

Tri-metallic Oxygen Carriers CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for Chemical Looping Combustion

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Abstract: Several tri-metallic ferrites with different ratios of Cu, Fe, and Mn were synthesized by direct decomposition method and tested for chemical looping combustion of methane, synthesis gas, and carbon. For comparison, several bi-metallic ferrites were also tested, and NiFe_2O_4 and CuFe_2O_4 showed the best performance. During a 55-cycle test, tri-metallic CuFeMnO_4 showed better overall performance than both NiFe_2O_4 and CuFe_2O_4 , which had shown the best performance among the bi-metallic ferrites for CLC of methane. From all the tri-metallic oxygen carriers with different atomic ratios of Cu, Fe, and Mn, CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed the best performance for CLC of methane. The oxygen carriers CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$, even without a support, showed very stable performance during a 100-cycle TGA test. The CuFeMnO_4 oxygen carrier also showed excellent performance during a multi-cycle CLC test with synthesis gas. CuFeMnO_4 is also suitable for CLC of a solid fuel, such as carbon, which showed stable performance during a ten-cycle test.

1. Introduction. Chemical looping combustion (CLC) is a promising technology that produces heat and energy with the significant advantage of producing concentrated CO₂ without requiring any major energy for its separation.¹ Large-scale application of CLC is dependent on the availability of a suitable oxygen carrier. The development of oxygen carriers with high reactivity, low fragmentation, and attrition, low tendency for agglomeration, low cost, and stable performance during repeated reduction/oxidation cycles at high temperature are critical for successful application of CLC in industry. The carrier should also be environmentally benign. Research on single metal oxide oxygen carriers that are traditionally used for CLC had already shown some issues, such as low reactivity with Fe₂O₃² and MnO₃³, low melting point and high agglomeration with CuO³, and health concerns with NiO⁴. Recently, scientists have been investigating mixed metal oxides instead of single metal oxides for CLC to potentially overcome the shortcomings associated with the single metal oxides. The mixture of single metal oxides may have several advantages due to synergetic effects, which could enhance the reactivity and stability, mechanical strength, and conversion of the fuel gas and lessen carbon deposition. The cost of the oxygen carrier can be low if low-cost single metal oxides are used for preparation. The environmental concerns can also be addressed if proper oxides are selected for preparation.

CuFe₂O₄ and NiFe₂O₄ are reported to have better overall performance than their single metal oxide varieties. The components of bi-metallic Cu–Fe oxygen carriers were optimized to achieve a better reactivity than Fe₂O₃ and better stability than CuO in cyclic methane CLC and coal/carbon CLC reactions.⁵⁻⁶ Superior performance of CuFe₂O₄, as compared to single-metal oxides of either CuO or Fe₂O₃, was also reported for H₂/air CLC application.⁷ Jin et al.⁸⁻⁹ investigated NiO/YSZ, CoO/YSZ, and NiO-CoO/YSZ for CLC. They found that NiO-CoO/YSZ had excellent overall performance with good reactivity, no carbon deposition, and significant regenerability for repeated

cycles of reduction and oxidation, while NiO/YSZ and CoO/YSZ have drawbacks of either higher carbon deposition or lower ability for regeneration, accompanied with increase in both the grain and pore sizes. Hossain et al.¹⁰ found the activation energies for Co–Ni/Al₂O₃ reduction to be significantly lower than that for the single metal oxide Ni/Al₂O₃ reduction, which confirms the favorable effect of Co on the reducibility of the bimetallic oxygen carrier.

The bimetallic Fe–Mn oxides supported on ZrO₂, sepiolite and Al₂O₃ prepared by solid-state mixing were found to be promising oxygen carriers for CLC using simulated synthesis gas, and MnO has a positive effect on the stability.¹⁰ In addition, combined Fe–Mn oxides with a molar ratio of Fe:Mn of 2:1 showed the best oxygen release ability, fluidizability, and methane conversion.¹¹ It was concluded that the mixed Fe–Mn oxides could contribute to faster fuel conversion, even though the total oxygen release was less compared to copper-based chemical looping with oxygen uncoupling (CLOU) materials during the tests with solid fuel. Nickel ferrite (NiFe₂O₄) had been investigated for its suitability as an oxygen carrier for CLC.¹² Redox cycling of NiFe₂O₄ oxygen carriers was performed by TGA with pure CH₄ gas and air. After five successive cycles, NiFe₂O₄ with a single phase spinel structure demonstrated higher redox cycling behavior and better stability than either standard NiO or Fe₂O₃. Iron-copper mixed metal oxide oxygen carriers were also studied with simulated synthesis gas derived from steam gasification of coal¹³. Bimetallic Fe–Cu/support oxygen carriers in this study showed higher reduction rates than Fe-support oxygen carriers. The carriers containing higher Cu content showed better stabilities and better reduction rates. The oxidation reaction was significantly faster than the reduction reaction for all supported Fe–Cu oxygen carriers. Carriers with higher Cu content had lower oxidation rates. Various oxygen carriers for different CLC applications have been summarized in the literature¹⁴⁻¹⁶.

In the current study, the tri-metallic ferrite oxygen carrier CuFeMnO_4 was synthesized to investigate its performance for CLC of methane, synthesis gas, and carbon. For comparison, eight oxygen carriers: second group bi-metallic ferrites (MgFe_2O_4 , CaFe_2O_4 , SrFe_2O_4 , and BaFe_2O_4) and transition metal bi-metallic ferrites (NiFe_2O_4 , CuFe_2O_4 , MnFeO_3 , and CoFe_2O_4) prepared by a direct decomposition method were also tested. Among these bi-metallic ferrites, NiFe_2O_4 showed the best performance for CH_4 conversion to CO_2 . However, there are safety and health concerns with nickel. The cost of oxygen carriers and the cost of the preparation method are also critical for the commercialization of CLC, and hence Fe, Cu, and Mn were chosen for the low-cost synthesis of various formulations of the tri-metallic oxygen carrier $\text{Cu}_x\text{Fe}_y\text{Mn}_z\text{O}_4$. To increase the stability, 20 % Al_2O_3 was also incorporated in some formulations. Tri-metallic oxygen carriers with different atomic ratios of Fe, Cu, and Mn were tested for their performance with methane, synthesis gas, and carbon to optimize the formulation.

2. Experimental

2.1 Synthesis of Oxygen Carriers. The direct decomposition method was used for the synthesis of both bi- and tri-metallic ferrite oxygen carriers because it is more cost effective and convenient. Metal nitrates or metal acetates were used as the precursors of oxygen carriers. Stoichiometric amounts of either metal nitrate or metal acetate were mixed with citric acid to enhance bonding and to prevent agglomeration at high temperature. The mixed metal salts (precursors of the tri-metallic ferrite oxygen carrier CuFeMnO_4) were decomposed at $500\text{ }^\circ\text{C}$ initially and were cooled to room temperature in air. After additional mixing of the cooled solid mixture, it was heated to $900\text{ }^\circ\text{C}$ at a ramping rate of $3\text{ }^\circ\text{C}/\text{min}$ in air and kept at $900\text{ }^\circ\text{C}$ for 6 hours. To decrease the agglomeration, 20 % Al_2O_3 was incorporated into tri-metallic oxygen carriers by

the solid reaction method: 80 weight % CuFeMnO_4 was mixed with 20 weight % Al_2O_3 and was heated to 950 °C under air and kept at 950 °C for 6 hours.

The tri-metallic oxygen carriers with different atomic ratios of Cu, Fe, and Mn were also prepared by decomposing the metal salts at 500 °C initially and cooling to room temperature in air. After additional mixing of the cooled solid mixture, it was heated to 1,000 °C at a ramping rate of 3 °C/min in air and kept at 1,000 °C for 8 hours. Calcination temperature of 1000 °C was chosen because there was no agglomeration during the tests with previous samples that were calcined at 950 °C and to ensure there is adequate interaction between the metal components.

2.2 Performance Tests of Oxygen Carriers

2.2.1 Fixed Bed Reactor Tests. The oxidation and reduction of oxygen carriers with air and CH_4 were performed in a fixed bed lab-scale reactor (Autoclave Engineering BTRS-JR-PC Laboratory Reactor Systems). A mass spectrometer (MS) was used to analyze the outlet gas composition during the tests. Helium was used as purge gas between oxidation and reduction cycles. CH_4 was used for the reducing gas, while house air was used for oxidation. Programmable switching was used to control the inlet flow using a mass flow controller to perform redox cycles of the oxygen carriers. Initially, 1–5g of sample was loaded in the reactor, coupled with MS, and heated to 750–850 °C at a ramp rate of 15 °C/min under 80–100 sccm (Standard cubic centimeters per minute, Temperature = 0 °C, Pressure= 1.01 bar) of helium. During typical reduction cycles, 80–100sccm of 15–20 % CH_4 balanced in helium was introduced to the reactor for 10–20 min, followed by 80–100 sccm of purge gas helium for 30 min. Then 100 sccm of house air was introduced into the reactor for oxidation of reduced oxygen carriers for 30 min, followed by 80–100 sccm of purge gas helium for 30 min prior to the next cycle.

2.2.2 Thermo-gravimetric analysis (TGA) Tests. The stability during cyclic tests of tri-metallic oxygen carriers with different atomic ratios of Cu, Fe, and Mn was evaluated in a TGA. The initial screening tests of the oxygen carriers with different atomic ratios of Cu, Fe, and Mn were performed for 20 cycles where 1 full cycle consists of a reduction followed by oxidation of the carrier. The sample in the TGA system was heated to the reaction temperature of 800 °C at 10 °C/min in 100 % N₂ flow and at a total flow rate of 100 sccm. Following heating to the reaction temperature, the reduction cycle was conducted using 20 % CH₄/balance N₂ for 20 min. After completion of the reduction cycle, the reactor was purged with 100 % N₂ flow at 100 sccm. The oxidation cycle was conducted with air at a flow rate of 100 sccm for 20 min. After completing the oxidation cycle, the reactor was purged with 100 % N₂ at a flow rate of 100 sccm prior to the next reduction cycle. After evaluation of the 20-cycle performance data of all the tri-metallic oxygen carriers, the carriers with the most stable and the best performance for CH₄ CLC were chosen for 100-cycle tests.

2.3 X-ray Diffraction Analysis

X-ray diffraction (XRD) analysis was carried out using a Panalytical PW 3040 X-Pert Pro SRD system equipped with a 60 kV PW 3373/00 3011/20 detector. The x-ray wavelength used was Cu K α -1 at 1.54056 Å. The maximum resolution was 0.003° (2 θ). System calibration was carried out using a polysilicon pressed disk with the Si(111) referenced to 28.443° (2 θ). Sample data was acquired at 40 kV and 45 m Å in a line-focus mode using a standard PW3071/60 powder diffraction stage. XRD patterns of the fresh and following 15 redox cycles were collected at room temperature.

2.4 Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy Analysis

Scanning electron microscope (SEM) energy-dispersive x-ray spectroscopy analysis was conducted using a JEOL 7600 FESEM system interfaced to a Thermo-Electron System 7

microanalysis system. The Thermo-Electron microanalysis system is equipped with a Thermo-Electron Ultra-dry Energy Dispersive Spectrometer (EDS) and an EDAX Electron Backscatter Diffraction system.

3. Results and Discussion

3.1 **Bench-Scale Flow Reactor Tests with CH₄/Air.** The XRD patterns of the fresh group II and transition metal ferrites¹⁷ indicated that the metal ferrites exist as a MFe₂O₄ (M=Mg, Ca, Sr, Ba, Co, Ni, Cu) structure except for Mn, which exists as FeMnO₃. Performance comparison tests were conducted with two single metal oxides (Fe₂O₃ and CuO), bimetallic group II metal ferrites (MgFe₂O₄, CaFe₂O₄, SrFe₂O₄, and BaFe₂O₄) and bimetallic transition metal ferrites (CuFe₂O₄, NiFe₂O₄, CoFe₂O₄, and MnFeO₃). 20 % CH₄ balanced in He at a total flow rate of 75 sccm for 20 min was used for the reduction step at 750 °C with 1 g of solid. As shown in Figure 1, Fe₂O₃ showed a drastic decrease in performance due to agglomeration. CuO showed an initial decrease but became stable after 7 cycles. Group II metal ferrites without support materials showed stable performance but with very low methane conversions. Transition metal ferrites without inert support materials showed more stable performance than either CuO or Fe₂O₃. NiFe₂O₄ showed the best overall performance among transition metal ferrites, but there are safety and environmental issues with NiFe₂O₄.

Our previous studies^{5,13} with CuO/Fe₂O₃/support with excess CuO had shown promising results for methane CLC. CuFe₂O₄ without excess CuO and support in the present study showed high capacities, but it decreased during cyclic tests, as shown in Figure 1. Mn ferrite showed stable reactivity even though it had low capacity. Therefore Mn was incorporated in CuFe₂O₄ to improve

cyclic stability. XRD analysis was conducted to investigate the phases formed during synthesis of CuFeMnO_4 by the direct decomposition method, and the results are shown in Figure 2. XRD data indicates that the main phase of tri-metal ferrite is CuFeMnO_4 . Because NiFe_2O_4 showed the best overall performance among transition metal ferrites and group II metal ferrites, CLC performance of NiFe_2O_4 was compared with that of CuFeMnO_4 . CH_4 CLC performance tests with 5 g of CuFeMnO_4 and NiFe_2O_4 without support materials were conducted at 750 °C using 20 % CH_4 at 100 sccm of total gas flow for 10 min. Data in Figure 3 indicates that CuFeMnO_4 has a better performance for CH_4 CLC than NiFe_2O_4 at 750 °C. NiFe_2O_4 showed very stable CLC performance after 4 cycles of reduction/oxidation reactions. However CuFeMnO_4 showed some decreased CLC performance even though it had a better oxygen transfer capacity than NiFe_2O_4 . To improve the stability of CH_4 CLC performance during cyclic tests, CaFe_2O_4 , Al_2O_3 , and bentonite were selected as support materials for CuFeMnO_4 . CaFe_2O_4 is not traditionally used as a support but it was selected because it showed stable and minimal reactivity during methane CLC tests as shown in Figure 1. Figure 4 illustrates the effect of support materials on the performance of CuFeMnO_4 for CH_4 CLC. Al_2O_3 , CaFe_2O_4 , and bentonite supports with CuFeMnO_4 increased the CLC performance stability of CuFeMnO_4 during the 10-cycle test. All three materials can be candidates as support materials for CuFeMnO_4 for CH_4 CLC to prevent performance degradation.

The data in Figure 5 illustrates the effect of temperature on the performance of 20 weight % $\text{CaFe}_2\text{O}_4/\text{CuFeMnO}_4$ for CH_4 CLC. The performance with CuFeMnO_4 at 800 °C is better than that at 750 °C, but the degradation was slightly more at 800 °C than that at 750 °C. However, CuFeMnO_4 with supports had relatively stable performance at both 800 °C and 750 °C.

3.2 TGA Stability Test of Tri-metallic Oxygen Carriers with Different Atomic Ratios.

Tri-metallic oxygen carriers with Cu-Fe-Mn demonstrated better CLC performance than bi-

metallic oxygen carriers for methane CLC. In this study, nine different tri-metallic oxygen carriers with different atomic ratios of Cu, Fe, and Mn were also synthesized using similar procedures in (2.1) and tested in TGA for CH₄ CLC. The data on 20-cycle CLC screening tests of tri-metallic oxygen carriers shown in Figure 6 indicated that CuFeMnO₄, CuFeMn₂O₄, and CuFe_{0.5}Mn_{1.5}O₄ have the best oxygen carrier capacities and stabilities during the cyclic tests. For comparison, the data with NiFeO₄, the best performing bimetallic oxygen carrier, is also shown in Figure 6, and it showed a decrease in carrier capacity during the cyclic tests at 800 °C. The tri-metallic Cu-Mn-Fe carriers with specific compositions had stable capacities even without an inert support material. The oxygen transfer capacities of various formulations of Cu-Fe-Mn carriers are listed in Table 1. CuFeMnO₄, CuFeMn₂O₄, and CuFe_{0.5}Mn_{1.5}O₄ showed the highest and most stable oxygen transfer capacities from all the oxygen carriers tested. The three formulations that had the best stability had both Cu/Mn and Fe/Mn ratios equal to or less than 1. When Mn concentration is higher than both Fe and Cu, the material appears to have a better performance stability. The only exception is Cu_{0.5}Mn_{1.5}FeO₄, which had poor stability even though the Fe/Mn and Cu/Mn was less than 1. However, this formulation also had a Cu/Fe ratio of 0.5, while the three formulations with the best performance had Cu/Fe \geq 1.

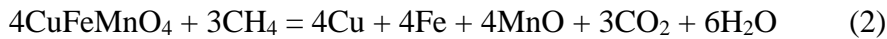
3.3 TGA 100-Cycle Test with CuFeMnO₄, CuFeMn₂O₄, and CuFe_{0.5}Mn_{1.5}O₄. Because CuFeMnO₄, CuFeMn₂O₄, and CuFe_{0.5}Mn_{1.5}O₄ showed promising results during the 20-cycle test, 100-cycle CLC tests with methane/air were conducted with these three materials. The three oxygen carriers were calcined at 1000 C for 14 hours prior to 100 cycle tests in order to make sure there will be no agglomeration during the long-term cyclic tests. The test data are shown in Figures 7, 8, and 9. All three materials showed very stable oxygen transfer capacity during the 100-cycle test at 800 °C. Achieving high stability with these materials during 100-cycles even without an inert

support is remarkable. The addition of Mn in the Cu-Fe material may play an important role in the performance stability in the 100-cycle CLC tests. Mn oxide³ showed a lower conversion rate than Fe₂O₃ and CuO, so Mn may act as inert support with a minimal contribution to the performance of CLC in Cu-Fe-Mn oxygen carriers. As also shown in Table 1, the three compositions with higher Mn (Cu/Mn < 1 and Fe/Mn < 1) showed the most stable performance. In addition, it also appears that the formulations with Cu/Fe>1 are preferable.

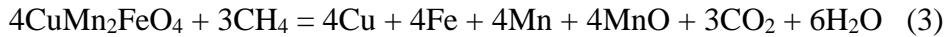
Theoretical and experimental oxygen transfer capacities for various reduction states of Cu-Fe-Mn tri-metallic oxygen carriers are listed in Table 2. The stoichiometric values of the CuFe_{0.5}Mn_{1.5}O₄ formulation matches well with oxidation states of Cu₂O, FeO, and MnO₂. Its theoretical oxygen transfer capacity for reduction to Cu, Fe, and MnO states matches well with its experimental oxygen transfer capacity. Thus, the reduction reaction could be the following:



The stoichiometric values of the CuFeMnO₄ formulation corresponds well with CuO, FeO, and MnO₂, and the oxygen transfer values during reduction correspond well with reduction states Cu, Fe, and MnO. Thus, the reduction reaction may proceed as follow:



The oxidation states of CuMn₂FeO₄ correspond well with CuO, MnO, and FeO. When reacting with CH₄, the oxygen transfer capacity matches well with the reduction states: Cu, Fe, FeO, Mn, and MnO. Thus, the reaction of CuFeMnO₄ with CH₄ could be the following:



3.4 Chemical Looping Oxygen Uncoupling (CLOU) Property Tests. To understand the CLOU properties, CuFeMnO₄ was heated to 800 °C in He (100 sccm) in the bench-scale flow reactor. The data in Figure 10 represents the amount of oxygen that can be released from 5 g of

20 % Al₂O₃/ 80 % CuFeMnO₄ at 800 °C in He (without any fuel). Oxygen release time in He was limited to 40 minutes for each cycle; then 100 sccm of house air was introduced into the reactor for oxidation of the reduced sample. This was followed by 80–100 sccm of purge gas helium for 30 min prior to the next cycle test. Oxygen from the outlet gas stream was measured using the mass spectrometer. Using the area of the peaks calculated from the triangulation method, oxygen %age release was calculated to be about 3.98 % per gram of CuFeMnO₄. The oxygen release from CuO in CuFeMnO₄ is about 3.36 %, according to the reaction $4\text{CuO} = 2\text{Cu}_2\text{O} + \text{O}_2$, so the data indicates that most of the oxygen release is contributed by CuO in CuFeMnO₄. TGA tests were also conducted with CuO and CuFeMnO₄ to understand the CLOU properties. During the 5-cycle TGA test as shown in Figure 11, the weight loss in helium was only due to the oxygen release from the CuO component, and weight gain was only due to the oxygen uptake in air of the Cu component.

3.5 Bench-Scale Flow Reactor Studies with Synthesis Gas/Air. The reaction of synthesis gas with 5 g of CuFeMnO₄, CuO, and Fe₂O₃ (without support materials) at 800 °C was evaluated because the synthesis gas reaction is important for coal CLC applications. Syngas consisting of 10.28 % H₂, 6.39 % CO, and 2.04 % CO₂ balanced by He (simulated synthesis gas derived from steam gasification of Janina coal from Poland) was introduced into the reactor at a flow rate of 100 sccm at 800 °C for 10 min for reduction, and 100 sccm of house air was used for oxidation of reduced samples. The data in Figure 12 indicates that H₂ conversion was 100 % with both Fe₂O₃ and CuFeMnO₄, while 90 % of CO was converted into CO₂ with both CuFeMnO₄ and Fe₂O₃. CuO without support showed less conversion of both CO and H₂, possibly due to some agglomeration. The data indicates that CuFeMnO₄ is an excellent oxygen carrier for synthesis gas CLC.

3.6 TGA Data of Carbon CLC with Metal Ferrites. The cyclic performance of carbon CLC with CuFeMnO_4 was tested in the TGA. Carbon was selected for this cyclic study instead of coal to avoid complications with ash accumulation during the cyclic reactions. 1.25g of 20 % $\text{Al}_2\text{O}_3/\text{CuFeMnO}_4$ was mixed with 100 mg carbon and was loaded in the TGA. Then the TGA was heated to 1,000 °C at a ramp rate of 5 °C/min under N_2 at a flow rate of 100 sccm and kept at 1,000 °C until there was no weight loss. The zero-grade air at a flow rate of 200 sccm was introduced for oxidation. The reaction rate of the oxygen carrier with carbon was calculated using TGA data as follows:

$$\text{Reduction rate} = dx/dt, X = (M_o - M)/(M_o - M_f)$$

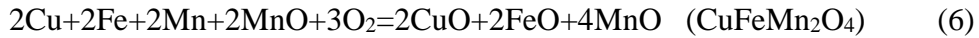
$$\text{Oxidation rate} = dx/dt, X = (M - M_f)/(M_{\text{oxd}} - M_f)$$

Where M is the instantaneous weight of the oxygen carrier-carbon mixture, M_o is the initial weight of the oxygen carrier-carbon mixture, M_f is the weight of the reduced metal after the reduction, and M_{oxd} is the weight of the completed oxidized sample after introducing air. The reaction rate dx/dt was calculated by differentiating the fifth-order polynomial equation. Figure 13 illustrates the maximum reduction and oxidation rates and reaction temperature corresponding to the maximum reaction rate during cyclic TGA tests of carbon with 20 % $\text{Al}_2\text{O}_3/\text{CuFeMnO}_4$. CuFeMnO_4 showed stable reduction rates with carbon during cyclic tests. The maximum reaction temperature increased slightly with increasing cycles up to the 4th cycle but remained constant after that. Initial temperature increase may be due to some agglomeration of the particles. CuFeMnO_4 appears to be a suitable oxygen carrier for carbon/coal CLC.

3.7 Thermodynamic Analysis. Heats of reactions of the oxygen carrier with fuel and oxygen are important parameters for the CLC process. Heat management in the CLC reactor is

easier when the reaction of the oxygen carrier with fuel is exothermic. Only a limited number of oxygen carriers have exothermic reactions with fuel.

In order to understand the heats of reaction and feasibility of reactions at various temperatures, thermodynamic analysis was performed by Factsage 6.0 for the reduction reaction (1), (2), (3) and oxidation reaction (4), (5), (6) with the best oxygen carriers CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$.



Because no data were available for CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the Factsage database, all the calculations were based on the corresponding components of Cu_2O , CuO , FeO , MnO , or MnO_2 instead of compounds CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as shown in Table 2. Heats of reaction (ΔH) and free energy (ΔG) values were computed for the three $\text{Cu}_x\text{Fe}_y\text{Mn}_z\text{O}_4$ compounds for the reactions with methane and O_2 and are shown in Figure 14. The heats of reactions with methane for all the reduction and oxidation reactions are exothermic in the temperature range of 500–900 °C, except for the reduction reaction (3) which is endothermic. This indicates that the heat only had to be provided for the reduction of $\text{CuMn}_2\text{FeO}_4$, while the formulations CuFeMnO_4 and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ do not require heat for reduction with methane. All oxidation and reduction reactions had negative free energy values in the temperature range 500–900 °C except for the reduction reaction with $\text{CuMn}_2\text{FeO}_4$, which had a positive free energy value below 600 °C.

4. Conclusions. Various compositions of the tri-metallic oxygen carrier $\text{Cu}_x\text{Fe}_y\text{Mn}_z\text{O}_4$ synthesized by the direct decomposition method were evaluated for CH_4 CLC reactions. For

comparison, eight bi-metallic oxygen carriers, selected from group II metal ferrites (MgFe_2O_4 , CaFe_2O_4 , SrFe_2O_4 , and BaFe_2O_4) and transition metal ferrites (NiFe_2O_4 , CuFe_2O_4 , MnFeO_3 , and CoFe_2O_4), also synthesized by the direct decomposition method were evaluated for CH_4 CLC reactions. In addition, tri-metallic oxygen carriers with various compositions of Cu-Fe-Mn were also evaluated for methane CLC reactions. A summary of the results are listed below:

- CuFeMnO_4 showed better CLC performance than all eight bi-metallic ferrites. Among these eight bi-metallic ferrites, NiFe_2O_4 showed the best CH_4 CLC performance, but performance of CuFeMnO_4 was the best overall.
- 55-cycle testing of CuFeMnO_4 showed stable performance and low agglomeration for CH_4 CLC reaction, and the cyclic performance was better than that with NiFe_2O_4 and CuFe_2O_4 .
- Tri-metallic oxygen carriers with different ratio of Cu, Fe, and Mn were also tested; CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed the highest oxygen transfer capacities and best stability during the 20-cycle TGA CLC tests.
- These three compositions had Cu/Mn and Fe/Mn ratios less than 1 and also $\text{Cu/Fe} \geq 1$, indicating that compositions with higher Mn than Fe and Cu had better stability.
- CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also showed very stable performance during 100-cycle CLC tests.
- Tri-metallic ferrites of $\text{Cu}_x\text{Fe}_y\text{Mn}_z\text{O}_4$ were prepared from readily available materials, which would contribute to low cost and is also environmentally benign.
- $\text{Cu}_x\text{Fe}_y\text{Mn}_z\text{O}_4$ oxygen carriers also showed good CLC performance with synthesis gas and coal.

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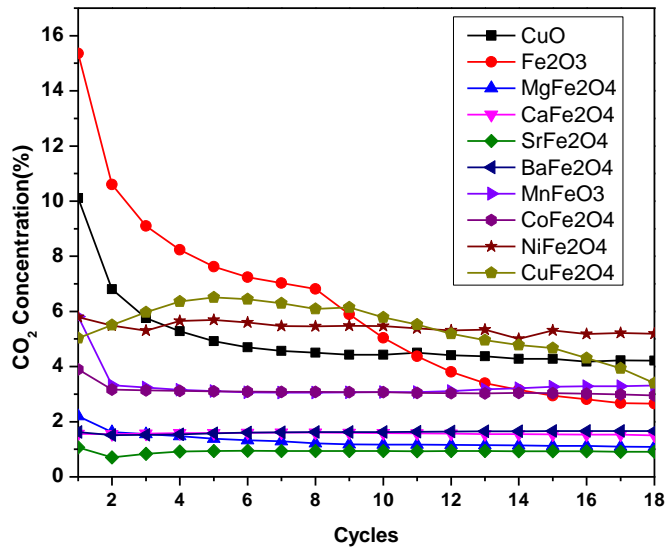


Fig.1. Comparison of CH₄ CLC reduction performance among single metal oxides, group II metal ferrites, and transitional metal ferrites at 750 °C.

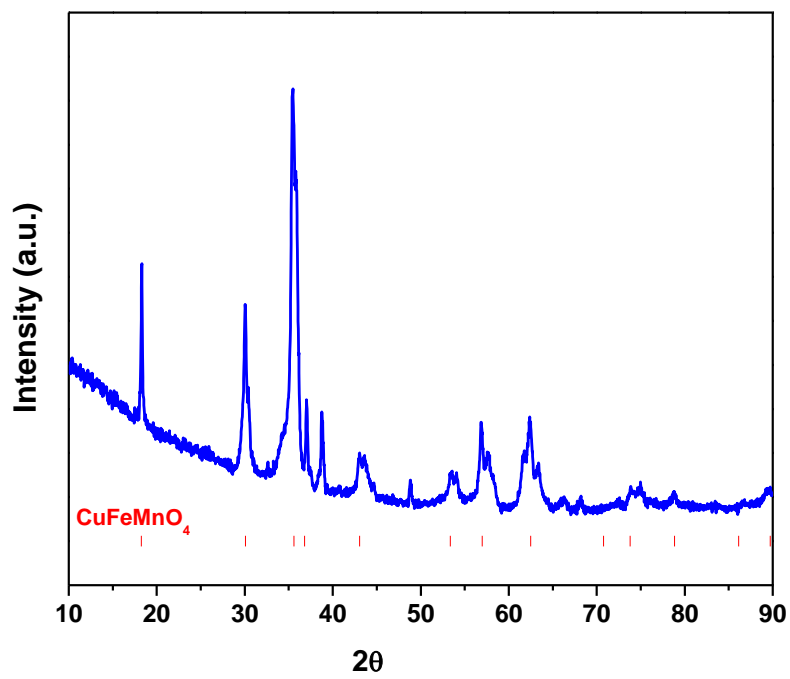


Fig.2. XRD of CuFeMnO₄ synthesized by the direct decomposition method.

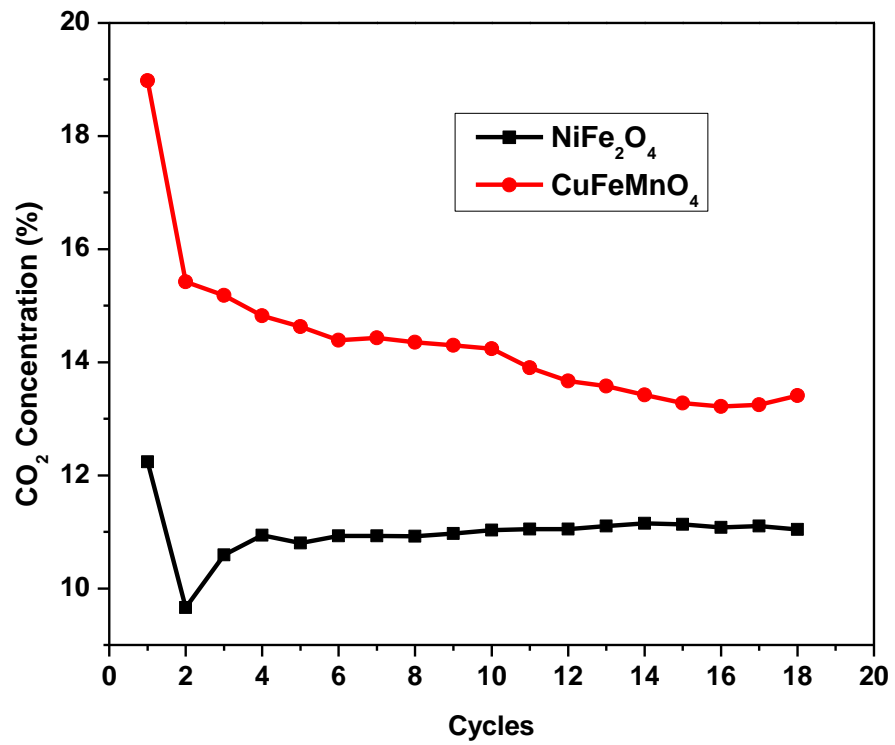


Fig.3. Comparison of CH₄ CLC performance between NiFe₂O₄ and CuFeMnO₄ at 750 °C with 20 % CH₄ and air for oxidation.

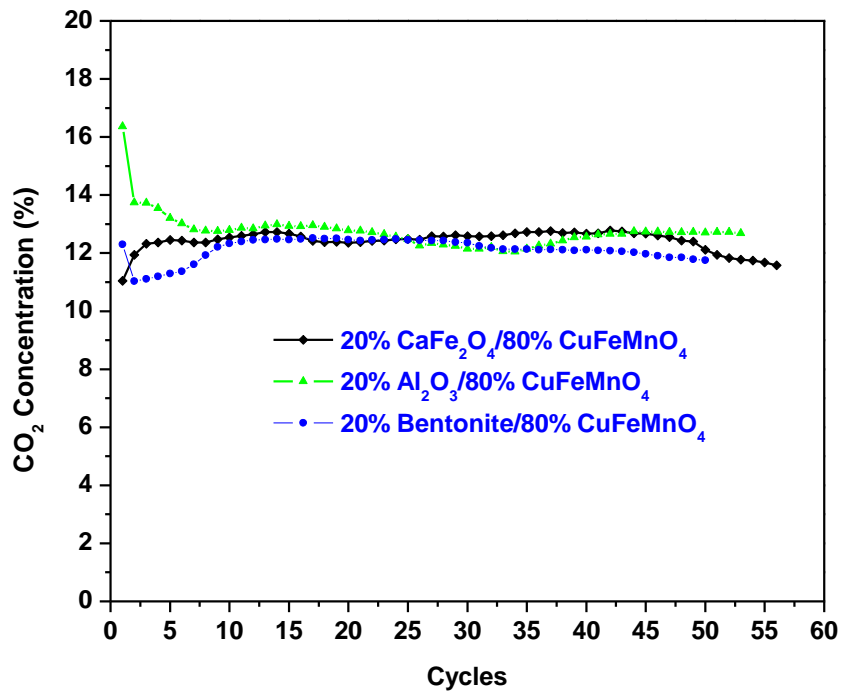


Fig.4. Effect of support materials on CH₄ CLC performance of CuFeMnO₄ at 750 °C.

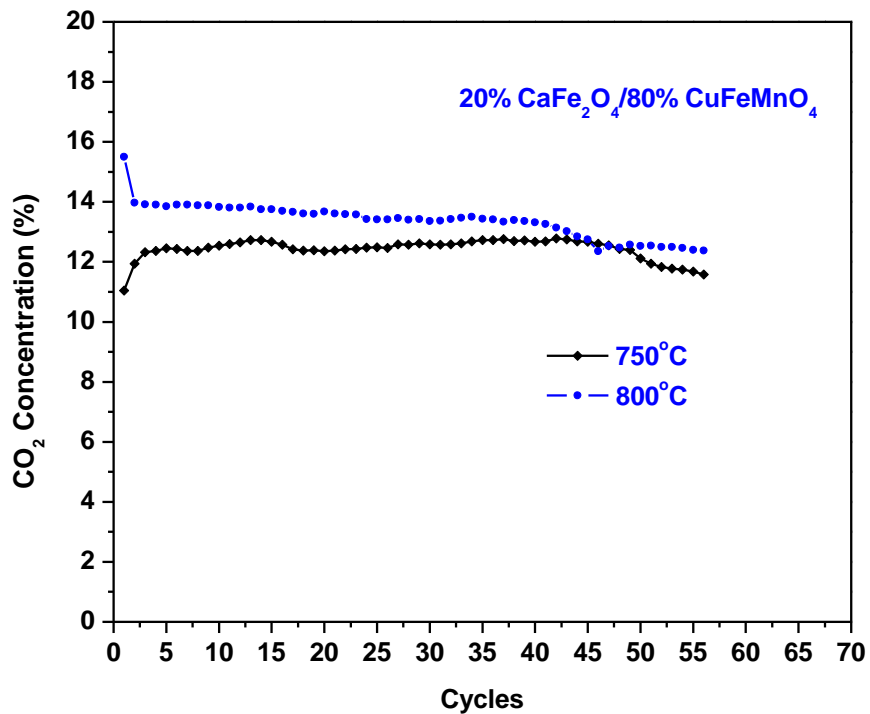


Fig.5. Effect of temperature on the performance of 20 % CaFe₂O₄/CuFeMnO₄ with CH₄.

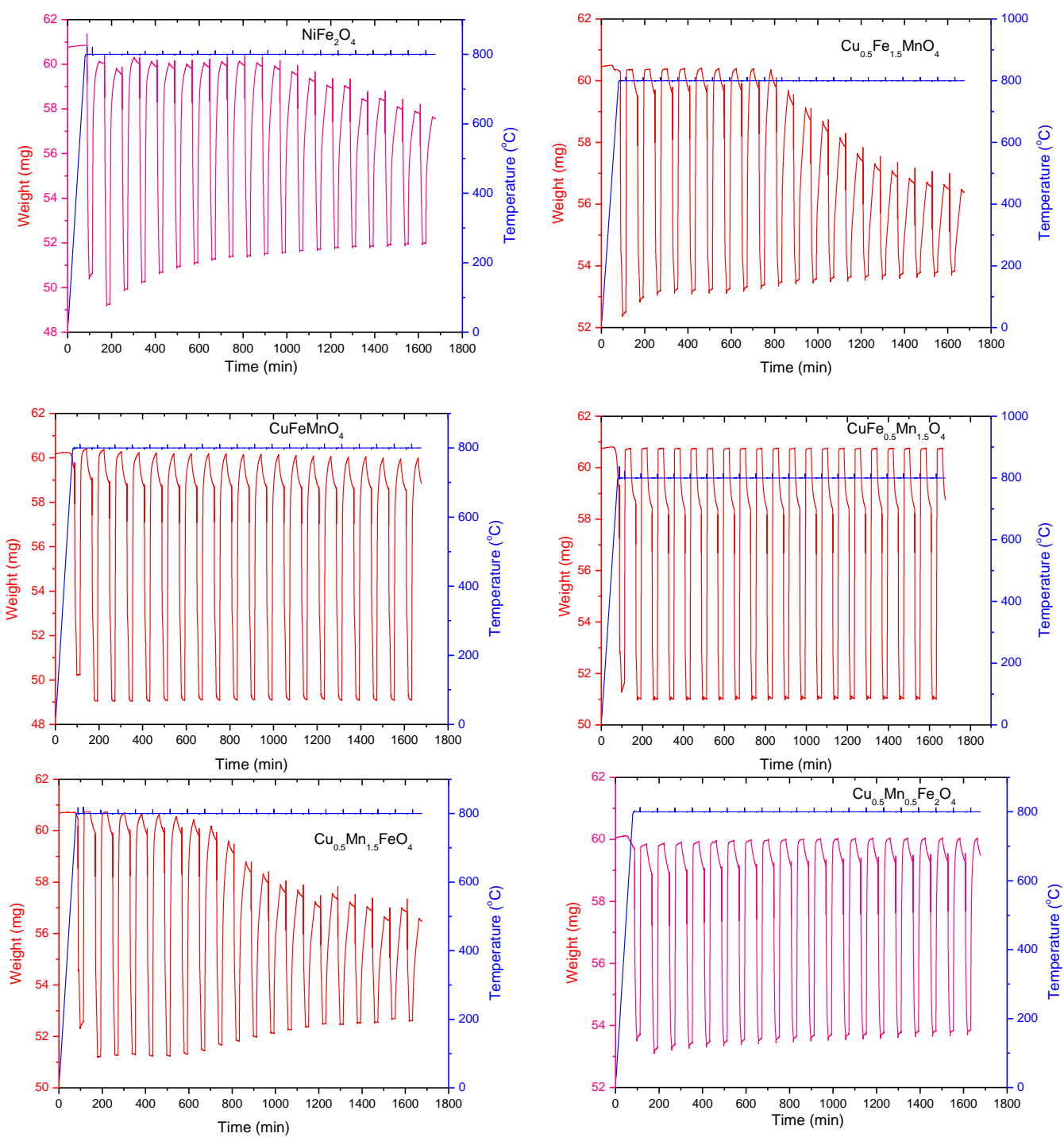


Fig.6. 20-cycle CLC TGA screening test data with methane/air with various composition of Cu-Mn-Fe tri-metallic oxygen carriers

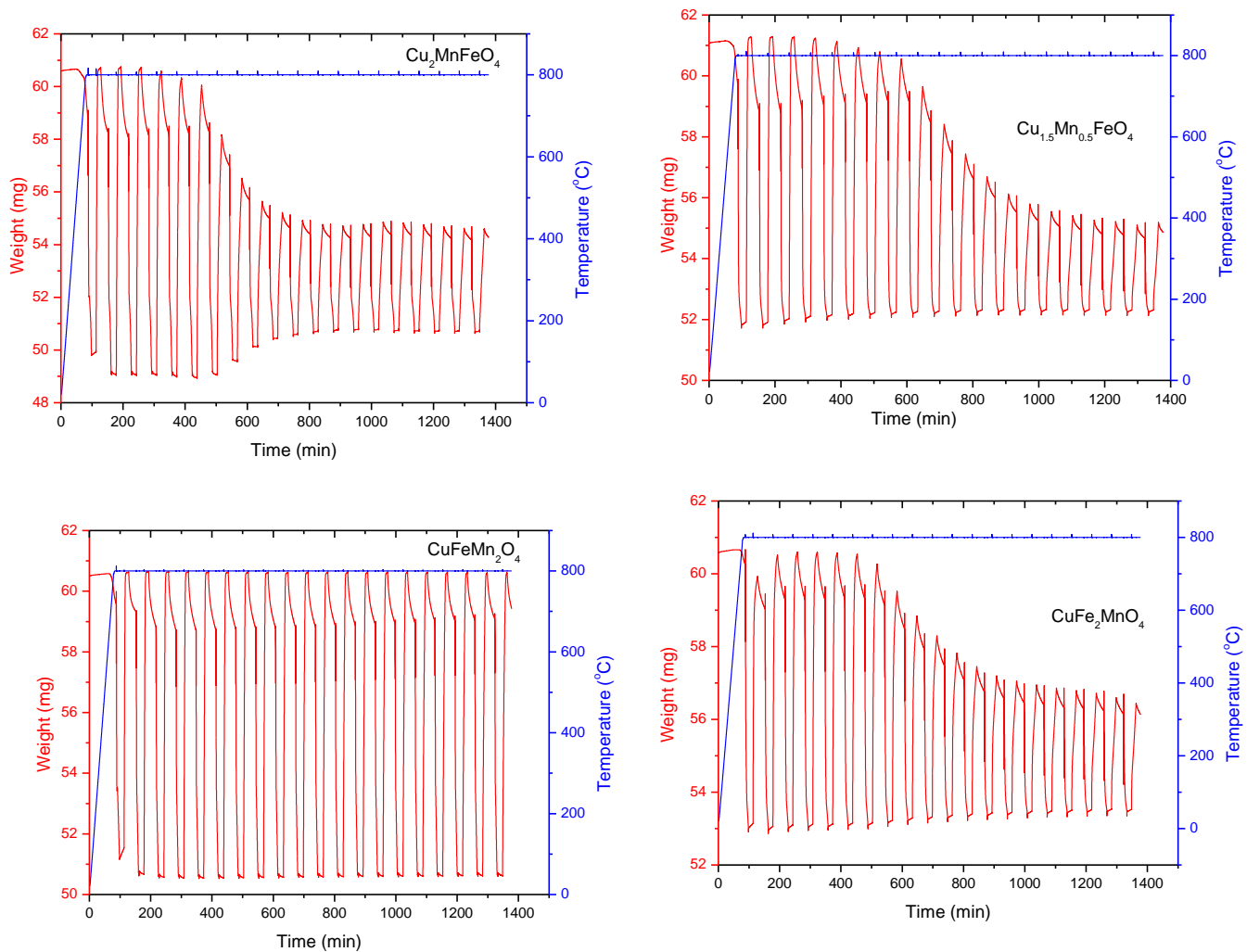


Fig.6 (continued). 20-cycle CLC TGA screening test data with methane/air with various composition of Cu-Mn-Fe tri-metallic oxygen carriers

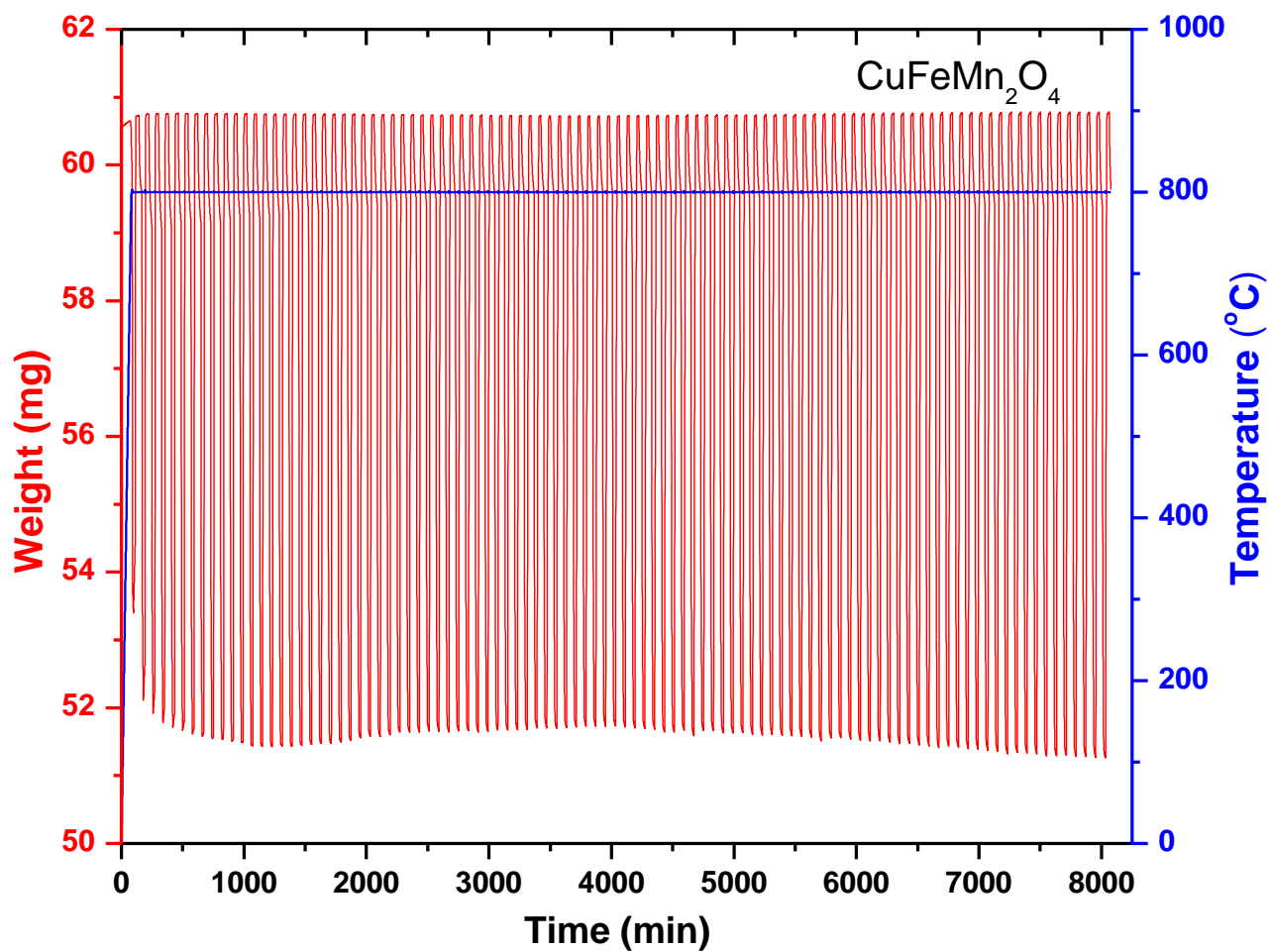


Fig.7. TGA 100-cycle methane/air CLC test for $\text{CuFeMn}_2\text{O}_4$ at 800 $^{\circ}\text{C}$

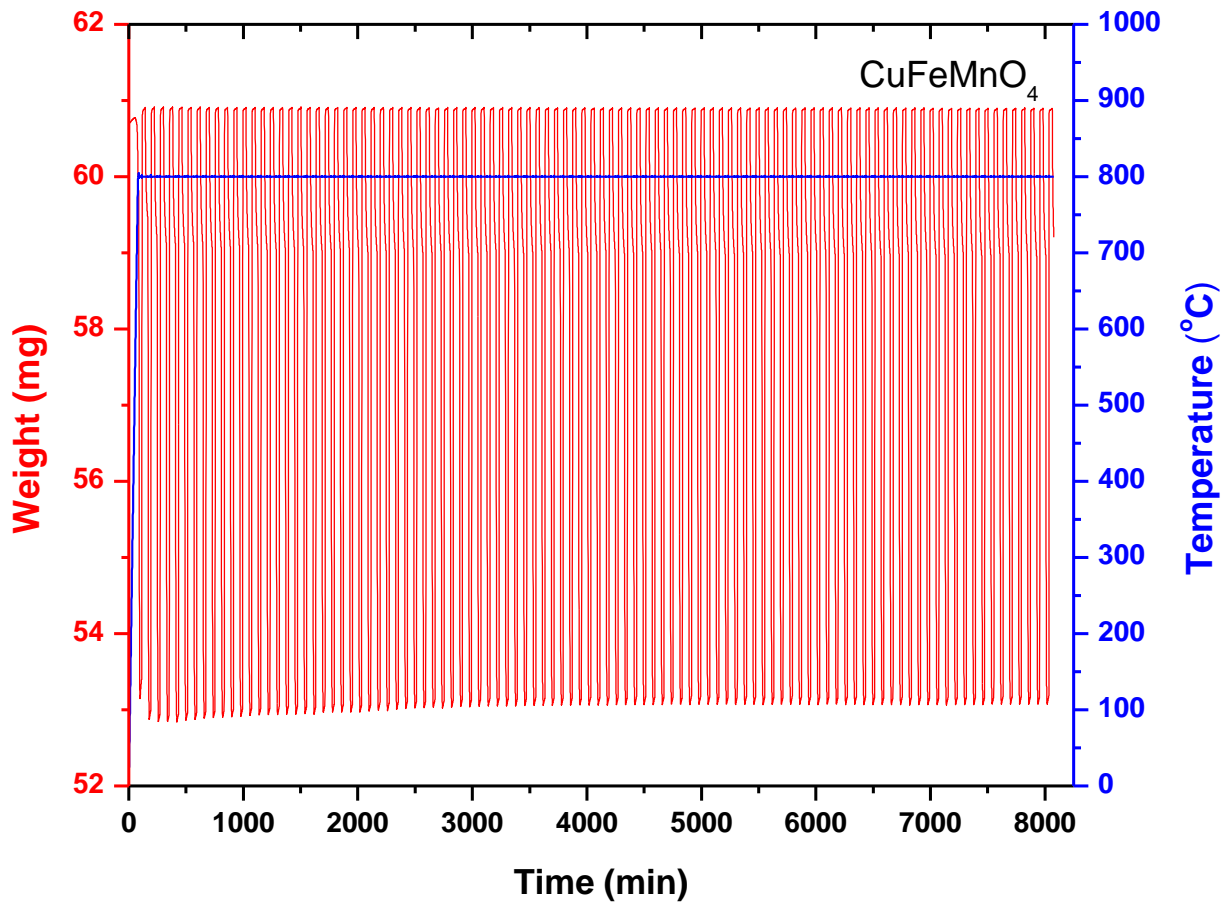


Fig.8. TGA 100-cycle methane/air CLC test for CuFeMnO_4 at $800\text{ }^\circ\text{C}$

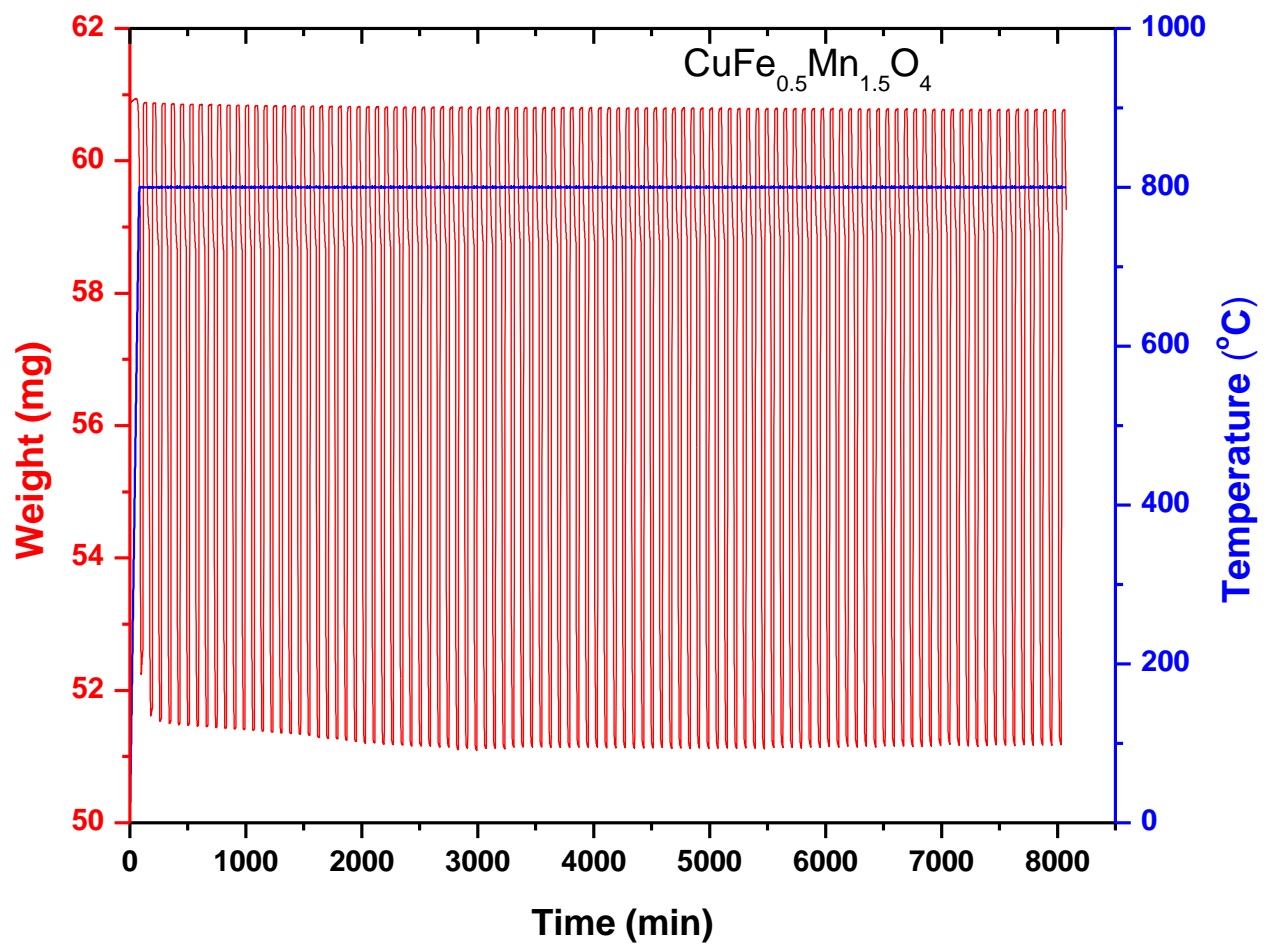


Fig.9. TGA 100-cycle methane/air CLC test for $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 800 °C

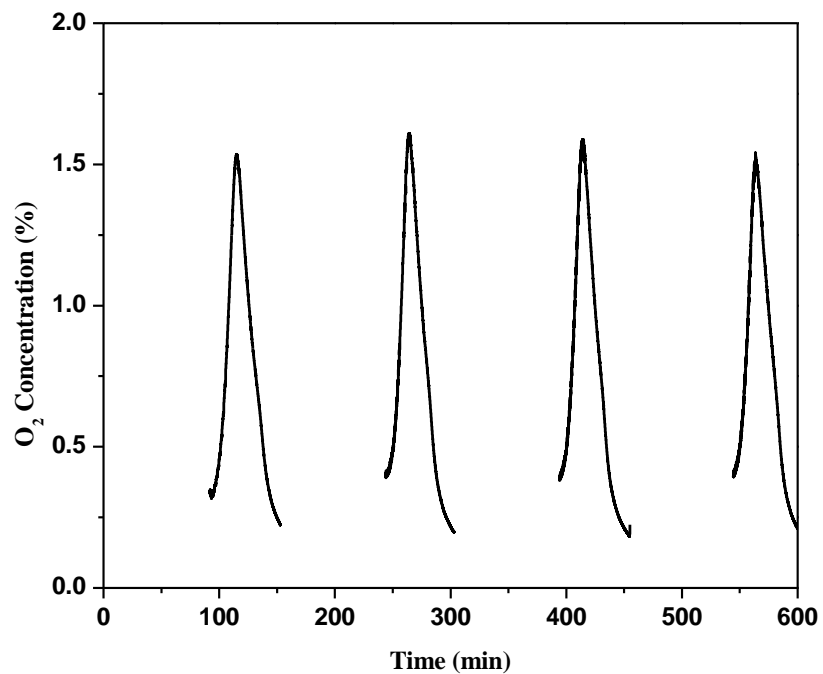
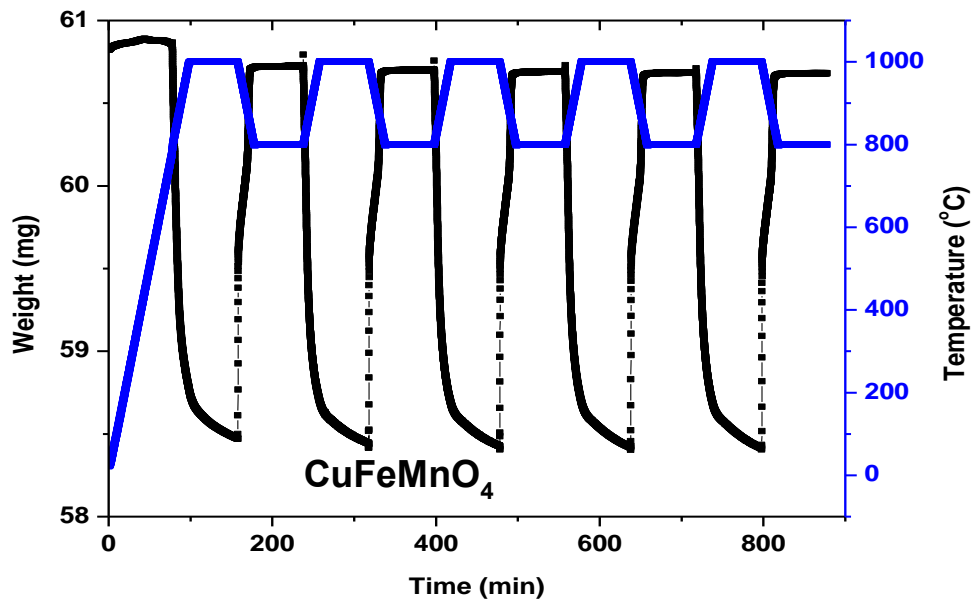
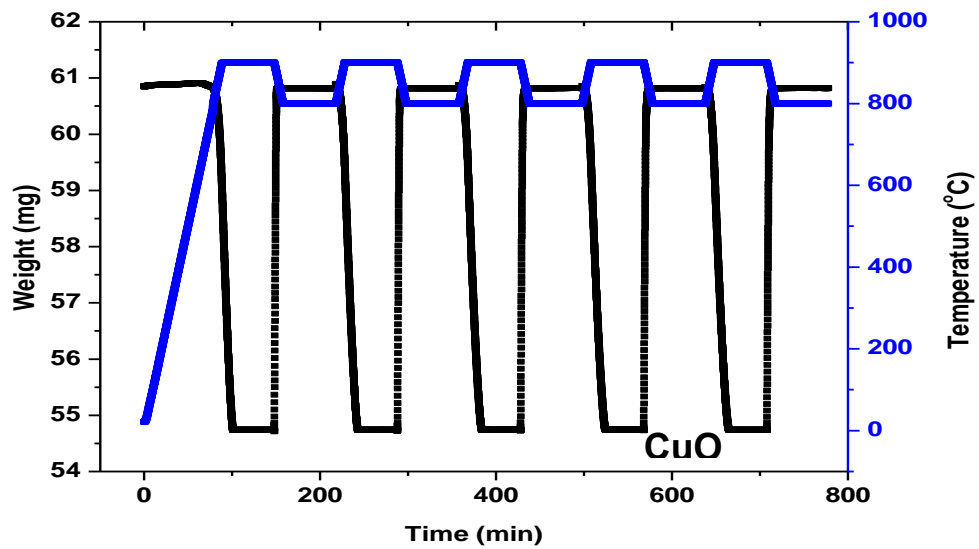


Fig.10. CLOU performance test in fixed bed reactor with 20 % Al₂O₃/CuFeMnO₄ during heating to 800 °C.



Released oxygen %age per gram of CuFeMnO₄: 3.7%

Released oxygen %age per gram of CuO: 9.5%

Fig.11. CLOU performance test in TGA reactor with CuFeMnO₄ during heating to 1,000 °C.

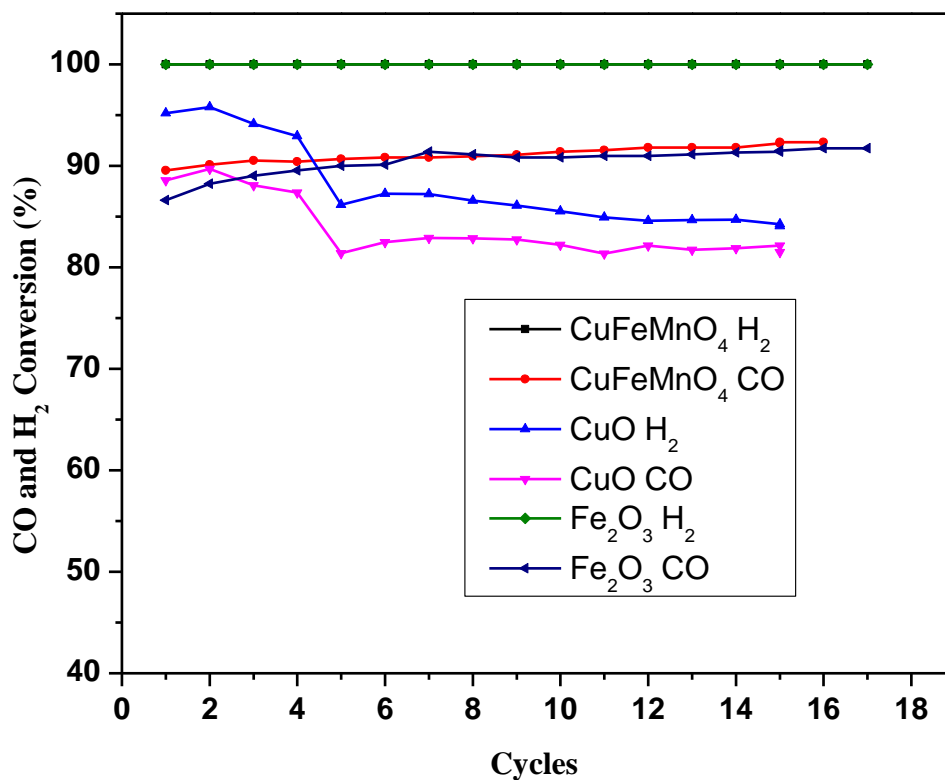


Fig.12. Cyclic CLC performance test of CuFeMnO₄ with syngas.

Reaction Condition:

Syngas: 100 sccm

Syngas components: H₂: 10.28%, CO: 6.39%, CO₂: 2.04% with He balanced

Temperature: 800 °C

Reaction time: 10 min

Oxygen Carrier: 5 g

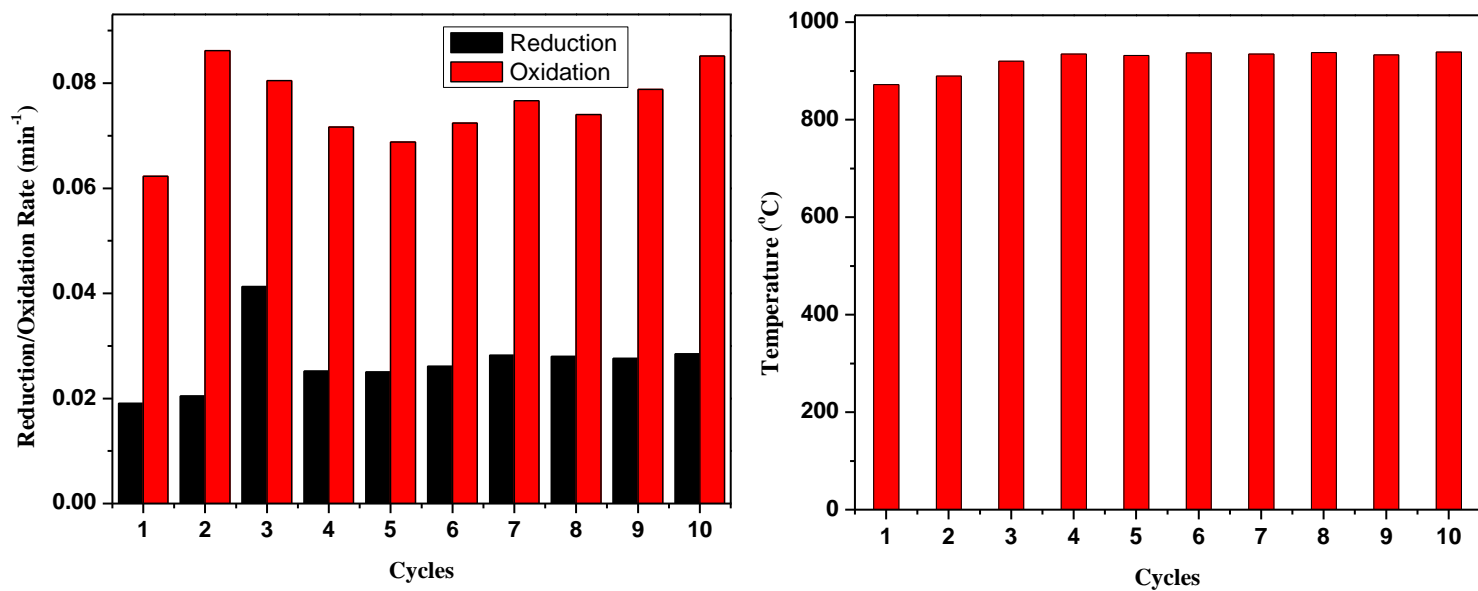


Fig.13. Reduction/oxidation rates and reaction temperatures corresponding to the maximum reaction rate for the reaction of 20 % Al₂O₃/CuFeMnO₄ with carbon.

Table 1 – Oxygen transfer capacity data for the various compositions of Cu-Fe-Mn tri-metallic oxygen carriers

Samples		EDX (based on atomic ratio)	Maximum theoretical oxygen transfer capacity (wt%) – (wt%)	Actual oxygen transfer capacity (wt%) – 2 nd cycle	Actual oxygen transfer capacity (wt%) – 10 th cycle	Actual oxygen transfer capacity (wt%) – 20 th cycle	Cu./Mn	Fe/Mn	Cu/Fe
Cu _{1-x} Mn _x Fe ₂ O ₄ (0 ≤ X ≤ 1)	Cu _{0.5} Mn _{0.5} Fe ₂ O ₄	Cu: 0.5 Fe: 2.0 Mn: 0.5	27.24	10.997	10.599	10.339	=1	>2	0.25
CuFe _x Mn _{2-x} O ₄ (0 ≤ X ≤ 1)	CuFe _{0.5} Mn _{1.5} O ₄	Cu: 1 Fe: 0.6 Mn: 1.7	26.9	15.95	15.9	15.94	<1	<1	1.6
	CuFeMnO ₄	Cu:1 Fe:1 Mn:1	26.85	18.71	18.38	18.03	=1	=1	1
Cu _{1+x} Mn _x FeO ₄ (0 < X ≤ 1)	Cu ₂ MnFeO ₄	Cu: 2.6 Fe: 1.0 Mn: 1.0	21.2	19.12	9.3	7.09	>1	=1	2.6
	Cu _{1.5} Mn _{0.5} FeO ₄	Cu: 2.3 Fe: 1.0 Mn: 0.6	26.38	15.34	12.41	5.06	>1	>1	2.3
Cu _x Mn _{1-x} Fe ₂ O ₄ (0 ≤ X ≤ 1)	Cu _{0.5} Mn _{0.5} Fe ₂ O ₄	Cu: 0.5 Fe: 2.0 Mn: 0.5	27.24	10.997	10.599	10.339	=1	>2	0.25

Cu _x Mn _{1+x} FeO ₄ (0<X≤1)	CuMn ₂ FeO ₄	Cu:0.8 Fe: 1.0 Mn: 2.0	21.82	16.41	16.48	16.42	<1	<1	0.8
	Cu _{0.5} Mn _{1.5} FeO ₄	Cu: 0.5 Fe: 1.0 Mn: 1.42	27.35	15.68	12.98	7.72	<1	<1	0.5
Cu _x Fe _{1+x} MnO ₄ (0<X≤1)	CuFe ₂ MnO ₄	Cu:1.0 Mn:1.0 Fe: 2.0	21.76	11.51	9.4	5.48	=1	=2	1
	Cu _{0.5} Fe _{1.5} MnO ₄	Cu: 0.5 Fe: 1.5 Mn: 1.0	27.29	12.31	11.41	4.83	<1	>1	0.3

Table 2– Theoretical and experimental oxygen transfer capacity for various reduction states of Cu-Fe-Mn tri-metallic oxygen carriers

Samples	Initial State	Reducing state	Theoretical oxygen transfer capacity (wt%)	Experimental oxygen transfer capacity (wt%)
CuFe _{0.5} Mn _{1.5} O ₄	Cu ₂ O, FeO, MnO ₂	Cu, Fe, Mn	26.9	15.8
		Cu, Fe, MnO	16.81	
		Cu, FeO, Mn	23.54	
		Cu ₂ O, Fe, MnO	13.45	
CuFeMnO ₄	CuO, FeO, MnO ₂	Cu, Fe, Mn	27.24	18.3
		Cu ₂ O, Fe, Mn	23.49	
		Cu, Fe, MnO	20.14	
		Cu ₂ O, Fe, MnO	16.78	
CuMn ₂ FeO ₄	CuO, MnO, FeO	Cu, Fe, Mn	21.82	16.1
		Cu ₂ O, Mn, Fe	19.09	
		Cu ₂ O, Fe, MnO	8.18	
		Cu, Fe, MnO	10.91	
		Cu, Fe, FeO, Mn, MnO	16.37	

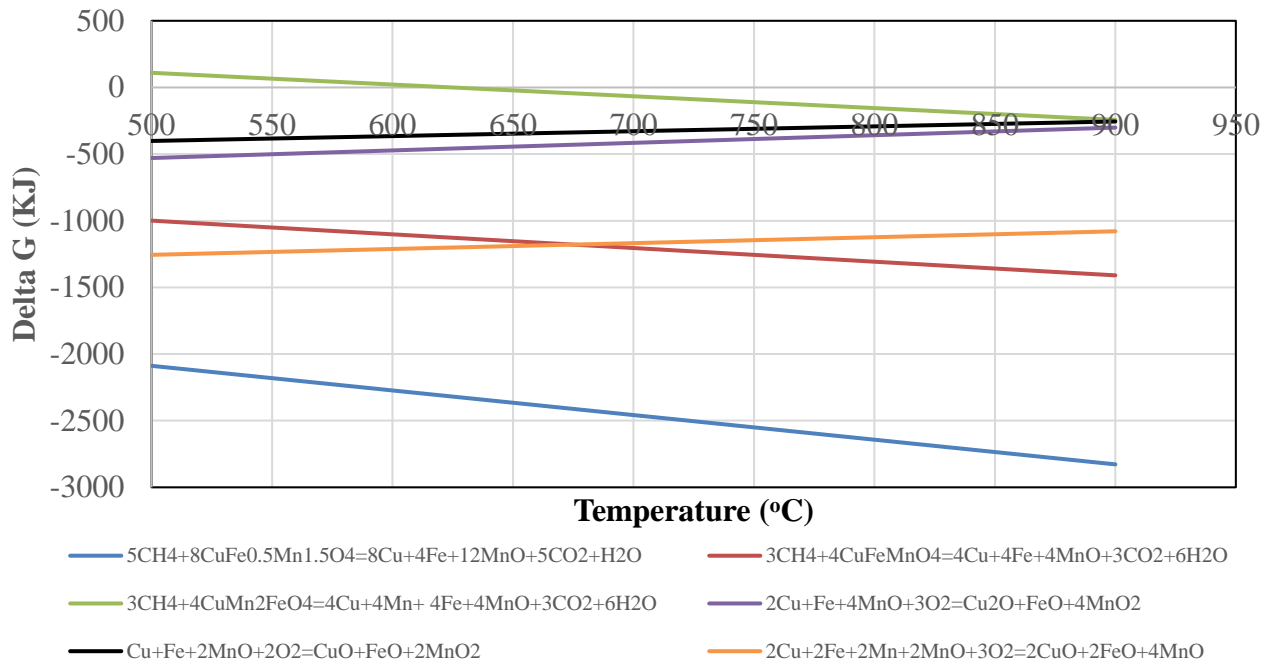
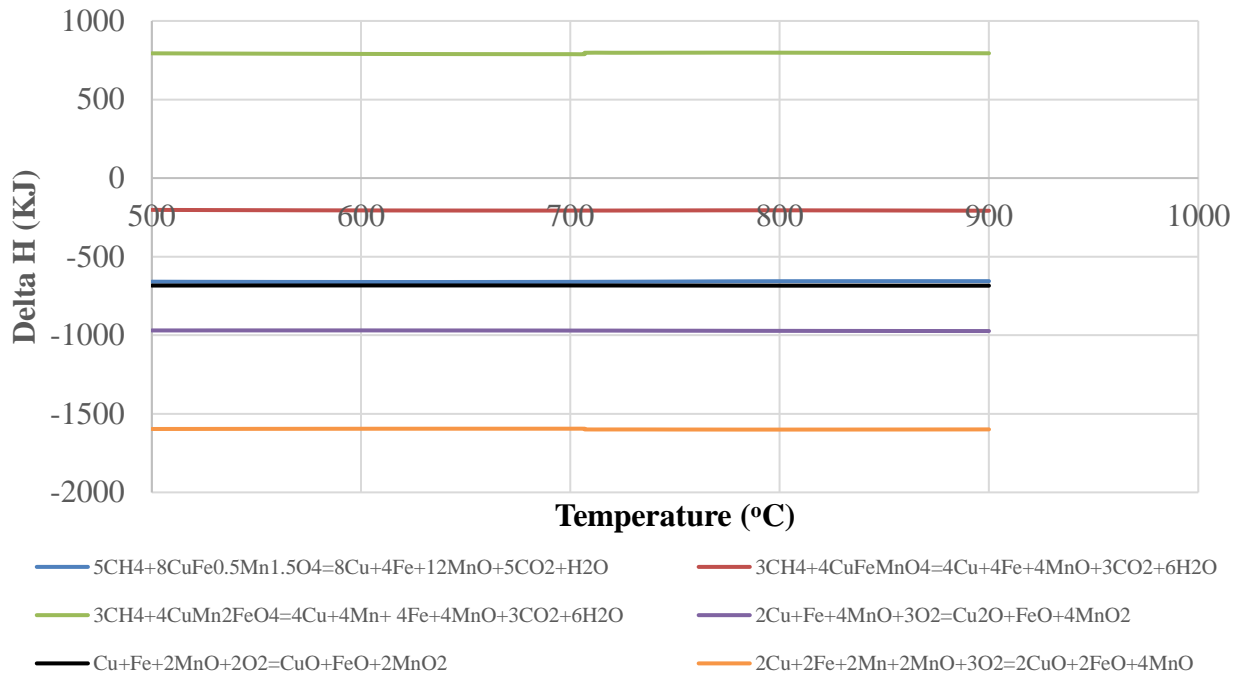


Fig.14. Thermodynamic analysis (ΔG and ΔH versus temperature) of reduction reaction with CH_4 and oxidation reaction with O_2 with CuFeMnO_4 , $\text{CuFeMn}_2\text{O}_4$, and $\text{CuFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$.