理想与还原 $\text{Fe}_2\text{O}_3[001]$ 表面上汞吸附协同催化 CO 分解作用李继红¹ 林常枫¹ 覃 昊^{1,*} 肖显斌¹ 魏 利^{2,*}⁽¹⁾华北电力大学可再生能源学院, 生物质发电成套设备国家工程实验室, 北京 102206;⁽²⁾哈尔滨工业大学, 城市水资源与水环境国家重点实验室, 哈尔滨 150090)

摘要: 煤化学链燃烧必然释放汞, 汞与载氧体表面相互作用, 影响界面的氧化还原反应。本文采用密度泛函理论计算, 研究汞(Hg^0)在理想表面($\text{Fe}_2\text{O}_3[001]$)和一系列被还原表面($\text{Fe}_2\text{O}_{2.75}$ 、 $\text{Fe}_2\text{O}_{2.5}$ 、 $\text{Fe}_2\text{O}_{2.25}$ 、 $\text{Fe}_2\text{O}_{1.625}$ 、 $\text{Fe}_2\text{O}_{0.875}$ 、 $\text{Fe}_2\text{O}_{0.375}$ 和 Fe)的吸附, 以及 Hg^0 对 $\text{Fe}_2\text{O}_{1.625}$ 、 $\text{Fe}_2\text{O}_{0.875}$ 、 $\text{Fe}_2\text{O}_{0.375}$ 和 Fe 等表面催化 CO 分解反应的协同作用机理。 Hg^0 物理吸附在理想 $\text{Fe}_2\text{O}_3[001]$ 表面。随着 $\text{Fe}_2\text{O}_3[001]$ 表面不断被还原, Hg^0 发生化学吸附。 Hg^0 吸附降低了 CO 与 Fe_2O_3 、 $\text{Fe}_2\text{O}_{2.75}$ 、 $\text{Fe}_2\text{O}_{2.5}$ 和 $\text{Fe}_2\text{O}_{2.25}$ 等表面之间的相互作用, 抑制 O 传递氧化 CO 为 CO_2 的反应; 载氧体进一步还原过程中, Hg^0 吸附促进了 CO 与 $\text{Fe}_2\text{O}_{1.625}$ 、 $\text{Fe}_2\text{O}_{0.875}$ 、 $\text{Fe}_2\text{O}_{0.375}$ 及 Fe 等表面之间的相互作用, 进而促进了表面对 CO 的催化分解反应, 加速了载氧体表面的积碳, 降低了化学链燃烧效率。因此, 合理控制载氧体的还原程度既可以减弱 Hg^0 的吸附, 也可以抑制积碳的形成, 这对化学链燃烧的操作优化至关重要。

关键词: 化学链燃烧; 载氧体; 汞; CO_2 捕集; 密度泛函理论

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Synergetic Effect of Mercury Adsorption on the Catalytic Decomposition of CO over Perfect and Reduced $\text{Fe}_2\text{O}_3[001]$ SurfaceLI Ji-Hong¹ LIN Chang-Feng¹ QIN Wu^{1,*} XIAO Xian-Bin¹ WEI Li^{2,*}⁽¹⁾National Engineering Laboratory for Biomass Power Generation Equipment, School of Renewable Energy Engineering, North China Electric Power University, Beijing 102206, P. R. China; ⁽²⁾State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, P. R. China)

Abstract: Mercury emission from coal during chemical-looping combustion (CLC) is an inevitable process, which can lead to adverse interactions with the surface of the oxygen carrier, thereby affecting the interfacial redox reactions. Density functional theory calculations were performed to investigate the mechanism of elemental mercury (Hg^0) adsorption and the synergetic effect of Hg^0 on the catalytic decomposition of CO over a perfect surface ($\text{Fe}_2\text{O}_3[001]$), as well as a series of reduced surfaces ($\text{Fe}_2\text{O}_{2.75}$, $\text{Fe}_2\text{O}_{2.5}$, $\text{Fe}_2\text{O}_{2.25}$, $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$ and Fe) during a deep CLC process. In this study, Hg^0 was physically adsorbed on to a perfect Fe_2O_3 surface, and then chemically adsorbed on to a series of reduced surfaces. The adsorption of Hg^0 inhibited the formation of meaningful interactions between CO and Fe_2O_3 [$\text{Fe}_2\text{O}_{2.75}$, $\text{Fe}_2\text{O}_{2.5}$ and $\text{Fe}_2\text{O}_{2.25}$] and hindered the efficient transport of oxygen to oxidize CO into CO_2 . In contrast, this process promoted the interactions between CO and $\text{Fe}_2\text{O}_{1.625}$ [$\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe], favoring the catalytic decomposition of CO on these surfaces, which accelerated the carbon deposit reducing CLC efficiency. Rationally controlling the reduction degree of the oxygen carrier could therefore be used to either decrease the adsorption of Hg^0 or depress the deposition of carbon, which are both crucial for the optimization of CLC processes.

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Key Words: Chemical looping combustion; Oxygen carrier; Mercury; CO₂ capture; Density functional theory

1 Introduction

In comparison with conventional combustion techniques and carbon dioxide removal techniques, chemical looping combustion (CLC) has received great attention because of its distinctive merit of efficient use of energy with *in-situ* CO₂ capture¹⁻³. CLC produces heat and energy using oxygen carriers (OCs), usually the oxides of Fe, Ni, Co, Cu, Mn, and Cd, to supply oxygen instead of air for the combustion of fuel. CLC of fuel results in generation of CO₂ and H₂O that is not diluted with N₂ or flue gas, and reduces NO_x emissions⁴⁻¹⁰. These properties render CLC highly desirable as possible candidate for low-cost coal combustion and carbon capture¹¹⁻¹³. Fe₂O₃ is the most promising OC used in CLC process due to its low cost and environmental compatibility^{14,15}. Fig.1 depicts the schematic process of coal CLC using Fe₂O₃ as OC, where Fe₂O₃ is transferred from the air reactor (AR) to the fuel reactor (FR) to realize the full conversion of coal into CO₂ and steam. After condensation, the pure CO₂ can be obtained without extra energy consumption. The reduced Fe₂O_{3-x} is transported back to the AR and regenerated therein for initiation of the next coal combustion cycle.

Nevertheless, coal CLC researches are at their very beginning, many problems and challenges lie ahead before their commercial adoption. For example, it is known that mercury exists in coal at the range of 0.02 to 1.0 mg·kg⁻¹¹⁶, which usually assumes three forms in flue gas: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺), and particulate mercury (Hg^p). Mercury is released into fuel gas as Hg⁰ during coal combustion¹⁷, emitted into the atmosphere, and then bioaccumulated through the food chain, which affects human health and generates long-lasting effects¹⁸. Mendiara detected the mercury released from CLC of coal and then quantitatively tested the emissions from the fuel reactor and air reactor¹⁹. However, whether there are certain interactions happening between mercury and OC during CLC processes, and if they have certain interactions, and how these interactions affect the related reactions of CLC process, remain unknown. Usually, OC could be generally reduced into lower oxidation state during deep CLC processes, and interfacial interactions would happen to these reduced OC surfaces. Therefore, it is necessary to detect the adsorption of mercury on the perfect and reduced OC surface at different reduction states, and the effect of mercury adsorption on the further reactions between

fuel molecule and the reduced OC surface, which are fundamental understandings of the coal CLC system.

Considering that mercury firstly releases into fuel gas as Hg⁰ during coal combustion¹⁷, and Fe₂O₃[001] is one of the dominant growth faces of the natural α -Fe₂O₃¹⁸, we herein elucidated the detailed Hg⁰ adsorption on the gradually reduced Fe₂O₃[001] surface and its effect on carbon deposition during CLC by using density functional theory (DFT) calculations. Results will provide insights into the mechanism of mercury adsorption and its effect on catalytic decomposition of CO during deep reduction of Fe₂O₃. The correlation between adsorption, decomposition, and reduction degree provides fundamental understanding to such complex CLC combustion processes. This study can serve as a reference for CLC optimization.

2 Computational models and method

2.1 Theoretical models

The pure Fe₂O₃[001]-*p*(2 × 2) surface with 32 Fe atoms and 48 O atoms was modeled. To eliminate the spurious interaction between periodic images in the *z* direction, the vacuum space is set no less than 1.5 nm, and dipole correction is used as well. A series of reduced Fe₂O₃[001]-*p*(2 × 2) surfaces was obtained by gradually removing the O atoms on the outer surface layer to do annealing under constant pressure and temperature (NPT) until their equilibrium states were reached, where the initial temperature was 300 K and the mid-cycle temperature was 1073 K (the temperature for real CLC). Further geometric optimizations were performed using DFT calculations. After geometric optimization, the stable configurations of Fe₂O₃, Fe₂O_{2.75}, Fe₂O_{2.5}, Fe₂O_{2.25}, Fe₂O_{1.625}, Fe₂O_{0.875}, Fe₂O_{0.375}, and Fe are shown in Fig.2. Then the Hg⁰ adsorption, CO adsorption, and catalytic decomposition of CO on these surfaces were investigated.

2.2 Parameters setting

We used the CASTEP program package for all calculations performed with a plane-wave pseudo potential method based on dispersion-corrected DFT¹⁹, which was combined with the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE)^{20,21}. Ultrasoft vanderbilt pseudopotentials²² were used to describe core orbitals. To correct the strong correlation between 3*d*-electrons of Fe atom, a Hubbard *U* was adopted to provide an on-site Coulomb repulsion to the DFT Hamiltonian. Previous investigations suggested that DFT + *U* method with *U* = 5 eV could accurately reproduce the experimental value of bandgap (2.2 eV) and band structure of hematite²³⁻²⁷. We have therefore adopted *U* = 5 eV to conduct our calculations in this work. Previous studies have confirmed the cut-off energy of 350 eV and *k* meshes of 4 × 4 × 1 in α -Fe₂O₃ surface reaction field can obtain satisfied results²⁸. Therefore, a cutoff of 350 eV was employed with smearing width of 0.1 eV, while the Brillouin zone integration of the surfaces was calculated using

Fig.1 Schematic diagram for CLC of coal using Fe₂O₃ as OC

Fig.2 Top and side views of the perfect four-layer $\text{Fe}_2\text{O}_3[001]-p(2 \times 2)$ surface model (a) and the reduced surfaces: (b) $\text{Fe}_2\text{O}_{2.636}$, (c) Fe_2O_2 , (d) $\text{Fe}_2\text{O}_{1.364}$, (e) $\text{Fe}_2\text{O}_{0.909}$, (f) $\text{Fe}_2\text{O}_{0.182}$, and (g) Fe
color online

$4 \times 4 \times 1$ Monkhorst-Pack k -point meshes. 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^{29–32}, + and – designated up-spin and down-spin directions with respect to the z -axis. The convergence criteria for the structure optimization and energy calculation were set to (a) an energy tolerance of $2.0 \times 10^{-5} \text{ eV} \cdot \text{atom}^{-1}$, (b) a SCF tolerance of $2.0 \times 10^{-6} \text{ eV} \cdot \text{atom}^{-1}$, (c) a maximum force tolerance of $0.5 \text{ eV} \cdot \text{atom}^{-1}$, and (d) a maximum displacement tolerance of 0.0002 nm . A linear synchronous transit or quadratic synchronous transit approach (LST/QST)³³ is used to get closer to the quadratic region of the transition state and then quasi-newton or eigenvector following methods are used to complete the optimization to ensure one and only one imaginary vibrational frequency.

The adsorption energy for the studied systems was calculated by using the following equation:

$$E_{\text{ads}} = E_{\text{compound}} - E_{\text{slab}} - E_{\text{x}} \quad (1)$$

where E_{compound} , E_{slab} , and E_{x} are the total energy for the substrate with adsorbate, the substrate, and the adsorbate, respectively. More negative adsorption energy represents stronger interaction.

3 Results and discussion

3.1 Hg^0 adsorption on perfect and reduced $\text{Fe}_2\text{O}_3[001]$ surfaces

Since $\text{Fe}_2\text{O}_3[001]$ will be gradually reduced in the fuel reactor during CLC, the adsorptions of Hg^0 on the perfect and the reduced $\text{Fe}_2\text{O}_3[001]$ surfaces were investigated. Previous work showed that Hg atom is more inclined to bind to Fe atom than O atom on oxide surface³⁴. We approached Hg^0 to different Fe atomic sites of these surfaces. Fig.3 illustrated the most stable configurations for the Hg^0 - Fe_2O_3 , Hg^0 - $\text{Fe}_2\text{O}_{2.75}$, Hg^0 - $\text{Fe}_2\text{O}_{2.5}$, Hg^0 - $\text{Fe}_2\text{O}_{2.25}$, Hg^0 - $\text{Fe}_2\text{O}_{1.625}$, Hg^0 - $\text{Fe}_2\text{O}_{0.875}$, Hg^0 - $\text{Fe}_2\text{O}_{0.375}$, and Hg^0 -Fe adsorption systems, respectively.

The corresponding calculated adsorption energies are presented in Fig.4. For Hg^0 - Fe_2O_3 adsorption system, Hg^0 is physically adsorbed on Fe-top site of $\text{Fe}_2\text{O}_3[001]$ surface with the minimum distance (L_{min}) of 0.3012 nm and E_{ads} of -0.36 eV close to the reported value of -0.39 eV ³⁴. Then, the interaction between Hg^0 and reduced surface becomes stronger. For example, in the Hg^0 - $\text{Fe}_2\text{O}_{2.75}$ system, weak chemisorption happens between Hg^0 and Fe atom of $\text{Fe}_2\text{O}_{2.75}$, with the Hg^0 -Fe bond length of 0.2846 nm and E_{ads} of -0.65 eV , while the Hg^0 - $\text{Fe}_2\text{O}_{2.5}$ with the bond length of 0.283 nm and E_{ads} of -0.76 eV . Further reduction of $\text{Fe}_2\text{O}_{2.5}$ into $\text{Fe}_2\text{O}_{2.25}$, $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe promotes the adsorption of Hg^0 on these surfaces, resulting in forming multi-coordinated Hg-Fe bonds on these surfaces. In the Hg^0 - $\text{Fe}_2\text{O}_{2.25}$ configuration, the E_{ads} is -1.04 eV and two Hg-Fe bonds (0.275 and 0.286 nm) formed on the surface, giving the average value $\bar{L}_{2f}$ of 0.280 nm .

Fig.3 Stable configurations for Hg^0 on (a) $\text{Fe}_2\text{O}_3[001]$, (b) $\text{Fe}_2\text{O}_{2.75}$, (c) $\text{Fe}_2\text{O}_{2.5}$, (d) $\text{Fe}_2\text{O}_{2.25}$, (e) $\text{Fe}_2\text{O}_{1.625}$, (f) $\text{Fe}_2\text{O}_{0.875}$, (g) $\text{Fe}_2\text{O}_{0.375}$, and (h) Fe
color online

Fig.4 E_{ads} for Hg^0 adsorption on the perfect and the reduced $\text{Fe}_2\text{O}_3[001]$ surfaces

In the $\text{Hg}^0\text{-Fe}_2\text{O}_{1.625}$ configuration, the E_{ads} is -1.44 eV and five $\text{Hg}\text{—Fe}$ bonds (0.269, 0.304, 0.315, 0.274, and 0.287 nm) formed on the surface, giving the average value $\bar{L}_{\text{sf}}$ of 0.290 nm. The $\text{Hg}^0\text{-Fe}_2\text{O}_{0.875}$, $\text{Hg}^0\text{-Fe}_2\text{O}_{0.375}$, and $\text{Hg}^0\text{-Fe}$ configurations show the average bond lengths $\bar{L}_{\text{bf}}$ of 0.289 nm, $\bar{L}_{\text{bf}}$ of 0.279 nm, $\bar{L}_{\text{sf}}$ of 0.283 nm, respectively, which result in the corresponding E_{ads} of -1.72 , -2.20 , and -2.02 eV. After Fe_2O_3 was reduced into the oxidation state that lower than Fe_2O_2 (such as $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe), stable chemisorption appears, where Hg^0 binds firmly to the Fe-accumulated area on the reduced surface.

To further understand the interaction between Hg^0 and the surfaces, we analyzed the partial density of state (PDOS) of the adsorbed Hg^0 , which is plotted in Fig.5. As observed in Fig.5, 4s-DOS curve for the Hg^0 adsorbed on $\text{Fe}_2\text{O}_3[001]$ overlaps to that for the pure Hg^0 ³⁵, while 4s-DOS for $\text{Fe}_2\text{O}_{2.75}$ and $\text{Fe}_2\text{O}_{2.5}$ splits around Fermi level ($E_f = 0$ eV) suggesting obvious electronic interaction between Hg^0 and surface. Therefore, $\text{Hg}^0\text{-Fe}_2\text{O}_{2.75}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{2.5}$ can be assigned to chemisorption. With further reduction of Fe_2O_3 into $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe, 4s-DOS of Hg^0 split into bonding orbital and anti-bonding orbital, implying that stronger interaction happens between Hg^0 and surface. These results further verify that the interactions between Hg^0 and the deeply reduced surfaces ($\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe) are stronger than those between Hg^0 and the surfaces at relatively higher oxidation state (Fe_2O_3 ,

Fig.5 4s-DOS for the adsorbed Hg^0 on the perfect and the reduced $\text{Fe}_2\text{O}_3[001]$ surfaces

$\text{Fe}_2\text{O}_{2.75}$, $\text{Fe}_2\text{O}_{2.5}$, and $\text{Fe}_2\text{O}_{2.25}$). Our results first reveal the relationship between the adsorption of Hg^0 and the iron oxide surface at different reduction degrees. While iron oxide is used as oxygen carrier for coal combustion, deeper reduction of iron oxide into low oxidation state can result in higher adsorption quantity of Hg^0 .

Stable Hg^0 adsorption alters the electronic property of the surfaces, which can hence affect the adsorption and decomposition processes of CO. In our simulations, the stable CO chemisorption occurs through hybrid between C atom and Fe atom of surface, corresponding to that CO prefers to bind to transition metal site of the surface^{36,37}. Fig.6 compares the adsorption energies for the stable configurations of CO adsorption on Fe_2O_3 , $\text{Fe}_2\text{O}_{2.75}$, $\text{Fe}_2\text{O}_{2.5}$, $\text{Fe}_2\text{O}_{2.25}$, $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe with and without the adsorption of Hg^0 , respectively. It can be observed that E_{ads} shows an interesting trend for CO adsorption on $\text{Fe}_2\text{O}_3[001]$, $\text{Fe}_2\text{O}_{2.75}$, $\text{Fe}_2\text{O}_{2.5}$, $\text{Fe}_2\text{O}_{2.25}$, $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe, as the trend for Hg^0 adsorption on these surfaces shown in Fig.4.

According to Fig.6, the reduced surfaces favor the adsorption of CO while compared to the perfect surface. With reduction of Fe_2O_3 into Fe, E_{ads} (-1.58 eV) for CO adsorption on Fe is close to the reported value of -1.56 eV for CO adsorption on Fe[110]³⁸, but lower than the value (-2.54 eV) for CO adsorption on Fe[100]³⁹.

However, the adsorption of Hg^0 decreases the interaction between CO and Fe_2O_3 [$\text{Fe}_2\text{O}_{2.75}$, $\text{Fe}_2\text{O}_{2.5}$, and $\text{Fe}_2\text{O}_{2.25}$], while promotes the interaction between CO and $\text{Fe}_2\text{O}_{1.625}$ [$\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe]. The distinct effect of Hg^0 on CO adsorption can be attributed to the relativistic effect of Hg^0 . The band structure of the reduced surfaces shows that the band near and closed to the Fermi level between the *M* and *K* points in the brillouin zone is almost completely flat, indicating extremely high electron effective mass. While Hg^0 chemically bound to Fe atoms of these reduced surfaces at relatively higher oxidation state, the bands near and closed to the Fermi level become less dispersive (for example, the band structures for $\text{Fe}_2\text{O}_{2.5}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{2.5}$ in Fig.1Sa (Supporting Information)), which depress electron and hole transport through the interface, hence decreasing the interaction between CO and the surface. During the first reduction stage (from Fe_2O_3 to $\text{Fe}_2\text{O}_{1.625}$), Hg^0 acts as electron donor decreasing the oxidizability of the

Fig.6 E_{ads} for CO adsorption on the perfect and reduced Fe_2O_3 surfaces, and the perfect and reduced $\text{Hg}^0\text{-Fe}_2\text{O}_3$ surfaces

surfaces before $\text{Fe}_2\text{O}_{1.625}$. Then during the last reduction state (from $\text{Fe}_2\text{O}_{1.625}$ to Fe), Hg^0 chemically bound to Fe on the surfaces, the bands near and closed to the Fermi level become more dispersive (for example, the band structures for $\text{Fe}_2\text{O}_{0.375}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{0.375}$ in Fig. 1Sb (in Supporting Information)), promoting electron and hole transport through the interface, where Hg^0 acts as electron acceptor increasing the oxidizability of the reduced surfaces favoring the hybridization between C and Fe, hence promoting the interaction between CO and the reduced surface.

Fig. 7 describes the relationship between the reduction degree, charge population (on C atom and O atom of the adsorbed CO molecule, and the total population on the adsorbed CO molecule), and bond length (of the adsorbed CO molecule and the new formed Fe—C bond). Generally, it is accepted that strong interaction corresponds to high value of E_{ads} , lengthening of the C—O bond, and obvious charge transport cross the interface. According to Fig. 7a, little charge transfer happens on the perfect Fe_2O_3 and the $\text{Hg}^0\text{-Fe}_2\text{O}_3$ surfaces, corresponding to small E_{ads} value above, which verified the physisorption. Then charge transfer becomes more obvious with the reduction of the surface. The representative interaction district appears after $\text{Fe}_2\text{O}_{2.25}$, where the E_{ads} , charge density transfers from surface to the adsorbed CO molecule, and the lengthening of C—O bond is more obvious than the cases before $\text{Fe}_2\text{O}_{2.25}$. The strong interaction and activation of CO will favor the catalytic decomposition of CO and result in carbon deposit on surfaces of the reduced OC, corresponding to an obvious weight increase according to the thermogravimetric analysis of $\text{CO-Fe}_2\text{O}_3$ ²⁸. According to Fig. 7b, interaction between CO and the reduced Hg^0 -doped surface also lengthens the CO bond after $\text{Hg}^0\text{-Fe}_2\text{O}_{2.25}$ with obvious charge transfer across the interface and charge repopulation during this reduction period, which hence activates the CO bond for further decomposition.

3.2 Effect of mercury on catalytic CO decomposition

It is generally agreed that, with the reduction of iron oxide, CO decomposes on the reduced surface and acts as the key step for carbon deposit during CLC^{40,41}. Therefore, we considered the

Fig. 7 Charge population (Q) for the C atom, O atom, and CO molecule, and the lengths of C—Fe bond and C—O bond
(a) over the perfect and reduced Fe_2O_3 surfaces,
(b) over the perfect and reduced $\text{Hg}^0\text{-Fe}_2\text{O}_3$ surfaces

following reaction mechanism on the reduced $\text{Fe}_2\text{O}_3[001]$ surface

where $*$ denotes a free step site. Catalytic decomposition of CO may result in a wide range of products. We have neglected the further interaction between C^* , O^* , and CO that forms CO_2 or carbonate species on the reduced surface.

Since carbon deposit hardly generates on the iron oxide at high oxidation state²⁸, and stable Hg^0 adsorption happens on the reduced surfaces $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe (seen in Fig. 3), we discussed the catalytic decomposition of CO on these reduced surfaces. The reaction initiates from the most stable CO adsorption models, and the product corresponds to the decomposition of CO^* into C^* and O^* at the most stable state. Then transition state (TS) search calculations were performed to detect the energy profiles for the CO^* decomposition reaction on these reduced surfaces with and without the adsorption of Hg^0 . The barrier energy (E_a) and reaction enthalpy (E_r) for the two reaction cases related to catalytic decomposition of CO on Hg^0 -doped surfaces and the undoped surfaces are listed in Fig. 8. It is clear that the adsorption of Hg^0 decreases the E_a for catalytic decomposition of CO on $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe. For example, E_a for catalytic CO decomposition on $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, and Fe are 3.01, 2.76, 1.43, and 1.51 eV, while the E_a for $\text{Hg}^0\text{-Fe}_2\text{O}_{1.625}$, $\text{Hg}^0\text{-Fe}_2\text{O}_{0.875}$, $\text{Hg}^0\text{-Fe}_2\text{O}_{0.375}$, and $\text{Hg}^0\text{-Fe}$ are 2.60, 2.39, 1.07, and 1.23 eV, respectively. E_a for CO decomposition on Fe is higher than that for CO dissociation on Fe(100) (1.14 eV reported by,³⁸ 1.07 eV reported by Sorescu *et al.*⁴², and 1.14 eV reported by Moon *et al.*⁴³). The general decrease of E_a on the Hg^0 -doped reduce surfaces could be attributed to the obvious charge transfer and charge repopulation on the adsorbed CO that activates the C—O bond for easier decomposition (as shown above in Fig. 7b). Except for CO decomposition on Fe surface, the reaction energy is in proportion to the barrier energy for CO decomposition on the reduced iron oxide surfaces. CO decompositions on $\text{Fe}_2\text{O}_{1.625}$ and $\text{Fe}_2\text{O}_{0.875}$ are endothermic processes, which need high temperature acting as driving force for the reactions. However, the adsorption of Hg^0 reduces the barrier energy for CO decomposition making the reaction exo-

Fig. 8 E_a and E_r for CO adsorption on (a) the perfect and reduced Fe_2O_3 surfaces, and (b) the perfect and reduced $\text{Hg}^0\text{-Fe}_2\text{O}_3$ surfaces

thermic. Both kinetics and energetics analysis imply that carbon deposit is more energetically realized on the Hg^0 -doped reduced iron oxide surface.

Because of the low E_a , obvious carbon deposit will happen after the reduction period around $\text{Fe}_2\text{O}_{1.625}$, which corresponds to the conversion rate (χ) around 46% (calculated by $\chi = \frac{m_{\text{ox}} - m}{m_{\text{ox}} - m_{\text{red}}} \times 100\%$, according to our previous works^{28,44,45}). Hg^0 promotes catalytic decomposition of CO for carbon deposit on the surfaces and depresses the efficiency of CLC.

To address the trends in CO^* decomposition more accurately, a kinetic model is required in order to treat the different time scales associated with the reduction of Fe_2O_3 at different degrees during CLC. We applied a simple phenomenological model to bring out the trends. The net reaction rates for reactions (R1 and R2) are written as

$$r_1 = k_1 \theta' p_{\text{CO}} - k_{-1} \theta_{\text{CO}} \quad (1)$$

$$r_2 = k_2 \theta_{\text{CO}} - k_{-2} \theta_{\text{C}} \theta_{\text{O}} \quad (2)$$

where k_i ($i = 1, 2$) are forward rate constants for Reaction-1 and Reaction-2 while k_{-i} ($i = 1, 2$) are the rate constants for the backward reactions. p and θ denote the pressure and surface coverage, respectively. Specially, θ' denotes the ratio of exposed active site.

The rate constants may be written as

$$k_i = \frac{k_{\text{BT}}}{h} \frac{f^{\ddagger}}{\prod f_j} \exp\left(\frac{-E_i}{RT}\right) \quad (3)$$

where E_i is the activation free energy of reaction step i . h is the Planck constant ($6.63 \times 10^{-34} \text{ J} \cdot \text{s}$), k_{B} is Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$). The degree of freedom for the reaction component j in each reaction step is given by

$$f_j = f_t \cdot f_r \cdot f_v$$

where f_t , f_r , and f_v are the translational, rotational, and vibrational degree of freedom, respectively.

For the CO desorption step (the backward reaction of step (1)), we use a rate constant given by

$$k_{-1} = \nu \exp\left(-\frac{E_{\text{CO}}}{k_{\text{B}}T}\right)$$

where E_{CO} is the CO binding energy and $\nu = 10^{13} \text{ s}^{-1}$ is set as a typical pre-exponential factor for CO desorption.

With the above approximations, Reaction-2 is the rate-determining step for CO evolution. Since chemical looping combustion experiments were usually performed around 1073 K in our previous works^{28,45}, the reaction rate is calculated according to the barrier energy for the decomposition of CO (ΔE_{CO^*}) under 1073 K and the given condition $\theta_{\text{CO}} = 0.5$, $\theta_{\text{O}} = 0.25$, $\theta_{\text{C}} = 0.25$, and $P_{\text{CO}} = 1.01 \times 10^5 \text{ Pa}$. The results are shown in Fig.9. For the catalytic decomposition of CO on the reduced Fe_2O_3 surfaces (the red curve), high decomposition reaction rate can be realized during the period round $\text{Fe}_2\text{O}_{0.375}$ and closed to the complete reduction stage into iron. This red curve model describes the thermogravimetric trends observed experimentally well, where obvious weight increase due to carbon deposit occurred around and after $\text{Fe}_2\text{O}_{1.625}$. However, Hg^0 promotes the CO decomposition on these reduced surfaces (the black line). The adsorption of Hg^0 promotes the cat-

Fig.9 Reaction rate for CO decomposition on the reduced $\text{Fe}_2\text{O}_3[001]$ at $\theta_{\text{CO}} = 0.5$, $\theta_{\text{O}} = 0.25$, and $\theta_{\text{C}} = 0.25$ for the Reaction-2 under 1073 K
color online

alytic decomposition of CO, and reveals the relationship between catalytic CO decomposition reaction rate and reduction degree of iron oxide. The qualitative and quantitative results of Hg^0 adsorption and its effect on CO adsorption and decomposition will provide fundamental understanding for optimizing the CLC processes.

4 Conclusions

We investigated the adsorption of elemental mercury (Hg^0) on the perfect and reduced $\text{Fe}_2\text{O}_3[001]$ surfaces, and probed into the synergetic effect of the adsorbed Hg^0 on the catalytic decomposition of CO on the reduced $\text{Fe}_2\text{O}_3[001]$ surfaces during chemical looping combustion. Interaction between Hg^0 and surface increases with reduction of $\text{Fe}_2\text{O}_3[001]$ into lower oxidation state. Stable Hg^0 adsorption promotes the interaction between CO and the reduced surfaces, favoring charge transport from surface to the adsorbed CO, which activates the C—O bond for its decomposition. Hg^0 together with carbon will hence be carried into air reactor, depressing the efficiency of CLC. Reasonable control of reduction degree not only hinders Hg^0 binding to the surface of oxygen carrier but also decreases generation of carbon deposit. Results of the current DFT work provide fundamental understanding of interaction between Hg^0 and the perfect and reduced Fe_2O_3 surfaces, and synergetic effect of Hg^0 on the interaction between CO and these surfaces. For future studies, it is necessary to investigate the synergy of multiple elements included in coal such as K, Na, and Ca on mercury adsorption and its influence on the process of CLC.

Supporting Information: Band structures for $\text{Fe}_2\text{O}_{2.5}$, Hg^0 - $\text{Fe}_2\text{O}_{2.5}$, $\text{Fe}_2\text{O}_{0.375}$, and Hg^0 - $\text{Fe}_2\text{O}_{0.375}$, as well as geometric structures of initial state, transition state, and final state for CO decomposition on the reduced surfaces ($\text{Fe}_2\text{O}_{1.625}$, Hg^0 - $\text{Fe}_2\text{O}_{1.625}$, $\text{Fe}_2\text{O}_{0.875}$, Hg^0 - $\text{Fe}_2\text{O}_{0.875}$, $\text{Fe}_2\text{O}_{0.375}$, Hg^0 - $\text{Fe}_2\text{O}_{0.375}$, Fe, and Hg^0 -Fe) have been included. This information is available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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理想与还原 Fe_2O_3 [001]表面上汞吸附协同催化 CO 分解作用

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Synergetic Effect of Mercury Adsorption on the Catalytic Decomposition of CO over Perfect and Reduced Fe_2O_3 [001] Surface

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Fig.S1 Band structures for (a) $\text{Fe}_2\text{O}_{2.5}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{2.5}$ and (b) $\text{Fe}_2\text{O}_{0.375}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{0.375}$

Fig.S2 Geometric structures of initial state (IS), transition state (TS), and final state (FS) for CO decomposition on (a) $\text{Fe}_2\text{O}_{1.625}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{1.625}$, (b) $\text{Fe}_2\text{O}_{0.875}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{0.875}$, (c) $\text{Fe}_2\text{O}_{0.375}$ and $\text{Hg}^0\text{-Fe}_2\text{O}_{0.375}$, (d) Fe and $\text{Hg}^0\text{-Fe}$

The C-O bond length and the distance between C and Fe of the IS are given in Å. And the related bond distances for the TS and FS are also given in Å.