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Mixed Co, Cu and Mn-based Metal Oxides for Thermochemical Energy Storage Application

Laurie André¹, Stéphane Abanades^{1, a)} and Laurent Cassayre²

¹ *Processes, Materials, and Solar Energy Laboratory, PROMES-CNRS, 7 Rue du Four Solaire, 66120 Font-Romeu, France*

² *Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France*

^{a)}Corresponding author: stephane.abanades@promes.cnrs.fr

Abstract. The potential of metal oxides for thermochemical heat storage in solar power plants at high temperature via reversible redox reactions has been largely demonstrated, and cobalt oxide and manganese oxide commonly appear as the most attractive simple oxides. However, drawbacks of pure oxides such as slow reaction kinetics, low reversibility, loss-in-capacity over cycles or sintering, could be tackled by the addition of a secondary oxide. This work presents the experimental evaluation of mixed oxides from the Co-Cu-O, Mn-Cu-O, and Co-Mn-O systems. Within the studied series of mixed oxides, the Co-Cu-O system with low amounts of Cu (≤ 10 mol%) shows very good cycling stability and high reaction enthalpy (~ 570 kJ.kg⁻¹). Among the mixed oxides studied in the Mn-Cu-O system, the compositions with Cu amounts in the range 40-80 mol% feature promising redox properties with complete reaction reversibility, even though sintering remains an issue. In contrast, compositions with Cu amounts below 30 mol% cannot be cycled because of the formation of the hausmannite phase during reduction, which inhibits further reoxidation. The compositions with less than 40% Mn in the Co-Mn-O system retain an interesting enthalpy for thermochemical energy storage in CSP plants for a cheaper material than pure cobalt oxide, but the reaction enthalpy decreases with the Mn content. In this system, the cycling ability is lost over 70 mol% Mn due to hausmannite phase formation, similarly to the case of Mn-Cu-O system.

INTRODUCTION

Thermal energy storage (TES) in solar power plants allows electricity production depending on the needs during off-sun hours, by storing solar energy within a stable solid material during on-sun hours. Using the exothermal and endothermal steps of reversible redox reactions (Eq. 1 and 2), thermochemical energy storage (TCES), combined with concentrated solar power (CSP), is one of the three main routes existing for thermal energy storage [1] and is the focus of this study. The energy captured/released corresponds to the reaction enthalpy that is stored in the reaction products during the heat charge, which can next be released during the discharge if the reaction is reversible.



Some of the advantages of using thermochemical energy storage are the access to high energy storage density, the possibility to store energy at room temperature in chemical bonds, and the long term storage in a large temperature range (up to $>1000^\circ\text{C}$) with a constant restitution temperature.

Among many potential transition metal oxides, cobalt and manganese oxides are considered as the most promising materials for TCES applications [2-7]. However, the improvement of reaction kinetics, the tuning of the reaction temperature, the cycling stability, and the cost of the raw materials, are relevant issues in order to fit to large

scale and long term application, e.g. in concentrated solar power plants. As such improvement of redox performance has been shown to be possible by mixing the oxides [2-10], this work was dedicated to the study of materials in the Co-Cu-O, Mn-Cu-O, and Mn-Co-O systems.

With fast reaction kinetics and complete reaction reversibility, $\text{Co}_3\text{O}_4/\text{CoO}$ has been proven to be the most suited pure metal oxide system for TCES application. However, cobalt oxide is considered as potentially toxic and would not be cost effective for large scale storage, since the price of cobalt keeps dramatically increasing as of today, which prompts research for the development and optimization of alternative energy storage materials. Although some improvements of the redox performances can be achieved by controlled morphology through synthesis and stabilization with inert material, another method to modify the properties of the pure oxides is the addition of a transition metal [6, 11-12]. For example, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ can benefit from the addition of iron with molar contents higher than 20% to enhance its reaction kinetics and cycling stability [12-13].

The present study aims at investigating the effects of Cu, Co or Mn addition on the performances and thermodynamic properties of Co and Mn-based mixed metal oxides. The objective of this experimental work is to determine the optimal mixed metal oxide compositions in order to reach high performances and suitability for TCES applications, such as high reaction enthalpy, stability upon cycling, reaction temperature tuning, and lower temperature hysteresis between the reduction and oxidation steps. The effect of Cu on cobalt oxide, Co_3O_4 , has been shown to affect the reaction temperature and the oxygen exchange capacity [1-3]. The addition of Cu to Mn_2O_3 was also reported to affect the reaction temperature and to enhance the reaction kinetics of the oxide [2-4]. The addition of low cobalt content to manganese oxide enhanced the thermal stability of the oxide but the material showed loss in cyclability with higher Co content. When compared with the pure metal oxides, especially, Co_3O_4 , the mixed manganese-cobalt oxide showed lesser performances [5,10].

The utilization of metal oxides for TCES allows operating with an open-loop system, using air as both the heat transfer fluid and the reactant for the redox reactions. In this study, the experiments were thus conducted in a mixture of 20% O_2 and 80% Ar, which has similar redox properties as air. The experimental STA measurements (simultaneous thermal analysis) presented here consisted in determining the mass loss/gain (O_2 storage capacity) of the materials upon heating and cooling during reduction/oxidation reactions, the temperature of the reduction (charging step), and oxidation (discharging step), and the enthalpies of reaction. Synthesis and characterization

Mixed metal oxides based on Cu-Mn-O, Cu-Co-O, and Mn-Co-O systems were synthesized by the Pechini method [14], using metal nitrates, citric acid and ethylene glycol in aqueous solution. The synthesized powders were calcined at 750°C for 4h and were then characterized by XRD (X-ray diffraction) before being studied in redox cycles. XRD analysis was performed at room temperature using a PANanalytical XPert Pro diffractometer (CuK α radiation, $\lambda = 0.15418$ nm). XRD measurements of θ - θ symmetrical scans were made over an angular range of 10 to 80° . The step size and the time per step were fixed at 0.01° and 20 s respectively. The contribution from K α_2 was removed and the X-ray diffractograms were recorded and studied using the PANanalytical software. The instrumental function was determined using a reference material (SRM 660, lanthanum hexaboride, LaB6 polycrystalline sample) and can be expressed by a polynomial function [15].

As shown in Fig. 1, the synthesized Co-Cu-O mixed oxides are composed of a mixture of Co_3O_4 and CuO, which is in accordance with the phase diagram reproduced in Fig. 2 [16]. The mixed oxides synthesized for the Mn-Cu-O system are composed of the bixbyite Mn_2O_3 and a spinel when $x(\text{Mn})$ is below 0.4, in accordance with [17]. When $x(\text{Mn})$ is equal or higher than 0.4, the material is composed of a mixture of spinel and CuO. The synthesized mixed oxides of the Co-Mn-O system correspond to the structure of a cubic spinel solution $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ from $x(\text{Mn})=0.05$ to 0.5. Between $0.7 \leq x(\text{Mn}) \leq 0.9$ the phases are identified as a mixture of hausmannite and cubic Mn_2O_3 . In addition, SEM observations reveal that the initial synthesized powders are composed of small particles (~ 120 nm) that can form large agglomerates (~ 10 μm).

The influence of the addition of Cu, Co and Mn to pure metal oxides on the reaction reversibility, cycling stability, reaction temperature, and heat storage capacity was investigated by conducting simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), using a Netzsch STA 449 F3 System.

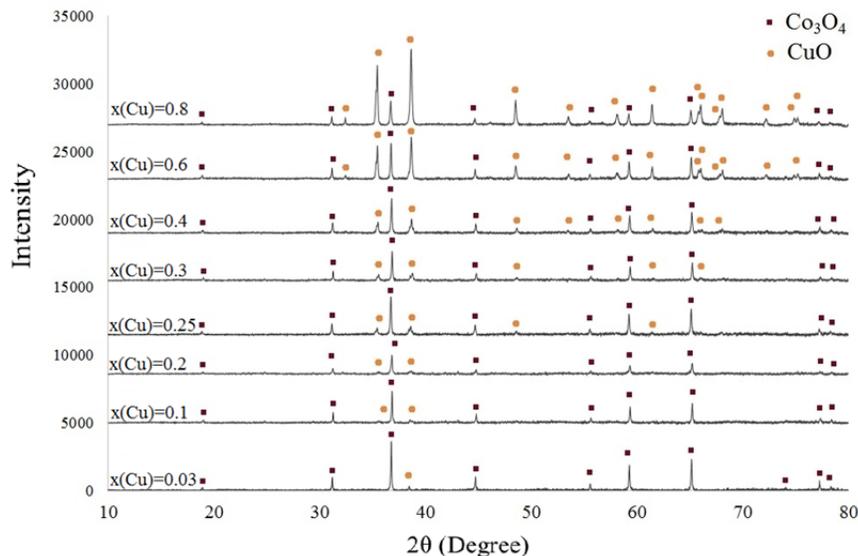


FIGURE 1. XRD of the prepared mixed Co-Cu oxides after calcination at 750°C.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental data concerning transition temperatures during redox process, oxygen storage capacity of redox materials and reaction enthalpies were obtained by TGA/DSC averaged over the course of three reduction/oxidation cycles for each material. The studied samples were pure cobalt oxide, manganese oxide and copper oxide, and mixed oxides of the systems Co-Cu-O (with $x(\text{Cu}) = 0, 0.03, 0.1, 0.2, 0.25, 0.3, 0.4, 0.6, 0.8$ and 1), Mn-Cu-O (with $x(\text{Cu}) = 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8$, and 1) and Co-Mn-O (with $x(\text{Mn}) = 0, 0.05, 0.1, 0.2, 0.4, 0.5, 0.7, 0.8, 0.9$ and 1). About 40 mg of powder was placed into an alumina crucible and then analyzed in TGA coupled with DSC. The heating rate was 20°C/min for the reduction step, and the cooling rate was 10°C/min for the re-oxidation step. For the Co-Cu-O system, reduction-oxidation cycles were performed in a 20%O₂/Ar atmosphere (10 Nml/min for O₂ and 40 Nml/min for Ar), between 700°C and 950°C. For the Mn-Cu-O system, the cycles were performed between 700°C and 1050°C under same atmosphere. For the more complex Co-Mn-O system, reduction-oxidation cycles were first performed between 650°C and 1000°C for compositions between 5 mol% and 20 mol% of Mn. These conditions were not suitable for the reduction of samples with higher Mn amounts. The mixed oxides of the Co-Mn-O system with 40 and 50 mol% Mn were thus reduced using a 1000°C isotherm under argon.

The interpretation of experimental data was supported by the help of published phase diagrams and thermodynamic models from [13-15], in order to provide further insights into the role of the metal oxides composition on the transition temperatures, oxygen storage capacities and reaction enthalpies.

Co-Cu-O System

The pure oxide currently considered as being the most promising for TCES applications among several other metal oxide candidates is cobalt oxide, mainly due to its high gravimetric storage density and high cycling stability. The reduction temperature of Co₃O₄ to CoO in air atmosphere is known to be between 880 and 930°C [8, 10, 19, 20]. The Co-Cu-O phase diagram in air published by Zabdyr *et al.* [16] (Fig. 2) shows that the content of Cu does not change the phase assemblage in the starting material up to 847°C: it is a mixture of Co₃O₄ and a Cu_xCo_{1-x}O phase, with $x \sim 0.99$.

The Co-Cu mixed oxide powders show good reaction reversibility independently of the Cu content (Fig. 3). However, the amount of O₂ released, or mass change (Δm), by the mixed oxides is inferior to that of the pure oxides, with the lowest being for the composition $x(\text{Cu}) = 0.8$. Since cobalt oxide is the reactive component in the material at these temperatures, the higher the amount of Cu, the lower the mass of active redox species [3]. It can be noted

that the phases identified by XRD (Fig. 4) are not in perfect accordance with the phase diagram. Indeed, the diagram indicates the existence of a Cu_2CoO_3 phase for $x(\text{Cu}) > 0.38$ and $T > 915^\circ\text{C}$, while XRD shows that the phase assemblage at 950°C is a mixture of $\text{Co}(\text{Cu})\text{O}$ and $\text{Cu}(\text{Co})\text{O}$. However, the formation of Cu_2CoO_3 from CuO and CoO does not lead to any oxygen release, and thus does not affect the oxygen storage properties. Thus, these results confirm that adding copper to cobalt oxide in large quantities greatly reduces the capacity of the material to store and release oxygen.

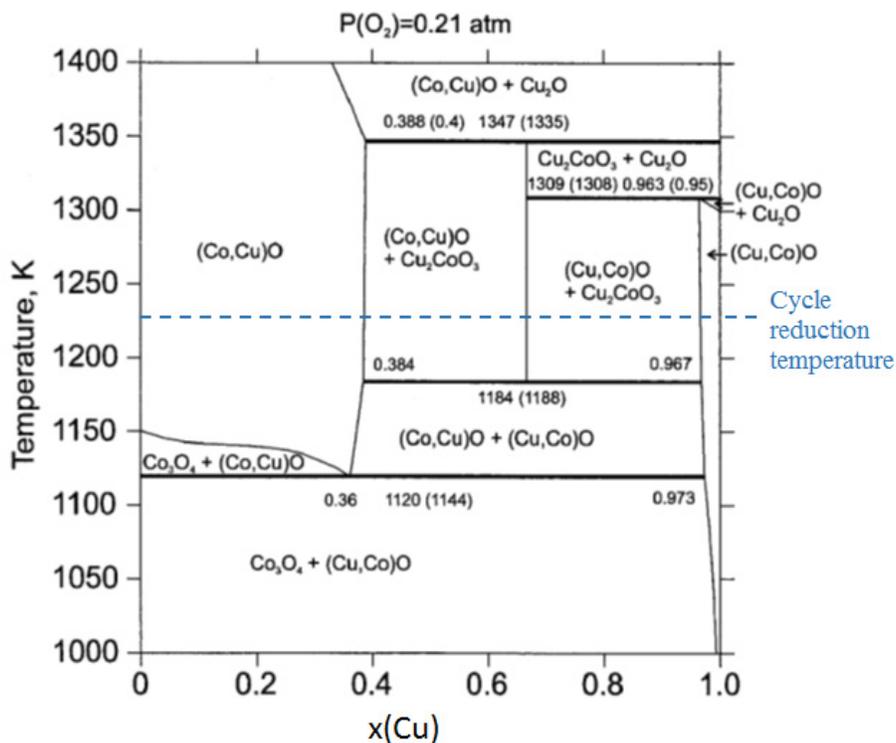


FIGURE 2. Co-Cu-O phase diagram in air [16].

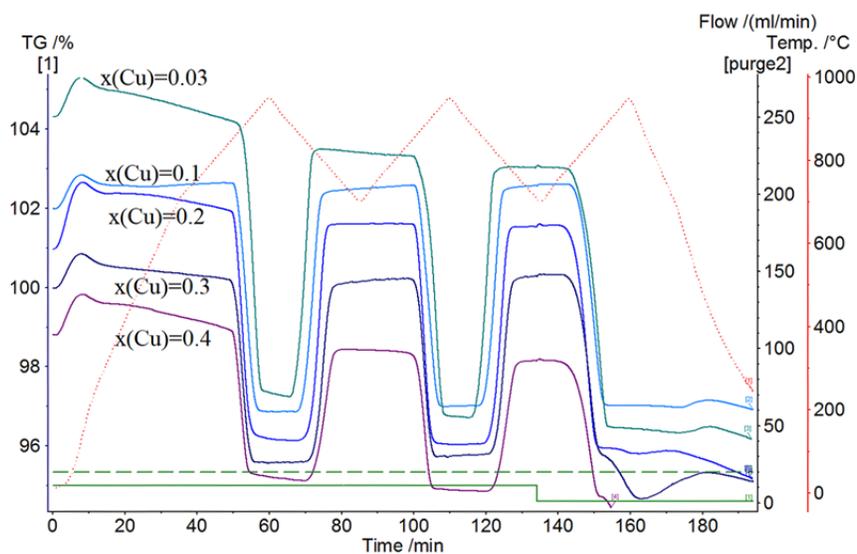


FIGURE 3. Example of TGA measurements: cobalt oxide with addition of various amounts of Cu (last reduction step in Ar).

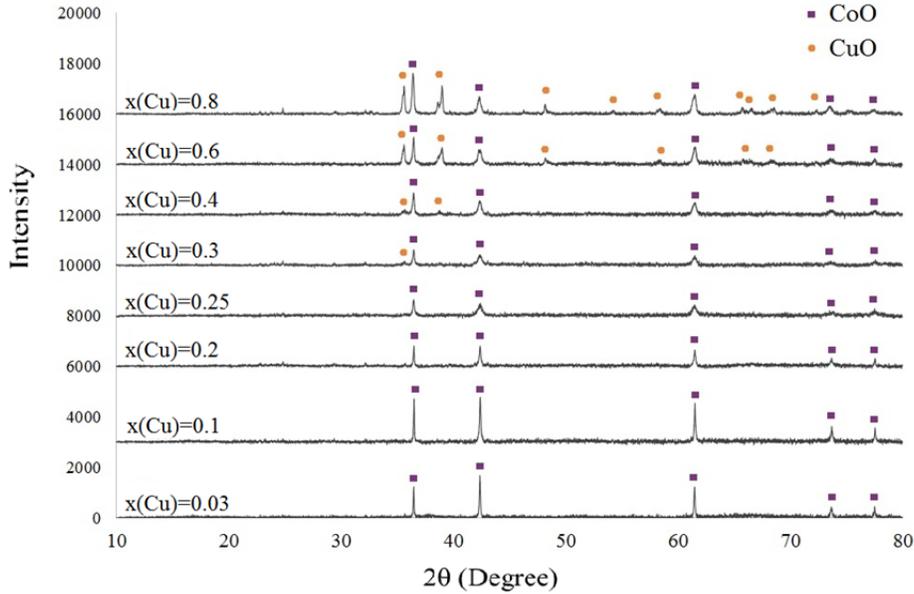


FIGURE 4. XRD of mixed Co-Cu oxides after TGA with last reduction step at 950°C in Ar

Figure 5 shows both the mass variations and the onset temperatures measured during reduction and oxidation reactions. As already discussed, the amount of oxygen exchanged in the Co-Cu-O system decreases when increasing the amount of Cu, except for pure CuO (Fig. 5a) which is converted into Cu₂O at higher temperature (1032°C, Fig. 5b). The reaction temperature is also affected by the composition of the system: the reduction temperature decreases and then remains stable, around 863°C, between $x(\text{Cu}) = 0.1$ and 0.8. The oxidation temperature decreases slightly before stabilizing, around 820°C, between $x(\text{Cu}) = 0.3$ and 0.8 (Fig. 5b). These temperatures are close to the eutectoid ($x=0.36$) decomposition temperature, at around 847°C (Fig. 2). The variations in temperature with the addition of Cu allows reducing the gap in temperature between the reduction and oxidation steps, especially for the mixed oxide with $x(\text{Cu}) = 0.1$ (Fig. 5b).

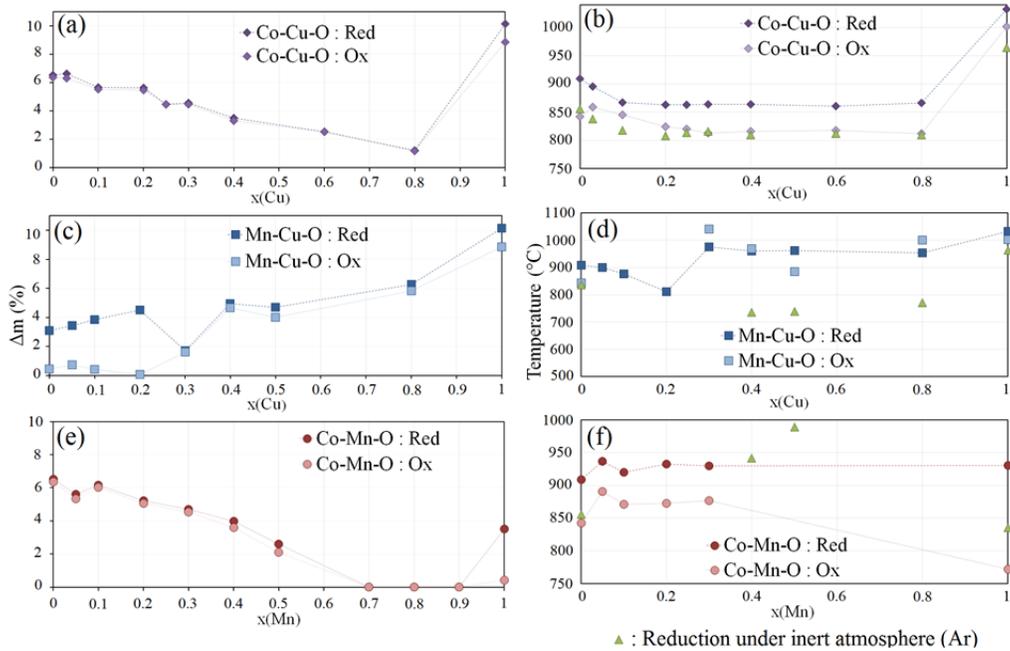


FIGURE 5. Oxygen storage capacity (Δm) and onset temperatures for oxidation and reduction steps of the systems (a, b) Co-Cu-O, (c, d) Mn-Cu-O, (e, f) Co-Mn-O.

When increasing the Cu amounts in the Co-Cu-O system, the heat storage capacity reduces, as also observed for the oxygen storage capacity in a very similar trend (Fig. 5a and 6). Nonetheless, the Co-Cu-O mixed oxides show very good cycling stability and the reaction enthalpies measured for all the compositions studied here are high enough to be interesting for TCES application, thus providing an additional option to reduce the toxicity and cost of cobalt-based materials.

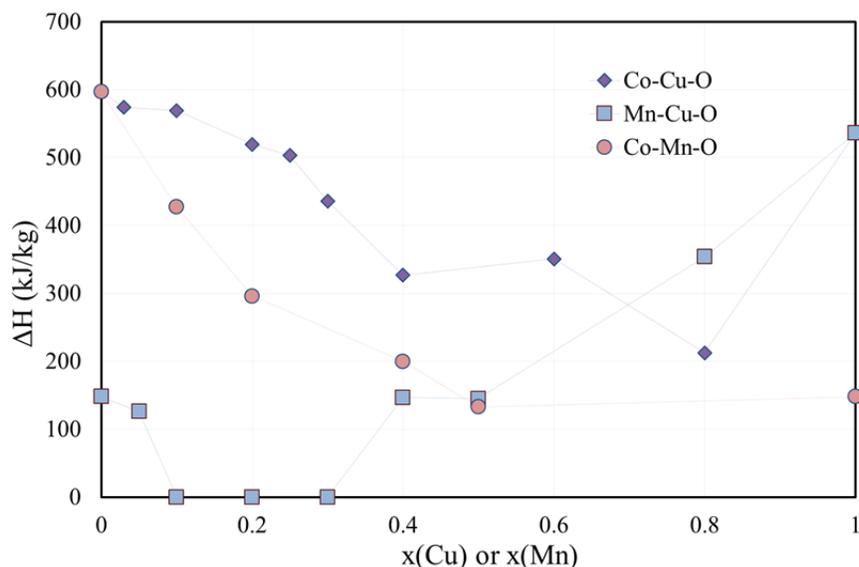


FIGURE 6. Experimental maximum reaction enthalpies measured by DSC (ΔH) as a function of either $x(\text{Cu})$ for Co-Cu-O and Mn-Cu-O systems or $x(\text{Mn})$ for Co-Mn-O system.

Mn-Cu-O System

Mn-Cu-O powders with amounts of Cu varying from 0 to 20 mol% were heated at 950°C under air and showed little sign of re-oxidation (Fig. 5c). The phase diagram presented in Fig. 7 (from [17]) indicates that up to 30 mol% of Cu, the initial bixbyite + spinel reduces into hausmannite and spinel phases. As evidenced in a previous work [12], the hausmannite phase strongly inhibits reoxidation reaction. Upon heating, the composition with $x(\text{Cu}) = 0.3$ first shows two reduction steps, but only the mass lost during the second reduction is regained during oxidation.

The powders with $x(\text{Cu}) = 0.4, 0.5$ and 0.8 showed complete re-oxidation and these compositions also resulted in significantly enhanced reaction enthalpies (Fig. 6). The composition with $x(\text{Cu}) = 0.8$ exhibits the highest oxygen storage capacity, but reduction happens in two steps with a first reaction around 954°C and a second transition at 1033°C (under 20%O₂/Ar) (Fig. 5d), which corresponds to the transition into delafossite (CuMnO₂) + Cu₂O phases.

As opposed to the mixed oxides of the Co-Cu-O system, the mixed oxides of the Mn-Cu-O system strongly suffer from sintering, and the sample with $x(\text{Cu}) = 0.8$ was the most sintered among these mixed oxides, after TGA (probably also due to the required higher temperatures being used).

The reduction temperature decreases when adding Cu to manganese oxide from $x(\text{Cu}) = 0.05$ to $x(\text{Cu}) = 0.2$, and then increases and remains stable from $x(\text{Cu}) = 0.3$ to $x(\text{Cu}) = 0.8$ (Fig. 5d). The lowest gap in temperature between reduction and oxidation is observed for the mixed oxide with $x(\text{Cu}) = 0.4$. For the compositions $x(\text{Cu}) = 0.3$ and $x(\text{Cu}) = 0.8$, the onset temperature of the re-oxidation is higher than that of the reduction step, because the oxidation begins promptly during the cooling down from high temperature. It can also be noticed that for these two compositions, the reduction occurs in two steps. For the composition $x(\text{Cu}) = 0.3$, only the second mass loss is regained by the material during the performed cycles with good cycling stability, whereas the material recovers the whole mass lost for the composition $x(\text{Cu}) = 0.8$.

The reaction enthalpy measured for the compositions $x(\text{Cu}) = 0.4$ and $x(\text{Cu}) = 0.5$ (147 and 145 kJ.kg⁻¹ respectively) are comparable to that of pure manganese oxide (148 kJ.kg⁻¹ for pure Mn₂O₃/Mn₃O₄), while the

reaction enthalpy of the composition $x(\text{Cu}) = 0.8$ is significantly higher (354 kJ.kg^{-1}) (Fig. 6). The reaction enthalpy for the compositions between $x(\text{Cu}) = 0.1$ and $x(\text{Cu}) = 0.3$ could not be measured.

The mixed oxides within the Mn-Cu-O system show interesting reaction enthalpy and cycling stability over three cycles at high temperature for compositions ranging from $x(\text{Cu}) = 0.4$ to 0.8 . However, strong sintering remains a critical issue that needs to be addressed.

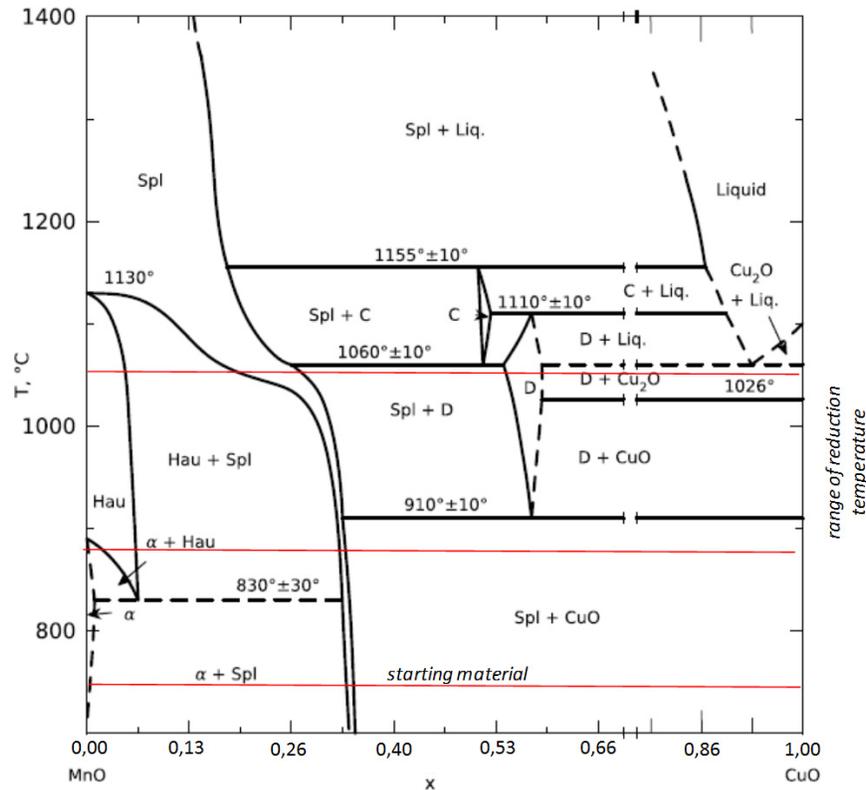


FIGURE 7. Mn-Cu-O phase diagram in air; α = Bixbyite ; Hau = Hausmannite ; Spl : Spinel ; D = Delafossite ; C = Crednerite (from [17]).

Co-Mn-O System

The Co-Mn-O oxides showed complete reaction reversibility up to Mn contents exceeding 50% (Fig. 5e). This can again be explained by the formation of a hausmannite phase upon reduction in this composition range and the poor re-oxidation capability of hausmannite to bixbyite [12]. Furthermore, the oxygen storage capacity decreases from $x(\text{Mn}) = 0.2$ to $x(\text{Mn}) = 0.5$, and it is lower than that of pure cobalt oxide. However, the temperatures required to reduce the mixed oxides are significantly higher, especially for $x(\text{Mn}) = 0.4, 0.5$. The reduction of the mixed compounds with 40 mol% and 50 mol% Mn were not achieved at 1000°C under air atmosphere and these compositions were thus reduced under argon atmosphere around 942°C and 989°C respectively.

The temperature of reaction increased with increasing amounts of Mn, in accordance with the phase diagram proposed by [18]. The gap in temperature was not significantly reduced (Fig. 5f). The energy storage capacity decreases when increasing the Mn content but the materials still present a higher enthalpy of reaction than pure manganese oxide (Fig. 6) (148 kJ.kg^{-1}). However, the performances of pure cobalt oxide remain far better than those of the Co-Mn-O mixed oxides. The measured reaction enthalpies of mixed oxides are higher than that of pure manganese oxide but lower than that of pure cobalt oxide.

CONCLUSION

This study aimed at investigating mixed oxide materials for improving chemical stability during cycling and heat storage density, compared to the pure oxide materials considered for high-temperature thermochemical storage of solar energy. Experimental studies on mixed metal oxides are valuable to envisage optimal composition fitting the characteristics of the targeted TCES application. In this work, the effect of secondary oxide addition to Co and Mn-based oxides was characterized and suitable mixed oxide compositions for TCES application were identified.

Similarly to the case of Mn-Fe system studied previously [12], the present work confirms that Mn-based systems with amounts of Co or Cu below ~30 mol% show poor re-oxidation capabilities, due to the formation of a hausmannite phase clearly described in published phase diagrams. Therefore, the reaction reversibility of Mn-Cu-O and Mn-Co-O systems is strongly improved with amounts of Co and Cu above 30 mol%.

Besides, the study of several mixed oxide systems, both in the present study and in previous work [12], points out a strong correlation between the variations of the enthalpy and the oxygen exchange capacity for each system. As an example, when the oxygen storage capacity tends to decrease with the variation of the composition, so does the reaction enthalpy.

The Co-Cu-O system globally features high enthalpy, good cycling stability and low temperature hysteresis between the reduction and oxidation step. Although copper is also a costly raw material, the reduction of the amount of cobalt in the materials by the addition of copper would allow for reducing materials toxicity and cost for TCES. For the Mn-Cu-O system, compositions with Cu contents between 40 and 80 mol% could be interesting for TCES application. However, the sintering issue affecting these materials during the cycling needs to be alleviated. Concerning the Co-Mn-O system, low amounts of Mn should be favored, as the reaction enthalpy decreases significantly when increasing the Mn content. However, these Co-Mn-O compositions with $x(\text{Mn}) < 0.7$ are interesting as they show good cycling stability and could thus provide more cost-effective and less toxic materials for TCES applications.

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