Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Copper-Manganese Mixed Oxides: CO_2-selectivity, Stable, and Cyclic Performance for Chemical Looping Combustion of Methane

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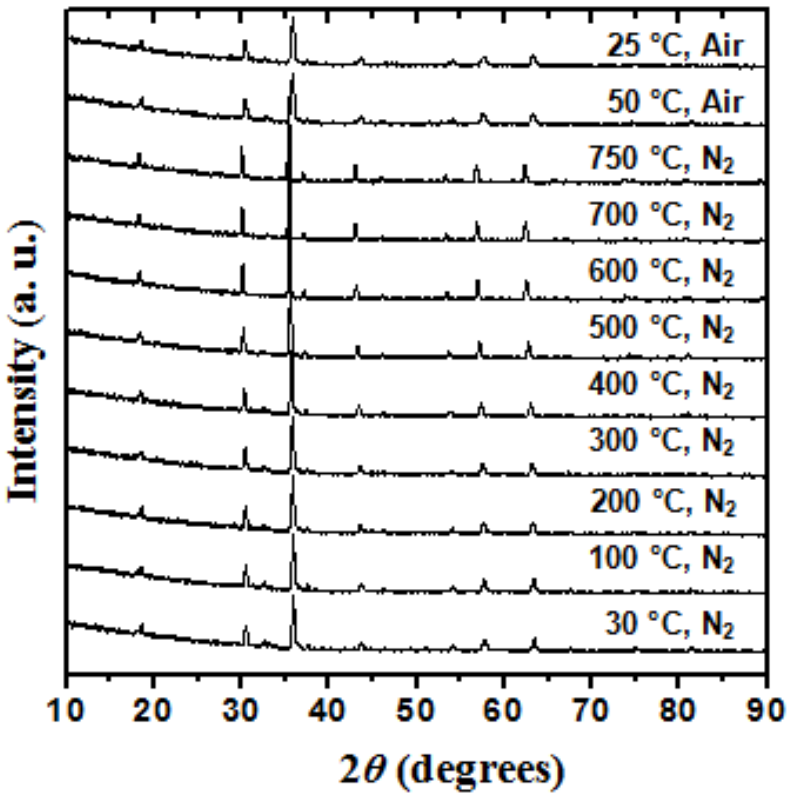

Figure S1. Temperature controlled *p*XRD profiles of $CuMn_2O_4$ at various temperatures in the presence of N_2 and air. $CuMn_2O_4$ was heated in the presence of N_2 up to 750 °C and cooled down to 25 °C in the presence of air.

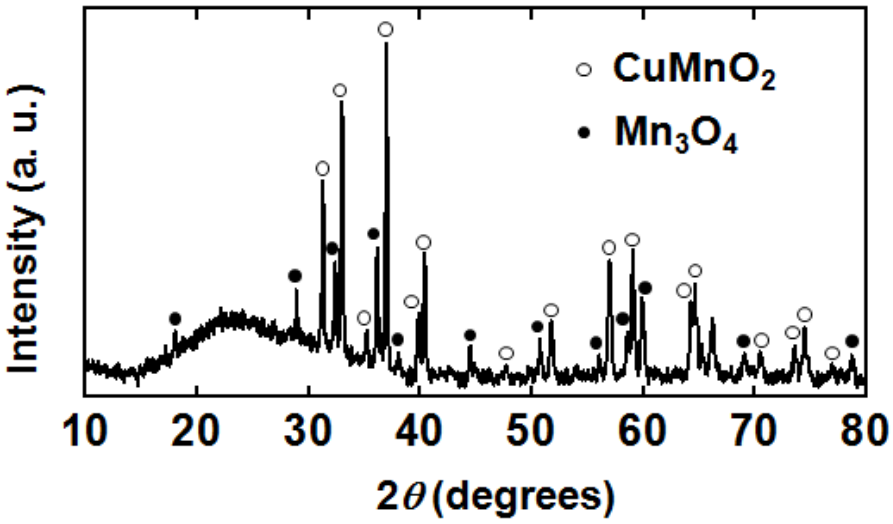

Figure S2. *p*XRD profile of $CuMn_2O_4$ after O_2-TPD experiments.

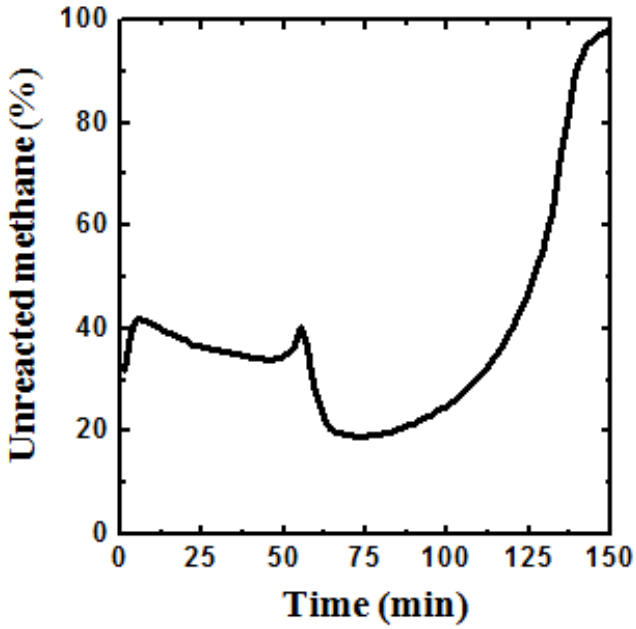

Figure S3. The dependence of un-reacted methane in the effluent stream of the outlet of the reactor as a function of time.

Figure S3 shows the percentage of un-reacted CH_4 in the effluent stream of the reactor outlet as a function of time. Approximately, 30 to 40% of un-reacted CH_4 was observed during initial stage of CH_4 combustion, however, the concentration of un-reacted CH_4 was decreased up to 20 % at around 75 min. The concentration of un-reacted CH_4 was reached 100 % at a later stage of CH_4 combustion reaction of CM. The observed trend is again consistent with the trends observed from CH_4 combustion performance (Figure 5).

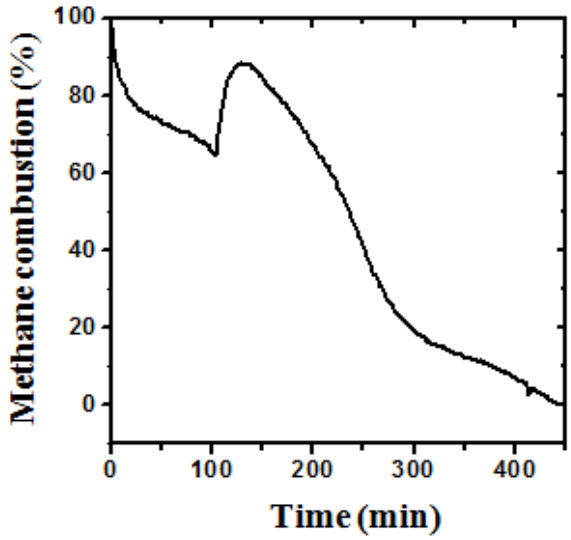

Figure S4. The CH_4 combustion efficiency for $CuMn_2O_4$ at the concentration of 2.5 % of CH_4 in the effluent stream as a function of time.

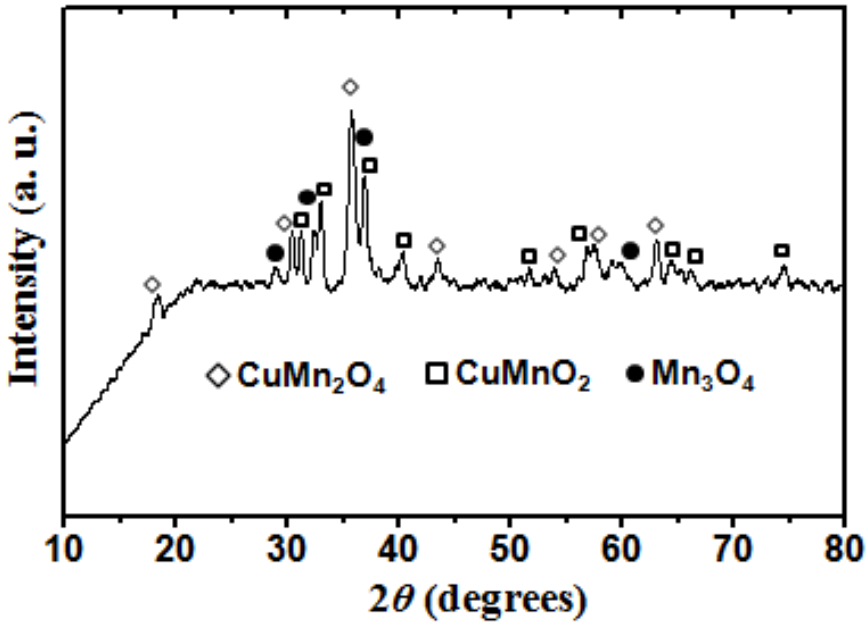

Figure S5. *p*XRD profile of the intermediate product recovered at 20 min.

*p*XRD analysis was performed to identify the structures of CM at the intermediate stage after at 20 min. as shown in Figure S5. The CH_4 combustion reaction was intentionally terminated at 20 min and the materials were recovered to perform *p*XRD analysis to identify the intermediate products. In addition to the characteristic peaks for $CuMn_2O_4$ (Figure 1), the material recovered at 20 min also showed the characteristic peaks of $CuMnO_2$, (J. Töpfer, M. Trari, P. Gravereau, J. P. Chaminade and J. P. Doumerc, *Crystalline Materials*, 1995, **210**, 184-187.) and Mn_3O_4. $CuMn_2O_4$ is thermally decomposed into the products of $CuMnO_2$ and Mn_3O_4 (Figure 4*a*) during CLC reaction for methane.

Figure S6*a* shows the *p*XRD profile for CMO (re-oxidized $CuMn_2O_4$), which is virtually consistent with the *p*XRD profile of original material CM (see Figure 1). CMO showed the characteristic peaks at 18.4°, 30.3°, 35.7°, 37.3°, 43.4°,53.8°, 57.4°, 63°, and 74.6° for the reflection planes of (111), (220), (311), (222), (400), (422), (511), (440) and (533) respectively, correspond to CM. These results clearly indicate that CMO possesses Cu-Mn-O phase similar to CM after re-oxidation of CMR. Therefore, Cu-Mn-O phase can be readily reinstated by annealing of CMR at 900 °C in the presence of air, which makes it a potential material for CLC applications.

CMO was examined further to observe their morphology after reduction and re-oxidation cycles. Figure S6*b-c* represents the FE-SEM images of CMO that showed the large-sized, agglomerated particles, which are again in irregular shapes as similar to CM (Figure 2*a*). The morphology of CM was not retained after CLC evaluation and re-oxidation; however, the particles are having the dense surfaces as shown in the magnified FE-SEM image (Figure S6*c*). These results suggest that Cu-Mn-O phase can be retained without affecting their structure after reduction and re-oxidation cycles.

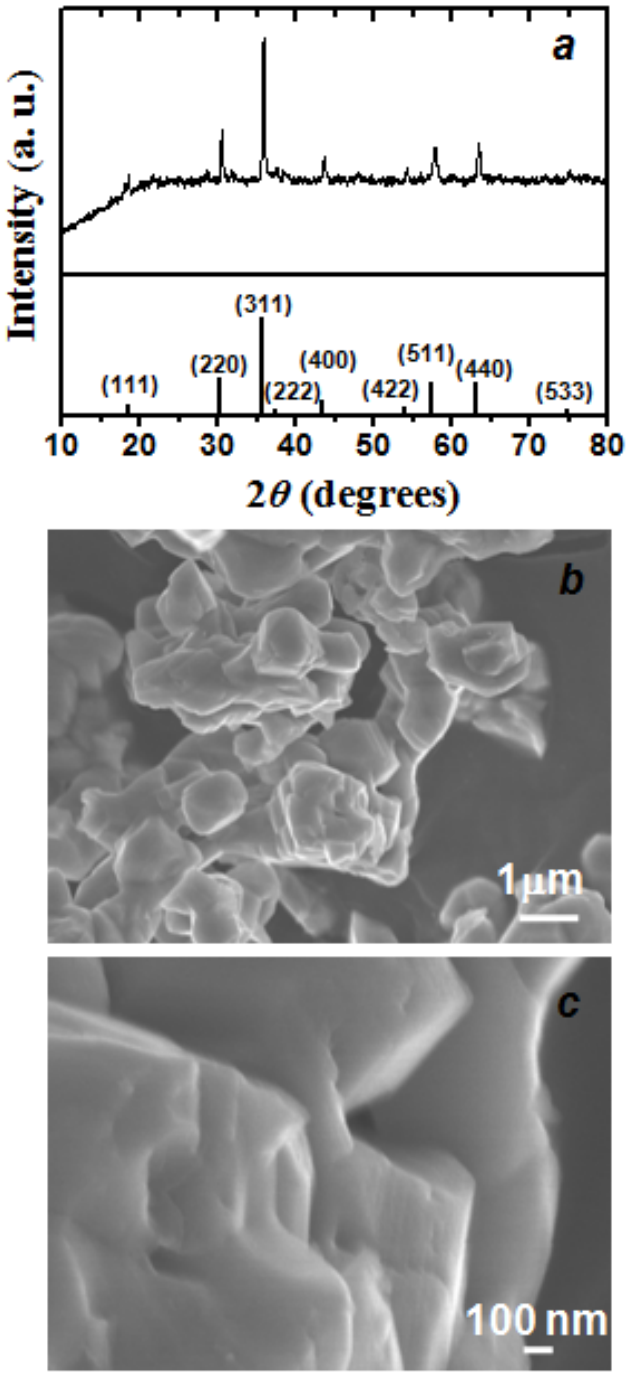

Figure S6. (*a*) *p*XRD profile of CMO (re-oxidized $CuMn_2O_4$). The simulated XRD lines for pure $CuMn_2O_4$ are shown by solid lines. (*b*-*c*) FE-SEM images of CMO.

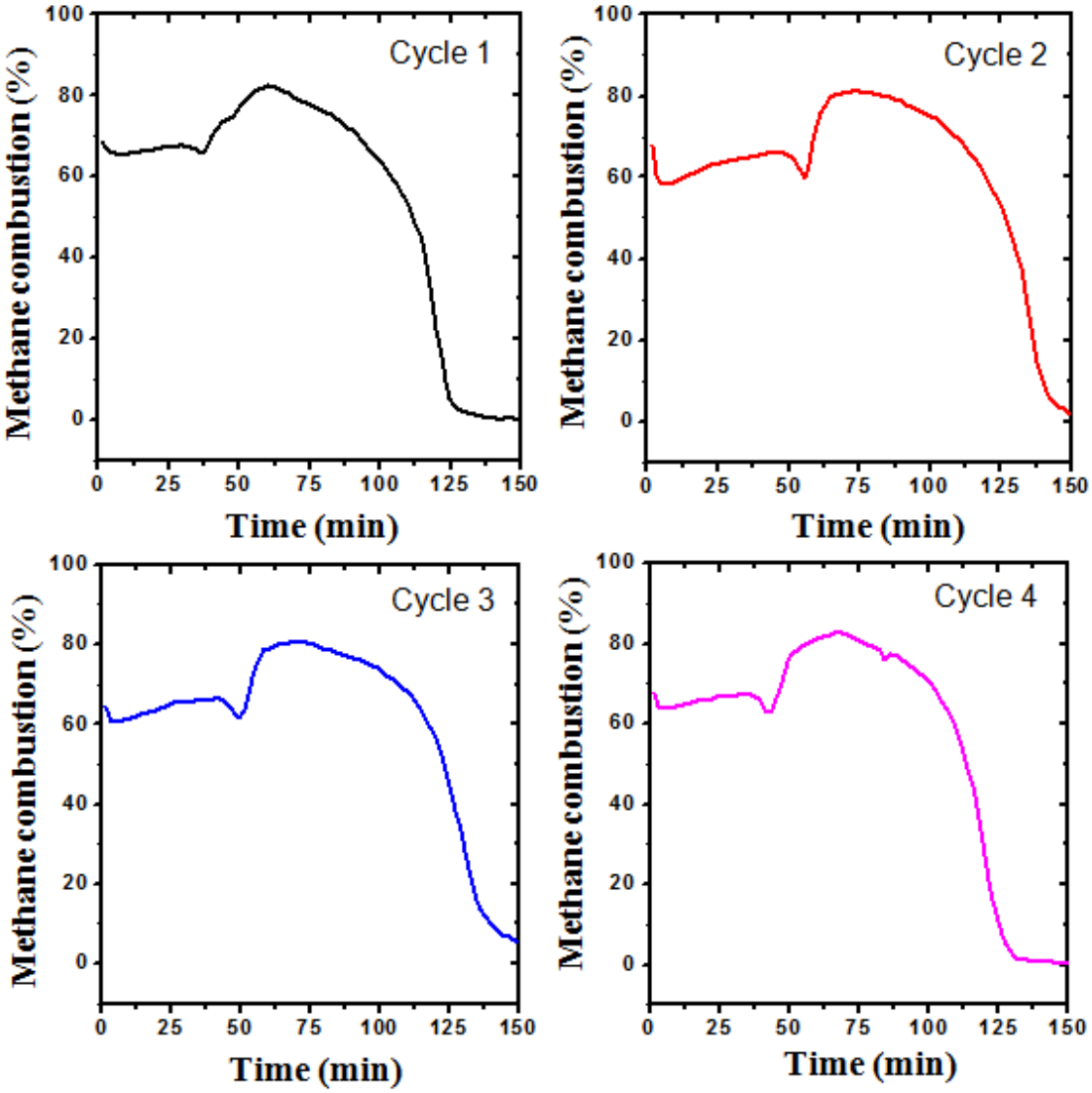

Figure S7. Multi-cycle CH_4 combustion performance of $CuMn_2O_4$ as a function of time.