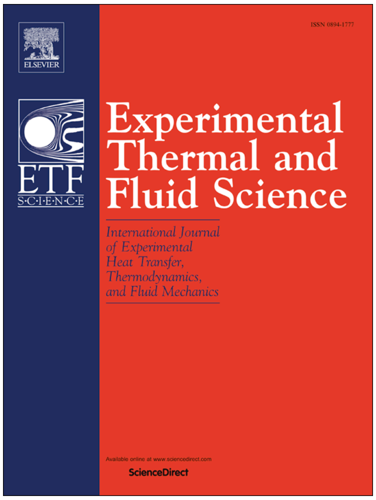

Crystallization of urea from an evaporative aqueous solution sessile droplet at sub-boiling temperatures and surfaces with different wettability

J. Schmid, I. Zarikos, A. Terzis, N. Roth, B. Weigand

PII: S0894-1777(17)30304-7
DOI: https://doi.org/10.1016/j.expthermflusci.2017.10.008
Reference: ETF 9232

To appear in: *Experimental Thermal and Fluid Science*

Received Date: 7 July 2017
Accepted Date: 10 October 2017

Please cite this article as: J. Schmid, I. Zarikos, A. Terzis, N. Roth, B. Weigand, Crystallization of urea from an evaporative aqueous solution sessile droplet at sub-boiling temperatures and surfaces with different wettability, *Experimental Thermal and Fluid Science* (2017), doi: https://doi.org/10.1016/j.expthermflusci.2017.10.008

Crystallization of urea from an evaporative aqueous solution sessile droplet at sub-boiling temperatures and surfaces with different wettability

J. Schmid[a], I. Zarikos[b], A. Terzis[a], N. Roth[a], B. Weigand[a]

[a]*Institute of Aerospace Thermodynamics, University of Stuttgart, 70569 Stuttgart, Germany*
[b]*Department of Earth Sciences, University of Utrecht, 3584 CD Utrecht, The Netherlands*

Abstract

The injection of urea-water-solution sprays in the exhaust pipe of modern diesel engines eliminates NO_x emissions in a very great extent. However, as water evaporates from the solution, urea is crystallized and causes wall-deposit formations hindering the performance of selective-catalytic-reaction. In this study, the crystallization of urea from an evaporative aqueous solution droplet placed on a heated wall is experimentally investigated, aiming to understand macroscopically the morphology of crystal growth at various conditions. Using optical and thermal imaging, urea crystallization patterns are examined at sub-boiling temperatures and substrates with different wettability. In all cases, the macroscopic initiation of crystal growth starts at the solid-liquid interface when urea concentration has reached supersaturated conditions. The experiments indicate two different crystallization modes depending on surface temperature and wettability as well as a significant heat release at the solidification front due the exothermic character of the process.

Keywords: AdBlue, crystallization, wettability, thermodynamics

---

1. Introduction

Selective-catalytic-reaction (SCR) is the most promising technique for reducing NO_x emissions of automotive diesel engines [1–3]. Using ammonia (NH_3) as a reducing agent, the NO_x emissions can be converted into harmless diatomic nitrogen (N_2) and water. For safety reasons, the source of ammonia for mobile engines is supplied by the thermal decomposition of urea (CH_4N_2O) [4–8], which is injected in the exhaust pipes as an aqueous solution.

Apart from the mixing efficiency between the reducing agent and the exhaust gases, where a number of studies focused on fluid dynamic aspects of SCR-sprays injected in a crossflow [9–15], another crucial factor for optimal $DeNO_x$ performance of an urea-dosing system is the mitigation of solid-deposit formation [16–22]. The latter is a direct consequence of the spray/wall interactions which are unavoidable due to the modern compact design requirements [23]. Under certain circumstances, as water evaporates supersaturated urea-water-solution (UWS) droplets are generated causing solidification of urea decomposition products on the pipe walls. Depending on the engine load (pressure and temperature), these include compounds such as biuret, cyanuric acid, ammelide, ammeline, melamine as well as more complex polymerisation products [16, 21]. Apart from material damage, wall deposits impede the flow of exhaust gases, and hence the uniformity of UWS supply, reducing the SCR performance over time [24].

In order to control such mechanisms, a very good knowledge of crystallization process at a fundamental level is required. Previous studies focused on solid deposit formation [15–22] examined the amount and type of deposition under different engine loads, demonstrating actually a “before-after” injection condition of the exhaust pipes. Although several molecular dynamic simulation studies investigated the onset of nucleation and growth morphology of crystalline urea from aqueous solutions at a molecular scale [25–29], experimental investigations of urea crystallization on engineering surfaces are limited in literature. Lodaya et al. [30] observed needle-like and dendritic growth urea crystals from supercooled water solutions at a macroscopic level, providing also a correlation for the nucleation rate. Garetz et al. [31] demonstrated a new photo-physical phenomenon in which laser pulses are able to induce crystallization in supersaturated solutions. Using infrared spectroscopy (IR) methods, Groen and Roberts [32] detected the onset of crystallization associated with the depletion of the solution concentration, while Sun and Xue [33] showed that the formation of crystalline urea is proceeded via the assembly of urea molecules, which allows the formation of 1D molecular chains, prior to their further aggregation into 2D plane-like and 3D net-like clusters. In addition, Lai et al. [34] used a reaction calorimetric technique and observed that the heat released upon crystallization is directly proportional to the amount of crystals formed, thus enabling measurements of urea solution supersaturation. Apparently, contrary to salt-solutions [35–39], the crystallization process of urea from an evaporative water solution on engineering surfaces at a macroscopic level is far from

---

*corresponding author. Tel.: +49 (0) 711 685-62315
Email addresses: `st108129@stud.uni-stuttgart.de` (J. Schmid), `alexandros.terzis@me.com` (A. Terzis)