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Co_3O_4 nanoparticles as oxygen carriers for chemical looping combustion: A materials characterization approach to understanding oxygen carrier performance

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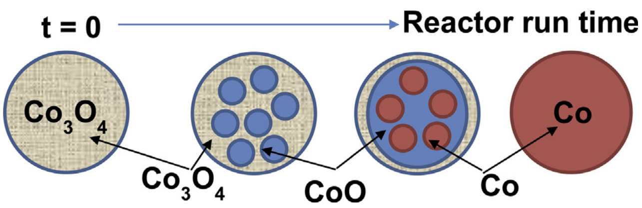
HIGHLIGHTS

- Co_3O_4 reduction proceeded through CoO then to metallic Co during CLC.
- Superior performance of CoO/Co mixed phases.
- CoO reduction to Co follows a nucleation and nuclei growth mechanism.
- Mixed metal-metal oxide phases may help to improve reactivity.
- Continued performance of Co_3O_4 through several cycles, illustrates its potential.

GRAPHICAL ABSTRACT



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ABSTRACT

Currently, there is relatively limited information about the use of Co_3O_4 as an oxygen carrier for chemical looping combustion, with the promise afforded by its high oxygen capacity often overlooked because of its moderate temperature of decomposition. Here, we employ a materials characterization approach to investigate the coupled surface chemical and bulk material processes influencing the oxidation of methane by Co_3O_4 (CO_2 yield and reactive longevity). Methane (CH_4) oxidation by Co_3O_4 was studied in a continuous flow reactor across a range of temperatures (500–700 °C) and gas hourly space velocities (125–375 h^{-1}). At the highest temperatures considered (700 °C), Co_3O_4 reduction proceeded through CoO to an ultimate end product of metallic Co, with the rate and extent of CH_4 oxidation to CO_2 decreasing monotonically with increasing CoO content because of its more highly coordinated lattice oxygen. In contrast, at lower temperatures (e.g., 500 °C) the initial decrease in CH_4 oxidation coinciding with Co_3O_4 conversion to CoO was followed by a period of increasing CO_2 yield as some CoO was further converted to Co, unexpected behavior not observed at higher temperatures. Complementary bulk and surface analyses indicate that CoO reduction to Co follows a nucleation and nuclei growth mechanism within the particle bulk. We thereby attribute the greater reactivity of lattice oxygen in mixed CoO/Co phases to a lower cohesive energy for oxygen atoms at the interface of these phases. Our results suggest that for CLC applications in lower temperature regimes, the use of mixed metal-metal oxide phases may help to improve reactivity. More practically, our results demonstrate the performance of Co_3O_4 through several cycles, illustrating its potential for use in CLC.

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1. Introduction

Chemical looping combustion (CLC) represents a promising method for improving the efficiency of CO_2 capture [1] while also minimizing unwanted byproduct greenhouse gases (e.g., nitrogen oxides). This process holds some advantages over more traditional catalytic oxidation processes, such as eliminating the oxygen production requirements and reduced energy demand and system costs [2]. The CLC process is performed in the temperature range from 600 to 1200 °C and consists of two steps, which are cycled back and forth. First is the reduction of the hydrocarbon gas by a metal oxide (Eq. (1)), which is followed by the subsequent regeneration of the metal oxide via its oxidation in air (Eq. (2)) [1].

$$(2n+m)Me_yO_x(\text{oxygen carrier}) + C_nH_{2m}(CH_4) \leftrightarrow (2n+m)Me_yO_{x-1} + mH_2O + nCO_2 \tag{1}$$

$$Me_yO_{x-1} + 1/2O_2(\text{from air}) \leftrightarrow Me_yO_x + (\text{air}: N_2 + \text{excess } O_2) \tag{2}$$

Several characteristics are desirable for solid-state oxygen carriers used in the CLC process. These include properties related to their reactivity, including high oxygen capacity and transport, their ease of reduction and re-oxidation, and practical considerations including their resistance to agglomeration and limiting carbon deposition during repeated cycling [3]. Several transition metal oxides (e.g., those of copper, cobalt, iron, manganese, and nickel) have all been identified as promising oxygen carrier candidates due to their tendency to be easily reduced [4,5]. Fe_2O_3 and CuO are among the most-investigated materials due to their low cost, but each has drawbacks that may limit their practical implementation at scale (e.g., low oxygen transport capacity of Fe_2O_3 [6] and adverse environmental implications for CuO) [7]. Despite its higher cost, NiO is also considered a good oxygen carrier due to its high oxygen content and reactivity.

Reduction of Co_3O_4 to Co metal provides the highest amount of available oxygen among common metal oxides used for CLC (i.e., Co_3O_4 offers the highest ratio of moles of available oxygen per mole of metal; see Eqs. S1–S4 in the Supporting Information or SI). In addition, Co_3O_4 holds several other potential advantages such as a lower tendency to sinter at high temperature compared to other transition metal oxides (e.g., copper or manganese), a larger thermodynamic driving force for reaction with hydrocarbon fuels [1,8], and greater rates of reduction and (re)oxidation [9]. Hongguang et al. [10] also report that cobalt oxide is more resistant to carbon deposition than NiO when reduced by CH_4. Nevertheless, Co_3O_4 has received relatively little attention for CLC application because of concerns over its cost [11] and its tendency to decompose at comparatively low temperatures [1], which may result in formation of less reactive CoO before contact with the hydrocarbon fuel. In addition, regenerating the Co_3O_4 phase after reduction may also be an issue limiting its use, with substrate re-oxidation typically occurring at temperatures greater than the decomposition temperature of Co_3O_4 [12]. Thus, use of Co_3O_4 for CLC has been mostly limited to doped materials with other transition metal oxides such as Fe_2O_3 and NiO [10,13,14]

We argue that the promise of Co_3O_4 as a CLC substrate may be better realized through improved understanding of how its surface and bulk chemical properties influence particle stability and reactivity during reaction. For example, current paradigms conceptualize the reduction of oxygen carriers during CLC as either a nucleation and nuclei growth model [15] or an unreacted shrinking core model [16]. The nucleation and nuclei growth model assumes that the reaction does not progress without formation of a new, reactive phase, after which the reaction proceeds at greater rates that scale with the number of nuclei (i.e., reactive product phases) that are randomly distributed across the substrate [17]. In contrast, the shrinking core model assumes that a metal–metal oxide interface moves toward the center of the oxygen carrier particles over the course of the reaction. As the reaction progresses, oxygen consumption at the particle surface forms a reduced layer of either a metal or metal oxide that gaseous reactants and products must then diffuse through [18]. We contend that elucidating the coupled surface and bulk chemical processes involved in Co_3O_4 reduction and methane combustion, as well as their impact on the transition from Co_3O_4 to CoO (and ultimately Co), is critical for optimizing the CO_2 yield and substrate stability, which may in turn help to alleviate concerns over the cost associated with using Co_3O_4 for CLC.

In the present work, we have investigated methane activation on unsupported Co_3O_4 nanoparticles using a continuous flow reactor while also analyzing the concentration profiles of reactants and products under CLC-relevant operating conditions. The activity and stability of Co_3O_4 were tested under different temperatures (500–700 °C) and flow rates (20–60 standard cubic centimeters per minute (sccm)) across a range of reduction/oxidation cycles (from five to ten cycles). Our goal was to determine the effect of system variables on the duration and rate of CH_4 conversion, mechanism of CH_4 transformation, including end products, and the evolution of Co_3O_4 bulk and surface chemical structure and phase during reduction by CH_4. To more completely understand the performance and stability of Co_3O_4 during application, we also considered the reactivity of CoO, which represents an anticipated intermediate in the reduction of Co_3O_4 to Co metal during CLC.

To evaluate changes in Co_3O_4 during CLC processing, we relied on a materials characterization approach that analyzed substrate particles before, during, and after reaction with CH_4 for their structure, morphology, surface area, bulk phase and surface chemical characteristics. A suite of materials characterization techniques were employed, including powder X-ray diffraction (p-XRD), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area analysis, thermal gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The current study provides new, fundamental understanding into CH_4 activation on Co_3O_4, particularly insights into the evolution of oxide particles in response to changes in operational variables. Collectively, we believe these coupled insights into Co_3O_4 structure and reactivity will help increase its feasibility in the CLC process, which may in turn ultimately help reduce the associated energy demand with this process by enabling optimized performance at lower combustion temperatures.

2. Materials and methods

2.1. Materials

Commercially available nanoparticles of Co_3O_4 (Aldrich) and CoO (SkySpring Nanomaterials, Inc) were used in this work. A mixture (P5 gas – Praxair) of methane (5%) in balance with argon (95%) was used to reduce the cobalt oxygen carrier, and synthetic air (Praxair) was used to re-oxidize the oxygen carrier, as well as during the preheating portion of our protocol. High purity nitrogen (Praxair 99.9%) was used to flush the reactor of air prior to the introduction of P5 to initiate reaction.

2.2. Characterization of cobalt oxide nanoparticles

Co_3O_4 and CoO nanoparticles were characterized by p-XRD (Bruker D8 Advance 206112) to examine the bulk crystalline phases before, during, and after reaction. This information on