Applied Energy 187 (2017) 1–9

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Probing cycle stability and reversibility in thermochemical energy storage – $CaC_2O_4{\cdot}H_2O$ as perfect match?

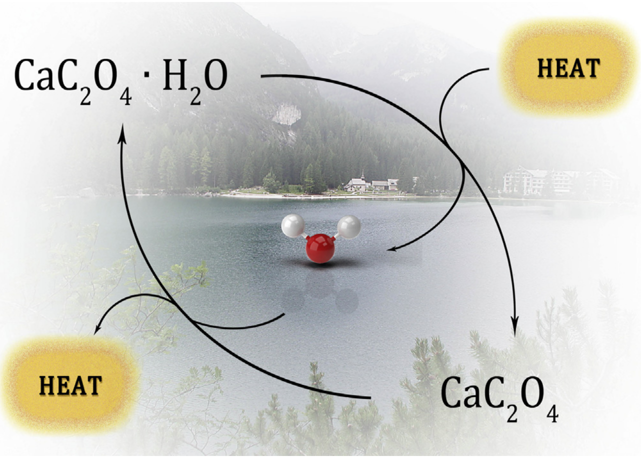
Christian Knoll [a,b], Danny Müller [a,*], Werner Artner [c], Jan M. Welch [d], Andreas Werner [e], Michael Harasek [b], Peter Weinberger [a]

[a] Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163-AC, A-1060 Vienna, Austria
[b] Institute of Chemical Engineering, TU Wien, Getreidemarkt 9/163-AC, A-1060 Vienna, Austria
[c] X-Ray Center, TU Wien, Getreidemarkt 9/163-AC, A-1060 Vienna, Austria
[d] Atominstitut, TU Wien, Stadionallee 2, 1020 Vienna, Austria
[e] Institute for Energy Systems and Thermodynamics, TU Wien, Getreidemarkt 9/163-AC, A-1060 Vienna, Austria

HIGHLIGHTS

- $CaC_2O_4{\cdot}H_2O$ dehydration is fully reversible between 25 °C and 200 °C.
- Isothermal cycling between hydrate and anhydrate phase can be triggered by the water vapour concentration.
- High reaction rates and full reversibility demonstrated over 100 cycles.
- Material shows no ageing effects or reactivity decrease.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 September 2016
Received in revised form 10 November 2016
Accepted 13 November 2016

Keywords:
Calcium oxalate monohydrate
Full reversibility
Cycle stability
Water vapour concentration
Chemical heat pump
Thermochemical energy storage

ABSTRACT

The dehydration and subsequent rehydration of calcium oxalate monohydrate has yet to find application in thermochemical energy storage. Unlike for many other salt hydrates, complete reversibility of the dehydration-rehydration reaction was observed. Additionally, it was found that the rehydration temperature is strongly affected by the water vapour concentration: Full reversibility is not only achieved at room-temperature, but, depending on the water vapour concentration, at up to 200 °C. This allows isothermal switching of the material between charging and discharging by a change of the H_2O-partial pressure. Cycle stability of the material was tested by a long-term stress experiment involving 100 charging and discharging cycles. No signs of material fatigue or reactivity loss were found. *In-situ* powder X-ray diffraction showed complete rehydration of the material within 300 s. The experimental findings indicate that the $CaC_2O_4{\cdot}H_2O/CaC_2O_4$ system is perfectly suited for technical application as a thermochemical energy storage medium.

1. Introduction

According to the international energy agency two-thirds of all energy produced energy is wasted due to inefficiency in production

---

* Corresponding author.
E-mail address: danny.mueller@tuwien.ac.at (D. Müller).

http://dx.doi.org/10.1016/j.apenergy.2016.11.053
0306-2619/

and conversion processes [1,2]. Increased attention to this issue by the scientific community and governmental organizations has led to different improvements such as increased focus on renewable energy sources and international agreements such as the Kyoto-protocol to limit greenhouse-gas emissions [3]. Nevertheless, the weak point in the overall energy balance the energy loss predominantly in form of unused waste heat is still widely ignored [4].

Utilization of waste heat is an attractive and effective approach to a more efficient energy balance. One method of achieving this objective could be storage and re-use of waste heat. Thermal energy storage transfers thermal energy to a storage medium, decoupling energy availability and demand [5,6]. The stored heat could be used for heating, cooling, or drying purposes, as well as for power generation. Generally, three types of thermal energy storage systems are employed: Sensible heat storage (using liquid or solid storage media) [7–9], latent heat storage (using phase-change materials) [10,11] and thermochemical heat storage (using reversible chemical reactions) [5,6].

Compared to latent or sensible heat storage, the major advantages of thermochemical energy storage systems (TCES) are the high storage density, long-term storage ability and finally the cost efficiency. According to the principle of a TCES-system given in Eq. (1) after separation of the products B and C no back-reaction can occur, decreasing the storage efficiency.

$$A + \Delta H \leftrightarrow B + C \tag{1}$$

In current literature many different potential materials for TCES-systems are discussed [6]. For a technically promising TCES-system high energy density, complete reversibility of the reaction, reasonably fast reaction kinetics and high cycle stability are required. Many systems may have these characteristics, nevertheless, only a limited number of materials have been systematically investigated.

To increase the scope of suitable materials for a TCES-application a search algorithm capable of a systematic database evaluation with subsequent extraction of potentially suitable reversible reactions was developed [12]. One possible hereto investigated candidate for energy storage applications, $CaC_2O_4{\cdot}H_2O$, was suggested by this search. Although dehydration of $CaC_2O_4{\cdot}H_2O$ should be reversible, to the best of our knowledge, the only report on this system in the context of energy storage relates to phase change materials, in which the application of $CaC_2O_4{\cdot}H_2O$ as nucleation inhibitor is investigated [13]. Several studies focus on the kinetics of the dehydration of $CaC_2O_4{\cdot}H_2O$ [13–22], whereas only a single study of rehydration kinetics appears in literature [23,24]. The scarcity of literature data and the results of our database search suggest the utility of a detailed study of the dehydration/rehydration behaviour of $CaC_2O_4{\cdot}H_2O$. The results achieved are very indicate that $CaC_2O_4{\cdot}H_2O$ is a promising material for TCES-application.

2. Experimental methodology

2.1. Material

Calcium oxalate monohydrate (CAS 5794-28-5) was obtained from Sigma-Aldrich and used as supplied. The anhydrous form was obtained by *in-situ* dehydration during the experiment unless otherwise stated.

2.2. Thermal analysis

Decomposition data were obtained using a Netzsch STA 449 F1 Jupiter® system equipped with an automatic sample changer and a combined TGA-DSC sample holder using open aluminium crucibles containing sample masses between 12 and 14 mg. Heating rates of 2, 5 and 10 $K\,min^{-1}$ under N_2 atmosphere between 25 °C and 500 °C have been applied.

All data thermoanalytical data, including those from rehydration experiments, were collected on a Netzsch STA 449 C Jupiter® instrument equipped with a combined TGA-DSC sample holder using open aluminium oxide crucibles containing sample masses between 19 and 21 mg. The system was equipped with a water vapour furnace, including an air-cooled double jacket and a heated vapour inlet. The oven is operable between 25 °C and 1250 °C, regulated by an S-type thermocouple. The steam was produced in an Adrop water vapour generator, which was set to 105 °C. The water vapour was transferred into the furnace via a heated transfer line and a heated collar, both of which were set to 100 °C. To prevent condensation of the water, a carrier gas stream of 100 ml N_2 min^{-1} was used. The protective gas stream was set to 5 ml N_2 min^{-1}.The gas flow was controlled using red-y smart series mass-flow controller by Voegtlin with an operable range between 2 and 100 ml min^{-1}.

All experiments reported were run at ambient pressure.

2.3. X-ray powder diffraction

The powder X-ray diffraction measurements were carried out on a PANalytical X'Pert Pro diffractometer in Bragg-Brentano geometry using Cu $K_{\alpha1,2}$ radiation and an X'Celerator linear detector with a Ni-filter. For the *in-situ* experiments an Anton Paar XRK 900 sample chamber was used. The sample is mounted on a hollow ceramic powder sample holder, allowing for complete perfusion of the sample with the reactive gas. The reaction chamber is operated between 25 and 900 °C and a pressure between 1 mbar and 10 bar. The sample temperature is controlled via a NiCr-NiAl thermocouple and direct environmental heating. The gas flow was set to 0.2 L min^{-1}, unless otherwise stated. For the moisture-setup a flow of 0.2 L min^{-1} helium was bubbled through a 20 cm high water tank and a subsequent droplet separator, before passing through the sample. At the entry of the reaction chamber the gas had a dew-point temperature of 23.2 °C. The diffractograms were evaluated using the PANalytical program suite HighScorePlus v3.0d. A background correction and a $K_{\alpha2}$ strip were performed.

2.4. Scanning electron microscopy

A JEOL JSM-5410 analogue scanning electron microscope equipped with a Bruker AXS digitalizing signal processing unit was used to obtain 2D images of the crystals shape of the powder samples. The samples were mounted on carbon pellets on top of the sample holder and plasma vacuum deposition was used to coat the samples with a thin layer of gold to ensure conductivity. The gold coating was performed using a Baltec Med020 sputtering system. The sample was held at $7{\cdot}10^{-4}$ mbar for 10 min, followed by adjustment of the pressure of $2{\cdot}10^{-2}$ mbar of argon. For the evaporation of the gold target a current of 150 mA for 150 s was used.

3. Results and discussion

3.1. Thermal dehydration of $CaC_2O_4{\cdot}H_2O$

Before focussing on rehydration behaviour, the thermal dehydration of $CaC_2O_4{\cdot}H_2O$ at variable heating rates was investigated. The dehydration process is well-known in literature [17] and often used as standard example of a TG-analysis [25].

The results of a typical TG-DSC experiment for the release of the hydrate water molecule are shown in Figs. 1 and 2. The quantitative TG-DSC data correspond to literature [17] and are given in