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Cobalt/cobaltous oxide based honeycombs for thermochemical heat storage in future concentrated solar power installations: Multi-cyclic assessment and semi-quantitative heat effects estimations

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ABSTRACT

The present study relates to the preparation and evaluation of small-scale honeycomb structures as compact reactors/heat exchangers via exploitation of the cobalt/cobaltous oxide (Co_3O_4/CoO) cyclic reduction–oxidation (redox) heat storage scheme. The structures considered included in-house extruded monoliths (pure cobalt oxide and cobalt oxide/alumina composites) and commercial cordierite substrates coated with Co_3O_4. The samples were subjected to multi-cyclic redox operation under air flow, in the temperature range of 700–1000 °C. Reduction occurred during heating up to 1000 °C, while oxidation took place during cooling. Redox performance was evaluated on the basis of on-line oxygen release/consumption measurements, while continuous monitoring of imposed air flow reactor inlet/outlet temperatures facilitated the preliminary estimation of heat dissipation in the duration and after completion of the exothermic reaction (oxidation). For all samples, redox performance remained stable in the course of multi-cyclic exposure. In terms of heat transfer, there is strong indication that both composition and the geometry of the honeycomb are important. The pure Co_3O_4 extruded honeycomb exhibited the highest heat dissipation efficiency but suffered from severe deformation upon multi-cyclic operation. The addition of a small amount of alumina in the aforementioned composition (10% on the basis of total initial mass of oxides), particularly when combined with an increase of the honeycomb wall thickness, substantially improved macro-structural stability upon thermal/redox cycling. The Co_3O_4-coated cordierite monoliths showed essentially the same normalised redox performance with the pure Co_3O_4 extruded honeycomb, however the overall heat dissipation achieved was lower. Regarding the effect of redox cycling on the structural stability of studied formulations, pure Co_3O_4 samples exhibited notable swelling. In the case of the extruded body, this resulted to structural collapse while for the coated cordierite honeycomb, expansion of the coating layer led to partial channels blocking. Based on relevant morphological and structural post-analysis, it was concluded that formation of cobalt aluminate largely reduced swelling intensity.

1. Introduction

Concentrated solar power (CSP) technology can be a low cost option for large-scale power production, in particular when plants are sited in locations with premium solar potential. As electricity cost from conventional generation technologies continues to rise, off-takers are becoming increasingly interested in CSP as a viable alternative to other renewable technology options (Cipollone et al., 2014). Owing to its intermittent nature, it is also of prime importance to develop technologies to store excess solar energy during on-sun operation. During off-sun conditions, this energy should be easily released and exploited controllably. Thus, plant capacity, efficiency and dispatchability would be significantly improved, thereby maximizing economic gains (Block et al., 2014).

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Thermal energy can be stored as sensible, latent or thermochemical heat (Gil et al., 2010; Kuravi et al., 2013). Thermochemical heat storage (TCS) has several advantages over both latent and sensible storage technologies (Yan et al., 2015). TCS is especially attractive due to its high energy storage density potential, thereby leading to more compact systems. Moreover, it can offer heat-pumping capability and more facile scalability (Abedin and Rosen, 2011). Storage of solar thermal energy and its on-demand release is achieved in three steps: charge via surplus heat exploitation, storage of charged material during idle operation (optional) and on-demand discharge. During charging, excess heat will be absorbed by an endothermic reaction and – when requested by the system – stored energy is controllably discharged via the reverse exothermic reaction.

At present, several commercial and demo systems are available but are mostly based on sensible storage concepts via gas–gas, liquid–liquid (Ramade et al., 1990; Prengle et al., 1980; Ervin, 1977), or gas–solid reaction systems (Laing et al., 2006; Zanganeh et al., 2012; Py et al., 2011; Zunft et al., 2010). For practical TCS implementation, complete reversibility of chemical reactions involved is a prerequisite. Several schemes have been proposed and typical examples are those of sulphates (Tmar et al., 1981), metal hydroxides (Murthy et al., 1986; Schaube et al., 2011, 2012a, 2012b) and carbonates (Edwards and Materić, 2012; Flamant et al., 1980; Kubota et al., 2000). However, decomposition reactions of such compounds produce gases, which in general have to be separated and stored (Agrafiotis et al., 2014).

An alternative gas–solid TCS system, providing an in-principle efficient means to store solar heat relates to redox reactions of multi-valent metal oxides (Fahim and Ford, 1983). Charging is achieved at a relatively high temperature via metal oxide reduction. Discharge proceeds by oxidation of the reduced oxide at a lower temperature. Several factors are important regarding the choice of the metal oxide used in redox TCS cycles: thermodynamics, energy storage density, materials cost, reaction kinetics, toxicity and cyclability (Wörner et al., 2012). Based on a combination of preliminarily evaluated thermochemical redox activity and economic potential, the redox couples of Co_3O_4/CoO, BaO_2/BaO, Mn_2O_3/Mn_3O_4, CuO/Cu_2O, Fe_2O_3/Fe_3O_4 and V_2O_5/V_2O_3 were those selected as in-principle suitable for further development studies (Wong, 2011). Recently, and under a similar redox TCS rationale, the use of perovskite-based compositions was proposed (Babiniec et al., 2015). Some first promising results on $La_xSr_{1-x}Co_yM_{1-y}O_{3-\delta}$ (M = Mn, Fe) were presented and appreciable energy densities (approximately 250 kJ/kg) were reported. Also reported was the requirement for very low oxygen partial pressures during discharging, so as to ensure adequately high reduction extent and, consequently, high energy storage density potential. From a practical point of view, this may be quite challenging.

It is important to highlight that for the multi-valent single metal oxide systems mentioned above, redox steps can take place under air flow, with temperature being the only control parameter for the reaction step to be promoted. This attribute further simplifies the operation of such systems and renders them especially compatible with central receiver power plants using air as heat transfer medium; e.g. the Solar Tower Jülich (STJ) demo installation. Among oxides mentioned, cobalt-oxide (Co_3O_4) is considered to be very promising, due to its high reaction enthalpy and consequently high energy density potential (maximum at approximately 844 kJ/kg), long-term/multi-cyclic material stability (Hutchings et al., 2006) and reasonably low conversion temperatures (Pelton et al., 1979; Kale et al., 1988; Tang et al., 2008). The latter characteristics render Co_3O_4 suitable for applications coupled with the new generation of volumetric-receivers, currently under development. This technology will have the potential to develop the required maximum temperatures of 950–1000 °C imposed by the reduction step of Co_3O_4 to CoO (Wang et al., 2012; Neises et al., 2012; Wong et al., 2010).

Most redox TCS studies up to date refer to either cobalt or manganese oxides and provide information on the intrinsic behaviour of the materials through small-scale tests, performed under idealised conditions (e.g. thermogravimetric analysis/TGA) with powder formulations. Doping of Co_3O_4 with other oxides (e.g. Ni, Mg and Cu) has an adverse effect on redox performance (Block et al., 2014), while the grade and source of cobalt oxide employed can also have measurable impact on performance and other important parameters such as cycle-to-cycle activity and redox onset temperatures (Agrafiotis et al., 2014; Pagkoura et al., 2014). A recent study (Carrillo et al., 2014) demonstrated that samples from pure Co_3O_4 show more stable cycle-to-cycle reduction and re-oxidation temperatures, faster reaction kinetics and very good cyclability versus doped ones. Mn-doped Co_3O_4 exhibited reaction kinetics deterioration, notably reduced heat storage potential and a shift towards higher redox onset temperatures. On the other hand, Co-doped manganese oxides showed better thermal stability but suffered from measurable cycle-to-cycle loss of redox performance. A common finding of all studies, performed so far under idealised TGA conditions with pure Co_3O_4, is its almost stoichiometric conversion upon redox cycling. However, additional lab-scale studies performed under more realistic conditions (Neises et al., 2012; Karagiannakis et al., 2014; Pagkoura et al., 2014) revealed that the reduction step is actually limited to Co_3O_4 conversions of about 50–65%, thereby decreasing maximum achievable energy density cf. to its theoretical value. On this basis, the maximum heat storage capacities in the range of 400–600 kJ/kg have been reported, also depend on the experimental setups used and, primarily, on the nature of Co_3O_4 grade.

A previous study of the present authors (Karagiannakis et al., 2014) proved that small-scale perforated cylindrical structures of pure cobalt oxide exhibited measurably faster redox kinetics, somewhat higher energy density (500 J/g) and improved cycle-to-cycle repeatability cf. to respective powder formulations. Furthermore (Pagkoura et al., 2014) it was demonstrated that, in such structures, alumina or iron oxide addition in relatively small amounts (10 wt%) can substantially improve structural stability. Naturally, this enhancement was at the expense of redox performance, however measured decrease was within acceptable levels. In line with this concept of structured formulations, two studies conducted by DLR/Cologne (Agrafiotis et al., 2015a, 2015b) evaluated the possibility of employing mini-specimens of various Co_3O_4 coated substrates as well as of small porous foams, manufactured entirely from the redox active material. Regarding coated structures, the choice of the substrate should be such that extensive interaction with the redox active phase is avoided. However, caution is required to also prevent significant resistance to air flow and/or coating entrainment. Such phenomena can be due to very high loadings that may induce extensive blocking of monolithic channels and/or insufficient adherence of the coating on the substrate. On the other hand, foams prepared from pure Co_3O_4 can ensure high volumetric energy density, however, based on reported results (Agrafiotis et al., 2015b) structural integrity under longer term exposure conditions may be an issue of concern. Promising findings of relevant recent studies promoted further interest on how the Co_3O_4 based TCS scheme could be integrated with solar electricity plants coupled with high-efficiency power cycles (Schrader et al., 2015; Muroyama et al., 2015). Thermodynamic calculations and kinetic considerations on the basis of experimental findings indicated that, despite technical challenges, the particular redox cycle can be directly and efficiently coupled with next generation CSP plants operating Air Brayton cycles.

The present work addresses aspects of multi-cyclic performance of in-house extruded and coated Co_3O_4 honeycomb structures to