Exploitation of thermochemical cycles based on solid oxide redox systems for thermochemical storage of solar heat. Part 1: Testing of cobalt oxide-based powders

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Abstract

Thermochemical storage of solar heat exploits the enthalpy effects of reversible chemical reactions for the storage of solar energy. Among the possible reversible gas–solid chemical reactions, utilization of a pair of reduction–oxidation (redox) reactions of solid oxides of multivalent metals can be directly coupled to Concentrated Solar Power (CSP) plants employing air as the heat transfer fluid avoiding thus the need for separate heat exchangers. The redox pair of cobalt oxides Co_3O_4/CoO in particular, is characterized by high reaction enthalpies and thus potential heat storage capacity.

Parametric testing of cobalt oxide-based powder compositions via Thermo-Gravimetric Analysis/Differential Scanning Calorimetry was performed to determine the temperature range for cyclic reduction–oxidation and optimize the process parameters for maximum reduction and re-oxidation extent. The heating/cooling rate is an important means to control the extent of the oxidation reaction which is slower than reduction. Complete re-oxidation was achieved within reasonable times by performing the two reactions at close temperatures and by controlling the heating/cooling rate. Under proper operating conditions Co_3O_4 powders exhibited long-term (30 cycles), complete and reproducible cyclic reduction/oxidation performance within the temperature range 800–1000 °C. No benefits occurred by using Ni, Mg and Cu cobaltates instead of "pure" Co_3O_4. The Co_3O_4 raw material's specific surface area is an influential factor on redox performance to which observed differences among powders from various sources could be attributed. Presence of Na was also shown to affect significantly the evolution of the products' microstructure, though not necessarily combined with improved redox performance.

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Keywords: Solar energy; Thermochemical cycles; Thermochemical heat storage; Redox reactions; Cobalt oxide; Cobaltates

1. Introduction

The identification of suitable materials and processes for efficient and economically viable exploitation of solar energy for hydrogen and so-called "solar fuels" production has been a subject of intense research activity (Centi and Perathoner, 2010). This broad concept includes among

other routes, the utilization of Concentrated Solar Power (CSP) as the heat source required for performing the high-temperature endothermic reactions of the so-called thermochemical cycles – multi-step processes of two or more chemical reactions that form a closed cycle (Kodama, 2003). The redox-oxide-pair based thermochemical cycles in particular, operate on the principle of transition between the oxidized (higher-valence, MeO_{ox}) and reduced (lower-valence, MeO_{red}) form of an oxide of a metal exhibiting multiple oxidation states (Steinfeld, 2005). In this concept,

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Nomenclature

English letters

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C	gas species concentration (moles of gas/m^3)
k	temperature-dependent reaction rate constant (m^3/moles/min)
R	reaction rate (moles of gas produced per minute per g of redox material)
T	absolute temperature (K)

Greek letters

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Ψ	maximum oxygen storage capacity of the redox material (moles of O$_2$ stored in the solid or "consumed from the gas phase" per g of redox material)
y	instantaneous actual oxygen storage capacity of the redox material normalized by the maximum one
ψ	instantaneous concentration of adsorbed oxygen (moles of O$_2$ per g of redox material).

Subscripts

H$_2$O	steam
O$_2$	oxygen
oxidant	gaseous oxidant, e.g. H$_2$O, CO$_2$, O$_2$
ox	oxidation/oxidized
red	reduction/reduced
redox	reduction–oxidation

during the first, higher-temperature, endothermic thermal reduction (TR) step, the oxidized form of the oxide MeO$_{ox}$, releases a quantity of oxygen and transforms to its reduced state under the supply of external heat, according to the generalized reaction scheme:

$$MeO_{ox} + (\Delta H) \rightarrow MeO_{red} + O_2(g) \qquad (1)$$
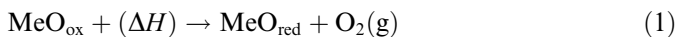
The second step involves (exothermic) oxidation of the reduced form of the oxide back to its oxidized state via an oxygen source (oxidant), establishing thus a cyclic process. If this oxygen source is water or CO$_2$ this step (water- or carbon dioxide splitting, respectively) produces hydrogen or CO. If oxygen (e.g. in air) is used as an oxidant according to the following reaction scheme:
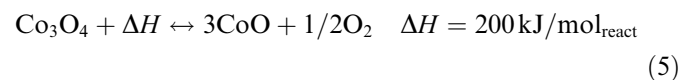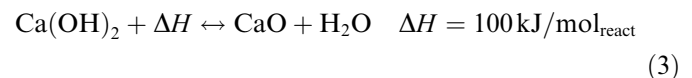
$$MeO_{red} + O_2(g) \rightarrow MeO_{ox} + (\Delta H) \qquad (2)$$
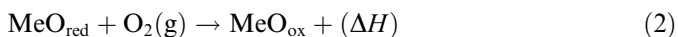
the "net" result of reactions (1)+(2) is not the production of a particular chemical but the exploitation of the heat effects of the reactions for the "storage" of solar heat via the so-called ThermoChemical Storage (TCS). The operation principle of such a cycle uses the heat produced by e.g. a solar receiver during on-sun operation to power an endothermic chemical reaction like (1); should this reaction be completely reversible like (2) the thermal energy can be recovered completely by the reverse reaction taking place during off-sun operation (Ervin, 1977; Wentworth and Chen, 1976).

Such a potential for Thermal Energy Storage (TES) integration within a Solar Thermal Power Plant (STPP) is one of the main differences between CSP and other renewable energy technologies. The concept of thermal storage is simple: throughout the day excess heat produced is diverted to a storage material. When electricity production is required after sunset, the stored heat is released into the steam cycle and the plant continues to produce electricity. Nowadays, most of the CSP plants have some ability to store heat energy for short periods of time and thus have

a "buffering" capacity that allows them to smooth electricity production and eliminate the short-term variations other solar technologies exhibit during cloudy days. In fact, there are three types of implementing this TES approach based on the "nature" of heat to be stored: sensible, latent and thermochemical heat, i.e. heat produced through reversible chemical reactions like the ones above. The characteristics and the latest developments of these technologies are described in several recent reviews (Bauer et al., 2012; Fernandes et al., 2012; Gil et al., 2010; Kuravi et al., 2013; Petrasch and Klausner, 2012; Siegel, 2012).

For TCS implementation is necessary that the chemical reactions involved are completely reversible. Several reversible reactions with significant heat effects have been proposed for exploitation: the most typical among gas–solid decomposition ones are those of metal hydroxides (Murthy et al., 1986), carbonates (Schaube et al., 2011) and oxides (Wentworth and Chen, 1976), under the reaction schemes (3)–(5) respectively:

$$Ca(OH)_2 + \Delta H \leftrightarrow CaO + H_2O \quad \Delta H = 100\,kJ/mol_{react} \qquad (3)$$

$$CaCO_3 + \Delta H \leftrightarrow CaO + CO_2 \quad \Delta H = 167\,kJ/mol_{react} \qquad (4)$$

$$Co_3O_4 + \Delta H \leftrightarrow 3CoO + 1/2O_2 \quad \Delta H = 200\,kJ/mol_{react} \qquad (5)$$

Thermochemical heat storage has several advantages over latent and sensible heat storage technologies: higher storage energy densities achievable, indefinitely long storage duration at near ambient temperature, heat-pumping capability and suitability for large scale. Solar thermal technologies via thermochemical conversion paths offer the prospect of inherent energy storage for continuous (24 h) generation of electricity, an increasingly significant issue as the world moves towards a truly renewable energy based economy.