



Isothermal Redox Kinetics of $\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3$ Nano-Composite as a Thermochemical Heat Storage Material

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ABSTRACT

Isothermal redox kinetics of as-received Co_3O_4 (AC), 1 h ball milled Co_3O_4 (BC), and 1 h ball milled $\text{Co}_3\text{O}_4\text{-15wt.\% Fe}_2\text{O}_3$ (BCF) was investigated at various temperatures (1130, 1100, 1070, and 1040 °C for reduction and 830, 860, and 890°C for re-oxidation) by thermogravimetric method. It was found that mechanical activation with and without Fe_2O_3 addition decreases the rate of reduction in all isothermal reduction temperatures, while it improves the rate of re-oxidation in lower re-oxidation temperatures. Mechanical activation with and without Fe_2O_3 addition preserves and decreases the rate of re-oxidation at higher re-oxidation temperatures, respectively. In addition, according to the results, the re-oxidation k^2 was slower than reduction kinetics. A model-free method was used to calculate the redox ΔH energies. It was found that mechanical activation individually increases the reduction ΔH energy, while mechanical activation along with Fe_2O_3 addition decreases the reduction ΔH energy in comparison with as-received Co_3O_4 . The results showed that reduction activation ΔH of AC, BC, and BCF samples varies depending on the reacted fraction (α) and are in the range -166.6 kJ/mol, 175.5 – 213.7 kJ/mol and 111.5 – 121.3 kJ/mol, respectively. The results also show that although both mechanical activations with and without Fe_2O_3 addition decreases the re-oxidation ΔH energy in comparison with as-received cobalt oxide, but the impact of mechanical activation without Fe_2O_3 addition on activation energy decline, is higher. Moreover, it was found that ΔH energies for the re-oxidation of AC, BC, and BCF samples are negative, variations depending on the reacted fraction (α), and are in the range of -76.8 to -133.5 kJ/mol, -440.2 to -471.9 kJ/mol, and -196.05 kJ/mol, respectively.

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1. INTRODUCTION

The fast growth in energy consumption, concerns due to greenhouse gases emissions and global warming have made the world to obtain the energy from renewable sources. Thus, developing the new environmentally friendly technologies working with renewable energies will have a major role to produce clean energy in the future. Concentrated solar power (CSP) along with thermal energy storage (TES) to produce electricity is one of these technologies. Thermochemical energy storage as a heat storage method plays a major role in the research and development of CSP plants because of improving the dispatch-ability of solar power plants. Thermochemical heat storage works based on the redox

reactions of reversible chemical reactions and has advantages of higher energy storage, suitability for large-scale application, long storage duration and long-range transport at ambient temperature, and higher working temperature ranges [1-4].

Metal oxides are capable of O_2 desorbing (reduction) and O_2 absorbing (re-oxidation) during redox reactions, but only a few of them, such as Co_3O_4 , BaO_2 , Mn_2O_3 , CuO , Fe_2O_3 , Mn_3O_4 , and V_2O_5 have the necessary conditions for use as a thermochemical heat storage material. Cobalt oxide is one of the most promising materials for thermochemical heat storage. Cobalt oxide has a better redox kinetics and reversibility than other metal oxides and temperature required for its redox reactions of cobalt oxides is in the range of 885- 905 °C

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that is close to the practical temperature (900-1000 °C) of CSP plants. Redox reaction of cobalt oxides is as follows [5-12]:



Although cobalt oxide is a proper option for thermochemical heat storage, but long redox cycles increase the particle size and sintering of cobalt oxide powder. This leads to a loss of redox kinetics in long-term cycles and weakens the properties of cobalt oxide as a heat storage material. To eliminate this defect, various additives such as Fe₂O₃ have been added to cobalt oxide to prevent particles growth and sintering (sintering inhibitor). Also, different oxide valence and ionic radius of additive phase in comparison with cobalt oxide respectively cause to electrical charge imbalance (increases anionic vacancies) and lattice strain (increase atomic distance) in cobalt oxide structure. These factors increase the mass transfer of oxygen in cobalt oxide structure [1-5].

The effect of Fe₂O₃ addition to cobalt oxide has been studied by Block et al. [13]. They found that addition of Fe₂O₃ reduces the redox enthalpy compared with pure cobalt oxide. They reported that cobalt oxide containing 10 mol % Fe₂O₃ is a proper composition as a thermochemical heat storage material. Pagkoura et al. [14] reported the sample prepared by adding 10-20 wt. % Fe₂O₃ to cobalt oxide exhibits good thermo-mechanical stability for 10 redox cycles, and thermochemical heat storage properties of cobalt oxide are also retained. Recently, Nekokar et al. [15] studied the mechanical activation effect on cobalt oxide redox behavior. They found that mechanical activation of cobalt oxide powder for a short time (less than 2 h) slightly improves the redox behavior, but in a long time, it greatly reduces cobalt oxide redox performance.

In another study [16], they found that addition of Fe₂O₃ to Co₃O₄ eliminates the negative effect of long time mechanical activation. This means that positive effects of mechanical activation, such as reduction of particle size and the uniform spread of secondary phase in the cobalt oxide, were maintained, and better redox behavior were obtained for the material.

Kinetics study is useful for a deep understanding of the reaction mechanism and their practical applications. Various researches [5, 7, 17-24] have been carried out to study the kinetics of reduction and re-oxidation of cobalt oxide powder and single crystals during 1971 to 2015. They reported various kinetics models and mechanisms along with redox activation energies. The summary of the most important studies is presented in Table 1. According to Table 1, the values of activation energy and reaction mechanisms are different in the various studies. This difference is due to the type, size, and purity of cobalt oxide, reaction environment, method used for study, and accuracy of used equipments. In fact, the information

presented in Table 1 only shows the energy activation range of reduction and re-oxidation of cobalt oxide and probable reaction mechanisms.

TABLE 1. Summary of some researches on Co₃O₄/CoO redox kinetics

Step	Year	Material type and activation energy	Model or mechanism	Ref.
Reduction	1971	Powder: 366 kJ/mol	Chemical reaction	[18]
		Powder: 627-1254 kJ/mol		
	1977	Single crystal: 309 kJ/mol (α < 0.35) 384 kJ/mol (α > 0.35)	Ash layer diffusion	[20]
	1978	Powder: 393 kJ/mol	Chemical reaction	[19]
		Powder: 410-460 kJ/mol		
	1985	Single crystal: 445-495 kJ/mol (α=0.1-0.8)	Ash layer diffusion	[17]
		Powder: E _d =22.8 kJ/mol (diffusion mechanism) E _r =153 kJ/mol (reaction mechanism)	Ash layer diffusion	
	1990	Single crystal: E _d =11.8 kJ/mol, E _r =164 kJ/mol	Chemical reaction	[21]
		Powder: In air: 439 kJ/mol In oxygen: 892 kJ/mol	Heat transfer and nucleation rate	[5]
	2006	Pure Co ₃ O ₄ : E _a =960 kJ/mol Co ₃ O ₄ -5 wt. % Al ₂ O ₃ : E _a = 731 kJ/mol	3D nucleation-shrinking core model	[24]
Re-oxidation	2015	powder 247.21 kJ/mol	Avrami-Erofeyev nucleation model	[7]
	1979	---	Nuclei-growth-controlled	[23]
	1985	powder 70-80 kJ/mol	Ash layer diffusion	[22]
	2006	---	Heat transfer and nucleation rate	[5]
	2011	Co ₃ O ₄ -5 wt. % Al ₂ O ₃ : E _a = 165 kJ/mol	3D nucleation-shrinking core model	[24]
	2015	powder 58.07 kJ/mol	Ash layer diffusion	[7]

Recently, model-free (isoconversional) methods for kinetic analysis have been used extensively due to their ability to calculate the energy of activation without the need to determine the kinetics model governing a process. Isoconversional methods are model-free methods that evaluate the activation energy (E_a) at progressive reacted fraction (α) values [25, 26].

To the best of our knowledge, the effects of mechanical activation and addition of Fe_2O_3 on cobalt oxide redox kinetics parameters such as reacted fraction, redox rate, and activation energy have not been reported yet. Previous studies have not investigated the mechanical activation effect with and without addition of Fe_2O_3 on the kinetics parameters of cobalt oxide as a thermochemical heat storage material. In this study, the effect of mechanical activation with and without Fe_2O_3 addition on redox reactions of cobalt oxide is investigated at various isothermal temperatures. Results of this study will determine how raw material preparation and composition change the required activation energy for redox reactions of cobalt oxide.

2. EXPERIMENTAL METHODS

2. 1. Materials and Preparation Cobalt oxide (Co_3O_4 , 99.5 wt.%, <10 μm , Merck) and Iron oxide (Fe_2O_3 , 99.5 wt.%, <10 μm , Blulux) were used as raw materials. Samples were encoded as *AC* (as-received Co_3O_4), *BC* (1 h ball milled Co_3O_4), and *BCF* (1 h ball milled Co_3O_4 -15wt.% Fe_2O_3). It should be noted that Fe_2O_3 content of 15 wt.% and mechanical activation time of one hour are selected as optimum values based on the results of previous works [13, 15, 16].

Iron oxide containing sample was prepared by adding 15 wt.% of Fe_2O_3 to Co_3O_4 , and the mixture was ball milled (mechanical activated) for 1 h using a high energy planetary ball mill (Restch PM 100) equipped with a stainless steel vial (150 ml) and steel balls (diameter of 10 and 20 mm). Ball milling was performed using a ball to powder weight ratio of 20 and a rotation speed of 300 rpm under atmospheric condition. In addition, a 1 h-mechanical activated Co_3O_4 sample was prepared according to the above-mentioned conditions. Isothermal redox reactions of all samples were studied at reduction temperature of 1040, 1070, 1100, and 1130°C and re-oxidation temperature of 830, 860, and 890 °C. In the reduction process, 5 g of a sample was poured in an alumina crucible (5×10×100 mm), placed inside a tube furnace (Azar furnace 1250) with a certain reduction temperature, and maintained for as long as no weight change was observed. During the process, the sample weight was recorded by a digital balance connected to a laptop by software application. Samples needed to study the re-oxidation process were prepared by placing *AC*, *BC*, and *BCF* samples at a temperature of 1130 °C for as

long as no weight change was observed (close to 20 min for conversion to CoO). Samples were removed from the furnace and cooled quickly to prevent the reduction reaction. Then they were used as a starting materials for re-oxidation process similar to above mentioned procedure. Scanning Electron Microscopy (Jeol JSM-840A) was used to study the size and morphology of the samples.

Reacted fraction (α) at a certain time was calculated by dividing the actual weight change into the theoretical weight change (6.64 wt. %). Subsequently, α curve versus time was depicted for each sample at an isothermal temperature. A model-free method was used to calculate the activation energy.

The temperature dependence of the rate constant (k) is usually given by Arrhenius equation [25, 26]:

$$k = A \exp(-E_a/RT) \quad (2)$$

Where, A is the pre-exponential (frequency) factor, E_a is the activation energy, T is the absolute temperature, and R is the gas constant.

For the integral reaction model the following equation is used:

$$g(\alpha) = kt \quad (3)$$

Substitution Equation (2) into Equation (1) gives:

$$g(\alpha) = A \exp(-E_a/RT) \cdot t \quad (4)$$

Then, the model-free method can be derived by taking the natural logarithm of the isothermal rate law (Equation (4)):

$$\ln g(\alpha) = \ln A - E_a/RT + \ln t \quad (5)$$

This is re-arranged to:

$$-\ln t = \ln [A/g(\alpha)] - E_a/RT \quad (6)$$

The slope of $-\ln t$ versus $1/RT$ for specific α , gives $-E_a$ according to Equation (7):

$$-\ln t_\alpha = \ln [A/g(\alpha)]_\alpha - E_{a\alpha}/RT_\alpha \quad (7)$$

3. RESULTS AND DISCUSSION

3. 1. Reacted Fraction (α) Figure 1 shows the reacted fraction (α) versus time during reduction and re-oxidation reactions of as-received Co_3O_4 , 1 h ball milled Co_3O_4 and 1 h ball milled Co_3O_4 -15 % Fe_2O_3 at various temperatures. As seen, not only the reacted fraction curves of each sample were different at various temperatures, but also they were entirely different from sample to sample.

3. 1. 1. Reacted Fraction (α) of Reduction Process

According to Figure 1, maximum α value of reduction for *AC* sample is approximately 0.80 after 8 minutes at

temperatures of 1070, 1100, and 1130 °C, while it is about 0.60 after 14 minutes at 1040 °C. BC sample has the maximum α value close to 0.78 after 8 and 9 minutes, respectively at 1130 °C and 1100 °C, while it has the maximum α value close to 0.74 and 0.42 after 10 and 16 minutes at 1070 °C and 1040 °C, respectively. The maximum α values for BCF sample were 0.60, 0.67, 0.68, and 0.58 after 7, 8, 10, and 14 at 1130 °C, 1100 °C, 1070 °C, and 1040 °C, respectively. In fact, α value decreases with decreasing the reaction temperature because the reduction process is endothermic according to Eq. (1). In addition, the type of sample also affects the α value of reduction process. As it is seen from Figure 1, the final α value for AC and BC samples is close to 0.80 at temperatures of 1070, 1100, and 1130 °C, while the final α value for mentioned samples is close to 0.60 and 0.44 at 1040 °C, respectively. This means that at temperatures below 1070 °C, the final α value in the AC and BC samples suddenly decreases. However, the reduction behavior of BCF sample indicates that final α value in this sample at temperatures of 1070 and 1100 °C is about 0.7, and at temperatures of 1040 and 1130 °C is about 0.60. Low final α value in BCF sample is partly attributed to the presence of iron oxide in the sample that does not participate in the reduction reaction. According to Figure 1, mechanical activation without Fe₂O₃ addition reduces α value at low reduction temperatures, but the mechanical activation with Fe₂O₃ causes α to return to the same amount of as-received cobalt oxide.

It is also possible to discuss about the time it takes to reach maximum α in different samples. As shown in Figure 1, AC, BC, and BCF samples, respectively, have reached the maximum value of α at shorter times. In fact, difference in the reduction behavior partly is due to particle size difference of various samples. Different researchers [13, 15, 16, 24] have shown that heat treatment increases the sample particle size and sintering in redox cycles. The smaller the particle size, the greater the growth and particle sintering unless the sample contains an inhibitor agent (such as Fe₂O₃). This increase in particle size and sintering, which can vary sample to sample and is discussed in later sections, greatly affects the redox behavior.

3. 1. 2. Reacted Fraction (α) of Re-oxidation Process

As it is seen in Figure 2, by increasing the re-oxidation temperature, the maximum α value after 60 min decreases because the re-oxidation reaction is exothermic, and with increasing temperature, this reaction is undesirable thermodynamically. In addition, according to Figure 2, the re-oxidation behaviors of the AC, BC, and BCF samples are different and reacted fraction (α) of them after 60 minutes at 830 °C is 0.64, 0.98, and 0.78; at 860 °C is 0.55, 0.45, and 0.48; and at 890 °C is 0.46, 0.17, and 0.44, respectively. Therefore, it is obvious that mechanical activation and Fe₂O₃ addition

in low re-oxidation temperatures have a positive effect on increasing α value. Reducing the particle size due to mechanical activation and the positive role of iron oxide in preventing growth and sintering of particles have led to differences in the behavior of BCF sample [15, 16]. BC sample has poor performance at high temperatures than samples AC and BCF, and this agrees with the results of Nekokar et al. [15, 16]. In fact, mechanical activation with addition of Fe₂O₃, improves the performance of cobalt oxide at lower temperatures and maintains its performance at high temperatures.

3. 2. Rate of Reaction Rate of the reduction and re-oxidation processes was calculated by dividing the maximum weight decrease/increase value to the time needed to reach that value. The rate of reduction and re-oxidation versus temperature are derived from Figures 1 and 2; then, it was shown as Figures 3 and 4, respectively. According to Figures 3 and 4, the behavior of the samples in reduction and re-oxidation processes is different and the reduction rate is totally higher than re-oxidation rate. Another difference is that reduction rate increases with increasing temperature, while the rate of re-oxidation decreases with increasing temperature. Also, as stated earlier, the low re-oxidation rate of cobalt oxide is its main drawback as a thermochemical heat storage material. The difference in rate of redox reactions in various samples is described below.

3. 2. 1. Rate of Reduction Process Figure 3 shows the rate of reduction (wt.%/min) for AC, BC, and BCF samples at 1040, 1070, 1100, and 1130 °C. As it is seen, the reduction rate depending on sample type and reduction temperature varies as follows:

- The reduction rate of AC sample increases from 0.50 to 1.30 wt.%/min with increasing the reduction temperature from 1040 to 1130 °C.
- The reduction rate of BC sample increases from 0.24 to 0.80 wt.%/min with increasing the reduction temperature from 1040 to 1100 °C and then decreases to 0.70 wt.%/min with increasing the reduction temperature from 1100 to 1130 °C.
- The reduction rate of BCF sample increases from 0.35 to 0.75 wt.%/min with increasing the reduction temperature from 1040 to 1100 °C and then is almost constant with increasing the reduction temperature from 1100 to 1130 °C.

As shown in Figure 3, the reduction rate of AC sample is higher than that of BC and BCF samples. Also, the reduction rates of BC and BCF samples are close together. The equilibrium temperature of Co₃O₄ and CoO conversion reaction (Equation (1)) is close to 890 °C. Therefore, as the temperature increases, the reaction goes to the right. Although in the isothermal redox experiments, AC sample has a better performance than other samples, but according to other research [15] in

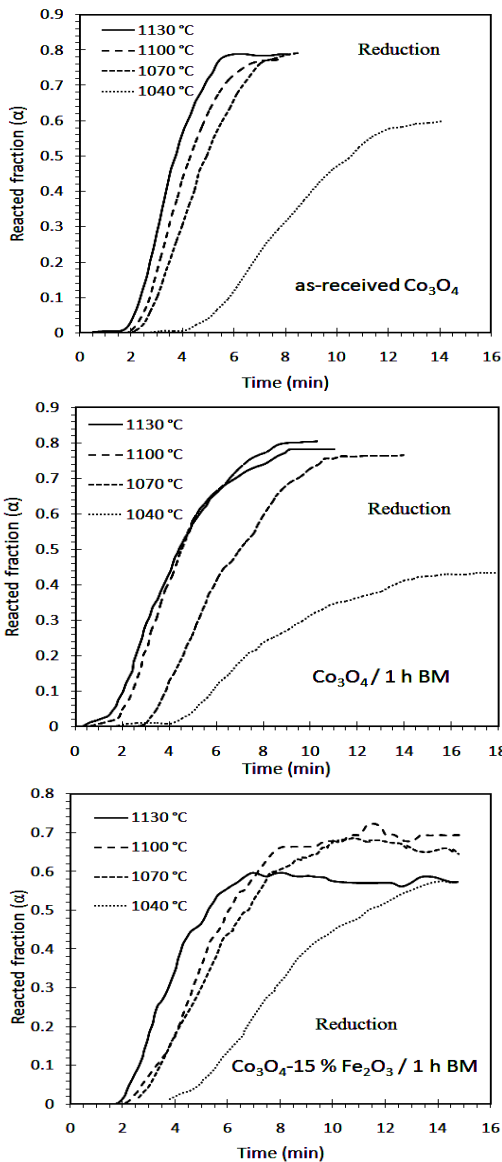


Figure 1. Reacted fraction (α) versus time for various samples during reduction

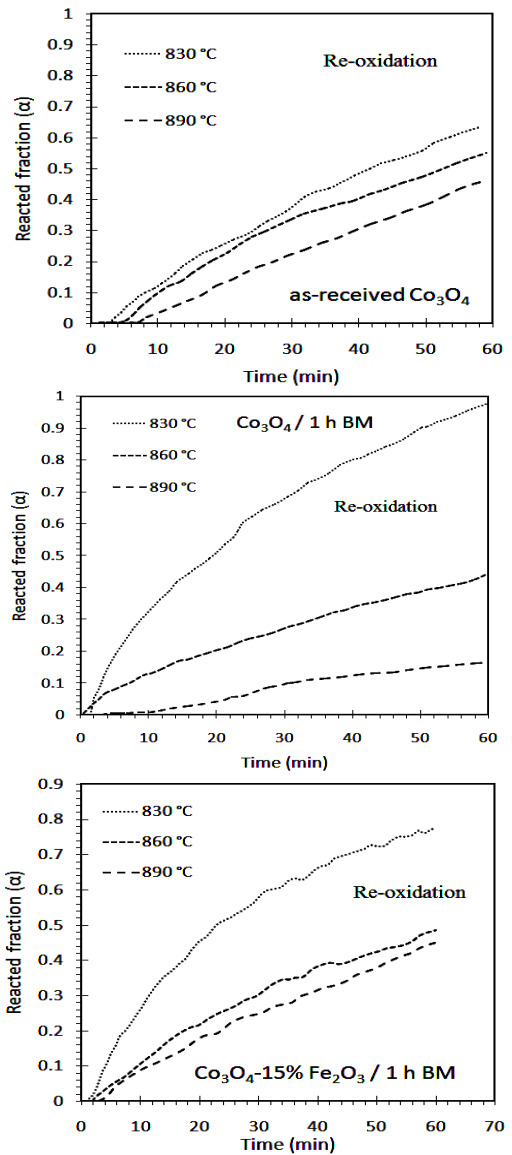


Figure 2. Reacted fraction (α) versus time for various samples during re-oxidation

long redox cycles the mechanical activated samples (similar to BC sample) always have a lower performance than as-received cobalt oxide (similar to AC), while the sample containing iron oxide in the long redox cycles performs better than the as-received cobalt oxide. Mechanical activation alone increases the growth of particles and sintering, but the addition of iron oxide along with mechanical activation prevents them. In fact, the iron oxide is placed around the cobalt oxide particles and prevents particle growth and sintering due to its high melting point. In long-term redox cycles, the positive effect of mechanical activation on samples containing iron oxide has been confirmed [16].

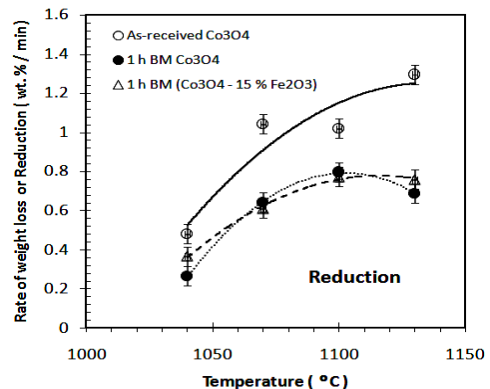


Figure 3. Reduction rate versus reduction isothermal temperature

3. 2. 2. Rate of Re-oxidation Process Figure 4 shows the rate of re-oxidation versus temperature for AC, BC, and BCF samples at various temperatures. As it is seen in Figure 4, the re-oxidation rate of all samples decreases with increasing the re-oxidation temperature from 830 to 890 °C; but, that decreasing is different depending on the sample. At low temperatures, the samples exhibit high re-oxidation rates because thermodynamically, the exothermic reactions progress well at lower temperatures. Different behavior of samples is related to the difference in particle size and the possibility of sintering during the redox. As shown in Figure 4, BC and BCF samples performed better than AC sample at the lower temperatures and BCF has a performance close to AC at high temperatures.

The better performance of BC at low temperatures can be due to its fine particle size and its poor performance at high temperatures is due to its high sintering capability. The performance of BCF, at 860 and 890 °C, is almost the same and close to that of AC sample because the presence of iron oxide in this sample prevents the particle sintering. According to other researches [13, 16], the effect of adding Fe₂O₃ in long redox cycles is evident, but in these experiments, the positive effect of iron oxide after one cycles is also clear.

3. 3. Activation Energy Arrhenius plots for reduction and re-oxidation processes of AC, BC, and BCF samples are shown in Figures 5 and 6, respectively. The corresponding curves were plotted using different reacted fraction values based on Equation (7) as described in experimental section. Then, the activation energy of samples was calculated using the slope of the fitting trend lines. As shown in Figures 5 and 6, the Arrhenius curves of the samples were shifted to the lower values with increasing α value, while the slope may change slightly. In fact, the slope of the curves represents the amount of $-E_a$.

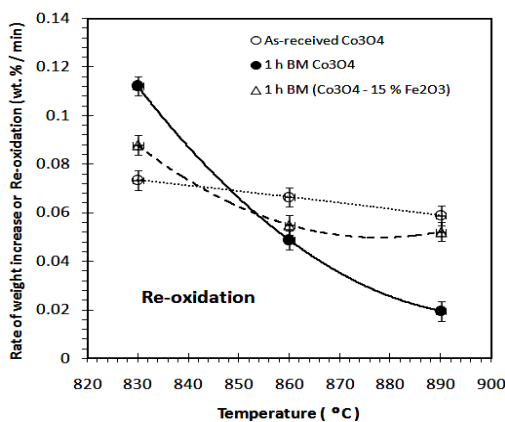


Figure 4. Re-oxidation rate versus isothermal re-oxidation temperature

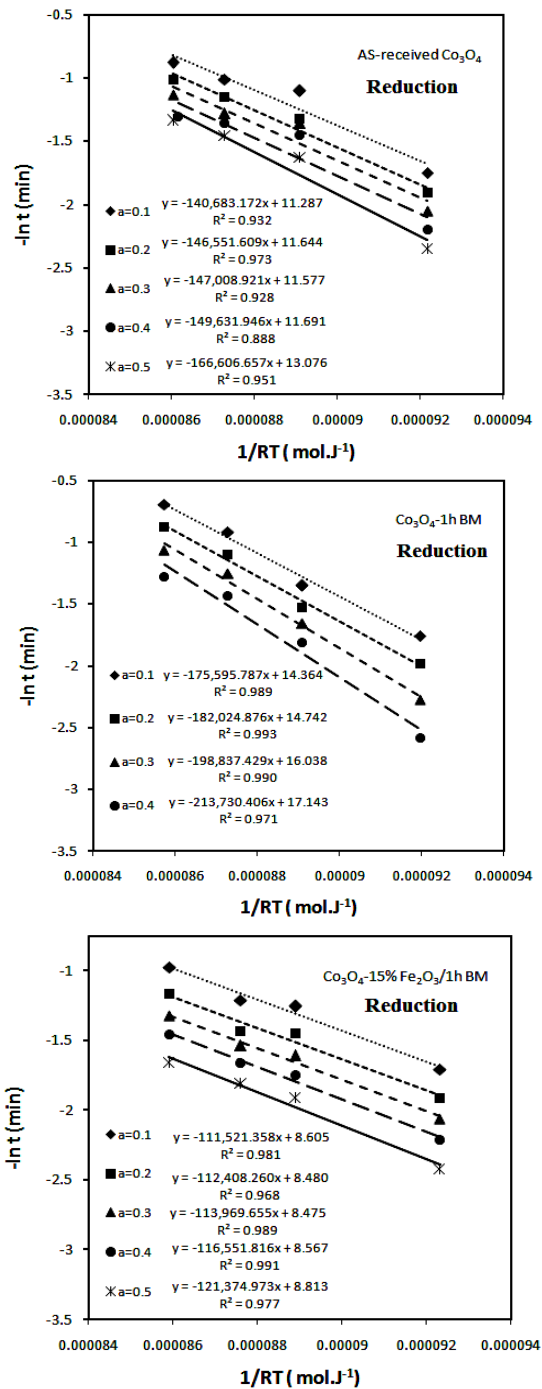


Figure 5. Arrhenius plots for reduction and re-oxidation of as-received Co₃O₄, 1 h BM Co₃O₄, and 1 h BM Co₃O₄- 15 % Fe₂O₃ samples

3. 3. 1. Activation Energy of Reduction According to Figure 7, the activation energy of the reduction process increases with increasing α value for various samples, although this increase is small for BCF sample. This means that Co₃O₄ reduction to CoO will require additional energy as the reduction reaction progresses.

This additional energy is reduced for samples BC, AC and BCF, respectively. Also, increasing the activation energy by increasing α value means that temperature should increase to raise the reduction rate or to maintain it. The reduction activation energy of AC, BC, and BCF samples depending on α value at the reduction

temperature range of this research experiments is between 140.6 - 166.6 kJ/mol, 175.5 - 213.7 kJ/mol and 111.5- 121.3 kJ/mol, respectively. Therefore, mechanical activation process increases the reduction activation energy, while mechanical activation along with Fe₂O₃ addition decreases the reduction activation energy in comparison with as-received Co₃O₄. This is clearly seen in Figure 7, so that curve of BCF sample is below the curves of other samples.

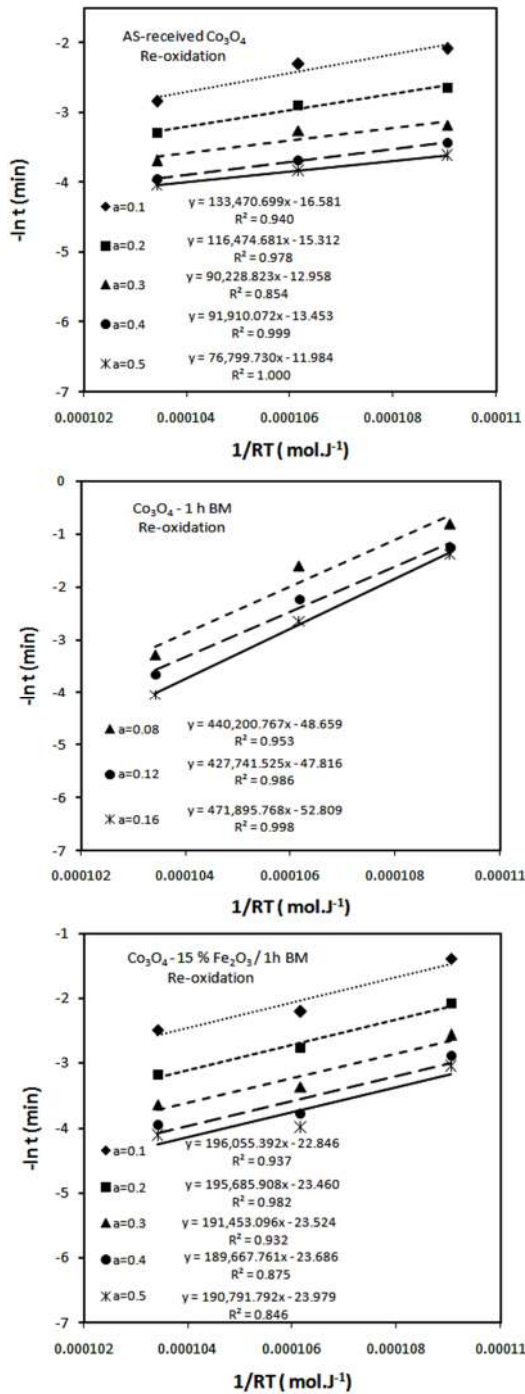


Figure 6. Arrhenius plots for reduction and re-oxidation of as-received Co₃O₄, 1 h BM Co₃O₄, and 1 h BM Co₃O₄- 15 % Fe₂O₃ samples

3.3.2. Activation Energy of Re-oxidation Figure 8 shows the re-oxidation activation energy versus α value. Although the re-oxidation activation energy of all samples is negative, their behavior is different with increasing α value. The re-oxidation activation energy of BCF remains constant with increasing α value, while the re-oxidation activation energy of AC and BC samples increases and decreases with increase of α , respectively. Increasing the activation energy by increasing α indicates a decline in the re-oxidation rate, while decreasing the activation energy by increasing α indicates an increase in the oxidation reaction rate.

According to Figure 8, the activation energy value for the re-oxidation of AC, BC, and BCF at the studied re-oxidation temperature range is between -76.8 to -133.5 kJ/mol, -440.2 to -471.9 kJ/mol, and -190.8 to -196.05 kJ/mol, respectively. The activation energy of the re-oxidation reaction of all samples is negative. The negative activation energy value means that rate of re-oxidation reaction declines with increasing the temperature. In most chemical processes, the reaction rates increase at higher temperatures, which is equivalent to the positive activation energy. In fact, according to experience, chemical processes are generally accelerated by heating. However, some reactions progress at higher temperatures at a lower rate, which means they have negative activation energy. Reactions with negative activation energy are present and happen [27].

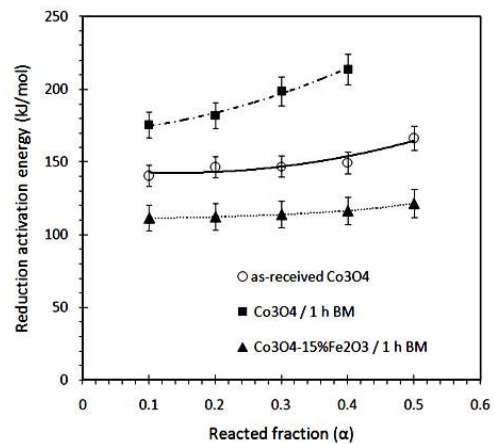


Figure 7. Reduction activation energy versus reacted fraction (α) for various samples

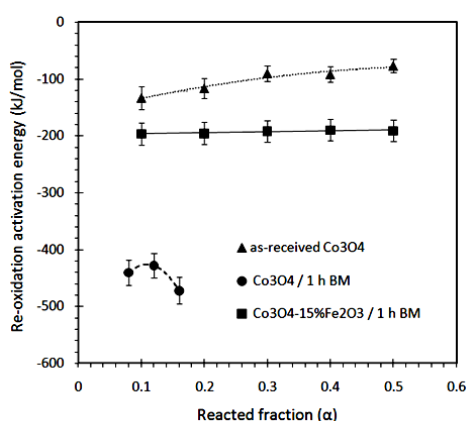


Figure 8. Re-oxidation activation energy versus reacted fraction (α) for various samples

It is clearly seen that re-oxidation activation energy value of BCF and BC samples are more negative than that of AC sample. In addition, re-oxidation activation energy of BC sample is more negative than that of BCF sample. As it is seen from Figure 8, the re-oxidation activation energy of BCF sample is relatively constant with increasing α value. It means that BCF behavior will be almost constant during the re-oxidation process that is a positive performance in view of thermochemical heat storage performance. These results confirm the data in Figure 4, in which the re-oxidation rate of BC sample decreases with increasing temperature over other samples.

Comparison of activation energies obtained in this research with the activation energy values cited in Table 1, shows that however, the activation energy values sometimes are close to each other but, in fact the sample type, pre-treatment, method, sample size, and other parameters affect on the activation energy of redox reactions of cobalt oxide. Therefore, the difference between activation energies calculated by various researchers is quite logical. The important difference between the present study and other studies that have worked on kinetics of cobalt oxide redox is that re-oxidation activation energy in this research is negative, while other studies have indicated a positive amount for it. Because of exothermic nature of re-oxidation process and use of the isothermal method for calculating the activation energy, the negative activation energy for re-oxidation activation appears to be correct [27].

3. 4. Particle Morphology Sintering of cobalt oxide particles during reduction and re-oxidation reactions plays an important role in the kinetics of redox process. Particle growth through sintering increases the oxygen diffusion distance that results in prolonging the reactions. Therefore, the particle size and their sintering during the

reactions are effective in the activation energy. One of the reasons for changing the activation energy by increasing the reacted fraction (α) is the particle sintering during the reactions. According to previous researches [15, 16], ball milling increases the sintering of particles, but Fe₂O₃ addition to ball milled Co₃O₄ prevents the growth of the cobalt oxide particles. These effects are obviously seen in Figures 9 and 10.

Figure 9 shows the particles morphology of samples before and after redox reactions. It is seen that redox process increases the size and sintering of the particles. The particle size of AC and BC samples after the redox process is greater than that of the BCF sample. SEM images confirm the results of Figure 7. As particles of BC sample sinter and grow more, over time, the energy required to oxygen diffusion in the reduction stage of BC sample increases. The increase in activation energy required for the re-oxidation stage is not visible because the re-oxidation reaction is an exothermic process and released heat during re-oxidation may compensate for the required energy for oxygen diffusion.

Figure 10 shows the variation in sample particle size of BCF sample before and after redox. According to this figure, BCF sample before redox reactions has particles with a size of less than 100 nm, while after the redox reactions; the size of the particles reaches to hundred nanometers. If the addition of iron oxide decreases the growth and particle sintering; however, the particle size after the redox is increased, which is not avoidable, but the particle growth rate and sintering are lower than other samples. Therefore, BCF sample can maintain its performance in long-term cycles.

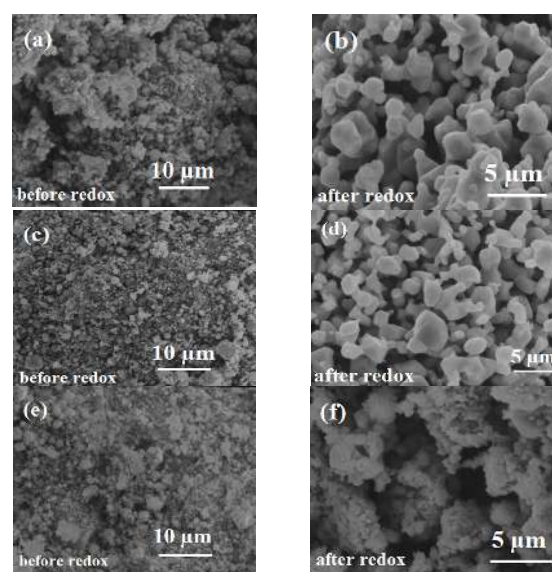


Figure 9. SEM images of AC (a, b), BC (c, d), and BCF (e, f) samples before and after redox

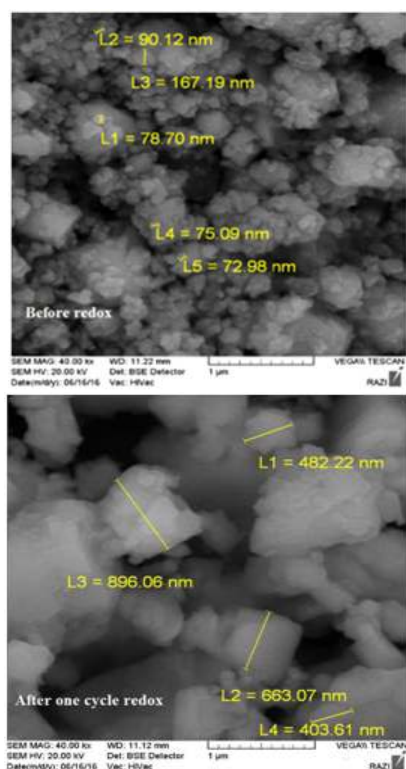


Figure 10. EM images of Co_3O_4 -15 wt.% Fe_2O_3 before and after redox

4. CONCLUSIONS

The following results were obtained from this research:

1. Mechanical activation with and without Fe_2O_3 addition decreases the rate of reduction in all isothermal reduction temperatures, while it improves the rate of re-oxidation in lower re-oxidation temperatures.
2. Mechanical activation with and without Fe_2O_3 addition decreases and preserves the rate of re-oxidation at higher re-oxidation temperatures, respectively.
3. Mechanical activation individually increases the reduction activation energy, while it along with Fe_2O_3 addition decreases the reduction activation energy in comparison with as-received Co_3O_4 .
4. Reduction activation energies vary depending on the reacted fraction (α) and are in the range of 140.6 – 166.6 kJ/mol, 175.5 – 213.7 kJ/mol and 111.5 – 121.3 kJ/mol for AC, BC, and BCF samples, respectively.
5. The results also showed that although both mechanical activations with and without Fe_2O_3 addition in comparison with as-received cobalt oxide decreases the re-oxidation activation energy, but the impact of mechanical activation without Fe_2O_3 on activation energy decline is higher.
6. Activation energies for re-oxidation step are negative, varies depending on the reacted fraction (α) and, are in the range of -76.8 to -133.5 kJ, -440.2 to -471.9 kJ, and

-190.8 to -196.05 kJ for AC, BC, and BCF samples, respectively.

5. ACKNOWLEDGEMENTS

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Isothermal Redox Kinetics of $\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3$ Nano-Composite as a Thermochemical Heat Storage Material

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در این تحقیق سینتیک احیا و اکسیداسیون اکسید کبالت اولیه (AC)، اکسید کبالت یک ساعت آسیاکاری شده (BC) و اکسید کبالت حاوی ۱۵ درصد وزنی اکسید آهن (BCF) در حالت ایزوترمال در دماهای مختلف (۱۱۳۰، ۱۱۰۰، ۱۰۷۰ و ۱۰۴۰ درجه سانتیگراد برای احیا و ۸۳۰، ۸۶۰ و ۸۹۰ درجه سانتیگراد برای اکسیداسیون مجدد) بوسیله گرمای سنجی مورد مطالعه قرار گرفت. مشخص شد که فعالسازی مکانیکی با و بدون افزودن اکسید آهن سرعت احیا را در کلیه دماهای مورد آزمایش، کاهش می دهد، این در حالی است که فعالسازی مکانیکی موجب بهبود سرعت اکسیداسیون مجدد در دماهای پایین می شود. فعالسازی مکانیکی با و بدون افزودن اکسید آهن به ترتیب موجب حفظ و کاهش سرعت اکسیداسیون مجدد در دماهای بالاتر اکسیداسیون می شود. علاوه بر این، مطابق نتایج حاصل سرعت اکسیداسیون مجدد از سرعت احیا کمتر است. برای محاسبه انرژی اکتیواسیون احیا و اکسیداسیون از روش "بدون مدل" استفاده شد. مطالعات نشان داد که تنها استفاده از فعالسازی مکانیکی انرژی اکتیواسیون احیا را افزایش می دهد، در حالی که فعالسازی مکانیکی همراه با افزودن اکسید آهن انرژی اکتیواسیون احیا را در مقایسه با اکسید کبالت اولیه کاهش می دهد. انرژی های اکتیواسیون احیا نمونه های AC، BCF و BC بسته به کسر واکنش (a) به ترتیب در محدوده ۱۴۰/۶-۱۶۶/۶ kJ/mol، ۱۷۵/۵-۲۱۳/۷ kJ/mol و ۱۱۱/۳-۱۲۱/۳ kJ/mol محاسبه شد. علاوه بر این نتایج نشان داد اگر چه فعالسازی مکانیکی با و بدون اکسید آهن انرژی اکتیواسیون اکسیداسیون مجدد را در مقایسه با اکسید کبالت اولیه کاهش می دهد ولی اثر فعالسازی مکانیکی در کاهش انرژی اکتیواسیون، بدون وجود اکسید آهن، بیشتر است. هم چنین مشخص شد که انرژی های اکتیواسیون اکسیداسیون مجدد نمونه های AC، BC و BCF منفی هستند و بسته به مقدار کسر واکنش به ترتیب در محدوده ۷۶/۸- تا ۱۳۳/۵، -۴۴۰/۲ تا -۴۷۱/۹ و -۱۹۰/۸ تا -۱۹۶/۰۵ کیلوژول به ازای مول هستند.

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