Kinetic modeling and simulation of high-temperature by-product formation from urea decomposition

C. Kuntz 1, C. Kuhn 1, H. Weickenmeier 1, S. Tischer 2, M. Börnhorst 1, O. Deutschmann 1,2

Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76128 Karlsruhe, Germany

HIGHLIGHTS

• Investigation of high-temperature urea by-products by TG, DSC and MS.
• Evaluation of kinetics for the decomposition of high-temperature urea by-products.
• Development of a reaction mechanism over the whole SCR relevant temperature range.
• Simulations with multiphase tank reactor model in good agreement with exp. data.

PHOTOGRAPHICAL ABSTRACT

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ABSTRACT

The Selective catalytic reduction (SCR) technique is widely applied in exhaust gas after-treatment of diesel engines. Depending on operating conditions, injected urea-water solution (UWS) can form liquid films on mixer blades and the pipe wall. Evaporation and subsequent reactions in the wall film can lead to deposits of urea and by-products, respectively. Especially deposits that are not decomposed up to high temperatures are challenging for the SCR technique. Thermogravimetric experiments are conducted for these stable urea by-products, such as ammelide, ammeline and their by-products, such as cyanamide or melamine. An analysis of the evolving gases during thermal decomposition led to a more detailed understanding of the kinetics. The postulated mechanism is able to predict the thermogravimetric analyses results and the effects of variation of the experimental conditions such as initial sample mass and heating rates. The evaluated kinetics, together with the recently developed kinetics for the urea/biuret/triuret/cyanuric acid system Tischer et al. (2019), can now be integrated into CFD simulations of SCR systems to numerically simulate all relevant physical and chemical processes in UWS equipped aftertreatment systems for a wide range of conditions.

1. Introduction

The control of emissions of nitrogen oxides ($\text{NO}_x$) is a challenge in every combustion using air as oxidizer. The need for efficient and reliable aftertreatment of $\text{NO}_x$ emissions became obvious to
the broad public in the last years concerning diesel fueled internal combustion (IC) engines and this need will remain in the future, in particular for the increasing number of IC engines fueled with natural gas and (green) hydrogen. Selective catalytic reduction (SCR) catalysts use ammonia to reduce the NO\textsubscript{x} emission from IC engines.

Today, this ammonia is most commonly supplied in form of a 32.5\% urea-water solution (UWS), which is sprayed into the hot exhaust pipe. Thermolysis and hydrolysis yield the necessary reducing agent NH\textsubscript{3} and CO\textsubscript{2}. However, incomplete evaporation and decomposition of UWS droplets lead to spray-wall interaction and film formation, depending on the boundary conditions (Birkhold, 2007; Börnhorst et al., 2016; Brack et al., 2016; Lundström et al., 2011; Postrioti et al., 2015; Quissek et al., 2019). Over time, condensed urea and by-product deposits can be formed from the UWS film, which reduce the ammonia uniformity and bear the risk of increased pressure drop, up to a complete blockage of the exhaust pipe (Schaber et al., 2004; Lundström et al., 2009; Bernhard et al., 2012; Ebrahimian et al., 2012; Brack et al., 2014). Although the amount of formed high-temperature by-products of the initial injected urea mass is rather small, it is especially very important to understand their formation and decomposition, since these will only decompose at temperatures above 400 °C, which is only rarely achieved in normal SCR systems. Alternative manual removal is expensive and should be avoided. Many authors studied the formation and decomposition of urea and its by-products, giving an insight in possible reactions and kinetics (Ostrogovich and Bacaloglu, 1965; Stradella and Argentero, 1993; Fang and DaCosta, 2003; Schaber et al., 2004; Eichelbaum et al., 2010; Ebrahimian et al., 2012; Bernhard et al., 2012; Brack et al., 2014; Börnhorst and Deutschmann, 2018; Tischer et al., 2019; Wang et al., 2019; Krum et al., 2021).

Ostrogovich and Bacaloglu (1965) published one of the first semi-detailed reaction mechanism describing the thermolysis of urea with the formation of biuret, guanidine, cyanuric acid, ammelide, ammeline, melamine and several intermediate species. They investigated the yield of these deposits over time at different temperatures and established equations to calculate the respective percentage. Several years later Schaber et al. (2004) investigated the thermal decomposition of urea in an open reaction vessel using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) coupled with mass spectrometry (MS), FT-IR spectroscopy, high performance liquid chromatography (HPLC) to analyze the originated residues and ammonium ISE (ion-selective electrode) measurements. They developed a reaction scheme which is divided in four temperature regions: Up to 190 °C urea melts and decomposes, from 190 °C to 250 °C biuret decomposes and forms cyanuric acid and ammelide, from 250 °C to 360 °C cyanuric acid sublimates and in the last range above 360 °C high-temperature deposits like ammelide and ammeline are decomposed.

First detailed kinetic models for urea decomposition were developed by Ebrahimian et al. (2012) and Brack et al. (2014). Both models are based on systematic analysis of TGA experiments and evolving gases during heat up of various urea by-products, but vary in their specific reactions implemented. Several later publications either used the one or the other as basis for further development or implementation into CFD (Börnhorst et al., 2020; Budziakou et al., 2020; Habchi et al., 2015; Sun et al., 2018).

Our recent study Tischer et al. (2019) proposes a reaction mechanism for urea decomposition, that accounts for thermodynamic effects of deposit formation such as phase transitions. The presence of an eutectic mixture of urea and biuret was revealed to explain the experimental observations by Schaber et al. (2004) and Brack et al. (2014) of biuret decomposition starting at 193 °C and the formation of a foam like structure at around 210 °C. The new approach does not depend on the addition of a kind of arbitrary “matrix” species (Schaber et al., 2004; Brack et al., 2014). Furthermore a second eutectic mixture with triuret was proposed but, due to a lack of data for the thermodynamic potentials of biuret and triuret, not yet integrated to the model. It is shown that cyanuric acid rather sublimates than being decomposed, as assumed before (Ostrogovich and Bacaloglu, 1965; Eichelbaum et al., 2010). Hence, the proposed reaction mechanism can explain more effects with less assumptions than the kinetics published before. A recent study by Krum et al. (2021) modified the mechanism by (Brack et al., 2014), applying it to experiments with higher heating rates. However, all those mechanism have in common, that they do not propose any detailed scheme that goes beyond the sublimation or decomposition of ammeline and melamine, that means at temperatures above 400 °C.

Actually, Liebig (1834) was the first who published possible formation and decomposition reactions of ammelide, ammeline, melamine, melam, melem and melon, in 1834, when studying urea and its derivatives as a naturally occurring product, which could be extracted from urine. In the next 160 years, molecules with C-N bonds often were of interest to many researchers, e.g., Liu and Cohen (1989) reported a theoretical study suggesting that carbon nitride structures (C\textsubscript{3}N\textsubscript{4}) could have a compressibility comparable to diamond. Different modifications of C\textsubscript{3}N\textsubscript{4} (Liu and Cohen, 1989; Yin et al., 2003; Yin et al., 2003) were synthesised and characterized, such as graphitic carbon nitride (g – C\textsubscript{3}N\textsubscript{4}) from urea or its byproducts (Gross and Höppe, 2020; Jürgens et al., 2003; Lotsch, 2006; Miller et al., 2017; Zhu et al., 2014). Furthermore g – C\textsubscript{3}N\textsubscript{4} was found as a metal free catalyst and optoelectronic semiconduc-

tor (Zhang et al., 2014; Zhu et al., 2014; Ruan et al., 2015).

Lotsch and Schnick (Lotsch, 2006) work on precursors for, and the formation of, carbon nitride networks (Lotsch and Schnick, 2005; Lotsch and Schnick, 2007). A mechanism describing reactions from melamine, over the formation of melam or directly, to g – C\textsubscript{3}N\textsubscript{4} via the gradual deam-
monation and polymerization was proposed and validated through several analytical, crystallographic, spectrometric, thermal and calorimetric methods.

Zhu et al. (2014) published a review paper on the synthesis, properties and applications in catalysis of graphitic carbon nitride. Several synthesis routes from cyanamide, guanidine hydrochloride, surfactants and pure urea are gathered and discussed. Furthermore they discuss the physicochemical properties of g-C₃N₄. A study using TGA coupled with MS revealed that g-C₃N₄ can withstand temperatures up to 600 °C without significant mass loss, even in oxidizing atmosphere. It is furthermore depicted that g-C₃N₄ rather decomposes than being oxidized with O₂. The analysis of the evolving gases with MS supports this assumption by showing the formation of NH₃, CNH and C₂N₂ and no signal for oxides like CO or CO₂.

In this work we combine the published mechanisms on urea decomposition up to ammeline with a novel mechanism for the deamination and polymerization reactions of melamine to graphitic carbon nitride. To the best of our knowledge, for the first time a detailed kinetic scheme is proposed to capture the decomposition of urea and its by-products up to temperatures of 750 °C.

2. Experiments

For kinetic and thermodynamic investigation of high-temperature urea deposits experimental data are derived from thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and mass spectroscopy (MS). All TG experiments follow the same procedure for each experiment. The sample is ground and 5mg to 100mg initial mass is placed in a corundum crucible. With a constant heating rate between 2 and 10K min⁻¹ the samples are heated from room temperature to 750 °C. Surrounding the crucible a purge gas flow of 100mL min⁻¹ of synthetic air (20.5% O₂ in N₂) flows, if not further specified.

Pure ammelid (Dr. Ehrenstorfer GmbH, 99.4%), ammeline (Sigma Aldrich, 97.9%), cyanamide (Sigma Aldrich, 99%), dicyandiamide (Sigma Aldrich, 99%), melamin (Fluka AG, 99%) and melem (Chemos GmbH & Co. KG, 98.2%) are used for the measurements.

A Mettler DSC 30 is used to investigate the thermal behaviour of the samples during heat up. DSC, as a thermo-analytical measurement technique, can detect exothermic or endothermic heat flows in comparison to a reference, which allows to gather data on heat capacities, heat of transition, heat of reaction or heat of a phase change (sublimation, melting or vaporization). Like in the TG experiments, the samples with an initial mass of 5 to 10mg are heated from room temperature to 750 °C with an surrounding synthetic air flow. For better heat flow measurement aluminum crucibles are used for sample and reference. Equipped to the DSC is a Netzsch QMS 403 Aëolos Quadro mass spectrometer to analyze the evolving gases, which are produced from the sample during heat-up.

A list of all experiments conducted in this study is given in Table 1. There, the type of the experiment, crucible type, substance, initial weight and the heating ramp is given. Experiments are either conducted as TG or DSC measurements, where the DSC experiments however include TG and MS measurements as well. The substance was either placed in a cylinder-type crucible (6mm inner diameter and 12mm height) or in a plate-type crucible (15mm inner diameter and 5mm height) in the specified setup. For each species several experiments, differing in initial mass or heating rate, are conducted to investigate the decomposition under different conditions.

3. Numerical Model

The TG and DSC experiments are simulated by our zero-dimensional batch-type reactor model (Tischer et al., 2019), which is implemented as DETCHEMMPTR (MPTR: multi-phase tank reactor) in the DETCHEM software package (Deutschmann et al., 2018). Each species Si is grouped into a specific phase Pi. Mixtures of species within a phase are considered ideal. However, by using multiple phases for liquid, aqueous and the different solid species, this assumption can be justified. A phase change of a substance is handled by two different species in two different phases. Thermo-dynamic data, namely specific heat, enthalpy and entropy, for each species are calculated based on assigned NASA-polynomials (Eqs. (1)–(3)).

\[
\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4
\]

\[
\frac{H_m}{R} = a_1 T + \frac{a_2 T^2}{2} + \frac{a_3 T^3}{3} + \frac{a_4 T^4}{4} + \frac{a_5 T^5}{5} + a_6
\]

\[
\frac{S_m}{R} = a_1 \ln T + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_6
\]

Species conservation (Eq. 4) and enthalpy conservation (Eq. 5) are handled by two different species in two different phases. Thermo-dynamic data, namely specific heat, enthalpy and entropy, for each species are calculated based on assigned NASA-polynomials (Eqs. (1)–(3)).
$k_p = 200 \text{ W m}^{-2}\text{K}^{-1}$ is chosen. DSC signals is the (negative) enthalpy change of all condensed species in the system. Since gas phase reactions shall not be considered in this study, the DSC signal equals the change of the total enthalpy minus the power to heat the gas (Eq. 7).

$$p_{\text{DSC}} = -\frac{dH}{dT} + \left(\sum_{i} R_i C_{pi}\right) \frac{dT}{dt} \tag{7}$$

For more information about the reactor model and calculation of the reaction rates we refer to our previous paper Tischer et al. (2019).

4. Thermodynamics and reaction mechanism

From our former study Tischer et al. (2019), we know, that thermodynamics, in particular phase transitions and eutectica, play a significant role in decomposition of urea and its by-products. With the availability of DSC measurements, the phase change, sublimation and reaction enthalpies can be considered and integrated into the thermodynamic properties of all species involved. The thermodynamic data for fundamental gaseous species, namely water $H_2O(g)$, ammonia $NH_3(g)$ and isocyanic acid HNCO(g), as well as their liquid or aqueous phases are taken from thermodynamic databases Tischer et al., 2019; Burcat, 2006.

In the following, the considerations, calculations and assumptions for thermodynamic properties of involved high-temperature urea by-products are discussed, a summary is given in Table 2. NASA coefficients for these species were estimated for a temperature range from 273K to 1023K (see thermdata in the supplemental information).

The proposed reaction mechanism is based on the given literature data and the experimental findings in this work, a summary of all involved reactions can be found in Table 3.

4.1. Ammeline and Ammeline

Ammeline and Ammeline (the chemical structure is given in the Supplemental Information Fig. A1) are both well known species from existing decomposition mechanisms of urea and its by-products. Their decomposition was often described as simple sublimation process (Brack et al., 2014) or as a 1-step decomposition reaction (Ebrahimian et al., 2012). Schaber et al. (2004) described the reaction from ammeline to ammeline as ammoniation, however these reactions only occur at elevated pressures, which is rarely the case in SCR applications. The reaction of ammeline to ammeline is given by Eq. 8 as used in this work (Tischer et al., 2019). Furthermore a direct reaction to melem (Eq. 9) is implemented. Both reactions are clearly global reactions, but can describe the experimental findings sufficiently well.

$$3\text{amm}(s) \rightarrow 2\text{amm}(s) + \text{Cyd}(s) + 2\text{CO}_2 \quad \Delta_h(300^oC) = -140.8\text{kJ mol}^{-1} \tag{8}$$

Only few literature mechanisms include ammonium decomposition. Schaber et al. (2004) stated an ammoniation reaction of ammeline to melamine, which however is unlikely to happen solely, due to low ammonia concentrations. A simultaneous decomposition and polymerization of ammeline with increasing temperature is more likely. A decomposition reaction of ammeline to HNCO and Cyd is proposed (Eq. 10). Furthermore an equally occurring polymerization to melam (Eq. 11) and melam (Eq. 12) is assumed.

$$\text{amm}(s) \rightarrow \text{HNCO} + 2\text{Cyd}(s) \quad \Delta_h(300^oC) = 237.0\text{kJ mol}^{-1} \tag{10}$$

$$3\text{amm}(s) \rightarrow \text{melem}(s) + 3\text{HNCO} \quad \Delta_h(300^oC) = 174.5\text{kJ mol}^{-1} \tag{11}$$

$$3\text{amm}(s) \rightarrow \text{melem}(s) + 3\text{HNCO} + 3\text{NH}_3 \quad \Delta_h(300^oC) = 139.4\text{kJ mol}^{-1} \tag{12}$$

4.2. Cyanamide and Dicyandiamide

Cyanamide (Cyd) is a rather simple molecule consisting of only a primary amino- and a nitrile group, which are directly connected
Table 3
Kinetic parameters of the proposed reaction scheme. Reactions and kinetics for the low-temperature range up to 400 °C, indicated by a *, are taken from Tischer et al. (2019).

| Reaction | $n_b$ | $A_b$ | $\beta_b$ | $E_{SA}$ [kJ mol⁻¹] |
|----------|------|------|---------|---------------------|
| **Homogeneous phase** | | | | |
| ammd(s) → 2HNCO + 2Cyd(s) | 1 | $4.0 \times 10^{10}$ | 0 | 175.67 |
| 3ammd(s) → 2ammn(s)+ Cyd(s) + 2CO₂ | 3 | $1.0 \times 10^{6}$ | 0 | 185.67 |
| 3ammn(s) → melem(s) + Cyd(s) + 2CO₂ + H₂O | 1 | $1.5 \times 10^{14}$ | 0 | 185.67 |
| ammn(s) → HNCO + 2Cyd(s) | 1 | $8.0 \times 10^{10}$ | 0 | 187.67 |
| 3ammn(s) → melem(s) + 3HNCO + 2NH₃ | 1 | $1.0 \times 10^{13}$ | 0 | 200.67 |
| 3ammn(s) → melem(s) + 3HNCO + NH₃ | 1 | $1.0 \times 10^{13}$ | 0 | 200.67 |
| 2Cyd(l) → Dcd(s) | 2 | 9.0 × 10⁶ | 0 | 115.67 |
| 3Dcd(l) → 2mela(s) | 1 | 2.0 × 10¹² | 0 | 165.67 |
| 3Dcd(l) → melam(s) + NH₃ | 1 | 4.0 × 10¹² | 0 | 165.67 |
| 2mela(s) → melam(s) + NH₃ | 1 | 2.0 × 10⁹ | 0 | 157.67 |
| melam(s) → melam(s) + NH₃ | 1 | 3.0 × 10¹² | 0 | 215.67 |
| melam(s) → 6HCN + NH₃ + 2N₂ | 1 | 0.6 × 10¹² | 0 | 215.67 |
| melem(s) → melon(s) + NH₃ | 1 | 2.5 × 10⁹ | 0 | 130.71 |
| melem(s) → 2g – C₄N₄(s) + 2NH₃ | 1 | 1.2 × 10⁹ | 0 | 130.71 |
| * urea(l) + HNCO(l) → biu(s) | 1 + 1 | 1.0 × 10⁴ | 0 | 0 |
| * urea(l) + HNCO(l) → biu(l) | 1 + 1 | 1.0 × 10⁴ | 0 | 0 |
| * biu(l) + HNCO(l) → triu(s) | 1 + 1 | 1.0 × 10⁴ | 0 | 0 |
| * triu(s) → cyu(s) + NH₃ | 1 | 1.2 × 10⁹ | 0 | 45 |
| * triu(s) → ammd(s) + H₂O | 1 | 3.0 × 10⁹ | 0 | 45 |
| **Surface** | | | | |
| mela(s) → mela(g) | 1 | 9.0 × 10⁶ | 0 | 141.3 |
| melon(s) → 2g – C₄N₄(s) + NH₃ | 1 | 7.5 × 10⁹ | 0 | 149.7 |
| 5melon(s) → 9C₃N₂ + 12HCN + NH₃ + 7N₂ | 1 | 3.0 × 10⁹ | 0 | 149.7 |
| 2g – C₃N₄(s) → 3C₂N₂ + N₂ | 1 | 2.8 × 10⁹ | 0 | 149.7 |
| * 2urea(l) → biu(l) + NH₃ | 2 | 3.5 × 10⁹ | 0 | 99.0 |
| * biu(l) + urea(l) → triu(l) + NH₃ | 1 + 1 | 2.0 × 10⁹ | 0 | 116.5 |
| * cyu(l) → cyu(g) | 1 | 3.0 × 10⁹ | 0 | 141.3 |
| **Phase change** | | | | |
| Cyd(s) → Cyd(l) | 1 | $8.8 \times 10^{-2}$ | 0 | 0 |
| Dcd(s) → Dcd(l) | 1 | $8.8 \times 10^{-2}$ | 0 | 0 |
| * H₂O(g) → H₂O(l) | 1 | $8.6 \times 10^{-2}$ | 0.5 | 0 |
| * urea(g) → urea(l) | 1 | $4.7 \times 10^{-2}$ | 0.5 | 0 |
| * HNCO(g) → HNCO(l) | 1 | $5.5 \times 10^{-2}$ | 0.5 | 0 |
| * urea(l) → urea(s) | 1 | $1.0 \times 10^{-6}$ | 0 | 0 |
| * biu(l) → biu(s) | 1 | $1.0 \times 10^{-6}$ | 0 | 0 |

The specific heat, obtained by DSC, is given in SK-steps from 305K to 465K as 122.49-171.02J K⁻¹ mol⁻¹, which can be approximated up to its melting point by a linear regression function as given in Table 2. The specific heat of 264.57J K⁻¹ mol⁻¹ at 495K can be interpreted as the liquid phase one. Calculated Gibbs free energies for Cyd and Dcd, both for solid and liquid phase, are shown in Fig. 1. Melting points, marked by the temperature where curves for solid and liquid phase intercept, are highlighted with black circles and given as previously discussed. TG curves of Cyd and Dcd at different heating rates and initial masses, as well as a DSC curve for Dcd, are given in Fig. 2.

As can be denoted from the TG curves the decomposition of Cyd and Dcd is overlapping and it can be clearly seen, that Cyd dimerizes to Dcd (Eq. 14). Furthermore, melting of Dcd (Eq. 15) can be observed at about 211 °C, which is also in good agreement with literature data (Zhang et al., 1997; Güthner and Mertschenk, 2000; Zhang et al., 2014). As soon as Dcd melts, first decomposition starts. As shown in Bojdyss (2009), Dcd can react either to melamine (Eq. 16) or directly to melam (Eq. 17). In addition, small parts are directly decomposed to gaseous HCN, NH₃ and nitrogen (Eq. 18).
ammonia and a lemon-colored residue. Later on, several works discussed either a decomposition (Smolin and Rapoport, 1959) or a sublimation (Mccellan, 1940; Crews et al., 2000). For this work both approaches are used and implemented, as described in Bann and Miller (1958) with “When heated, melamine sublimes with some decomposition”. TG data of melamine for various heating rates and initial masses (Fig. 3) show that less than 5% is decomposed or polymerized and the most of it sublimes. Low heating rates and therefore more time at polymerization temperatures promote the formation of a residual and vice versa, for example for high heating rates the sublimation prevails and occurs almost exclusively. Furthermore, one can see that a high heating rate and a high initial mass shift the TG curve to higher temperatures, whereas with low heating rates and low initial masses the decomposition takes place at lower temperatures, as it is closer to an equilibrium state. (see Fig. 4).

The sublimation of melamine and its respective reaction enthalpy is denoted in Eq. 19. As polymerization product either melam (Smolin and Rapoport, 1959; Lotsch, 2006; Wirnhier et al., 2013) and/or melem (Smolin and Rapoport, 1959; Lotsch, 2006) is given in the literature. Several reports claim that they produced melam by pyrolyzing melamine, which was later identified as melam by IR and UV spectroscopy. In contrast to that, May (1959) reported the formation of melam, melem and melon as pyrolysis products of melamine at 360 °C, 400 °C and 500 °C, respectively. Therefore the decomposition of melamine is described for both possible routes, to melam (Eq. 20) and to melem (Eq. 21).

\[
mela(s) \rightarrow \mela(g) \quad \Delta_{\text{r}}H(340 \degree C) = 121.3 \text{kJ mol}^{-1} \quad (19)
\]

\[
2\mela(s) \rightarrow \melam(s) + \text{NH}_3(g) \quad \Delta_{\text{r}}H(200 \degree C) = 43.0 \text{kJ mol}^{-1} \quad (20)
\]

\[
2\mela(s) \rightarrow \melem(s) + 2\text{NH}_3(g) \quad \Delta_{\text{r}}H(200 \degree C) = 23.4 \text{kJ mol}^{-1} \quad (21)
\]

Thermodynamic data for solid melamine is obtained from Salley and Gray (1948) and Smolin and Rapoport (1959). Based on solid melamine’s sublimation enthalpy of 121.3kJ mol⁻¹ at 340 °C from Smolin and Rapoport (1959) and melamine’s gas phase standard enthalphy of formation of 70.1kJ mol⁻¹ from Gratzfeld and Olzmann (2017), the thermodynamic data for gaseous melamine are calculated. Due to the lack of sufficient literature data a 2nd

4.3. Deammonation process to graphitic carbon nitride

Since the work of Liu and Cohen (1989) proposed carbon nitrides as super-hard materials, many researchers were emphasized to work on synthesis routes to form them from C/N/H species. But already about 150 years earlier research was done on different nitrogen molecules.

Melamine was first prepared by Liebig (1834) in 1834. During heat up, he described a melt that pulls itself up on the walls of the tube, without sublimation, but decomposition with evolving
order polynomial for specific heat is used. Starting from melamine, the deamination process leads to melam, then melem, then melon and last of all to graphitic carbon nitride. During this process the H-content is successively decreasing, leaving only C-N bonds behind. Melam, as the first product of the elimination of ammonia, is formed by linking two molecules of melamine as a "ditriazinylamine"-type structure (Eq. 20). Melem can be formed either from melam by release of one ammonia (Eq. 22) or by direct deamination of two molecules of melamin with release of two ammonia (Eq. 21). Melam and melem are structural and thermodynamically very similar, therefore they are assigned the same specific heat in this work. In general, there are only few studies on thermodynamic data for decompositions in the literature. Therefore the thermodynamic data from graphs are used. Selivanov et al., 1973, there is no thermodynamical data for melon, since both are very similar in their structure.

\[
\text{melon(s) \rightarrow 2g-C}_3\text{N}_4(s) + \text{NH}_3, \quad \Delta_h H(400 \, ^\circ\text{C}) = 519.2 \text{kJ mol}^{-1}
\]

(26)

\[
\text{5melon(s) \rightarrow 9C}_2\text{N}_2 + 12\text{HCN} + \text{NH}_3 + 7\text{N}_2, \quad \Delta_h H(400 \, ^\circ\text{C}) = 408.4 \text{kJ mol}^{-1}
\]

(27)

\[
2g-C}_3\text{N}_4(s) \rightarrow 3C}_2\text{N}_2 + \text{N}_2, \quad \Delta_h H(400 \, ^\circ\text{C}) = -88.0 \text{kJ mol}^{-1}
\]

(28)

Thermodynamic data for g – C\N\N are well described in the theoretical study by Ruan et al. (2015), who calculated heat capacity, enthalpy, entropy and Gibbs free energy. From this, the necessary NASA polynomial is calculated with very good agreement in the temperature range from 0 °C to 750 °C.

As a result of the investigations in this work, the authors came up with a reaction scheme of the decomposition of urea and its by-products (Fig. 5). The gathered and calculated thermodynamic data for all mentioned species is summarized in Table 2. All involved reactions for the formation and decomposition of high temperature urea by-products and their kinetic data is shown in Table 3. For each reaction the reaction order \( n_{\text{EA}} \), pre-exponential factor \( A_{\text{EA}} \) in SI-units and the activation energy \( E_{\text{A}} \) are given. After the kinetic data were adjusted to agree to the main characteristics of DSC and TG experimental data, no significant improvement was achieved by a following automated parameter optimization, which is why the manually fitted parameter are used in this publication.

5. Simulation results

All simulations presented in the following were performed with the DETCHEM software package described in Section 3 and the reaction mechanism and kinetic data from Table 3.

Starting from the decomposition of g – C\N\N, the simulation of every species involved in the published mechanism is compared to available experimental data. In all following figures the experimental and simulated TG results are normalized by the initial mass of the experiment and plotted against the temperature. Additional experimental and simulation results, e.g. different heating rates, and the gas composition during experiments can be found in the supplemental information section D.
5.1. Graphitic carbon nitride

Graphitic carbon nitride is the most thermal stable solid product of the deammonation process and consists, theoretically, of only C – N bonds. Zhu et al. (2014) showed that g-C$_3$N$_4$ is not harmed by oxidizing atmosphere and pyrolizes with evolution of C$_2$N$_2$, HCN and ammonia. The occurrence of H atoms in the pyrolysis gas can be attributed to an incomplete deammonation and existence of melon in the investigated sample. For the simulation pure g-C$_3$N$_4$ is used, therefore no HCN or ammonia but only C$_2$N$_2$ and nitrogen are formed. A comparison of the experiment from Zhu et al. (2010) and the simulation is shown in Fig. 6.

The initial mass reduction in the experiment is attributable to evaporating water due to humidity and is not considered in the simulation. For the following decomposition in a 1-step reaction a very good agreement between experiment and simulation is accomplished.

5.2. Melem

Since no literature data of pure melon decomposition nor the species itself for experiments is available, the next discussed species is melem. It is the third most thermal stable species in the deammonation process and melon is directly formed from melem together with g-C$_3$N$_4$ and ammonia. Melem decomposition slowly starts at around 400°C, but takes to 500°C for a mass loss of 10% and to 600°C to have all melem and resulting products converted, as can be seen in Fig. 7.

The simulation of melem decomposition is in very good agreement with the experimental results. Kinetics are designed, that one third of melem reacts directly to 2 g-C$_3$N$_4$ and evolving ammonia, and two third react to melon as intermediate species. This distribution ensures a gas evolution of C$_2$N$_2$, HCN and NH$_3$ during the further decomposition of melon and g-C$_3$N$_4$ similar to the experiment.

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**Fig. 5.** Proposed reaction scheme of the decomposition of urea and its by-products. Adapted and extended from Tischer et al. (2019).

**Fig. 6.** Mass loss of graphitic carbon nitride as function of temperature measured by TG (cylinder crucible, 20mg, 10K min$^{-1}$), dashed line, and simulation results of the total mass loss of g-C$_3$N$_4$ during decomposition, solid lines. Experimental data from (Zhu et al., 2010).

**Fig. 7.** Mass loss of melem as function of temperature measured by TG (cylinder crucible, 7.5mg, 2K min$^{-1}$), dashed line, and simulation results of the total mass loss and mixture composition during decomposition, solid lines.
5.3. Melam

Melam is the intermediate species of the deammoniation of melamin to melem and further products. It consists of two melamine rings connected by elimination of ammonia. Wirnhier et al. (2013) synthesized the rather unstable melam by thermal treatment of Dcd in an autoclave. Subsequent thermal analysis revealed the decomposition behavior, as it can be seen in Fig. 8. Melam starts to react at about $370^\circ C$ with a mass loss of $22.6\%$ up to $410^\circ C$. This corresponds well with evolution of either $3\text{mol}$ of ammonia (calc. $21.7\%$ (Wirnhier et al., 2013)) or $1\text{mol}$ ammonia, $1\text{mol}$ HCN and $1/3\text{mole}$ $N_2$ (calc. $22.7\%$) per mole of melam. The latter is used in this work, which is implemented via the deammoniation reaction of melam to melem (Eq. 22) and decomposition of melam (Eq. 23).

![Fig. 8. Mass loss of melam as function of temperature measured by TG (cylinder crucible, 24mg, 5K min$^{-1}$), dashed line, and simulation results of the total mass loss and mixture composition during decomposition, solid lines. Experimental data from Wirnhier et al. (2013).](image)

5.4. Melamine

A comparison between experimental data and simulation results for melamine decomposition is shown in Fig. 9. Melamine starts to react at about $250^\circ C$. From many literature studies it is known that it mostly sublimates and only a fraction reacts to melam in open vessels. This behavior is well described in the simulation, where the mass loss of $96.25\%$ up to $350^\circ C$ overlaps with the experiment. In the following, the produced melam reacts further to melem, melon and $g-C_{3}N_{4}$ and decomposes. Though, the last decomposition step of melon and $g-C_{3}N_{4}$ is slightly overpredicted and shifted to lower temperature. This is most probably caused by the low remaining mass and definition of the reactions on the surface, which results in high surface/volume ratios and therefore increased reactions rates.

![Fig. 9. Mass loss of melamine as function of temperature measured by TG (cylinder crucible, 25.9mg, 2K min$^{-1}$), dashed line, and simulation results of the total mass loss and mixture composition during decomposition, solid lines.](image)

5.5. Cyanamid

Decomposition of Cyanamide involves several stages and intermediate species. Starting from room temperature, Cyd melts at $47^\circ C$ to liquid Cyd. Simultaneously, water evaporates slowly from Cyd, even after drying, since it is a strongly hygroscopic species. Since this phenomenon could not be included in the simulation, it is always a bit above the experimental curve, which can be seen in the following. At around $100^\circ C$ liquid Cyd begins to dimerize to dicyandiamide. Interestingly, although solid Dcd is formed from the dimerization, the thermodynamic equilibrium is on the liquid Dcd side until 50% of Cyd is converted. That is caused by the liquid phase definitions and algorithm in the used model, but could occur in the experiment as well. With increasing temperature solid Dcd starts to melt at $211^\circ C$ and slowly polymerizes to melamin and decomposes in small amounts. The following mass loss due to sublimation of melamin fits very well with the experimental mass loss around $300^\circ C$. The next stage during melam formation and decomposition to melem is in good agreement with the experiment, as can be see in Fig. 10. The last large mass loss step, starting at $400^\circ C$, due to the formation and decomposition of melem, melon and $g-C_{3}N_{4}$, is again slightly overpredicted and shifted to lower temperatures, due to the mentioned problems with water and the $g-C_{3}N_{4}$ decomposition. Furthermore, due to the high reactivity

![Fig. 10. Mass loss of cyanamide as function of temperature measured by TG (cylinder crucible, 20.1mg, 2K min$^{-1}$), dashed line, and simulation results of the total mass loss and mixture composition during decomposition, solid lines.](image)
of Cyd with its two reactive centres it can form a diversity of side-products, which is not included in this mechanism.

The decomposition of Dcd follows the curve of Cyd in the experiment as well as in the simulation. It includes the exact same stages and formed products in the temperature ranges and is therefore not further discussed. A comparison between experiment and simulation of two measurements of Dcd decomposition, including DSC/MS data, can be found in the supplemental information.

5.6. Ammelide

Ammelide is one of the species which is already included in former reaction mechanisms. However, its decomposition was often modeled as a pure sublimation, as a simplification of the more complex real process. From the experiment in Fig. 11 it can be clearly seen, that ammelide decomposition involves more than just one reaction or stage. The simulation can reproduce this behavior with a very good agreement. Starting at about 320 °C, ammd decomposes to ammn with release of Cyd and CO₂. Simultaneously, a small part reacts directly to melem, while another part decomposes to HNCO and Cyd. Through the release of Cyd in the reactions many side products can be formed, as already discussed above. The two overlapping, but recognisable, stages in the experiment during the first decomposition of ammd could not be separated in the simulation in that way. However, the overall mass loss of 75% up to 470 °C in the experiment is well met with the simulation (72.1%). The start of the last stage of decomposition is in good agreement, even if the mass loss with increasing temperature occurs slightly slower in the experiment than in the simulation. Residual mass in the experiment is presumably due to measurement inaccuracy. Results of the DSC/MS-measurement and a TG experiment with higher heating rate, together with corresponding simulations, can be found in the supplemental information. (see Fig. 12).

5.7. Ammeline

Ammeline decomposition starts at about 375 °C and loses 58% of its initial mass up to 475 °C. The simulation is in very good agreement (56% mass loss) with the experiment by modeling the decomposition by equal shares of melam and melem. Furthermore, ammeline pyrolizes to HNCO and Cyd as its building blocks to form other byproducts. Formed melam reacts quickly to melem by deammoniation. The following decomposition stage of melem is in good agreement, but again slightly shifted to lower temperatures as already described above.

5.8. Urea

The comparison between experiment and simulation for urea decomposition is shown in Fig. 13, which is the initiating species for solid deposits in SCR applications. For the simulation of urea decomposition up to ammelide formation, our recently published kinetics (Tischer et al., 2019) are used, while subsequent reactions are taken from this study. The first decomposition stage between 133 °C and 220 °C with a mass loss of 48% is well described by the model. But especially for the second decomposition stage, where biuret and triuret react, there is a significant deviation between experiment and simulation. The mechanism by Tischer et al. (2019) is not able to precisely reproduce this second stage...
with a mass loss of about 13%, but forms cya and ammd earlier instead. Due to missing thermodynamic data of biuret and triuret in solid and liquid phase, no eutectic mixture of these compounds could be established as suggested (Tischer et al., 2019). The following decomposition stage involves the sublimation of cya and further decomposition of ammd. Especially above 400 °C, where all cya has sublimated, there is a good agreement between experiment and simulation. This suggests that the amount of ammd is correctly predicted by the mechanism of Tischer et al. (2019). Though, above 400 °C only 5% of the initial urea mass is left as a deposit, it is important to have a good correlation for the formation and decomposition of these high-temperature urea by-products.

6. Conclusion

This study presents a new kinetic model for high-temperature urea deposit formation and decomposition starting from ammelide. Based on TG- and DSC-measurements of the urea by-products ammelide, ammeline, cyanamide, dicyandiamid, melamine and melem and MS analysis of the evolving gases a mechanism is developed. All experiments are simulated with the DETCHEM® code (Tischer et al., 2019) and kinetics are manually adjusted to agree with the main characteristics of TG- and DSC data. No significant improvement of the results was achieved by a following automated parameter optimization, which is why the manually fitted parameters are used in this publication to prevent overfitting.

Other mechanisms in the literature are often limited to reactions up to the formation of ammelide or melamine and their direct decomposition into the gas phase. High-temperature by-products are not taken into account. Even if this high-temperature species make less than 5% of the initially injected urea mass, over time they can accumulate and build deposits that can only be removed by temperatures much higher than 400 °C or by expensive manual removal. This study attempts to fill the gap of literature mechanisms by involving the formation and decomposition of 11 different species (Ammelide, Ammeline, Cyanamide solid and liquid, Dicyandiamide solid and liquid, Melamine, Melam, Melem, Melon and Graphitic Carbon Nitride), including two phase changes and the evolution of 6 different gases (CO₂, HNCO, NH₃, HCN, C₂N₂ and N₂). It therefore consists of 14 homogeneous and 6 interphase reactions in addition to the mechanism by Tischer et al. (2019) comprising urea reactions below 400 °C. For each species, thermodynamic data was gathered from the literature and NASA-polynomials are calculated. However, data is not available for every species and some assumptions based on similarities to other species had to be made. All performed TGA- and DSC measurements are very well described by the postulated mechanism. Even changes of initial mass or heating rate can be reproduced well. In combination with the Tischer mechanism (Tischer et al., 2019) the proposed overall reaction scheme for urea decomposition up to 750 °C gathers 21 different solid, liquid and aqueous species, 10 gaseous species, 19 homogeneous reactions, 7 interphase reactions and 7 phase change reactions.

This study presents the first reaction mechanism for decomposition of urea and formation and decomposition of its by-products over the whole SCR-relevant temperature range from room temperature to 750 °C. Kinetics for low-temperature reactions are taken from our previous study (Tischer et al., 2019), while high-temperature reactions are developed in the present study. There is still some uncertainty in the second stage of urea decomposition, especially concerning the interplay of the mixture of urea, biuret and triuret. A major issue therefore is the unavailability of thermodynamic data for certain species, in particular for triuret. More experiments, in open and closed vessels, should be done to determine the nature and gather more data of a possible eutectic mixture of biuret and triuret. Nevertheless the mechanism used in this study can reproduce all important processes during decomposition of urea and its by-products. Further investigation of the addressed problems could complete the uncertain parts of the mechanism, make it more robust and enhance its area of application. An implementation of this extended urea decomposition mechanism into CFD simulations of SCR systems could further improve the accuracy of existing models in order to match the experimental deposit composition, help to avoid the formation of high-temperature by-products and make the development process more cost-efficient.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ces.2021.116876.

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