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First experimental studies of solar redox reactions of copper oxides for thermochemical energy storage

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Abstract

Thermochemical redox processes are currently considered one of the most promising methods for thermal storage of solar energy. Among the different types of materials available for this purpose, metal oxides allow higher operation temperatures in CSP systems. This is in agreement with the new R&D trends that focus on increasing the temperature to augment the efficiency. Copper oxide was previously proposed as a valid metal oxide for thermochemical storage. However, no demonstrative experiments had been carried out so far under solar radiation. In this work, the suitability of copper oxide was proved in a solar furnace. The employed solar reactor was a rotary kiln device with direct radiation absorption on reactive particles, which is a configuration that guarantees higher operation temperatures than other types of solar reactors. Given results include the performance of the CuO reduction in the rotary kiln under argon atmosphere and the cyclability of the pair CuO/Cu_2O in air.

Keywords: Thermochemical storage; Copper oxide; Solar reactor; Solar furnace

1. Introduction

CSP uses concentrated solar energy to generate electricity while producing very low levels of greenhouse-gas emissions. When combined with thermal energy storage capacity, CSP plants can still produce electricity when clouds block the sun or after sundown, what is a very significant advantage (Romero and Steinfeld, 2012; Zaversky et al., 2013). Thus, investigation on reliable and economically feasible thermal storage systems is currently one of the key challenges for the efficient and sustainable use of concentrating solar energy into the future (Agrafiotis et al., 2015; Cabeza et al., 2015; Galione et al., 2014; Karagiannakis et al., 2014).

There are three main types of thermal energy storage (TES) technologies available: Sensible heat storage (SHS), latent heat storage (LHS) and thermochemical storage (TCS) (Gil et al., 2010). TCS is a relatively new technology with much research and development ongoing (Aydin et al., 2015). Its advantages and potentiality are certain. Energy stored density of TCS can be up to fifteen times higher than SHS and six times higher than LHS (Abedin and Rosen, 2011). Also, heat can be recovered at higher temperature and in a different range depending on the material employed to store. Finally, heat can be stored indefinitely in the form of chemical energy (Nagel et al., 2013).

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Nomenclature

P_{RR}	power input to the solar reactor	$[O_2]$	instantaneous concentration of oxygen
F_f	solar furnace factor	υ	gasflow in the reaction chamber
Q_i	ideal power of the solar furnace	ρ	density of an ideal gas
X_A	chemical conversion of reactant “A”		

The redox pairs of metal oxides have been proposed as a promising concept for thermochemical energy storage at high temperature. The system employs cycles of reduction and oxidation (redox) reactions to store and release heat. Operating temperature is in a range of 623–1373 K depending on the equilibrium temperature of the selected redox pair (Pardo et al., 2014). The general pathway of TCS based on metal oxides is:

$$\text{Reduction}: \quad M_xO_y \rightarrow M_xO_{y-1} + 1/2O_2 \quad \Delta H > 0 \tag{1}$$

$$\text{Oxidation}: \quad M_xO_{y-1} + 1/2O_2 \rightarrow M_xO_y \quad \Delta H < 0 \tag{2}$$

Wong et al. (2010) and Wong (2011) analyzed sixteen oxides as possible candidates for this application. Among them, only BaO_2, Co_3O_4, Mn_2O_3, CuO, Fe_2O_3, and Mn_3O_4 demonstrated a suitable performance as TCS materials. Then, Co_3O_4 was retained for further studies since it exhibited the best performance in terms of reversibility and energy storage density (Agrafiotis et al., 2014; Block et al., 2014; Neises et al., 2012). Neises et al. (2012) performed several cycles of reduction/oxidation irradiating the material with concentrated solar radiation. Mn_2O_3 cyclability has been also recently proved by TGA tests and the influence of particle size has been analyzed (Carrillo et al., 2014). Relating to copper oxide pair (CuO/Cu_2O), Wong (2011) indicated that re-oxidation of Cu_2O seems to take place at temperature significantly lower than equilibrium transition. Since this capacity would provide flexibility in the design and operation of the storage system, they pointed out the potential of CuO as TCS candidate. Theoretical transition temperature is established in 1120 °C in air and the storage density is 811 kJ/kg (844 kJ/kg for Co_3O_4 and 202 kJ/kg for Mn_3O_4) according to Wong (2011). Moreover, copper oxide is widely available in areas of emerging CPS markets with very high solar resource, as México and North of Chile, what could decrease its price compared with other TCS metal oxides.

Apart from advanced TES materials, another key challenge of CSP concerns the increase of the thermal fluid temperature because it is favorable for improving thermal conversion efficiency. Investigation on this direction involves receiver materials and efficient designs or new thermal fluids proposals (Romero and Steinfeld, 2012). Hence, energy storage development should be also oriented to higher temperature systems.

Metal oxides redox systems are conceived to be coupled with high temperature solar receivers where air is the thermal fluid. For example, volumetric receivers made of metallic or ceramic materials may increase the thermal fluid temperature above 1000 °C. In addition, recent investigations are focused on CSP tower plants with direct-absorption receiver using solid particles. Regarding to that, Ehrhart et al. (2014) proposed to combine the air-particles heat transfer media with solid thermochemical storage. According to their approach, a thermochemically active material is charged in a direct-absorption solar receiver/reactor by means of an endothermic chemical reaction. Then, the material is stored until heat must be recovered for the power block, when it is released through an exothermic chemical reaction.

Among the different types of direct absorption particles solar reactors that were classified in Alonso and Romero (2015a,b), rotary kilns have the advantages of versatility, long life of components and low cost of maintenance. In fact, Neises et al. (2012) investigated the reduction and oxidation of Co_3O_4/CoO for thermochemical energy storage with a solar operated rotary kiln. For the reactor selection they justified that it favors the heat transfer between the gas and solid phase with a high reactive surface area. Moreover the particles motion should decrease their sintering. This feature is very interesting in case of working with copper oxides because the melting point of Cu_2O is close to the transition temperature and sintering or partial melting could pose problems to the physical operation of the TCS system. Finally, the feasibility of solar heated rotary kilns for thermochemical application was shown in several cases (Chambon et al., 2010; Flamant, 1980; Meier et al., 2004).

According to the above pointed out, in this study, the potential of the metal oxide redox pair CuO/Cu_2O for TCS is evaluated, for the first time, under solar conditions with direct radiation absorption. A solar reactor was employed for experimental tests. It consists of a rotary cavity closed by a quartz window. The reactor was set up at the HoSIER solar furnace of the Renewable Energy Institute of the National University of México (IER-UNAM). Experiences acquired with the first approach to the solar-driven reduction of CuO into Cu_2O are reported in this paper. Then, results of reduction/oxidation cycles in air according to the following reaction

$$CuO \leftrightarrow Cu_2O + 1/2O_2 \tag{3}$$

are also presented and discussed.