Evaluating the reactivity of CuO-TiO$_2$ oxygen carrier for energy production technology with CO$_2$ capture

Avaliação da reatividade do Transporta Sólido de Oxigênio CuO-TiO$_2$ para tecnologia de produção de energia com captura de CO$_2$

Evaluación de la reactividad del portador de oxígeno CuO-TiO$_2$ para la tecnología de producción de energía con captura de CO$_2$

Abstract

Chemical looping combustion (CLC) processes have been shown to be promising and effective in reducing CO$_2$ production from the combustion of various fuels associated with the growing global demand for energy, as it promotes indirect fuel combustion through solid oxygen carriers (SOC). Thus, this study aims to synthesize, characterize and evaluate mixed copper and titanium oxide as a solid oxygen carrier for use in combustion processes with chemical looping. The SOC was synthesized based on stoichiometric calculations by the polymeric precursor method and characterized by: X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM-FEG) with EDS, and Programmed Temperature Reduction (PTR). The oxygen carrying capacity (ROC) and the speed index of the reduction and oxidation cycles were evaluated by Thermogravimetric Reactivity (TGA). The main reactive phase identified was: The CuO phase for the mixed copper and titanium oxide were identified and confirmed by X-ray diffraction using the Rietveld refinement method. The reactivity of the CuO-TiO$_2$ system was high, obtaining a CH$_4$ conversion rate above 90% and a speed index of 40%/min. Due to the structural characteristics and the reactivity tests of this material, it is concluded that mixed copper and titanium oxide have the necessary requirements to be used in chemical looping combustion (CLC) processes.

Keywords: CO$_2$ capture; Chemical looping combustion; Solid oxygen carriers; CuO-TiO$_2$ system.

Resumo

Os processos de combustão por recirculação química (CRQ), tem-se mostrado promissor e eficiente na diminuição da produção de CO$_2$ proveniente da combustão de diversos combustíveis , associada à demanda global crescente de
energia, pois promove a combustão indireta do combustível por meio de transportadores sólidos de oxigênio (TSO). Desta forma, este estudo tem como objetivo sintetizar, caracterizar e avaliar o óxido misto de cobre e titânio como transportador sólido de oxigênio para utilização em processos de combustão com recirculação química. O TSO foi sintetizado com base em cálculos estequiométricos pelo método dos precursors poliméricos e caracterizados por: Fluorescência de raio X (FRX), Difração de raio X (DRX), Microscopia Eletrônica de Varredura (MEV-FEG) com EDS, Redução à Temperatura Programada (RTP). A capacidade de transporte de Oxigênio (Roc) e o índice de velocidade dos ciclos de redução e oxidação foram avaliados por Reactividade por Termogravimetria (TGA). A principal fase reativa identificadas foi: A fase CuO para o óxido misto de cobre e titânio foram identificadas e confirmadas por Difractometria de raio X utilizando o método de refinamento Rietveld. A reatividade do sistema CuO-TiO₂ foi elevada, obtendo uma conversão de CH₄ acima de 90% e índice de velocidade de 40% /min. Pelas características estruturais e pelos testes de reatividade desse material, conclui-se que o óxido misto de cobre e titânio possuem os requisitos necessários para serem utilizados nos processos de combustão por recirculação química (CLC).

Palavras-chave: Captura de CO₂; Combustão por recirculação química; Transportadores sólidos de oxigênio; Sistema CuO-TiO₂.

1. Introduction

Climate change has caused significant impacts on natural and human systems on all continents and across the oceans in recent decades, and a large part of these changes are caused by one of the environmental issues that most concern humanity: the intensification of global warming. Due to the increase in CO₂ emissions, the new IPCC report (2021) states that the global temperature temporarily exceeds or surpasses 1.5°C and no longer 2°C as described at COP21 in 2015 (International Energy Agency, 2019; IPCC, 2018; Page et al., n.d.).

Due to the huge dependence on the use of fossil fuels in generating energy, CO₂ Capture and Storage (CCS) technologies have emerged as an important option to reduce global CO₂ emissions. In order to achieve this goal, Chemical Looping Combustion (CLC) has emerged as a promising technology for CO₂ capture in power plants and industrial applications, with low energy penalties compared to other competing CO₂ Capture and Storage (CCS) techniques (Juan Adánez & Abad, 2019). The CLC process scheme is shown in Figure. 1.
CLC technology describes cyclic redox processes between two interconnected reactors, as shown in Figure 1, and its principle is the use of a metal oxide (MeOx), known as a solid oxygen carrier (SOC), to transfer the necessary oxygen from the air (Reaction 1) and oxidize the fuel into CO₂ and H₂O (Reaction 2) in order to avoid direct contact between the air and the fuel. Its main advantage is the inherent CO₂ capture, bypassing the energy penalty.

\[
\text{Me}_x\text{O}_{y-1} + 1/2\text{O}_2 \rightarrow \text{Me}_x\text{O}_y \quad \text{(Reaction 1)}
\]
\[
(2n+m)\text{Me}_x\text{O}_x + \text{C}_n\text{H}_{2m} \rightarrow (2n+m)\text{Me}_x\text{O}_{y-1} + m\text{H}_2\text{O} + n\text{CO}_2 \quad \text{(Reaction 2)}
\]

Correctly selecting the solid oxygen carrier (SOC) is the key to proper functioning of the chemical looping combustion system. This carrier must have favorable thermodynamics and stability through several reduction/oxidation cycles, high oxygen carrier capacity, high fuel conversion with selectivity for the intended product, zero or low carbon deposition, good mechanical properties in fluidized beds, not present agglomeration and still be of low cost to obtain and be environmentally safe. Based on these characteristics, some possible oxides (such as oxides based on Ni, Fe, Cu, Co and Mn) supported in inert materials (such as SiO₂, Al₂O₃, TiO₂, ZrO₂) were evaluated to improve their reactivity and lifetime of solid oxygen carriers (J. Adánez et al., 2018a). In our previous works we evaluated other systems such as La₂NiO₄, NiO-Fe₂O₃/MgAl₂O₄, Mg₆MnO₈ and Mn₂O₃-MgAl₂O₄, in which we observed new structural characteristics that helped to develop and study new materials and processing forms (Costa et al., 2021; Medeiros et al., 2017, 2020; Melo et al., 2018; Nascimento et al., 2020).

In the literature, solid oxygen carriers based on Cu and TiO₂ have good reaction rates and much higher oxygen carrier capacity than other carriers based on Fe and Mn, in addition to not having thermodynamic restrictions for complete conversion of fuel to CO₂ and H₂O. In addition, TiO₂ has been used as an inert support, which can increase the reactivity of oxygen carriers by increasing porosity, surface area and mechanical strength. Moreover, copper is cheaper than other materials used for CLC such as nickel and cobalt, and its use in oxygen carriers has fewer environmental problems (J. Adánez et al., 2018a; Tian et al., 2018; Tijani et al., 2018; Xu et al., 2015).

Therefore, in order to contribute to the development of materials for CLC technology aiming to evolve to industrial applications, this work aims to evaluate the reactivity of the CuO-TiO₂ system as a solid oxygen carrier.
2. Method

2.1 Preparation of oxygen carriers

The solid oxygen carrier CuO-TiO$_2$ (named TCu) was prepared by stoichiometric calculations by the polymeric precursor method (M.P. Pechini, 1967) using copper nitrate III - Cu(NO$_3$)$_2$.3H$_2$O (VETEC, PA = 99%), titanium isopropoxide - C$_{12}$H$_{28}$O$_4$Ti (ALFA AESA, PA = 97.5%), ethylene glycol - HOCH$_2$CH$_2$OH (SYNTH, PA = 99%) and citric acid - C$_6$H$_{10}$O$_8$ (SYNTH, PA = 99%). The synthesized material has a particle size range between 100 and 300 µm to be used in the reactivity test.

The citric acid was first dissolved in distilled water heated to 80°C in a beaker. The solution was subjected to constant stirring for 30 minutes. After the acid had dissolved, copper II nitrate was slowly added to produce the mixed copper and titanium oxide. Ethylene glycol was subsequently added for solution polymerization under 1 hour of agitation and a temperature of approximately 110°C, forming a polymeric gel. The resins obtained in the syntheses were initially subjected to a thermal treatment in a dryer at 100°C for 24 hours to evaporate excess water. Then, the resins were calcined in a muffle furnace at 350°C for 2h at a rate of 5°C/min to eliminate organic components. The obtained powders were then calcined in an oven at 900°C for 4 h at a heating rate of 10 °C/min in order to achieve high mechanical strength.

The composition of the calcined TCu SOC was determined by X-ray fluorescence. Table 1 shows the XRF analysis results of the mixed copper and titanium oxide (TCu) with the percentages by mass.

| Sample/Composition | TiO$_2$ | Fe$_2$O$_3$ | CuO | MnO | SiO$_2$ | Al$_2$O$_3$ | Na$_2$O | MgO | outros |
|--------------------|--------|------------|-----|-----|--------|------------|--------|-----|--------|
| TCu                | 72.68  | 0.16       | 22.86 | 0.5 | 1.58   | 1.29       | -      | -   | 0.93   |

Source: Authors (2021).

2.2 Characterization of the solid oxygen carrier

Physical and chemical characterizations were performed on the solid oxygen carrier particles. The SOC chemical composition was determined by X-ray fluorescence in a Bruker S2 Ranger instrument using Pd or Ag anode radiation, maximum power of 50 W, maximum voltage of 50 kV, maximum current of 2 mA, and a XFlash® Silicon Drift Detector. The crystalline chemical phases were detected by X-Ray Diffraction (XRD) using a Shimadzu XRD-7000 X-ray diffractometer with Cukα radiation (λ = 1.5409 Å). The Joint Committee on Power Diffraction Standards (JCPDS) was used to designate the crystalline phases with the Inorganic Crystal Structure Database (ICSD) database. The refinement of the structure was carried out by applying the Rietveld treatment (Rietveld, 1969), using the MAUD software program.

The temperature programmed reduction (TPR) profile of the SOC was evaluated on a Micromeritics AUTOCHEM II 2920 equipped with a TCD (Thermal Conductivity Detector). The analyzes were performed by varying the temperature from 100 to 900°C under a flow of 50 mL.min$^{-1}$ of a mixture of 10% H$_2$ in Argon. It was then possible to estimate the oxygen carrier capacity of metal oxides (RO) through the consumption of H$_2$ according to the equations below.

\[ C_{H_2} (\text{mol}) = C_{H_2} \left( \text{cm}^3 \text{g}^{-1} \right) \times 1 \text{ml} \times \frac{1L}{1000 \text{ml}} \times \frac{1\text{mol}}{22.4L} \quad (\text{Equation 1}) \]

\[ RO = \frac{m_{\text{oxi}} - m_{\text{red}}}{m_{\text{oxi}}} = \frac{\Delta m}{m_{\text{oxi}}} \quad (\text{Equation 2}) \]
\[
\Delta m = C_{H_2} \text{(mol)} \times \frac{16g}{\text{mol}} \\
R_{\text{OC}} = X_{\text{TO}} \times R_{\text{O}}
\]

In which: \(C_{H_2} \text{(mol)}\) represents the \(H_2\) consumption by mol, \(C_{H_2} \text{(cm}^3\text{g)}\) is the volume of \(H_2\) consumed experimentally, \(m_{\text{ox}}\) and \(m_{\text{red}}\) is the mass of the solid oxygen carrier when it is fully oxidized and reduced, respectively, ROC is the oxygen carrying capacity of the materials, XTO is the fraction of active phases present in the carrier. The morphology and distribution of the CuO and TiO\(_2\) phases in the solid was evaluated by scanning electron microscopy (SEM) on a SHIMADZU SSX-550 microscope with a voltage of 15KV, equipped with an Oxford Link-Isis energy dispersive X-ray spectroscopy (EDS) analyzer.

### 2.3 Solid oxygen carrier reactivity test

The reactivity tests of the solid oxygen carrier were carried out using a thermogravimetric analyzer (TGA, CI Eletronics), with the experimental configuration shown in Figure 2.

**Figure 2 – Operating diagram of the thermogravimetric analyzer.**

![Operating diagram of the thermogravimetric analyzer](image)

Source: Authors (2021).

In Figura 2: (1) oven; (2) Pt basket with OC; (3) vaporizer; (4) microbalance; (5) condenser; (6) gas outlet; (7) temperature control; and (8) data collector.

Approximately 50 mg of sample was used in the experiments, which was heated to the study temperature in synthetic air flow. The experiments started when the desired temperature was reached and the system stability was verified, with the oxygen carriers being submitted to successive reduction and oxidation stages. Nitrogen was introduced for 2 minutes after the reduction and oxidation steps to avoid mixing the reduction and oxidation gases.
Table 2 details the conditions of the experiments performed on the thermogravimetric analyzer sample.

**Table 2** – Experimental conditions performed with oxygen carriers in the thermogravimetric analyzer.

| Temperature (°C) | Reduction          | Oxidation  | Cycles |
|------------------|--------------------|------------|--------|
| 900              | 10%CH₄+90%N₂ (25L/h) | Ar sintético | 3      |

Source: Authors (2021).

Gas flows were maintained at 25 L/hour during the experiments with the aim of reducing oscillations when gas changes occurred and minimizing the resistance to external diffusion of the gases. In addition, CH₄ was used as a reducing gas, synthetic air as an oxidizer and pure nitrogen to purge the system and avoid contact between the reducing and oxidizing gases. The water vapor used is to simulate the conditions existing in the reduction reactor in a CLC system and/or to prevent carbon deposition. For studying and treating the data, it was considered that the 100% mass would correspond to the sample in its highest oxidation state at the analyzed temperature, and that any loss of mass is due to the reaction of active phase oxygen (copper oxides) with the reducing gas. It was possible to determine several important parameters through the thermogravimetry results, such as: amount of effective metal oxide, speed index and the oxygen carrier capacity of each carrier.

### 3. Results and Discussion

#### 3.1 SOC reactivity with CH₄ in TGA

Figure 3 shows the conversion of the mixed copper and titanium oxide solid oxygen carrier as a function of time over three reactivity test cycles in TGA, reacting with methane (CH₄) during the reduction step, and synthetic air in the oxidation step.

**Figure 3** – Conversion curves (%) as a function of time obtained by TGA for the TCu oxygen carrier using CH₄ as reducing gas and synthetic air with oxidant.

![Conversion curves](image)

Source: Authors (2021).

Were calculated from the possible redox reactions involved (1-2 reactions) according to their oxidation degree and in terms of the sample mass variation as shown in Figure 4. The reactions responsible for mass variations in the thermobalance are as follows (Gayán et al., 2012):
In the reduction of TCu with CH₄:

\[
\text{CH}_4 (g) + 4 \text{CuO} (s) \rightarrow \text{CO}_2 (g) + 2 \text{H}_2\text{O}(g) + 4 \text{Cu} (s): \quad \text{Reaction 3}
\]

In the oxidation of TCu with O₂:

\[
\text{Cu} (s) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{CuO} (s): \quad \text{Reaction 4}
\]

According to (J. Adánez et al., 2018b), the reduction and oxidation rate in CLC processes must be sufficiently fast, which was observed in the thermogravimetric experiments for the TCu solid oxygen carrier shown in Figure 3, as its total oxidation occurred in less than 1 minute. The TCu solid oxygen carrier showed better reactivity than the copper oxide carriers supported on diatomite (Cu-D) and kaolin particles (Cu-K) (Costa et al., 2021), making this material very promising for its application in chemical looping combustion (CLC) processes.

The evolution of the oxygen carrier capacity obtained by the TCu SOC was evaluated over time for the three cycles according to Table 3.

| Solid oxygen carrier | State     | 1° cycle | 2°cycle | 3° cycle |
|----------------------|-----------|----------|---------|----------|
| TCu                  | Reduction | 11,36    | 11,41   | 11,37    |
|                      | oxidation | 11,36    | 11,34   | 11,40    |

Source: Authors (2021).

It was found that there are generally small variations with an increase in ROC at each cycle. These obtained values correspond to the amount of oxygen needed to completely convert the fuel into CO₂ and H₂O. The CuO-TiO₂ system has CuO as its active phase, so the mass loss suffered by this material corresponds to the reduction of copper oxide to metallic copper, according to the XRD result in Figure 4 and the TPR pattern in Figure 5 presented later.

3.2 Oxygen carrier characterizations

The XRD patterns corresponding to the mixed copper and titanium oxide (TCu) calcined at 900°C reduced and oxidized after the third cycle in the thermobalance are shown in Figure 4.
Figure 4 – X-ray diffractograms of the reduced calcined TCu solid oxygen carrier and after the reactivity test.

Table 4 presents the reference sheets, chemical formulas and the crystal structure of each phase used in the identification of the diffractograms, the percentage of phases and the Sig of the Rietveld refinement of the mixed copper and titanium oxide.

Table 4 – Presentation of the crystalline phases present in the TCu SOC.

| oxygen carrier | State   | Phases | % Phases | Sig     | Letter JCPDS | Cell types | CIF     |
|----------------|---------|--------|----------|---------|--------------|------------|---------|
| TCU            | Calcined| CuO    | 32,00    | 1.02    | 01-080-0076  | Monoclinic | 067850  |
|                |         | TiO2   | 21,00    |         | 01-071-0650  | Tetragonal | 009161  |
|                |         | Ti3O5  | 47,00    |         | 01-082-1137  | Monoclinic | 055193  |
| Reduced        |         | Cu     | 49,20    | 1,13    | 01-089-2838  | Cubic      | 043493  |
|                |         | TiO2   | 50,80    |         | 01-077-0440  | Tetragonal | 039166  |
| Oxidized       |         | CuO    | 55,74    | 1,14    | 01-080-1916  | Monoclinic | 069757  |
|                |         | TiO2   | 44,26    |         | 01-077-0442  | Tetragonal | 039168  |

Source: Authors (2021).

We can see in Figure 4 that the calcined TCu diffractogram shows the Ti3O5, TiO2 and CuO phases with main peaks at 25.64°, 27.44° and 32.45° with monoclinic, tetragonal and monoclinic structures, respectively. Table 4 presents a mass percentage of 47% Ti3O5 and 21% TiO2 which differs from the XRF result, which presents a percentage for the TiO2 phase of...
72.68%; as the XRF is a semi-quantitative analysis of the oxides presented in sample, this does not distinguish between titanium oxides.

According to Stem et al. (2014), rutile titanium dioxide and near-stoichiometric TiO$_{2-x}$ are stable forms of TiO$_2$ with a small number of point defects. However, as the number of point defects increases, rearrangements in the crystal structure (crystallographic shear planes - CSPs) are observed to accommodate them. Point defects are often correlated with oxygen deficiencies, such as Ti interstitials and oxygen vacancies or a combination of both, and are also associated with oxygen diffusion or doping. Oxygen vacancies can be doubled or ionized, resulting in titanium interstitials in Ti(III) or Ti(IV) states, depending on the reaction. However, when the concentrations of these vacancies in the CSP increase enough, there is formation of TinO$_{2n-1}$ compounds (Ti$_3$O$_5$, Ti$_4$O$_7$, Ti$_5$O$_9$, Ti$_6$O$_{11}$), which justifies the formation of the Ti$_3$O$_5$ phase (Stem et al., 2014).

The reducible crystalline phases correspond to rutile (TiO$_2$) and metallic copper (Cu) with the main peaks at 27.40° and 43.29°, and tetragonal and monoclinic structures, respectively. However, there were considerable changes in the regenerated TCu particles compared to the calcined particles. The Ti$_3$O$_5$ phase was not regenerated, and according to Table 4, we have a mass percentage of 55.74% CuO and 44.26% TiO$_2$.

Regarding the active phase found in mixed copper and titanium oxide, CuO acts as the active phase and titanium oxides as inert supports. Likewise, there are transitions between their oxidation states when subjecting these solid oxygen carriers to reducing conditions, depending on the concentration of fuel gas and the reaction temperature, according to Reaction 3 (Edelmannová et al., 2018).

For the reduction with H$_2$ we have:

$$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$$

Reaction 5

Therefore, the mixed copper and titanium oxide diffractograms reveal that the choice of uses with a calcination temperature of 900°C may be relevant for CLC applications due to the presence of a greater predominance of the CuO oxidation state than when reduced to Cu, providing complete fuel conversion. Figure 5 shows the H$_2$-TPR profiles of the solid oxygen carrier from Cu.
According to the XRD results presented in Figure 4 and Table 4, the mixed copper and titanium oxide presents titanium oxide (Ti$_3$O$_5$), titanium oxide (TiO$_2$) and copper oxide (CuO) as the most oxidized phase. The active phase for this mixed oxide is copper oxide (CuO). The copper oxide in this temperature programmed reduction experiment takes place following the reaction below:

$$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$$

The Figure 5 shows the reduced SOC reduction profile. The presence of a single reduction peak is observed with a maximum temperature of 273°C, which corresponds to the reduction of copper oxide (CuO) to metallic copper (Cu).

The TPR results of Figures 5 are in accordance with the phases identified by XRD, literature reports and thermodynamic data, showing characteristic profiles of CuO (Andache et al., 2019). The surface morphology and energy-dispersed chemical analysis (SEM-EDS) of the TCu oxygen carrier were evaluated by Scanning Electron Microscopy (SEM), as shown in Figure 6 and 7, respectively.
Figure 6 – Field emission scanning electron microscopy of TCu: (a) TCu calcined at 900°C with 5000x; (b) TCu after redox cycles in TGA at 900°C with 5000x; (c) and (d) highlighted region with 30000x.

In the analyzed region, the TCu morphology (Figure 6-(a) and (b)) illustrates heterogeneous, rounded and regular surfaces without sintering signs, indicating thermal stability, which in turn suggests that there was no change in the surface area. Microstructures with geometric characteristics of quadratic and hexagonal shape can be seen after enlarging the regions highlighted in figures (a) and (b), Figure 5 - c and d, respectively. The TCu morphology formed in this work showed morphological similarity with the mixed oxides of copper and titanium produced by Mahmoudabadi et al. (2019) and Zeng et al. (2017) (Mahmoudabadi & Eslami, 2019; Zeng et al., 2017).
Figure 7 – TCu EDS mass percentage.

The EDS of Figure 6 (e) and (f) show the characteristic copper, titanium and oxygen peaks corresponding to TCu without any contamination. A variation in mass of these elements was observed, whose values are shown in Figure 5. This variation occurred due to the reduction and oxidation reactions of the elements.

4. Conclusion

Reactivities during reduction and oxidation reactions of solid oxygen carriers based on mixed copper and titanium oxide were analyzed by thermogravimetry (TGA) and their physicochemical properties by XRD, SEM-EDS, and TPR. The copper oxide (CuO) particles synthesized with titanium oxide, according to the SEM-EDS results, presented appropriate mechanical strength and uniform distribution of the CuO particles on the oxygen carrier surface. It showed an increase in reactivity and its oxygen carrying capacity when subjected to three redox cycles, in addition to good stability after the third cycle. This reveals that there were no changes in the structure of oxygen carriers in this reaction period. The regeneration of CuO after the third cycle with CH₄ led to the full formation of copper oxide, so that the CuO-TiO₂ system diffractograms reveal that the choice of uses with a calcination temperature of 900°C may be pertinent for CLC applications due to the presence of a greater predominance of the CuO oxidation state which provides complete fuel conversion when reduced to Cu. From the structural characteristics and the reactivity tests reflective in methane conversion above 90% and ROC of 11.3 of this material, it is concluded that the CuO-TiO₂ system has the necessary requirements to be used in chemical looping combustion processes (CLC).

We can synthesize a larger amount of mixed copper and titanium oxide to act as solid oxygen carriers in reactors in future works in order to carry out many tests in multiple redox cycles, verifying the stability of samples in fluidized beds.

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