/DSC apparatus (NETZSCH STA 409 PC Luxx). The evolved gases were analyzed with a gas chromatograph (AGILENT 6890 series) equipped with a fused silica column (VARIAN CP7447) and coupled to a mass selective detector (AGILENT 5973Network). Solid decomposition products were characterized with an FTIR spectrometer (BIO-RAD FTS 6000) equipped with a DuraSamplIR Diamond ATR (attenuated total reflection). The reactor setup consisted of a gas delivery manifold, using N_2 (UHP grade), 1% NO in Ar (UHP), 1% NH_3 in Ar (UHP), and Air (Dry Grade), regulated by mass flow controllers (MKS Mass-Flo 1179A) connected to a multi gas controller (MKS 647C). NO_x conversion was measured with a NO-NO_2-NO_x analyzer (THERMO ELECTRON 42i-HL). A syringe pump (COLE PARMER 74900 series) was used to generate the desired amounts of steam or urea-containing steam. The SCR reactor consisted of a quartz glass tube, a furnace and heated stainless steel transfer lines. The catalysts investigated were commercial zeolites Y, Cu-Y, H-Beta, Na-Beta and Fe-Beta (all BASF) in powder form and wash-coated on monoliths.

Results and Discussion

The TGA/DTA curves in figure 1 show, that after the melting of urea at 133°C the sample starts to lose mass, and at about 200°C, a distinct endothermic DTA peak can be determined. This mass change is accompanied by the generation of huge amounts of NH_3 peaking at 200°C.



Figures 1, 2: TGA, DTA and GC/MS gas analysis of urea (left) and urea/zeolite y (right).

The first step of the urea decomposition is proposed to be the thermolysis to NH_3 and isocyanic acid: $CO(NH_2)_2 \rightarrow NH_3 + HNCO$ [2]. This reaction perfectly explains the high abundance of NH_3 in the evolved gas. However, only a minor amount of HNCO was detected between 210 and 270°C. The abundance of CO_2 at 200°C is most likely caused by the hydrolysis of HNCO to NH_3 and CO_2. However FTIR studies of solid urea decomposition products at 270°C indicated, that most of the HNCO reacted to cyanuric acid, CyA. CyA decomposes again after heating above 300°C. In Figure 1 the appropriate endothermic DTA peak of this reaction can be identified at 370°C, as well as the peak of the CyA decomposition product HNCO. At 500°C about 5% of the original mass remains as a yellowish solid residue. FTIR studies indicate it is a polymeric heptazine species such as melem or melon.

To study the influence of zeolites the urea sample was mixed with different zeolites and investigated by TGA-GC/MS and FTIR. Figure 2 shows that Zeolite Y significantly alters the urea decomposition process. First, both the urea thermolysis to NH_3 and the decomposition of CyA is shifted to lower temperatures (160 and 290°C instead of 200 and 370°C, respectively). Furthermore, the formation of the intermediate product CyA is decreased tremendously. This trend was also found for mixtures of urea with zeolites such as Cu-Y and Fe-Beta.

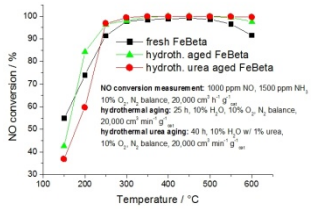


Figure 3: SCR activity of fresh and aged Fe-Beta.

Even though the catalyst improves the decomposition of urea to NH_3 and HNCO, there are still significant amounts of by-products left that might hinder the catalytic performance if deposited on the catalytic surface. NO_x conversion studies in a SCR reactor indeed showed, that NO_x conversion is reduced especially at lower temperatures after 25h aging at 750°C in a urea atmosphere (Figure 3). In the future, surface characterization of the aged catalysts should help to understand whether and how the urea decomposition products decrease the catalytic activity.

Significance

A profound knowledge of the urea decomposition process will help to understand the formation of solid products on the catalyst surface and the walls of the exhaust lines that can cause an increased consumption of urea, the sudden release of huge amounts of HNCO and NH_3 at abrupt exhaust temperature changes and/or the poisoning of catalytic sites.

References

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