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Kinetic modeling of urea decomposition based on systematic thermogravimetric analyses of urea and its most important by-products

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AUTHOR-HIGHLIGHTS

- A kinetic reaction model for thermal decomposition of urea is proposed.
- Thermogravimetric analyses of urea, biuret and cyanuric acid are predicted.
- Species concentrations during thermal decomposition of urea are captured.
- Variations in heating rate and initial sample mass can be reproduced.
- The influence of the surface area and the crucible geometry is captured.

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ABSTRACT

A kinetic reaction model for thermal decomposition of urea is presented. Systematic thermogravimetric analyses of urea and its most important by-products, such as biuret and cyanuric acid, are performed to gain the main reactions and their rates. Gaseous products are analyzed and the concentrations of solid products are determined. The reaction scheme, as well as the kinetic parameterization, is validated at different heating rates. The proposed kinetic reaction model matches all performed thermogravimetric analyses and it is also able to reproduce changes in the measurement conditions, such as differences in crucibles geometry or variations of the initial sample mass.

1. Introduction

The selective catalytic reduction (SCR) is a promising solution to fulfill the upcoming nitrogen oxide (NO_x) emission regulations for lean burning engines (Köbel et al., 2000; Moser et al., 2001) and is widely used for on- as well as off-highway applications. To supply the reducing agent ammonia, an aqueous 32.5 wt% urea solution (brand name: AdBlue) is used for reasons of toxicity and safety. Owing to the variety of different exhaust gas configurations, their development and application require appropriate support from numerical simulation in order to obtain the required objectives, i.e. functionality, cost-effectiveness and robustness.

Therefore, it is necessary to assess the SCR performance, the risk of deposits and the pressure drop of the exhaust gas system during the early stages of the product development process through simulation methods. The evaluation of spray preparation by numerical simulation, especially the uniformity of the reducing agent and the flow field in front of the SCR catalyst, has become state-of-the-art (Weltens et al., 1993; Birkhold et al., 2006, 2007). Chemical reactions inside the SCR catalyst are well known and can be described by simulation models (Köbel and Elsener, 1998; Ciardelli et al., 2004). In contrast, a reliable prediction of the deposit risk through numerical simulation still remains a topic of research.

Urea deposits occur under unfavorable conditions, when a urea water solution is sprayed into the exhaust system. This can lead to a failure of the dosing strategy. Consequently, the SCR system cannot reach the maximum possible NO_x conversion and the decomposition of existing urea by-products can result in a higher

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ammonia slip. Moreover, the formed deposits may clog the exhaust gas pipe, or at least, increase the pressure drop.

Since the impingement of spray on the wall as well as the formation of a liquid wall film cannot be avoided in many cases, it is necessary to consider the competitive processes of wall film evaporation and chemical conversion into solids to increase the simulation reliability regarding the deposit risk. Urea deposits appear if the rate of formation of thermally stable urea by-products from the impinged AdBlue exceeds the rate of evaporation and decomposition of the products. This strongly depends on the thermal behavior of the wall and the chemical reactions of the urea in the film. However, a suitable chemical kinetic scheme for the decomposition of urea is not available yet, even though the possible reactions of urea decomposition are well known (Koryakin et al., 1971; Stradella and Argentero, 1993; Schaber et al., 2004; Eichelbaum et al., 2010; Bernhard et al., 2012).

Koryakin et al. (1971), Stradella and Argentero (1993) and Schaber et al. (2004) studied the decomposition of urea and its by-products biuret, cyanuric acid, ammelide and triuret by thermogravimetric analyses. To identify the reactions, different analysis methods were used, which differed in the measurement conditions, such as heating rates, crucible geometries or initial sample masses. This must be regarded in a critical manner, as Lundström et al. (2009) have shown that urea decomposition depends strongly on the measurement conditions.

Furthermore, Koryakin et al. (1971) and Eichelbaum et al. (2010) found a strong influence of the geometric structure of the crucible on the urea decomposition behavior. Koryakin et al. (1971) assumed that this phenomenon results from an increasing triuret production in thin layers, in accordance with the findings of Spasskaya (1969). According to Eichelbaum et al. (2010), this effect can be attributed to the enlarged sample surface, which causes a quick removal of gaseous products. The observed steps of decomposition also depend on the used heating rate, as shown by the comparison of the available measurement data (Koryakin et al., 1971; Stradella and Argentero, 1993; Schaber et al., 2004; Eichelbaum et al., 2010). Consequently, a profound knowledge of these phenomena is necessary for a suitable modeling of urea decomposition.

Ebrahimian et al. (2012) made the first attempt to derive a kinetic scheme for urea decomposition. They suggested a semi-detailed kinetic scheme, which considers, besides global reactions, the formation of intermediates like ammonium and cyanate ions. The model was tested against the data made available by Schaber et al. (2004) and Lundström et al. (2009) and was able to depict the impact of a higher heating rate that causes an enhanced formation of solid by-products. This kinetic modeling depends on the initial sample mass, which limits the practical use of the model. In contrast to thermogravimetric analyses, the instantaneous wall film mass varies in a SCR system because of the dosing strategy. Furthermore, the necessity of different activation energies for urea and aqueous urea solution reveals the lack of a suitable description of the evaporation phenomena.

Nevertheless, the concentration profiles as well as the thermogravimetric analyses of urea, both done by Schaber et al. (2004), can be reproduced. But the model fails to predict the qualitative decomposition behavior of heavier by-products like biuret, cyanuric acid and ammelide.

The model cannot describe the absorption and desorption of a non-reacting gaseous species at the interface between the solid phase and the gas phase. However, it is necessary to describe the geometry dependency of urea decomposition, as shown by the crucible variations of Koryakin et al. (1971) and Eichelbaum et al. (2010). Hence, without a method to capture such geometric effects, the portability of the kinetic model towards an exhaust gas system seems to be problematic.

A suitable description of urea decomposition through simulation has to fulfill the following requirements:

- Description of the mass decrease of urea and its solid by-products during thermal decomposition.
- Prediction of the release of gaseous products as well as of the concentration profiles of the solids and liquids during urea decomposition, in order to confirm the used reactions.
- Reproduction of variations in heating rate and initial sample mass to guarantee the reliability of the kinetic approach and parameterization.
- Capturing of geometric effects, such as the influence of the surface area, to guarantee the portability of the kinetic model towards an exhaust gas system.
- Independence of the kinetic modeling from initialization data, so that it could be easily integrated into a computational fluid dynamics code.

Accordingly, the decomposition processes of urea and its most important by-products, such as cyanuric acid and biuret, are investigated in detail in this study. The main reaction paths are identified at consistent measurement conditions by collection of data characterizing the gases evolved during the thermal decomposition and by analysis of the selected solid phase concentration profiles. Based on the systematic thermogravimetric analyses, including variations of the heating rate and initial sample mass, a global kinetic scheme for urea decomposition is developed. To guarantee the portability of the kinetic scheme towards different geometries, the used continuously stirred-tank reactor (CSTR) approach is extended by an evaporation model for isocyanic acid. Furthermore, the kinetic parameterization does not depend on the initial sample mass. Consequently, the kinetic model can easily be integrated into a computational fluid dynamics code.

2. Methods

2.1. Experimental

The thermogravimetric analyses (TGA) were performed on a TG/DTA 6300R from Seiko Instruments Inc, under nitrogen atmosphere (250 $\mathrm{ml_N/min}$), with a cylinder-like alumina crucible (crucible area = 14.52 $\mathrm{mm^2}$).

The gaseous products were analyzed by using a Fourier transform infrared spectrometer (FTIR) of Bruker (Bruker FTIR TENSOR) coupled with a thermogravimetric analyzer of Netzsch (Netzsch TG 209 F1 IRIS). The measurements are done under nitrogen atmosphere (70 $\mathrm{ml_N/min}$) with a cylinder-like alumina crucible (crucible area = 50.27 $\mathrm{mm^2}$). As the measurement window misted up, reliable FTIR measurements were only possible up to 260 °C.

At the same measuring conditions, thermogravimetric analyses are performed by using a Netzsch STA F3 JUPITER. At characteristic temperatures corresponding to minima of the differential thermal gravimetric (DTG) curve, the sample was quenched at room temperature. Afterward, the remaining sample mass was qualitatively and quantitatively analyzed by using high-performance liquid chromatography (HPLC).

The samples were purchased from Merck KGaA (urea $>99.5\%$ purity), from Sigma-Aldrich Co. (biuret $>98.5\%$ purity) as well as from Merck Schuchardt OHG (cyanuric acid $>98\%$ purity), and were used without further purification.

2.2. Simulation

For kinetic simulations, the numerical simulation package DETCHEM (Deutschmann et al., 2011) is extended by DETCHEM$^{\mathrm{EVAPORATOR}}$ which calculates the time evolution of a