Development of Cu-based Oxygen Carriers for Chemical-Looping Combustion

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Abstract

In a chemical-looping combustion (CLC) process, gas (natural gas, syngas, etc) is burnt in two reactors. In the first one, a metallic oxide that is used as oxygen source is reduced by the feeding gas to a lower oxidation state, being CO_2 and steam the reaction products. In the second reactor, the reduced solid is regenerated with air to the fresh oxide, and the process can be repeated for many successive cycles. CO_2 can be easily recovered from the outlet gas coming from the first reactor by simple steam condensation. Consequently, CLC is a clean process for the combustion of carbon containing fuels preventing the CO_2 emissions to atmosphere. The main drawback of the overall process is that the carriers are subjected to strong chemical and thermal stresses in every cycle and the performance and mechanical strength can decay down to unacceptable levels after enough number of cycles in use.

In this paper the behaviour of CuO as an oxygen carrier for a CLC process has been analysed in a thermogravimetric analyser (TGA). The effects of carrier composition and preparation method used have been investigated to develop Cu-based carriers exhibiting high reduction and oxidation rates without substantial changes in the chemical, structural and mechanical properties for a high number of oxidation-reduction cycles. It has been observed that the carriers prepared by mechanical mixing or by coprecipitation showed an excellent chemical stability in multicycle tests in thermobalance, however, the mechanical properties of these carriers were highly degraded to unacceptable levels. On the other hand, the carriers prepared by impregnation exhibited excellent chemical stability without substantial decay of the mechanical strength in multicycle testing. These results suggest that copper based carriers prepared by impregnation are good candidates for chemical-looping combustion process.

Keywords: Chemical-looping combustion; CO_2 capture; Copper oxide.

1. Introduction

It is generally accepted that a reduction of gas emissions promoting the greenhouse effect is a necessity in the industrial countries. Carbon dioxide coming from fossil fuel combustion is one of the most important greenhouse gases contributing to global warming. Until now, the main attention for decreasing CO_2 emissions to atmosphere has been focused on the use of alternative energies and the increase of the efficiency in the conversion and use of energy. However, because it is not clear if it is possible to reach the desired low levels in CO_2 emissions only by these ways, it is nowadays increasing the interest in using CO_2 capture and sequestration from the combustion of fossil fuels as an alternative process [1]. For the capture and separation of CO_2 from flue gases there are different techniques [2], however, the current processes of CO_2 capture usually require a considerable energy consumption, leading to a reduction of the plant efficiency and increasing the cost of energy production [3].

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Chemical-looping combustion (CLC) was a process firstly proposed as a way to increase thermal efficiency in power generation [4-5], but later the possibility of using this combustion process for inherent CO_2 separation without substantial energy losses was also recognised. This technology involves the use of a metal oxide as an oxygen carrier, which transfers oxygen from the air to the fuel avoiding the direct contact between fuel and air. The CLC system is made of two interconnected reactors, designated as air and fuel reactors. In the fuel reactor, the fuel gas is oxidised to CO_2 and H_2O by a metal oxide through the chemical reaction:

$$CH_4\ (CO, H_2) + MeO \rightarrow CO_2 + H_2O\ (CO_2, H_2O) + Me \qquad (1)$$

where Me represents a metal or a reduced form of MeO.

This metal or reduced oxide is further transferred into the air reactor in which it is oxidised with air:

$$Me + \tfrac{1}{2}\, O_2 \rightarrow MeO \qquad (2)$$

and the material regenerated is ready to start a new cycle.

The flue gas leaving the air reactor contains N_2 and probably unreacted O_2. The exit gas from the fuel reactor contains CO_2 and H_2O, which are kept apart from the rest of the flue gas. After water condensation, almost pure CO_2 can be obtained with little energy lost for component separation.

Different metal oxides have been proposed in the literature as potential candidates for CLC [4-6]: CuO, CdO, NiO, Mn_2O_3, Fe_2O_3 and CoO. In general, these metal oxides are prepared with an inert which acts as a porous binder enhancing the reactivity of the active phase and, probably, as an ionic conductor for oxygen [7-8]. Additionally, this inactive binder increases the mechanical strength and the attrition resistance of the oxygen carrier.

Depending upon the chemical nature of the metal oxide used, reaction 1 can be endothermic or exothermic, while reaction 2 is always exothermic. The total amount of heat evolved over the two reactors in CLC process is the same as in conventional combustion, however, thermodynamic considerations show that the exergy destructions in CLC are much lower than in conventional combustion, giving chance to increase the net power efficiency [4-5,9]. The only drawback of the overall CLC process is that the materials are subjected to strong chemical and thermal stresses in every cycle and the performance could be poor after enough number of cycles in use.

Mattisson and co-workers [10-12] have investigated the behaviour of natural and synthetic iron oxides in a CLC process using CH_4 and air as feeding gases in fixed-bed and fluidised-bed reactors. They found for synthetic samples higher reaction rates and lower particle breakage as compared with the performance exhibited by natural samples. Recently, these authors [13] prepared NiO, CuO, CoO, and Mn_3O_4 based carriers on alumina support by dry impregnation, and their reactivity was studied in a thermogravimetric analyser (TGA). They observed that the Ni or Cu containing materials showed high reactivity at all temperatures tested, however, Mn and Co containing carriers showed a rather poor reactivity. Ishida and co-workers [7,14-18] have investigated the effect of temperature, particle size, gas composition and pressure on the reduction and oxidation rates and on carbon deposition of Fe, Ni, and Co oxides in a TGA, using H_2, CO, or CH_4 as fuels and air as oxidising gas. The effect of the inert used as a binder and its concentration was also analysed [7]. They concluded that the carbon deposition and the reaction rates and conversions, in addition to the operating conditions used (temperature, particle size, gas composition, total pressure, etc), depended strongly on the chemical nature of the solid materials [16-17].

Among the different metal oxides that have been proposed in the literature as potential candidates for CLC process, CuO and Fe_2O_3 are the less expensive having good oxygen capacities.

The aim of this paper was the study of the behaviour of some potential Cu-based oxygen carriers for a CLC process. The effects of the carrier composition and the preparation method used were investigated to develop oxygen carriers exhibiting high reduction and oxidation rates while maintaining their mechanical properties for a high number of successive oxidation-reduction cycles.

2. Experimental

2.1. Preparation of oxygen carriers

The prepared oxygen carriers are composed of CuO as active phase and an inert as a binder to increase the mechanical strength. The studied oxygen carriers will be designated with the chemical symbol referred to the active metal oxide (Cu), followed by the weight concentration of CuO, and a symbol referred to the binder used (Al=alumina, Si=silica, Se=sepiolite, Ti=titania, and Zr=zirconia). Finally, the preparation method used (M=mechanical mixing, C=coprecipitation, and I=impregnation) is also included. For example, a sample designated as Cu60Se-M means a carrier composed of 60 wt% of CuO and 40 wt% of sepiolite and prepared by mechanical mixing.

Mechanical mixing. Oxygen carriers were prepared from commercial pure products as powders of particle size < 10 μm including CuO as active phase and Al_2O_3, sepiolite, SiO_2, TiO_2, or ZrO_2 as binders. Graphite was added during preparation, as a pore-forming additive, to create during calcination a suitable macroporosity that, presumably, may enhance the carrier reactivity in the two involved processes included in CLC. A powder mixture including the CuO and the binder in the desired concentration together with a 10 wt% of graphite was converted by water addition into a paste of suitable viscosity to be extruded in a syringe for obtaining cylindrical extrudates of about 2 mm diameter. These extrudates were softly dried at 80 ^{o}C overnight, cut at the desired length (about 1-2 mm), and calcined at 950 ºC for 6 h in a muffle oven. We have prepared these carriers in three different CuO/inert ratios (40/60, 60/40, and 80/20).

Coprecipitation. A sample Cu40Si-C was also prepared by coprecipitation of $Cu(NO_3)_2$ and colloidal SiO_2 from an aqueous solution followed by filtration, washing, and drying. The powder mixture obtained was further subjected to the same procedure as that applied to samples prepared by mechanical mixing.

Impregnation. In this case fresh extrudates of silica and titania as porous binders were prepared following the same method described for samples prepared by mechanical mixing, but calcining at 1100 ºC. The extrudates were subsequently crushed, ground and sieved into particles of 200-400 μm in size, in order to increase the efficiency of the subsequent impregnation with a saturated aqueous solution of $Cu(NO_3)_2$. The desired active phase loading was achieved by applying successive wet impregnations followed by calcination at 500 ^{o}C to decompose the impregnated copper nitrate into insoluble copper oxide.

2.2. Characterization of oxygen carriers

The crushing strength of the oxygen carriers as extrudates was determined by using the ASTM D-4179 method, which allows the measurement of the minimum normal force required to crush a cylindrical extrudate placed between two horizontal plates. The crushing strength was obtained dividing the applied force by the extrudate length. The final measure was obtained from the average of at least 15 different measurements undertaken on different extrudates randomly chosen.

The morphology and distribution of the elements of interest in the fresh oxygen carriers were studied in a scanning electron microscope (SEM) coupled to an Si(Li) X-ray detector and a PGT SUN Sparcstation 5 for energy-dispersive X-ray (EDX) analysis. Identification and quantitative analysis of crystalline phases in the fresh samples were carried out by powder

X-ray diffraction (XRD) in a diffractometer Seifert 3000 using Ni-filtered Cu Kα radiation and a graphite monochromator.

2.3. Reactivity tests

Experimental set-up. Reactivity tests of the oxygen carriers were carried out in a thermogravimetric analyser (TGA), CI Electronics type, showed in Fig. 1. The TGA consisted of a quartz tube (24 mm i.d.) placed in an oven, which can be operated at temperatures up to 1100 °C. The sample holder was a wire mesh platinum basket (14 mm diameter and 8 mm height) to reduce mass transfer resistance around the solid sample. The temperature and sample weight were continuously recorded in a computer. N_2 (9 nL/h) flowed through the microbalance head to keep the electronic parts free of the reactant gas. The flow rate of the reacting gas mixture (25 nL/h) was controlled by electronic mass flow controllers and it was introduced at the upper part of the reaction tube. The gas was heated up to the desired temperature flowing down through the external annulus of the reactor before entering in contact with the sample located at the bottom of the reactor. The gas left the reactor through an internal quartz tube (10 mm i.d.) after mixing with the gas coming from the head of the balance.

Procedure: For the reactivity experiments, the oxygen carrier (20-40 mg) was loaded in the platinum basket and heated to the set operating temperature in air atmosphere. After stabilisation, the experiment was started by exposing the oxygen carrier to alternating reducing and oxidising conditions. To avoid mixing of combustible gas and air, nitrogen was introduced for two minutes after each reducing and oxidising period. Some experiments without sample were initially carried out to detect the buoyancy effects due to the change of the reacting gases.

The composition of the gas used was CH_4, H_2, or $CO+H_2$ for reduction and pure air for oxidation. The reducing gas was saturated in water by bubbling through a water containing saturator at the selected temperature to reach the desired water concentration (30 wt%). This H_2O avoids or minimises the possible carbon deposition during the reduction reaction [13] and normally acts as an inert gas for the carrier reduction. The experiments were carried out at 800 ºC because at higher operating temperatures CuO, although stable in air, decomposes in N_2 atmosphere into Cu_2O with the subsequent loss of oxygen transport capacity of the carrier.

3. Results and discussion

At least five cycles of reduction and oxidation were carried out with each carrier. It was detected that the carriers normally stabilised after the first cycle, for which the reduction reaction rate was usually slower than the others. This feature was maybe due to the different changes produced in the structure of the fresh oxygen carriers during their first reduction reaction as compared with the different formation of the metal oxide during regeneration in successive cycles. In this work, the oxygen carrier reactivity corresponding to the cycle 5 was used for comparison purposes.

Data in reduction-oxidation TGA tests is directly obtained as a sample weight evolution as a function of the time. These weight data can be transformed into conversion data by using the following equations:

For reduction: $$X = \frac{m_{ox} - m}{m_{ox} - m_{red}} \tag{3}$$

For oxidation: $$X = 1 - \frac{m_{ox} - m}{m_{ox} - m_{red}} \tag{4}$$

where m is the actual mass of sample, m_{ox} is the mass of the sample fully oxidized and m_{red} the mass of the sample in the reduced form. Reactions 5 and 6 show the reactants and products involved in the reactions of the Cu-based oxygen carriers using CH_4 as reducing gas.

$$CH_4 + 4\ CuO \rightarrow CO_2 + 2\ H_2O + 4\ Cu \quad (5)$$

$$4\ Cu + 2\ O_2 \rightarrow 4\ CuO \quad (6)$$

3.1. Effect of the binder

Fig. 2 shows the reactivity of pure CuO extrudates (without inert) as a function of the number of successive reduction-oxidation cycles in a typical multicycle test in TGA. In this case, the conversion X* plotted against the reaction time was defined as $X^*=(m- m_{red})/(m_{ox}-m_{red})$. As can be seen, for the reduction of CuO the result indicates that the particles reached complete conversion, however, the behaviour observed during the oxidation was different. The oxidation reaction rate of pure CuO decreased quickly with increasing the number of cycles and after three cycles of reaction the reactivity of the extrudates was extremely low, reaching conversions of only 10% in more than 20 min. Similar results were found by Ishida and Jin [8] working with pure NiO. These researchers observed that the addition of a binder increased the oxidation rate and concluded that the binder plays dual roles: the role as an oxygen-permeable material and the role as a material to enhance the mechanical strength of the particle for cyclic use and against abrasion. As a drawback, it is worth noting that an increase in the amount of binder also yields a decrease in the oxygen transport capacity of the carrier.

Fig. 3 shows the reactivity data, obtained in TGA during the reduction and the oxidation reactions, for some of the oxygen carriers prepared by mechanical mixing using different binders and CuO concentrations as active phase. As can be seen in the figures, the reactivity of all carriers prepared using binders was very much higher than the reactivity of pure CuO particles. It may be concluded that the reduction and oxidation rates of the oxygen carriers prepared by mechanical mixing were highly dependent on the degree of conversion, and the binder type but, in general terms, all Cu-based carriers studied exhibited high reactivities in reduction and oxidation. The reaction times for complete conversion in the reduction process were lower than 1 minute for all carriers and the oxidation conversion obtained at 1 minute of reaction time varied from 70 to 100%. In most of the carriers the final oxidation rate was slower, probably by diffusional effects.

The identification of crystalline phases and their concentrations in some of the prepared carriers have been determined by powder XRD as shown in Table 1. Silica and alumina used as binders are microcrystalline giving diffuse X-ray patterns in opposition to zirconia and rutile that present very intense reflections allowing easy identification. Additionally, the active phase, CuO, also presents a well-defined pattern. In sample Cu40Al-M the presence of a spinel-structure $CuAl_2O_4$ was clearly evidenced indicating that in this sample there was interaction between the active phase and binder through the formation of this mixed oxide. This effect could strongly alter the carrier behaviour on reduction, however, the corresponding plot in Fig. 3 shows complete conversion in reduction indicating that this spinel phase is also reducible by the feeding gas.

In addition to the studied reactivity, the mechanical strength of the carriers is another important parameter to be accounted as a criterion for material selection. Table 2 shows the crushing strength of all fresh extrudates prepared by mechanical mixing. The crushing strength mainly depended on the type of binder used and the carriers only showed appreciable crushing strength when using SiO_2 and TiO_2 as binders. These results in the case of TiO_2 could be associated with some structural changes occurring for this binder during calcination at 950 ºC. X-ray diffraction patterns (Table 1) revealed that TiO_2, present as anatase in the raw titanium oxide, was converted into rutile during calcination at high temperature. However, it is not so apparent when SiO_2 was used as binder. Using these binders the crushing strength increased with the CuO content indicating that the CuO as active phase also plays an important role in the mechanical properties exhibited by the fresh extrudates. In general, a higher sintering temperature produces an increase in the crushing strength of the oxygen carriers, however, for the Cu-based oxygen carriers the sintering temperature is limited by the decomposition or melting of the particles.

Based on the reactivity tests in thermobalance and crushing strength measurements it may be concluded that CuO based oxygen carriers prepared by mechanical mixing using SiO_2 or TiO_2 as binders are the most promising studied carriers to be used in CLC.

3.2. Effect of the gas composition

The effect of the gas composition on reactivity of sample Cu40Si-M is shown in Fig. 4. Two possible feeding gases to be used in a CLC process, CH_4 as the main component of the natural gas and a mixture of CO and H_2 simulating the coal gas composition from gasification, were analysed. In addition, H_2 was also used as a reference. In reduction, complete conversion of the carrier was reached rapidly with all gases studied, however, the reaction rate depended upon the gas composition being lower for CH_4 than for H_2 or H_2+CO. The gas composition of the gas used in reduction, however, did not affect the rate of oxidation apparently in the subsequent process to complete the cycle.

3.3. Effect of the preparation method

The preparation method used may affect the degree of dispersion of the active phase (CuO) in the oxygen carrier. To study this effect, a sample Cu40Si-C has been prepared by coprecipitation with identical composition of sample Cu40Si-M prepared by mechanical mixing. SEM-EDX line profiles of Cu Kα and Si Kα taken from the two samples revealed that Si and Cu were not chemically associated. XRD analysis confirmed the presence of CuO and SiO_2. Additionally, the degree of dispersion of the Cu containing phase, CuO, in sample

Cu40Si-C was slightly higher than in sample Cu40Si-M. This different degree of dispersion of the active phase may affect both the chemical reactivity and the mechanical strength of the carriers.

Fig. 5 shows the reactivity data of both samples. During reduction the reactivity of the sample prepared by coprecipitation was slightly lower than the prepared by mechanical mixing, however, during the oxidation the reactivity was almost identical for both samples. Additionally, the mechanical strength of samples prepared by the two different methods (see Table 2) was not so much different and, consequently, both samples were selected to carry out further studies in multicycle tests in TGA.

The oxygen carriers exhibiting acceptable crushing strengths and high conversions and reactivities were further selected for 100-cycles testing in successive oxidation-reduction tests in TGA. In every cycle the carrier undergoes important chemical and structural changes at high operating temperature and, consequently, important changes in the performance of the carriers with the number of cycles are expected. Fig. 6 shows the reactivity of the sample Cu40Si-M in several selected cycles for reduction and oxidation. The curves are almost coincident revealing that the carrier reactivity was not affected substantially by the number of cycles in use. Similar results were observed with other carriers prepared by mechanical mixing and coprecipitation.

Fig. 7 shows the appearance at low magnification of samples Cu40Si-M and Cu40Ti-M fresh and after 100 and 20 cycles, respectively. As can be observed, the original cylindrical shape of the fresh extrudates was completely converted in an amorphous powder pile after reaction indicating that the mechanical strength of the carrier was severely affected. This effect was especially important using titania as binder. With this binder the mechanical strength of the fresh sample was high but, unfortunately, it decreased after few cycles in use. Additional information on the microscopic appearance of fresh and after-use carriers at higher magnification was obtained from SEM pictures shown in Fig. 8 taken from cross sections of samples Cu40Si-M and Cu40Si-C. As can be seen, the surface of the fresh extrudates appears granular and compact while the surface of the reacted particles contains large holes and cracks probably formed by thermal stress.

From these multicycle tests it can be concluded that Cu-based oxygen carriers prepared by mechanical mixing or coprecipitation exhibit high reactivity and excellent chemical stability but poor mechanical strength. Consequently, the method of preparation must be improved to decrease the unacceptable rapid degradation of the mechanical properties of carriers as the number of cycles increases.

The effects of the accumulative chemical and thermal stresses in every cycle could be minimised if CuO as active phase is retained within the porous texture of an inert support. In this case, the inert support could be calcined at higher temperature to increase substantially its mechanical strength. Thermal sintering is not detrimental because the active phase CuO has not been incorporated yet and, additionally, the presence of macropores in the support could be assured. On the other hand, the reactivity of the active phase could be kept high in every cycle since the porous and rigid support would allow gas diffusion without rate limitations.

In this work, samples of titania and silica impregnated with CuO were prepared following the conventional method commented above. Fig. 9 shows the reactivity in 100-cycles tests in TGA of samples Cu30Ti-I and Cu20Si-I. As can be observed in this figure, these carriers showed good chemical stabilities and high reactivities, similar to or even higher than those prepared by mechanical mixing or coprecipitation and calcined at lower temperature. Fig. 10 shows SEM micrographs of surfaces of the fresh and after-use Cu20Si-I and Cu30Ti-I carriers. The presence of holes or cracks clearly are not evidenced in after-use samples and crush strength measurements revealed that the mechanical properties of the fresh carriers were preserved after reaction in multicycle tests. These results suggest that carriers prepared by wet impregnation on rigid and porous supports are potential candidates for chemical-looping combustion. However, more experimental work is needed to analyse the behaviour of these carriers with respect to agglomeration during fluidised bed cyclic reactions.

4. Conclusions

The possibility of using CuO as an oxygen carrier for a CLC process was analysed in a thermogravimetric analyser (TGA). It was found that the oxidation rate of pure CuO extrudates decreased quickly with increasing the number of cycles and after three cycles the reaction rate becomes extremely low. The oxidation rate and maximum conversion for all studied carriers were dramatically increased by the addition of a binder.

The effects of carrier composition and preparation method were investigated in order to develop oxygen carriers exhibiting high reduction and oxidation rates but maintaining the mechanical properties for a high number of oxidation-reduction cycles. It was observed that all carriers prepared by mechanical mixing or coprecipitation exhibited excellent chemical stabilities, high reactivities, and complete conversions during the cyclic process, independently on the type of binder and on the CuO concentration. However, these carriers underwent unacceptable degradation of the mechanical properties in multicycle tests in thermobalance.

To reduce the effect of chemical and thermal stresses, CuO based carriers were prepared by wet impregnation using titania and silica as supports. These new carriers exhibited high reactivities and complete conversions in multicycle tests in TGA. In addition, they maintained the chemical and mechanical properties of the fresh carriers, suggesting that impregnated carriers are good candidates for chemical-looping combustion.

Acknowledgements

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Table 1. Crystalline phases and concentrations (wt%) in some of the studied carriers as determined by powder XRD.

Sample	Composition
Cu40Al-M	CuO= 26 %, $CuAl_2O_4$= 74 %, amorphous Al_2O_3
Cu40Se-M	CuO= 100 %, amorphous sepiolite
Cu40Si-M	CuO= 100 %, amorphous silica
Cu40Ti-M	CuO= 40 %, rutile= 60 %
Cu40Zr-M	CuO= 41 %, ZrO_2= 59 %

Table 2. Crushing strength (N/mm) of the extrudates prepared by different methods and using different binders.

Preparation method	CuO (wt %)	Binder				
		Al_2O_3	Sepiolite	SiO_2	TiO_2	ZrO_2
M	80	3	4	22	66	6
M	60	0	0	20	59	2
M	40	0	0	17	43	1
C	40	-	-	14	-	-
I	20	-	-	27	-	-
I	30	-	-	-	60	-

Captions of the figures

Figure 1. Schematic drawing of the thermogravimetric analyzer.

Figure 2. Reactivity of pure CuO extrudates as a function of the number of reduction-oxidation cycles, using CH_4 as fuel.

Figure 3. Effect of the type of binder and CuO content on the reactivity of Cu-based oxygen carriers prepared by mechanical mixing, using CH_4 as fuel.

Figure 4. Effect of gas composition on the reactivity of Cu-based oxygen carriers.

Figure 5. Comparison of the reactivity of the samples Cu40Si-M and Cu40Si-C, using CH_4 as fuel.

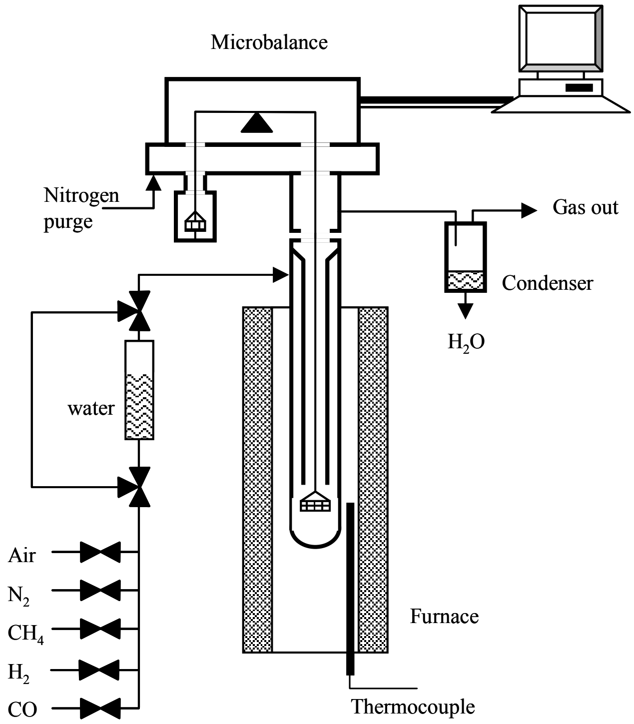
Figure 6. Effect of number of reduction-oxidation cycles on reactivity of sample Cu40Si-M, using CH_4 as fuel.

Figure 7. Photographs of fresh and after reaction carrier particles prepared by mechanical mixing.

Figure 8. SEM micrographs of fresh and after 100 cycles tests in TGA of samples Cu80Si-M and Cu40Si-C.

Figure 9. Effect of number of reduction-oxidation cycles on reactivity of samples prepared by impregnation, using CH_4 as fuel.

Figure 10. SEM micrographs of fresh and after 100 cycles tests in TGA of samples Cu20Si-I and Cu30Ti-I prepared by impregnation.


Microbalance
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Gas out
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H_2O
water
Air
N_2
CH_4
H_2
CO
Furnace
Thermocouple

Figure 1.

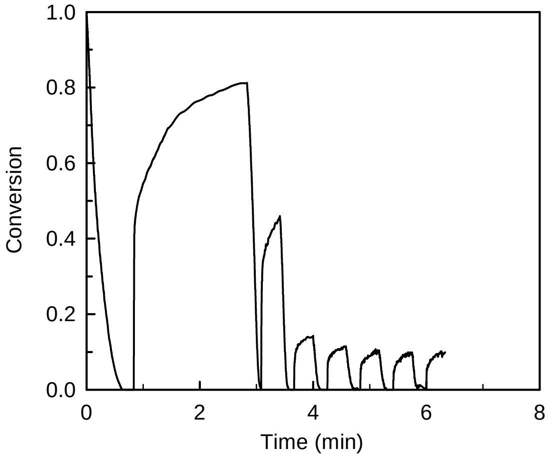

Figure 2.

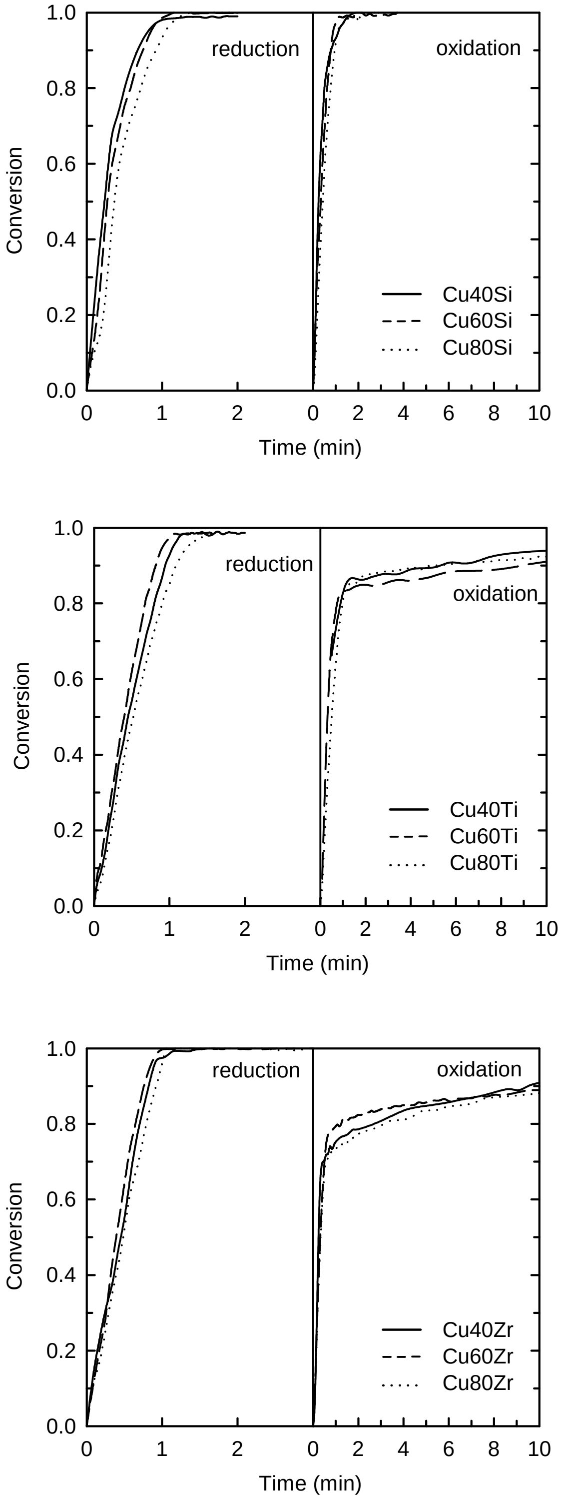
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Figure 3.

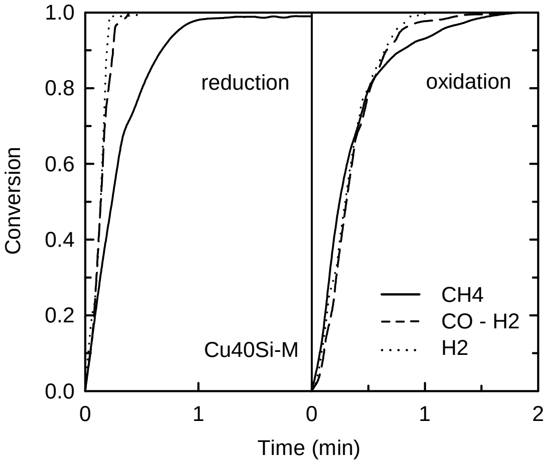
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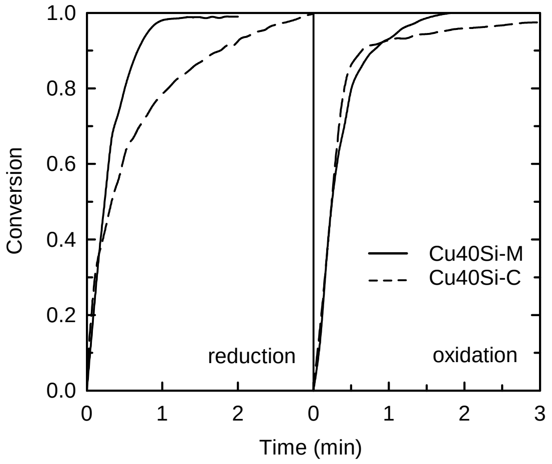
Figure 4.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reduction
oxidation
Cu40Si-M
Cu40Si-C

Figure 5.

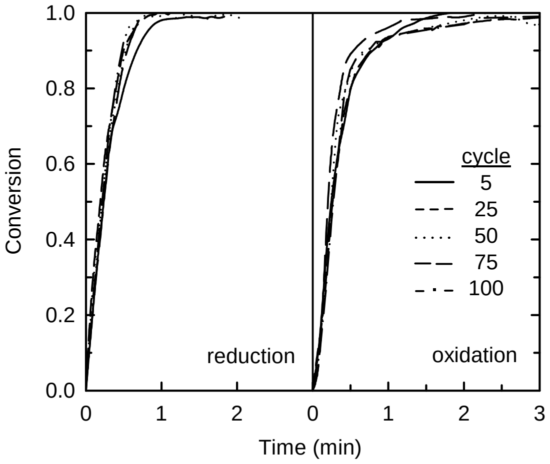

1.0
0.8
0.6
0.4
0.2
0.0
Conversion
0
1
2
0
1
2
3
Time (min)
reduction
oxidation
cycle
5
25
50
75
100

Figure 6.

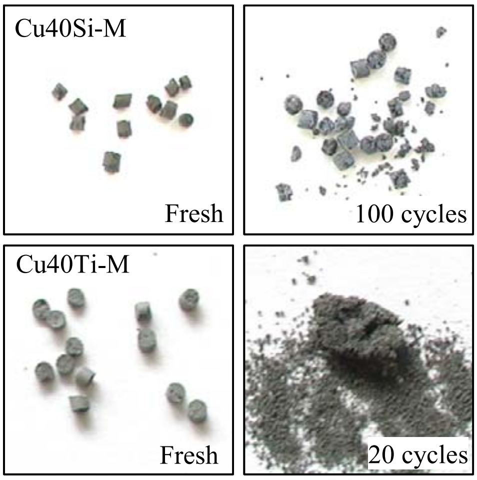


Figure 7.

Development of Cu-based Oxygen Carriers for Chemical-Looping Combustion.
Luis F. de Diego et al.

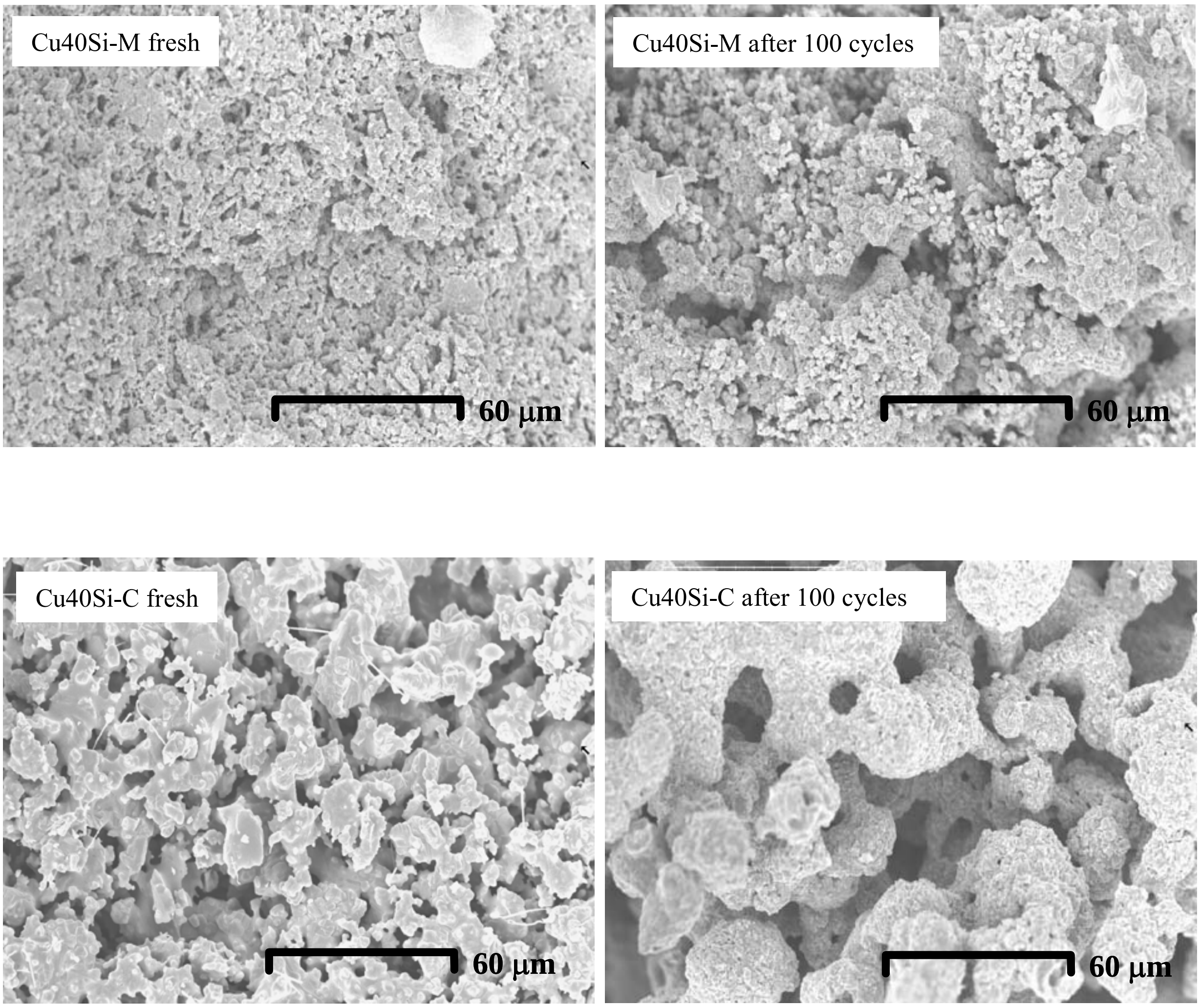
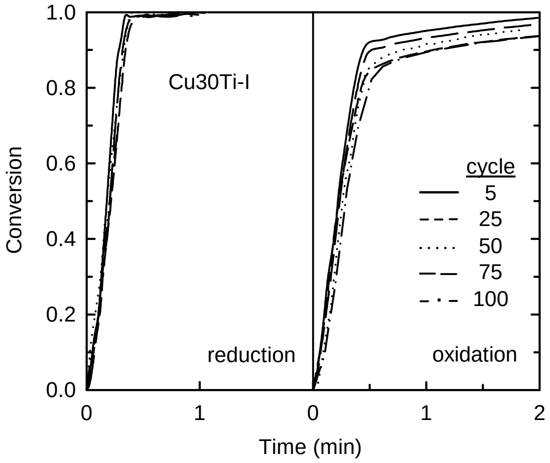


Figure 8.


Cu30Ti-I
Conversion
0.0
0.2
0.4
0.6
0.8
1.0
Time (min)
0
1
0
1
2
reduction
oxidation
cycle
5
25
50
75
100

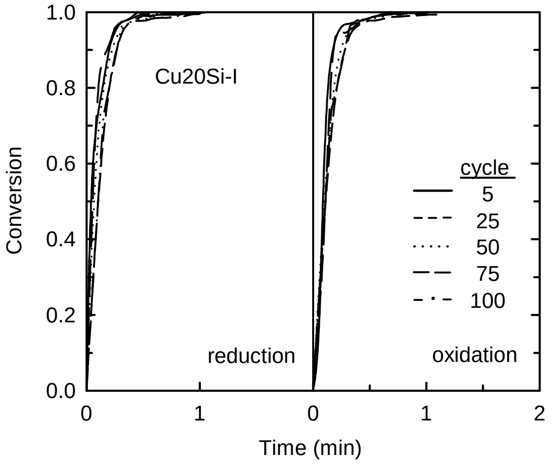

Cu20Si-I
Conversion
0.0
0.2
0.4
0.6
0.8
1.0
Time (min)
0
1
0
1
2
reduction
oxidation
cycle
5
25
50
75
100

Figure 9.

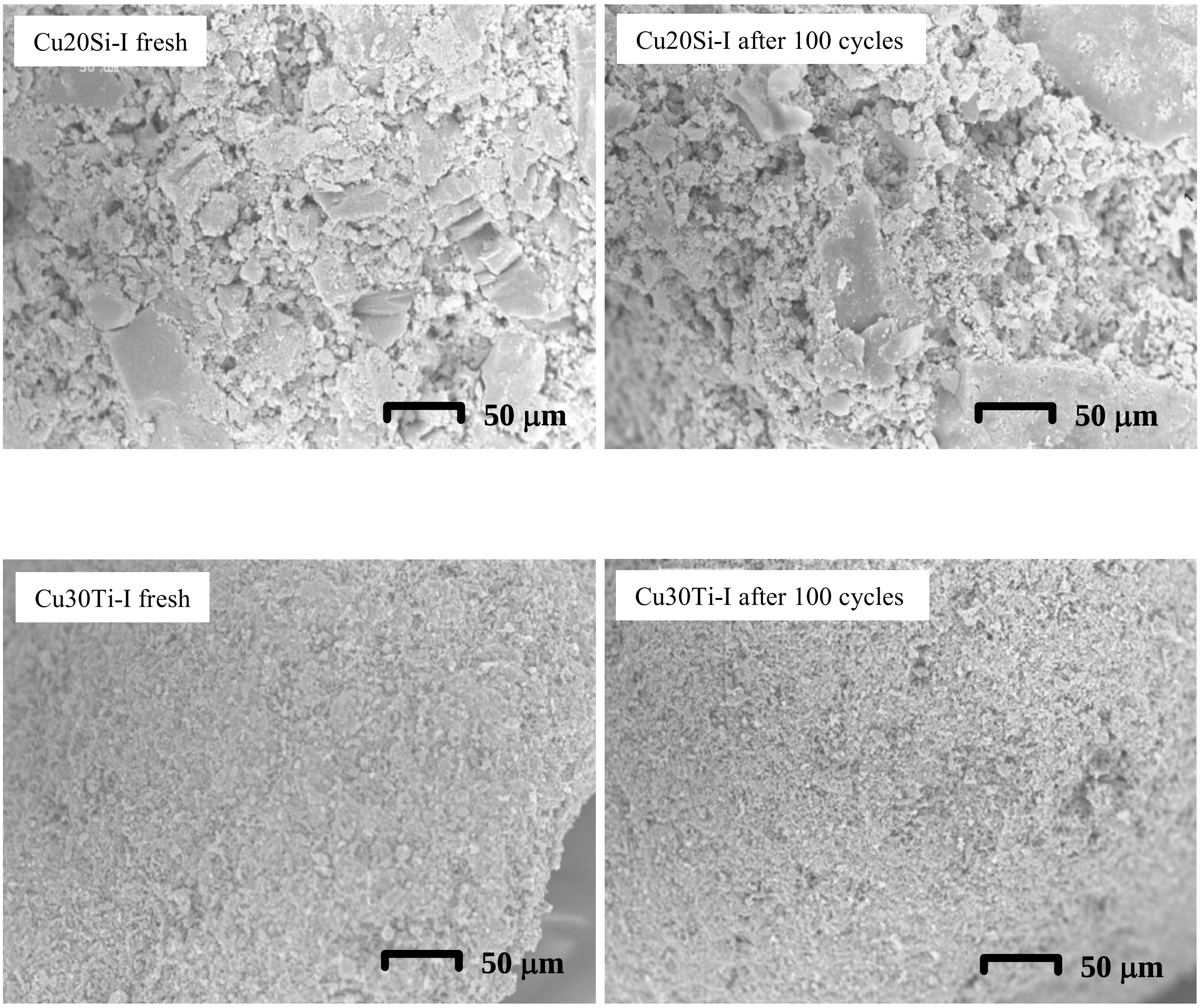

Cu20Si-I fresh
50 µm
Cu20Si-I after 100 cycles
50 µm
Cu30Ti-I fresh
50 µm
Cu30Ti-I after 100 cycles
50 µm

Figure 10.