Thermochimica Acta 560 (2013) 34–42

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

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

$LiNO_3$–$NaNO_3$–KNO_3 salt for thermal energy storage: Thermal stability evaluation in different atmospheres

Rene I. Olivares*, William Edwards

CSIRO Energy Centre, Newcastle, Australia

A R T I C L E I N F O

Article history:
Received 20 November 2012
Received in revised form 20 February 2013
Accepted 26 February 2013
Available online 16 March 2013

Keywords:
Thermal energy storage (TES)
Heat transfer fluid (HTF)
Concentrating solar power (CSP)
Eutectic $LiNO_3$–$NaNO_3$–KNO_3
Thermal stability

A B S T R A C T

The thermal stability of the eutectic $LiNO_3$–$NaNO_3$–KNO_3 salt was investigated by simultaneous differential scanning calorimetry, thermogravimetry and mass spectrometry (DSC/TG–MS). The work was carried out between room temperature and 1000 °C in blanket gas atmospheres of argon, nitrogen, oxygen and air. The stability of the salt, as measured by the gases evolving from the melt, was influenced by the atmosphere. Evolution of the main gaseous species NO was detected at 325 °C in an atmosphere of argon, at 425 °C in an atmosphere of nitrogen, at 475 °C in an atmosphere of air and at 540 °C in an atmosphere of oxygen. Prior to melting, the eutectic underwent endothermic (α/β) solid–solid type transformation at 87 °C. The melting point was 121 °C, and the solidification point 98 °C. Under-cooling of the salt coincided with the onset of the (α/β) solid–solid transformation upon heating. At a temperature of 500 °C in air, TG analysis showed that the long-term stability of the salt was limited and this was confirmed by DSC. Uncertainty analysis indicated that the measurement of temperature is accurate to ±2.7 °C.

1. Introduction

Solar thermal plants which concentrate the Sun's energy to produce steam and electricity often use molten salt mixtures as a heat transfer fluid (HTF) and/or as thermal energy storage (TES) medium [1–3]. It is desirable that such a salt should have a low melting point in addition to being stable at the highest possible temperature.

Nitrates based salts are generally used at temperatures below 500 °C. Operating such salts at temperatures higher than 500 °C may be possible by rigorous control of the atmosphere. In previous contribution [4], using the same methodology described in this work, it was shown that atmosphere had an important effect on the thermal stability of the nitrite/nitrates based ternary salt ($NaNO_2$–$NaNO_3$–KNO_3) allowing for the maximum operating range of the salt to be extended at high pO_2. Oxidising atmosphere however changed the chemistry of the salt by converting nitrite (NO_2^-) to nitrate (NO_3^-) increasing the melting point. In this work, we revise the low melting point nitrates only, eutectic $LiNO_3$–$NaNO_3$–KNO_3, under the influence of different gas atmospheres.

A low melting point salt that is stable at temperatures higher than 700 °C is needed to increase the heat-to-electricity conversion efficiency for Rankine cycle systems, for use in Brayton cycle systems and to supply high grade heat to industrial processes. The high temperature thermal stability of the salt is then an important aspect that requires consideration given that it will determine the long term viability of its use in a high temperature storage system. Numerous reports addressing thermal stability for nitrate based systems are available [5–8], albeit that some ambiguous conclusions have been made as well. It is therefore essential that the thermo-chemical behaviour, thermal stability, and mode of decomposition of the salt are studied in some detail. For this, the low melting point ternary eutectic system $LiNO_3$–$NaNO_3$–KNO_3 was characterised in the present work between room temperature and 1000 °C under various gas atmospheres.

1.1. Literature

The principal mode of thermal decomposition in nitrate salts has been agreed amongst researchers [5–10]; to correspond to the main reaction: $NO_3^- \leftrightarrow NO_2^- + 1/2\ O_2$. Further decomposition also takes place with the evolution of the oxides of nitrogen, particularly at higher temperatures [11].

In some studies [5,12,13] the decomposition temperature has been reported as the temperature at which oxygen, nitrogen or nitrous oxide is detected in the gas phase. In the work of Gordon and Campbell [12] the single salts alkali metal nitrates were observed to undergo a thermal reaction at temperatures 100–300 °C above their melting points as indicated by bubbling of the molten salt. The evolution of nitrous fumes observed by Gordon and Campbell [12], occurred at temperatures ranging from about 200–350 °C above

---

* Corresponding author at: 10 Murray Dwyer Circuit, Steel River Estate, Mayfield West, NSW 2304, Australia. Tel.: +61 2 4960 6253.
E-mail address: Rene.Olivares@csiro.au (R.I. Olivares).

0040-6031/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2013.02.029

Table 1
Eutectic $LiNO_3$–$NaNO_3$–KNO_3 formulation.

Compound	wt%	mol%
LiNO_3	30	37
NaNO_3	18	14
KNO_3	52	49

Note: Compositions were determined using phase diagrams calculated with FactSage software (Fig. 1).

the initial bubbling reaction. This was claimed to be as a result of the decomposition of the nitrate and/or nitrite to oxide. The later stage of the decomposition of these nitrates was still occurring at temperatures as high as 900 °C which was the upper limit of the apparatus employed [12].

Kust and Burke [14] conducted experiments with a pure equimolar sodium potassium nitrate melt in an oxygen rich atmosphere (pO_2 at 0.85 atm) and measured high oxide ion concentration (O^{2-}) in the molten salt which corresponded to the dissociation constant for nitrite ion (NO_2^-); based on the equilibrium $NO_3^- \rightarrow NO_2^- + O^{2-}$, (nitrite ion concentration reached equilibrium within 7–16 h at temperatures between 295 °C and 340 °C in Kust and Burke experiments [14]) demonstrating that nitrate ion (NO_3^-) could decompose to a measurable extent at temperatures as low as 295 °C.

The thermal stability of binary mixes of alkali metal nitrates as investigated by Abe et al. [15], by means of differential thermal analysis (DTA) and evolved gas analysis (EGA), concluded that the nitrate melts are thermally unstable. The evolved gas analysis measurements [15] indicated that the decomposition of nitrates took place independently and followed the ranking order of thermodynamic stability as determined by the reactions sequence $\mathbf{M}NO_3 \rightarrow \mathbf{M}NO_2 + 1/2O_2$ followed by $2\mathbf{M}NO_2 \rightarrow \mathbf{M_2}O + NO + NO_2$. On this basis the decomposition of a mixture of $LiNO_3$–$NaNO_3$–KNO_3 would be determined by the least thermodynamically stable species, in this case **Li**NO_3 followed by **Na**NO_3 and then **K**NO_3, a possibility if the solution is close to ideal.

Most recently the thermal stability of the eutectic composition in $LiNO_3$–$NaNO_3$–KNO_3 ternary salt was reported by Wang et al. [16], after studies where temperature was cycled between 75 °C and 500 °C in argon gas atmosphere, using a TG/DTA method. Wang et al. [16] observed that once the salt had lost its water content after the first melting cycle it reached a stable condition. In long term stability tests at 500 °C though, there was a weight change of ~8.6 wt% and [16] concluded that the salt was unstable beyond this point. Given that weight loss alone as a measure of stability may be compromised due to some salt evaporation, further analysis is required before the practical limit of salt stability can be ascertained.

In the present work the thermo-chemical behaviour and thermal stability of the $LiNO_3$–$NaNO_3$–KNO_3 eutectic was studied from at least three different points of view: (i) the temperature at which the rapid evolution of gases, NO and/or NO_2 and O_2, are detected by means of mass spectrometry (MS), (ii) the temperature of the melt at which an irreversible endothermic peak of decomposition is resolved by differential scanning calorimetry (DSC), and (iii) the temperature at which rapid weight loss is observed in a thermogravimetric curve (TG). A combination of these three criteria is used for elucidation of the limiting temperature for operation of the salt as would apply in a TES installation. The chemistry and equilibrium reactions by which molten nitrites/nitrates may interact with the atmosphere can be found in Refs. [4,17,18,26].

2. Experimental

The eutectic salt composition was prepared by mixing the individual components in the weight proportions given in Table 1. Analytical reagent grade chemicals $LiNO_3$–$NaNO_3$–KNO_3 supplied by Ajax (UNIVAR) were dried overnight in vacuum prior to weighing and mixing.

2.1. Experimental procedure

A 20 g mixture of the pre-dried pure chemicals was melted inside an alumina crucible in a muffle furnace and allowed to equilibrate in air at 250 °C for 2 h before casting into a stainless steel mould to quench and solidify. The solidified salt was kept under vacuum at 65 °C at all times from which a small sub-sample was taken and used for simultaneous DSC/TG–MS experimentation as needed. About 15–25 mg were ground and loaded into a 100 μL Al_2O_3 crucible in a SETARAM DSC/TG SETSYS Evolution analyser, coupled with a Pfeiffer QUADSTAR-422 mass spectrometer. Due to the presence of $LiNO_3$, the sample was highly hygroscopic and it was inevitable that upon handling the sub-sample, moisture was absorbed. The data acquisition was done by programming the MS to scan for masses from 1 to 60 (amu) to cover the range of possible gaseous species reporting to the gas phase. Identification of gaseous species was done by matching the relative Ion Current Intensities measured by the MS, with the corresponding spectra available in the QUADSTAR-422 MS library database.

The experiments were carried out from room temperature up to 1000 °C at a heating-rate of 10 °C/min in atmospheres of argon, nitrogen, air and oxygen respectively. Once the atmosphere around the sample was set, the gas was allowed to flow at a rate of 30 ml/min.

Five melting–solidification cycles were initially carried out between 50 °C and 400 °C before the full decomposition up to 1000 °C was completed. At all times during heating and cooling the carrier gas was maintained at 30 ml/min and the heating rate was at 10 °C/min. A weight loss in the first heating cycle of between 1 and 2 wt% corresponded to the evolution of water absorbed during sample handling; this was detected by the MS, and was not considered in the analysis. The subsequent four remaining cycles did not show any weight loss or water evolution and were used for determination of the melting and solidification points and to check reproducibility of the measurement. At the end of each decomposition run, contamination of the DSC platinum sensor was evident by a dark stain around the sensor that had to be thoroughly cleaned between runs by first soaking in hot water and then heating to 1200 °C in oxygen to remove any residue.

2.2. Experimental error and uncertainty

Temperature and heat flow calibration of the DSC was carried out as per the standard method for this type of analysis [19,20] using certified reference materials (CRM) listed in Table 2 to cover the temperature range 100–1050 °C. All calibration curve parameters were estimated by a least-squares optimisation routine (build in Calisto Software–SETARAM). The uncertainty on the temperature and heat flow measurements were calculated from the standard error of the estimate, s, according to:

$$s^2 = \frac{1}{N-(n+1)} \sum (Y_{\text{corr}} - Y_{\text{std}})^2$$

where s is the standard error of the estimate; N, number of data points; n, number of independent variables; Y_{corr}, corrected temperature of melting, T_{corr}; or, corrected energy of melting, ΔH_{corr}; and Y_{std}, melting temperature of standard, T_{std}; or, energy of melting of standard, ΔH_{std}.

From these and using the calculation procedure described, the uncertainty for the temperature is ±2.7 °C and the uncertainty for the energy is ±2.3 J/g. The uncertainty of the standard (see Table 2)