In-situ X-ray absorption spectroscopy study of Na-doped and Al_2O_3-stabilized, CuO-based oxygen carriers for chemical looping combustion and chemical looping with oxygen uncoupling

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Abstract

Chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) are emerging carbon capture and storage (CCS) technologies that are conceptually linked to oxy-fuel combustion. In CLC, hydro-carbonaceous fuels are combusted using the lattice oxygen of an oxygen carrier, typically a transition metal oxide. In the case of CLOU, the hydro-carbonaceous fuel is combusted with molecular oxygen derived from the decomposition reaction of a transition metal oxide. The CuO-Cu_2O-Cu system is very suitable for both CLC and CLOU owing to its (i) high oxygen carrying and uncoupling capacity of, respectively, 0.2 g O_2/g CuO and 0.1 g O_2/g CuO and fast kinetics for the reduction and decomposition reactions. However, CuO has one main disadvantage, *i.e.* the low Tammann temperature of CuO of 526 °C. Therefore, CuO requires stabilization by a high Tammann temperature support, *e.g.* Al_2O_3 or $MgAl_2O_4$. Al_2O_3-stabilized, CuO-based oxygen carriers have received considerable attention owing to the low cost of Al_2O_3.[i] However, Al_2O_3 can form mixed oxides with CuO, *viz.* $CuAl_2O_4$ (spinel) and $CuAlO_2$ (delafossite). Compared to the CuO-Cu_2O couple, the $CuAl_2O_4$-$CuAlO_2$ couple possesses a low oxygen equilibrium partial pressure and a slow decomposition/re-oxidation kinetics. Therefore, the formation of $CuAl_2O_4$ negatively affects the CLOU performance of Al_2O_3-stabilized, CuO-based oxygen carriers. Interestingly, the formation of the $CuAl_2O_4$ spinel can be inhibited by the incorporation of Na^+ or K^+ ions in the CuO-Al_2O_3 matrix. Here, we utilized a sol-gel technique to synthesize Na^+ promoted (1-5 wt. %) and Al_2O_3-stabilized, CuO-based oxygen carriers containing 80 wt. % CuO. The synthesized oxygen carriers were characterized using powder X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), N_2 adsorption and temperature programmed decomposition. The cyclic oxygen uncoupling capacity of the synthesized materials was evaluated in a thermo-gravimetric analyzer (TGA) at 900 °C. The oxygen uncoupling capacity of Al_2O_3-stabilized CuO decreased with cycle number owing to the slow oxidation kinetics of $CuAlO_2$. On the other hand, Na^+ promoted, CuO-based oxygen carriers showed a stable oxygen uncoupling capacity with cycle number. *In-situ* X-ray

absorption spectroscopy (XAS) revealed that the presence of Na^+ ions not only inhibits the formation of $CuAl_2O_4$ but also promotes the reduction of CuO and Cu_2O. Owing to its high and stable oxygen uncoupling capacity and fast kinetcis, Na^+ doped and Al_2O_3-stabilized CuO was identified as a very promising oxygen carrier for CLC and CLOU.

[i] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L. F. de Diego, Prog. Energy Combust. Sci. 2012, 38, 215 – 282.