Supplementary file

Development of MgAl₂O₄-stabilized, Cu-doped, Fe₂O₃-based

oxygen carriers for thermochemical water-splitting

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Figure S1: Schematic diagram of the experimental set-up.

The reactor (i.d. 19.8 mm, length 590 mm) was made of recrystallized alumina and contained a perforated frit to support the bed. The reactor was heated by an electric furnace (Carbolite MTF tube furnace), the temperature of the bed being controlled via an N-type thermocouple. For all experiments, 0.5 g of an oxygen carrier (+300, -425 μ m) was mixed with 5 g of Al₂O₃ $(+300, -425 \ \mu\text{m})$. This mixture was then sandwiched between layers of $+1.4, -1.7 \ \text{mm} \ \text{Al}_2\text{O}_3$. The lower layer comprising Al₂O₃ and quartz wool prevented the material from falling through the holes in the perforated frit. The upper layer preheated the inlet gas which was supplied from the top of the reactor. The flow rates of the gases, viz. (i) 10 % CH₄ in N₂, (ii) N₂ and (iii) 5 % O₂ in N₂ were recorded using calibrated mass flow meters (AWM5101VN, Honeywell). Liquid water was pumped at a rate of 12 mL/h via a syringe pump into an evaporator maintained at 210 °C. The resulting mixture comprising 15 vol. % steam in N2 was fed via a heated line (also maintained at 210 °C) into the reactor. The atmosphere in the reactor was switched via a computer-controlled setup comprising solenoid valves and a switch box. Steam present in the outlet gas was removed first by condensation *via* an ice bath and subsequently *via* a CaCl₂ trap. The composition of the effluent stream was analyzed continuously using (i) a non-dispersive infrared (NDIR) analyzer measuring CO, CO₂ and CH₄ (ABB Uras26), (ii) a paramagnetic analyzer measuring O₂ (ABB Magnos27) and (iii) a thermal conductivity analyzer measuring H₂ (ABB Caldos27).



Figure S2: Scanning electron micrographs of the calcined oxygen carriers: (a) Fe70MgAl30, (b) Fe71Cu02MgAl27, (c) Fe71Cu08MgAl21, (d) Fe73Cu17MgAl10, (e) Fe75Cu25, (f) pure, *i.e.* unsupported Fe₂O₃ and (g) pure CuO. The materials were calcined at 900 °C for 2 h.



Figure S3: CH₄-TPR profiles of (——) pure, *i.e.* unsupported Fe₂O₃, (……) pure CuO and (– · –) commercial CuFe₂O₄.



Figure S4: Reaction steps identified in the CH_4 -TPR profiles of the synthesized oxygen carriers: (a) Fe70MgAl30, (b) Fe71Cu02MgAl27, (c) Fe71Cu08MgAl21, (d) Fe73Cu17MgAl10 and (e) Fe75Cu25.



Figure S5: X-ray diffractograms of the reduced oxygen carriers: (a) Fe70MgAl30, (b) Fe71Cu02MgAl27, (c) Fe71Cu08MgAl21, (d) Fe73Cu17MgAl10 and (e) Fe75Cu25. The following compounds were identified: (**a**) Fe, (**a**) Fe₃C, (**•**) MgAl₂O₄, (**•**) Cu and (-) FeO.



Figure S6: CO_x yield during re-oxidation using 15 vol. % steam in N₂. The experiments were performed in a packed bed at 900 °C and the duration of the steam oxidation reaction was fixed to 8 min: (•) Fe70MgAl30, (×) Fe71Cu02MgAl27, (•) Fe71Cu08MgAl21, (•) Fe73Cu17MgAl10 and (\blacktriangle) Fe75Cu25.

oxygen carriers, as determined by refining theoretical EXAFS functions.										
Na		R ^b [Å]		σ ^{2, c}	k-range	R-factor ^d				
$Fe - Fe_1$	$Fe - Fe_2$	$Fe - Fe_1$	$Fe - Fe_2$	[Å ²]	[Å-1]	[%]				
Fe foil										
8.0	6.0	2.46 ± 0.01	2.85 ± 0.01	0.0049 ± 0.0002	2.7 - 13.0	1.04				
Fe70MgA130										
8.0	6.0	2.47 ± 0.01	2.83 ± 0.01	0.0066 ± 0.0003	2.7 - 14.0	1.04				
Fe73Cu17MgAl10										
8.0	6.0	2.47 ± 0.01	2.83 ± 0.01	0.0074 ± 0.0003	2.7 - 14.0	1.04				

Table S1. Structural parameters for the first Fe-Fe shell in the reference Fe foil and reduced

^aN = coordination number, fixed; ^bR = Fe-Fe distance; ^c σ^2 = EXAFS Debye-Waller factor; ^dRfactor indicates the normalized sum of residuals.

Table S2. Structural parameters for the first Cu-Cu shell in the reference Cu foil and reduced									
Fe73Cu17MgA110, as determined by refining theoretical EXAFS functions.									
	Na	R ^b	σ ^{2, c}	k-range	R-factor ^d				
		[Å]	$[Å^2]$	[Å-1]	[%]				
Cu foil	12.0	2.54 ± 0.01	0.0074 ± 0.0003	3.0 - 13.5	1.90				
Fe73Cu17MgAl10	12.0	2.54 ± 0.01	0.0086 ± 0.0007	3.0 - 13.5	1.90				
^a N = coordination number, fixed; ^b R = Fe-Fe distance; ^c σ^2 = EXAFS Debye-Waller factor;									
^d R-factor indicates the normalized sum of residuals.									



Figure S7: Scanning electron micrographs of cycled oxygen carriers (oxidized form): (a) Fe70MgAl30, (b) Fe71Cu02MgAl27, (c) Fe71Cu08MgAl21, (d) Fe73Cu17MgAl10 and (e) Fe75Cu25.



Figure S8: Gas composition of the effluent gas during steam oxidation (15th cycle): (a) Fe70MgAl30 and (b) Fe71Cu08MgAl21. The experiments were performed in a packed bed at 900 °C. The duration of the steam oxidation was fixed to 8 min: (-) H₂, (-) CO and (-) CO₂.



Figure S9: Raman spectra of oxygen carriers exposed to 10 vol. % CH_4 in N_2 for 1 h at 900 °C in a TGA: (a) Fe70MgAl30, (b) Fe71Cu08MgAl21, (c) Fe73Cu17MgAl10 and (d) Fe75Cu25.

The Raman spectrum of reduced Fe70MgAl30 confirms the deposition of graphite on its surface. The Raman shift at 1582 cm⁻¹ (G band) corresponds to the sp² carbon networks of graphite. The so-called D and D' bands (at 1310 cm⁻¹ and 1620 cm⁻¹, respectively) are the defect induced Raman features of graphite. The Raman spectra indicate that graphite was also deposited on the surface of Fe70Cu10MgAl20 and Fe70Cu20MgAl10. However, the propensity for coke deposition decreased with increasing Cu content. No carbon deposition was observed for the reference material Fe70Cu30 as it was not fully reduced to metallic Fe and Cu at the end of the experiment (1 h of reduction with 10 % CH₄ in N₂).