Facet-dependent diffusion of atomic oxygen on Ag surfaces

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ABSTRACT

It has been proposed that the introduction of surface and subsurface atomic oxygen into Ag catalysts is crucial for selectivity enhancement of ethylene epoxidation towards ethylene oxide. However, the diffusion of atomic oxygen on various Ag crystal surfaces, which is an essential process to form surface and subsurface atomic oxygen, has not been systematically investigated. In this work, we have employed density functional theory (DFT) to study the horizontal diffusion as well as downward diffusion of oxygen atom on different crystal facets of Ag, including (1 1 1), (1 1 0), (1 0 0) and (2 1 1) surfaces. Among all studied crystal facets, the horizontal diffusion of surface atomic oxygen is most favorable on Ag (1 1 1) surface, while Ag (1 1 0) surface is the most beneficial to horizontal diffusion of subsurface atomic oxygen. It is also found that the atomic oxygen prefers to downward diffuse on Ag (1 1 0) surface rather than downward diffuse on other surfaces. The deep insight revealed here may guide to engineer Ag surface to promote the formation of surface and subsurface atomic oxygen, and accordingly pave the avenue for the rational design of Ag catalyst for ethylene epoxidation.

1. Introduction

Ethylene epoxidation reaction is a crucial heterogeneous catalytic process, since its selective product, ethylene oxide (EO), has a wide application in the chemical industry [1]. The competition between the desired epoxidation reaction and the undesired complete combustion reaction of ethylene decides the selectivity towards EO in the ethylene epoxidation reaction [2]. Ag is a remarkably efficient catalyst for this reaction, with a selectivity up to 50% [3,4]. Accordingly, a rational design of Ag catalysts for ethylene epoxidation reaction, which can therefore enhance the selectivity toward EO, has attracted great interest from both experimental and theoretical fields [5–7].

According to the detection by the spectroscopic methods [8,9], researchers have reached a consensus that the surface O atom (O_s) is the active species in Ag catalyst during the ethylene epoxidation reaction [10–15]. Early studies [16–18] found that the selectivity toward EO is dependent on surface oxygen coverage (θ_{O_s}). Later, the experimental and theoretical [19–21] works have shown that the selectivity to EO would be enhanced with the increase of the θ_{O_s}. Jacob and his coworkers [19] used the aberration-corrected transmission electron microscope (AC-TEM) and density functional theory (DFT) calculations to study the role of O_s in Ag surfaces during the ethylene epoxidation. They demonstrated that O_s is beneficial to improve the selectivity to

EO. Moreover, the subsurface atomic oxygen (O_{sub}) has also been characterized in previous studies by using X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption spectroscopy (TPD), which found that the O_{sub} would play an important role in selectivity improvement [19,22–25]. The significant effect of the O_{sub} on the ethylene epoxidation as well as the electronic structure of O_{sub} has also been explored theoretically, which indicated that the O_{sub} is crucial to enhance the selectivity to EO [10,19,25–28]. In addition, Ozbek et al. [29–31] have studied the atomic-scale mechanism on oxidation state of Ag catalysts during ethylene epoxidation, and found that the selectivity to EO on Ag surfaces accompanied by surface and subsurface O atom is higher than that on pure Ag surfaces. Despite the great progress made by the systematic researches above, a full understanding of the adsorption and diffusion of atomic oxygen, the essential process to form O_s and O_{sub}, remains elusive, which may hinder the approach to rationally design Ag catalysts with enhanced selectivity through exposing appropriate crystal surfaces.

In our work, we investigate the adsorption and diffusion of atomic oxygen on different Ag crystal facets, including Ag (1 1 1), (1 1 0), (1 0 0) and (2 1 1) surfaces, by using DFT calculations. We first study the stability of surface and subsurface atomic oxygen on different Ag crystal facets. In the following, the horizontal diffusion as well as the downward diffusion of O_s and O_{sub} has been discussed. This work may

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Table 1

The adsorption energies (E_{ads}, in eV), average lengths of AgsbndO bonds (d_{Ag-O}, in Å) and perpendicular distance (d_{o-sur}, in Å) between atomic oxygen and corresponding nearest Ag surface. For the oxygen atom on first and second subsurface, the adsorption site of fcc, hcp, B, 3F and 4F represent the adsorption sites which are under corresponding surface adsorption site: fcc, hcp, B, 3F and 4F, respectively. The symbol "–" represent unstable adsorption sites for the atomic oxygen.

	Surface O			First subsurface O			Second subsurface O		
	E_{ads}	d_{Ag-O}	d_{o-sur}	E_{ads}	d_{Ag-O}	d_{o-sur}	E_{ads}	d_{Ag-O}	d_{o-sur}
Ag (1 1 1)									
fcc	−3.38(−3.61[a])	2.16[b]	1.16	−2.83[b]	2.25	1.59	−1.83	2.11	1.98
B	−3.38(fcc)	2.16	1.16	−2.83	2.25	1.60	−1.83	2.11	2.02
hcp	−3.27(−3.43[a])	2.16	1.19	−2.73	2.11	1.73	−2.37	2.27	2.25
Ag (1 1 0)									
4F	−3.23	2.71	1.23	–	–	–	–	–	–
LB	−3.19	2.22	0.82	–	–	–	−2.50	2.15	0.52
SB	−2.80	2.76	1.33	−2.53	2.14	0.66	−2.28	2.25	0.67
Ag (1 0 0)									
B	−3.61(4F$_1$)	–	–	–	–	–	−1.79	2.10	0.91
4F	−3.61(−3.47[c])	2.12	0.69	–	–	–	−2.14	2.23	0.81
Ag (2 1 1)									
B$_1$	−3.20(3F$_2$)	2.34	1.01	–	–	–	−1.14	2.10	0.93
B$_2$	–	–	–	–	–	–	−2.55	1.85	1.06
B$_3$	−3.39(4F$_2$)	2.29	1.21	–	–	–	−2.31	2.09	1.02
3F$_1$	−3.13	2.36	1.40	–	–	–	−2.16	1.80	1.71
3F$_2$	−3.20	2.34	1.02	–	–	–	−1.15	2.10	1.30
4F	−3.39	2.29	1.20	–	–	–	−1.04	2.09	1.03

[a] Ref. [22].
[b] Ref. [23].
[c] Ref. [48].

provide helpful information to further understand the facet-dependent formation of the surface and subsurface O atoms on Ag surface during ethylene epoxidation reaction.

2. Theoretical methods

The periodic density functional theory (DFT) calculations were performed by the PWscf (Plane-Wave Self-consistent Field) code in the Quantum ESPRESSO (QE) package [32]. The Perdew-Burke-Ernzerhof (PBE) [33] exchange-correction functional and the ultrasoft pseudo potentials (USPP, from PSlibrary) [34–37] of Generalized gradient approximation (GGA) were employed. The theoretical lattice constant of Ag was calculated to be 4.16 Å, which agrees well with the experimental value (4.09 Å) [6,38,39]. Ag (1 1 1), (1 1 0), (1 0 0), and (2 1 1) surfaces were simulated by using a symmetric periodic slab model with a vacuum region of 15 Å between the slabs in order to eliminate the dipole moment and the surface-surface interaction. Ag (1 1 1), (1 1 0), (1 0 0) and (2 1 1) surfaces were modeled containing a five-layers-thick p (3 × 3) slab to achieve the periodicity (see Fig. S1). For the Ag (2 1 1) surface, we regarded each adjacent three atomic layers as one layer. Monkhorst-Pack [40] 3 × 3 × 1 k-point gird was chosen to sample the Brillouin zone for optimizing the geometry while 12 × 12 × 1 k-point was used to calculate the density of state (DOS). The d-band center was calculated by analyzing the projected DOSs on d-orbital of the surface atoms based on the following equation

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} \rho_{DOS} E dE}{\int_{-\infty}^{+\infty} \rho_{DOS} dE} \quad (1)$$

in which the ε_d is the d-band center, ρ_{DOS} is the projected d-band DOS, and E is energy level. Self-consistent-field (SCF) procedure was employed until the total energy is converged to be 1×10^{-6} Ry. During the structural optimization, all atoms except the bottom two Ag layers were fully relaxed until the maximum force component of the system converge to be 0.02 eV/A. The values of 45 and 450 Ry were used as the energy cutoffs to describe the wave function and the electron density, respectively. The free oxygen molecule in ground state is triplet and the adsorption of atomic oxygen on Ag surfaces may also have spin density, therefore, the spin polarized was considered in our calculations. The Fermi energy level was broadened using the Gaussian smearing technique with a smearing parameter of 0.002 Ry.

The adsorption energy (ΔE_{ads}) was calculated using the following formula

$$\Delta E_{ads} = E_{slab+adsorbate} - E_{adsorbate} - E_{slab} \quad (2)$$

where $E_{slab+adsorbate}$ is the total energy of the slab and adsorbate system, $E_{adsorbate}$ is the energy of the adsorbate, and E_{slab} is the energy of the slab. According to this definition, a negative (positive) value of ΔE_{ads} indicates that the adsorption is exothermic (endothermic).

To investigate the minimum-energy pathways (MEP) of atomic oxygen diffusion, the climbing image nudged elastic band (CI-NEB) method was used. Meanwhile, seven configurations including endpoints were used to describe the pathway between the different states. And the simulation would stop until the force orthogonal is less than 0.01 eV/Å. Vibrational frequency analysis was done to verify the identified translation state (TS). The activation energy barrier (ΔE_a) for each reaction step was calculated according to the following equation

$$\Delta E_a = E_{TS} - E_{IS} \quad (3)$$

in which IS and TS represent the initial and transition state of the reaction, respectively.

The surface energy was calculated by using the following equation [41–43]:

$$E_{surf} = \frac{\left[E_{slab} - \left(\frac{N_{slab}}{N_{bulk}} \right) E_{bulk} \right]}{2 A} \quad (4)$$

where E_{surf}, E_{slab}, N_{slab}, N_{bulk}, and A are the surface energy, the total