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Evaluating the reactivity of $CuO\text{-}TiO_2$ oxygen carrier for energy production technology with CO_2 capture

Avaliação da reatividade do Transporta Sólido de Oxigênio CuO-TiO2 para tecnologia de produção de energia com captura de CO2

Evaluación de la reactividad del portador de oxígeno $CuO\text{-}TiO_2$ para la tecnología de producción de energía con captura de CO_2

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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 $CuO\text{-}TiO_2$ 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; $CuO\text{-}TiO_2$ system.

Resumo

Os processos de combustão por recirculação química (CRQ), tem-se mostrado promissor e efeiciente 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 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 precursores 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 (R_{oc}) e o índice de velocidade dos ciclos de redução e oxidação foram avaliados por Reatividade 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 Difratometria 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 %/mim. 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 $CO_{2;}$ Combustão por recirculação química; Transportadores sólidos de oxigênio; Sistema $CuO-TiO_2$.

Resumen

Se ha demostrado que los procesos de combustión por recirculación química (CRQ) son prometedores y efectivos para reducir la producción de CO_2 a partir de la combustión de varios combustibles, asociada con la creciente demanda mundial de energía, ya que promueve la combustión indirecta del combustible a través de transportadores. Sólidos de oxígeno (TSO). Así, este estudio tiene como objetivo sintetizar, caracterizar y evaluar una mezcla de óxido de cobre y titanio como transportador sólido de oxígeno para su uso en procesos de combustión con recirculación química. El TSO se sintetizó en base a cálculos estequiométricos por el método del precursor polimérico y se caracterizó por: fluorescencia de rayos X (FRX), difracción de rayos X (DRX), Microscopía electrónica de barrido (SEM-FEG) con EDS, Reducción de temperatura programada (RTP). La capacidad de transporte de oxígeno (Roc) y el índice de velocidad de los ciclos de reducción y oxidación fueron evaluados por Reactividad Termogravimétrica (TGA). La principal fase reactiva identificada fue: La fase CuO para la mezcla de óxido de cobre y titanio se identificó y confirmó mediante difracción de rayos X utilizando el método de refinamiento de Rietveld. La reactividad del sistema CuO-TiO2 fue alta, obteniendo una conversión de CH4 superior al 90% y un índice de velocidad de 40% / min. De las características estructurales y las pruebas de reactividad de este material, se concluye que la mezcla de óxido de cobre y titanio tiene los requisitos necesarios para ser utilizada en procesos de combustión por recirculación química (CRQ).

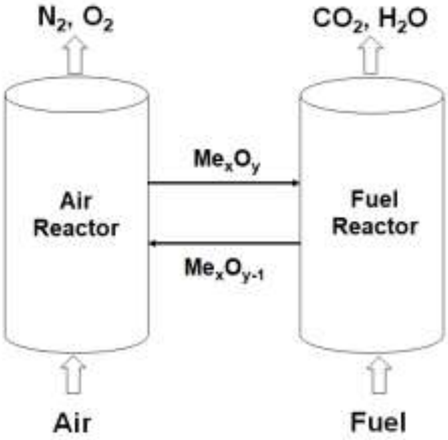
Palabras clave: Captura de CO_2; Combustión por recirculación química; Transportadores sólidos de oxígeno; Sistema $CuO-TiO_2$.

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 CO_2 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, CO_2 Capture and Storage (CCS) technologies have emerged as an important option to reduce global CO_2 emissions. In order to achieve this goal, Chemical Looping Combustion (CLC) has emerged as a promising technology for CO_2 capture in power plants and industrial applications, with low energy penalties compared to other competing CO_2 Capture and Storage (CCS) techniques (Juan Adánez & Abad, 2019). The CLC process scheme is shown in Figure. 1.

Figure 1 – CLC process scheme.



Source: Adapted from Adanez *et al*. (2012).

CLC technology describes cyclical redox processes between two interconnected reactors, as shown in Figure 1, and its principle is the use of a metal oxide (M_xO_y), known as a solid oxygen carrier (SOC), to transfer the necessary oxygen from the air (Reaction 1) and oxidize the fuel into CO_2 and H_2O (Reaction 2) in order to avoid direct contact between the air and the fuel. Its main advantage is the inherent CO_2 capture, bypassing the energy penalty.

$Me_xO_{y-1} + 1/2O_2 \rightarrow Me_xO_y$ (Reaction 1)

$(2n+m)Me_xO_x + C_nH_{2m} \rightarrow (2n+m)Me_xO_{y-1} + mH_2O + nCO_2$ (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 SiO_2, Al_2O_3, TiO_2, ZrO_2) 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 La_2NiO_4, $NiO\text{-}Fe_2O_3/MgAl_2O_4$, Mg_6MnO_8 and $Mn_2O_3\text{-}MgAl_2O_4$, 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 TiO_2 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 CO_2 and H_2O. In addition, TiO_2 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 $CuO\text{-}TiO_2$ 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 - $Cu(NO_3)_2.3H_2O$ (VETEC, PA = 99%), titanium isopropoxide - $C_{12}H_{28}O_4Ti$ (ALFA AESA, PA = 97.5%), ethylene glycol - $HOCH_2CH_2OH$ (SYNTH, PA = 99%) and citric acid - $C_6H_{10}O_8$ (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.

Table 1 – Chemical analysis of synthesis products by XRF (mass%).

Sample/Composition	TiO_2	Fe_2O_3	CuO	MnO	SiO_2	Al_2O_3	Na_2O	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.

$$C_{H_2\,(\mathrm{mol})} = C_{\mathrm{H2}\left(\frac{\mathrm{cm^3}}{\mathrm{g}}\right)} \times 1\mathrm{ml} \times \frac{1\mathrm{L}}{1000\mathrm{mL}} \times \frac{1\mathrm{mol}}{22{,}4\mathrm{L}} \qquad \text{(Equation 1)}$$

$$R_O = \frac{m_{oxi} - m_{red}}{m_{oxi}} = \frac{\Delta m}{m_{oxi}} \qquad \text{(Equation 2)}$$

$$\Delta m = C_{H2\,(mol)} \times \frac{16g}{mol} \qquad \text{(Equation 3)}$$

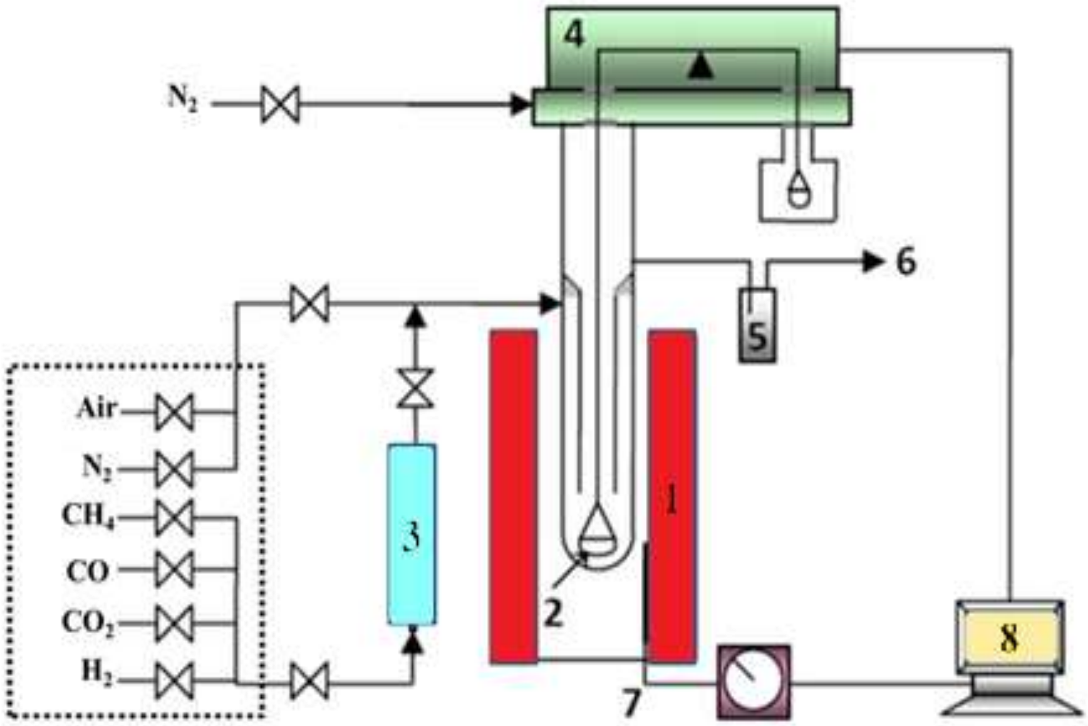
$$R_{OC} = X_{TO} \times R_O \qquad \text{(Equation 4)}$$

In which: $C_{H_2\,(mol)}$ representes the H_2 consumption by mol, $C_{H2\left(\frac{cm^3}{g}\right)}$ is the volume of H_2 consumed experimentally, m_{oxy} and m_{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.



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 **c**onditions performed with oxygen carriers in the thermogravimetric analyzer.

Temperature (°C)	Reduction	Oxidation	Cycles
900	10%CH_4 +90%N_2(25L/h)	Ar sintético	3

Source: Authors (2021).

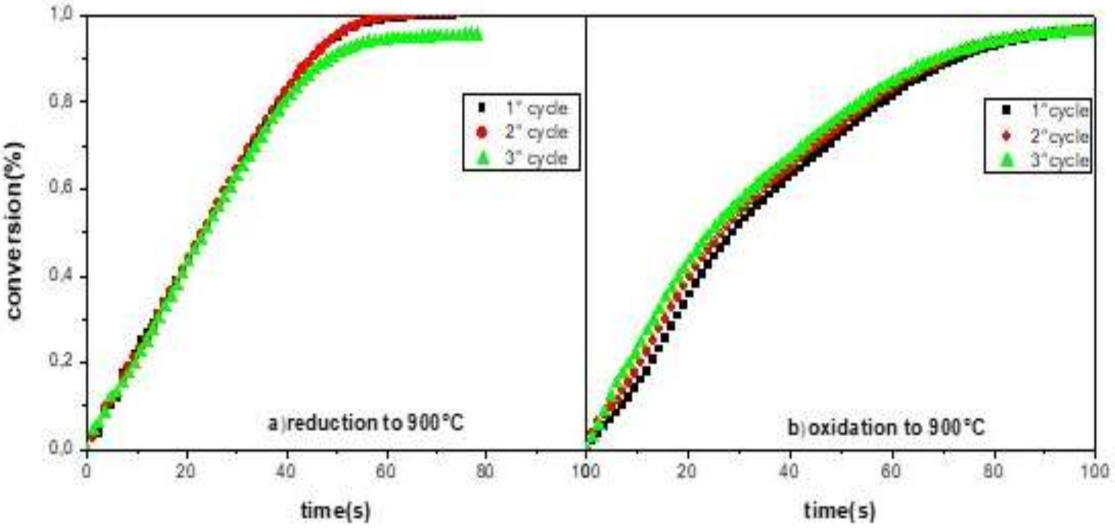
Gas flows were maintained at 25 L/hour during the experiments with the aim of reducing oscillations when gas changes occurred and minimizing the resistance to external diffusion of the gases. In addition, CH_4 was used as a reducing gas, synthetic air as an oxidizer and pure nitrogen to purge the system 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 CH_4 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 (CH_4) 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 CH_4 as reducing gas and synthetic air with oxidant.



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 CH_4:

$CH_4 (g) + 4\ CuO (s) \rightarrow CO_2 (g) + 2\ H_2O(g) + 4\ Cu (s)$: Reaction 3

In the oxidation of TCu with O_2:
Cu (s) + ½ O2 (g) → CuO (s): 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.

Table 3 – Oxygen Carrying Capacity (ROC) data.

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

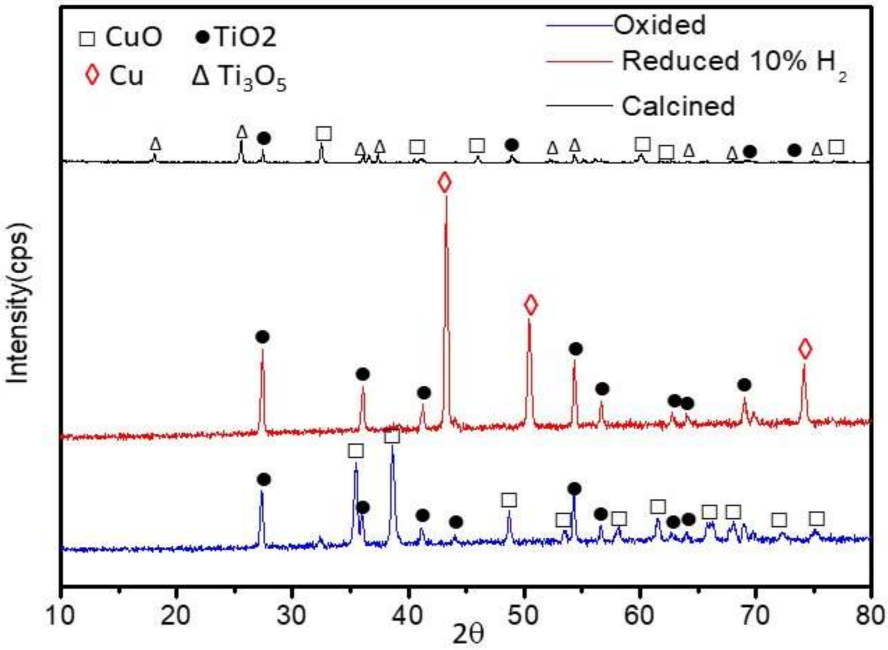
Source: Authors (2021).

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 CO_2 and H_2O. The CuO-TiO_2 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.



Source: Authors (2021).

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 XRD.

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	Monoclínic	067850
		TiO_2	21,00		01-071-0650	Tetragonal	009161
		Ti_3O_5	47,00		01-082-1137	Monoclínic	055193
	Reduced	Cu	49,20	1,13	01-089-2838	Cubic	043493
		TiO_2	50,80		01-077-0440	Tetragonal	039166
	Oxided	CuO	55,74	1,14	01-080-1916	Monoclínic	069757
		TiO_2	44,26		01-077-0442	Tetragonal	039168

Source: Authors (2021).

We can see in Figure 4 that the calcined TCu diffractogram shows the Ti_3O_5, TiO_2 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% Ti_3O_5 and 21% TiO_2 which differs from the XRF result, which presents a percentage for the TiO_2 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_3O_5, Ti_4O_7, Ti_5O_9, Ti_6O_{11}), which justifies the formation of the Ti_3O_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_3O_5 phase was not regenerated, and according to Table 4, we have a mass percentage of 55.74% CuO and 44.26% TiO_2.

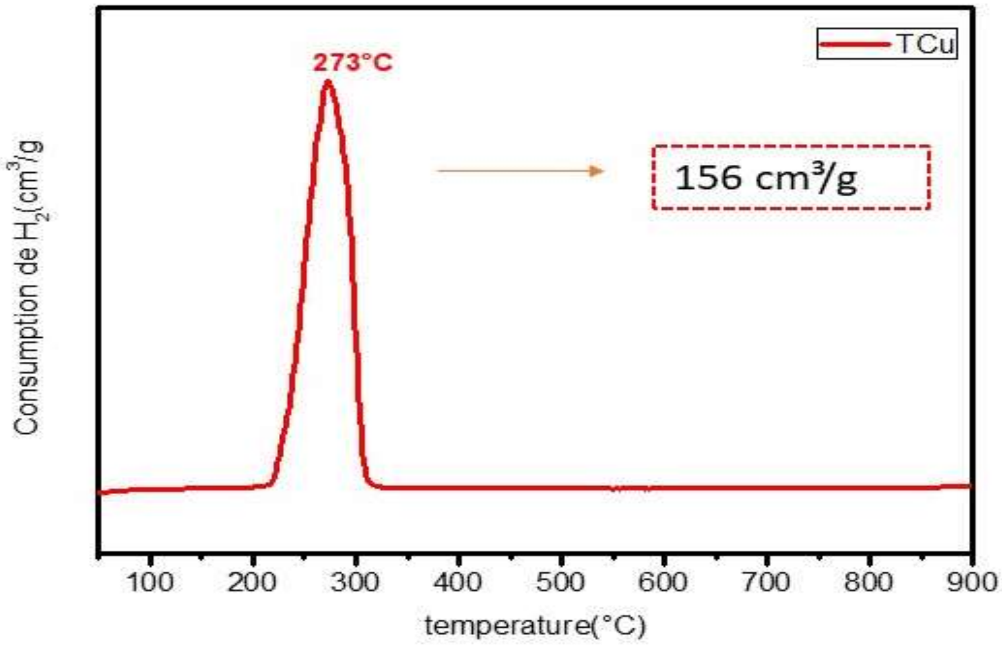
Regarding the active phase found in mixed copper and titanium oxide, CuO acts as the active phase and titanium oxides as inert supports. Likewise, there are transitions between their oxidation states when subjecting these solid oxygen carriers to reducing conditions, depending on the concentration of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

For the reduction with H_2 we have:

$$CuO + H_2 \longrightarrow Cu + H_2O \qquad \text{Reaction 5}$$

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.

Figure 5 – Temperature Programmed Reduction for the CuO-TiO_2 system.



Source: Authors (2021).

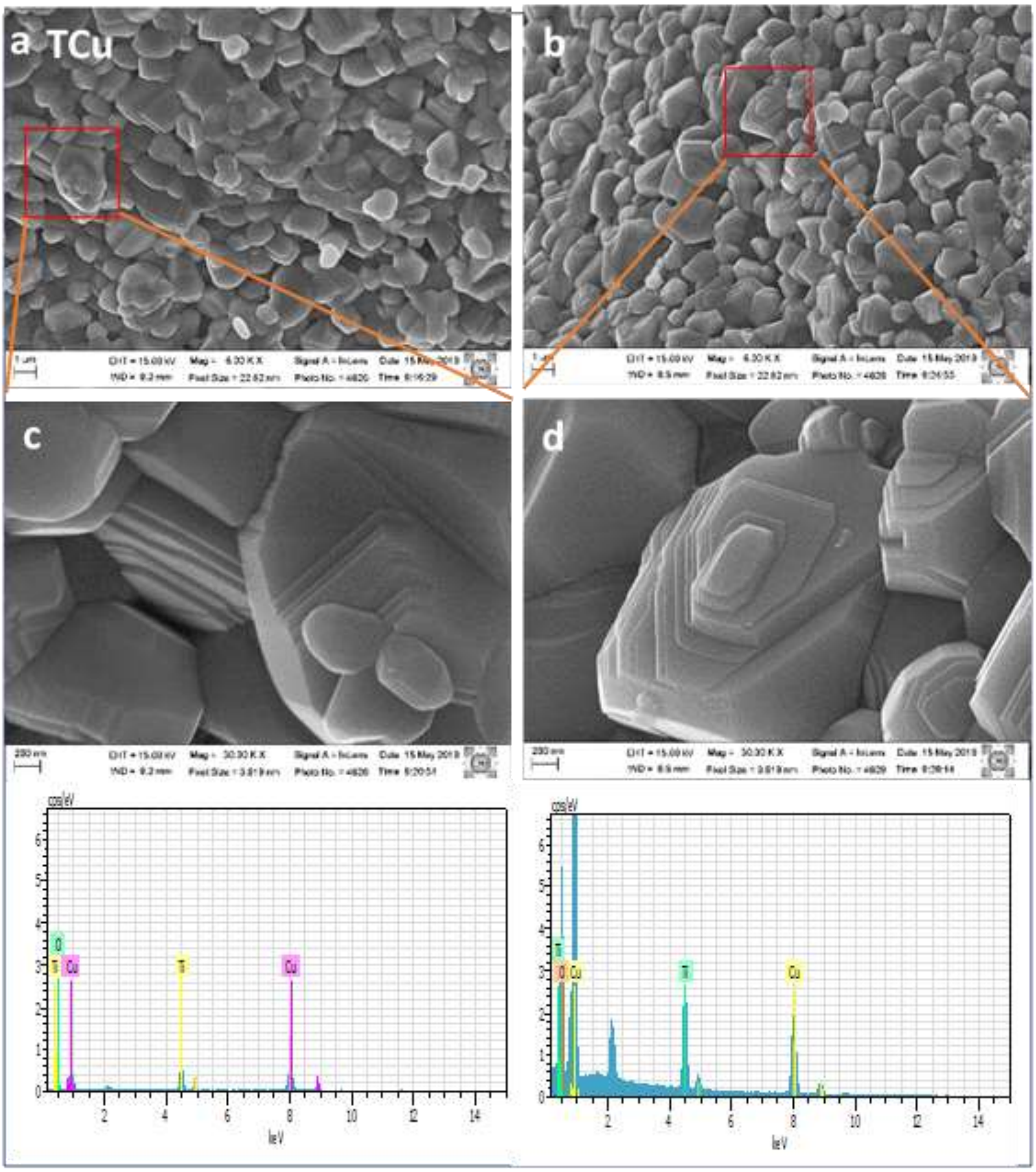
According to the XRD results presented in Figure 4 and Table 4, the mixed copper and titanium oxide presents titanium oxide (Ti_3O_5), titanium oxide (TiO_2) and copper oxide (CuO) as the most oxidized phase. The active phase for this mixed oxide is copper oxide (CuO). The copper oxide in this temperature programmed reduction experiment takes place following the reaction below:

$CuO + H_2 \rightarrow Cu + H_2O$ Reaction 6

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.

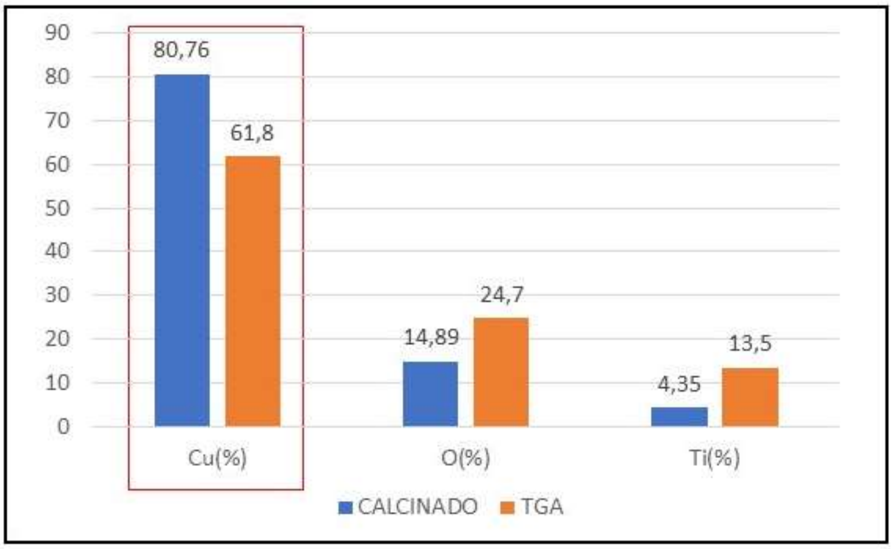
Figure 6 – Field emission scanning electron microscopy of TCu: (a) TCu calcined at 900°C with 5000x; (b) TCu after redox cycles in TGA at 900°C with 5000x; (c) and (d) highlighted region with 30000x.



Source: Authors (2021).

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.



Source: Authors (2021).

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 CH_4 led to the full formation of copper oxide, so that the CuO-TiO_2 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-TiO_2 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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References

Adánez, J., Abad, A., Mendiara, T., Gayán, P., de Diego, L. F., & García-Labiano, F. (2018a). Chemical looping combustion of solid fuels. *Progress in Energy and Combustion Science*, *65*, 6–66. https://doi.org/10.1016/j.pecs.2017.07.005

Adánez, J., Abad, A., Mendiara, T., Gayán, P., de Diego, L. F., & García-Labiano, F. (2018b). Chemical looping combustion of solid fuels. *Progress in Energy and Combustion Science*, *65*, 6–66. https://doi.org/10.1016/J.PECS.2017.07.005

Adánez, Juan, & Abad, A. (2019). Chemical-looping combustion: Status and research needs. *Proceedings of the Combustion Institute*. https://doi.org/10.1016/j.proci.2018.09.002

Andache, M., Nemati Kharat, A., & Rezaei, M. (2019). Preparation of mesoporous nanocrystalline CuO–ZnO–Al2O3 catalysts for the H2 purification using catalytic preferential oxidation of CO (CO-PROX). *International Journal of Hydrogen Energy*. https://doi.org/10.1016/j.ijhydene.2019.08.197

Costa, R. C. P. da, Nascimento, R. A. B. do, Melo, D. M. de A., Albuquerque, D. S., Medeiros, R. L. B. de A., Melo, M. A. de F., & Adánez, J. (2021). Development of CuO-based oxygen carriers supported on diatomite and kaolin for chemical looping combustion. *Research, Society and Development*, *10*(4), e15110412831. https://doi.org/10.33448/rsd-v10i4.12831

Edelmannová, M., Lin, K.-Y., Wu, J. C. S., Troppová, I., Čapek, L., & Kočí, K. (2018). Photocatalytic hydrogenation and reduction of CO2 over CuO/ TiO2 photocatalysts. *Applied Surface Science*, *454*, 313–318. https://doi.org/10.1016/J.APSUSC.2018.05.123

Gayán, P., Adánez-Rubio, I., Abad, A., De Diego, L. F., García-Labiano, F., & Adánez, J. (2012). Development of Cu-based oxygen carriers for Chemical-Looping with Oxygen Uncoupling (CLOU) process. *Fuel*. https://doi.org/10.1016/j.fuel.2012.01.021

International Energy Agency. (2019). Global Energy and CO2 Status Report. The latest trends in energy and emissions in 2018. *World Energy Outlook*.

IPCC. (2018). IPCC Special Report 1.5 - Summary for Policymakers. In *Global warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change,*. https://doi.org/10.1017/CBO9781107415324

M. P. Pechini. (1967). Method of Preparing Lead and Alkaline Earth Titanates and. In *U.S. Patent nº 3,330.697*.

Mahmoudabadi, Z. D., & Eslami, E. (2019). One-step synthesis of CuO/TiO2 nanocomposite by atmospheric microplasma electrochemistry – Its application as photoanode in dye-sensitized solar cell. *Journal of Alloys and Compounds*, *793*, 336–342. https://doi.org/10.1016/J.JALLCOM.2019.04.185

Medeiros, R. L. B. A., Macedo, H. P., Figueredo, G. P., Costa, T. R., Braga, R. M., Melo, M. A. F., & Melo, D. M. A. (2017). Study of the reactivity by pulse of CH4 over NiO/Fe-doped MgAl2O4 oxygen carriers for hydrogen production. *International Journal of Hydrogen Energy*, *42*(39), 24823–24829. https://doi.org/https://doi.org/10.1016/j.ijhydene.2017.08.019

Medeiros, R. L. B. A., Melo, V. R. M., Melo, D. M. A., Macedo, H. P., Moure, G. T., Adánez-Rubio, I., Melo, M. A. F., & Adánez, J. (2020). Double perovskite (La2-xCa-Bax)NiO4 oxygen carriers for chemical looping reforming applications. *International Journal of Hydrogen Energy*, *45*(3), 1681–1696. https://doi.org/https://doi.org/10.1016/j.ijhydene.2019.11.004

Melo, V. R. M., Medeiros, R. L. B. A., Braga, R. M., Macedo, H. P., Ruiz, J. A. C., Moure, G. T., Melo, M. A. F., & Melo, D. M. A. (2018). Study of the reactivity of Double-perovskite type oxide La1−xMxNiO4 (M = Ca or Sr) for chemical looping hydrogen production. *International Journal of Hydrogen Energy*, *43*(3), 1406–1414. https://doi.org/10.1016/J.IJHYDENE.2017.11.132

Nascimento, R. A. B., Medeiros, R. L. B. A., Costa, T. R., Oliveira, Â. A. S., Macedo, H. P., Melo, M. A. F., & Melo, D. M. A. (2020). Mn/MgAl2O4 oxygen carriers for chemical looping combustion using coal: influence of the thermal treatment on the structure and reactivity. *Journal of Thermal Analysis and Calorimetry*, *140*(6), 2673–2685. https://doi.org/10.1007/s10973-019-09014-w

Page, S. P. M., Chapter, L., & Page, M. C. (n.d.). *P54/WGI-14 - Changes to the underlying scientific-technical assessment to ensure consistency with the approved SPM These trickle backs will be implemented in the Chapter during copy-editing. August 2021*.

Rietveld, H. M. (1969). A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*. https://doi.org/10.1107/s0021889869006558

Stem, N., de Souza, M. L., de Faria, D. L. A., & dos Santos Filho, S. G. (2014). Formation of Ti(III) and Ti(IV) states in Ti3O5 nano- and microfibers obtained from hydrothermal annealing of C-doped TiO2 on Si. *Thin Solid Films*, *558*, 67–74. https://doi.org/10.1016/J.TSF.2014.02.077

Tian, X., Wei, Y., & Zhao, H. (2018). Using a hierarchically-structured CuO@TiO2-Al2O3 oxygen carrier for chemical looping air separation in a paralleled fluidized bed reactor. *Chemical Engineering Journal*. https://doi.org/10.1016/j.cej.2017.10.084

Tijani, M. M., Aqsha, A., & Mahinpey, N. (2018). X-ray diffraction and TGA kinetic analyses for chemical looping combustion applications. *Data in Brief*. https://doi.org/10.1016/j.dib.2017.12.044

Xu, Z., Zhao, H., Wei, Y., & Zheng, C. (2015). Self-assembly template combustion synthesis of a core–shell CuO@TiO2–Al2O3 hierarchical structure as an oxygen carrier for the chemical-looping processes. *Combustion and Flame*, *162*(8), 3030–3045. https://doi.org/10.1016/J.COMBUSTFLAME.2015.05.006

Zeng, Y., Wang, T., Zhang, S., Wang, Y., & Zhong, Q. (2017). Sol–gel synthesis of CuO-TiO2 catalyst with high dispersion CuO species for selective catalytic oxidation of NO. *Applied Surface Science*, *411*, 227–234. https://doi.org/10.1016/J.APSUSC.2017.03.107