Graphical Abstract

**Co₃O₄ Nanoparticles as Oxygen Carriers for Chemical Looping Combustion:
A Materials Characterization Approach to Understanding Oxygen Carrier Performance**

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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 to 700 °C) and gas hourly space velocities (125 to 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.

Keywords: cobalt oxides, nucleation and nuclei growth model, chemical looping combustion, methane oxidation, nanotechnology, surface spectroscopy

1. INTRODUCTION

Chemical looping combustion (CLC) represents a promising method for improving the efficiency of CO₂ 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].

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]. Fe₂O₃ 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 Fe₂O₃ [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 progresses 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 towards 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 a metallic/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 a commonly observed 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 CH₄ activation on Co₃O₄, particularly insights into the evolution of oxide particles in response to changes in operational variables. Collectively, we believe these coupled insights into Co₃O₄ 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 Co₃O₄ (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

Co₃O₄ 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 changes to the bulk composition of the particles was complemented by XPS analysis, which provided information about how the surface composition of particles evolved over the reaction duration. The surface analysis chamber of the XPS instrument (Kratos Axis

Ultra XPS) is equipped with an aluminum $K\alpha$ source with a 500 mm Rowland circle silicon single crystal monochromator that produces a monochromatic X-ray beam of 1486.6 eV. The X-ray gun was operated using a 10 mA emission current at an accelerating voltage of 15 kV. XPS spectra of cobalt oxides were calibrated using the adventitious C 1s peak at 285.0 eV.

High resolution TEM (HRTEM; JEOL 2100F) with an accelerating voltage of 200 kV was used to determine particle size distributions of cobalt oxide samples by measuring at least 125 randomly chosen particles. HRTEM samples were prepared after sonication of nanoparticle suspensions in ethanol for 15 minutes at room temperature. SEM (Hitachi S-4800) was used to examine the extent of sintering for oxygen carriers after multiple cycles of reduction and re-oxidation reactions, as the extensive growth observed in some instances precluded use of HRTEM. Samples were imaged on an Au-coated silicon wafer and the particle size was determined by measuring at least 100 randomly chosen particles of the reacted oxygen carriers. Specific surface area of cobalt oxides was determined using the Brunauer-Emmett-Teller (BET) adsorption isotherm method, where particles were first degassed for 3 h at 110 °C. A seven point BET isotherm was used to determine the specific surface area using N_2 (g) as the adsorbate. Thermal gravimetric analysis (TGA) of the as-received Co_3O_4 and CoO nanoparticles were carried out on a Q5000 Thermogravimetric Analyzer from TA Instruments at a heating rate of 5 °C/min from room temperature to 900 °C in N_2 to investigate the stability of Co_3O_4 . TGA was also used to analyze the re-oxidation of the spent oxygen carrier using an air stream at the same heating rate between room temperature and 700 °C.

2.3. Continuous Flow Reactor Operation

To examine the performance of Co_3O_4 and CoO as oxygen carriers for CLC, reactions with methane were conducted in a tube furnace (Thermolyne, type 21100- 15 inch long) fitted with a quartz tube reactor (1/4 inch in diameter, and 18 inch long; see Figure S1 in SI). The reactor inlet was connected to a three-way valve, which allowed control of the inlet gas composition.

Reactions between cobalt oxides and methane were conducted as a function of gas hourly space velocity (GHSV) and temperature. Mass flow controllers (MKS) with a range up to 100 sccm were used to introduce gases into the reactor. P5 gas was used at a flow rate between 20 to 60 sccm, and the typical metal oxide loading in the reactor was one gram. These conditions produce GHSV values between 125 to 375 h^{-1} , where values were calculated based on the volumetric methane flow rate normalized to the reactor bed volume (i.e., the volume of the cobalt oxide). The range of reaction temperatures investigated was from 500 to 700 $^{\circ}\text{C}$, all of which are below the stability of Co_3O_4 and CoO . Based on our thermal gravimetric analysis (TGA), the decompose temperature of Co_3O_4 and CoO are 750 and 900 $^{\circ}\text{C}$ respectively.

The long-term stability of cobalt oxides as oxygen carriers during full conversion of CH_4 was also investigated. These stability experiments were conducted both as a function of time (of a single cobalt oxide/ CH_4 oxidation process step) and as a function of the number of complete cobalt oxide reduction/re-oxidation cycles. These stability tests were conducted at reaction temperatures of 600 and 700 $^{\circ}\text{C}$ and with P5 gas at a flow rate ranging from 20 to 60 sccm (GHSV = 125 to 375 h^{-1} respectively). Experiment monitoring cobalt oxide stability as a function of reaction time monitored reaction progress until CH_4 conversion reduced to 0% (i.e., until there was no longer any oxidation of CH_4 by the cobalt oxide). For experiments evaluating stability across sequential oxide reduction/re-oxidation cycles, the reaction was monitored to determine

the duration over which there was 100% conversion of CH_4 to CO_2 (typically 10 – 60 minutes depending on reaction conditions). Once incomplete CH_4 conversion was observed, the P5 was shut off to the reactor and air was introduced at a flow rate of 60 sccm for the same time period of the initial reduction reaction. Prior to reintroducing P5 to the reactor to initiate the next reduction/re-oxidation cycle, N_2 was passed through the reactor at a flow rate of 60 sccm for 5 minutes. This sequence was repeated for all additional cycles until cobalt oxide reactivity dose not regenerated well enough to capture 100% of CO_2 for all the durations of cycles (depending on the conditions, after 5 to 10 cycles).

To conduct a reaction, the tube reactor was filled with Co_3O_4 or CoO as oxygen carriers and then heated to the desired temperature under a stream of air or nitrogen (60 sccm), respectively. When the desired temperature was achieved, the air flow was stopped (in the case of using Co_3O_4) and N_2 was introduced at the same flow rate for 5 min prior to introducing the P5 gas. Upon introduction of P5, samples were taken periodically for gas chromatography analysis (as described below) to monitor effluent concentration of CH_4 , CO_2 and other potential reaction byproducts (e.g., CO and H_2). When samples of the oxygen carrier were needed to characterize changes in morphology and composition along the reaction coordinate, the reactor was cooled down under N_2 stream and the samples were stored under vacuum until analysis. Each set of experiments was conducted at least twice and good repeatability of results was observed.

2.4. Gas Chromatography (GC) Analysis

Agilent 6890N Network Gas Chromatograph (GC) equipped with 4m *118'' *0.085'' Porpak Q packed column (Alltech) and thermal conductivity detector (TCD) were used. Helium (He) was used as a carrier gas. The reactor outlet was connected to a three way valve, which allowed

control of the outlet gas composition and a gastight syringe (0.25 ml) was used to sample the reaction gas products.

3. RESULTS AND DISCUSSION

3.1. Characterizations of Cobalt Oxides

From TEM analysis, the average projected area diameter (i.e., measured from the two-dimensional area of particles in TEM images by projecting their shapes onto an arbitrary plane) of Co_3O_4 and CoO nanoparticles before reaction (i.e., “as received” particles) were $50 (\pm 10)$ and $50 (\pm 17)$ nm, respectively (see Fig. S2). We chose similarly sized Co_3O_4 and CoO to avoid any possible influence of oxygen carrier particle size on reactivity, which would complicate performance comparisons. Accordingly, specific surface areas measured via N_2 BET adsorption were also comparable for as-received Co_3O_4 and CoO , measuring $26 (\pm 1)$ and $19.0 (\pm 1) \text{ m}^2/\text{g}$, respectively (values represent average and standard deviation of at least three measurements). Finally, p-XRD validated the phase of each commercial material, with patterns for as-received Co_3O_4 and CoO nanoparticles matching those of the cubic reference diffraction pattern (JCPDS card 00-042-1467) and the rock salt reference diffraction pattern (JCPDS card 00-048-1719), respectively.

3.2. Temperature and Flow Rate Dependent Trends in CH_4 Oxidation by Co_3O_4 .

Figure 1 shows the effect of temperature and flow rate (as GHSV) on the oxidation of CH_4 (present at 5% in a standard P5 gas mixture) to CO_2 by Co_3O_4 . Data are shown for temperatures from 500-700 °C and across flow rates from 20-60 sccm ($125\text{-}375 \text{ h}^{-1}$ as GHSV).

Results from at least duplicate reactions are presented, with all concentration data representing averages (with standard deviation) from these experiments.

Generally, and as might be expected, conversion of CH_4 to CO_2 (as percent) was greatest in magnitude and sustained over longer durations at higher temperatures and lower flow rates (corresponding to trials shown toward the bottom left-hand corner of **Figure 1**). At 500 °C, for example, the duration over which CH_4 conversion to CO_2 was complete (i.e., 100% CO_2 yield) decreased from 20 (± 1) minutes to 7 (± 1) minutes as flow increased from 20 to 60 sccm. After this period of complete CH_4 conversion, a rapid decrease in CO_2 concentration in the reactor effluent occurred concomitantly with CH_4 breakthrough, indicative of an exhausted (or at least considerably less reactive) oxygen-carrier substrate over longer timescales.

Notably, these results illustrate that reduction of Co_3O_4 to CoO occurs readily at 500 °C upon exposure to CH_4 , a temperature threshold below the minimum typically proposed for CLC (~600 °C). Indeed, according to theoretical mass balance calculations [i.e., using the presumed reaction stoichiometry shown in eq. S5 in SI], the measured durations for complete CH_4 oxidation matched expectations for the mass flux of CH_4 necessary to reduce completely Co_3O_4 to CoO at each of the flow rates considered. Also consistent with these calculations, p-XRD patterns collected as a function of the extent of reaction at 500 °C illustrate the progression from Co_3O_4 to CoO along the reaction coordinate (**Figure 2a**). Thus, we ascribe the marked decrease in CH_4 oxidation over time to the lower inherent activity of CoO ; lattice O in CoO is more coordinated than in Co_3O_4 [19] and thereby not as labile for formation of O vacancy sites on the surface.

To establish the influence of temperature on Co_3O_4 performance, it is illustrative to first examine results at the highest reaction temperature considered at each flow rate (600 °C for 125

h^{-1} and $700\text{ }^{\circ}\text{C}$ for both 250 and 375 h^{-1}). At these highest temperatures, concentration profiles for CH_4 and CO_2 generally resemble those at $500\text{ }^{\circ}\text{C}$; there is an extended period of complete CH_4 conversion to CO_2 , after which CO_2 yield declines while CH_4 concentration in the reactor effluent increases to nearly influent concentration levels. While the duration of complete CH_4 conversion once again decreases with increasing flow rate [e.g., from $20 (\pm 1)$ minutes to $7 (\pm 1)$ across 125 to 375 h^{-1}], unique behavior at more elevated temperatures is the production of hydrogen gas (H_2) at intermediate timescales of reactor operation. This production of H_2 results from the cracking reaction (eq. 3), which is catalyzed by the fully reduced oxygen carrier Co metal [i.e., $\text{Co}(0)$] [20, 21]. We note that the formation of carbon, a product of the cracking reaction, was confirmed by re-oxidizing the spent (i.e., reduced) oxygen carrier in air, during which we observed formation of CO and CO_2 from surface carbon oxidation. In addition, TG analysis of re-oxidizing the spent oxygen carrier also suggests the formation of carbon (see Fig. S3 and associated discussion in SI).

Furthermore, p-XRD conducted at timescales corresponding to observations of H_2 production (as well as analysis conducted well after CH_4 breakthrough in the effluent) indicate the formation of Co as an end product of Co_3O_4 reduction, proceeding through intermediate CoO . Notably, at these elevated temperatures, H_2 formation either precedes or is concurrent to the detection of CO_2 in the reactor effluent, suggesting a substrate with multiple, distinct reactive sites for simultaneous transformation processes (i.e., oxide for CH_4 oxidation and metal for CH_4 reduction).

We also note that carbon monoxide (CO), which can be produced from the partial oxidation of CH_4 (eq. 4) [22], was only detected in trace amounts near the conclusion of these

experiments (i.e., when oxygen was no longer available from the cobalt carrier). This suggests that Co_3O_4 does not promote the partial oxidation of CH_4 , which we interpret as evidence of a relatively fast rate of oxygen release from the lattice of cobalt oxides under these operating conditions.

At intermediate temperatures (e.g., 550 °C at 125 h⁻¹ and 600 °C for 250 and 375 h⁻¹), more complex concentration profiles for CH_4 conversion to CO_2 were observed. After periods of 100% CH_4 conversion to CO_2 , subsequent decreases in CO_2 production were not monotonic. Rather, CO_2 effluent profiles exhibited an initial decrease that was offset by a later increase, which was ultimately followed by a period of relatively stable but incomplete CH_4 conversion (see regions labeled A, B, and C, respectively, in **Figure 1a**). For instance, at 550 °C and 20 sccm (or GHSV = 125 h⁻¹) full conversion of CH_4 to CO_2 and H_2O occurred over the first 20 minutes, after which CO_2 concentration in the influent sharply decreased from 20-60 min before rebounding to ~60% over the remainder of the experiment. Although the duration of complete CH_4 conversion was shortened at higher flow rates, the pattern of an initial decrease in conversion followed by a rebound in performance was still observed under these conditions.

We attribute these concentration profiles to the unique evolution of the Co substrate's oxidation state and phase over the course of the reaction progress at these intermediate temperatures. Initially, Co_3O_4 is reduced to CoO (as supported by p-XRD analysis (**Figure 2b**)), as was observed at higher temperatures. This phase change corresponds to the initial loss in CH_4 conversion because CoO is a less reactive oxygen carrier, as we previously noted. The subsequent rebound or increase in CH_4 conversion coincides with a period when not only CoO but also Co metal is produced from Co_3O_4 reduction, as detected via p-XRD (**Figure 2b**) and

consistent with observed H_2 formation via methane cracking over the same timescales. Thus, it appears that the formation of Co metal produces a mixed solid phase (along with CoO and residual Co_3O_4) with lattice oxygen more prone to release, leading to the rebound in CH_4 conversion. To better understand this phenomenon, additional experiments were conducted simultaneously evaluating the surface and bulk chemical composition of CoO and Co_3O_4 during oxidation of CH_4 .

3.3. Characterization of CoO Surface and Bulk Composition during CH_4 Oxidation.

Results pertaining to CH_4 oxidation on CoO are shown in **Figure 3a**, collected using the same experimental conditions as those used in experiments with Co_3O_4 . Initially, as expected given its poorer performance as an oxygen carrier, very little conversion of CH_4 occurred on CoO (i.e., 75% of influent CH_4 was present in the effluent of the reactor at our initial sampling point of ~5 min). However, as with Co_3O_4 performance at this intermediate temperature, this initial decrease in reactivity was followed by a more sustained period of improving CH_4 conversion, with effluent CH_4 levels decreasing from ~90% to ~5% of the influent between 20 and 60 min of reactor operation. This decrease in effluent CH_4 was matched by a corresponding increase in effluent CO_2 over this same time period, suggesting that CH_4 loss resulted from its oxidation to CO_2 by the substrate. Finally, at the longest timescales considered (beyond 60 min), although CH_4 in the effluent remained low, there was a shift in the product distribution from CO_2 (the oxidation product) to H_2 (the product of methane cracking) as would be expected for the near complete transformation of CoO to metallic Co.

The increase in CH_4 conversion from 20 to 60 min coincides clearly with the formation of Co metal, with p-XRD analysis revealing diffraction lines for both Co metal and CoO after 45 min of reaction (**Figure 3b**) when near-peak system performance was achieved (with over 90%

CH₄ conversion to CO₂). Because Co metal cannot participate in the oxidation of CH₄ to CO₂, it was unexpected to see its formation promote reaction. We are left to conclude, as we inferred from results with Co₃O₄, that a mixed phase containing CoO with metallic Co inclusions possesses lattice oxygen more easily released for CH₄ oxidation relative to pure CoO. We hypothesize that lattice oxygen adjacent to metallic Co produced via CoO reduction is more reactive due to its lower cohesion energy relative to that initially present in CoO.

A common mechanism proposed for oxygen carrier structural evolution during the CLC process is a core-shell model, where products of oxygen carrier reduction form a thin layer, or shell, on the particle surface, with the shell increasing in thickness as the extent of reaction increases. Because Co metal cannot directly oxidize CH₄ to CO₂, it is unlikely such a model is at play in the CoO system as a metallic core would effectively inhibit, not promote, CO₂ formation over time. In fact, corresponding XPS analysis (**Figure 3c**) suggests that metallic Co is only detectable on the substrate surface over very long reaction timescales (most clearly after 90 min), at which point H₂ from CH₄ cracking is the major reaction product. Specifically, the 2p_{3/2} signal with features at 780.8 and 778.8 eV is assigned to CoO and Co metal, respectively [23]. This is in contrast to corresponding p-XRD data, which indicates the formation of metallic Co at earlier times.

Evidence from material characterization suggests, therefore, that formation of metallic Co occurs first in the particle bulk, rather than the surface. Accordingly, initially low rates of oxygen release at the beginning of the reaction correspond to the required time to generate and propagate new reactive sites within the substrate [24-26]. Presumably, as these clusters of metallic Co grow in the particle bulk, oxygen at their interface becomes more labile for CH₄ oxidation to CO₂.

Only after extensive, prolonged conversion of CoO does metallic persist on the particle surface, allowing it to promote CH₄ cracking to H₂.

3.4. Characterization of Co₃O₄ Surface and Bulk Composition during CH₄ Oxidation.

Guided by insights from experiments with CoO, analogous complementary analyses of bulk and surface composition were also conducted with Co₃O₄ during reaction with CH₄ at 40 sccm and 700 °C (**Figure 4**). **Figure 4a** reveals the evolution of cobalt oxides phases over time, with persistence of Co₃O₄ in the particle bulk (from p-XRD) over 30 minutes of reaction. Also over this period, both CoO and metallic Co were detected in the bulk of the substrate as early as 15 min into the reaction.

Materials characterization data for Co₃O₄ systems further support the release of lattice oxygen following a nucleation and nuclei growth [27] rather than a core-shell model. As with CoO, concurrent XPS analysis suggests that the reactive substrate surface evolves in a manner distinct from the particle bulk. XPS data of the Co 2p binding energy region (**Figure 4b**) indicate the presence of only Co(II) and Co(III) on the particle surface after 30 minutes of reaction, over which conversion of CH₄ to CO₂ was complete (i.e., 100% conversion). Specifically, the 2p_{3/2} signal at 780.1 eV can be fitted as the sum of two peaks commonly assigned to Co(III) and Co(II) present in Co₃O₄ [23, 28-30]. There is also another peak at 795.0 eV attributable to the 2p_{1/2} signal of these two oxidation states, as well as two associated satellite peaks at 787.3 and 803.3 eV [31, 32]. Co 2p_{3/2} and 2p_{1/2} signals of CoO are typically around 1 eV higher than that of Co₃O₄ [33], which explains the observed shift in the peaks in XPS spectra with time. The Co 2p_{3/2} metal signal, present as a shoulder at a binding energy 778.8 eV [23], first appears on the particle surface after 45 minutes of reaction. Finally, after 60 minutes of reaction, effluent CO₂ concentration had fallen to zero, and XPS revealed mainly metallic cobalt based on its

characteristic Co 2p_{3/2} and 2p_{1/2} signals at 778.8 and 793.8 eV, respectively [23]. Taken together, results from bulk (p-XRD) and surface (XPS) analysis suggest that a restructuring of the CoO phase occurs during reaction, pushing lattice oxygen molecules from the particle bulk to the particle surface, thereby maintaining the surface at a higher average oxidation state than the bulk.

Given the importance of lattice oxygen in CH₄ oxidation, we also explored the O (1s) region in XPS spectra. The oxygen binding energy region of the as received samples exhibits a wide peak which can be described as the sum of four peaks (not shown here) with maxima at 530.2, 530.8, 531.8, and 532.2 eV. These peaks are typically assigned to oxygen lattice atoms, hydroxyl groups, the oxygen–carbon bond in surface carbonate species [34, 35], and adsorbed water [36], respectively. As show in **Figure 4c**, the oxygen peak is reduced in magnitude after 15 minutes of reaction while also growing a shoulder peak around 532.2 eV due to an increase in the carbonate species and adsorbed water produced via the CH₄ oxidation reaction. After 60 minutes of the reaction, the O peak is almost entirely diminished, leaving only a small peak due to adsorbed water and carbonate species. We note that the persistence of a small amount of surface oxygen on spent substrates (those reacted for 60 minutes, corresponding to when CO₂ formation was zero) is consistent with our hypothesis about bulk oxygen being primarily depleted for oxidation, while higher oxidation states persist at the surface. However, we also cannot rule out a trace surface oxidation that may have occurred during sample preparation and analysis. Finally, XPS analysis of the C (1s) region of both samples (Fig S4) revealed a sharp increase in the carbon peak at 285 eV by the conclusion of the reaction, which we attribute to the formation and deposition of carbon on the surface as a result of the cracking reaction.

3.5. Mechanistic Insights and Practical Implications for Cobalt Oxides in CLC Process.

Key indicators for Co_3O_4 use in CLC applications are summarized in **Figure 5**, which illustrates the duration (in minutes) over which complete conversion of CH_4 to CO_2 (i.e., 100% yield) was observed (**Figure 5a**) and the corresponding percentage (on a molar basis) of lattice oxygen utilized over this time period (**Figure 5b**). Data in **Figure 5a** estimate the substrate residence time in the reactor before it would need to be regenerated (otherwise incomplete CH_4 conversion would occur), while **Figure 5b** assesses the extent of lattice oxygen utilization over this residence time.

Generally, the timescale for 100% CO_2 yield is maximized at higher temperatures and lower flows, ranging from a maximum interval of 80 min to a minimum under 10 min for the reactor conditions explored (**Figure 5a**). Perhaps more notable are trends in lattice oxygen utilization. For example, while reduction of Co_3O_4 to CoO occurred at 500 °C, mass balance estimates suggest only a small fraction of lattice oxygen (~20 %) is available under these conditions. Increasing the reaction temperature to 600 °C results in far more complete utilization of Co_3O_4 lattice oxygen (~80%), albeit at low flow rates (20 sccm), whereas near-complete utilization of lattice oxygen (~80%) is observed at 700 °C regardless of flow rate.

In combination with our materials characterization results, these data help to establish the rate-limiting step in CH_4 oxidation on Co_3O_4 in our experimental systems. Breaking of the Co-O bond appears to be, at least in part, rate determining, where increasing temperature promotes oxygen release from the substrate. Because characterization suggests that reduction of Co_3O_4 and CoO occurs preferentially in the bulk of the particle, migration of oxygen from the particle bulk to the surface may also limit CH_4 oxidation, as the rate of this migration would also be expected to increase with temperature. Our data illustrate that the rate of CH_4 oxidation is also increased on mixed CoO and Co metal phases (e.g., see **Figure 3**). We propose that the Co-O bonds in

such mixed phases are less stable, and thus easier to dissociate at lower temperature, which would explain the increase in CH₄ oxidation observed with increasing Co metal content at 500 °C.

Additional tests considered more practical aspects associated with the use of Co₃O₄ in CLC. Table 1 considers particle stability during multiple substrate reduction/oxidation cycles, including BET surface area and average size of the particles after five to ten CLC cycles. The duration of the reaction in these trials corresponded to the observed duration of 100% CO₂ yield, thereby avoiding the formation of any residual surface carbon from the cracking reaction. Substrate regeneration was examined using reduction and oxidation cycles performed at the same temperatures and durations. Generally, under these conditions, Co₃O₄ particles exhibited reversible reduction/oxidation through all CLC cycles (see Fig. S5 in SI) and sustained reactivity toward CH₄ (i.e., 100% CO₂ yield) across all of the cycles noted in Table 1.

Despite sustained and re-generable use, we note that there were clear changes in particle characteristics in response to repeated cycling. For example, simply heating the Co₃O₄ nanoparticles (at 600 °C followed by cooling under an air stream without exposure to CH₄) altered particle surface area and particle size. For these heated (but unreacted) samples, BET surface area and projected area diameter calculated from SEM images (Fig S6-a in SI) changed considerably (4.8 ± 0.2 m²/g and 127 ± 43 nm, respectively) relative to as received values (26 ± 1 m²/g and 50 ± 10 nm, respectively). Similarly, characterization of reacted oxygen carriers after 5 to 10 cycles at 600 and 700 °C revealed a large reduction in particle surface area, producing values < 0.6 m²/g in all cases. Likewise, the projected area diameter from SEM images of these reacted Co₃O₄ substrates decreased to ≤ 0.5 (± 0.2) and (1 ± 0.5) micron respectively (e.g., see Figure S6-b and S6-c in SI). These marked reductions in surface area and particle size were due

to the agglomeration and sintering of the Co_3O_4 nanoparticles at high temperatures (above 600 °C). Thus, these results highlight the need to use Co_3O_4 nanoparticles in the CLC process at temperatures below these values (e.g., 500 °C) or in a supported platform that helps to minimize agglomeration during use.

4. CONCLUSIONS

Herein, we explored the feasibility of using Co_3O_4 as a solid state oxygen carrier in the CLC process. For commercial Co_3O_4 nanoparticles, we observed the rate and extent of CH_4 oxidation to CO_2 to be greatest at higher temperatures (700 °C) and lower flow rates (20 sccm), conditions that promoted the near-complete utilization of lattice oxygen within Co_3O_4 prior to breakthrough of CH_4 in the reactor effluent. Through complementary material characterization, CH_4 oxidation coincided with the reduction of Co_3O_4 to CoO , and ultimately metallic Co , at all temperatures, even those (e.g., 500 °C) below the range typically proposed for CLC (600 - 1200 °C). This phase transition was reversible via air oxidation of spent substrates, as we demonstrated for Co_3O_4 through repeated reduction-oxidation cycles to simulate the CLC process, during which sustained CH_4 conversion was observed.

At lower operating temperatures, which may be desirable for limiting the associated energy demand of the CLC process, we observed rates of CH_4 oxidation to vary non-linearly in response to phase changes in Co_3O_4 along the reaction coordinate. This behavior is attributed to the preferential reduction of CoO to metallic Co within the particle bulk rather than at the particle surface, which produces new, more reactive oxygen sites at the interface of these phases according to a traditional nucleation and nuclei growth model. Fundamentally, we attribute the greater reactivity of lattice oxygen at the CoO-Co phase boundary to a lower degree of cohesive energy, which makes the cobalt-oxygen bond more prone to dissociation and migration to the

substrate surface to participate in CH₄ oxidation. More practically, the preferred initial formation of Co in the particle bulks is also significant, as it helps to suppress the CH₄ cracking reaction (i.e., reduction of CH₄ to unwanted byproducts C and H₂) until much further along the reaction coordinate when metallic Co is finally persists on the particle surface. Finally, extending these findings beyond the Co₃O₄ system, the greater reactivity of mixed metal-metal oxide phases toward CH₄ may indicate a promising new class of solid-state oxygen carriers better suited for low temperature CLC applications, a proposal that merits further investigation.

For Co₃O₄ application at higher temperatures, despite high and sustained yields of CO₂, challenges related to nanoparticle application remain. These include loss of reactive surface area from extensive nanoparticle agglomeration and sintering. Thus, for high temperature applications, addition of an appropriate binder [37, 38] or use of supported catalysts may be necessary to prevent changes in the physicochemical structure of Co₃O₄ particles that are likely to inhibit their in the CLC process as oxygen carriers.

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Table and Figures

Table 1. Conditions of oxygen carrier stability tests and results of material characterization conducted after cycling experiments.

Case #	T (°C)	Flow rate (sccm)	Reaction durations (min)	No. of cycles	Total operational time (h)	BET Surface Area (m ² /g)	Particle size (micron)
1	600	20	60	5	11	0.6	0.5 ± 0.2
2	600	40	10	10	4.5	0.5	0.5 ± 0.2
3	700	40	35	5	7	0.4	1 ± 0.5
4	700	60	20	5	4.5	0.5	1 ± 0.5

Figure 1. Concentration profiles for methane, carbon dioxide, and hydrogen during reaction with Co_3O_4 at (a) 20 sccm (GHSV = 125 h^{-1}), (b) 40 sccm (GHSV = 250 h^{-1}), and (c) 60 sccm (GHSV = 375 h^{-1}). Profiles are shown as a function of temperature (as indicated). Error bars represent standard deviation of values from triplicate experiments.

Figure 2. p-XRD of Co_3O_4 before and after reaction with P5 (i.e., 5% CH_4) at a flow rate of 40 sccm and a temperature of (a) 500 °C, and (b) 600 °C. Diffraction patterns show evolution of particle phase over time, with diffraction lines of reaction products CoO , and Co indicated.

Figure 3. (a) Concentration profiles for methane, carbon dioxide, and hydrogen for reaction of P5 (i.e., 5% methane) with CoO at 40 sccm ($\text{GHSV} = 250 \text{ h}^{-1}$) and 600 °C. Vertical dashed lines show various regions of reactivity corresponding to evolution of particle phase, as described in the text. (b) p-XRD of CoO as a function of reaction time, showing evolution of Co metal (as noted) with reaction progress. (c) XPS spectra of the cobalt ion region (2p) as a function of reaction time, revealing low binding energy Co metal peak on the substrate surface only after extended periods of reaction.

Figure 4: Materials characterization of Co_3O_4 as a function of reaction time with P5 (i.e., 5% methane) at 40 sccm (GHSV = 250 h^{-1}) and 700°C . Shown are results of (a) bulk characterization via p-XRD and surface characterization via XPS of the (b) Co 2p, and (c) O 1s regions.

Figure 5. Effect of increasing reactor flow rate on (a) the duration over which methane oxidation on Co₃O₄ results in complete CO₂ conversion (i.e., 100% yield) and (b) the percentage of O₂ released from Co₃O₄ (on a molar basis based on mass balance calculations) during this period of 100% CO₂ yield. Data are shown as a function of reaction temperature. Error bars represent standard deviation from triplicate measurements.

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