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高指数晶面结构氧化铁化学链燃烧反应活性及深层还原反应机理

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摘要: 采用密度泛函理论计算和实验研究形貌可控制备氧化铁作为高效载氧体用于化学链燃烧的可行性. 首先从理论上对比分析 Fe_2O_3 高指数晶面[104]和低指数晶面[001]的反应活性及深层还原反应机理. 表面反应结果显示, Fe_2O_3 [104]氧化 CO 的反应活性远高于 Fe_2O_3 [001], Fe_2O_3 [104]被还原成为低价的铁氧化物或单质, 这些低价的铁氧化物或单质可被 O_2 氧化再生. 载氧体和 CO 深层反应结果显示 Fe_2O_3 [104]可被 CO 彻底还原成 Fe 单质, Fe_2O_3 [104]释放氧能力强, 反应活性高; 而 Fe_2O_3 [001]还原到一定程度后反应能垒高, 抑制表面进一步还原, 释放氧能力有限. 最后, 实验结果进一步证明了 Fe_2O_3 [104]作为载氧体用于化学链燃烧的高反应活性及稳定性.

关键词: 燃烧; 表面; 吸附; Fe_2O_3 ; 密度泛函理论
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Reaction Activity and Deep Reduction Reaction Mechanism of a High Index Iron Oxide Surface in Chemical Looping Combustion

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Abstract: The possibility of morphological control of iron oxide as an oxygen carrier for chemical looping combustion was investigated using density functional theory and experiment. First, we calculated the reactivity of Fe_2O_3 with high-index facets [104] and low-index facets [001], as well as the deep reduction reaction mechanism of these two facets. Surface reaction results show that the activity of Fe_2O_3 [104] for oxidizing CO is greater than that of Fe_2O_3 [001]. Fe_2O_3 [104] was reduced into iron oxide at lower oxidation state or into iron, which could then be regenerated after being oxidized by O_2 . The deep reduction reaction mechanism between oxygen carrier and CO shows that Fe_2O_3 [104] can be completely reduced into Fe, and Fe_2O_3 [104] exhibits high oxygen transfer ability. However, Fe_2O_3 [001] can only be reduced to a limited extent, with a high energy barrier preventing further reduction, while it also exhibits limited oxygen transfer capacity. Results of experiments further verify the high reactivity and stability of Fe_2O_3 [104].

Key Words: Combustion; Surface; Adsorption; Fe_2O_3 ; Density functional theory

1 Introduction

Chemical looping combustion (CLC) has received great attraction for its efficient use of energy and inherent separation of CO_2 .^{1–3} CLC is a promising technology that produces heat and

energy using oxygen carrier (OC) to supply oxygen instead of air for combustion of fuel, which results in the generation of a sequestration-ready stream of CO_2 that is not diluted with N_2 or flue gas and also reduces NO_x emissions.^{4–10} Fig.1 shows the principle

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Fig.1 Principle of chemical-looping combustion
Me: metal

of CLC.

OC acts as one of the most important factors deciding the efficiency of CLC. Till now, many OCs mainly including the oxides of Fe, Ni, Co, Cu, Mn, and Cd, have been developed for CLC. Among these OCs, NiO exhibits high reactivity but thermodynamic limitation and potential carcinogenic tendency of NiO,¹¹ CuO shows exothermic characteristic but low melting point and thus is low resistance to sintering,¹² CoO shows satisfactory reactivity and oxygen transfer capacity but high cost,¹³ Fe₂O₃ becomes the candidate for CLC process recently due to its environmentally harmlessness, high oxygen capacity, good mechanical strength, and low price.¹⁴ However, enhancing the oxygen transfer capacity and reactivity of Fe₂O₃ becomes urgent problem.

Loaded Fe₂O₃ and combined iron based OC have received great interest for their enhanced reactivity, avoidance of carbon deposition, and good repeatability.^{15–26} But the application of these compounds in CLC systems may not be feasible due to expensive production cost. Recently, controlled synthesis of metal oxide with a large percentage of certain exposed facets causes researcher's attention, owing to their scientific importance associated with highly reactive surfaces.^{27,28} The surface energies of hematite calculated based on density functional theory (DFT) for [001], [101], and [104] facets are 1.146, 1.308, 1.453 J·m⁻², respectively,²⁹ which shows that surface energy of the [104] facet is higher than those of [001] and [101] facets. Single crystals of hematite with exposed [104] facets have been prepared for potential application as carbon-alternative anode materials for lithium ion batteries, showing high capacity, improved cyclability, and good rate performance.³⁰ The unique α -Fe₂O₃ crystals with [104] high-index facets are highly advantageous for gas sensors with high performance.³¹ Single crystals of hematite with nearly 100% exposed [012] facets show improved photocatalytic properties over nanoplates with dominant [001] facets.³²

Fe₂O₃ with high-index facets shows a noticeable catalytic activity. However, differing from catalytic reaction course, Fe₂O₃ is gradually reduced and structurally destroyed during CLC process. Whether such high index Fe₂O₃ surface is active enough for fuel CLC and whether the reduced surface can be regenerated remain unknown. In addition, the reaction mechanism between fuel molecule and the high index Fe₂O₃ surface, especially the deep reduction reaction mechanism of the high index Fe₂O₃ surface, has not been investigated before. To address these problems, we compared the electronic properties, surface reaction activity,

oxygen transfer, and deep reduction of the high index Fe₂O₃ surface [104] with those of the low index Fe₂O₃ surface [001], one of the dominant growth faces of the natural hematite.³³ Then we experimentally verified the enhanced performance and re-use property of the high index Fe₂O₃ surface.

2 Experimental and computational details

2.1 Preparation and chemical looping combustion

According to the reported method,³¹ 5.38 g FeCl₃·6H₂O (AR, Sinopharm Chemical Reagent Beijing Co., Ltd.) and 5.82 g urea (AR, Sinopharm Chemical Reagent Beijing Co., Ltd.) were dissolved in 200 mL of distilled water to form a clear yellow solution, and then appropriate amount of Al₂O₃ (AR, Sinopharm Chemical Reagent Beijing Co., Ltd.) and 7.25 g formamide (AR, Sinopharm Chemical Reagent Beijing Co., Ltd.) were added. The reacting solution was transferred to 200 mL Teflon-lined stainless autoclave and heated to 120 °C for 12 h. After cooled down to room temperature, the product was collected by centrifugation and washed with distilled water and absolute ethanol (AR, Sinopharm Chemical Reagent Beijing Co., Ltd.) 4 times, and then dried at 80 °C for several hours. The obtained solid was sintered at 900 °C for 2 h. Finally, the as-synthesized Fe₂O₃[104]/Al₂O₃ (60%, mass fraction) samples were further ground and sieved to 63–106 μ m for use.

The referenced Fe₂O₃/Al₂O₃ was prepared following the traditional precipitation method.³⁴ The morphological characterizations of the prepared and the regenerated OCs were performed by LEO-1450 scanning electron microscope (SEM, LEO, USA), H-9000NAR high-resolution transmission electron microscopy (HRTEM, Hitachi, Japan), D/MAX-RB X-ray diffraction (XRD, Rigaku, Japan), and Autosorb-iQ-MP Brunauer-Emmett-Teller (BET, Quantachrome, USA).

The reaction between the synthesized OCs and CO was conducted in a simultaneous thermal analyzer (TGQ500) under N₂ at 900 °C. The flow rate of N₂ is 100 mL·min⁻¹. As comparison, reaction between CO and the referenced Fe₂O₃/Al₂O₃ was also performed under the same conditions. Reactivity data as a function of time were obtained from the mass variations during the reduction-oxidation cycles. The degree of solid conversion χ is defined as follow:

$$\chi = \frac{m_{\text{ox}} - m}{m_{\text{ox}} - m_{\text{red}}} \times 100\% \quad (1)$$

where m is the actual mass of sample, m_{ox} is the mass of the sample when it was fully oxidized; m_{red} is the mass of the sample in the fully reduced form.

2.2 Computational model and methods

All density functional theory calculations were performed by the CASTEP³⁵ with the generalized gradient approximation (GGA)³⁶ for describing electron–electron interactions, since GGA can predict the ground state of bulk iron more accurately than local density approximation (LDA) or local spin density approximation (LSDA).³⁷ Hubbard parameter (U_{eff}) was set to be 4.5 eV in our calculation, which provides the best match to the experimental

Fig.2 3-layer model and site terminology of the stoichiometric (a) $\text{Fe}_2\text{O}_3[001]$ 2×2 super-cell surface and (b) $\text{Fe}_2\text{O}_3[104]$ 1×2 super-cell surface

band gaps of hematite.³⁸ The magnetic configuration (+−+−) was set for Fe atoms in the rhombohedral unit cell of Fe_2O_3 , which makes the optimized cell at the lowest total energy,^{39–42} + and − designated up- and down-spin directions with respect to the z -axis. The interaction between the valence electrons and the ionic core was described by the Perdew, Burke, and Ernzerhof (PBE) gradient-corrected functional and the effective core potential (ECP).⁴³ Valence electron wave functions were expanded by double numeric with polarization (DNP). The kinetic energy cut-off (E_{cut}) was 350 eV; the Monkhorst-Pack k -mesh was $4\times 4\times 1$. Calculation used an energy convergence tolerance of 1×10^{-4} eV and a gradient convergence of 5×10^{-1} eV $\cdot\text{nm}^{-1}$. The formulation of the linear synchronous transit (LST) and quadratic synchronous transit (QST) methods were used to search the transition states for each reaction.⁴⁴

$\text{Fe}_2\text{O}_3[104]$ 2×1 super-cell surface and $\text{Fe}_2\text{O}_3[001]$ 2×2 super-cell surface slabs were cleaved from the optimized α - Fe_2O_3 bulk structure, as shown in Fig.2. The stoichiometric [001] surface exhibits two nonequivalent Fe sites ($\text{Fe}_{4\text{-folded}}-1$ and $\text{Fe}_{4\text{-folded}}-2$) that bond to three O atoms on the top layer and one O atom on the second layer. The stoichiometric [104] surface exhibits four different Fe sites, including two nonequivalent $\text{Fe}_{5\text{-folded}}-1$ and $\text{Fe}_{5\text{-folded}}-2$ that bond to four O atoms on the top layer and one O atom on

the second layer, respectively, $\text{Fe}_{4\text{-folded}}-1$ that bonds to three O atoms on the top layer and one O atom on the second layer, and $\text{Fe}_{4\text{-folded}}-2$ that bonds to four O atoms on the top layer. All the Fe atoms on [001] surface or [104] surface are unsaturated, since the coordination number of bulk Fe is six. Geometry optimization was performed using DFT calculations and the optimized structure was obtained after fully relaxation by minimizing total energy. Then the electronic properties, reaction behavior, and oxygen transfer were detected.

3 Results and discussion

3.1 Electronic property

C atom of CO prefers to binding to the metal site of oxide mainly due to σ donation from $3p_z$ of CO and $3d_z$ of metal oxide surface.⁴⁵ Therefore, we compared the partial density of states (PDOS) for these Fe atoms of $\text{Fe}_2\text{O}_3[104]$ and $\text{Fe}_2\text{O}_3[001]$, as shown in Fig.3. For $\text{Fe}_2\text{O}_3[104]$, the DOS curves show that the $3d$ electrons of Fe atoms on the top layer delocalizes below and near the Fermi level ($E_f=0.0$ eV). The highest occupation molecular orbital (HOMO) of $\text{Fe}_{5\text{-folded}}-1$ is at higher energy level than those of $\text{Fe}_{5\text{-folded}}-2$, $\text{Fe}_{4\text{-folded}}-1$, and $\text{Fe}_{4\text{-folded}}-2$, while the lowest unoccupied molecular orbital (LUMO) of $\text{Fe}_{5\text{-folded}}-1$ appears at lower energy level than those of $\text{Fe}_{5\text{-folded}}-2$, $\text{Fe}_{4\text{-folded}}-1$, and $\text{Fe}_{4\text{-folded}}-2$ above the

Fig.3 $3d_{\text{Fe}}$ -DOS of (a) $\text{Fe}_2\text{O}_3[104]$ and (b) $\text{Fe}_2\text{O}_3[001]$

Fermi level (0.0 eV). Therefore, the energy gap (E_{gap}) between HOMO and LUMO for Fe_{5-folded}-1 is the smallest (~1.0 eV), while E_{gap} for Fe_{5-folded}-2 is ~1.5 eV, and E_{gap} for Fe_{4-folded}-1 and Fe_{4-folded}-2 is about 2.0 eV.

The calculated E_{gap} of Fe_{4-folded}-1 and Fe_{4-folded}-2 of Fe₂O₃[001] are about 2.0 eV, close to the results of 2.0–2.1 eV,^{46,47} which is larger than that of Fe_{5-folded}-1 on Fe₂O₃[104]. The small E_{gap} for the Fe_{5-folded}-1 atom of Fe₂O₃[104] will benefit the acceptance of electron. We adopt LUMO energies of Fe₂O₃[104] and Fe₂O₃[001] to characterize their Lewis acidity and the HOMO energy of CO to characterize their Lewis basicity, respectively. The energy gap between the two orbitals can be used to predict how CO interacts with Fe₂O₃, which can be calculated using the equation below:

$$E_{\text{LUMO-HOMO}} = E_{\text{LUMO}}(\text{Fe}_2\text{O}_3) - E_{\text{HOMO}}(\text{CO}) \quad (2)$$

where $E_{\text{LUMO}}(\text{Fe}_2\text{O}_3)$ and $E_{\text{HOMO}}(\text{CO})$ are the LUMO energy of Fe₂O₃ and the HOMO energy of CO, respectively. The $E_{\text{LUMO-HOMO}}$ of the CO-Fe₂O₃[104] system is -3.82 eV, while the $E_{\text{LUMO-HOMO}}$ of the CO-Fe₂O₃[001] system is -4.91 eV. The $E_{\text{LUMO-HOMO}}$ implies that Fe₂O₃[104] will be more active than Fe₂O₃[001] for initiating CLC reaction of CO.

3.2 Reaction activity of surface

CO was approached to the active site Fe_{5-folded}-1 of Fe₂O₃[104] and Fe_{4-folded}-1 of Fe₂O₃[001] to do optimization. Results show that CO binds to Fe_{5-folded}-1 and Fe_{4-folded}-1, respectively. For the stable configuration of CO-Fe₂O₃[104], the tilt angle is 171°41', the bond length of the adsorbed CO is 0.115 nm, the distance between CO and Fe_{5-folded}-1 is 0.180 nm. For the stable configuration of CO-Fe₂O₃[001], the tilt angle is 171°41', the bond length of the adsorbed CO is 0.116 nm, the distance between CO and Fe_{4-folded}-1 is 0.186 nm. Hybrid occurred between C and Fe for both the CO-Fe₂O₃[104] interaction system and the CO-Fe₂O₃[001] interaction system. The hybrid weakened the CO bond, resulting in a red shift of the C—O bond of the adsorbed CO to lower wavenumbers with respect to that of the gas-phase CO.

The binding energy for CO on Fe₂O₃[104] and Fe₂O₃[001], $E_{\text{bind-CO}}$, was calculated respectively using the following expression as mentioned in previous works:^{48,49}

$$E_{\text{bind-CO}} = E(\text{CO-OC}) - E(\text{OC}) - E(\text{CO}) \quad (3)$$

where $E(\text{CO-OC})$ and $E(\text{OC})$ are the total energies of the Fe₂O₃[104] or Fe₂O₃[001] with and without the presence of CO molecule, respectively, and $E(\text{CO})$ is the total energy of an isolated CO molecule. The interaction between CO and Fe₂O₃[104], in terms of binding energies, is -0.221 eV, while $E_{\text{bind-CO}}$ for the interaction between CO and Fe₂O₃[001] is -0.786 eV. Both the absorption of CO on Fe₂O₃[104] and the absorption of CO on Fe₂O₃[001] are exothermic processes. The less heat release from the absorption process of CO on Fe₂O₃[104] will lead to better adsorption of CO on the surface at high temperature during CLC, while compared to the CO-Fe₂O₃[001] case.

Then we discussed the oxidation of CO into CO₂ by the surface lattice oxygen (①, ②, ③, and ④) bonded to Fe_{5-folded}-1 on Fe₂O₃[104], and by the surface lattice oxygen atom (①, ②, and ③) bonded to Fe_{4-folded}-1 on Fe₂O₃[001], respectively. The reaction

initiates from the stable adsorption configurations of CO on Fe_{5-folded}-1 of Fe₂O₃[104] and CO on Fe_{4-folded}-1 of Fe₂O₃[001]. Fig. 4 shows the calculated potential energy profiles for the most accessible channels of CO oxidation into CO₂ on Fe_{5-folded}-1 of Fe₂O₃[104] and on Fe_{4-folded}-1 of Fe₂O₃[001]. A qualitatively similar two-step reaction mechanism for the reaction between CO and Fe₂O₃[104] {and Fe₂O₃[001]} was obtained. The first step relates to the conversion from the initial state (IS) to a carbonate species at the intermediate state (MS). The second reaction step initiated from the MS and changed into the final state (FS) with the release of CO₂ from the surface. The total activation energy (E_a) and reaction enthalpy (E_r) for CO+Fe₂O₃[104]→CO₂+Fe₂O₃[104]_{red} (reduced Fe₂O₃[104]) are 0.681 and -0.776 eV, respectively, while E_a and E_r for CO+Fe₂O₃[001]→CO₂+Fe₂O₃[001]_{red} (reduced Fe₂O₃[001]) are 1.203 and -0.392 eV, respectively. The latter E_a is almost twice as high as the former, which suggests that the oxidation of CO by Fe₂O₃[104] is more accessible than by Fe₂O₃[001]. The reaction CO+Fe₂O₃[104]→CO₂+Fe₂O₃[104]_{red} releases more energy than CO+Fe₂O₃[001]→CO₂+Fe₂O₃[001]_{red}. Results show that Fe₂O₃[104] surface is more chemically active than Fe₂O₃[001] surface for oxidizing CO during CLC.

3.3 Regeneration behavior

During CLC processes, after the CO was oxidized by Fe₂O₃[104] and Fe₂O₃[001], Fe₂O₃[104]_{red} and Fe₂O₃[001]_{red} were reduced; then the reduced Fe₂O₃[104]_{red} and Fe₂O₃[001]_{red} would be transferred to the air reactor, where Fe₂O₃[104]_{red} and Fe₂O₃[001]_{red} would be oxidized by O₂ into Fe₂O₃[104] and Fe₂O₃[001]. Therefore, the regeneration reaction was initiated from the adsorption of O₂ on Fe₂O₃[104]_{red} and Fe₂O₃[001]_{red}, which were then oxidized by the adsorbed O₂. Actually, only one O atom is needed for oxidizing Fe₂O₃[104]_{red} or Fe₂O₃[001]_{red} into Fe₂O₃[104] or Fe₂O₃[001]. We pushed one O of O₂ to the defected site of Fe₂O₃[104]_{red} or [Fe₂O₃[001]_{red} to do geometrical optimization to define the final reaction state. At the stable final configuration of the O₂-Fe₂O₃[104]_{red} system, one O atom from O₂ fixes into the defected site of Fe₂O₃[104]_{red} very well in an one-step oxidation reaction mecha-

Fig. 4 Calculated potential energy profiles for CO oxidation on Fe_{5-folded}-1 of Fe₂O₃[104] and on Fe_{4-folded}-1 of Fe₂O₃[001]

The IS, TS, MS, and FS denote the initial state, transition state, intermediate species, and final state, respectively. The data are the energies for the crucial points referenced to the initial state set at 0.000 eV.

Fig.5 (a) Potential energy profiles for the oxidation of $\text{Fe}_2\text{O}_3[104]_{\text{red}}$ and $\text{Fe}_2\text{O}_3[001]_{\text{red}}$ by O_2 , and (b) comparison of DOS for the fresh and the regenerated OC

nism, as shown in the upper reaction path in Fig.5a. However, the oxidation reaction of $\text{Fe}_2\text{O}_3[001]_{\text{red}}$ crossed the barrier of 0.374 eV at the MS which subsequently overcome a barrier of 0.397 eV into the final state (FS), as shown in the lower reaction path in Fig.5a. At the final state of $\text{O}_2\text{-Fe}_2\text{O}_3[001]_{\text{red}}$, one O atom of O_2 embedded into the surface of $\text{Fe}_2\text{O}_3[001]_{\text{red}}$ and the other excess O atom is adsorbed on the top layer. Both the oxidation of $\text{Fe}_2\text{O}_3[104]_{\text{red}}$ and the oxidation of $\text{Fe}_2\text{O}_3[001]_{\text{red}}$ by O_2 are energetically accessible.

However, surface reconstructions help in understanding surface chemistry of oxygen carriers, especially in the case where the surfaces can be structurally regenerated. Table 1 lists the average relaxation of Fe and O atoms on the regenerated surfaces in the direction vertically to the slab models. The average relaxations of Fe and O atoms on $\text{Fe}_2\text{O}_3[104]_{\text{red}}$ are smaller than those on $\text{Fe}_2\text{O}_3[001]_{\text{red}}$. But, in general, both $\text{Fe}_2\text{O}_3[104]_{\text{red}}$ and $\text{Fe}_2\text{O}_3[001]_{\text{red}}$ underwent slight surface atom relaxation after regeneration. The change of electronic state will therefore occur with the atom re-

Table 1 Average relaxation of Fe and O atoms on the regenerated surfaces in the direction vertically to the slab models

	Fe atom	O atom
$\text{Fe}_2\text{O}_3[104]_{\text{red}}$	0.2%	1.2%
$\text{Fe}_2\text{O}_3[001]_{\text{red}}$	2.1%	2.9%

laxation, as the DOS shown in Fig.5b. Except for little change happened to the DOS before and after regeneration, the DOS of the regenerated surface, especially the regenerated $\text{Fe}_2\text{O}_3[104]$, matches that of the fresh surface very well. Results of the oxidation reactions energetically and structurally verified that the possibility of regeneration of the reduced $\text{Fe}_2\text{O}_3[104]$.

3.4 Oxygen transfer

Oxygen carrying capacity and transfer in the OC system plays an important role in CLC. We examined the oxygen transfer on the surfaces of $\text{Fe}_2\text{O}_3[104]$ and $\text{Fe}_2\text{O}_3[001]$ by gradually removing the top layer O atoms to form non-stoichiometric surfaces during the further reductions of $\text{Fe}_2\text{O}_3[104]$ and $\text{Fe}_2\text{O}_3[001]$, results of which are listed in Fig.6. In Fig.6a, after the top layer O atoms of $\text{Fe}_{22}\text{O}_{33}$, $\text{Fe}_{22}\text{O}_{29}$, $\text{Fe}_{22}\text{O}_{22}$, and $\text{Fe}_{22}\text{O}_{15}$ are removed, oxygen atoms of the inner layers transfer to the top layer. Then, Fe atom dominates the top layer after $\text{Fe}_{22}\text{O}_{15}$. In Fig.6b, the optimized $\text{Fe}_{32}\text{O}_{48}$, $\text{Fe}_{32}\text{O}_{44}$, and $\text{Fe}_{32}\text{O}_{36}$ show relatively high O atom coverage; then the surface of the optimized $\text{Fe}_{32}\text{O}_{26}$ is almost completely covered by Fe atoms except for only one O atom. Fe atoms hinder further oxidation of CO into CO_2 . Instead, hybrid between CO and Fe would promote Fe-catalyzed carbon deposit reaction ($2\text{CO} \xrightarrow{\text{Fe}} \text{C} + \text{CO}_2$),⁴⁸ rather than CO oxidation reaction. In comparison with the low oxygen transfer on $\text{Fe}_2\text{O}_3[001]$, the higher oxygen transfer capacity of $\text{Fe}_2\text{O}_3[104]$ would result in more complete reduction of $\text{Fe}_2\text{O}_3[104]$.

3.5 Deep reduction

To further investigate the deep reduction of $\text{Fe}_2\text{O}_3[104]$ and $\text{Fe}_2\text{O}_3[001]$, we initiated the reactions from the stable physisorption of CO on the top layers of $\text{Fe}_{22}\text{O}_{33}$, $\text{Fe}_{22}\text{O}_{29}$, $\text{Fe}_{22}\text{O}_{20}$, $\text{Fe}_{22}\text{O}_{15}$, $\text{Fe}_{22}\text{O}_{10}$, $\text{Fe}_{32}\text{O}_{48}$, $\text{Fe}_{32}\text{O}_{44}$, $\text{Fe}_{32}\text{O}_{36}$, and $\text{Fe}_{32}\text{O}_{26}$, respectively. The energy profiles for the most possible redox reaction (with the lowest E_a) on these surfaces are illustrated in Fig.7, respectively, where y-ordinate is the energy in eV and the x-ordinate is the gradual reduction reaction coordinate for $\text{Fe}_2\text{O}_3[104]$ and $\text{Fe}_2\text{O}_3[001]$ by CO. Reduction of $\text{Fe}_{22}\text{O}_{33}$, $\text{Fe}_{22}\text{O}_{29}$, $\text{Fe}_{22}\text{O}_{20}$, $\text{Fe}_{22}\text{O}_{15}$, and $\text{Fe}_{22}\text{O}_{10}$ by CO followed a two-step reaction mechanism, where the first step led to the generation of carbonate species on the surfaces while the second step was for the desorption of the carbonate species that changed into a free CO_2 , which is similar to our previous discovery on $\text{Fe}_2\text{O}_3[1\bar{1}2]$ ⁴⁹ and Fe_2O_3 cluster³⁴. E_a for every reaction step on $\text{Fe}_{22}\text{O}_{33}$, $\text{Fe}_{22}\text{O}_{29}$, $\text{Fe}_{22}\text{O}_{20}$, $\text{Fe}_{22}\text{O}_{15}$, and $\text{Fe}_{22}\text{O}_{10}$ is below 2 eV. Results show that E_a increases slightly with the decrease of the valence states (Q_v) of Fe atoms of $\text{Fe}_{22}\text{O}_{33}$, $\text{Fe}_{22}\text{O}_{29}$, $\text{Fe}_{22}\text{O}_{20}$, $\text{Fe}_{22}\text{O}_{15}$, and $\text{Fe}_{22}\text{O}_{10}$.

The reduction of $\text{Fe}_{32}\text{O}_{48}$, $\text{Fe}_{32}\text{O}_{44}$, and $\text{Fe}_{32}\text{O}_{36}$ by CO followed a two-step reaction mechanism, while the reduction of $\text{Fe}_{32}\text{O}_{26}$ followed a one-step reaction mechanism. E_a for the reduction of $\text{Fe}_{32}\text{O}_{48}$ and $\text{Fe}_{32}\text{O}_{40}$ is below 2 eV, respectively, while E_a for the reduction of $\text{Fe}_{32}\text{O}_{44}$ and $\text{Fe}_{32}\text{O}_{36}$ is a bit higher than 2 eV. However, the reaction between CO and $\text{Fe}_{32}\text{O}_{26}$ crossed rather high barrier ($E_a > 14$ eV). The high E_a together with the limited oxygen carrying capacity decides the lower reaction activity and reduction degree of $\text{Fe}_2\text{O}_3[001]$, in comparison with $\text{Fe}_2\text{O}_3[104]$. If completely

Fig.6 Oxygen transfer on (a) Fe_2O_3 [104] and (b) Fe_2O_3 [001]

geom. opt.: geometry optimization

covered by the [001] facet, the reduction of the single crystal iron-based oxygen carrier should be very limited. However, it is known that different facets (including low and high index facets) expose on the iron-based oxygen carrier used for the chemical looping combustion in previous research works,^{14,34} where the high index

facet could benefit the deep reduction of Fe_2O_3 into Fe. Obviously, surface morphology greatly decides the reaction performance of iron-based OC during CLC.

3.6 Experimental control

Fig.8a shows the CLC reactions between CO and Fe_2O_3 [104]/

Fig.7 Energy profile for oxidation of CO using (a) Fe_2O_3 [104] and (b) Fe_2O_3 [001]

Fig.8 (a) Conversion (χ) as a function of reaction time for the reaction between CO and $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$, and the referenced reaction between CO and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, at 900 °C; (b) re-use of $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ at 900 °C

Fig.9 (a) SEM image (with the inset HRTEM image) and (b) XRD pattern of $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$, (c) SEM image (with the inset HRTEM image) and (d) XRD pattern of the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$

Al_2O_3 and the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, which were conducted in a simultaneous thermal analyzer at 900 °C. It could be observed that $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ reached a conversion (χ) of 100% without carbon deposit after 4 min, implying that $\text{Fe}_2\text{O}_3[104]$ could be completely reduced by CO into metallic iron ($\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$). Compared to $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$, a two-stage reaction process was identified for the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. The first stage shows a rapid rise of reaction rates at the first minute, reaching the χ of 33.3%. The second reduction stage is at a relatively consistent reaction rate, showing an indicator of its poor reactivity, where the maximum χ is 72.0% and the formation of carbon should be in the ascendancy.⁵⁰ Results correspond to the theoretical analysis of oxygen transfer and deep reduction above.

Five reduction-oxidation cycles were further performed to detect the effect of re-use of $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ on CLC, results of which are depicted in Fig.8b. The weight loss of 2% was found after its first use, whereas, the activity differences were inconspicuous among the second to the fifth re-use of $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$, which implies the stability of $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ for further cycles.

Fig.9 depicts the XRD patterns, SEM images, and HRTEM images of the fresh $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ and the regenerated $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ after five reduction-oxidation cycles, in comparison with those of the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. The SEM image shows that porosity of this rough structure mainly oriented along [104] on the surface of the prepared $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ according to the inset HRTEM images in Fig.9a. Fig.9b shows that all the iden-

tified diffraction peaks of Fe_2O_3 can be assigned to $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS card No. 33-0664), no other phase is observed, indicating a high phase purity and the well dispersion of Fe_2O_3 on the support Al_2O_3 . The sharp diffraction peaks suggest good crystallinity of the prepared $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ and confirm the regenerated renewable of the used $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$. Fig.9c shows that the surface of the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ is also porous but smoother than $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$, and the surface of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ is oriented along different crystallographic directions. XRD pattern in Fig.9d verifies the high crystallization and regeneration of the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. Further, the regenerated $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ and the referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ keep a specific surface area of around $40 \text{ m}^2 \cdot \text{g}^{-1}$ as those for the fresh $\text{Fe}_2\text{O}_3[104]/\text{Al}_2\text{O}_3$ and the fresh referenced $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$.

4 Conclusions

We have theoretically and experimentally demonstrated that morphological control of Fe_2O_3 is very rewarding: $\text{Fe}_2\text{O}_3[104]$ exhibits surprisingly high activity for CO CLC and can be regenerated for further reuse. The fundamental understanding shows that morphological control of metal oxides allows preferential exposure of active sites, improves reaction activity and oxygen transfer, decreases carbon deposit during chemical looping combustion.

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