DEHYDRATION PERFORMANCE OF A NOVEL SOLID SOLUTION LIBRARY OF MIXED AND SUPPORTED TUTTON SALTS AS THERMOCHEMICAL HEAT STORAGE MATERIALS

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ABSTRACT

Since the first industrial revolution in the mid-to-late 18th century, the demand for energy in the form of electricity or heat has soared at a considerable rate. The need for establishing robust energy facilities to cater to this increasing consumption is therefore greater, especially in the context of climate change.

The materials we are developing are involved in chemical reactions between a gas and a solid. This process is known as thermochemical energy storage (TCES). In particular, we are characterizing Tutton's salts with the formula $A_2M(XO_4)_2 \cdot 6H_2O$ (X = S or Se), where M is a divalent cation. We are investigating mixed-cation substitutions of the form $K_2Zn_{1-x}M_x(SO_4)_2 \cdot 6H_2O$ (M = Mg, Co, Ni, Cu) for low-temperature, timescale-unlimited energy storage applications. Additionally, we are exploring monovalent cation substitution (A = Na, K, NH_4, $MeNH_3$...) to broaden our material library.

Two trends have been readily observed: increasing the amount of nickel leads to a predictable increase in the dehydration onset temperature while preserving the simple single-step dehydration behavior. Conversely, the use of copper leads to a predictable decrease in dehydration onset temperature. We have also incorporated these salt hydrates into γ-alumina and silica matrices to investigate potential performance improvements for TCES applications.

Key words: Thermochemistry, Energy, Storage, Salt hydrates, Composites

INTRODUCTION

Thermochemical energy storage is one the newest thermal energy storage methods with the potential to meaningfully contribute to improving the energy efficiency of our infrastructure and thus mitigate climate change. In contrast to other technologies such as sensible heat storage and latent heat storage, TCES offers much higher potential energy storage densities and lossless long-term storage. TCES has thus been reviewed extensively [[1],[2]].

A general representation of most TCES reactions involves using waste heat for the endothermic decomposition of substance A to yield two products B and C, which can be stored separately and, when heat is required, united to produce the original substance A: (1) $A + \Delta H \rightleftharpoons B + C$.

Tutton salts, with the composition $A_2M(XO_4)_2 \cdot 6H_2O$, have been synthesized with various monovalent (A+) and divalent (M²+) cations, and oxyanions (XO_4^{2-}) containing sulfur (S), selenium (Se), or chromium (Cr). They all crystallize in the same monoclinic system with space group $P2_1/a$ [3]. However, a systematic investigation focusing on the relationship between the divalent cation composition and the thermochemical properties of Tutton salts for low-temperature thermochemical energy storage applications has not been previously reported, as in the works by Babiniec et al. or Müller et al. [4, 5]. Our work addresses this gap by presenting the first characterization of a large library of Tutton salts where each salt contains a mixture of two divalent cations. In this study, we describe the thermal behavior of pure Zn, Mg, Ni, Co, Cu salts and all salt mixes ranging from $K_2Zn_{0,1}M_{0,9}(SO_4)_2 \cdot 6H_2O$ to $K_2Zn_{0,9}M_{0,1}(SO_4)_2 \cdot 6H_2O$ with an 0.1 systematic increase in Zn content.

The relationship between the chosen cations and the temperature dependence of dehydration for each TCES material is analyzed and extrapolated, and initial tests on the dehydration of these salts supported on gamma alumina and silica are performed so as to evaluate the impact on energy density.

EXPERIMENTAL
1. Synthesis of Tutton salts and composite materials

To theoretically yield a total of 33 mmol of the desired Tutton salt product, the corresponding molar ratio of the salts (combinations of K_2SO_4 or Na_2SO_4 or $(NH_4)_2SO_4$ with $MgSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, and $ZnSO_4 \cdot 6H_2O$) was dissolved in boiling deionized water. When the volume of the solution sank to ca. 30 ml, the product was allowed to crystallize at room temperature and then at 8 °C for 16 h to yield the TCES materials in a timely fashion, in contrast to the literature [6]. Filtration, washing with acetone, and drying in vacuum yielded the crystalline products. Using the incipient wetness technique, a saturated solution of a previously isolated Tutton salt of the desired composition was added to the support materials, which had been dried at 120°C for 1 h prior to preparation of the composite material.

2. Phase analysis via powder X-ray diffraction

A Panalytical MPD Pro diffractometer was used to perform the powder X-ray diffraction (PXRD) in Bragg-Brentano geometry with a scattering angle of $5° < 2\theta < 60°$ for Cu $K_{\alpha 1,2}$-radiation. The instrumental resolution was defined by a ½° fixed divergent entrance slit followed by a 0.04 rad Soller slit. A 0.04 rad Soller slit was placed before the X-Celerator detector operated in the 1D continuous line mode. The detector to sample distance for this instrument is 220 mm. Rietveld refinement was carried out with Panalytical HighScore Plus version 5.1.

3. Elemental analysis via X-ray fluorescence

The ratio of bivalent cations of the salts was determined by X-ray fluorescence analysis (XRF) using a Panalytical Axios Advanced device with a Rh tube, an excitation voltage of 50 kV, a tube current of 50 mA, a wavelength dispersive X-ray spectrometer, and a vacuum of <10 Pa. Finely ground Tutton salt (10 g) was shaken with Panalytical Ultra-Wax (1 g) in a Turbula shaker with agate grinding balls for 30 min and compacted to a disc at 20 t for measurement with an irradiated circle of 27 mm diameter.

4. Simultaneous thermal analysis

Simultaneous thermal analysis (STA) with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449 F1 Jupiter device equipped with a steel furnace, an automatic sample changer, and a combined TGA-DSC sample holder using aluminum crucibles containing sample masses of ca. 10 mg. A heating rate of 2.5 K/min in a N_2 atmosphere between 25 °C and 220 °C was applied. The device was calibrated with Zn, In, Sn, CsCl, and adamantane standards.

RESULTS AND DISCUSSION

To begin, we consider the dehydration of compounds with only one bivalent metal, which provides a foundation for understanding mixtures (Fig. 1). As reported in the literature, the pure Mg salt undergoes four well-separated dehydration steps, the Co salt two to three, the Ni salt one, the Cu salt two, and the Zn salt one to two [6, 7, 8]. To illustrate the variation in thermodynamic properties, we measure STA for each salt mixture. Additionally, we measure

the dehydration enthalpy of supported $K_2Zn(SO_4)_2 \cdot 6H_2O$ and supported $K_2Fe_{0.5}Zn_{0.5}(SO_4)_2 \cdot 6H_2O$.
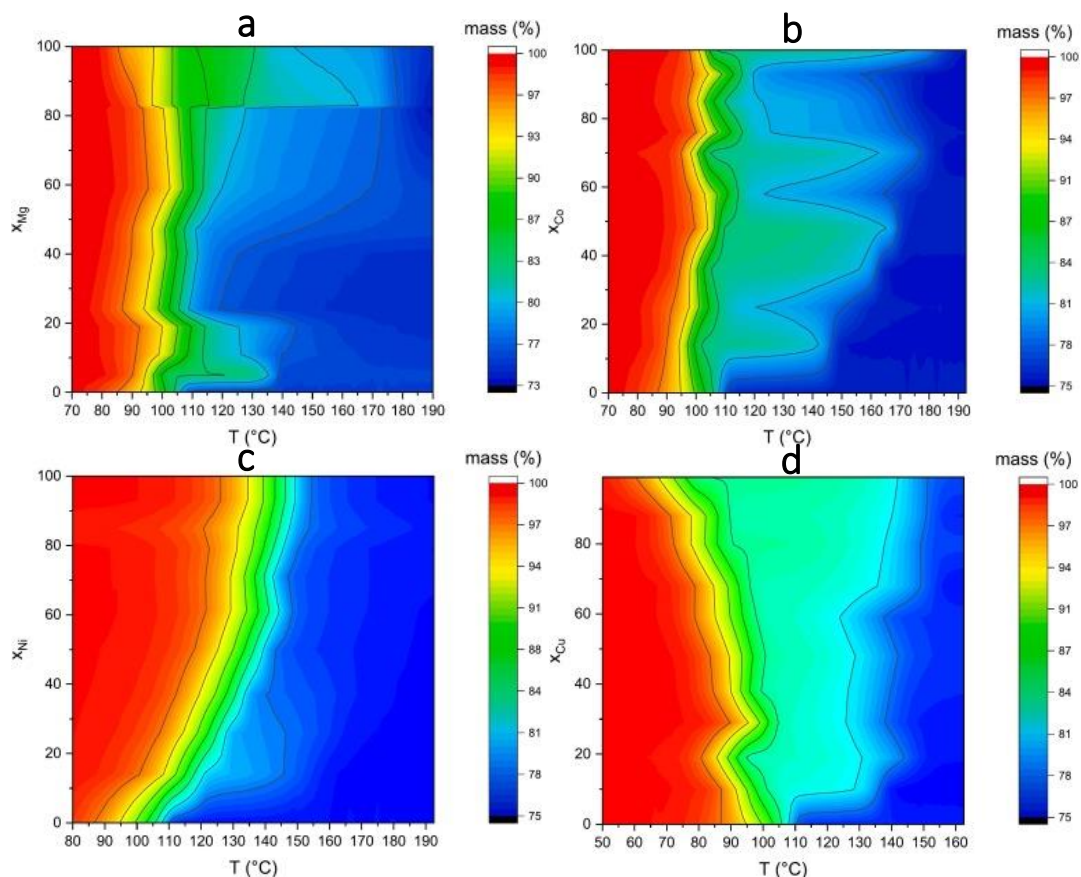

Figure.1. Example of thermogravimetric analysis of $K_2Zn_{1-x}Mg_x(SO_4)_2 \cdot 6H_2O$, $K_2Zn_{1-x}Co_x(SO_4)_2 \cdot 6H_2O$, of $K_2Zn_{1-x}Ni_x(SO_4)_2 \cdot 6H_2O$ and $K_2Zn_{1-x}Cu_x(SO_4)_2 \cdot 6H_2O$.
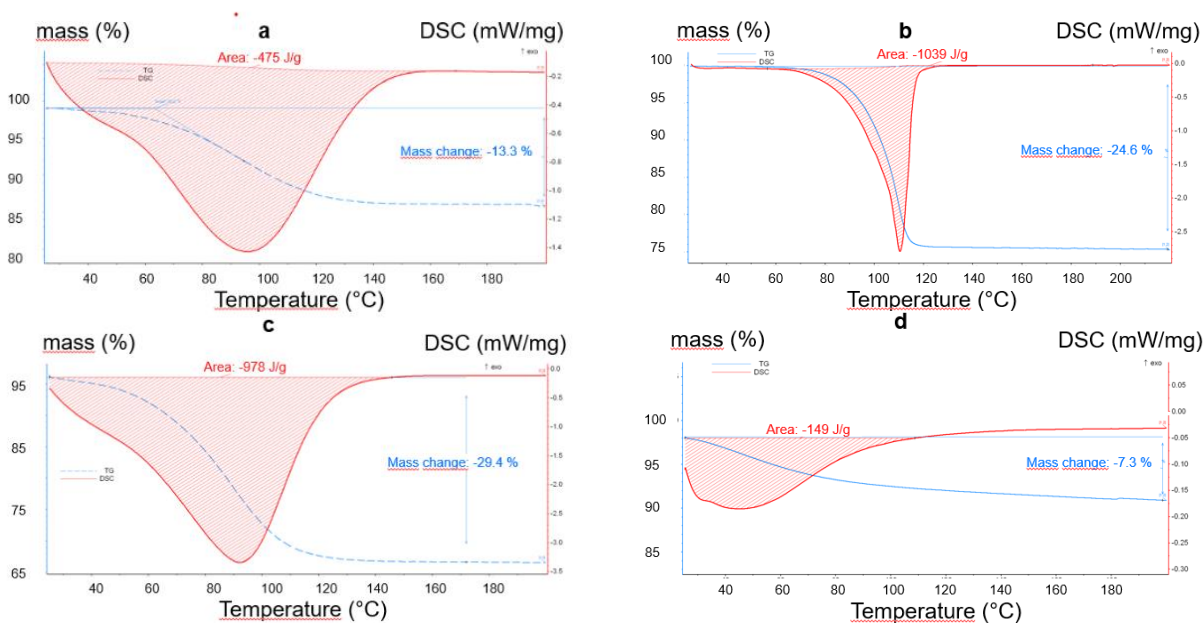

Figure.2. Dehydration of silica and supported Tutton's salts: mass loss as a function of time for : **a** SiO_2
b $K_2Zn(SO_4)_2 \cdot 6H_2O$ **c** $K_2Zn_{0.5}Fe_{0.5}(SO_4)_2 \cdot 6H_2O$ supported on SiO_2 **d** $K_2Zn(SO_4)_2 \cdot 6H_2O$ supported on ɣ-alumina

Figure 1. shows that the initial dehydration temperatures (onset temperatures) vary significantly depending on the cation combination in the mixed salts. As the proportion of zinc changes in the structures containing Mg, Co, Ni, and Cu, we observe a range of first average dehydration temperatures: 93°C for Mg, 95.3°C for Co, 120.2°C for Ni, and 81.5°C for Cu. Notably, the difference between the Ni and Cu salts is a remarkable 38,7°C, highlighting the potential for tailoring the initial dehydration temperature in these materials. Figure 2 further demonstrates that incorporating $K_2Zn_{0.5}Fe_{0.5}(SO_4)_2 \cdot 6H_2O$ onto SiO_2 and $K_2Zn(SO_4)_2 \cdot 6H_2O$ into γ-alumina, similar to the $CaCl_2$ case studied by Courbon et al. [9], affects the composite material's dehydration enthalpy and onset dehydration temperature.

CONCLUSION

This study efficiently synthesized Tutton salts with the formula $A_2Zn_{1-x}M_x(SO_4)_2 \cdot 6H_2O$, where M represents Mg, Co, Ni, or Cu, and A is either Na or NH_4. PXRD and XRF confirmed the phase and elemental composition of the synthesized materials. For potassium salts, STA measurements revealed that combining different bivalent cations within a single Tutton salt results in a variation of dehydration behaviors. These tailorable materials have potential applications in various small- and mid-sized industries with thermal processes generating waste heat at different temperatures. Each application can be matched with a specific Tutton salt composition that offers the dehydration temperature that best suits the energy requirements. To further expand on this research, we plan to immobilize several salts from the library into various matrices and measure the resulting composite's dehydration enthalpy values and onset temperature differences.

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