# Preparation and Performance of CuMn2O4 Composite Oxygen Carrier for Chemical Looping Oxidative Dehydrogenation of Ethane

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**Abstract.** In chemical looping oxidative dehydrogenation (CL-ODH), an alkali metal molten shell material is typically employed to improve the reactivity of oxygen carrier. However, the existence of a molten shell necessitates reaction at a higher melting temperature than that of the shell itself, thereby increasing the oxygen-releasing temperature of the oxygen carrier. In this study, a novel oxygen carrier for ethane CL-ODH, $CuMn_2O_4$ promoted by non-molten shells of $MnMoO_4$ and $SrMoO_4$ was prepared and investigated. $CuMn_2O_4$ with high oxygen capacity releases lattice oxygen, while the adding Mo activates the C-H bond of ethane regulates ethylene selectivity. With $CuMn_2O_4$@$MnMoO_4$ as oxygen carrier, the ethane conversion and ethylene selectivity with oxygen carrier are 40.3% and 93.7%, respectively, and the maximum instantaneous yield of ethylene can reach 9.72 mol$C_2H_4$/kg-cat/h at 700℃. Sr-modified $CuMn_2O_4$ oxygen carrier significantly increases the alkaline site on the surface, thereby enhancing the adsorption and desorption ability of ethane and ethylene. The prepared $CuMn_2O_4$@$SrMoO_4$ oxygen carrier obtained 44.6% ethane conversion and 88.94% ethylene selectivity at 700℃. The instantaneous yield of ethylene is as high as 9.32 mol$C_2H_4$/kg-cat/h, and the oxygen capacity is 7.5 wt.%.

**Keywords:** ethane; chemical looping oxidative dehydrogenation; composite oxygen carrier; core-shell structure.

## 1. Introduction

The proposed process of chemical looping oxidative dehydrogenation (CL-ODH) overcomes the disadvantages of traditional oxidative dehydrogenation (ODH) [1]. The ethane CL-ODH process consists of an ODH reactor and an oxidation regeneration reactor [2]. In the ODH reactor, lattice oxygen is released by the oxygen carrier ($MeO_x$) to selectively oxidize ethane to produce ethylene and water, and then the reduced oxygen carrier ($MeO_{X-1}$) is fed into the oxidation regeneration reactor, which uses air for oxidation regeneration to supplement lattice oxygen and release heat [3]. Ethane CL-ODH avoids direct contact between ethane and oxygen, and self-heating operation of the ethane CL-ODH system can be achieved when more than 70% of the hydrogen byproducts are oxidized in situ. At the same time, the gaseous products can be reduced by about 40%, reducing the energy consumption of subsequent product separation [4].

In the ethane CL-ODH reaction, the amount of oxygen carried by the oxygen carrier is an important consideration, and the level of oxygen carried affects the amount of oxygen carrier and the switching frequency of reduction oxidation [5]. The effect of surface adsorbed oxygen on the chemical looping dehydrogenation of ethane is reduced by high oxygen load, and the ethane processing capacity is higher in the continuous reaction. The polyvalent state of manganese indicates that it has excellent oxygen storage capacity, so manganese oxide is usually used as a high oxygen carrier for ethane chemical looping oxidation dehydrogenation process [6]. Wang et al [7]. reported an oxygen carrier $Na_2WO_4/CuMn_2O_4$ with high oxygen carrying capacity. $CuMn_2O_4$ with spinel structure has a relatively higher oxygen capacity (13.5 wt.%) than $ABO_3$ type perovskite structure. At 720°C, the selectivity of ethylene is 86.4% and the conversion of ethane is 58.8%. $CuMn_2O_4$ is regarded as a promising oxygen nucleus due to its high oxygen carrying capacity.

During ethane CL-ODH, high oxygen carriers usually rapidly release a large number of non-selectively oxidized electrophilic oxygen species and spread to the surface of the oxygen carrier, resulting in excessive oxidation of ethane to $CO_x$, resulting in reduced ethylene selectivity. In order to ensure the high ethylene selectivity of CL-ODH, it is necessary to cover the oxygen nucleus with an accelerator that can reduce the number of electrophilic oxygen species on the surface and limit the lattice oxygen transfer. Gao et al [8]. used mixed metal oxide $La_{0.8}Sr_{0.2}FeO_3$ coated with molten $Li_2CO_3$ as oxygen carrier to improve the ethylene selectivity, and obtained 86% ethylene selectivity and 60% ethane conversion at 750℃, but its oxygen carrier was only 0.65 wt.%. However, the modification of alkali metal salt melt shell accelerator makes the composite oxygen carrier easy to be lost during the oxidation reduction cycle and leads to the decrease of its oxygen carrying capacity.

In view of the problems existing in the modification of molten shell, modified metal oxides were proposed as oxygen carriers of ethane CL-ODH. Mo element is beneficial to activate the C-H bond of ethane, inhibit the fracture of C-C bond, and improve the selectivity of ethylene. Novotny et al [9,10]. significantly improved ethylene selectivity by impregnating $MoO_3$ onto $\alpha$-$Fe_2O_3$ support to form a surface layer rich in $MoO_3$ and $Fe_2(MoO_4)_2$. At 600℃, 62% ethylene selectivity can be achieved, but the oxygen carrier is only 0.62 wt.%. After using $MoO_x/Al_2O_3$ as oxygen carrier, ethylene selectivity of 94.5% and ethane conversion of 66.5% can be achieved, but the ethylene yield decreases significantly after multiple pulses.

In this study, we reported that $CuMn_2O_4$ promoted by non-molten shells of $MnMoO_4$ and $SrMoO_4$ was used as oxygen carrier for ethane CL-ODH, which solved the problem of easy loss and high oxygen carrying in molten shells of oxygen carriers. The core-shell structure and surface morphology of the oxygen carrier were characterized by X-ray diffraction (XRD), and high-resolution transmission electron microscopy (H-TEM).

## 2. Experimental Testing

### 2.1 Oxygen Carriers Synthesis

The $CuMn_2O_4$ oxygen carrier was prepared via the sol-gel technique as follows: $Cu(NO_3)_2 \cdot 3H_2O$ (99.5%, Sinopharm) and $Mn(NO_3)_2$ (50 wt.% in $H_2O$, Sinopharm) with a stoichiometric ratio of 1:2 were dissolved in deionized water at room temperature. After complete dissolution, citric acid (99.5%, Sinopharm), equivalent to 1.5 times the amount of the metal ions ($Cu^{2+}$ and $Mn^{2+}$), was added to the solution, which was vigorously stirred at 80℃ until a highly viscous gel formed. The obtained gel was dried in an oven at 85℃, followed by calcination in a muffle furnace at 300℃ for one hour, and then at 850℃ for 6 hours. Finally, the sample was cooled to room temperature and crushed into particles sized between 60-120 mesh.

The specific preparation steps of the core-shezll structure $CuMn_2O_4$@$MnMoO_4$ are as follows: A certain amount of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$(AR, 99.0%, Sinopharm) is ground and calcined in a tube furnace at 550℃ for 1 hour to obtain $MoO_3$. Then the prepared $CuMn_2O_4$ and $MoO_3$ are added to the mortar in proportion to fully grind for half an hour. In order to obtain a stable oxygen carrier, calcined at a rate of 5℃/min in air between room temperature and 700℃ for 1 hour, finally cooled to room temperature, crushed and used (60-120 mesh).

The specific preparation steps of the core-shell $CuMn_2O_4$@$SrMoO_4$ oxygen carrier are as follows: a certain proportion of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$(AR, 99.0%, Sinopharm) and $Sr(NO_3)_2$(AR, 99.5%, Sinopharm) are weighed and dissolved in deionized water at room temperature. After complete dissolution, urea (AR, 99.5%, Sinopharm), equivalent to 1.5 times the amount of the metal ions ($Sr^{2+}$ and $Mo^{6+}$), was added to the solution, and then a certain amount of prepared $CuMn_2O_4$ composite metal oxide was added to the solution, and the solution was vigorously stirred at 80℃ until it was dried. The obtained solids are dried in an oven at 85℃ and then calcined in a tubular furnace at 800°C for 1 hour after grinding. After cooling to room temperature and grinding, the core-shell composite oxygen carrier with particle size of 60-120 was prepared.

### 2.2 Experimental Testing

The ethane CL-ODH test was performed in an 8 mm I.D. fixed-bed quartz tube reactor. The quartz reactor is placed in a furnace and electrically heated. The reaction temperature is monitored using a type K thermocouple near the sample bed. Each test used 0.5 g (about 1 mL in volume) oxygen carrier, in which quartz cotton was added to the void space on both sides of the quartz tube reactor to limit the dead volume in the heating zone and to fix the oxygen carrier. For comparison, a blank test using $CuMn_2O_4$ as the bed material was also carried out under the same reaction conditions, and the gas flow rate and gas composition were controlled by mass flowmeter. During the CL-ODH reaction test, the fixed bed reactor is purged and heated to the desired temperature at 50 ml/min Ar and kept at that temperature for 10 minutes to eliminate the adsorbed substances on the surface of the oxygen carrier and obtain stable physical and chemical properties. Pulse experiments were performed on oxygen carriers at five different reaction temperatures (600, 650, 700, 750 and 800°C). For each pulse experiment, 5 ml of $C_2H_6$ and 5 ml of internal standard gas ($N_2$) were injected into the reactor, followed by a 50 ml/min Ar purge for 10 min and an air bag to collect the outlet gas for analysis. In the continuous ODH experiment, 10 vol%$C_2H_4$/Ar was continuously injected into the fixed bed reactor (total flow rate was 50 ml/min) and the outlet gas was collected by air bag every 2 min.

The gas collected in gas sampling bag was analyzed by gas chromatograph (GC), and the performance of oxygen carrier in fixed bed reactor was evaluated by internal standard method. The conversion of ethane, selectivity of ethylene, yield of ethylene, and conversion of hydrogen are calculated as follows:

$$\text{Conversion of ethane (\%)} = \frac{\text{introduced ethane - residual ethane}}{\text{introduced ethane}} \times 100\% \tag{1}$$

$$\text{Selectivity of ethylene (\%)} = \frac{\text{moles of ethylene}}{\text{moles of converted ethane}} \times 100\% \tag{2}$$

$$\text{Ethylene yield} = \text{conversion of ethane} \times \text{selectivity of ethylene} \tag{3}$$

$$H_2 \text{ conversion} = 1 - \frac{(H_2)_{out}}{(H_2)_{gen}} \times 100\% \tag{4}$$

## 3. Results and Discussion

### 3.1 Characterization of the prepared oxygen carriers

X-ray diffraction patterns of fresh $CuMn_2O_4$ bimetallic oxides and $CuMn_2O_4$@$MnMoO_4$ and $CuMn_2O_4$@$SrMoO_4$ composite oxygen carriers were prepared by sol-gel method, as shown in Fig. 1. The characteristic peaks of the tetragonal $CuMn_2O_4$ phase (JCPDS PDF#84-0543) confirmed the successful preparation of $CuMn_2O_4$ with spinel structure [11]. By adding $MoO_3$, a new phase $MnMoO_4$(JCPDS PDF#72-0285) with scheelite structure was formed. For $CuMn_2O_4$@$SrMoO_4$ complex oxygen carrier, the spinel $CuMn_2O_4$ phase and scheelite $SrMoO_4$ phase (JCPDS PDF#85-0809) are exhibited [12]. The addition of $SrMoO_4$ decreased the peak strength of $CuMn_2O_4$ compared with fresh $CuMn_2O_4$.

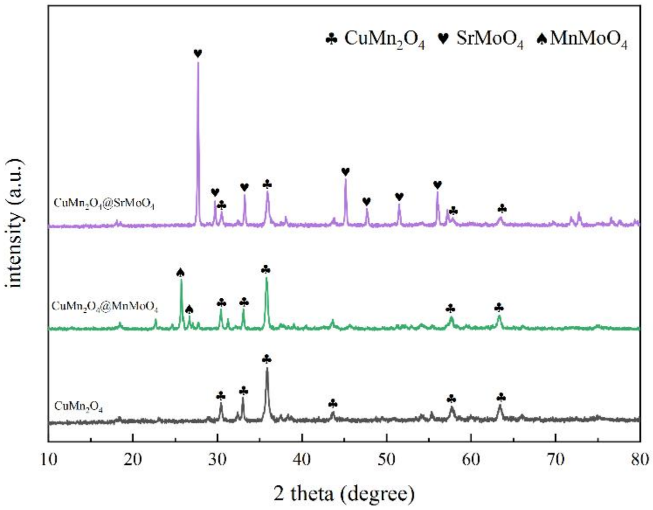

Fig. 1 XRD of CuMn2O4, CuMnO4@MnMoO4 and CuMnO4@SrMoO4 oxygen carriers

Fresh oxygen carriers $CuMn_2O_4$@$MnMoO_4$ and $CuMn_2O_4$@$SrMoO_4$ were characterized by HTEM, respectively. The formation of coreshell structure can be clearly observed in Fig. 2. For $CuMn_2O_4$@$MnMoO_4$ oxygen carrier, the outermost lattice spacing is 0.500 nm, corresponding to the $MnMoO_4$(2 0 0) plane, while the inner lattice spacing is 0.282 nm, corresponding to the $CuMn_2O_4$(2 2 0) plane. It can also be inferred that the thickness of $MnMoO_4$ layer is about 20 nm. For the $CuMn_2O_4$@$SrMoO_4$ oxygen carrier, the spacing of two different crystal lattice can be clearly observed, 0.332 nm is the $SrMoO_4$(1 1 2) plane, 0.282 nm is the $CuMn_2O_4$(2 2 0) plane, confirming that the prepared composite oxygen carrier has a core-shell structure.

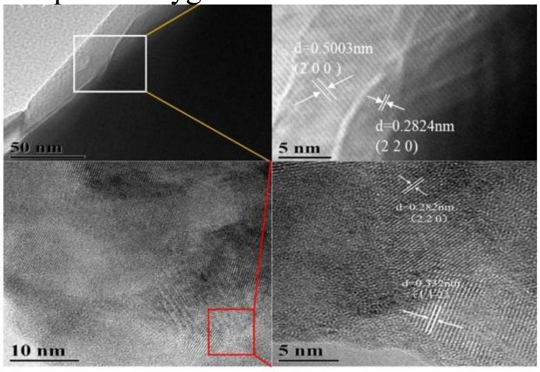

Fig. 2 HTEM images of CuMn2O4@MnMoO4(left) and CuMn2O4@SrMoO4(right)

### 3.2 Reactivity of composite oxygen carrier

A series of fixed bed pulse experiments were carried out in the range of 600-800℃ to investigate the reaction performance of the prepared oxygen carrier for chemical looping oxidative dehydrogenation of ethane. The relationship between ethane conversion, ethylene selectivity and reaction temperature of oxygen carriers is shown in Fig. 3. The ethane conversion rate of $CuMn_2O_4$ oxygen carriers is higher than that of $CuMn_2O_4$@$MnMoO_4$ and $CuMn_2O_4$@$SrMoO_4$ in the whole temperature range, but the ethylene selectivity of $CuMn_2O_4$ is below 20%. This is because $CuMn_2O_4$ releases a large number of non-selective electrophilic oxygen species to completely oxidize ethane into $CO_2$ and $H_2O$. The yield of ethylene did not reach 10% under all experimental conditions. However, due to its high oxygen carrying capacity and activity to ethane, it is an ideal oxygen carrying core. Compared with $CuMn_2O_4$, the $CuMn_2O_4$ oxygen carrier is modified by adding $MoO_3$, and the surface of the oxygen carrier is covered with a layer of $MnMoO_4$ non-molten shell, which can effectively inhibit the direct contact between ethane and $CuMn_2O_4$, reduce the excessive oxidation of ethane, and then increase the ethylene selectivity[13]. With the increase of temperature, ethylene selectivity first increased and then decreased, and reached the best value of

80.7% at 700℃. At the same time, the addition of Mo element also further activated the C-H bond of ethane, thus increasing the conversion rate of ethane. The ethylene yield reached 33.3% at 700℃ and 54.4% at 750℃. The results show that $CuMn_2O_4$@$SrMoO_4$ oxygen carrier achieves the best ethylene selectivity (86.8%) and hydrogen conversion rate (94.6%) at 700℃. Compared with $CuMn_2O_4$@$MnMoO_4$, the conversion rate of ethane increases from 39.1% to 45.3% at the same reaction temperature, which further proves that the addition of alkali earth metal Sr is beneficial to the conversion of ethane.

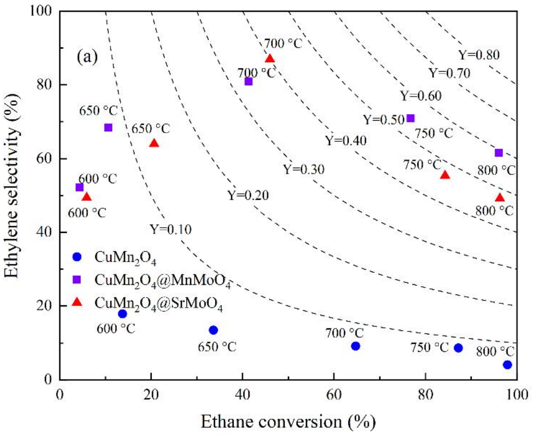

Fig. 3 Ethane conversion and ethylene selectivity of CuMn2O4, CuMn2O4@MnMoO4 and CuMn2O4@SrMoO4 oxygen carriers at different temperatures

### 3.3 Continuous reduction of composite oxygen carrier

Fig. 4 shows the ethane chemical looping oxidative dehydrogenation properties of $CuMn_2O_4$, $CuMn_2O_4$@$MnMoO_4$ and $CuMn_2O_4$@$SrMoO_4$ oxygen carrier and the instantaneous ethylene yield under continuous ethane reaction. As shown in Fig. 4(a), $CuMn_2O_4$ releases a large amount of non-selective molecular oxygen in the first four minutes, which causes nearly 70% of ethane to be over-oxidized to produce a large amount of COx, but at the same time, it also achieves close to 100% hydrogen conversion. With the rapid consumption of oxygen, the activity of the oxygen carrier also decreases, and the conversion rate of ethane decreases to 29.3% after 10 min. The hydrogen conversion rate decreased to 0, indicating that the oxygen carrier was completely reduced, and the subsequent reaction was all ethane pyrolysis.

$CuMn_2O_4$@$MnMoO_4$ The continuous reaction of the oxygen carrier is shown in Fig. 4(b). In the first 3 minutes, nearly half of the ethane is completely oxidized to $CO_2$. The presence of adsorbed oxygen on the surface of the oxygen carrier completely oxidizes the ethane. Selective lattice oxygen plays a major role in oxidative dehydrogenation due to the rapid consumption of non-selective oxygen. The ethylene selectivity was increased to 90.4%, while the ethane conversion was reduced to 41.5%. At the 12th minute of reaction, with the consumption of lattice oxygen, the hydrogen conversion gradually drops to zero, and the lattice oxygen released by the oxygen carrier is no longer enough to support the chemical looping oxidative dehydrogenation of ethane.

$CuMn_2O_4$@$SrMoO_4$ The continuous reaction of the oxygen carrier is shown in Fig. 4(c). Compared with $CuMn_2O_4$@$MnMoO_4$ oxygen carrier, some lattice oxygen tends to over-oxidize at the initial stage of the reaction, resulting in low ethylene selectivity [5]. The oxygen carrier coated with $SrMoO_4$ metal oxide shell greatly improves the proportion of selective oxygen in the oxygen carrier, which enables the selective oxidation of ethane at the initial stage of the reaction. With the progress of the reaction, the ethylene selectivity was further improved. At the 8th minute, the ethane conversion reached 48.5%, the ethylene selectivity reached 85.7%, and the maximum instantaneous yield of ethylene was as high as 9.32 mol$C_2H_4$/kg-cat/h, breaking through the blank equilibrium yield (28.9%) under the same conditions, breaking the thermodynamic limit. With the continuous consumption of lattice oxygen, the hydrogen conversion rate gradually decreases. However, unlike the $CuMn_2O_4$ oxygen carrier, the hydrogen conversion rate of $CuMn_2O_4$@$SrMoO_4$ oxygen carrier does not drop to 0% rapidly, which indicates that the covering of $SrMoO_4$ shell can effectively limit the transfer rate of lattice oxygen, so that lattice oxygen can be slowly released to the surface of the oxygen carrier for chemical looping oxidative dehydrogenation.

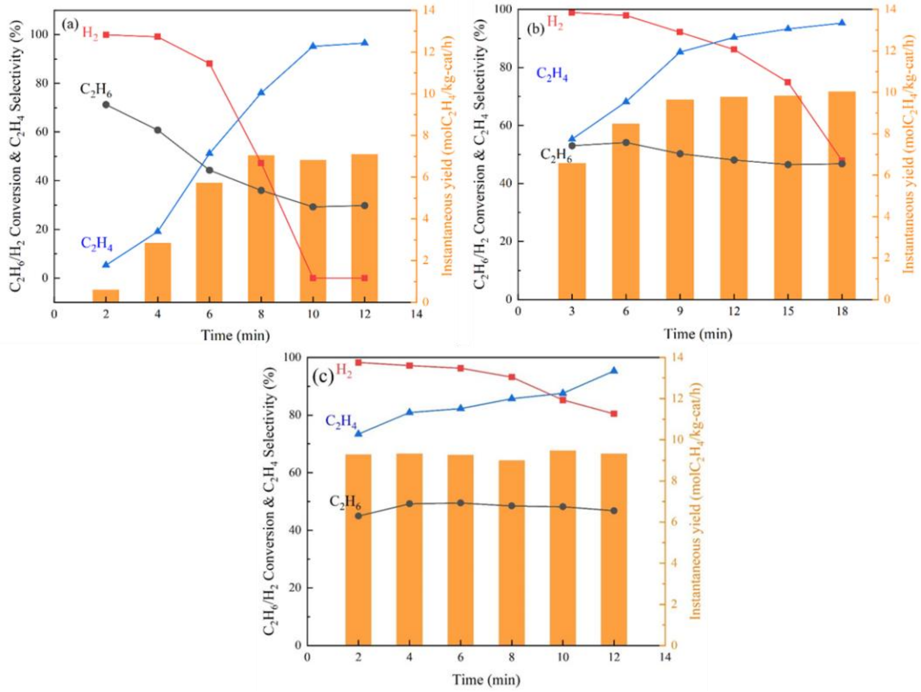

Fig. 4. Ethane conversion, ethylene selectivity, H2 conversion and ethylene instantaneous yield of CuMn2O4(a), CuMn2O4@MnMoO4 and CuMn2O4@SrMoO4(b) continuous reactions

## 4. Conclusions

The composite oxygen carriers $CuMn_2O_4$@$MnMoO_4$ and $CuMn_2O_4$@$SrMoO_4$ with $CuMn_2O_4$ as oxygen-carrying core metal oxide non-molten shell have been prepared, characterized, analyzed and experimentally studied. The C-H bond of ethane is activated by the addition of Mo, which plays a key role in regulating ethylene selectivity. At 700℃ $CuMn_2O_4$@$MnMoO_4$ the conversion of ethane and ethylene selectivity are 40.3% and 93.7%, respectively. At the same time, excellent chemical looping oxidation performance was also shown in continuous reaction experiments, and the maximum instantaneous yield of ethylene was 9.72 mol$C_2H_4$/kg-cat/h. The addition of Sr further improves the alkaline site on the surface of the oxygen carrier, is more conducive to the absorption and desorption of ethane and ethylene, improves the conversion rate of ethane, and reduces the occurrence of side reactions. This results in a significant increase in ethylene selectivity while ensuring that the oxygen carrier has a high oxygen load (7.5 wt.%) and high activity. At 700℃, 45.1% ethane conversion and 87.9% ethylene selectivity were obtained, and high ethylene selectivity was obtained in the early stage of continuous reaction. The maximum instantaneous yield of ethylene was as high as 9.32 mol$C_2H_4$/kg-cat/h.

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