Urea-Selective Catalytic Reduction (SCR) for NO_x Diesel Emission Control: Urea-Zeolite Interactions

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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. 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.

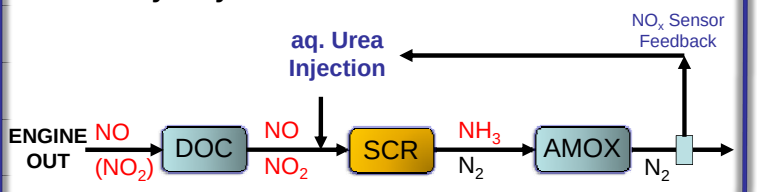
In power plants and stationary sources, SCR is already used to reduce NO_x with NH_3. For diesel vehicles it is proposed to use an aqueous urea solution as the NH_3 source because it is non-toxic and can be much more easily and safely transported. After the injection of the urea solution into the hot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

Experimental

- ***Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA):*** NETZSCH Simultaneous TGA-DTA/DSC Apparatus STA 409PC/4/H Luxx
- ***TGA Evolved Gas Analysis – Gas Chromatography (GC):*** AGILENT 6890 Series Gas Chromatograph with GC capillary column VARIAN WCOT Fused-Silica 30mx0.32mm ID coating CP-Volamine
- ***TGA Evolved Gas Analysis - Mass Spectrometry (MS):*** AGILENT 5973*Network* Mass Selective Detector
- ***Attenuated Total Reflectance (ATR) – Fourier Transform Infrared Spectroscopy (FTIR):*** BIO-RAD FTS 6000 near-IR and mid-IR with DuraSamplIR Diamond ATR

Urea-SCR for NOx abatement

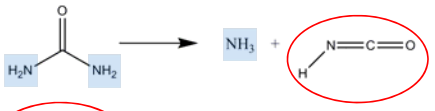
Three Catalyst System for Diesel Cars:



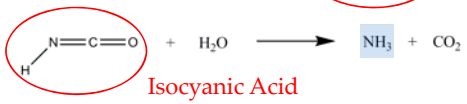
DOC = diesel oxidation catalyst
SCR = selective catalytic reduction of NO_x using NH_3 in the form of liquid urea
AMOX = Ammonia oxidation catalyst to destroy any breakthrough NH_3

- **Ideal overall urea decomposition:**
  $(NH_2)_2CO \rightarrow 2\ NH_3 + CO_2$

1. Step: Thermolysis (fast)



2. Step: Hydrolysis (slow)



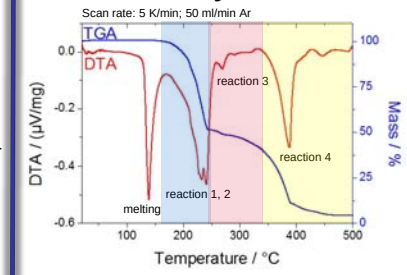
- **Selective catalytic NO_x reduction:**

Standard SCR: $4\ NO + 4\ NH_3 + O_2 \longrightarrow 4\ N_2 + 6\ H_2O$
Fast SCR: $2\ NO + 2\ NO_2 + 4\ NH_3 \longrightarrow 4\ N_2 + 6\ H_2O$
Slow SCR: $3\ NO_2 + 4\ NH_3 \longrightarrow 3.5\ N_2 + 6\ H_2O$

- **SCR catalysts:** Commercial BASF Zeolite Y, Zeolite Cu-Y, Fe-Beta, H-Beta, Na-Beta

Decomposition of Pure Solid Urea

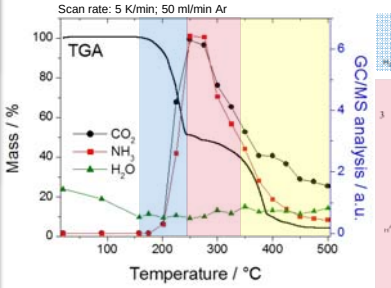
TGA/DTA study



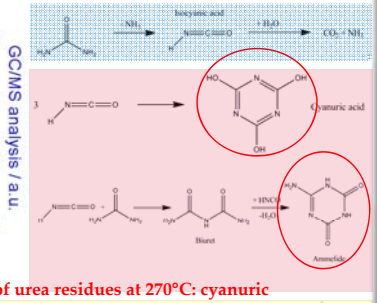
- **2-step decomposition:**
  1) 300°C: only about 50% decomposed
  2) 500°C: ~5% solid residues
- **5 distinct endothermic DTA peaks:**
  133°C: melting point of urea; 230/240°C; 270 °C; 380°C

TGA/GC-MS* study

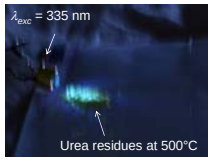
* of evolved gases during decomposition

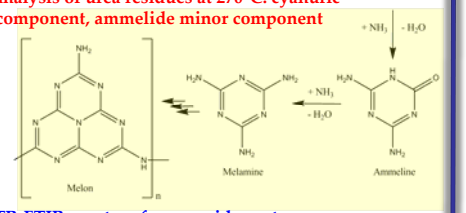


Proposed reactions during decomposition:



ATR-FTIR analysis of urea residues at 270°C: cyanuric acid major component, ammelide minor component

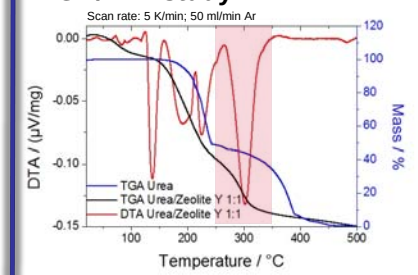




Green luminescence and ATR-FTIR spectra of urea residues at 500°C point to formation of heptazines like melon

Decomposition of Urea/Zeolite Y Mixtures

TGA/DTA study

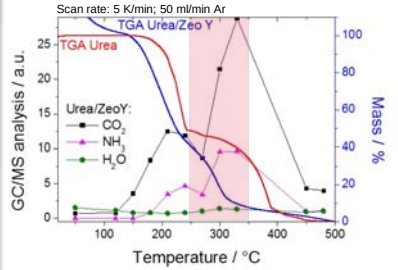


- **almost 1-step decomposition:**
  1) 300°C: about 80% of original urea decomposed
  2) 500°C: ~5% solid urea residues
- **4 distinct endothermic DTA peaks:**
  133°C: melting point of urea; 190°C; 225°C; 300°C

Zeolite Y inhibits the formation of solid by-products (cyanuric acid) at 250-350°C and boosts the generation of NH_3 and CO_2 at 300-400°C

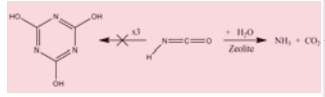
TGA/GC-MS* study

* of evolved gases during decomposition

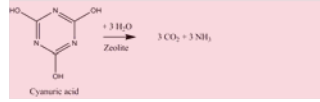


Explanations:

Zeolites could catalyze the hydrolysis of isocyanic acid preventing its polymerization:



and/or catalyze the decomposition of triazines such as cyanuric acid::



Summary & Outlook

- 2-step urea decomposition process: at 250-350°C only ~ 50% decomposed
- Solid decomposition products at 270°C: cyanuric acid and ammelide
- Zeolites catalyze the hydrolysis of cyanuric acid and/or isocyanic acid preventing the formation of urea-decomposition intermediate products
- *Future:* Study of the influence of urea decomposition products on zeolite SCR activity

We are grateful to BASF SE and Columbia University for funding this project.