



Research paper

Bifunctional Co- and Ni- ferrites for catalyst-assisted chemical looping with alcohols



N.V.R. Aditya Dharanipragada^a, Vladimir V. Galvita^{a,*}, Hilde Poelman^a, Lukas C. Buelens^a, Christophe Detavernier^b, Guy B. Marin^a

^a Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052, Ghent, Belgium

^b Department of Solid State Sciences, Ghent University, Krijgslaan 281, S1, B-9000, Ghent, Belgium

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ABSTRACT

Ferrite materials were applied for catalyst-assisted chemical looping with two different alcohol fuels, methanol and an ethanol-water mixture (1:1 mol ratio), at 550 °C and 750 °C respectively. CO₂ was used for reoxidation, resulting in the production of CO. The structural characteristics, CO formation and stability of a range of x CoFe₂O₄/NiFe₂O₄ (x = 20 – 100 wt%) modified with CeZrO₂ were investigated through STEM and in situ XRD. Crystallographic changes during two consecutive H₂-TPR and CO₂-TPO cycles were followed using in situ XRD. Further, the long term stability was assessed during one hundred isothermal chemical looping redox cycles using H₂ for reduction and CO₂ for reoxidation. The 20 wt% CoFe₂O₄ material could be reduced and reoxidized to the as prepared state without loss in oxygen storage capacity. In 80 wt% CoFe₂O₄ however, deactivation due to phase segregation into Co and Fe₃O₄ along with material sintering occurred. On the other hand, all NiFe₂O₄ materials modified with CeZrO₂ suffered from sintering as well as phase segregation into separate Ni and Fe₃O₄ phases, which could not be restored into the original spinel (NiFe₂O₄) phase. During chemical looping with methanol, carbon formation was observed on CoFe₂O₄/NiFe₂O₄ ferrites modified with CeZrO₂. 20 wt% CoFe₂O₄ was the best performing material with a CO yield of ~40 mol CO kg⁻¹_{CoFe₂O₄}, i.e. almost twice the theoretical amount. This high CO yield was ascribed to the oxidation of carbon formed upon material reduction. During chemical looping with the ethanol-water mixture however, the CO yield remained low (~13 mol CO kg⁻¹_{CoFe₂O₄}) because of incomplete conversion of CH₄ and water. A pre-catalyst bed configuration for complete conversion of CH₄ and water is proposed.

1. Introduction

Since the industrial revolution, human dependence on fossil fuels has increased exponentially. This has resulted in increased emission of greenhouse gases like CO₂ and CH₄, which contribute to global warming [1,2]. Hence, there is a need to minimize our dependence on fossil fuels and to shift towards more clean energy sources [3,4]. The potential technologies which can achieve this reduction in greenhouse gas emission by minimizing the consumption of fossil fuels are fuel cell driven processes. Fuel cells are the most efficient way of directly converting chemical energy to electrical energy. The most common fuel cells are based on proton conducting electrolytes (PEMFC: proton-exchange membrane fuel cell), which require high purity hydrogen as fuel. Solid oxide fuel cells (SOFCs) on the other hand are fuel flexible and can oxidize essentially any fuel containing a mixture of hydrocarbons and even carbon, because the electrolyte transports an oxygen

ion. SOFCs capability of achieving high power densities is based on oxygen-ion conductors that operate at high temperature. Over the past decade, considerable progress has been achieved in bringing down the working temperature to an intermediate range between 350 °C–700 °C [5–7] and in reaching high stability of the anode under fuels other than hydrogen [8–10]. It has been established that even CO can be used as a fuel in SOFCs [8,11–14].

The latter can be generated from renewable fuels (biogas and bio-ethanol) and carbon dioxide through dry reforming. An attractive alternative process which can produce CO from CO₂ for SOFC technologies is chemical looping [15–17]. This is a two-step cyclic process where in the first step, an oxygen storage material is reduced by fuel (Fig. 1). In the second step, CO₂ is used for reoxidation to regenerate the material resulting in production of CO, which can serve as fuel for the SOFC. Iron oxides are the most widely preferred oxygen carriers in chemical looping CO₂ utilization, due to their redox activity with CO₂,

* Corresponding author.

E-mail address: Vladimir.Galvita@UGent.be (V.V. Galvita).

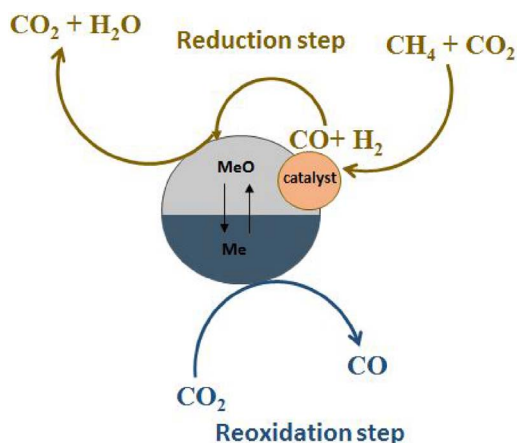


Fig. 1. Catalyst-assisted chemical looping using a bifunctional material.

high oxygen storage capacity, abundant availability and environmentally friendly nature [18–22]. When natural hydrocarbon containing feeds (e.g. biogas, $\text{CH}_4 + \text{CO}_2$) are employed for reduction, the overall production of CO is determined by the kinetics of the slower step, i.e. the reduction of iron oxide with CH_4 [23–26]. The presence of CO_2 in the feed and product stream slows down the reduction rate. In order to improve the kinetics of this step, an extra catalyst component (e.g. Ni, Co) can be added to the oxygen storage material to first convert CH_4 [24,27,28].

Addition of such a catalyst component to the iron oxide assists in CH_4 conversion to CO and H_2 through catalytic dry reforming. Subsequently, this mixture of $\text{CO} + \text{H}_2$ reduces the iron oxide oxygen storage material, producing CO_2 and H_2O (Fig. 1). The material thus acts both as an oxygen carrier and as a catalyst, hence it is termed bifunctional material and the process is called catalyst-assisted chemical looping [24,29].

In view of designing materials with both catalytic and oxygen storage properties, ferrites can be of interest as they offer both these properties. They have Co or Ni as a catalyst component and an oxygen storage component in the form of Fe. Moreover, ferrites are widely used as bifunctional materials due to their high oxygen storage capacity, easy reducibility ($350\text{ }^\circ\text{C}$ – $550\text{ }^\circ\text{C}$) [30,31]. To improve the stability of the Co- and Ni-ferrites, which tend to deactivate rapidly, promoter elements can be added. Among the promoter candidates, CeZrO_2 stands out as it shows high stability along with redox activity in a CO_2 environment and also possesses desired mechanical properties [32].

As for chemical looping fuel, feedstocks containing alcohols, especially methanol and ethanol, are promising towards clean energy production due to their high hydrogen to carbon ratio, easy biomass derivability, high energy density as liquid fuel and easy storage [33–35]. Both methanol and ethanol have been applied as fuel in chemical looping over ferrite materials towards high purity hydrogen production [30,31,36–38].

In the present study, the applicability of CeZrO_2 modified Ni- and Co-ferrites in catalyst assisted chemical looping with ethanol, ethanol-water and methanol for CO_2 conversion to CO has been investigated. In the first step, methanol or ethanol are used as reducing agents. Methanol decomposes into CO and H_2 , whereas ethanol decomposes into CH_4 in addition to CO and H_2 . The decomposition reactions are enabled by the catalyst component. The mixtures of $\text{CO} + \text{H}_2$ or $\text{CH}_4 + \text{CO} + \text{H}_2$ reduce the oxygen storage component, thereby being converted to CO_2 and H_2O . The amount of CO that is produced in the second step of chemical looping, depends on the oxygen storage capacity and the degree of reduction that can be achieved in the first step. Therefore, this investigation is focused on the assessment of material stability and activity of CeZrO_2 promoted ferrite materials towards catalyst assisted chemical looping processes.

2. Experimental procedures

2.1. Material preparation

Ferrite materials with varying loadings ($x\text{CoFe}_2\text{O}_4/\text{NiFe}_2\text{O}_4 - \text{CeZrO}_2$, $x = 20, 50, 80$ and $100\text{ wt}\%$) were synthesized by means of coprecipitation. The following precursors were used: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.99 + %, Sigma-Aldrich[®]), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich[®]), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich[®]), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich[®]) and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich[®]). The pH was controlled by dropwise addition of NH_4OH under stirring. The precipitate obtained was recovered and dried in an oven at $120\text{ }^\circ\text{C}$ for 12 h. All materials were then calcined at $650\text{ }^\circ\text{C}$ for 6 h and at $750\text{ }^\circ\text{C}$ for the chemical looping process with ethanol. The ferrite materials modified with CeZrO_2 are represented as $x\text{wt}\% \text{CoFe}_2\text{O}_4/\text{NiFe}_2\text{O}_4$, where x represents the ferrite loading.

2.2. Characterization: x-Ray diffraction (XRD), scanning transmission electron microscopy (STEM) and brunauer–Emmett–Teller (BET)

The crystalline phases were determined using a Siemens Diffractometer Kristalloflex D5000, with $\text{Cu K}\alpha$ ($\lambda = 0.154\text{ nm}$) radiation. The XRD patterns were collected in a 2θ range from 10° to 80° with a step of 0.04° . The crystallite size was calculated using the Scherrer equation by fitting a Gaussian function to the four most intense characteristic peaks to obtain the peak width at half maximum.

Morphological and local elemental analysis were performed using a JEOL JEM-2200FS: Cs-corrected, operated at 200 kV, equipped with a Schottky-type field-emission gun (FEG), EDX JEOL JED-2300D and JEOL in-column omega filter (EELS). Specimens were prepared by immersion of a lacey carbon film on copper support grid and particles sticking to the grid were investigated. Elemental mapping was performed by EDX. A beryllium specimen retainer was used to remove secondary X-ray fluorescence.

The Brunauer–Emmett–Teller (BET) surface area was determined by N_2 adsorption (five point BET method) using a Micromeritics Gemini 2360. Before carrying out the experiment, samples were outgassed for 3 h at $200\text{ }^\circ\text{C}$ in order to remove the adsorbates.

2.3. Redox properties

The redox properties of the ferrite materials were investigated using in situ XRD and conventional TPR-TPO techniques. The phase changes during the redox processes were identified using in situ XRD and the bulk consumption was monitored using conventional TPR-TPO. Finally, the phase transformations were correlated to bulk consumption. The total amount of available oxygen is tabulated below.

2.3.1. In situ X-Ray diffraction (XRD) analysis

The crystallographic transformations during H_2 -TPR and CO_2 -TPO were followed by in situ XRD (Bruker-AXS D8 Discover) with $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154\text{ nm}$). The setup consisted of a homebuilt reaction chamber with a Kapton foil window for X-ray transmission and a linear Vantec detector covering 20° with an angular resolution of 0.1° in 2θ . Approximately 10 mg of powder was spread on a single crystal Si wafer. No interaction between the Si wafer and sample was observed. Prior to the start of experiment, the chamber was pumped down to a base pressure of 5 Pa and purged with helium. 10 mol% H_2/He and pure CO_2 were employed for reduction and oxidation treatment. All gas flows were maintained at 30 Nml/s.

A uniform ramp rate of $20\text{ }^\circ\text{C}/\text{min}$ up to a temperature of $700\text{ }^\circ\text{C}$ was used during H_2 -TPR and CO_2 -TPO. Full XRD scans (10° to 65° with a step of 0.1°) were performed after each H_2 -TPR and CO_2 -TPO at room temperature under helium flow. The materials were subjected to repeated redox treatments, with two cycles of H_2 -TPR and CO_2 -TPO to study the phase transformations during these treatments.

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