

Measurement and modeling of decomposition kinetics for copper oxide-based chemical looping with oxygen uncoupling



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HIGHLIGHTS

- By experimental approach kinetic equations of two copper-based oxygen carriers were defined.
- The dual effects of temperature (kinetic and thermodynamic) were separated.
- The developed kinetic equations were then used to predict the rates of two other carriers.
- It may be reasonable to assume a universal rate equation for all copper-based oxygen carriers.

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ABSTRACT

Chemical looping combustion with oxygen uncoupling (CLOU) is a promising CO₂-capture ready energy technology that employs oxygen carriers with thermodynamic properties that cause oxygen to be spontaneously liberated as gaseous O₂ in the fuel reactor, where it can react directly with solid fuels. One of the promising CLOU carrier metals is copper, cycling between CuO and Cu₂O. Experimentally-determined rate expressions for these reactions are needed for proper development, modeling and scale-up of CLOU technology. The CuO–Cu₂O system presents an interesting challenge in that the rate of decomposition depends on the thermodynamic driving force imparted by the difference between equilibrium and actual partial pressures of oxygen, and the equilibrium partial pressure is strongly temperature dependent in the range useful for combustion. This study investigates decomposition of two different copper-based oxygen carriers, from CuO to Cu₂O oxidation states, to develop a universal kinetic expression to describe the observed rate of reaction as a function of temperature, conversion and gas environment. The kinetic model developed is compared to results of a third support type (silica) using two different CuO wt% loadings (64 wt% CuO and 16 wt% CuO) to demonstrate applicability to other support types and copper oxide loadings.

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1. Introduction

Chemical looping combustion (CLC) is promising technology for CO₂-capture ready processing of carbonaceous fuels for energy production, and has been recognized as having potentially lower energy demand and offering a lower cost of electricity than oxy-fuel combustion, IGCC and flue gas CO₂ removal by amine scrubbing [1,2]. The most common configuration for a CLC system involves two interconnected fluidized beds, the so-called air reactor and fuel reactor, with metal-based “oxygen carrier” particles cycling between them [3]. The metal is oxidized in the air reactor, the product gas of which is oxygen-depleted air. The oxidized carrier particles are transported to the fuel reactor via a loop seal, thus keeping nitrogen from entering the fuel reactor. In

the fuel reactor, the oxygen carrier is reduced by a gaseous fuel such as natural gas, effectively combusting the fuel to CO₂ and H₂O, resulting in a product stream of nearly pure CO₂ once water vapor is condensed. The reduced carrier is returned to the air reactor.

Because solid–solid reactions are inefficient, CLC is not suitable for processing solid fuels unless the fuels are converted to syngas in an upstream reactor or in situ in the fuel reactor. Another, more promising approach is so-called Chemical Looping with Oxygen Uncoupling (CLOU), a variant of CLC, that involves use of specific metal–metal oxide complexes to spontaneously release (“uncouple”) oxygen as gaseous O₂ in the fuel reactor [4]. This is possible because the equilibrium behavior of the carrier oxidation/reduction reaction is such that gaseous O₂ is favored at high temperature, low-O₂ conditions such as those existing in the fuel reactor of a CLC system. In the air reactor, the high O₂ partial pressure favors the oxidized metal. The advantage of CLOU carriers

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over conventional CLC carriers is that the released oxygen can react directly with solid fuel or char, thereby avoiding the need to convert the solid to gas through relatively slow gasification reactions.

Only a few metal complexes that exhibit this CLOU behavior in the range of chemical looping combustion temperatures have been identified. Mattisson et al. [4] discussed the ability of CuO, MnO and CoO to perform the spontaneous liberation of oxygen. CLOU Copper oxide is attractive due its fast reaction rates and it is thermodynamically favored to completely convert gaseous hydrocarbons to CO₂ and H₂O [5]. Most notably, however, copper oxide looping is overall exothermic in both the air reactor and fuel reactor, whereas other materials are exothermic in the air reactor, but would require heat input to the fuel reactor since the heat required to reduce the carrier exceeds that given off by the fuel as it combusts [6].

When used as a CLOU carrier, copper cycles between the Cu⁺² cupric (CuO) and Cu⁺¹ cuprous (Cu₂O) states:



The equilibrium curve for this reaction is shown in Fig. 1. At temperatures above approximately 800 °C, in otherwise low-O₂ environments (such as the fuel reactor of a chemical looping system), the left side of the above reaction is favored, generating O₂. If the O₂ continues to be consumed (e.g., by reaction with fuel), the CuO decomposition reaction will continue to progress. The use of the Cu₂O–CuO system to generate carbon dioxide was first recognized by Lewis and Gilliland in 1954 [7]. Application to CLC was first demonstrated by Mattisson et al. [4], who showed that conversion of petcoke by CLOU is as much as 50 times faster than conversion by conventional CLC with an iron-based carrier, which requires in situ conversion of petcoke to syngas by relatively slow gasification reactions. Several groups have since continued in the investigation of CLOU using either Co, Mn or Cu-based carriers in their studies ultimately concluding that either Mn or Cu may be suitable choices [8–13].

For proper design and modeling of chemical looping systems, it is valuable to understand the intrinsic chemical kinetics of both the forward (oxidation) and reverse (reduction) reactions shown in reaction (1). Ideally, it would be useful to develop general rate expressions applicable across a broad range of conditions, for example of the form below for cupric oxide decomposition:

$$\text{rate} = A \exp(-E_a/RT) [\text{CuO}]^\alpha (P_{\text{O}_2, \text{eq}} - P_{\text{O}_2})^\beta \quad (2)$$

where A is a pre-exponential constant, E_a is the activation energy and α and β are reaction orders. The challenge lies in experimentally determining these constants. The inclusion of the oxygen concentration term in Eq. (2) may not initially be obvious. Because reaction (1) is reversible, the thermodynamic behavior shown in Fig. 1

affects the rate of the carrier oxidation and decomposition (uncoupling) reactions. It is well understood that rates of reversible reactions such as reaction (1) are affected by the difference between the actual and equilibrium concentrations of reacting species, the so-called “driving force.” This has also been observed to occur with copper-based oxygen carriers operating in the CLOU regime [14]. Due to the effect of temperature on the equilibrium partial pressure of oxygen the oxygen concentration term in Eq. (2) takes the form shown as a difference between the equilibrium partial pressure and the observed partial pressure of oxygen.

The dependence of Cu₂O oxidation and CuO decomposition on the oxygen driving force makes identification of intrinsic kinetics of the respective oxidation and reduction reactions challenging. For example, several groups studying CLOU have reported a decrease in the rate of oxidation by air at higher temperatures [12,14–16], which is due at least in part to a decrease in the difference between the equilibrium O₂ partial pressure and air’s partial pressure of 0.21 atm. Similarly, in certain types of experiments the rate of cupric oxide reduction to release O₂ is affected by that released O₂. Adánez-Rubio et al. [17] demonstrated a decrease in the decomposition rate of CuO with an increase in the supplied partial pressure of oxygen. They suggested that the decrease in reaction rate be ascribed to a decrease in the driving force between the equilibrium partial pressure and supplied partial pressures of oxygen.

Using results obtained from the decomposition of a zirconia-supported copper oxide-based carrier in a batch fluidized bed with Mexican Petcoke as a fuel Sahir et al. [18] suggested that the apparent activation energy observed during CuO decomposition is a combined effect from the activation energy as well as the influence of the oxygen partial pressure driving force. Their analysis suggests that the energy required to overcome both the thermodynamic (oxygen partial pressure driving force) and kinetic (activation energy) barriers to reaction is 280 kJ/mole. They report that by separating the influences of these two barriers they were able to obtain a kinetic barrier of 20 kJ/mole and a thermodynamic barrier of 260 kJ/mole. This work reports results obtained using a sample of the oxygen carrier material used in that analysis.

It has been observed that the rate of CuO decomposition is slower than that of Cu₂O oxidation in the temperature range of interest to copper looping systems, so it is especially critical for proper design of the fuel reactor that decomposition rates are well understood and can be modeled. The objective of this study is therefore to gain a better understanding of the chemical mechanisms associated with decomposition of cupric oxide. The desired kinetic model should adequately represent the characteristics of a copper-based oxygen carrier regardless of variability in characteristics such as support type, copper loading and production method. It is the goal of this work to provide such a model.

2. Experimental

In order to gain a better understanding of the decomposition mechanism and to compare carriers under a variety of conditions, two copper-based oxygen carriers were studied under a variety of experimental conditions.

2.1. Samples

Two different CuO-based carriers, prepared by different methods, were evaluated. Properties of the carriers are presented in Table 1. The MgO stabilized ZrO₂ material was produced using a freeze granulation method and provided by Chalmers University, Sweden. This material was reported to be very stable while maintaining physical strength and high chemical reactivity. Johansson

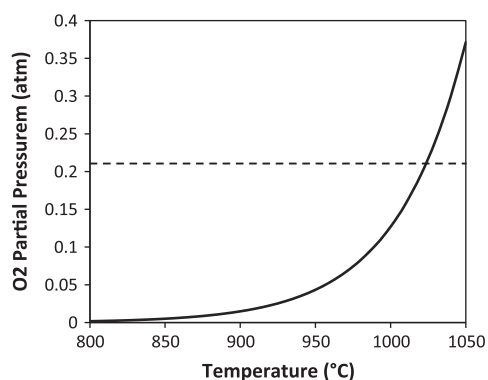


Fig. 1. Equilibrium curve for Cu₂O–CuO system. From data in Ref. [4].

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