

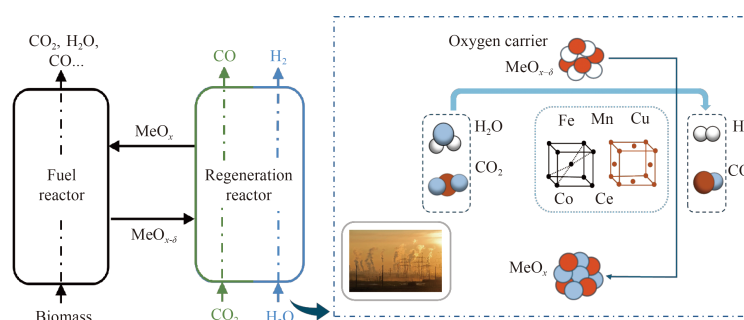
Screening of oxygen carriers for chemical looping CO_2 conversion and hydrogen production *via* water splitting based on Gibbs free energy analysis

WANG Peng^{1,2}, PU Ditao², WANG Yixin², HU Qiang^{2,*}, YANG Yang², YANG Haiping², CHEN Hanping²

¹ China-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, Wuhan 430074, China;

² School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

Abstract: Chemical looping, with its advantages of efficient product separation and low energy consumption, has emerged as a crucial technical pathway for the CO_2 conversion and hydrogen production *via* water splitting. Oxygen carriers, functioning within the chemical looping cycle, undertaking oxygen storage and transfer and participating in the redox reactions, serve as a key component that



determines the reaction rates and product selectivity. To screen high-performance oxygen carriers, this study employed the Gibbs free energy analysis method to thermodynamically investigate the chemical looping reactions involving typical metals and corresponding oxides for the CO_2 conversion and hydrogen production *via* water splitting. Based on the Ellingham diagrams, the feasibility of the conversion reactions and the performance of various metal-based oxygen carriers were evaluated. The Gibbs free energies for the oxidation of metals (such as iron, vanadium, manganese, cobalt, copper and cerium) and that for the reactions between these metals and water were obtained. The feasibility and critical temperatures of the reactions of various metals and their oxides with CO_2 and water across different temperature ranges were clarified, which revealed the superior capability of the Fe/Mn-based oxygen carriers for CO_2 reduction at high temperatures and the great hydrogen production potential of Mn/Cu/Ce-based oxygen carriers at low temperatures. The results indicate that high temperatures can promote the reduction of CO_2 by iron, manganese, and their reduced oxides, with initial reaction temperatures of 708 °C for Fe and 935 °C for Mn; in addition, the promoting effect becomes more pronounced at higher temperatures. Thermodynamically, manganese, copper, and cerium can spontaneously decompose water to produce hydrogen at relatively low temperatures. This study delineates the relative redox performance of various metals with CO_2 and H_2O at different temperatures, providing a thermodynamic theoretical basis for the screening and optimization of oxygen carriers in the chemical looping reactions.

Key words: Gibbs free energy; chemical looping reaction; carbon dioxide conversion; hydrogen production by water splitting; oxygen carriers

Carbon capture and utilization is one of the key technologies for achieving the goal of carbon neutrality. In this aspect, the CO_2 conversion technology enables the recycling of carbon resources^[1] and water splitting for hydrogen production yields zero-carbon-emission hydrogen energy, providing crucial support for addressing the

intermittency of renewable energy and building a new energy system. Both the CO_2 conversion and the water splitting are important technical means for achieving the goal of “dual carbon”. Chemical looping technology, through the redox reactions of metal oxide oxygen carriers^[2], can reduce CO_2 or H_2O to obtain CO or H_2 ,

Received: 2025-11-25; Revised: 2026-01-07

* Corresponding author. E-mail: huqiang2008@hust.edu.cn.

DOI: 10.1016/S1872-5813(26)60696-2 CSTR: 32157.14.2097-213X.2026.JFCT.0055 Associated Data DOI: 10.57760/sciencedb.j00124.00430

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

making it a significant technology for the CO₂ conversion to CO and water splitting to produce hydrogen^[3]. Won et al.^[4] achieved the CO₂ conversion to CO using a nickel-based oxygen carrier in a bubbling fluidized bed, reaching a CO₂ conversion of 78% at 900 °C. Pomiro et al.^[5] prepared Ce/Pr mixed oxygen carriers for the chemical looping reverse water-gas shift, finding that Pr enhanced oxygen mobility in CeO₂, thereby promoting the dissociation of the C=O bonds in CO₂, achieving a CO₂ conversion of 78%. Han et al.^[6] prepared Cr-doped spinel oxygen carriers MgFe_xCr_{2-x}O₄ for the chemical looping water splitting to produce hydrogen. Cr doping simultaneously promoted the dissolution of Fe⁰ nanoparticles and the formation of Fe-O_v-Cr species, which activated H₂O through a relay catalysis mechanism, significantly improving the lattice oxygen recovery rate. The peak H₂ generation rate reached 4.65 mmol/(min·g), with good stability maintained over multiple cycles. Therefore, chemical looping technology has broad application prospects in the CO₂ conversion and water splitting for hydrogen production.

In the processes of chemical looping CO₂ conversion and water splitting to produce hydrogen, the oxygen carriers have important functions. They not only undertake the storage and transfer of lattice oxygen, passing oxygen atoms through changes in their own oxidation states^[7], but also act as heat carriers to maintain thermal balance between reactors. Furthermore, some metal oxide oxygen carriers (such as iron-based and nickel-based carriers) have catalytic effects on the chemical looping reactions, catalyzing the cracking and reforming of hydrocarbons and carbon-oxygen compounds^[8-9]. Therefore, the oxygen carrier is an important factor affecting the overall reaction performance^[10], playing a crucial role in achieving efficient, clean CO₂ conversion and green hydrogen production *via* water splitting. Currently, commonly used oxygen carriers in the chemical looping processes mainly include metal elements such as Fe, Co, Cu, Ni and Ce. Among them, iron-based oxygen carriers are one of the most widely used single-metal carriers due to their abundance as raw materials, low cost, environmental friendliness, and strong oxygen-carrying capacity; however, but they also suffer from issues like easy agglomeration at high temperatures and deactivation over prolonged reaction^[11-13]. Cobalt-based oxygen carriers display lower reaction temperatures and excellent oxygen release performance in the medium-to-low temperature range, but suffer from poor activity and stability and high raw material costs, making their large-scale application difficult^[14]. Copper-based oxygen carriers show strong resistance to carbon deposition and moderate cost. Qiu et al.^[15] verified through temperature-programmed reduction that copper can promote the reduction process at moderate temperatures; however, copper is prone to deactivation by sintering at high temperatures. Nickel-based oxygen carriers exhibit outstanding catalytic activity and can significantly increase the hydrogen ratio in syngas, but they are sensitive to impurities like sulfur and chlorine, making them susceptible to poisoning. Cerium-based oxygen carriers

have strong chemical stability; for example, CeO₂ is a good catalyst material because it can store and release lattice oxygen through the Ce⁴⁺/Ce³⁺ shift, optimizing the material's electronic properties and promoting electron transfer^[16]. However, cerium-based oxygen carriers have low oxygen transfer capacity and are difficult to meet the requirements for efficient reactions when used alone. Yan et al.^[17] prepared uniformly distributed CeO₂-modified CaO/Ca₁₂Al₁₄O₃₃ material *via* wet mixing. During the gasification of sugarcane bagasse char, the presence of CeO₂ was beneficial for maintaining efficient and stable CO₂ capture capacity over multiple cycles. The redox activity of metal oxygen carriers is directly related to the efficiency of chemical looping CO₂ conversion and water splitting for hydrogen production. Research on the reaction performance of metal oxygen carriers is key to optimizing the chemical looping processes.

Efficient and directional control of chemical looping processes can be achieved through thermodynamic material regulation. Zhu et al.^[18] found that in the syngas preparation, by regulating the equilibrium oxygen partial pressure of perovskite-type oxides, over-oxidation of syngas products could be suppressed without relying on their surface characteristics. On the other hand, the oxygen carriers with high equilibrium oxygen partial pressure spontaneously release gaseous oxygen of high activity during their reduction. Therefore, the oxygen carriers with high equilibrium oxygen partial pressure can also generate partially oxidized products under the conditions far from thermodynamic equilibrium. Through thermodynamic calculations, Zhu et al.^[18] found that the lattice oxygen released during the reduction of manganese oxides was either too oxidative (high oxygen partial pressure, e.g., MnO₂, Mn₂O₃) or insufficiently reactive (low oxygen partial pressure, e.g., MnO), while the perovskite material CaMnO₃ possessed ideal redox characteristics suitable for chemical looping oxygen uncoupling. Imtiaz et al.^[19] pointed out that replacing the original cations in CaMnO₃ with Sr, Fe, Ti, or Mg cations could significantly enhance the oxygen absorption/release performance and stability of perovskite-based oxygen carriers in the chemical looping oxygen uncoupling and chemical looping combustion. Qiu et al.^[15] found that in the structure of Cu_{0.4}Co_{0.6}FeO₄ spinel, Cu doping significantly reduced the reduction activation energy of cobalt-iron oxygen carriers and improved the structural reversibility and reaction rate during the oxygen carrier regeneration stage, achieving thermodynamic matching between the reduction and oxidation steps. This synergistic regulation allowed the material to maintain a high CO₂ decomposition rate while enabling stable cycling under mild conditions, demonstrating the feasibility of achieving efficient CO₂ conversion through precise transition metal doping and component design to regulate the reaction pathway. In recent years, researchers have been able to adjust material thermodynamic parameters on demand, such as equilibrium oxygen partial pressure and redox activation energy, through structural design of multi-metal structures

like perovskites and spinels, thereby directly regulating the driving force, pathway, and cycling stability of the redox reactions. The thermodynamic analysis framework based on Gibbs free energy in this paper aims to provide key theoretical basis and screening guidance for subsequent in-depth rational design and optimization.

Gibbs free energy (G), as a physical quantity describing the spontaneity of isothermal and isobaric systems, can directly judge the feasibility and driving force of a reaction through the change in Gibbs free energy (ΔG). Meanwhile, the Ellingham diagram constructed based on Gibbs free energy^[20] can intuitively present the relative redox performance of metals and oxides at different temperatures, providing a reliable thermodynamic tool for evaluating and screening oxygen carrier reaction activity. Most existing studies on the thermodynamic analysis of chemical looping oxygen carriers focus on single-valence metal oxides, with less comparative analysis of the reaction performance of different valence state oxides of the same metal and a relative lack of research on the reaction performance of different metals with $\text{CO}_2/\text{H}_2\text{O}$. Therefore, this study uses the Gibbs free energy analysis method to systematically investigate the performance differences of oxygen carriers of the same metal but different valence states in the two reaction systems of CO_2 conversion and water splitting for hydrogen production, providing theoretical support for the optimization and screening of metal oxygen carriers.

In summary, this study takes single-metal oxygen carriers in the chemical looping CO_2 conversion and water splitting for hydrogen production as the research object. Based on the principle of Gibbs free energy minimization, it calculates the Gibbs free energy changes for the participation of various typical single metals and their different valence state oxides, including iron, cobalt, copper, nickel, manganese, vanadium and cerium, in the CO_2 conversion and water splitting for hydrogen production^[21]. By constructing Ellingham diagrams, the reaction trends, critical reaction temperatures, and redox performance of various metal oxygen carriers in different temperature ranges are analyzed and the reaction differences of different valence state oxides of the same metal are clarified; the thermodynamic performance of each single-metal oxygen carrier is then evaluated, which provides a thermodynamic theoretical basis for the screening and optimization of efficient oxygen carriers in the chemical looping CO_2 conversion and water splitting for hydrogen production.

1 Gibbs free energy calculation and analysis method

1.1 Principle of Gibbs free energy

The Ellingham diagram is an effective analytical tool for screening oxygen carriers in the chemical looping conversion reactions. By examining the Gibbs free energy

curves of various reactions in the diagram, the relative redox performance of all the components in the chemical looping reactions at different temperatures can be judged. Simultaneously, the minimum Gibbs free energy method^[22] can be used to preliminarily assess the feasibility and extent of reactions.

The Ellingham diagram is plotted based on the Gibbs free energy. Gibbs free energy is a thermodynamic state function describing the thermodynamic state of a closed system under isothermal and isobaric conditions. It can be used to describe the energy level of a system in a given state and the spontaneity of the system transitioning from one state to another. The change in Gibbs free energy (ΔG) can be calculated by Equation (1):

$$\Delta G = U + pV - SdT = \Delta H - T\Delta S \quad (1)$$

where U is the internal energy of the system, p is pressure, V is volume, S is entropy, T is temperature and H is enthalpy. The Ellingham diagram depicts the standard Gibbs free energy of the formation of metal oxides (calculated per consumption of 1 mol O_2) as a function of temperature^[23–24]. Each line in the diagram represents a metal oxidation reaction, as in Equation (2):



where Me is the metal element and Me_aO_b is the corresponding metal oxide. The data involved in this study mainly come from NIST Chemistry WebBook and CRC Handbook of Chemistry and Physics.

This study adopts the linear expression $\Delta G = \Delta H - T\Delta S$ for clear comparison of multiple systems. This expression essentially assumes that within the discussed temperature range, ΔH and ΔS of the reaction do not change with temperature, i.e., ignoring the influence of the heat capacity difference ΔC_p . To evaluate the error brought by this simplification, we took some reactions as examples for verification, using HSC Chemistry 6.0 software to call the thermodynamic database, which contains temperature-dependent C_p functions for each component, to precisely calculate the ΔG values. The comparison results are shown in Table 1. In Table 1, ΔG_c denotes the value calculated in this work, whereas ΔG_{HSC} denotes the value calculated using the HSC Chemistry software. Within the core temperature range of 500 to 1500 K, the absolute deviation between the two cases is less than 15 kJ/mol O_2 , with most relative errors within 2.5%. This indicates that within the temperature range concerned in this study, the linear approximation can reliably reflect the trend and relative magnitude of the reaction free energy change, sufficient to support conclusions from qualitative comparisons and critical temperature judgments.

1.2 Thermodynamic calculation and reaction process simulation

Thermodynamic equilibrium calculations were performed using HSC Chemistry 6.0 to study the changes in the

chemical composition of metals and gas products during the CO₂ conversion process. Based on the fundamental thermodynamic data for given materials, the thermodynamic behavior of each component was fitted

under chemical equilibrium conditions. The equilibrium phase composition module was used, set to 50 steps and 1.0 bar pressure, to simulate the variation of chemical composition with temperature.

Table 1 Validation of linear ΔG approximation for metal oxidation reactions (Comparison between this study and HSC database)

Reaction	Temperature/K	$\Delta G_e/(\text{kJ}\cdot\text{mol}^{-1} \text{O}_2)$	$\Delta G_{\text{HSC}}/(\text{kJ}\cdot\text{mol}^{-1} \text{O}_2)$	Deviation/%
$\text{Fe}+\text{O}_2\rightarrow\text{Fe}_3\text{O}_4$	673	-442.80	-444.43	0.36
	873	-408.21	-413.64	1.31
	1073	-373.62	-383.97	2.70
$\text{Mn}+\text{O}_2\rightarrow\text{Mn}_3\text{O}_4$	673	-575.90	-576.32	0.07
	873	-530.82	-542.05	2.07
	1073	-505.76	-507.70	0.38
$\text{Cu}+\text{O}_2\rightarrow\text{CuO}$	673	-189.30	-188.49	0.43
	873	-152.06	-153.957	1.23
	1073	-114.82	-120.245	4.51
$\text{Ce}+\text{O}_2\rightarrow\text{CeO}_2$	673	-944.44	-948.985	0.48
	873	-901.48	-908.255	0.75
	1073	-858.52	-867.646	1.05

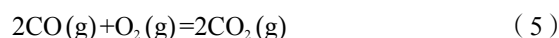
1.3 Analysis method

The core of the Ellingham diagram is to use the change in Gibbs free energy (ΔG) to determine the reaction direction. $\Delta G < 0$ indicates that the forward reaction can proceed spontaneously; the smaller its value, the stronger the thermodynamic driving force is. $\Delta G = 0$ means that the reaction reaches equilibrium. $\Delta G > 0$ suggests that the reverse reaction is spontaneous^[25–26]. In the Ellingham diagram, the lower the position of a metal oxidation line, the smaller its ΔG value is, meaning the stronger the reducibility of the metal is in its elemental state, and the more stable its oxide is. For metals with multiple valence state oxides, thermodynamically, the formation of the oxide with a smaller ΔG (lower position in the diagram) is favored.

In the Ellingham diagram, to evaluate a metal's ability to reduce CO₂, the metal oxidation line needs to be compared with the carbon oxidation line and the CO oxidation line. The relevant reactions and their standard Gibbs free energy changes (in kJ/mol O₂) are as follows:



$$\Delta G = -221 - 0.17872T \quad (4)$$



$$\Delta G = -565.96 + 0.17295T \quad (6)$$

As shown in Figure 1, based on their oxidative performance in the chemical looping reactions, all metals can be divided into three reaction zones, corresponding to the non-CO₂ decomposition zone (Zone I, also called the complete oxidation zone), the CO₂ decomposition zone (Zone II, also called the partial oxidation zone), and the inert zone (Zone III)

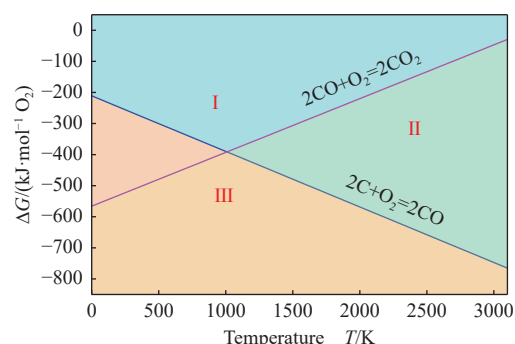


Fig. 1 Reaction partition diagram for the chemical looping reactions: Zone I, CO₂ decomposition zone; Zone II, the partial oxidation zone; Zone III, the inert zone

Metal oxides in Zone I, such as nickel oxide, copper oxide, and ferric oxide, have strong oxidizing ability and can oxidize C and CO to CO₂. Using Zone II metal oxides, carbon can only be partially oxidized to CO. Therefore, Zone II metals or non-highest valence metal oxides can reduce CO₂ to generate CO, making them ideal choices for achieving the CO₂ conversion^[27]. Metal oxides in the inert zone exist stably in the CO/CO₂ atmospheres and do not react with CO or CO₂.

As shown in Equation (1), the slope of the ΔG - T line in the Ellingham diagram is $-\Delta S$. Meanwhile, the reaction between metal and oxygen is usually a gas molecule number decreasing process. For example, the reaction of iron with oxygen to form magnetite significantly reduces the amount of gaseous substance, leading to a significant decrease of entropy ($\Delta S < 0$), which gives a positive slope for the ΔG - T line. In contrast, the reaction of $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ is a gas molecule number increasing process, with entropy increase ($\Delta S > 0$), leading to a negative slope for the ΔG - T line. Accordingly, the ΔG - T line for the reaction of $2\text{C} + \text{O}_2 = 2\text{CO}$ with a negative slope intersects with that

of most metal oxidation reactions with a positive slope. At a temperature above the intersection point, the ΔG value of the $2C + O_2 = 2CO$ reaction is lower than that of the metal oxidation reaction, meaning that the metal or its partially reduced oxide can thermodynamically reduce CO_2 to CO . Therefore, this intersection temperature is the key thermodynamic critical temperature for judging whether a metal or its partially reduced oxide can react with CO_2 to generate CO ^[28].

In subsequent work, metal elements such as Fe, Cu, Co, Ni, Mo, K, V, Ti, Cr, Zn, Pb, Si and Ca were considered, and the Gibbs free energy changes for the formation of corresponding oxides were calculated^[29], as shown in Figure 2, which are compared with the $2C + O_2 = 2CO$ reaction to judge whether the metal can reduce CO_2 to CO .

This study uses the comparison between the metal oxidation line and the $2C + O_2 = 2CO$ line to judge the capability of the metal oxides to reduce CO_2 . Its thermodynamic essence is completely equivalent to the direct calculation of the ΔG value for the reaction of $CO_2 + Me_xO_y = Me_xO_{y-1} + CO$. Kang et al.^[30] pointed out that the overall Gibbs free energy change of the reaction between the reaction gas and the oxygen carrier metal can be calculated by subtracting the ΔG value of the reaction between the reaction gas and oxygen from the ΔG value of the reaction between the oxygen carrier metal and oxygen, thereby eliminating oxygen from the reaction equation. This method facilitates the evaluation of the thermodynamic properties of different metal oxides as chemical looping oxygen carriers within a unified framework. Taking the iron-based oxygen carrier studied in this paper as an example:

The target reaction is:



This reaction can be obtained by combining the lines of two reactions in the diagram:



A formula of $6FeO + 2CO_2 \rightarrow 2Fe_3O_4 + 2CO$ was obtained through (8), (9), which can be simplified to Equation (7) after rearrangement. Therefore, the Gibbs free energy change of the reaction shown in Equation (7) is: $\Delta G_7 = (\Delta G_8 - \Delta G_9)/2$. When the FeO oxidation line in the diagram is below the CO oxidation line (i.e., $\Delta G_8 < \Delta G_9$), then $\Delta G_7 < 0$, meaning the reaction shown in Equation (7) can proceed spontaneously, that is, FeO can reduce CO_2 . This method of referencing oxygen potential lines is an intuitive and sufficient criterion for judging the capability of the metal oxides to reduce CO_2 , especially suitable for parallel comparison of the relative performance of multiple metals in a single diagram. For water splitting to produce hydrogen, the Gibbs free energy of the reaction between steam and metals is selected, and the reactants and products are calculated and analyzed to judge the thermodynamic performance of the reaction between metals and water to generate hydrogen.

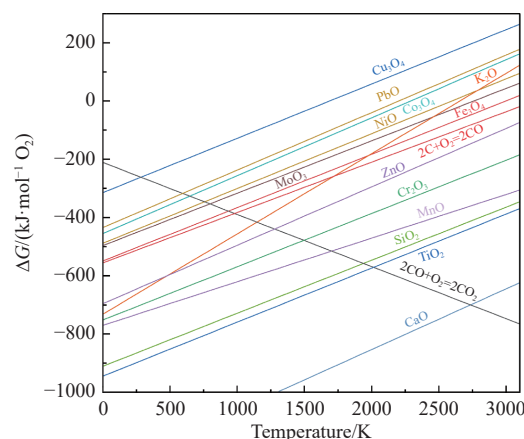


Fig. 2 Ellingham diagram for the reaction of metals with oxygen to form oxides

2 Results and discussion

2.1 Screening of oxygen carriers for chemical looping CO_2 conversion

To construct the Ellingham diagrams, the standard Gibbs free energy change (ΔG) for the reaction of metal elements with oxygen to form oxides of different valence states was calculated. To unify the baseline, all reactions were standardized to correspond to the consumption of 1 mol O_2 . The calculation results are given in Table 2.

As shown in Figure 3(a), the enthalpy change (ΔH) for forming Fe_3O_4 differs from that for the reaction $2CO + O_2 = 2CO_2$ by only 3 kJ/mol O_2 , and their entropy changes differ by only 0.0005 kJ/mol O_2 .

Table 2 ΔG value of the reactions between metals and oxygen to form metal oxides

Reaction	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1} O_2)$
$Fe + O_2 \rightarrow Fe_3O_4$	$-559.2 + 0.17295T$
$Fe + O_2 \rightarrow FeO$	$-544 + 0.1383T$
$Fe + O_2 \rightarrow Fe_2O_3$	$-549.5 + 0.1833T$
$V + O_2 \rightarrow V_2O_5$	$-620.24 + 0.17586T$
$V + O_2 \rightarrow V_2O_3$	$-812.93 + 0.178T$
$V + O_2 \rightarrow VO_2$	$-944 + 0.18314T$
$Co + O_2 \rightarrow CoO_2$	$-300 + 0.17514T$
$Co + O_2 \rightarrow Co_3O_4$	$-445.5 + 0.19895T$
$Co + O_2 \rightarrow CoO$	$-475.88 + 0.15914T$
$Co + O_2 \rightarrow Co_2O_3$	$-594 + 0.1704T$
$Mn + O_2 \rightarrow MnO_2$	$-520.3 + 0.1841T$
$Mn + O_2 \rightarrow MnO$	$-549.5 + 0.19294T$
$Mn + O_2 \rightarrow Mn_2O_3$	$-647.4 + 0.17414T$
$Mn + O_2 \rightarrow Mn_3O_4$	$-693.9 + 0.17534T$
$Cu + O_2 \rightarrow CuO$	$-314.6 + 0.18618T$
$Cu + O_2 \rightarrow Cu_2O$	$-337.2 + 0.15146T$
$Ce + O_2 \rightarrow CeO_2$	$-1089 + 0.2148T$
$Ce + O_2 \rightarrow Ce_2O_3$	$-1193.3 + 0.2011T$

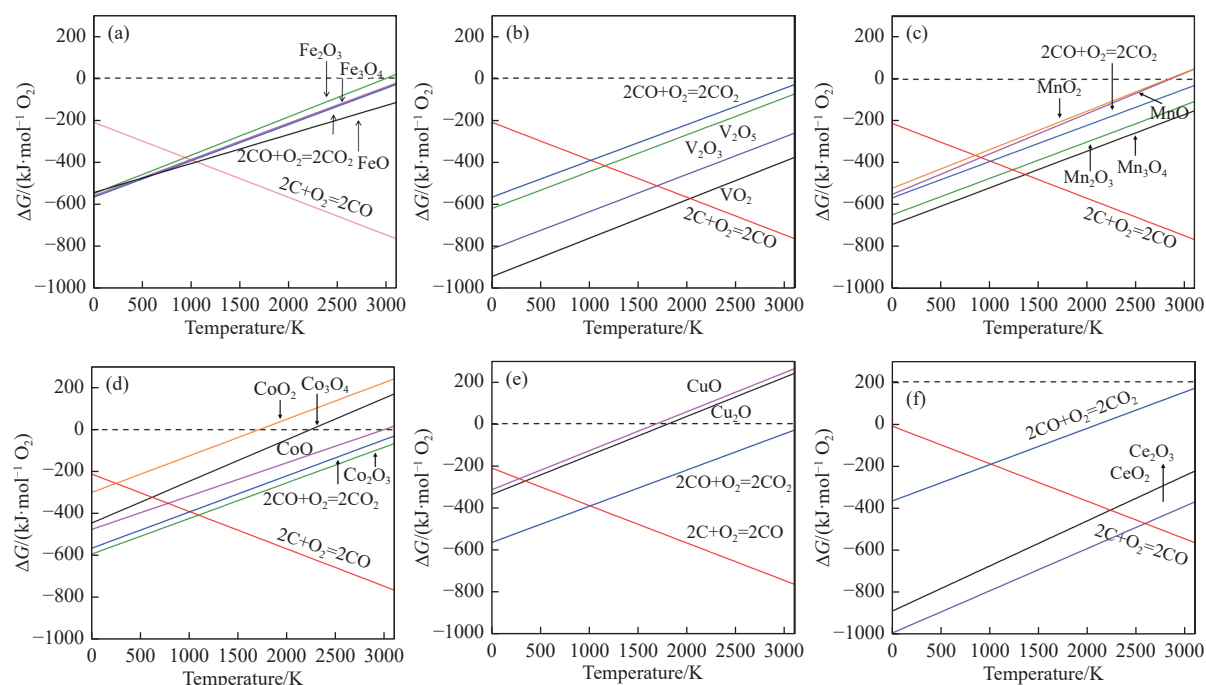


Fig. 3 Ellingham diagram for the reaction of metals with oxygen to form oxides: (a) Fe, (b) V, (c) Mn, (d) Co, (e) Cu, (f) Ce

Therefore, these two lines nearly coincide in the diagram, indicating that two reactions are thermodynamically similar in the redox performance. At 952.46 K, the lines for $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $2\text{C} + \text{O}_2 = 2\text{CO}$ intersect. Below 952.46 K, the ΔG value for $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ is less than that for $2\text{C} + \text{O}_2 = 2\text{CO}$, so CO would be oxidized to CO_2 . The ΔG value for the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ is calculated as $172.45 - 0.17586T$. For $\text{CO}_2 + \text{C} = 2\text{CO}$, ΔG equals zero at 980.60 K, making 980.60 K the critical point at which CO_2 can be reduced to CO by the reducing agents. Above 980.60 K, CO is thermodynamically more stable than CO_2 .

FeO is in the partial oxidation zone at high temperatures. When the temperature is below 1018.86 K, the ΔG value to form FeO is greater than that for $2\text{C} + \text{O}_2 = 2\text{CO}$. The line for the reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and that for the FeO formation intersect at 345.82 K. Below 345.82 K, their maximum difference is only 12 kJ/mol O_2 , indicating that two reactions are close in the redox performance. Thus, below 1018.86 K, FeO can be further oxidized and does not react with CO; above 1018.86 K, however, the ΔG value for forming FeO is greater than that for $2\text{C} + \text{O}_2 = 2\text{CO}$ but less than that for $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, meaning FeO will be oxidized by CO_2 . As the temperature increases, the thermodynamic driving force for the reaction strengthens and the tendency for the forward reaction becomes more significant.

When the elemental iron reacts with CO_2 , the trend for the amount of each component changing with the temperature is shown in Figure 4.

For vanadium oxides (Figure 3(b)), above 1659.37 K, V_2O_5 undergoes a reduction reaction with CO_2 to generate CO. When the temperature rises above 1998.01 K, V_2O_5 can be oxidized by CO_2 . It is worth noting that the critical decomposition temperature of V_2O_5 is 2023 K, at which

V_2O_5 thermally decomposes to form VO_2 . Therefore, under conditions above 2023 K, the reaction of V with CO_2 mainly produces VO_2 and CO.

Manganese-based materials have the advantages of high-temperature stability, environmental friendliness, and low cost, with theoretically higher oxygen transport capacity than iron. Within the temperature range below 3000 K, the redox performance of MnO_2 and MnO becomes nearly identical as the temperature increases, with both being in the complete oxidation zone at high temperatures (Figure 3(c)). Mn_2O_3 and Mn_3O_4 are in the partial oxidation zone at high temperatures, enabling CO_2 reduction. Below 1208.41 K, Mn_2O_3 does not react with CO_2 or CO; above 1208.41 K, CO_2 can react with Mn_2O_3 to generate CO. Below 1340.19 K, Mn_3O_4 does not react with CO_2 or CO; above 1340.19 K, CO_2 can react with Mn_3O_4 to generate CO, and the generation potential increases with rising temperature^[31].

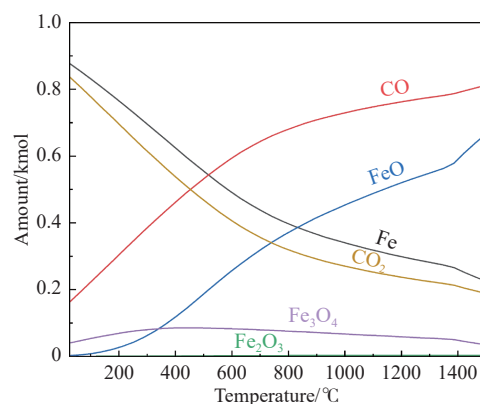


Fig. 4 Variation of the amount of each component in the reaction between iron and carbon dioxide with the temperature

CoO₂, Co₃O₄ and CoO are all in the complete oxidation zone and exhibit similar properties below the critical temperature at which they can be reduced by carbon (the temperature at which their oxidation lines intersect with 2C + O₂ = 2CO), all capable of oxidizing CO to CO₂ (Figure 3(d)). Co₂O₃ is in the partial oxidation zone above 755.62 K. Below 755.62 K, Co₂O₃ does not react with CO₂ or CO. Above 755.62 K, although the ΔG value for the Co₂O₃ formation reaction is less than that for the CO₂ formation reaction, the Co element in Co₂O₃ is already at its highest valence state, so it does not react with CO₂.

Copper oxides are easily reduced, with the elemental metal being more stable than its oxides. The theoretical intersection temperature of the CuO oxidation line with 2C + O₂ = 2CO is very low (256.50 K), indicating that CuO is thermodynamically very easily reduced (Figure 3(e)). Although thermodynamics predicts the reaction can occur at low temperatures, significant reduction of CuO by CO to generate Cu and CO₂ is only observed experimentally above 400 °C, which may be due to the kinetic barriers. Despite being easily reduced, the copper-based oxygen carriers have the advantages of high oxygen-carrying capacity, fast reaction rates, and relatively low cost^[10], making them suitable for composite use as oxygen carriers in the CO₂ conversion.

The standard Gibbs free energy change for the reactions of cerium oxide formation is lower compared to that of other metal oxides, placing them in the inert zone under experimental conditions (Figure 3(f)). The strong reducibility of Ce can reduce CO₂ to generate CO under high-temperature conditions, and both CeO₂ and Ce₂O₃ are very stable. Only at extremely high temperatures, e.g., above 2559.90 K, Ce₂O₃ can reduce CO₂ to generate CO, and even higher temperatures are needed to promote the reaction. Therefore, cerium is rarely used as a standalone oxygen carrier in the chemical looping reactions due to its low oxygen transfer capacity^[32], in contrast, it is often doped with other metals for modification. Zhang et al.^[33–34] observed that multi-metal cerium-based oxygen carriers Ce₇Fe₃O₈ and Ce₇Fe₃Cu_{0.5}O₈ exhibited good reaction activity and cycling characteristics, with improved lattice oxygen mobility. In addition, Ce₇Fe₃O₈ could enter the thermal weight stabilization stage earlier compared to CeO₂.

2.2 Screening of oxygen carriers for chemical looping water splitting for hydrogen production

For the chemical looping water splitting to produce hydrogen, the ΔG value for the reaction of metal elements with water to generate hydrogen and metal oxides, viz., $a\text{Me(s)} + b\text{H}_2\text{O(g)} \rightleftharpoons \text{Me}_a\text{O}_b\text{(s)} + b\text{H}_2\text{(g)}$, is calculated and given in Table 3 and Figure 5(a). Most of the studied metal elements have a thermodynamic tendency for spontaneous water splitting reaction within a certain temperature range, except for a few metals like cobalt and nickel. Among them, zinc and manganese elements show particularly significant reaction spontaneity.

Table 3 ΔG values of the reactions between metals and water to form metal oxides and hydrogen

Reaction	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1} \text{O}_2)$
Ni+H ₂ O→NiO+H ₂	327.3+0.0008 <i>T</i>
Sn+H ₂ O→SnO ₂ +H ₂	-48.53+0.054295 <i>T</i>
Zn+H ₂ O→ZnO+H ₂	-106.46+0.05614 <i>T</i>
W+H ₂ O→WO ₃ +H ₂	-38.71+0.04099 <i>T</i>
Ti+H ₂ O→TiO ₂ +H ₂	-230.18+0.0483 <i>T</i>
Fe+H ₂ O→Fe ₃ O ₄ +H ₂	-37.8+0.041925 <i>T</i>
Fe+H ₂ O→FeO+H ₂	-30.18+0.0247 <i>T</i>
Fe+H ₂ O→Fe ₂ O ₃ +H ₂	-32.91+0.04722 <i>T</i>
Co+H ₂ O→Co ₃ O ₄ +H ₂	19.05+0.0551 <i>T</i>
Co+H ₂ O→CoO+H ₂	3.88+0.03522 <i>T</i>
Mn+H ₂ O→MnO ₂ +H ₂	-18.195+0.04763 <i>T</i>
Mn+H ₂ O→MnO+H ₂	-143.4+0.03045 <i>T</i>
Mn+H ₂ O→Mn ₂ O ₃ +H ₂	-81.98+0.04266 <i>T</i>
Mn+H ₂ O→Mn ₃ O ₄ +H ₂	-105.03+0.0448575 <i>T</i>
Cu+H ₂ O→CuO+H ₂	-84.52+0.04867 <i>T</i>
Cu+H ₂ O→Cu ₂ O+H ₂	-73.22+0.03131 <i>T</i>
Ce+H ₂ O→CeO ₂ +H ₂	-302.7+0.06295 <i>T</i>
Ce+H ₂ O→Ce ₂ O ₃ +H ₂	-354.87+0.0561 <i>T</i>

For the reaction of iron with water vapor (Figure 5(b)), the Gibbs free energy change has a small negative value throughout the temperature range, with the maximum absolute value at 0 K being only about -38 kJ/mol O₂, indicating a weak thermodynamic driving force for this reaction. Therefore, although the reaction is thermodynamically feasible, its equilibrium hydrogen production yield is limited. As the temperature increases, the ΔG values increases gradually and becomes positive above 1221.86 K, meaning that the reaction will no longer be spontaneous at such a high temperature. Between 0 and 442.38 K, the main decomposition product of iron with water is Fe₃O₄; between 442.38 and 1221.86 K, the main product is FeO; above 1221.86 K, the ΔG value for all three decomposition reactions is greater than 0, meaning that these reactions are then not spontaneous any more.

The decomposition reaction of manganese with water occurs spontaneously over a wide temperature range until 4709.4 K (Figure 5(c)), at which point the ΔG value for all four hydrolysis reactions becomes greater than 0. The reaction H₂O + Mn → MnO + H₂ has the lowest ΔG value, with MnO of the divalent manganese as the main product, accompanied by a small amount of Mn₃O₄ (a mixture of divalent and trivalent manganese). Among the different water decomposition reaction paths for manganese, the reaction 2Mn + 2H₂O → MnO₂ + 2H₂ for generating MnO₂ has the highest ΔG value that becomes greater than zero above 382.01 K, indicating that this path is not thermodynamically feasible over most practical temperature ranges. Therefore, MnO₂ does not appear in the products of manganese-water reactions at a high temperature; thermodynamically, the formation of lower valence manganese oxides like MnO and Mn₃O₄ is favored.

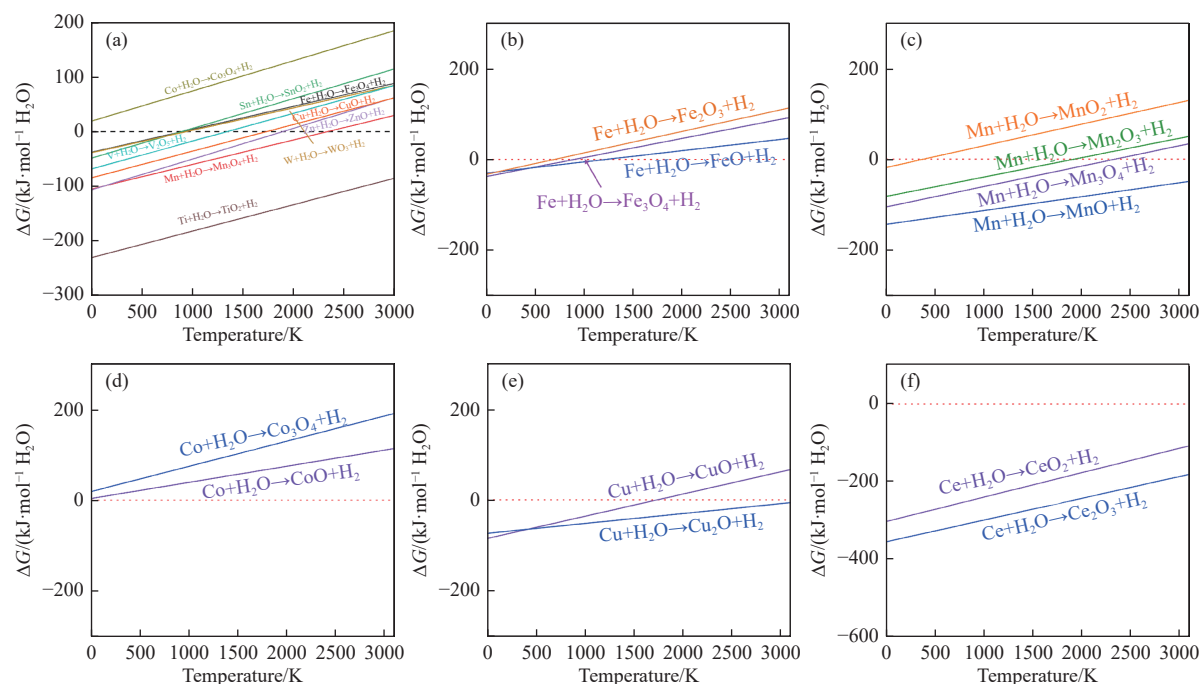


Fig. 5 Ellingham diagram for the reactions of metals with water to form oxides and hydrogen: (a) Overview of all metals considered in this work, (b) Fe, (c) Mn, (d) Co, (e) Cu and (f) Ce

For cobalt, the ΔG value for the reaction of elemental Co with water to generate CoO or Co_3O_4 is greater than zero over all practical temperature ranges (Figure 5(d)), indicating that these reactions are thermodynamically non-spontaneous. Therefore, cobalt is not suitable as a reducing agent for the chemical looping water splitting for hydrogen production.

The reaction of copper metal with water vapor has thermodynamic spontaneity over a wide temperature window up to 3380.42 K (Figure 5(e)), showing good hydrogen production potential. At 418.36 K, the reaction lines for generating CuO and Cu_2O intersect. Below this temperature, the formation of CuO is thermodynamically favored; above it, the formation of Cu_2O is favored.

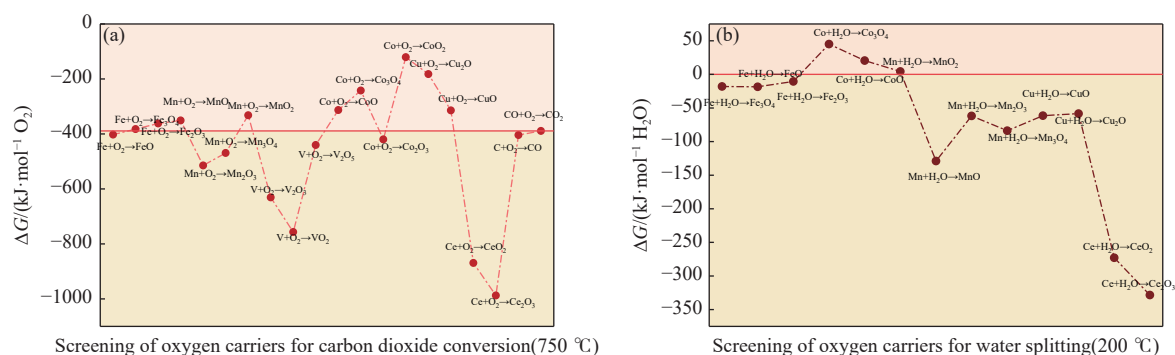
Cerium metal exhibits extremely strong reducibility. The ΔG value for its reaction with water to generate CeO_2 or Ce_2O_3 is as low as approximately -302.7 and -354.9 kJ/mol O_2 at 0 K, respectively, far exceeding other metals (Figure 5 (f)), indicating a huge thermodynamic driving force for this reaction. The spontaneity of this reaction can be maintained up to extremely high temperatures, until about 6325 K. From a thermodynamic perspective, cerium is an ideal reducing agent for water splitting to produce hydrogen. However, its practical application is also influenced by the factors such as reaction kinetics, reaction systems, material costs, and cycling stability.

2.3 Analysis and discussion

The thermodynamic feasibility of the CO_2 conversion reaction is determined by the relative magnitude of the Gibbs free energy change between the metal oxide

formation and carbon oxidation reactions. As shown in Figure 6(a) and Table 4, in the CO_2 conversion reaction, the metals or low-valence oxides whose oxidation reaction formation free energy is lower than that of $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ reaction possess the ability to reduce CO_2 , but the lower their free energy, the higher the temperature required to drive the reaction. FeO (1018.86 K), Mn_2O_3 (1208.41 K), and other metal oxides need to reach specific starting temperatures to gain CO_2 reduction capability, and low-valence oxides of metals like Fe, Mn and V more easily drive the reaction in the high-temperature regions, with enhanced thermodynamic driving force at high temperatures. This result is consistent with the phenomenon of increased CO yield at a higher temperature observed by Huang et al.^[29] in the chemical looping gasification with Fe_2O_3 as the oxygen carrier. As shown in Figure 6(b) and Table 5, in the water splitting for hydrogen production, Mn-, Cu- and Ce-based low-valence oxides show significant advantages. For example, the spontaneous reaction of MnO with H_2O can proceed below 4709.36 K, Ce_2O_3 up to 6325.6 K, and CuO and Cu_2O also maintain reaction spontaneity below 1736.59 and 2338.55 K, respectively, showing good low-temperature hydrogen production potential.

To screen excellent oxygen carrier materials, metals should possess sufficient reducing ability to drive the reaction, but excessively strong reducing ability can lead to extremely stable oxidized states, making it difficult to reduce the metal back to a low valence state^[35]. For example, Ce_2O_3 has strong reducing ability and can react efficiently with H_2O or CO_2 . However, its corresponding oxidized state, CeO_2 , is very stable.

Fig. 6 Analysis of metals on (a) the CO₂ conversion and (b) the water splitting reactionsTable 4 Initial temperature for the reduction of CO₂ by metals

Metal category	Metal oxide category	Initial temperature for the CO ₂ reduction/K
Fe	Fe ₃ O ₄	980.6
	FeO	1018.86
	Fe ₂ O ₃	—
Mn	Mn ₂ O ₃	1208.41
	Mn ₃ O ₄	1340.19
	MnO	—
V	MnO ₂	—
	V ₂ O ₅	—
	V ₂ O ₃	1659.37
Co	VO ₂	1998.01
	CoO ₂	—
	Co ₃ O ₄	—
Cu	CoO	—
	Co ₂ O ₃	—
	CuO	—
Ce	Cu ₂ O	—
	CeO ₂	—
	Ce ₂ O ₃	2259.9

Table 5 Termination temperature of spontaneous reaction between metals and H₂O

Metal category	Metal oxide category	Termination temperature for the spontaneous reaction with H ₂ O/K
Fe	Fe ₃ O ₄	901.6
	FeO	1221.86
	Fe ₂ O ₃	696.95
Mn	Mn ₂ O ₃	1921.71
	Mn ₃ O ₄	2341.41
	MnO	4709.36
Co	MnO ₂	382.01
	CoO	—
	Co ₃ O ₄	—
Cu	CuO	1736.59
	Cu ₂ O	2338.55
Ce	CeO ₂	4808.58
	Ce ₂ O ₃	6325.6

Removing lattice oxygen from CeO₂ requires extremely high energy, which not only increases the energy consumption but may also adversely affect the structural stability of the oxygen carrier. Long-term cycling can easily lead to CeO₂ particle agglomeration, decrease the specific surface area, and consequently impact the oxygen-carrying performance^[36]. In contrast, for the oxygen carrier systems like Fe₂O₃/Fe₃O₄ and Mn₃O₄/MnO, the conversion between their reduced and oxidized states during the chemical looping cycle for the CO₂ conversion and water splitting can be achieved under relatively mild conditions to regenerate the oxygen carrier while maintaining good cycling stability. For instance, in an air atmosphere, Fe₃O₄ can be rapidly oxidized to Fe₂O₃ at 800 °C, with a Gibbs free energy change ΔG value of $-172.0 \text{ kJ/mol O}_2$ for this regeneration reaction at 800 °C, indicating sufficient reaction driving force. Morales et al.^[37] prepared an oxygen carrier with Fe₂O₃ as the matrix by combining tungsten with iron. A solid solution of tungsten formed in the matrix, providing higher mechanical stability. It performed well over multiple cycles, with minimal changes in the crystal structure and particle morphology, and slow decay in the oxygen-carrying capacity. Taking copper-based oxygen carrier CuO/Cu₂O as an example, its reducing ability is weaker than that of Fe and Mn systems. The ΔG value for reducing CuO to Cu₂O is -132 kJ/mol O_2 at 500 °C, but the regeneration conditions are milder; Cu₂O can be oxidized to CuO in an air atmosphere at 600–700 °C, and it has outstanding resistance to carbon deposition. For the systems with excessively strong reducing ability, like Ce-based ones, doping can be used to adjust and reduce the reduction difficulty, achieving a balance between high oxygen-carrying capacity and acceptable regeneration energy consumption.

Strong thermodynamic spontaneity, i.e., a large negative Gibbs free energy change, is necessary for fast reactions, but the actual reaction rate is controlled by kinetic activation energy. Taking cerium-based oxygen carriers as an example, they exhibit extremely strong thermodynamic driving force in the water splitting, but the overall reaction is often rather slow due to the limited oxygen ion bulk diffusion rates. Zhu et al.^[18] pointed out that the oxygen ion diffusion coefficient of pure CeO₂ is low at 800 °C, mainly due to its limited oxygen vacancy migration rate, leading to

insufficient lattice oxygen conduction capacity, thereby constraining its overall redox reaction rate. In contrast, copper-based oxygen carriers have moderate thermodynamic driving force but often exhibit superior surface reaction kinetics at suitable temperatures. Adánez et al.^[38] observed in fluidized bed experiments that CuO/Al₂O₃ oxygen carriers had extremely high initial reaction rates in the chemical looping combustion, attributed to copper's good redox activity and relatively low activation energy, enabling the redox cycle to proceed rapidly at relatively low temperatures.

Thermodynamic phase stability, usually manifested as a high free energy of formation, helps oxygen carriers maintain chemical structural stability under the reaction conditions, avoiding over-reduction or decomposition. Under the specific temperature and oxygen partial pressure of the chemical looping cycle, only thermodynamically stable phases can exist long-term. If the reaction is conducted under the conditions where the oxygen carrier is in the thermodynamically unstable phase, uncontrollable phase transitions, decomposition, or reactions with the support may occur, leading to structural collapse and activity decay. At high temperatures, grain sintering and particle coarsening are the main causes for the oxygen carrier deactivation, driven by the reduction of the system's Gibbs free energy, i.e., the system tends toward stability by reducing surface energy. The free energy change between different valence state oxides indirectly reflects the lattice strain energy during the phase transitions. The larger the absolute value of the free energy change before and after the reaction and the more severe the phase transition, the greater the structural stress is, which exacerbates the atomic migration process that leads to sintering.

Furthermore, the resistance of oxygen carriers against carbon deposition is fundamentally constrained by thermodynamic equilibrium. The Gibbs free energy of formation of metal oxides, i.e., the oxygen chemical potential, must be higher than the critical value for the carbon gasification ($C + O_2 \rightarrow CO_2$, $C + O_2 \rightarrow CO$) to avoid the thermodynamic spontaneous tendency of carbon deposition. Simultaneously, in the chemical looping reaction process, whether during oxygen carrier regeneration or the fuel reaction stage, it is necessary to avoid the occurrence of the Boudouard reaction ($2CO \rightarrow C + CO_2$) leading to carbon deposition. Therefore, it is necessary to increase the effective oxygen chemical potential of the oxygen carrier, providing strong oxygen supply capacity, and avoid entering the thermodynamic stability region of carbon. For example, at a lower temperature, iron-based oxygen carriers like FeO have too low an oxygen chemical potential to inhibit the Boudouard reaction, making carbon deposition a thermodynamically spontaneous process, leading to carbon deposition. Therefore, through thermodynamic calculations, more stable composite systems can be predicted and designed. For example, combining active components with inert supports or forming solid solutions can thermodynamically alter the

system's phase equilibrium and free energy, physically separating active particles to inhibit their contact and agglomeration. The low surface energy characteristic of the support itself can also reduce the total surface energy of the system, thereby suppressing sintering and carbon deposition tendencies, and enhancing the material's cycling stability.

3 Conclusions

Thermodynamic properties are crucial for evaluating oxygen carriers in the chemical looping reactions. In this study, based on the principle of Gibbs free energy minimization, potential metal oxygen carriers were classified and screened according to the thermodynamic feasibility of the reactions. The thermodynamic performance of various metals and their oxides in the chemical looping CO₂ conversion and water splitting for hydrogen production was evaluated and following conclusions were obtained:

In the chemical looping CO₂ conversion process, increasing temperature favors the reduction of CO₂ by metals such as Fe and Mn. Fe-based oxygen carriers begin to show significant CO₂ reduction capability at ≥ 708 °C, and Mn-based ones at ≥ 935 °C, with enhanced thermodynamic driving force at elevated temperatures.

In the chemical looping water splitting for hydrogen production, most metal oxides, except cobalt and nickel, possess thermodynamic feasibility for water vapor decomposition to produce hydrogen under certain temperature conditions. Thermodynamically, manganese, copper, and cerium can spontaneously decompose water to produce hydrogen at relatively low temperatures.

Through systematic Gibbs free energy analysis, the feasible temperature windows and reaction driving forces for different metal oxygen carriers in the CO₂ conversion and water splitting reactions were clarified, providing a reliable theoretical basis for the directional design and screening of oxygen carriers. By determining the favorable temperature ranges for different oxygen carrier reactions, it helps to guide the selection of oxygen carriers and optimization of operating conditions in the CO₂ reduction and water splitting for hydrogen productions, providing a thermodynamic foundation for the development of processes for efficient energy conversion and carbon recycling under the "dual carbon" goals.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] SANSANIWAL S K, PAL K, ROSEN M A, et al. Recent advances in the development of biomass gasification technology: A comprehensive review[J]. Renewable

- Sustainable Energy Rev, 2017, 72: 363–384.
- [2] ERSAN S, PARK J O. Light-independent biological conversion of CO₂[J]. *Joule*, 2020, 4(10): 2047–2051.
- [3] NIU Y, CHI Z, LI M. Advancements in biomass gasification research utilizing iron-based oxygen carriers in chemical looping: A review[J]. *Mater Rep Energy*, 2024, 4(3): 100282.
- [4] WON Y, LEE K R, RYU H J, et al. CO₂-to-CO conversion using a Ni-based oxygen carrier in a bubbling fluidized bed and its integration potential with chemical looping combustion[J]. *Chem Eng J*, 2025, 522: 167771.
- [5] POMIRO F J, FOUGA G G, TAMIETTI A E, et al. Conversion of CO₂(g) to CO(g) via reverse water–gas shift cycle on mixed cerium/praseodymium oxides at 500 °C[J]. *Chem Eng J*, 2024, 498: 155222.
- [6] HAN Y, ZONG T, WANG Y, et al. Enhanced hydrogen production of Fe-based spinel by relay catalysis of Fe⁰ and Fe–O_x–Cr species in chemical looping H₂O splitting[J]. *J Catal*, 2024, 436: 115614.
- [7] ZENG L, CHENG Z, FAN J A, et al. Metal oxide redox chemistry for chemical looping processes[J]. *Nat Rev Chem*, 2018, 2: 349–364.
- [8] MENDIARA T, JOHANSEN J M, UTRILLA R, et al. Evaluation of different oxygen carriers for biomass tar reforming (II): Carbon deposition in experiments with methane and other gases[J]. *Fuel*, 2011, 90(4): 1370–1382.
- [9] PARK H J, PARK S H, SOHN J M, et al. Steam reforming of biomass gasification tar using benzene as a model compound over various Ni supported metal oxide catalysts[J]. *Bioresour Technol*, 2010, 101(Suppl.): S101–S103.
- [10] TANG M, XU L, FAN M. Progress in oxygen carrier development of methane-based chemical-looping reforming: A review[J]. *Appl Energy*, 2015, 151: 143–156.
- [11] WANG S, WU F, WANG X. Experimental and kinetics analysis on biomass chemical looping gasification using lean iron ore as oxygen carrier[J]. *Chem Eng J*, 2023, 474: 145855.
- [12] REN Z, GAO Z-H, GUO Z-L, et al. Sustainable hydrogen production from waste plastics via staged chemical looping gasification with iron-based oxygen carrier[J]. *Appl Energy Combust Sci*, 2025, 23: 100362.
- [13] CHEN X, WANG L, LIN Y, et al. Migration of lattice oxygen during chemical looping dry reforming of methane with Ca₂Fe₂O₃/Zr_{0.5}Ce_{0.5}O₂ oxygen carrier[J]. *Fuel Process Technol*, 2023, 244: 107706.
- [14] WONG Y J, KOH M K, KHAVARIAN M, et al. Investigation on cobalt aluminate as an oxygen carrier catalyst for dry reforming of methane[J]. *Int J Hydrogen Energy*, 2017, 42(47): 28363–28376.
- [15] QIU Y, MA L, ZENG D, et al. Efficient CO₂ to CO conversion at moderate temperatures enabled by the cobalt and copper co-doped ferrite oxygen carrier[J]. *J Energy Chem*, 2020, 46: 123–132.
- [16] GUO H, KOU X, ZHAO Y, et al. Effect of synergistic interaction between Ce and Mn on the CO₂ capture of calcium-based sorbent: Textural properties, electron donation, and oxygen vacancy[J]. *Chem Eng J*, 2018, 334: 237–246.
- [17] YAN X, LI Y, MA X, et al. CeO₂-modified CaO/Ca₁₂Al₁₄O₃₃ bi-functional material for CO₂ capture and H₂ production in sorption-enhanced steam gasification of biomass[J]. *Energy*, 2020, 192: 116664.
- [18] ZHU X, LI K, NEAL L, et al. Perovskites as geo-inspired oxygen storage materials for chemical looping and three-way catalysis: A perspective[J]. *ACS Catal*, 2018, 8(9): 8213–8236.
- [19] IMTIAZ Q, HOSSEINI D, MULLER C R. Review of oxygen carriers for chemical looping with oxygen uncoupling (CLOU): Thermodynamics, material development, and synthesis[J]. *Energy Technol*, 2013, 1: 633–647.
- [20] EPIFANO E, MONCEAU D. Ellingham diagram: A new look at an old tool[J]. *Corros Sci*, 2023, 217: 111113.
- [21] HUANG Z, HE F, FENG Y, et al. Characteristics of biomass gasification using chemical looping with iron ore as an oxygen carrier[J]. *Int J Hydrogen Energy*, 2013, 38(34): 14568–14575.
- [22] WANG K, YU Q, QIN Q, et al. Thermodynamic analysis of syngas generation from biomass using chemical looping gasification method[J]. *Int J Hydrogen Energy*, 2016, 41(24): 10346–10353.
- [23] STRATTON P. Ellingham diagrams-their use and misuse[J]. *Int Heat Treat Surf Eng*, 2013, 7(2): 70–73.
- [24] BACKMAN L, OPILA E J. Thermodynamic assessment of the group IV, V and VI oxides for the design of oxidation resistant multi-principal component materials[J]. *J Eur Ceram Soc*, 2019, 39(5): 1796–1802.
- [25] ZENG J, XIAO R, ZHANG H, et al. Chemical looping pyrolysis-gasification of biomass for high H₂/CO syngas production[J]. *Fuel Process Technol*, 2017, 168: 116–122.
- [26] SARAFRAZ M M, CHRISTO F C, et al. Thermodynamic assessment and techno-economic analysis of a liquid indium-based chemical looping system for biomass gasification[J]. *Energy Convers Manag*, 2020, 225: 113428.
- [27] ZHAO X, ZHOU H, SIKARWAR V S, et al. Biomass-based chemical looping technologies: The good, the bad and the future[J]. *Energy Environ Sci*, 2017, 10(9): 1885–1910.
- [28] ZENG L, TONG A, KATHE M, et al. Iron oxide looping for natural gas conversion in a countercurrent moving bed reactor[J]. *Appl Energy*, 2015, 157: 338–347.
- [29] HUANG Z, HE F, ZHU H, et al. Thermodynamic analysis and thermogravimetric investigation on chemical looping gasification of biomass char under different atmospheres with Fe₂O₃ oxygen carrier[J]. *Appl Energy*, 2015, 157: 546–553.
- [30] KANG K, SAMPEI H, SEKINE Y, et al. CO₂ conversion to CO by reverse water gas shift and dry reforming using chemical looping[J]. *RSC Sustainable*, 2025, 3(4): 1598–1628.
- [31] LI X, FENG S, GUO Y, et al. Thermomechanical and thermodynamic analysis of the sintering process of Mn-based oxygen carrier in chemical looping gasification of biomass[J]. *Fuel*, 2024, 374: 132422.
- [32] MA S, CHEN S, ZHU M, et al. Enhanced sintering resistance of Fe₂O₃/CeO₂ oxygen carrier for chemical looping hydrogen generation using core-shell structure[J]. *Int J Hydrogen Energy*, 2019, 44(13): 6491–6504.

- [33] ZHANG H, TIAN Y, GAO Y, et al. Thermal analysis kinetics of cerium-based oxygen carriers in chemical-looping reforming[J]. Low-Carbon Chem Chem Eng, 2019, 44(6): 64–69.
- [34] LI B, ZHANG H, LV P, et al. Performances of Ce-based oxygen carrier prepared by direct ball milling in chemical looping reforming of methane to syngas[J]. Low-Carbon Chem Chem Eng, 2019, 44(6): 1–7+19.
- [35] ZHAO Y, LIU D, FENG Y, et al. Behavior and design of Fe-based oxygen carriers in chemical looping combustion: A review[J]. Chem Eng J, 2024, 499: 156582.
- [36] MA S, CHENG F, LU P, et al. Enhanced performance of hematite oxygen carrier by CeO₂ for chemical looping hydrogen generation[J]. Int J Hydrogen Energy, 2022, 47(8): 5130–5141.
- [37] MORALES CORONA J J, CAMPBELL K S, FENNELL P S. Enhancement of iron-based oxygen carriers through alloying with tungsten oxide for chemical looping applications including water splitting[J]. Greenhouse Gas Sci Technol, 2023, 13: 565–574.
- [38] ADÁNEZ J, ABAD A, GARCÍA-LABIANO F, et al. Progress in chemical-looping combustion and reforming technologies[J]. Prog Energy Combust Sci, 2012, 38(2): 215–282.

基于吉布斯自由能分析的化学链二氧化碳转化与水分解制氢的载氧体筛选

王 鹏^{1,2}, 蒲迪涛², 王亦歆², 胡 强^{2,*}, 杨 扬², 杨海平², 陈汉平²

(1. 华中科技大学 中欧清洁与可再生能源学院, 湖北 武汉 430074; 2. 华中科技大学 能源与动力工程学院, 湖北 武汉 430074)

摘 要: 化学链技术具有可实现产物的高效分离、降低能耗等优势, 成为二氧化碳转化与水分解制氢的重要技术路线。载氧体在化学链循环中承担氧的储存与传递、参与氧化还原反应, 成为决定反应速率与产物选择性的关键。为了筛选出性能优异的载氧体, 本研究采用吉布斯自由能分析方法, 从热力学上对典型金属及其氧化物参与二氧化碳转化与分解水制氢化学链反应展开研究。基于埃林汉姆图评估反应的可行性及各类金属载氧体的反应性能, 分别得出了铁、钒、锰、钴、铜、铈等金属氧化反应以及金属与水反应的吉布斯自由能, 借此明确不同温度区间内各金属及其氧化物与 CO₂、水的反应可行性及临界温度, 揭示了铁、锰基载氧体的高温 CO₂ 还原优势与锰、铜、铈基载氧体的低温制氢潜力。结果表明, 高温可促进铁、锰及还原态氧化物对二氧化碳的还原, 其反应起始温度分别为 708 和 935 °C, 温度越高效果越显著。热力学上锰、铜、铈可在较低温度下自发将水分解制备氢气。该研究展示了各金属与 CO₂、H₂O 在不同温度下的相对氧化还原性能, 为化学链反应中载氧体的筛选与优化提供了热力学理论依据。

关键词: 吉布斯自由能; 化学链反应; 二氧化碳转化; 水分解制氢; 载氧体

中图分类号: TQ511

文献标识码: A

作者简介:



王鹏(2000), 华中科技大学中欧清洁与可再生能源学院硕士研究生, 研究方向为化学链二氧化碳转化、基于机器学习的化学链载氧体筛选与优化, m202471771@hust.edu.cn。



胡强(1991), 华中科技大学能源与动力工程学院副教授、硕导, 新加坡国立大学环境研究所博士后。研究方向是热转化绿色制氢、制氢与捕碳协同耦合、基于机器学习的化工过程设计、低碳燃料负碳利用等, huqiang2008@hust.edu.cn。