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Development of a novel CO₂ splitting fixed-bed reactor based on copper-doped cerium oxide

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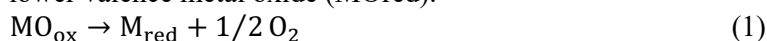
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Abstract. Global warming has received widespread attention in recent years due to the accumulation of carbon dioxide. Looking at the current energy landscape, new technologies must be developed to reduce CO₂ emissions. The present work is aimed to develop and test a new prototype of an innovative reactor for the conversion of CO₂ into CO, operating according to a two-phase thermochemical cycle. The innovative and main aspect of this study was the use of a reactor coupled with a new type of catalyst, a copper-doped cerium oxide (Cu_{δ+2}Ce_(1-δ)O₂), which allowed to decrease the temperature of the reaction up to 850°C, much lower than the models present in the literature, tested on 1300/1400°C and even beyond.

1. Introduction

Even today, the world's energy needs are still mainly satisfied by fossil sources, as coal, natural gas or oil, whose combustion determines the production of high quantities of CO₂ and other pollutants, which contribute to the so-called greenhouse effect phenomenon, as well as the increase in global warming [1,2]. In this regard, in recent decades, the scientific community has given greater prominence to climate problems, trying to develop new technologies and new alternatives, that can give them a solution [3]. Since fossil fuels are still the most abundant primary source, several systems have been developed trying to limit or reuse the produced CO₂. For example, CO₂ capture systems are capable to separate carbon dioxide from other combustion gases, forming a separate stream, suitable to be compressed and stored underground. Also, there are innovative technologies that allow treating CO₂ instead of simply storing it. The past concept of carbon capture and storage (CCS) is no longer adequate and it has already been amended to CCUS, involving significant carbon dioxide utilization: e.g. thermochemical processes, taking place in catalytic reactors, convert CO₂ into other substances, such as fuel or other chemicals, which can be reused for various purpose [4].

In the wake of the previously developed works [5,6], the present paper concerns the development of a fixed-bed reactor for the conversion of CO₂ to CO. It is currently known that carbon monoxide is mainly produced by dry reforming of natural gas or by partial oxidation of fossil fuels [7], but several processes have been studied and partially developed to produce it from CO₂ by means of thermal energy supply [8-10]. Among these, the two-step thermochemical processes, based on metal oxides, represent a viable option: in these processes, the first step is represented by an endothermic reduction of metal oxide (MO_{ox}) to metal or lower valence metal oxide (M_{red}).



The second exothermic step is the oxidation of the reduced metal oxide with CO₂ to form CO.





Thus, the reoxidized metal oxide can be recycled, returning to the first step. According to reactions (1) and (2), the overall reaction of the two-step cycle process can be written as:



In the last years, several thermochemical processes based on different catalysts (e.g. ferrites, zinc oxide, cerium oxide, etc.) have been studied to optimize the carbon reduction reaction, due to the high stability of the CO_2 [11-16]. Particularly, ceria-based cycles have given good and stable results, since ceria is a catalytic material with a high affinity to carbon dioxide and carbon monoxide, characterized by a very high melting temperature of about 2400°C , that retains its properties, even after several thermal processes [17].

In the first works where ceria has been used to achieve H_2O or CO_2 splitting, a significant reduction at very high temperature (more than 1400°C) was obtained, accompanied by negative consequences, such as practical problems in reactor design and sintering phenomena that decreased the reactive surface [18]. The high reduction and conversion temperatures are a major impediment to the diffusion of H_2O and CO_2 cleavage technology, due to the practical problem in reactor design and the structural modification phenomena of catalysts exposed to temperatures higher than 1000°C . Therefore, in recent years many researches have been carried out for the development of doped catalysts, capable of decreasing the temperature of the CO_2 reduction reaction. Several research groups [19-24] studied new technologies as the two-step water splitting process using several solid catalysts containing ceria and various transition doping-metal as Mn, Fe, Ni and Cu. A lot of catalysts have been synthesized, but it is quite evident the necessity to define a new type of catalyst properly functionalized, which coupled with a reactor developed *ad hoc*, allows to overcome disadvantages described so far, reducing the process temperatures and increasing the conversion efficiencies. Therefore, in this work, a new CO_2 solid sorbent was prepared by surfactant-templated method and its properties toward the carbon dioxide reduction were tested in a new fixed-bed reactor.

2. Experimental Section

The reactor was purpose-built, while the auxiliary components, such as N_2 and CO_2 cylinders, heat dissipator, flow meters, thermocouple and valves, needed to test this facility, were carefully selected. Several tests were carried out to evaluate the conversion capacity of the reactor, while the output gas was analyzed by means of a gas-chromatograph. Figure 1 shows a schematic of the reactor prototype.

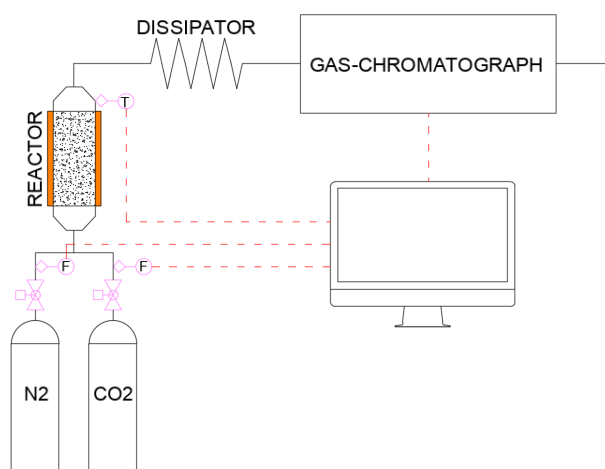


Figure 1. Schematic of the reactor prototype (F: flowmeter; T: thermocouple)

The reactor was made by using a special alloy tube with an inner diameter of 10 mm and an outer diameter of 12 mm; its active part, where the catalyst (copper-doped cerium oxide powder) was enclosed, was 152 mm long. Inside at the base of the reactor was placed a filter having a mesh size of a few μm . It supports the dust bed, also ensuring good gas distribution and preventing particles from falling below. Another internal filter was placed at the outlet of the reactor, with the purpose of retaining any solid particles suspended in the gas stream. The end of the reactor was sealed with a high-temperature mastic and sleeves connecting to the supply and exhaust lines. The reactor was then filled with copper-doped cerium oxide powder, placing the tubular ceramic heater surrounding the reactor, allowing it to be heated and brought to the desired internal temperature, 850°C . A thermocouple probe was also placed in the top of the reactor, which was essential for monitoring temperature levels. The reactor was insulated (Figure 2) all around with rock wool to reduce heat loss and avoid large thermal variations that would cause stress areas due to the expansion of the material. The whole was closed with a metal cover and fixed to a support structure (Figure 3).

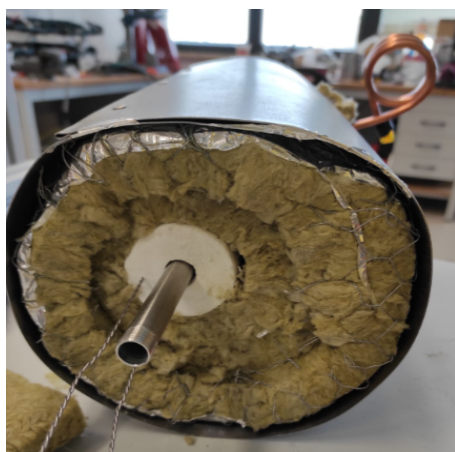


Figure 2. Reactor insulated with ceramic heater and rock wool.

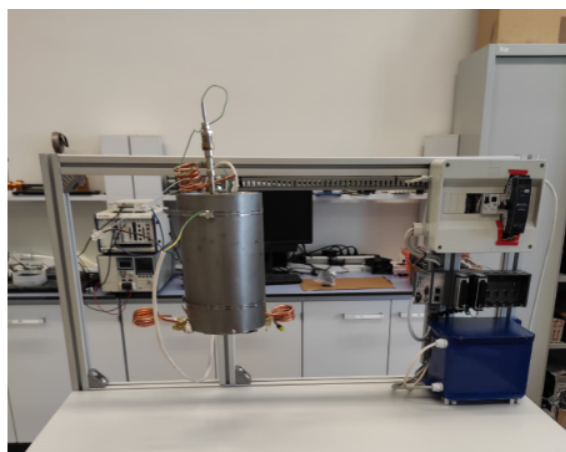


Figure 3. The full system: on the left the reactor, on the right the electrical panel and transformer.

The new catalyst was synthesized using the co-precipitation method. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR) were added to water at molar ratio of $\text{Cu}/(\text{Cu}+\text{Ce}) = 0.2$. Then, the salt solution was added to the CTAB solution (with a 1:1 ratio of CTAB to metal ions) under vigorous stirring for 30 min, giving a clear homogeneous solution. Afterwards, a 28% ammonia aqueous solution was added dropwise into the mixed solution at room temperature, under vigorous stirring, until pH reached 11 and temperature raised to 80°C . The obtained precipitate was then filtered and repeatedly washed with water and ethanol. Finally, the solid product was dried at 110°C for 12 h in the oven and calcined at 850°C for 3h. For calcination, the furnace was programmed at a rate of $1^\circ\text{C}/\text{min}$ up to reach 500°C , then the temperature was maintained stable for 1 h and finally it was further increased up to 850°C at a rate of $3^\circ\text{C}/\text{min}$ and kept stable for 3 h. After this step, the furnace was cooled down to room temperature at a rate of $3^\circ\text{C}/\text{min}$. The dry calcined powder, showed in Figure 4, appears grey.

A scanning electron microscope (SEM-Zeiss Germany) was used to investigate microstructural properties of the synthesized catalysts. It is evident in Figure 5 that the synthesized powder was nano meter in size, but aggregated to form micron sized particles. The x-ray diffractometric analysis was carried out by means of on Rigaku Ultima X- ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The XRD spectra (Figure 6) shows the crystalline peaks of ceria and a very low intense peaks of doped metal oxide.

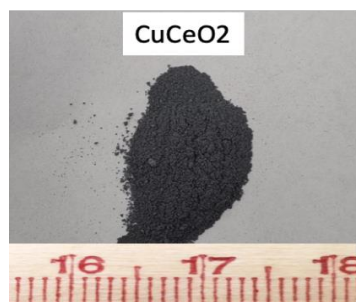


Figure 4. Picture of the final powder calcined at 850°C.

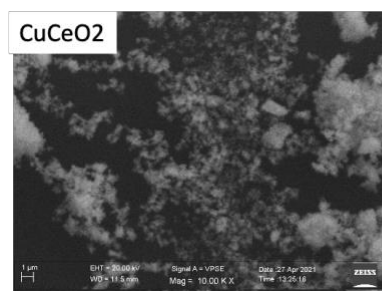


Figure 5. SEM images of synthesized catalyst.

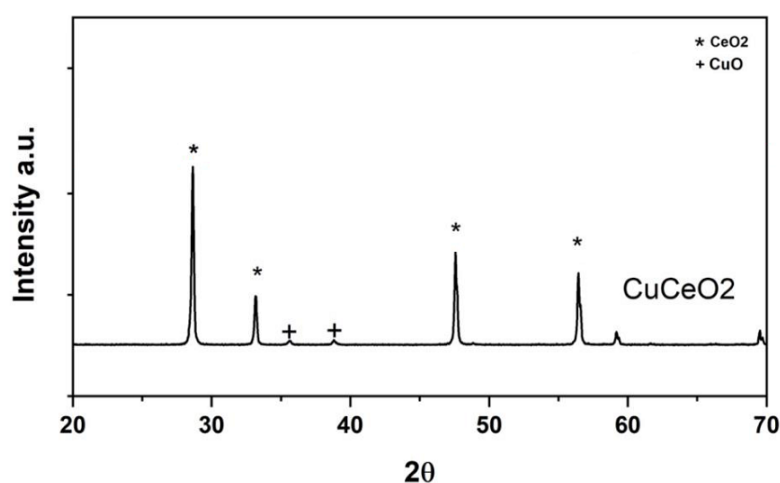


Figure 6. XRD spectra of the crystalline catalyst.

For microstructural analysis, the Nitrogen adsorption has been measured and the surface area has been calculated by means of the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05 to 0.25. The average pore size and pore volume were calculated using Barrett-Joyner-Halenda (BJH) method. The data about CuCeO_2 shows a very low specific surface area ($3.5 \text{ m}^2/\text{g}$), a low pore volume (0.011 cc/g) and a mean pore diameter of 3.71 nm .

To confirm the amount of doping and to verify the homogeneous distribution of doped ions in ceria, an elemental mapping was performed by using a Micro X-Ray fluorescence spectrometer (Bruker M4 Tornado, Berlin, Germany). The XRF analysis shows the percentage of each element: 79.1% for Ce, 20.9% for Cu; besides the mapping of elements shows homogenous distribution in micron scale (Figure 7).

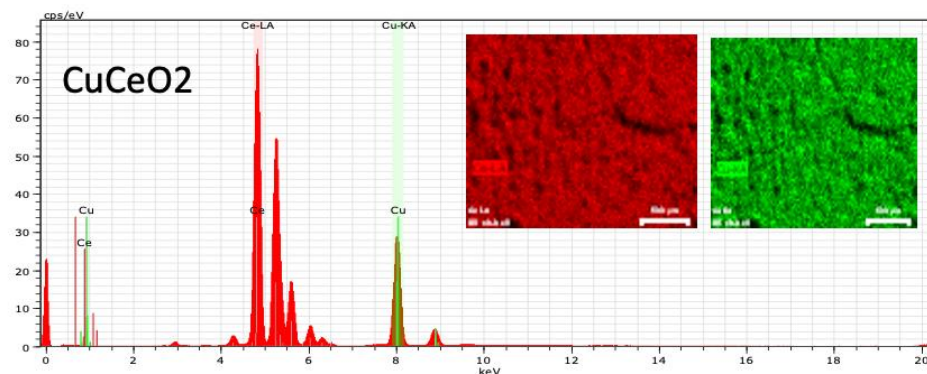


Figure 7. X-Ray fluorescence spectra and elemental mapping of synthesized catalysts.

Finally, a laser particle size analyzer (CILAS 1190) has been used to characterize the particles size: the results show the synthesized catalyst was micrometer sized. This may be due to the formation of aggregates during calcination at 850°C.

3. Discussion of the results

The experimental phase consisted primarily of verifying that, by performing the two-step thermochemical cycle described above, it was possible to convert CO₂ into CO. The first goal was to achieve a qualitative result rather than quantitative one. As mentioned above the cycle consists essentially of two steps, the first catalyst reduction during which nitrogen was flushed and heat was supplied, and the second oxidation, in which CO₂ oxidized the catalyst becoming CO.

CuCeO₂ powder was loaded in the reactor with a nitrogen flow rate of 100 mL/min providing heat to create a highly reactive environment and allowing the powder to reduce completely. After the reduction phase, the oxidation was carried out by interrupting the nitrogen flow and starting to flush CO₂ at a flow rate of 100 mL/min. Therefore, the gas at the exit of the reactor was sent to the gas chromatograph, which taken a sample and performed analysis on it.

Several tests were carried out: the first three tests were carried out by performing two steps, one of reduction with nitrogen and the other one of oxidation with CO₂, but changing progressively the CO₂ fluxing times, respectively from 5 min, to 10 min and finally 25 min. From the chromatograms (Figure 8a, 8b, 8c), it can be seen the presence of CO, in addition to CO₂ and N₂, and therefore the conversion took place. Particularly, the area under each peak is proportional to the amount of each analyte present in the chromatogram. Then, by calculating the area of the peaks, the concentrations of all analytes in the samples have been determined, according to the previously created calibration curves [25]. Therefore, a higher percentage of CO was found in the sample analyzed after 5 min of CO₂ fluxing and was equal to about 37%, while the sample analyzed after 10 min had 27% CO and the one analyzed after 25 min had <1% CO.

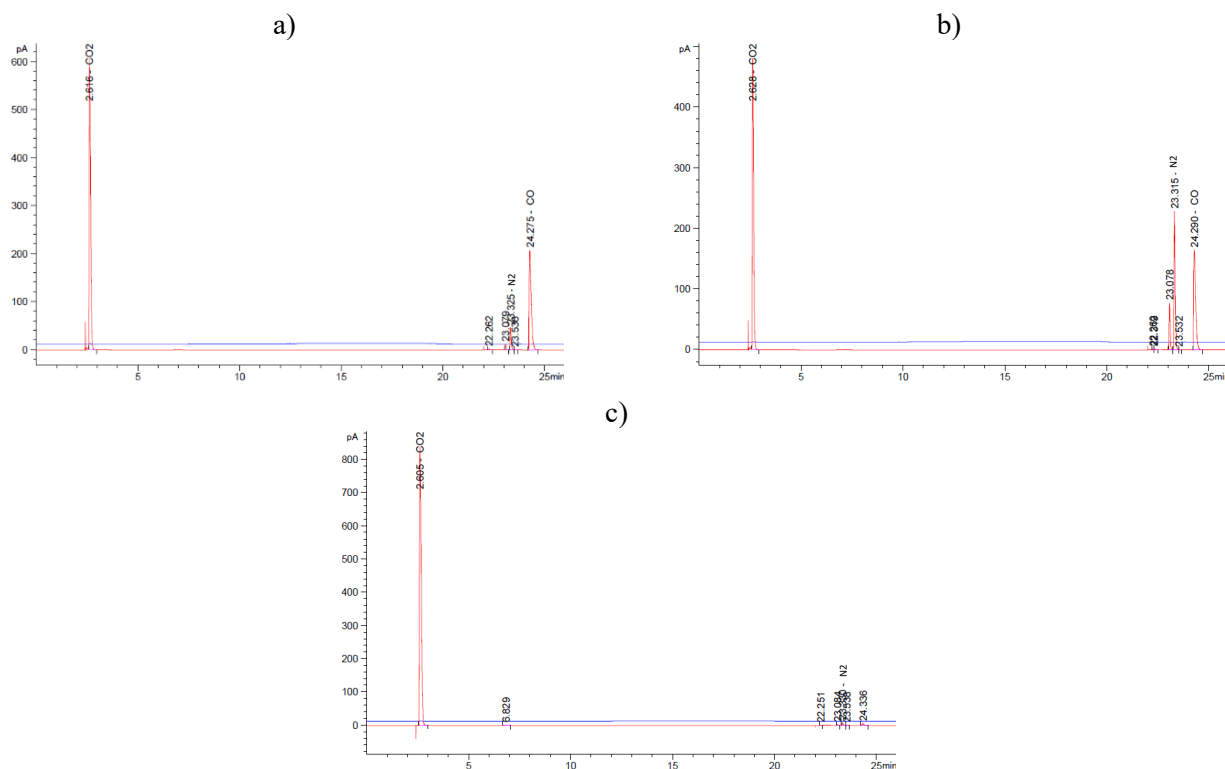


Figure 8. Chromatogram after 5 min (a), 10 min (b) and 25 min (c) of fluxing CO₂

When the oxidation phase begins and CO₂ is fluxed, this goes to oxidize the catalyst, in fact it gives up oxygen, which is bought by the reduced ceria, and is transformed into CO. It is obvious that once the ceria is oxidized it cannot acquire oxygen and therefore the conversion reaction of CO₂ into CO does not take place anymore. From here we can understand that as the reaction progresses, the samples have a lower percentage of CO, because most of it was produced in the early stages of CO₂ fluxing. Another test was carried out by performing the following cycles of continuous and alternating fluxing of N₂ and CO₂ in order to evaluate the regenerative capacity of the powder at the end of each reduction and oxidation step. From the chromatograms obtained (Figure 9a, 9b, 9c, 9d)) it can be seen that the amount of CO detected in the four analyses is 27%, 37%, 13%, 21% respectively. Therefore, the cerium oxide was able to regenerate quite well in the first 4 reduction/oxidation steps. Unfortunately, it is possible to see that the values are not fully reproducible even though the experiments were conducted under the same experimental conditions. Among all the possible causes, one may be that between two consecutive experiments the gases could follow different paths inside the reactor. Consequentially, the surface of the powder involved in the reactions could change.

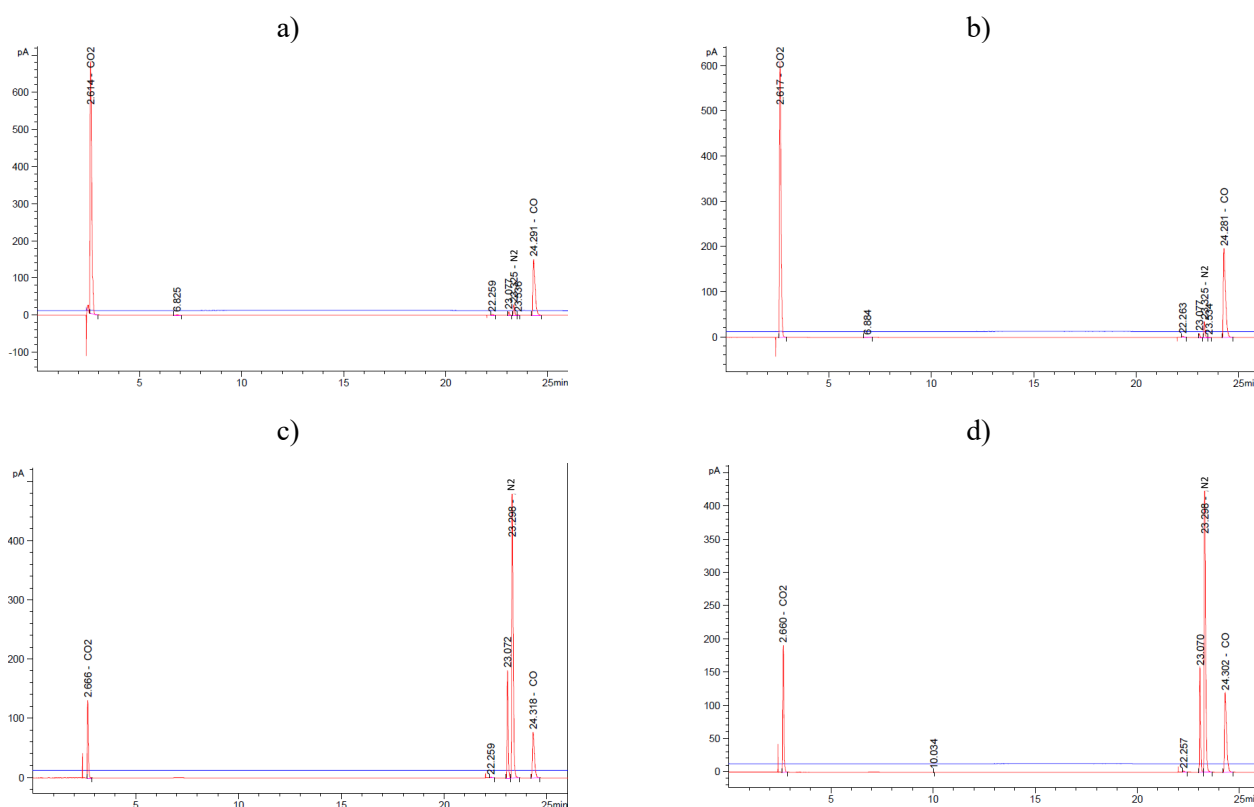


Figure 9. Chromatogram with 27% of CO (a), 37% of CO (b), 13% of CO (c) and 21% of CO detected (d).

Finally, a test was also conducted fluxing CO₂ and N₂ at the same time, always heating up to 850°C and then performing 3 analyses in sequence at 30 min interval each. The chromatograms related to these experiments (Figure 10a, 10b, 10c) show that the CO present is always about 4%, in all three analyses. These results show how the simultaneous fluxing mode is less performing than the alternating one.

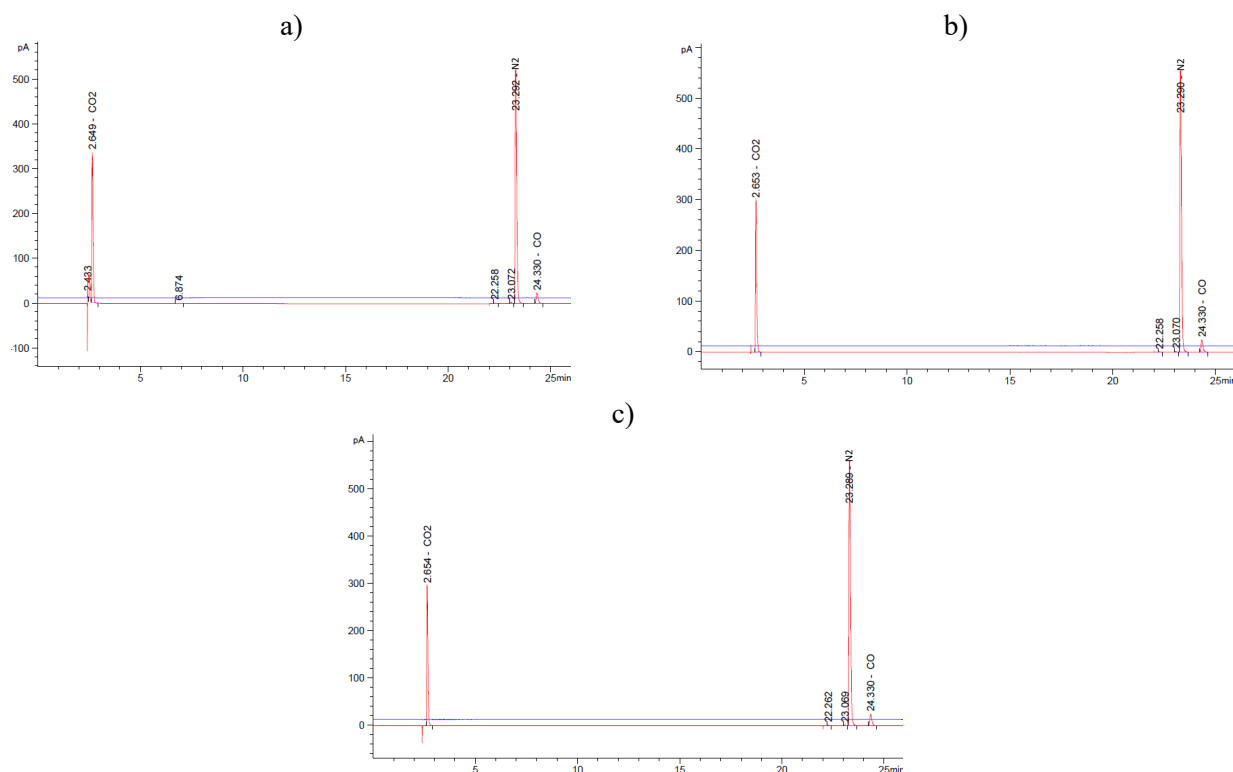


Figure 10. Chromatogram of the analyses with simultaneous flow of N₂ and CO₂: a) 1st analysis, b) 2nd analysis, c) 3rd analysis

4. Conclusions

On the basis of the numerous researches carried out in this area, in this work an innovative reactor prototype for the conversion of CO₂ into CO, operating according to a two-phase thermochemical cycle, was developed and tested. The innovative and main aspect was the use of a new type of catalyst, namely copper-doped cerium oxide (CuCeO₂), which allowed the temperature to be reduced much lower than the models described in literature and tested on 1400°C and even beyond. The high temperature is one of the main problems that does not facilitate diffusion and implementation of these technologies: this is because it requires very expensive materials and very high energy expenditure (due to heat losses), which makes the process unsustainable at an economic level.

The tests carried out in this work have activated the conversion of CO₂ into CO already at 850°C, obtaining good results, following a two-phase cycle of reduction and oxidation. Despite the experiment worked quite well, the measurements were not fully reproducible. The hypothesis of the different preferential paths could be a reasonable explanation, but it needs to be proved through further studies. Certainly, even better results could be obtained by implementing the fluidized-bed reactor instead of a fixed-bed reactor, allowing better interaction between powders and gases. Also, in our perspective, we would like to test new cerium oxide based materials and compare them with this catalyst to see which one can give higher CO₂ conversion at lower temperatures. To be fully successful on a large scale, these technologies must further decrease the reaction temperature and provide the heat needed for the reaction by harnessing solar energy, making the process more sustainable. Moreover, in our outlook, the produced CO could be mixed with green hydrogen to produce methanol to be used as fuel or to produce various chemicals such as polycarbonates, urea, salicylic acid and dimethyl carbonate.

5. References

- [1] Yoro KO, Daramola MO, Sekoai PT, Armah EK and Wilson UN 2021 *Ren and Sust En Rev* **147** 111241
- [2] Colangelo G, Spirto G, Milanese M and de Risi A 2021 *Energies* **14** 4270
- [3] Molina-Fernández C and Luis P 2021 *J CO₂ Utiliz* **47** 101475
- [4] Alper E and Orhan OY 2017 *Petroleum* **3** 109-126
- [5] Milanese M, Colangelo G, Laforgia D and de Risi A 2017 *Energy* **134** 919-932
- [6] Milanese M, Colangelo G, Iacobazzi F and de Risi A 2017 *Sol Ener Mat Sol Cel* **160** 174–181
- [7] Zhang H, Sun Z and Hu Y H 2021 *Renew Sust Ener Rev* **149** 111330
- [8] Villafán-Vidales HI, Arancibia-Bulnes CA, Riveros-Rosas D, Romero-Paredes H and Estrada CA 2017 *Renew Sust Ener Rev* **75** 894-908
- [9] Agrafiotis C, Roeb M and Sattler C 2015 *Renew Sust Ener Rev* 242-254
- [10] Smestad GP and Steinfeld A 2012 *Ind. Eng Chem Res* **51**(37) 11828-40
- [11] Loutzenhiser PG and Steinfeld 2011 *Int J Hydrog Ener* **36** 12141-47
- [12] Loutzenhiser PG, Galvez ME, Hischer I, Graf A and Steinfeld A 2010 *Chem Eng Sci* **65** 1855-64
- [13] Galvez ME, Loutzenhiser PG, Hischer I and Steinfeld A 2008 *En & Fuels* **22**(5) 3544-50
- [14] Chueh WC and Haile SM 2010 *Trans R Soc A Math Phys Eng Sci* **368**(1923) 3269-94
- [15] Stamatiou A, Loutzenhiser P G and Steinfeld A 2010 *Chem Mater* **22**(3) 851-859
- [16] Loutzenhiser PG, Meier A and Steinfeld A 2010 *Materials* **3**(11) 4922-38
- [17] Trovarelli A 1996 *Cat Rev* **38** 439-520
- [18] Kaneko H, Miura T, Ishihara H, Taku S, Yokoyama T, Nakajima H and Tamaura Y 2007 *Energy* **32** 656–663
- [19] Abanades S, Legal A, Cordier A, Peraudeau G, Flamant G and Julbe A 2010 *J Mater Sci* **45** 4163-73
- [20] Murray EP, Tsai T and Barnett SA 1999 *Nature* **400** 649-51
- [21] Park S, Vohs JM and Gorte RJ 2000 *Nature* **404** 265-267
- [22] Sharma S, Hilaire S, Vohs JM, Gorte RJ and Jen HW 2000 *J Cat* **190** 199-204
- [23] Demoulin O, Navez M, Mugabo JL and Ruiz P. 2007 *Appl Cat B* **70** 284-293
- [24] Lin M and Haussener S 2015 *Energy* **88** 667
- [25] Skoog DA, West DM, James Holler F and Crouch SR 2004 *Fundamentals of analytical chemistry* VIII ed. Brooks/Cole, a division of Thomson Learning