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Original Research Paper

Effect of mechanical activation on thermal energy storage of Co_3O_4/CoO system

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A B S T R A C T

The heat produced by a solar receiver during on-sun operation can be employed to drive the endothermic reduction reaction of Co_3O_4 to CoO; then the consumed thermal energy can be recovered completely by the exothermic reverse oxidation reaction of CoO to Co_3O_4 which can take place during off-sun operation. In this research, the effect of mechanical activation duration (1, 2, 4, 8, and 16 h) on thermal energy storage by Co_3O_4/CoO redox pair was investigated. It was found that increasing the mechanical activation duration increases the sintering and particle size of the cobalt oxide powder after one cycle redox, and subsequently the thermal energy storage properties are declined. The weight loss was about 4–5 wt.% for samples heated by 1, 3, and 5 °C/min, while it was about 2 wt.% for 10 °C/min heating rate and less than 1 wt.% for 15 °C/min heating rate. The comparison of cycleability of as-received and 1 h mechanical activated cobalt oxide showed that mechanical activation weakened the cycleability of redox reactions of cobalt oxide. The as-received cobalt oxide cycleability continued up to three cycles, although the reduction and oxidation capacities gradually declined. The cycleability of 1 h mechanical activated sample entirely diminished after two cycles.

1. Introduction

Increasing energy demands and the environmental impacts of fossil fuels is the direct driving force for the renewable energy sources. Thermal energy storage (TES) systems play a major role in the development of concentrated solar power (CSP) plants as a renewable energy technology since they improve the dispatch ability of power plants using solar energy [1].

The three most common modes of thermal energy storage systems are based on the storage of sensible heat, latent heat, and thermochemical heat. Thermochemical heat storage has several advantages over latent and sensible heat storage technologies including higher energy storage densities, long storage duration, heat-pumping capability and suitability for scale-up [2,3].

Thermochemical heat storage (TCS) technology exploits the reversible chemical transformations in the form of a redox cycle. The heat produced by a solar receiver during on-sun operation is employed to drive an endothermic chemical reaction; the consumed thermal energy can be recovered completely by the exothermic reverse reaction that can take place during off-sun operation [4].

It is also important that the reaction products can be stored, and heat can be retrieved when the reverse reaction takes place. Therefore, the reversibility of the reactions becomes important. The most important challenge is to find the appropriate reversible chemical reaction for the heat energy storage. Thermochemical reactions need high temperatures (greater than 400 °C) and the enthalpy of the reaction is in a high range also (100–500 kJ/mol). In addition, since the products of the reaction can be stored separately, the systems that use thermochemical heat storage materials (TCM) to store energy are also suitable as seasonal storage systems [5].

Several reversible reactions with significant heat effects were proposed for thermochemical heat storage which the most typical among gas–solid decomposition ones are those of metal hydroxides [6], carbonates [7] and oxides [8]. In a recent study, several oxide systems screened with respect to their thermochemical storage capability [9]. A number of oxides were eliminated either due to their low efficiency heat recovery of redox temperatures (Cr_5O_{12}, Li_2O_2, Mg_2O) or due to their high cost raw materials and processing (PtO_2, Rh_2O_3, UO_3). Based on the combination of thermochemical redox activity and economic aspects, Co_3O_4, BaO, Mn_2O_3, CuO, Fe_2O_3, Mn_3O_4 and V_2O_5 were selected for further developmental

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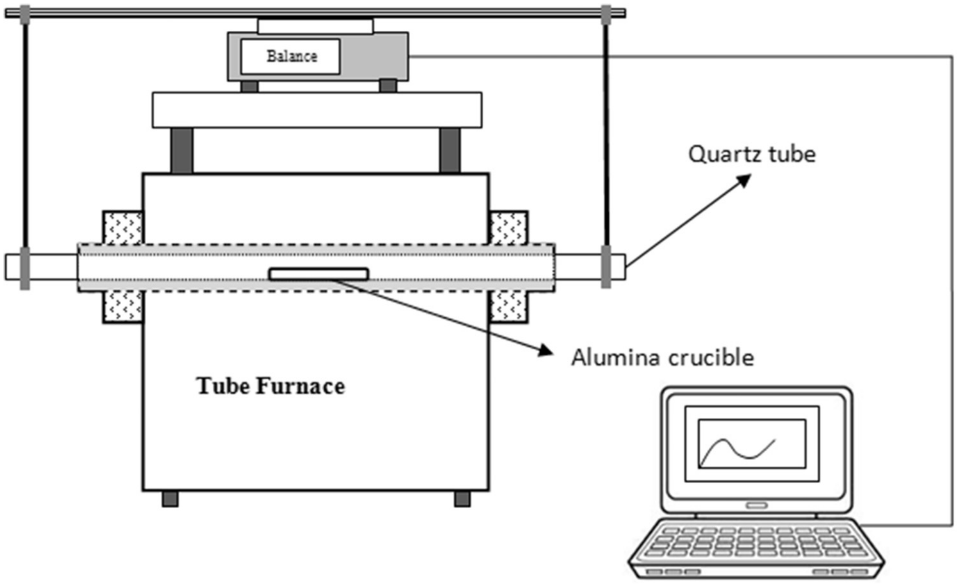

Fig. 1. Schematic of thermogravimetry setup.

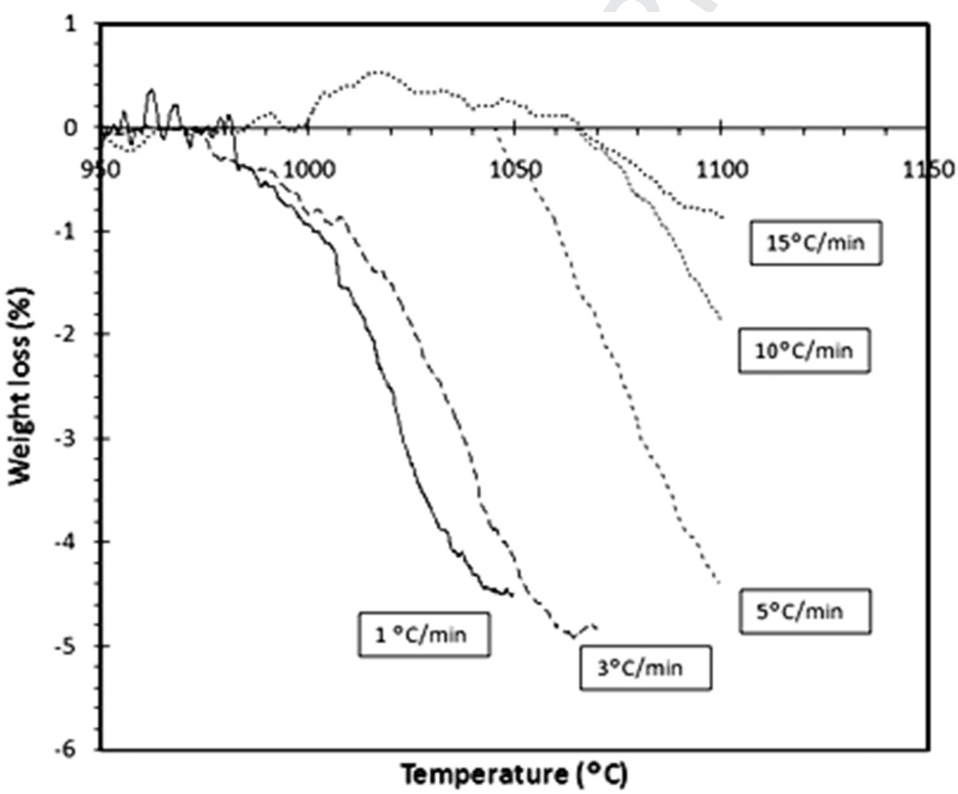

Fig. 2. Effect of heating rate on weight loss during Co_3O_4 reduction to CoO.

and design studies. Secondary oxide addition from abundant raw mineral sources was suggested to decrease the material cost while increasing materials performance, meeting eventually the US Department of Energy (DOE) storage cost and Levelized Cost of Electricity (LCOE) targets of $15/kWh and $0.09/kWh, respectively [3].

Cobalt oxides considered among the most attractive of these systems since its reduction in air under atmospheric pressure (Reaction 1) takes place at about 900 °C, a temperature that can achieve within the new generation of volumetric-receivers-based solar tower power plants. In addition, its energy density (844 kJ/kg) [9] is among the highest of such oxide systems. Also, the Co_3O_4/CoO redox pair is attractive due to its good reaction kinetics in short redox cycles [8] and long-term material stability [10]. Systems based on this pair have been recently tested for TCS applications via Thermo-Gravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC), either pure [4] or in combination with other oxides metals such as iron oxide [11], manganese oxide

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