

Supporting information

# CuO promoted Mn<sub>2</sub>O<sub>3</sub>-based materials for solid fuel combustion with inherent CO<sub>2</sub> capture

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## Experimental

### Chemicals

All chemicals were of analytical grade and were used without further purification. Aqueous solutions were prepared using reverse osmosis water (15 MΩ cm). Copper (II) nitrate hydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O) and sodium hydroxide (NaOH) were purchased from Fisher Scientific and manganese (II) nitrate hydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) from Sigma-Aldrich.

### Synthesis of the oxygen carriers

Cu-Mn-based oxygen carriers were synthesized *via* a co-precipitation technique at room temperature. The precipitating agent, NaOH (2 M), was added dropwise under vigorous stirring to an aqueous solution containing Cu(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (1 M) and Mn(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O (1 M) until a pH value of 13 was obtained. The quantities of Cu- and Mn-nitrate were adjusted such that the calcined oxygen carriers contained the following mass fractions of CuO, *viz.* 25, 34, 50, or 75 wt. %. The resulting slurry was aged for 2 h. Subsequently, the precipitate was filtered and washed several times with reverse osmosis water (15 MΩcm at 25 °C) to remove excess nitrate and Na<sup>+</sup> ions (the conductivity of the filtrate was <200 μS·cm<sup>-1</sup>). The washed precipitate was placed in an oven at 100 °C for 24 h. The dried oxygen carriers were subsequently calcined in a muffle furnace at 900 °C for 2 h (heating rate 5 °C/min). Finally, the calcined material was crushed and sieved into the size ranges of 53-106 μm, 300-425 μm and 500-600 μm. The nomenclature xCu-yMn refers to an oxygen carrier that contains x wt. % CuO and y wt. % Mn<sub>2</sub>O<sub>3</sub>. Additionally, an Al<sub>2</sub>O<sub>3</sub>-supported, Cu-based oxygen carrier (labelled CuAl) was synthesized according to the protocol reported by Imtiaz *et al.*<sup>22</sup> and used as a reference material. The CuAl oxygen carrier contained 70 wt. % CuO.

### Material characterization

Powder X-ray diffraction (XRD) patterns were acquired using a Bruker AXS D8 Advance X-ray diffractometer (Cu-K<sub>α</sub>, λ=0.1541 nm at 40 kV and 40 mA) scanning over a 2θ range from 10 to 80°. The step size was 0.0275°. Additionally, *in-situ* XRD patterns were obtained using a PANalytical X'Pert PRO θ-θ scan system (Cu-K<sub>α</sub>). The diffraction patterns were recorded from 2θ = 25 - 50° with an angular step size of 0.02626°. In a typical experiment 0.3 g of the sample (50-100 μm) was placed in a reactor chamber (XRK 900, Anton Paar). The flow of the reactive gases was metered *via* mass flow controllers (5850 TR, Brooks instrument). In a typical *in-situ* XRD experiment, the oxygen carriers were first heated to 850 °C in a flow of N<sub>2</sub> (100 mL/min) with a heating rate of 10 °C/min. The decomposition reaction was performed for 0.5 h at 850 °C in N<sub>2</sub>. Subsequently, the oxygen carrier was re-oxidized in air (100 mL/min) for 0.5 h. The decomposition and oxidation cycle was repeated three times.

Scanning electron micrographs were acquired with a FEI Quanta 200 FEG microscope operated at 10 kV. Prior to imaging the samples were sputter-coated with a thin layer of gold.

X-Ray absorption spectra at the Cu *K* and Mn *K*-edges were collected at the BM01B (Swiss Norwegian Beamlines, SNBL) beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The electron energy in the storage ring was 6 GeV with a maximum current of 200 mA. The measurements were performed in transmission mode using a Si(111)

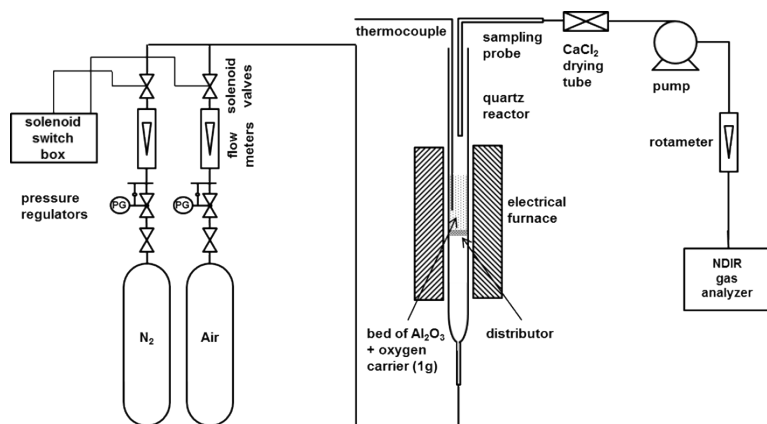
double crystal monochromator. The second crystal of the monochromator was detuned by 60% in order to suppress higher harmonic radiation. The intensities of the incident and transmitted X-rays were monitored with nitrogen- and argon-filled ionization chambers. All spectra were acquired in a continuous scanning mode from 6530 to 7000 eV for Mn *K*-edge and from 8970 to 9300 eV for Cu *K*-edge, with energy steps of 0.4 eV and an integration time of 400 ms. The samples were homogeneously mixed with small amounts of cellulose and pressed into pellets.

### Thermo-gravimetric analysis

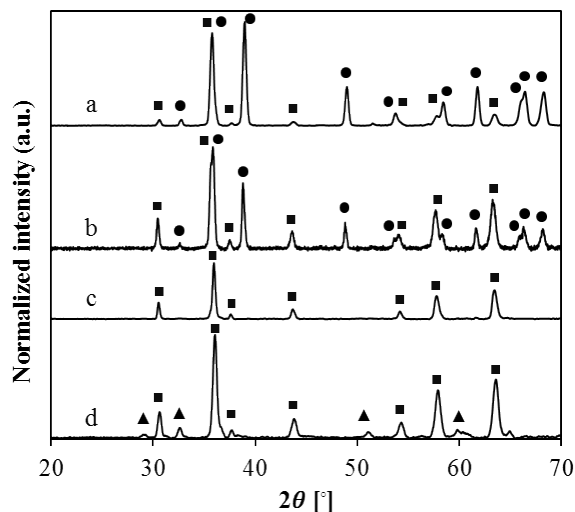
A thermo-gravimetric analyser (TGA, Mettler Toledo TGA/DSC 1) was used to determine the CLOU characteristics of the synthesized oxygen carriers at 850 °C over 10 cycles. Here, a sample of the oxygen carrier (~30 mg) was placed in an alumina crucible and heated to 850 °C at a rate of 10 °C/min in air (50 mL/min). Once the set temperature was reached, the oxygen carrier was allowed to decompose in a flow of N<sub>2</sub> (50 mL/min) for 25 min. Subsequently, the N<sub>2</sub> flow was stopped and the material was re-oxidized in air (50 mL/min) for 20 min. To determine the total oxygen carrying capacity and the decomposition characteristics of the oxygen carriers, temperature programmed decomposition (TPD) experiments were performed in a TGA (TGA, Mettler Toledo TGA/DSC 1). In a typical experiment, a small quantity (~30 mg) of the oxygen carrier was heated from room temperature to 1050 °C at a rate of 10 °C/min in a N<sub>2</sub> atmosphere (50 mL/min). To study the reducibility of the oxygen carriers, hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was conducted. In a typical TPR experiment, a small amount of oxygen carrier (<30 mg) was placed in an alumina crucible and heated to 1000 °C at a rate of 10 °C /min under a flow of 100 mL/min H<sub>2</sub> (8 vol. % H<sub>2</sub> in N<sub>2</sub>). The consumption of H<sub>2</sub> was recorded with a thermal conductivity analyser (ABB Caldos27).

### Fluidised and packed bed experiments

The equilibrium oxygen partial pressure of the oxygen carriers was determined in a packed bed reactor at 800 °C. In these experiments, 2.5 g of the oxygen carrier (300-425 µm) was used. In addition, 5 g of alumina (300-425 µm) was placed on top of the oxygen carrier to preheat the gas (0.5 L/min N<sub>2</sub>). To determine the CLOU characteristics of the synthesized oxygen carriers under practically relevant conditions, fluidised bed experiments were performed. The fluidized bed was made of quartz glass (i.d. 29.5 mm and length 460 mm). A porous frit served as the distributor and was located 300 mm above the bottom of the reactor. The reactor was heated in a tubular electric furnace and the temperature of the fluidized bed was controlled by a PID controller using a N-type thermocouple. The flow rates of the gases were recorded *via* flow meters (Honeywell AWM5101N). The off gas was sampled *via* a quartz tube. The sampled gas stream (1 L/min) was first pumped through a desiccating tube containing CaCl<sub>2</sub>. Subsequently, the dried gas stream passed through two non-dispersive infra-red (NDIR) gas analyzers (ABB EL3020 and AO2020) to measure the volume fraction of CO<sub>2</sub> and O<sub>2</sub> in the sampled gas stream. In these experiments, 1 g of the oxygen carrier (500-600 µm) was added to the fluidised bed (15 g of alumina, 300-425 µm). Experiments were performed at 850 °C or 950 °C under N<sub>2</sub> (2 L/min) and air (1.85 L/min) to decompose and re-oxidise the sample, respectively. A schematic sketch of the experimental setup is given in Figure S1. The CLOU performance of the Cu-Mn bimetallic oxygen carriers was investigated further by adding a solid fuel (50 mg charcoal 500-600 µm) to a fluidised bed that contained 10 g of the oxygen carrier (500-600 µm). The bed was operated isothermally at 800 °C. To re-oxidise the decomposed oxygen carrier a flow of 5% O<sub>2</sub> in N<sub>2</sub> was used. The sample of charcoal was fed to the fluidising bed once the oxygen concentration in the off-gas approached the equilibrium oxygen partial pressure, as determined in the packed bed experiments.



**Figure S1:** Schematic diagram of the fluidized bed setup.

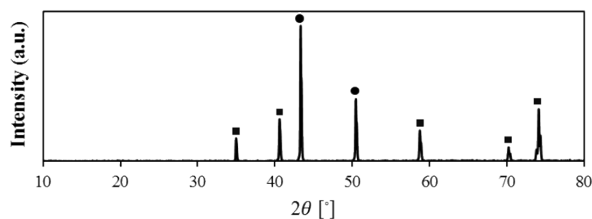


**Figure S2:** XRD patterns of the calcined oxygen carriers. (a) 75Cu-25Mn, (b) 50Cu-50Mn, (c) 34Cu-66Mn, (d) 25Cu-75Mn. The following phases were identified: (■)  $\text{CuMn}_2\text{O}_4$ , (▲)  $\text{Mn}_3\text{O}_4$ , (●)  $\text{CuO}$ .

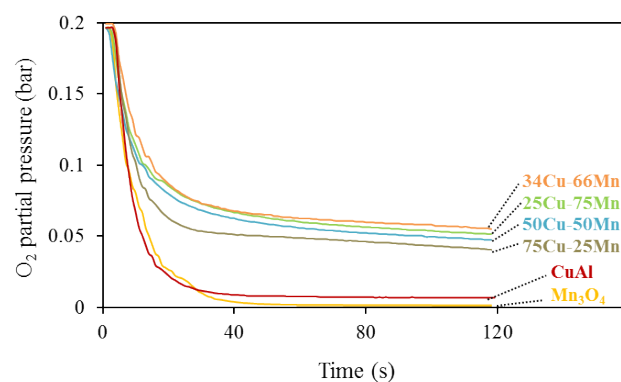
**Table S1:**  $\text{H}_2$ -TPR characteristics of the synthesized oxygen carriers: reduction temperatures and hydrogen consumption.

Oxygen carrier	Temperature of first reduction step [°C]	Temperature of second reduction step [°C]	Total $\text{H}_2$ consumed ( $\text{mmol.g}^{-1}$ ) <sup>a</sup>	Theoretical total $\text{H}_2$ consumption ( $\text{mmol.g}^{-1}$ ) <sup>b</sup>
$\text{CuO}$	335		12.3	12.5
75Cu-25Mn	290	330	12	10.8
50Cu-50Mn	290	327	10.2	9.3
34Cu-66Mn	290	324	10	8.3
25Cu-75Mn	290	320	9.5	7.9
$\text{Mn}_2\text{O}_3$	370	455	6.25	6.3

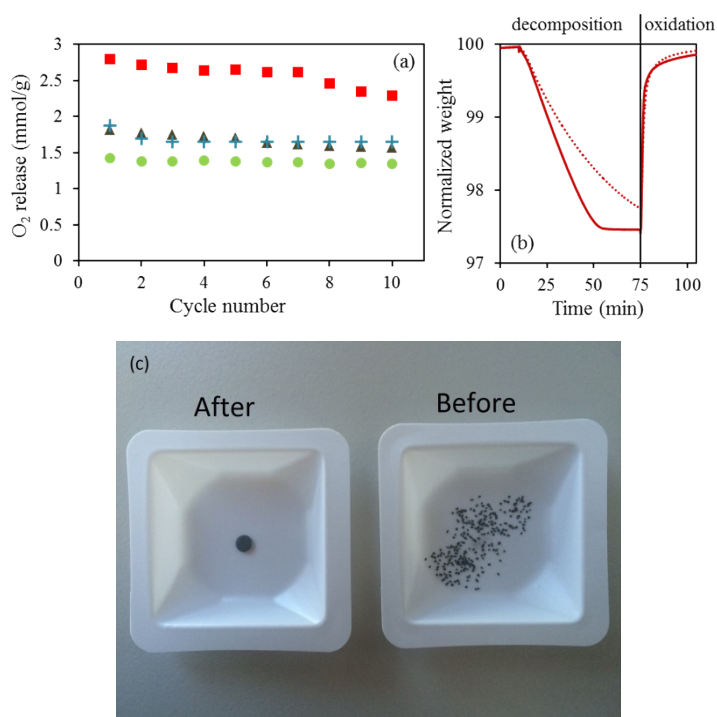
<sup>a</sup> calculated from the mass loss corresponding to the total amount of oxygen reacted with hydrogen.  
<sup>b</sup> calculated from the  $\text{CuO}$  and  $\text{Mn}_2\text{O}_3$  mass ratio in the synthesized oxygen carriers.



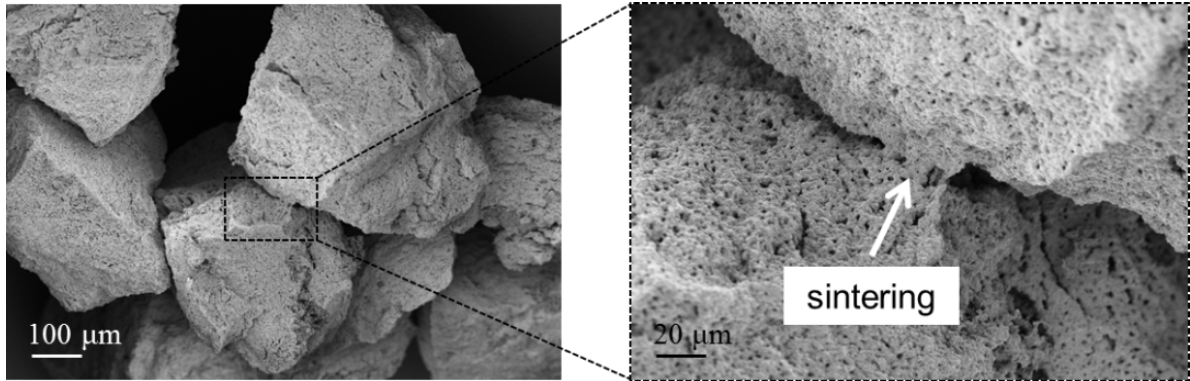
**Figure S3:** XRD pattern of 50Cu-50Mn after  $\text{H}_2$ -TPR: (■)  $\text{MnO}$ , (●)  $\text{Cu}$ .



**Figure S4:** Equilibrium  $O_2$  partial pressure of the oxygen carriers as determined in a packed bed operated at  $800\text{ }^\circ\text{C}$ .



**Figure S5:** (a) Cyclic CLOU characteristics of the bimetallic oxygen carriers as a function of cycle number: (●) 25Cu-75Mn, (+) 34Cu-66Mn (▲) 50Cu-50Mn, (■) 75Cu-25Mn. The theoretical values for 1 g oxygen carrier are 1.53, 1.67, 2.1 and 2.6 mmol for, respectively, 25Cu-75Mn, 34Cu-66Mn, 50Cu-50Mn and 75Cu-25Mn. (b) Decomposition and oxidation characteristics of 75Cu-25Mn as a function of cycle number: (—) 2<sup>nd</sup> cycle and (---) 10<sup>th</sup> cycle. (c) Optical images of the 75Cu-25Mn particles before and after CLOU cycles.



**Figure S6:** SEM image of the cycled 50Cu-50Mn oxygen carrier after being exposed to 25 cycles in a fluidised bed operated at 850 °C.