

Thermal decomposition of guanidinium salts as alternative solid promoters of ammonia for selective catalytic reduction of NO_x

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Introduction

Due to their higher efficiency, diesel engines have been attractive in automotive applications; however, NO_x abatement in this kind of emissions is a problem. Selective Catalytic Reduction with Ammonia (NH₃-SCR) has been a successful approach for NO_x transformation into harmless N₂ and H₂O; urea 32.5% aqueous is a commercial source of NH₃ [1]. However, alternative ammonia sources have been recently investigated, such as formamide or methanamide solutions, or even solid promoters [2].

Solid ammonia promoters have the advantage of potentially producing the same NH₃ amounts than aqueous solutions in a smaller space, therefore increasing the system effectiveness, and also reducing the safety issues related to the handling and transportation of the material [3]. Some guanidinium salts have been investigated due to their relative thermal stability and non-toxicity, compared to other alternative NH₃ promoters, like methanamide [4]. However, a deep characterization of the thermal decomposition of guanidinium salts has not been performed yet. We therefore present in this work the first comprehensive report on the thermal decomposition of the acetate, carbonate and chloride salts of guanidinium.

Materials and Methods

The guanidinium salts were heated in a crucible over a heating plate, from room temperature to approximately 350 °C, increasing 10 °C per minute, and leaving the system to reach equilibrium for 25 minutes every 50 °C. In all the cases, the system was in contact with the atmosphere. Samples from solid residues at different temperatures were collected and characterized using Thermogravimetric Analysis coupled with Differential Temperature Analysis (TGA/DTA), using a TA Instruments model 2690 analyzer, and a heating rate of 2 °C/min in a 100 mL/min N₂ atmosphere. Differential Scanning Calorimetry (DSC) was performed in a Perkin Elmer Sapphire Calorimeter, using a 100 mL/min flow of N₂ and a heating rate of 5 °C/min. Fourier Transform Infrared Spectrometry (FT-IR) was performed using a Thermo Scientific Nicolet 6700, and for X-Ray Diffractometry (XRD) tests, a Siemens model D-5000 diffractometer was used. The ammonia released by thermal decomposition was analyzed using a wet chemistry method.

Results and Discussion

TGA analysis showed guanidinium carbonate started decomposing at the lowest temperature, 165 °C. The decomposition consisted of only one step for the acetate and chloride salts, while guanidinium carbonate showed two decomposition steps. FT-IR and XRD helped

characterize the solid products, which are summarized on **Figure 1**. It can be observed that the solid decomposition products are in all cases triazines and heptazines, which have a high nitrogen content per molecule. Therefore, the potential as ammonia sources for this guanidinium salts may be lower than expected. Guanidinium carbonate shows the main ammonia release step to occur at a lower temperature (T > 185 °C). Released ammonia quantification tests showed that even when forming highly nitrogenated solid compounds, guanidinium carbonate releases the maximum ammonia (30,650 ppmv) compared to the other two salts (6,700 and 5,270 ppmv for guanidinium acetate and chloride, respectively).

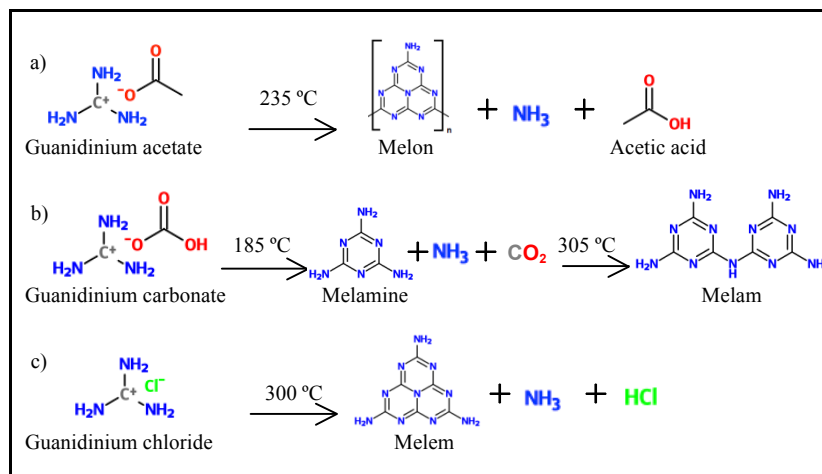


Figure 1. Decomposition schemes for guanidinium salts: a) acetate, b) carbonate, c) chloride.

Significance

Guanidinium carbonate shows potential as solid ammonia source, releasing high amounts of ammonia at a relatively low temperature (185 °C). All guanidinium salts polymerize at high temperatures to form heptazines, namely melon (acetate), melam (carbonate) and melem (chloride).

References

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