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The regeneration mechanisms of sulfurized α -Fe₂O₃ surfaces under O₂ atmosphere: A density functional theory study



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ABSTRACT

The regeneration mechanisms of sulfurized α -Fe₂O₃ desulfurization sorbent under O₂ atmosphere are systematically studied by density functional theory (DFT) slab calculation. The regeneration pathways are proposed for two sulfurized surfaces, "S-contained surface" and "S-adsorbed surface", which are derived from the substitution of surface O atom by S atom and the adsorption of S atom on the surface Fe atom, respectively. Our results show that two competitive regeneration pathways exist on each sulfurized surface. For the regeneration on the S-contained surface and the S-adsorbed surface, the rate-determining step is the dissociation of O₂ with the energy barriers of 136.7 and 227.3 kJ·mol⁻¹, respectively, suggesting that the regeneration on the Scontained surface is easier than that on the S-adsorbed surface. Then, the O vacancy on the α -Fe₂O₃(0001) surface can be repaired under O₂ atmosphere, and the reparation mechanism demonstrates that the dissociation of O₂ on the O-vacancy α -Fe₂O₃(0001) surface only needs to overcome a lower energy barrier of 49.8 kJ·mol⁻¹ than those (136.7 and 227.3 kJ·mol⁻¹) on two sulfurized surfaces. As a result, the presence of O vacancy on the α -Fe₂O₃(0001) surface can accelerate the dissociation of O₂, which is favorable to the regeneration of sulfurized surfaces.

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1. Introduction

Coal-derived gaseous products always contain sulfur-containing compounds, and the main component is H_2S [1,2]. It is necessary to reduce the content of H_2S to a low level due to its negative effects on the environment and the chemical processing [3–6].

At present, Fe₂O₃ is widely used as a desulfurization sorbent to remove sulfur species from gas streams [7–9]. α -Fe₂O₃ is the most stable form and main component of Fe₂O₃ [10–12]. The α -Fe₂O₃(0001) surface is the predominant and active surface, and the highly relaxed single-layer Fe-termination (Fe–O₃–Fe–R) is the inherently most stable surface configuration [11,13–15].

During desulfurization, two sulfurized surfaces can be formed on the α -Fe₂O₃(0001) surface by different mechanisms [16]. These sulfurized surfaces can also be formed during the interaction of H₂S with other metal oxides [17,18]. On the one hand, the favorable overlap between *p*-orbit of S atom and *d*-orbit of Fe atom results in the formation of a strong S – Fe bond, which makes S adsorb on the top of the surface Fe atom and leads to the blocking of active sites on the α -Fe₂O₃(0001) surface. On the other hand, the surface O atom is suffered from the

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substitution by S atom, which leads to the increment of the energy barrier for the H₂S dissociation on the desulfurization sorbent surface. Thus, the removal of adsorbed sulfur on the surface and regeneration of the substituted S surface are crucial for the recycling of the Fe₂O₃ desulfurization sorbent. What's more, the reparation of the O vacancy on the α -Fe₂O₃(0001) surface seems to be significant due to the negative influence of O vacancy on the desulfurization [19].

Up to now, the regeneration of desulfurization sorbents using H_2 [20], O₂ [21,22], H₂O [23,24] and SO₂ [25,26] has been extensively studied by experimental approaches. H₂S is formed during the regeneration under H₂ atmosphere, which is a disadvantage to desulfurize. While the regeneration of the sulfurized Fe₂O₃ sorbent by O₂ forming SO₂ is fast and cheap [25]. Besides, O vacancy on the Fe₂O₃ surface can be repaired and enhance its desulfurization performance. During the regeneration of Fe₂O₃ sorbent under O₂ atmosphere, SO₂ is the main and inevitable product. A deep understanding of the adsorption and dissociation of O₂ on the perfect and defective surfaces are important, and the regeneration mechanism of Fe₂O₃ sorbent under O₂ atmosphere is necessary to improve the behavior of desulfurizer. Through the adsorption of O₂ on the perfect α -Fe₂O₃(0001) surface [27], and the adsorption of product SO₂ on the CeO₂(111) [28], CaO(100) [29], MgO(100) [30], SnO₂(110) [31], and TiO₂(110) surfaces [32] have been investigated, the regeneration mechanism of the sorbent is not clear. In our previous work [33], the regeneration mechanism of the sulfurized ZnO surface has been

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Fig. 1. The optimized slab models of the α -Fe₂O₃(0001) surfaces. Top and sides views of (a) the perfect surface, (b) the S-contained surface, (c) the S-adsorbed surface and (d) the O-vacancy surface. The purple, red and yellow balls represents Fe, O and S atoms, respectively. As illustrated in (a) the perfect surface, four sites are presented. The denoted "Top-Fe", "Top-O", "Bridge–Os–Fe1" and "Bridge–Os–Fe2" on the perfect α -Fe₂O₃(0001) surface represent "the top site of the Fe atom", "the top site of the O atom", "the bridge site between the surface Os atom and the surface Fe1 atom" and "the bridge site between the surface Os- atom and the surface Fe2 atom", respectively. For the S-contained surface, six sites are designated. "Top-Fe", "Top-O" and "Top-S" represent the top sites of the surface Fe, O and S atoms, respectively. In addition, "Bridge–Fe–O", "Bridge–S–Fe1" and "Bridge–S–Fe2" represent the bridge sites between surface Fe 1 atom and surface O atom, between surface S atom and surface Fe1 atom, and between surface S atom and surface Fe2 atom, respectively. "Vacancy-O" represents the vacancy site of O atom on the O-vacancy surface.

studied. Herein, DFT is employed to investigate the regeneration mechanisms of sulfurized α -Fe₂O₃ surfaces including "S-contained surface" and "S-adsorbed surface" under O₂ atmosphere. Furthermore, the reparation mechanism for the O vacancy on the α -Fe₂O₃(0001) surface is also investigated.

2. Computational methods and models

2.1. Surface models

Based on the most stable and accurate antiferromagnetic arrangement (+ - - +) structure of α -Fe₂O₃ [34–36], where + and – are respectively assigned as the up-spin and down-spin directions of the Fe sites from the top to the bottom of the unit cell, the Fe-terminated nine atomic layer slab model of the perfect α -Fe₂O₃(0001) surface is built based on the optimized α -Fe₂O₃ bulk structure. According to the previous calculations [37–39], a $p(2 \times 2)$ super-cell is large enough to neglect the lateral adsorbate interaction and a vacuum space of 12 Å is introduced to prevent interaction between the slabs. Then, two sulfurized surfaces are constructed with S atom substituting the surface O atom and S atom being adsorbed at the Fe site of the α -Fe₂O₃(0001) surface, which are denoted as "S-contained surface" and "S-adsorbed surface", respectively. The S-contained surface is obtained by replacing one out of twelve O atoms in the surface according to our previous

Table 1	
Lattice parameters of α -Fe ₂ O ₃ using different cutoff energies and k-point.	

Cutoff energy	k-point spacing	a = b (Å)	c (Å)
400	$3 \times 3 \times 2$	5.017	13.891
400	$5 \times 5 \times 2$	5.015	13.894
400	$8 \times 8 \times 2$	5.015	13.895
450	$3 \times 3 \times 2$	5.006	13.910
450	$5 \times 5 \times 2$	5.008	13.898
450	$8 \times 8 \times 2$	5.009	13.899
500	$3 \times 3 \times 2$	5.009	13.879
500	$5 \times 5 \times 2$	5.008	13.882
500	$8\times8\times2$	5.008	13.882

calculations results. And the S-adsorbed surface is constructed by a S atom bonding to the surface Fe atom, which is the most stable configuration of S adsorbing on the α -Fe₂O₃(0001) surface. The O-vacancy α -Fe₂O₃(0001) surface is constructed by removing one surface O atom from the perfect surface. In all calculations, the outmost six layers and adsorbed species are fully relaxed while the bottom three layers are fixed to the bulk parameters. The side and top views for the four surfaces are shown in Fig. 1 with different adsorption sites.

2.2. Calculation methods

All calculations were performed with the CASTEP program package [40]. The generalized gradient approximation (GGA) [41] with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [42] was applied. The electronic wave functions were expanded in a plane wave basis set, and the ionic cores were described by ultrasoft

Table 2

Adsorption energies of different species on the S-contained surface, O-vacancy surface and perfect surface $(kJ \cdot mol^{-1})$.

S-contained su	urface	O-vacanc	y surface	Perfect surface	e
$Sc-O_2(a)$	117.4	V-02	86.1	P-O(a)	451.2
$Sc-O_2(b)$	107.0			P-O(b)	288.0
Sc-O(a)	472.8			$P-SO_2(a)$	90.5
Sc-O(b)	475.1			$P-SO_2(b)$	122.8
Sc-O(c)	477.5			$P-SO_2(c)$	70.7
Sc-O(d)	290.1			$P-SO_2(d)$	121.6
				$P-SO_2(e)$	50.3
				$P-O_2(a)$	103.9
				$P-O_2(b)$	71.4
				$P-O_2(c)$	68.2
				P-SO(a)	140.6
				P-SO(b)	130.0
				P-SO(c)	164.1
				P-SO(d)	166.3
				P-SO(e)	140.7
				P-S(a)	362.7
				P-S(b)	333.0
				P-S(c)	318.8

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Table 3

Co-adsorption energies of two O atoms on the S-contained surface, S/O₂ and SO/O on the perfect α -Fe₂O₃(0001) surface (kJ·mol⁻¹).

S-contained surface	ce	Perfect surface	Perfect surface			
Sc-20(a)	954.0	P-S/O2	451.8			
Sc-20(b)	1033.0	P-SO/O(a)	570.5			
		P-SO/O(b)	558.2			
		P-SO/O(c)	575.7			

pseudopotentials. A Fermi smearing of 0.1 eV was utilized to speed up convergence. The convergence criteria are set to medium quality with the tolerance for SCF, energy, maximum force, and maximum displacement of 2.0×10^{-6} eV/atom, 2.0×10^{-5} eV/atom, 0.05 eV/ Å and 2.0×10^{-3} Å, respectively. A series of different cutoff energies and k-point values has been used to optimize α -Fe₂O₃ bulk, and the results are shown in Table 1. It can be seen that lattice parameters with a = b = 5.009 Å and c = 13.879 Å are closer to experimental values using the cutoff energy of 500 eV and $3 \times 3 \times 2$ Monkhorst-Pack grid with 0.07 $Å^{-1}$ separation for structures than others. However, the cutoff energy of 450 eV and k-point of $3 \times 3 \times 2$ have been used in our study to improve the calculation efficiency. The calculated lattice parameters of α -Fe₂O₃ are a = b = 5.006 Å and c = 13.910 Å, which are comparable with the previous experimental values of a = b = 5.038and c = 13.772 Å [43] and in accordance with other theoretical values [44–46]. In addition, there is a little difference of 3.0 kJ \cdot mol⁻¹ for the adsorption energy of SO₂ on the perfect α -Fe₂O₃ surface using the cutoff energy of 500 and 450 eV. For the surface models, $2 \times 2 \times 1$ Monkhorst–Pack grid with the same separation for structure has been used [47]. It should be noted that the DFT–GGA level of theory provides reasonably accurate lattice constants and cohesive energies [48], and which has provided meaningful structural and energetic properties of α -Fe₂O₃ [38,45] as well as the reaction mechanisms on the α -Fe₂O₃ surfaces [49]. Therefore, the calculations in our study are based on the DFT–GGA level. In addition, the gas phase species were optimized in a large cell of $10 \times 10 \times 10$ Å, and energies of which could be obtained.

The adsorption energy is always regarded as a measure of the strength to adsorbate–substrate adsorption. The adsorption energy is defined as follows:

$$E_{\rm ads} = E_{\rm A} + E_{\rm slab} - E_{\rm A/slab} \tag{1}$$

where $E_{A/slab}$ is the total energy of the substrate together with the adsorbate in its equilibrium state, E_A is the total energy of the free adsorbate, and E_{slab} is the total energy of the bare substrate. By this definition, a positive E_{ads} value corresponds to an exothermic adsorption, and the more positive the E_{ads} is, the stronger the adsorption is.

The co-adsorption energy is defined as follows:

$$E_{\rm co-ads} = E_{\rm A} + E_{\rm B} + E_{\rm slab} - E_{\rm (A+B)/slab}$$
(2)

where E_A , E_B , E_{slab} and $E_{(A + B)/slab}$ are the energies for the free A, B, the slab with a $p(2 \times 2)$ super-cell and the co-adsorbed (A + B)/slab systems, respectively.



Fig. 2. The optimized adsorption structures of O₂ and atomic O on the S-contained surface. Bond lengths are given in angstrom.



Fig. 3. The optimized structures for the adsorptions of O₂ on the O-vacancy surface and O atom on the perfect surface. Bond lengths are given in angstrom.

Moreover, the transition states (TS) are searched by the complete LST/QST methods for reactions [50]. The reaction energy (ΔE) and the energy barrier (E_a) are defined as follows:

$$\Delta E = E_{\rm P} - E_{\rm R} \tag{3}$$

$$E_{\rm a} = E_{\rm TS} - E_{\rm R} \tag{4}$$

where E_P is the energy of the product in each reaction, E_R is the energy of the reactant in each reaction, and E_{TS} is the energy of the transition state in each elementary reaction.

3. Results and discussion

3.1. The mechanism for the regeneration on the S-contained surface under O_2 atmosphere

To investigate the regeneration mechanism of the S-contained surface, it is necessary to compare the adsorption of O_2 and O atoms at the different sites and obtain their most stable adsorption structures. Then, the co-adsorptions of two O atoms from O_2 on the S-contained surface are further probed to understand the atom transfer during the regeneration. The mechanism for regeneration is ultimately defined with the transition structures of the elementary reactions. Besides, the adsorptions of O_2 on the O-vacancy surface and O atom on the perfect surface are discussed. Adsorption energies and co-adsorption energies of different species on the different surfaces are shown in Tables 2 and 3.

3.1.1. O2 and O atom adsorption on the S-contained surface

3.1.1.1. O₂ adsorption. For the O₂ adsorption, the original structures with O₂ parallel, perpendicular and tilting to the S-contained surface are separately considered. O₂ only can interact with the surface Fe atom. Two stable structures are obtained, denoted as $Sc-O_2(a)$ and $Sc-O_2(b)$ (see Fig. 2). When the O_2 molecule is parallel to the surface in its initial configuration, it still maintains its posture after optimizing, which is Sc–O₂(a) with an adsorption energy of 117.4 kJ·mol⁻¹. In this structure, bond lengths of O1-O2, O1-Fe1 and O2-Fe1 are 1.384, 1.893 and 1.902 Å, respectively. However, when O_2 is perpendicular or tilting to the surface in the initial configuration, which are converted to the structure Sc–O₂(b) with an adsorption energy of 107.0 kJ·mol⁻¹. In this case, O1 atom is bonded to the surface Fe1 atom and formed bond length is 1.805 Å. The parallel adsorption of O_2 on the surface is more exothermic, suggesting that the configuration of $Sc-O_2(a)$ is more stable, which is similar to the previous result [27]. In this structure, the Mulliken charge of Oa and Ob are 0.30 e, and the spin are 0.07 and 0.10 for Oa and Ob, respectively. It is implied that O_2 is surperoxide.

3.1.1.2. O adsorption. As for the O atom adsorption, four adsorption structures on the S-contained surface are obtained, which are Sc–O(a), Sc–O(b), Sc–O(c) and Sc–O(d) shown in Fig. 2. The adsorption energy of Sc–O(a) is 472.8 kJ·mol⁻¹. In this structure, O atom is bonded with



Fig. 4. The optimized structures for the co-adsorptions of two O atoms on the S-contained surface. Bond lengths are given in angstrom.



Fig. 5. The reaction profiles of the mechanism for the regeneration of the S-contained surface under O₂ atmosphere.

Fe2 and S atoms simultaneously with O–Fe2 and O–S bond lengths of 2.092 and 1.568 Å, respectively. For Sc–O(b), O atom is at the "Top-Fe" site with a Fe1–O bond length of 1.633 Å, and its adsorption energy is 475.1 kJ·mol⁻¹. As to Sc–O(c), O atom bridges to S–Fe1 bond with the exothermic energy of 477.5 kJ·mol⁻¹. For Sc–O(d), it is observed that O atom is at the "Bridge–Fe–O" site bonding to Fe and O atoms with the adsorption energy of 290.1 kJ·mol⁻¹. Comparing the four cases, Sc–O(c) has the largest adsorption energy, indicating that O atom is the most favorably absorbed on the S-contained surface with Sc–O(c) configuration.

3.1.2. O₂ adsorption on the O-vacancy surface

As displayed in Fig. 1(d), on the optimized O-vacancy surface, the Fe atom surrounded around the O vacancy site collapses and migrates into the bulk. Nevertheless, previous experiments and calculations have revealed that sulfur species mainly interact with the metal centers of the oxide surfaces [51–54]. Therefore, the presence of O vacancy on the surface has an adverse effect on the desulfurization. O_2 molecularly adsorbs at the O-vacancy site in this coverage, and fills the vacancy site leading to the collapsed Fe atom on the O-vacancy surface move up to its original surface. The O– O bond has been elongated to 1.456 Å corresponding



Fig. 6. The structures of transition states and intermediates in the S-contained surface regeneration process. Bond lengths are given in angstrom.



Fig. 7. The optimized structures of SO₂ adsorption on the perfect α -Fe₂O₃(0001) surface. Bond lengths are given in angstrom.

to 1.237 Å of O₂ in gas phase. The adsorption mode is different from the case on the reduced rutile TiO₂(110) surface [55] and the O-vacancy ZnO(1010) surface [56], on which molecular and dissociative adsorption states are also investigated, and the latter is a more stable adsorption. The adsorption energy of "V-O₂" is 86.1 kJ·mol⁻¹. The Mulliken charge of Oa and Ob are -0.36 and -0.37, and the spin of which are -0.01 and -0.02, which show that the O₂ adsorption at the O vacancy site of α -Fe₂O₃(0001) surface is peroxide.

3.1.3. O atom adsorption on the perfect α -Fe₂O₃(0001) surface

For the O atom adsorption on the perfect α -Fe₂O₃(0001) surface, two stable configurations, "P–O(a)" and "P–O(b)", are presented in Fig. 3. P–O(a) has an adsorption energy of 451.2 kJ·mol⁻¹, in which O atom is located at the "Top-Fe" site with the O–Fe2 bond length of 1.631 Å. In P–O(b), the adsorbed O atom bridges to the surface Os- Fe2 bond with O–Os- and O–Fe2 bond lengths of 1.476 and 1.912 Å, respectively. The adsorption energy of P–O(b) is 288.0 kJ·mol⁻¹. The adsorption energy of P–O(b) is larger than that of P–O(b), which predicts that P–O(a) is more stable. The stable configuration is consistent with the result of Liu et al. [57].

3.1.4. 20 co-adsorption on the S-contained surface

Considering the adsorption of individual O on the S-contained surface and the formation process of SO_2 , the co-adsorption of two O

atoms on the S-contained surface is also investigated. Two co-adsorption structures, Sc-2O(a) and Sc-2O(b), are obtained and shown in Fig. 4. As to Sc-2O(a), O1 atom is located at the "Bridge–S–Fe2" site with O1–Fe2 and O1 – S bond lengths of 2.195 and 1.542 Å, respectively. Meanwhile, O2 is located at the top site of Fe1 atom with a O2–Fe1 bond length of 1.638 Å. For Sc-2O(b), O2 atom bridges to the S–Fe1 bond with O2–S, O2–Fe1, O1–S and O1–Fe2 bond lengths of 1.559, 1.956, 1.524 and 2.097 Å, respectively. Co-adsorption energies for Sc-2O(a) and Sc-2O(b) are 954.0 and 1033.0 kJ·mol⁻¹, respectively.

3.1.5. The mechanism for the regeneration on the S-contained surface under O_2 atmosphere

In this section, the reaction profiles (see Fig. 5) are constructed, and the involved transition states and intermediate structures are shown in Fig. 6. As shown in Fig. 5, two pathways for the regeneration on the S-contained α -Fe₂O₃(0001) surface under O₂ atmosphere are initiated with the adsorption of O₂, Sc–O₂(a). Then, the O₂ is dissociated with the migration of O1 atom to "Bridge–S–Fe2" site via transition state TS1 and bonding to Fe2 and S atoms in Sc–2O(a). In this step, the distance between O1 and O2 atoms is elongated from 1.384 Å in Sc– O₂(a) to 3.023 Å in Sc–2O(a). O2 atom is still located at the "Top-Fe" site in Sc–2O(a). This elementary reaction overcomes an energy barrier of 136.7 kJ·mol⁻¹ and is exothermic by 145.7 kJ·mol⁻¹. Subsequently, O2 atom is transferred from "Top-Fe" site to "Bridge–S–Fe1" site via TS2



Fig. 8. The optimized structures for the adsorption of O_2 on the perfect α -Fe₂ $O_3(0001)$ surface. Bond lengths are given in angstrom.



Fig. 9. The optimized structures of SO adsorbs on the perfect α -Fe₂O₃(0001) surface. Bond lengths are given in angstrom.



Fig. 10. The optimized structures for the adsorptions of S atom on the perfect α -Fe₂O₃(0001) surface. Bond lengths are given in angstrom.

with the energy barrier of 115.5 kJ·mol⁻¹. Simultaneously, the bond length of O2–Fe1 increases to 1.956 Å from 1.638 Å in Sc–2O(a) via 1.720 Å in TS2 leading to the formation of Sc–2O(b) with an exothermicity of 79.0 kJ·mol⁻¹. Actually, SO₂ rudiment has been formed on the surface in the structure Sc–2O(b).

In the first path (the black line), SO_2 can desorb from the surface and a vacancy is formed via TS3 with an energy barrier of 115.5 kJ·mol⁻¹ leading to the formation of IM1, which is an endothermic reaction with the energy of 52.8 kJ·mol⁻¹. Another O_2 subsequently adsorbs at the "Vacancy-O" site with the exothermic energy of 103.0 kJ·mol⁻¹. At last, the O3 atom in the adsorbed O_2 is transferred from the vacancy site in IM2 to "Top-Fe" site in P via TS4 by overcoming a mild energy barrier of 38.7 kJ·mol⁻¹.

Competitively (the red line), another O_2 can be adsorbed in the structure Sc–2O(b) leading to the formation of the stable intermediate IM3, followed by the desorption of SO₂ via TS5 with an energy barrier

of 58.3 kJ·mol⁻¹. At last, O3 atom transfers from the site of "Bridge– Os-–Fe2" in IM4 to the site of "Top–Fe" in P via TS6. This step overcomes a slight energy barrier of 10.3 kJ·mol⁻¹.

The dissociation of O_2 from Sc- $O_2(a)$ to Sc-2O(a) is the rate-determining step. Both the regeneration mechanisms should undergo TS1 with an energy barrier of 136.7 kJ·mol⁻¹, which means that they are two competitive pathways. Thus, reducing the energy barrier of O_2 dissociation on the surface is favorable to the regeneration of the S-contained surface.

3.2. The mechanism for regeneration on the S-adsorbed surface under O_2 atmosphere

As to the regeneration mechanism for the S-adsorbed surface, the individual adsorptions and co-adsorptions of the species involved in the



Fig. 11. The optimized coadsorption structures for S/O₂ and SO/O on the perfect α -Fe₂O₃(0001) surface. Bond lengths are given in angstrom.



Fig. 12. The reaction profile of the mechanism for the regeneration on the S-adsorbed surface under O₂ atmosphere.

regeneration reaction are also investigated. Every elementary reaction is analyzed.

3.2.1. The adsorptions of SO₂, O₂, SO, S and O on the perfect surface

3.2.1.1. SO₂ adsorption. In the case of SO₂, five optimized structures are obtained and presented in Fig. 7. In P-SO₂(a), S atom is bonded to the surface Os atom, and O1 is concurrently bonded with the near surface Fe1 atom. The adsorption energy is 90.5 kJ mol^{-1} with S–Os and O1-Fe1 bond lengths of 1.932 and 1.999 Å, respectively. As to P- $SO_2(b)$, S atom bonds with the surface Os atom and both O atoms in SO₂ bind with its near Fe atoms with O1-Fe1, O2-Fe2 and S-Os bond lengths of 2.108, 2.055 and 1.704 Å, respectively, which is exothermic with an energy of 122.8 kJ·mol⁻¹. In P-SO₂(c), the adsorbed SO₂ is nearly perpendicular to the surface with an adsorption energy of 70.7 kJ \cdot mol⁻¹. O1 atom is bonded with the surface Fe1 atom with the distance of 1.974 Å. Adsorption energies of $P-SO_2(d)$ and $P-SO_2(e)$ are 121.6 and 50.3 kJ \cdot mol⁻¹, respectively. For the adsorption structures of P-SO₂(a) and P-SO₂(b), S atoms are bonded to the surface Os atom leading to the formation of analogical SO₃ structure, which is compatible with the experimental observation using XPS [58]. Therefore, the most stable adsorption configuration of SO₂ on the α -Fe₂O₃(0001) surface is P- $SO_2(b)$, which is the same as its adsorption mode on the $CeO_2(111)$ and ZnO(1010) surfaces [28,33].

3.2.1.2. O_2 adsorption. For the O_2 adsorption, it can only adsorb at the "Top-Fe" site on the perfect surface just as that on the S-contained surface. The optimized structures with three different orientations are labeled as "P–O₂(a)", "P–O₂(b)", "P–O₂(c)" shown in Fig. 8. In P–O₂(a), O_2 is parallel to the surface and bonds to the surface Fe2 atom with O1 – Fe2 and O2 – Fe2 bond lengths of 1.861 and 1.946 Å, respectively, and the adsorption energy is 103.9 kJ·mol⁻¹. The adsorbed O_2 molecules in "P–O₂(b)" and "P–O₂(c)" are perpendicular and tilting to the surface with adsorption energies of 71.4 and 68.2 kJ·mol⁻¹, respectively. Therefore, P–O₂(a) is the most stable adsorption structure of O_2 on the perfect surface, which is consistent with the result of Bergermayer et al. [27].

3.2.1.3. SO adsorption. In the process of SO₂ formation, O atom bonding with S atom and forming SO are necessary. In this section, the adsorptions of SO at the different sites on the perfect α -Fe₂O₃(0001) surface are investigated. Five optimized structures (see Fig. 9) are obtained. In P–SO(a), S atom is bonded with the surface Os atom while O atom is bonded with the surface Fe2 atom with S–Os and O–Fe2 bond lengths of 1.582 and 2.039 Å, respectively. The adsorption energy is 140.6 kJ·mol⁻¹. In P–SO(b) and P–SO(e), both SO adsorb on the surface through S atom binding with the Fe2 atom with the corresponding adsorption energies of 130.0 and 140.7 kJ·mol⁻¹, respectively. For P–SO(c) and P–SO(d), both S atom and O atom are bonded to the surface Os atom and Fe1 atom, respectively. Adsorption energies for two structures are 164.1 and



Fig. 13. The structures of transition states and final product in the regeneration on the S-adsorbed surface. Bond lengths are given in angstrom.



Fig. 14. The reaction profile of the mechanism for the reparation on the O-vacancy surface under O₂ atmosphere.

166.3 kJ·mol⁻¹, respectively. In addition, it is clearly observed that the significantly changes occur on the surfaces in P-SO(c) and P-SO(d). Based on the above investigations, the structure of P-SO(d) is the most stable adsorption mode of SO.

3.2.1.4. Atomic S adsorption. As to the adsorption of atomic S on the perfect α -Fe₂O₃(0001) surface, there are three stable structures (see Fig. 10). In P–S(a), S atom is adsorbed at the "Top-Fe" site with the S–Fe2 bond length of 2.017 Å, which has an adsorption energy of 362.7 kJ·mol⁻¹. In P–S(b), S atom bridges to the Fe2–Os bond with an adsorption energy of 333.0 kJ·mol⁻¹. In the case of P–S(c), S atoms is located at the site of "Bridge–Os–Fe1" and bonded with the surface Os and Fe1 atoms. The adsorption energy is 318.8 kJ·mol⁻¹. Evaluating adsorption energies, P–S(a) is the most stable structure for the adsorption of S atom on the perfect α -Fe₂O₃(0001) surface.

3.2.1.5. Atomic O adsorption. The adsorptions of atomic O on the perfect α -Fe₂O₃(0001) surface have been investigated in Section 3.1.3.

3.2.2. The co-adsorption of S/O_2 and SO/O on the perfect $\alpha\text{-}Fe_2\text{O}_3(0001)$ surface

Herein, the co-adsorptions of S/O₂ and SO/O on the perfect α -Fe₂O₃(0001) surface are investigated. The optimized structures are shown in Fig. 11.

3.2.2.1. S/O_2 co-adsorption. Based on the above studies for the separate adsorptions of S and O₂ on the perfect α -Fe₂O₃(0001) surface, the co-adsorption structure for S atom and O₂ is constructed with the optimized structure presented in Fig. 11 and denoted as "P–S/O₂(a)". In P–S/O₂(a), S is placed at its most stable "Top-Fe" site bonding to Fe2 atom, meanwhile, the O₂ molecule is parallel to the surface Fe1 atom with the S–Fe2, O2–Fe1 and O1–Fe1 bonds lengths of 2.003, 1.963 and 1.862 Å, respectively. This structure has a co-adsorption energy of



Fig. 15. The structures of transition state for the reparation of the O-vacancy surface.

451.8 kJ·mol⁻¹. In this stable structure, the Mulliken charge of Oa and Ob are 0.24 e, and the spin are 0.18 and 0.21 for Oa and Ob, respectively. Therefore, it is surperoxide when O_2 adsorbs on the S-adsorbed surfaces.

3.2.2.2. SO/O co-adsorption. Before the formation of SO₂, the obtainment of intermediate SO/O is necessary. Therefore, the behaviors of SO and O co-adsorptions on the perfect α -Fe₂O₃(0001) surface are discussed. Different co-adsorption configurations of SO/O are constructed, and three optimized structures are obtained (see Fig. 11). In P–SO/O(a), O1 is adsorbed at the top site of Fe1 atom while SO is bridged to the Fe2–Os bond with O1–Fe1, S–Fe2 and S–Os bond lengths of 1.640, 2.327 and 1.594 Å, respectively, which has an adsorption energy of 570.5 kJ·mol⁻¹. As to P–SO/O(b) and P–SO/O(c), adsorption energies are 558.2 and 575.7 kJ·mol⁻¹, respectively. As a result, P–SO/O(c) is the most favorable structure for the co-adsorption of SO/O on the perfect α -Fe₂O₃(0001) surface.

3.2.3. The mechanism for the regeneration on the S-adsorbed surface under O_2 atmosphere

As shown in Fig. 12, two pathways are proposed for the regeneration process of the S-adsorbed surface under the O_2 atomphere. The transition states involved in this process are shown in Fig. 13. Starting with the co-adsorption structure of P–S/O₂, the dissociation process of O_2 on the S-adsorbed surface also occurs firstly. With the departure of O2 atom from Fe1 and O1 atoms, O2 approaches to the adsorbed S atom on the surface via the transition state TS1' by overcoming a fairly large energy barrier of 227.3 kJ·mol⁻¹. With the breakage of O1–O2 and O2–Fe1 bonds, the new O2–S bond is formed in the intermediate P–SO/O(b). In TS1', the length of O2–O1 bond increases to 2.116 from 1.352 Å in P–S/O₂(a), and the distance between O2 and S atoms decreases to 3.047 Å.

Then, there are two pathways for the transformation of P–SO/O(b). On the one hand (in the black line), P–SO/O(b) can be converted to a more stable intermediate P–SO/O(c) via a transition state TS2' by overcoming a low energy barrier of 5.6 kJ·mol⁻¹, subsequently forms SO₂ in P – SO₂(b) by the O1 atom in P–SO/O(c) approaching to the S atom via TS3' overcoming a much low energy barrier of 5.2 kJ·mol⁻¹. The transition state structures of TS2' and TS3' are shown in Fig. 13. On the other hand (in the red line), P–SO/O(b) can also be converted to P–SO/O(a) by overcoming a slight higher energy barrier of 58.8 kJ·mol⁻¹ via TS4' than that of TS2'. In TS4', the distance of S and the surface Os atoms is 2.421 Å, which is shorter than 2.884 Å in P–SO/O(b). Later, P–SO/O(a) converts to P–SO₂(a) through TS5' with a very low energy barrier of 5.2 kJ·mol⁻¹. At last, SO₂ is formed on the surfaces with the structures of P–SO₂(a) and P–SO₂(b).

Table 4

Thermodynamic properties of regeneration and reparation reactions on the S-contained, S-adsorbed and O-vacancy surfaces.

	$\Delta_{\rm r} H_{\rm m} (\rm kJ \cdot mol^{-1})$			$\Delta_{\rm r}G_{\rm m}(\rm kJ\cdot mol^{-1})$			lgK		
	298.15 K	500 K	1000 K	298.15 K	500 K	1000 K	298.15 K	500 K	1000 K
$\begin{array}{l} Sc-O_2(a) \rightarrow P \\ P-S/O_2 \rightarrow P' \\ V-O_2 \rightarrow P-O(a) \end{array}$	503.8 245.8 208.7	508.4 252.0 207.7	517.7 266.3 206.8	489.4 240.1 209.2	-478.3 -234.6 -209.9	-444.5 -211.5 -212.5	85.7 42.1 36.6	50.0 24.5 21.9	23.2 11.0 11.1

Later on, to facilitate the regeneration of the surface, SO_2 needs to transfer to an unstable site and subsequently desorbs from the surface. For this reason, the migration of SO_2 occurs to promoting the transition from P- $SO_2(b)$ to P- $SO_2(a)$. This step overcomes an energy barrier of 51.6 kJ·mol⁻¹ via TS6' with an endothermic energy of 32.3 kJ·mol⁻¹. During this course, the distance of O2 and Fe2 increases to 3.863 Å in P- $SO_2(a)$ from 2.055 Å in P- $SO_2(c)$ via TS7' with an energy barrier of 32.6 kJ·mol⁻¹. In TS7', the bond length of S – Os increases to 3.288 Å. At last, SO_2 in P- $SO_2(c)$ desorbs from the surface with an endothermic energy of 62.2 kJ·mol⁻¹.

From the reaction profile, it is clear that the highest energy point in the regeneration process of the S-adsorbed surface occurs at TS1', which is much higher than that on the S-contained surface. The ratedetermining step is also the dissociation of the adsorbed O_2 on the surface. Therefore, accelerating the dissociation of O_2 on the surface can facilitate the regeneration of the S-adsorbed surface.

3.3. The mechanism for the reparation on the O-vacancy surface under O_2 atmosphere

According to the former studies about the adsorption of O₂ on the O-vacancy surface and O atom on the perfect α -Fe₂O₃(0001) surface, the reparation mechanism for the O-vacancy surface is obtained (see Fig. 14). During the pathway, only one transition state TS* is involved (see Fig. 15). Firstly, one O₂ molecule is adsorbed at the "Vacancy-O" site and forms " $V-O_2$ " (see Fig. 3), in which the metal Fe atom has moved up to the surface with an exothermic energy of 86.1 k[\cdot mol⁻¹. It is observed that the metal active site reappears on the surface. Then, the adsorbed O_2 dissociates with the breakage of O1-O2 bond. O2atom migrates to the "Top-Fe" site via TS* by overcoming an energy barrier of 49.8 kJ·mol⁻¹, which makes contribution to the formation of P–O(a). In this step, the O1 – Fe bond length decreases from 1.844 Å in V–O₂ via 1.778 Å in TS* to 1.631 Å in P–O(a). During the reparation process, the energy barrier for the dissociation of O_2 on the O-vacancy surface is much lower than those on both sulfurized surfaces, namely the S-contained surface and the S-adsorbed surface, which means that the presence of oxygen vacancy on the surface is beneficial to the regeneration process.

3.4. The thermodynamic and kinetic analysis for the regeneration and reparation process

The thermodynamic data including reaction enthalpy, Gibbs free energies and the equilibrium constant, and the kinetic data including activation enthalpy, activation entropy and rate constant for the ratedetermining step of the regeneration and reparation reactions on three surfaces have been calculated using Dmol³ program, which are listed in Tables 4 and 5. The equilibrium constant *K* can be obtained from Eq. (5). According to the transition state theory, activation enthalpy $\Delta_r H^{\neq}_m$, activation entropy $\Delta_r S^{\neq}_m$ and rate constant *k* can be obtained from Eqs. (6), (7) and (8), respectively.

$$\Delta_r G^{\theta}_m(T) = -RT \ln K^{\theta} \tag{5}$$

[59]

$$\Delta_r H_m^{\neq} = H(TS) - H(R) \tag{6}$$

$$\Delta_r S_m^{\neq} = S(TS) - S(R) \tag{7}$$

$$k = \frac{k_b T}{h} \left(\frac{p^0}{RT}\right)^{1-n} \exp\left(\frac{-\Delta_r H_m^{\neq}}{RT}\right) \exp\left(\frac{\Delta_r S_m^{\neq}}{R}\right)$$
(8)

[60,61]

Where $\Delta_r G^{\theta}_{m}$ is Gibbs free energies, *K* is the equilibrium constant, *k* is the rate constant, *T* is reaction temperature, k_b , *h*, p^0 and R are Boltzman constant, Planck's constant, standard atmospheric pressure and fundamental gas constant, and *n* is the number of reactant.

From Table 4, it can be seen that lgK of the reaction on the Scontained surface is the largest, which shows that a large number of SO₂ can be formed in this surface. The rate constant for the dissociation of O₂ on the O-vacancy surface is the largest from Table 5, and which for the reaction on the S-adsorbed surface is the smallest, and that on the Scontained surface is the second. It is shown that the reparation of the Ovacancy surface is the easiest, and the regeneration of the S-contained surface is easier than that of the S-adsorbed surface. The rate constant lnk of rate-determining step increases with the temperature increasing, while the balance constant lgK decreases due to the exothermic reactions. Therefore, a proper regeneration temperature is very important. Tseng et al. [62] studied the regeneration of iron sulfide sorbent using O₂, which was oxidized to iron oxide at the temperature range 873-1173 K. Xie et al. [21] studied the regeneration of iron-based sorbents after sulfidation at 993 K and the iron sulfide can be regenerated well. The lowest temperature of 873 K was gotten to regenerate the sulfurized iron by White et al. [63].

4. Conclusions

DFT calculations have been carried out to investigate the regeneration mechanisms for two sulfurized α -Fe₂O₃(0001) surfaces and the reparation of the O-vacancy α -Fe₂O₃ surface under O₂ atmosphere. In

Table 5

The activation enthalpy, activation entropy and rate constant for every rate-determined step.

Rate-determining step	$\Delta_{\rm r} H^{\neq}{}_{\rm m} (\rm kJ \cdot mol^{-1})$			$\Delta_{\mathbf{r}} S^{\neq}{}_{\mathbf{m}} \left(\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1} \right)$			Lnk		
	298.15 K	500 K	1000 K	298.15 K	500 K	1000 K	298.15 K	500 K	1000 K
$Sc-O_2(a) \rightarrow Sc-2O(a)$	127.0	122.6	110.8	- 32.7	-43.8	-60.1	-25.7	-4.8	10.1
$P-S/O_2 \rightarrow P-SO/O(b)$	224.4	225.2	226.1	24.6	26.7	28.1	- 58.1	-21.0	6.8
$V-O_2 \rightarrow P-O(a)$	40.4	38.6	31.6	-1.4	-6.0	- 15.5	13.0	20.0	25.0

addition, the influence of the O-vacancy surface on the adsorption and dissociation of O_2 has been considered.

For the regeneration of two sulfurized surfaces of α -Fe₂O₃, the adsorptions and co-adsorptions of involved species in every pathway on the different surfaces have been investigated primarily. Then, the obtained structures are used as the reactants and intermediates to investigate regeneration mechanisms. Herein, two regeneration pathways are proposed to each sulfurized surface for α -Fe₂O₃. It is found that two pathways are competitive for each sulfurized surface, and the dissociation of O₂ is the rate-determining step with an energy barrier of 136.7 kJ·mol⁻¹ for the S-contained surface and 227.3 kJ·mol⁻¹ for the S-contained surface and the S-contained surface. Therefore, accelerating the dissociation of O₂ on the surface will do favor to the regeneration of two sulfurized surfaces.

For the O-vacancy surface, only a low energy barrier of 49.8 kJ·mol⁻¹ is required for the reparation, which clearly suggests that the reparation of the O-vacancy surface is very easy under O_2 atmosphere. What's more, the presence of O vacancy on the surface results in the easy dissociation of O_2 , which is beneficial to regeneration.

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