Effects of Fe$_2$O$_3$ addition and mechanical activation on thermochemical heat storage properties of the Co$_3$O$_4$/CoO system

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**HIGHLIGHTS**

- Effects of Fe$_2$O$_3$ addition and 1 h ball milling on redox reactions of Co$_3$O$_4$ were studied.
- Some of the Fe$_2$O$_3$ reduced to Fe$_3$O$_4$ during the reduction process.
- $\Delta H_{\text{Red}}$ of Co$_3$O$_4$, 1 h ball milled Co$_3$O$_4$, and 1 h ball milled Co$_3$O$_4$-15 wt% Fe$_2$O$_3$ are 622, 496, and 895 kJ/kg, respectively.
- Fe$_2$O$_3$ addition and ball milling improved the redox cyclability of Co$_3$O$_4$.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

Effects of Fe$_2$O$_3$ addition (2-20 wt%) with 1 h mechanical activation on redox reactions of Co$_3$O$_4$ were studied by TG/DSC, SEM, and XRD analyses. The results showed that a Fe$_2$O$_3$ addition from 2 to 15 wt% increases the oxygen release from 1.4 to 3.4 wt% and decreases the reduction onset temperature from 1030 to 960 °C, while it increases the oxygen uptake value and re-oxidation onset temperature respectively from 1.5 to 3.3 wt% and from 930 to 1010 °C. The increase in iron oxide to 20 wt% resulted in loss of heat storage properties due to significant reduction in oxygen release and uptake. Moreover, TG/DSC analyses revealed that reduction enthalpy of as-received Co$_3$O$_4$, 1 h ball milled Co$_3$O$_4$, and 1 h ball milled Co$_3$O$_4$-15% Fe$_2$O$_3$ are 622, 496, and 895 kJ/kg, respectively. Phase identification and TG experiments under argon atmosphere demonstrated that Fe$_2$O$_3$ participates in the reduction process. Furthermore, adding 15 wt% of iron oxide to cobalt oxide and 1 h mechanical activation improved the redox cyclability of cobalt oxide.

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1. Introduction

Fossil fuels supply most of the required energy consumption in the world. However, the increasing growth in energy consumption, environmental concerns due to greenhouse emissions and global warming, and depletion of fossil fuels reserves have caused the world to make a serious decision to obtain energy using renewable sources [1,2]. Therefore, it is very important to develop new environmental friendly technologies working with renewable energies. Using concentrated solar power (CSP) along with thermal energy storage (TES) to produce electricity is one of these technologies [3-7]. The main advantage of Solar Thermal Power Plants working with CSP rather than other solar energy technologies is that the heat originated from solar energy can be stored and converted to electricity in off-shine hours thus making dispatch-ability for solar power plants [2]. Among the various CSP technologies, solar towers offer the potential of high temperatures and thus high thermodynamic conversion efficiencies [8,9].

Three methods including sensible, latent, and thermochemical heat storage are used for thermal energy storage [10,11]. The concept of thermochemical heat storage was first introduced by Funk and Reinstorm in 1966 [12]. In fact, the thermochemical heat storage method is based on redox reactions and exploits the heat effects of reversible chemical reactions [10]. Thermochemical heat storage has the advantages of higher energy storage, suitability for large-scale applications, long storage duration and long-range transport at ambient temperature, and higher working temperature ranges in comparison with the other two storage methods [11,13].

Various reversible reactions have been studied for thermochemical heat storage. They include carbonation/decarbonation of metal oxides/carbonates [14,15], hydration/dehydration of metal hydroxides [16-18], decomposition/sulfation of metal sulfates/oxides [1,19], ammonia synthesis/dissociation [20] and reduction/oxidation (redox) of metal oxides [14]. Among these, metal oxides have the main advantage of incorporation with air-operated solar thermal power plants. Attractive mono-metallic redox pair oxides are those which are capable of taking up and releasing gas-phase O₂ at conditions relevant for generation of heat [14,21,22] including Co₃O₄/CoO [22-25], BaO₂/BaO [26], MnO₂/ Mn₃O₄ [2,27,28], CuO/Cu₂O [29], Fe₂O₃/Fe₃O₄ [30]. Multi-metallic redox oxides such as perovskites [31-33] have been recently investigated.

According to Wong et al. [34] only a few metal oxides have the required properties for thermochemical heat storage including Co₃O₄, BaO₂, MnO₂, CuO, Fe₂O₃, Mn₃O₄ and V₂O₅, with an emphasis that cobalt oxide shows the best re-oxidation kinetics. Cobalt oxide is one of the most promising materials for thermochemical heat storage. The redox temperature for the Co₃O₄/CoO pair is about 885-905 °C according to Eq. (1) [35]:

\[
\text{Co}_3\text{O}_4 + \Delta H \leftrightarrow 3 \text{CoO} + \frac{1}{2} \text{O}_2
\]

\[\Delta H = 200 \text{kJ/mol}_{\text{reac}} \text{ or } 844 \text{kJ/kg}_{\text{reac}}\]

Cobalt oxide has been studied using various reactors such as directly irradiated rotary kiln and powder-coated honeycomb reactors [24,36]. The reduction and re-oxidation of cobalt oxide powder for 30 cycles in a solar-heated rotary kiln were studied by Neises et al. [24]. They achieved a storage capacity of about 400 kJ/kg in a cycle with half reduced material due to insufficient mixing. Agrafiotis et al. [8,23,35] studied the porous foams and pellets made of Co₃O₄ for about 30 redox cycles. They found that foam retained its integrity and stoichiometric redox performance after the cycles, while pellets exhibited cracks after a few cycles. They also stated that when using foams or pellets of Co₃O₄, all the oxide is exploited for the thermochemical reaction. According to research by Karagiannakis et al. [37], a gravimetric energy storage density of 495 kJ/kg for the cobalt oxide powder and 515 kJ/kg for the pellets were achieved. More complex systems containing secondary oxide are being investigated to improve the properties or overcome the drawbacks of candidate materials for thermochemical heat storage. Generally, a secondary oxide addition to cobalt oxide was employed to increase anion vacancies concentration and increase oxygen mass transfer. Also, differences in oxidation state and atomic size cause a charge imbalance and lattice strain. The increased lattice vacancies density leads to higher oxygen mass transfer through the lattice. In addition to doping compounds, research continues in mixed metal oxides [38] and perovskites [39]. Basically, the cyclability of heat storage materials is improved by inhibiting grain growth using secondary oxide additions [1].
The effect of iron oxide addition to cobalt oxide was investigated by Block et al. [40]. They observed that the addition of iron oxide to cobalt oxide or the addition of cobalt oxide to iron oxide reduces the enthalpies of reaction in comparison with pure oxides. They reported that 10 mol% iron oxide doped cobalt oxide shows a high enthalpy of reaction and higher reduction/oxidation reversibility than pure cobalt oxide. The reversibility of the redox reactions of cobalt oxide pellets with the addition of alumina, ceria, iron oxide, manganese oxide, silicon carbide or zirconia in air flow and in the range of 800-1000 °C was also investigated by Pagkoura et al. [41]. They found that redox kinetics of cobalt oxide was improved with the addition of 25 wt% ceria, but the thermomechanical stability of the structured material did not improved. Also, they reported that cobalt oxide doped with 10-20 wt% of alumina or iron oxide showed good thermomechanical stability for 10 redox cycles while maintaining the thermochemical heat storage properties of cobalt oxide.

The main problem of cobalt oxide as a thermochemical heat storage material is low cyclability of redox reactions due to increasing grain size upon sintering during redox reactions. A large grain size reduces oxygen mass transfer and decreases the reaction kinetics specially the re-oxidation kinetics. Therefore, kinetics improvements are needed in order to make cobalt oxide usable as a thermochemical heat storage material. The re-oxidation kinetics of cobalt oxide is improved through the incorporation of secondary oxides [14].

Mechanical activation increases the reaction rates by making new features in the substance including structural disordering, structure relaxation, structural mobility, and an increase of specific surface area. These factors simultaneously affect the reactivity of a solid. Recently, mechanical activation has been used for improving the hydrogen desorption/absorption kinetics of hydrogen storage materials [42-45].

To the best knowledge of the authors, there is no report in the literature about effects of Fe$_2$O$_3$ addition and mechanical activation on the heat storage properties of cobalt oxide. Therefore, it seems that this research is a first attempt to evaluate the effect of mechanical activation along with Fe$_2$O$_3$ addition on the heat storage properties of cobalt oxide, which will provide useful background information on heat storage properties of cobalt oxide. The aim of the present work is to investigate the mechanical activation effect along with Fe$_2$O$_3$ addition on the heat storage properties of cobalt oxide such as oxygen release and uptake, particle morphology, and redox cyclability under air atmosphere.

2. Experimental methods

2.1. Materials and preparation

Cobalt oxide and iron oxide specifications used in this research are shown in Table 1. Cobalt oxide was mixed with 2, 6, 10, 15, and 20 wt% of Fe$_2$O$_3$ and ball milled for 1 h using a high energy planetary ball mill (Retsch PM 100) equipped with a stainless steel vial (150 ml) and steel balls (diameter of 10 and 20 mm). Ball milling was carried out using a ball to powder weight ratio of 20 and a rotation speed of 300 rpm under air atmosphere.

2.2. Thermal analysis

Thermal analysis experiments (TG/DSC) were carried out by TA Instruments (SDT-Q600) analyzer using a sample weight of 15 mg, a heating rate of 5 °C/min, and an alumina crucible under an argon flow rate of 100 mL/min. In addition, a home designed thermogravimetry setup was used for studying the reduction and re-oxidation of samples under air atmosphere [46]. A cubic acrylic glass was used to avoid the effects of environmental airflow on the weight measuring system isolated in the setup. In each experiment, 5 g of the sample was poured in an alumina crucible (5×10×100 mm) and placed inside a quartz tube located in a tube furnace (Azar furnace 1250). Subsequently, a temperature range of 750 to 1050 °C with a heating/cooling rate of 5 °C/min was used for the reduction and re-oxidation processes. The weight change was recorded in real time using a digital balance (A&D model EK-600i) and software (RS weight A&D) linked and installed on a laptop.

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity (wt%)</th>
<th>Particle size (μm)</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt oxide (Co$_3$O$_4$)</td>
<td>99.5</td>
<td>10</td>
<td>B.D.H</td>
</tr>
<tr>
<td>Iron oxide (Fe$_2$O$_3$)</td>
<td>99.5</td>
<td>10</td>
<td>Blulux</td>
</tr>
</tbody>
</table>
2.3. Materials characterization

The X-ray diffractometry (Italsstructures APD2000) with CuKα radiation (λ= 1.54 Å) and X’Pert high score software (1.0d) were used for phase identification. Scanning electron microscopy (Jeol JSM-840A) was used for studying the powder morphology. Energy-dispersive X-ray spectroscopy (EDS) was used for x-ray map analysis.

3. Results and discussion

3.1. Effect of Fe₂O₃ addition and mechanical activation on Co₃O₄ redox reactions

The effect of iron oxide (2, 6, 10, 15, and 20 wt%) addition and 1 h mechanical activation on the redox reactions of Co₃O₄ was investigated by thermogravimetric analysis. The resulting TG curves of as-received Co₃O₄, Co₃O₄/1h BM and Co₃O₄-15wt% Fe₂O₃/1 h BM samples are shown in Figure 1. The useful information including onset temperature of redox reactions and weight change are extracted from the TG curves and presented in Table 2. In Figure 1, the sample Co₃O₄/1 h BM shows weight increase in the early stage of the experiment. This phenomenon is due to CoO formation during ball milling and its re-oxidation in the early stage of the experiment. More details are provided in the previous work [46] of the authors.

According to Table 2, the reduction onset temperature of as-received Co₃O₄ and 1 h ball milled Co₃O₄ are 1030 and 1010 °C, respectively. Addition of 2 and 6 wt% of Fe₂O₃ to Co₃O₄ increases the reduction onset temperature to 1035 and 1050 °C, but addition of 10 and 15 wt% of Fe₂O₃ decreases the reduction onset temperature to 990 and 960 °C, respectively. More Fe₂O₃ addition (20 wt%) increases the reduction onset temperature to about

Table 2. Thermodynamic data obtained by thermogravimetry under air atmosphere.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset-T&lt;sub&gt;red&lt;/sub&gt; (°C)</th>
<th>Onset-T&lt;sub&gt;oxid&lt;/sub&gt; (°C)</th>
<th>Δm&lt;sub&gt;red&lt;/sub&gt; (%)</th>
<th>Δm&lt;sub&gt;re-oxid&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received Co₃O₄</td>
<td>1030</td>
<td>930</td>
<td>4.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Co₃O₄ -1 h BM</td>
<td>1010</td>
<td>950</td>
<td>3.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Co₃O₄ - 2 wt% Fe₂O₃</td>
<td>1035</td>
<td>930</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Co₃O₄ - 6 wt% Fe₂O₃</td>
<td>1050</td>
<td>980</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Co₃O₄ - 10 wt% Fe₂O₃</td>
<td>990</td>
<td>980</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Co₃O₄ - 15 wt% Fe₂O₃</td>
<td>960</td>
<td>1010</td>
<td>3.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Co₃O₄ - 20 wt% Fe₂O₃</td>
<td>1030</td>
<td>1010</td>
<td>0.9</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Fig. 1. TG curve of as-received Co₃O₄, Co₃O₄/1h BM and Co₃O₄-15wt% Fe₂O₃/1 h BM samples.
1030 °C again. Generally, it is clear that increasing the Fe₂O₃ content in the samples increases the oxidation onset temperature.

Another important result is a difference between onset temperature of reduction and re-oxidation. The closer reduction and re-oxidation onset temperature, the lower energy loss during charge and discharge. This is a very favorable effect in view of thermal energy storage. The difference between reduction and re-oxidation onset temperatures for as-received cobalt oxide is about 100 °C. It decreases as the Fe₂O₃ content of the samples increases.

Also, Table 2 shows that Fe₂O₃ addition from 2 to 15 wt% increases the oxygen release (Δmₒ₂) from 1.4 to 3.4 wt%. This means that Fe₂O₃ addition up to 15 wt% improves the oxygen release. However, increasing the Fe₂O₃ content to 20 wt% decreases the oxygen release to 0.9 wt%. In contrary, the oxygen release of as-received Co₃O₄ and 1 h BM Co₃O₄ are 4 and 3.5 wt%, respectively. It must be said that total theoretical weight change is 6.64 wt% during reduction and re-oxidation stages. Therefore, it is observed that all of the samples weight change is less than the theoretical value.

The oxygen uptake value increases from 1.5 to 3.3 wt% for samples containing 2 and 15 wt% Fe₂O₃, respectively. Addition of 20 wt% Fe₂O₃ decreased the oxygen uptake to 1 wt%. As previously stated, the main problem of Co₃O₄ as a heat storage material is its weak re-oxidation behavior. According to Table 2, although Fe₂O₃ addition decreases the oxygen release value in comparison with as-received cobalt oxide and 1 h ball milled cobalt oxide, Fe₂O₃ addition (up to 15 wt%) considerably improves the oxygen uptake value or re-oxidation behavior.

Another important point according to Table 2 is that oxygen release and uptake values for samples containing Fe₂O₃ are close, but their values are different for as-received Co₃O₄ and 1 h ball milled Co₃O₄. The reason for the similarity between oxygen release and uptake values for Fe₂O₃ containing samples are low sintering of particles. This phenomenon has been reported by various researchers [14,30,33].

The different behavior of samples containing 20 wt% Fe₂O₃ is most probably due to the formation of Co₃O₄ and Fe₂O₃ spinels (according to Figure 2) that release or uptake oxygen at high temperatures [40]. The formation range of the spinel phase in the Co₃O₄-Fe₂O₃ phase diagram has been investigated in various research works

![Fig. 2. Phase diagram of the Co–Fe–O system with material compositions (dotted lines) (S: spinel, CW: cobalt-wüsite, L: liquid) [40].](image)

[30,33], but it must be noted that mechanical activation may change the phase stability regions [44,45].

### 3.2. Morphology of particles

Figure 3 illustrates the particle morphologies of as-received Co₃O₄, 1 h ball milled Co₃O₄, and 1 h ball milled Co₃O₄-15 wt% Fe₂O₃ samples before and after redox. It is seen that the Fe₂O₃ containing sample was less sintered than the other two samples. Therefore, Fe₂O₃ addition plays a key role in decreasing the particle sintering and growth. According to Figure 3, the particle size of as-received Co₃O₄ and 1 h ball milled Co₃O₄ after redox are several times larger than before redox, while the particle size of 1 h ball milled Co₃O₄-15 wt% Fe₂O₃ show low growth after redox. In fact, Fe₂O₃ particles are placed among the Co₃O₄ particles and prevent the cobalt oxide particle adhesion and sintering due to a higher melting point than cobalt oxide. Figure 4 shows the x-ray map analysis for the Co₃O₄-15 wt% Fe₂O₃/1 h BM sample after redox. Figure 4 demonstrates that the iron oxide particles have dispersed uniformly in the sample and around the cobalt oxide particles.

### 3.3. TG/DSC analysis under argon atmosphere

For studying the synergistic effect of Fe₂O₃ addition and mechanical activation on the oxygen release and heat storage value under an oxygen partial pressure close to zero, three samples including as-received Co₃O₄, 1 h ball milled Co₃O₄, and 1 h ball milled Co₃O₄-15% Fe₂O₃ were analyzed by TG/DSC under argon...
atmosphere and heating rate of 5 °C/min. It should be noted that the oxidation reaction was not done, because the re-oxidation reaction takes place only in oxygen-containing environment. It was not possible to decide on the synergistic effect of Fe₂O₃ addition and mechanical activation according to the experiments carried out under air atmosphere, because the oxygen partial pressure is different in the reaction medium of various samples due to their different oxygen release.

According to Figure 5, total weight loss of the above mentioned samples are 6.5, 6.3, and 5.8 wt%, respectively. These values are different from the weight decrease presented in Table 2. This is due to the fact that argon gas dilutes the oxygen in the reaction medium while it facilitates the reaction of cobalt oxide reduction. In addition, the sample weight (15 mg versus 5 g) has an effective on the weight loss/increase value. At high sample weights, the heat transfer from outside/inside into the sample in the reduction/re-oxidation stage is important because it takes a long time. Moreover, the partial pressure of the oxygen around the samples tested under the air atmosphere is different, while it is alike in the experiments carried out under the argon atmosphere. Due to the above-mentioned reasons, the onset temperature of reduction is almost the same for the samples tested under the argon atmosphere and are different for the samples tested under the air atmosphere.

The theoretical weight loss of the Co₃O₄ is close to 6.64 wt%. If it is considered that only the Co₃O₄ fraction of Co₃O₄-15 wt% Fe₂O₃ participates in the reduction process, the theoretical loss weight of the sample will be 5.64 wt%. However, the practical obtained oxygen release value of the mentioned sample was 5.8 wt% (0.16 wt% more than the theoretical value). This only
happens when some of the Fe$_2$O$_3$ is reduced to Fe$_3$O$_4$. Therefore, it seems that in addition to cobalt oxide, Fe$_2$O$_3$ also participates in the reduction process. According to the difference (0.16 wt%) between theoretical and practical oxygen release, the amount of formed Fe$_3$O$_4$ will be about 5 wt%; and therefore, its XRD peaks have low intensity. According to Figure 6, only Fe$_2$O$_3$ phase peaks are seen in the XRD pattern related to before reduction; but after reduction both Fe$_2$O$_3$ and Fe$_3$O$_4$ peaks exist in the XRD pattern. It should be noted that the presence of Fe$_2$O$_3$ after reduction is based on the XRD patterns and TG results.

According to DSC results (Figure 7), the absorbed heat energy for reduction of as-received Co$_3$O$_4$, 1 h mechanical activated Co$_3$O$_4$, and 1 h ball milled Co$_3$O$_4$-15% Fe$_2$O$_3$ are 622, 496, and 895 kJ/kg, respectively. These values were taken directly from the device (SDT-Q600) and are proportional to the area under the endothermic peaks in Figure 7. As it is seen, 1 h ball milled Co$_3$O$_4$, in comparison with other two samples, has absorbed low heat energy because some part of the energy required for reduction is compensated by the energy stored in the Co$_3$O$_4$ structure during ball milling. It can also be seen that the 1 h ball milled Co$_3$O$_4$-15% Fe$_2$O$_3$ has absorbed higher heat energy, even higher than the theoretical value (717.4 kJ/kg), due to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$. The temperature of Fe$_2$O$_3$ reduction to Fe$_3$O$_4$ is about 100 °C higher than that of Co$_3$O$_4$ reduction to CoO [14]. The XRD patterns of Co$_3$O$_4$-15% Fe$_2$O$_3$ sample before and after redox shown in Figure 6 confirmed the presence of Fe$_2$O$_3$ after the reduction. In fact, the high energy ball milling decreases the temperature of Fe$_2$O$_3$ reduction to Fe$_3$O$_4$ [44,45].

Moreover, according to Figure 7, Fe$_2$O$_3$ addition has caused the heat energy absorption to take place in a wide range of temperature or time in comparison with the other two samples. This means that heat charge and discharge processes in samples containing iron oxide are more controllable.

### 3.4. Redox cyclability

The redox cyclability of the as-received Co$_3$O$_4$ and 1 h ball milled Co$_3$O$_4$-15% Fe$_2$O$_3$ samples under air atmosphere and a heating/cooling rate of 5 °C/min for 3 cycles were investigated. Figure 8 illustrates the cyclability results. It is seen that weight loss and weight increase of as-received Co$_3$O$_4$ decreased gradually as the cycle numbers increased and reached from 3 wt% at cycle one to about 1.5 wt% at cycle three. The cyclability of the 1 h ball milled sample disappears after two cycles. More details about the cyclability of this sample are found in the previous work of the authors [46]. However, the cyclability of Co$_3$O$_4$-15 wt% Fe$_2$O$_3$ is favorable in comparison with as-received and 1 h ball milled samples. The reason the cyclability improves with the addition of iron oxide is due to low particles growth and sintering.

### 4. Conclusions

This research obtained the following results:
- Fe$_2$O$_3$ addition from 2 to 15 wt% increased the
oxygen release from 1.4 to 3.4 wt% and decreased the reduction onset temperature from 1030 to 960 °C.

- Oxygen uptake value and re-oxidation onset temperature increased from 1.5 to 3.3 wt% and from 930 to 1010 °C for the samples containing 2 and 15 wt% Fe₂O₃, respectively.

- TG/DSC analysis under argon atmosphere revealed that enthalpy of reduction reaction of as-received Co₃O₄, 1 h ball milled Co₃O₄, and 1 h ball milled Co₃O₄-15 wt% Fe₂O₃ is 622, 496, and 895 kJ/kg, respectively.

- Phase identification by XRD and related TG analysis demonstrated that Fe₂O₃ participates in the reduction process.

- Fe₂O₃ addition prevented the cobalt oxide particle growth and sintering; subsequently, it improved the re-oxidation behavior.

- Addition of 15 wt% Fe₂O₃ to Co₃O₄ and ball milling of the mixture for 1 h improved the redox cyclability.

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References


