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Cobalt oxide based structured bodies as redox thermochemical heat storage medium for future CSP plants

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Abstract

The present work is an investigation of the redox performance of several cobalt oxide based compositions, as candidate materials for energy storage in future concentrated solar power plants. To this respect, various commercial and in-house synthesized grades were evaluated in the form of small structured perforated monolithic bodies (flow-through pellets) and assessed in terms of their capability to perform reversible cyclic reduction–oxidation reactions under air flow in the temperature range of 800–1000 °C. The compositions studied involved pure cobalt oxide as well as composites of cobalt oxide with ceria, zirconia, alumina, iron oxide, silicon carbide and manganese oxide. The main criterion for the evaluation of compositions considered was a combination of high redox reaction extent with good thermo-mechanical stability of fabricated structured bodies. Among the materials studied and based on this criterion, the most promising ones were the cobalt oxide–alumina and cobalt oxide–iron oxide composites. Although pure cobalt oxide, and especially one grade synthesized in the lab, exhibited the highest redox performance, the respective shaped structures did not manage to retain their macro-structural integrity in the course of 10 redox cycles. Moreover, it was found that, under certain conditions, the addition of ceria improved redox reaction kinetics, while total performance of cobalt oxide was not affected. However, the structural stability of cobalt oxide–ceria pellets was also problematic. It was also demonstrated that by varying the second oxide, the start-of-reduction/oxidation temperatures of cobalt oxide can be significantly altered. A preliminary simplified kinetic model was developed and its good agreement with pure cobalt oxide redox experimental data was also demonstrated. Post-characterization of used structured bodies confirmed the experimental findings of redox performance measurements and, to some extent, provided explanations regarding the main phenomena involved upon cyclic operation of different compositions employed.

Keywords: Thermochemical heat storage; Redox reactions; Cobalt oxide; Monolithic structured reactor

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Nomenclature

English letters

T	absolute temperature (K)
k	temperature-dependent reaction rate constant (s^{-1})
R	redox reaction rate (s^{-1})
p_1, p_2	phenomenological coefficients/kinetic model fitting parameters
E	kinetic model fitting parameter (K)

Greek letters

y	the fraction of Co_3O_4 transformed to CoO during reduction step

Subscripts

$MO_{oxidized}$	high valence metal oxide
$MO_{reduced}$	low valence metal oxide
O_2	oxygen
n_{O2}	oxygen moles
$\Delta H_{reaction}$	reaction enthalpy
$E_{released}$	maximum energy release during the oxidation step of the redox thermochemical cycle

1. Introduction

Similarly to virtually all energy production systems based on renewable energy resources, Concentrated Solar Power (CSP) installations are limited by the inherently intermittent nature of their driving source (i.e. solar energy). An efficient solution could be provided by a suitable, simple and high energy density system, with the ability of storing the excess of solar power during on-sun operation. Such concepts fall into the general category of Thermal Energy Storage (TES) and their importance is demonstrated by the fact that most CSP plants implemented during recent years incorporate such systems to avoid or mitigate inefficiencies due to intermittent operation. Current state-of-the-art TES systems are dominated by molten salts technology, however sensible heat systems based on a variety of different materials and formulations are also employed to some extent (Gil et al., 2010). Both approaches are characterized by relatively low energy densities (<200 J/g), which translate to substantially high amounts and volumes of storage media, with an obvious impact on capital costs for the construction of relevant systems, especially when the target is prolonged off-sun operation. Moreover, molten salts are also limited by the maximum allowable operation temperature (<600 °C) due to their decomposition.

A relatively recent and promising alternative to the above TES solutions, which in-principle efficiently addresses the above mentioned challenges of state-of-the-art storage concepts, is based on thermochemical heat storage (THS) schemes (Abedin and Rosen, 2011). Such approaches are based on multi-step reversible reactions that are able to store excess CSP-derived energy by driving endothermic reactions. When necessary, e.g. during off-sun operation, conditions are modified to favor the exothermic reactions step(s) and the energy stored previously is released and transferred to the CSP plant working fluid, thereby extending power production. Such examples are thermochemical concepts based on cyclic decomposition and synthesis of ammonia (Lovegrove et al., 2004) and hydration/dehydration (Schaube et al., 2012) or carbonation/calcination (Barker, 1974; Muller et al., 2011) of calcium oxide. In addition, a recently proposed approach (Wong et al., 2011) relates to cyclic reduction–oxidation of metal oxides (MO). A typical scheme for such a system is described by the following two-step thermochemical cycle:

$$MO_{oxidized} + Heat \rightarrow MO_{reduced} + O_2\,(\text{endothermic/energy storage step}, T = T_{high}) \quad (1)$$

$$MO_{reduced} + O_2 \rightarrow MO_{oxidized} + Heat\,(\text{exothermic/energy release step}, T = T_{low}) \quad (2)$$

One of the notable advantages of the above concept, as described by reactions (1) and (2) and particularly in comparison to the other above mentioned THS technologies, is the fact that both steps can occur in the presence of air, thus eliminating the need of switching atmospheres depending on the step to be promoted. In addition, this characteristic renders the particular approach notably compatible with CSP plants utilizing ambient air as heat transfer fluid, such as the demo installation of Jülich Solar tower (Schwarzboezl et al., 2010). Under the particular redox THS approach, the system can be regulated/designed in a way that during both steps, the air flow exiting the system maintains a relatively constant temperature. In general, all CSP plant designs/technologies, after proper customization and under the prerequisite that they can provide adequately high temperatures for the occurrence of the reduction step, could be compatible with such a storage concept.

Based on a preliminary theoretical and proof-of-principle experimental study (Wong et al., 2011), the cobalt (Co_3O_4/CoO) and manganese (MnO_2/Mn_3O_4/Mn_2O_3) oxides were qualified as the most promising ones, both from a practical and from a cost-effectiveness point-of-view. Indeed, the redox transition temperatures of these two systems lie in the range of 550–1000 °C and thus can be