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The cobalt-oxide/iron-oxide binary system for use as high temperature thermochemical energy storage material

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A B S T R A C T

The use of thermochemical reactions is a promising approach for heat storage applications. Redox-reactions involving multivalent cations are recently envisaged for high temperature applications. In temperature range of 900–1000 °C, however, where heat storage required for concentrated solar power (CSP) processes only few metal oxides with sufficient heat storage capabilities do exist. Binary systems, on the other hand, could provide a wider range of suitable materials. In the present experimental study the cobalt-oxide/iron-oxide binary system is investigated. For pure iron-oxide the transformation of Fe_2O_3/Fe_3O_4 occurs at 1392 °C with a reaction enthalpy of 599 J/g. The reaction temperature, however, is far too high for CSP applications. Cobalt-oxide, on the other hand, reacts from Co_3O_4/CoO at 915 °C with an enthalpy of 576 J/g. Iron-doped cobalt-oxides transform at similar temperature as pure cobalt-oxide but the reaction enthalpy gradually decreases with increasing iron content. Microstructural stability and related long-term reversibility of the chemical reaction, however, is higher with respect to pure cobalt-oxide. Compositions of around 10% iron-oxide were identified having appropriate enthalpies and being beneficial in terms of microstructural stability.

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1. Introduction

Suitable heat-storage systems are not only essential for concentrated solar power plants (CSP) they also can be used in future to minimize losses in industrial processes. Meanwhile sensible and latent heat storage systems are well established [1], while thermochemical storages are still in an early stage of development. For these type of storage system energy will be absorbed by endothermic reactions (preferentially solid–gas reactions) and released by the exothermic back reaction. For the low temperature range (<100 °C) adsorption reactions of silica gels or zeolites are in development [2]. At temperatures of 100–400 °C dehydration or dehydroxylation reactions such as $Cl_2 \cdot 2H_2O \leftrightarrow CaCl_2 \cdot H_2O + H_2O$ and $Mg(OH)_2 \leftrightarrow MgO + H_2O$ are of interest and may be used in future for industrial waste heat recovery (metal processing, paper manufacturing). Above 400 °C reactions of metal hydroxides ($Ba(OH)_2$), metal carbonates ($CaCO_3$) and metal oxides (Co_3O_4) are promising [1,2]. In general thermochemical storage material should fulfill these requirements:

- fast and reversible reactions in a particular temperature range,
- high energy conversions,
- mechanical stable, inexpensive and non-toxic [3].

Metal oxides of multivalent metals are potential substances for high temperature thermochemical storages, for example in CSP applications with temperatures up to 1000 °C. For this usage heat storage is essential to compensate off-sun hours. The redox-reaction of metal-oxides typically proceeds in an open system with air as the working fluid [1] according to M (=metal):

on-sun: $M_xO_{y+z} \rightarrow M_xO_y + z/2O_2$
off-sun: $M_xO_y + z/2O_2 \rightarrow M_xO_{y+z}$ [1,4]
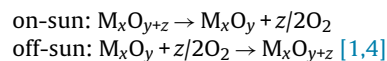
Among pure oxides cobalt-oxide is the most promising redox-material for thermochemical storage applications, because of its high reaction enthalpy and relatively low conversion temperatures [1,5–8]. Cobalt-oxide, however, is under suspicion being carcinogenic, as well as expensive. On the other hand, iron-oxide is cheap, nontoxic and has a high reaction enthalpy [5] as well, but the reaction temperature is far too high for the envisaged applications. A combination of iron- and cobalt-oxide in form of solid solutions or phase assemblages could be a suitable option to benefit from both metal oxide systems.

The aim of the present paper is to investigate mixtures of the binary cobalt-oxide/iron-oxide system in view of the application as a material for thermochemical high temperature storages.

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Composition dependent reaction enthalpies, reaction-temperatures, reaction kinetics, as well as microstructural changing are of special interest. SEM, XRD and STA where used to study thermal effects, phase development and microstructural effects.

2. Experimental

2.1. Synthesis

The materials were synthesized by a sol–gel-method, with citric acid as gel-forming agent [9,10]. For that purpose aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were mixed in the corresponding molar ratios with citric acid in solution by use of volumetric pipettes. After that the dissolutions were heated up in the following steps:

- 120 °C, 2 h → loss of external water
- 180 °C, 2 h → starting of gel-forming process and loss of internal water
- 220 °C, 2 h → outgassing of excess nitrous gases
- 450 °C, 2 h → completion of NO_x outgassing
- 800 °C, 2 h → calcination [9]

Compositions of investigated materials ($x =$ cation ratio, i.e. $Co/(Fe + Co)$) are labeled in the phase diagram (Fig. 1).

2.2. Simultaneous thermoanalysis – STA

DSC (Differential Scanning Calorimetry) and TG (Thermogravimetric Analysis) experiments were performed in STA 449 F3 Jupiter (Netzsch, Germany) with a SiC-furnace (maximal temperature 1550 °C) using platinum crucibles. For subsequent data analysis the Netzsch software Proteus 6 was utilized.

Fig. 2 shows a typical STA-experiment. Thermal analyses start with a heating ramp to 200 °C followed by an isothermal step (20 min) to adjust the system related to the gas flow in the hole system and especially at the balance. Subsequently three cycles between 1100 °C or 1400 °C, respectively and 500 °C were carried out, without holding times. The heating/cooling rates were
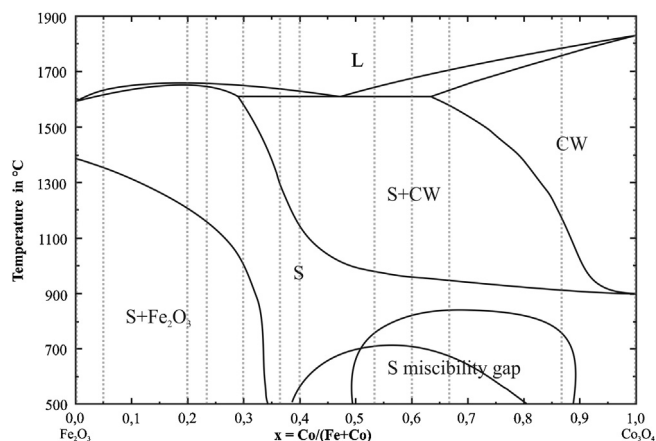

Fig. 1. Phase diagram of the Co–Fe–O-system with the investigated material compositions (dotted lines) after Jung et al. [12] (S – spinel, CW – cobalt-wüstite, L – liquid).

10 °C/min. All experiments were performed at atmospheric pressure ($p_{O_2} = 0.21$ atm) with a gas flow of 70 ml/min nitrogen and 30 ml/min oxygen. Before the last cooling step the oxygen supply was stopped and the nitrogen-flow increased correspondingly to 100 ml/min to prevent re-oxidation of the material (Fig. 2). This allows retaining the high temperature state of the material after reduction for subsequent microstructural investigations and to prove if it keeps metastable under room temperature conditions.

For detailed analyses shown below the second cycle of the STA run is used because the first cycle is not free from drift effects [11] (Fig. 2). This may result from first sintering reactions of the starting material. The third cycle, on the other hand, cannot be utilized since the re-oxidation step is suppressed because of cooling down under nitrogen.

STA provides information on reaction-enthalpy, mass-change, reaction-time, onset-temperature and reaction-temperature. The onset-temperature corresponds to the temperature of beginning reduction- or re-oxidation reaction. While the reaction-temperature means the temperature of maximum reaction rate, given by the maxima of DSC peaks.
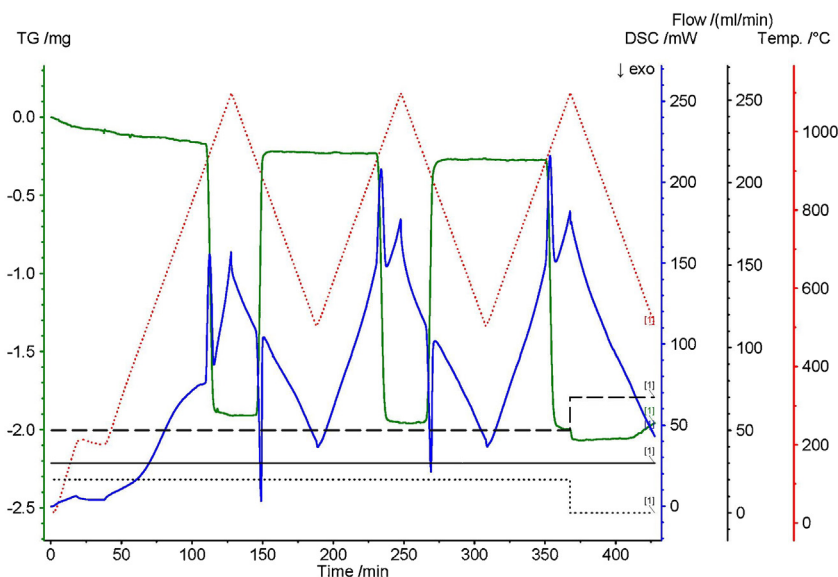

Fig. 2. Results from a STA experiment; red dotted line = temperature-program, green line = TG, blue line = DSC, black dashed line = N_2 (purge gas), black line = N_2 (purge gas), black dotted line = O_2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)