



Metal oxides for thermochemical energy storage: A comparison of several metal oxide systems

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Abstract

The reversible redox reactions of metal oxides show high potential as thermochemical storage material. At high temperatures oxides of suitable transition metals will undergo a reduction reaction and by that thermal energy is absorbed ($M_xO_{y+z} \rightarrow M_xO_y + z/2 O_2$ ($M = \text{Metal}$)). Below specific equilibrium temperatures the reoxidation ($M_xO_y + z/2 O_2 \rightarrow M_xO_{y+z}$) takes place and hence thermal energy will be delivered. Because of the gas–solid reaction and the fact that air can be used as heat transfer fluid thermochemical energy storage based on transition metal oxides are of special interest from the procedural point of view.

Among pure metal oxides only cobalt oxide, iron oxide, copper oxide and manganese oxide show suitable reaction temperatures, reaction enthalpies, cycling stabilities and material costs. To broaden the range of suitable metal oxides binary oxide systems were analyzed in the present study. In the following several compositions of eight binary metal oxide systems as well as the listed pure metal oxides were tested in terms of their ability to store energy thermochemically. Cobalt oxide/iron oxide, copper oxide/cobalt oxide, copper oxide/manganese oxide and manganese oxide/iron oxide are found to show high potential as thermochemical storage material. It was shown, however, that none of the tested systems fulfill all the requirements of an ideal storage material regarding storage capacity, costs and cycling stability.

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1. Introduction

Concentrated solar power (CSP) plays an important role for prospective renewable energy or heat generation. The released heat/energy could be stored by using sensible, latent or thermochemical processes. Actually, sensible storage materials are state of the art, e.g. silica fire bricks show an average heat capacity of 1.00 kJ/kg K between 200 °C (T_{Cold}) and 700 °C (T_{Hot}). Another storage approach is

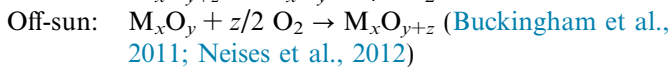
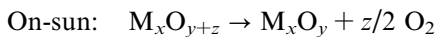
the latent heat storage system using a phase change of the chosen material. Those systems are more easy to handle at low temperatures, e.g. NaNO_3 (307 °C) 172 J/g, but they become more complicated at temperatures >600 °C, e.g. K_2CO_3 (897 °C) 235.8 J/g or Al (660 °C) 398 J/g (Gil et al., 2010; Kuravi et al., 2013). This affects especially the long term stability, in case of corrosion effects, of the surrounded reactor components that are directly in contact with the high temperature phase change materials. For high temperature storage applications thermochemical storage based on reversible chemical reactions is a promising approach for heat recovery. By thermochemical reactions high amounts of thermal energy can be stored while

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using various chemical reactions (e.g.: dehydration of salt hydrates or metal hydrates, decarboxylation of metal carbonates) for heat absorption and subsequent heat release (Kerskes et al., 2011). For temperatures >700 °C, however, redox reactions with metal oxides of multivalent metals are promising. Typically, the redox reactions of these metal oxides proceed in an open system, with an oxygen partial pressure of 0.21 atm using air as working fluid (Neises et al., 2012).

Possible applications for redox-based thermochemical storage systems are focused on industrial waste heat, on higher flexibility in power-heat cogeneration processes or on compensating off-sun hours in CSP plants (Kerskes et al., 2011; Schaube et al., 2011). In general, thermochemical storage materials should show high reaction enthalpy, fast reaction kinetics, long-term cycling stability and material costs as low as possible. For CSP applications, in particular, reaction temperatures of 700–1100 °C are envisaged. The redox reaction can be described as followed (M = Metal):



Among pure metal oxides cobalt oxide, manganese oxide, iron oxide and copper oxide appear most appropriate. But too high reaction temperatures for the envisaged applications, as well as low enthalpies or high material costs, which cannot compete with other approaches of energy storage, make these materials crucial for large-scale applications. To extent the spectrum of possible materials, binary metal oxide systems should be taken into account. The aim of this paper is to present eight different binary systems and to discuss their pros and cons as thermochemical storage materials with respect to the pure metal oxides mentioned before. Reaction temperatures, conversion enthalpies and redox kinetics will be analyzed. Furthermore microstructural development due to cyclic redox reactions will be studied.

2. Experimental

2.1. Synthesis

The materials were synthesized by a sol-gel-method, with citric acid as gel-forming agent. For that purpose aqueous solutions of metal nitrates were mixed in the corresponding molar ratios with citric acid in solution. After that the dissolutions were heated up in several sub-steps (Prasad et al., 1998) with a final calcination step at 800 °C.

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 1520 °C) using platinum crucibles. It was used an open pan, without any lid, to guarantee a better reactivity between the gaseous atmosphere and the metal oxide powder. For subsequent data analysis Netzsch software Proteus 6.1.0 was used.

Fig. 1 represents the results of a typical STA experiment. The performed thermal analysis experiments start with a heating ramp to 200 °C followed by an isothermal step of 20 min. A holding-time is required to adjust the STA system in view to the gas flow in the balance. Subsequently three thermal cycles between 1000 °C or 1450 °C, respectively and 500 °C were carried out, without holding times between the single segments. The heating/cooling rates were 10 °C/min. All experiments were performed at atmospheric pressure with a gas flow of 80 ml/min nitrogen and 20 ml/min oxygen. Before the last cooling step the oxygen supply was stopped and the nitrogen-flow was increased correspondingly to 100 ml/min to prevent reoxidation of the material (Fig. 1). This allows retaining the high temperature state of the material after reduction for subsequent microstructural investigations and to prove if the high temperature state can be retained metastable at room temperature.

To study reaction enthalpy, mass change, reaction time (reaction kinetics), onset temperature and reaction temperature, the second cycle of the STA run is used because the first cycle is not free from drift effects (Subramanian and Dieckmann, 1994) (Fig. 1) possibly due to powder sintering. The third cycle, on the other hand, cannot be used since the reoxidation step is suppressed due to cooling down under nitrogen. Onset temperatures correspond to temperatures of beginning reactions while the reaction temperature describes the temperature of maximum reaction rate, given by the maxima of DSC peaks.

2.3. X-ray diffraction (XRD) and scanning electron microscopy (SEM)

For XRD-analyses a Siemens Kristalloflex D5000 and a Bruker D8 Advance diffractometer with Cu-radiation was used. For high temperature in-situ XRD analyses the Bruker D8 Advance unit was equipped with a heating chamber of the Type HTK1200 (Anton Paar).

Microstructures of the materials were investigated by using a Zeiss Ultra 55 scanning electron microscope. For secondary electron imaging 5.0 kV acceleration voltage and 8.0 mm working distance were used.

Both methods were employed to analyze composition-dependent phase assemblages and microstructures of starting materials (800 °C) and of metastable high temperature conditions (1000–1450 °C).

3. Results and discussion

The most limiting factors for using metal oxides as thermochemical storage materials are material costs, suitable enthalpies, health and safety issues and reaction

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