materials

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Supplementary Materials

Theoretical Study of As_2O_3 Adsorption Mechanisms on CaO surface

Yaming Fan [1,2,†], Qiyu Weng [2,3,4,†], Yuqun Zhuo [2,3,4,*], Songtao Dong [1], Pengbo Hu [2,3,4] and Duanle Li [2,3,4]

1 Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China; fanymthu@163.com (Y.F.); dongst.ripp@sinopec.com (S.D.)
2 Key Laboratory for Thermal Science and Power Engineering of the Ministry of Education, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China; wqy17@mails.tsinghua.edu.cn (Q.W.); hupb18@mails.tsinghua.edu.cn (P.H.); liduanle@163.com (D.L.)
3 Tsinghua University-University of Waterloo Joint Research Center for Micro/Nano Energy and Environment Technology, Tsinghua University, Beijing 100084, China
4 Beijing Engineering Research Center for Ecological Restoration and Carbon Fixation of Saline–alkaline and Desert Land, Tsinghua University, Beijing 100084, China
* Correspondence: zhuoyq@mail.tsinghua.edu.cn
† These authors contributed equally to this work

Optimization of slab model

CaO (001) is a typical surface in describing CaO [1,2] surface. The surface size (1×1, 2×2, 3×3, 4×4) and layers (2, 3, 4, 5 and 6) of the slab models were optimized to their physical and chemical properties. The physical property included the z_{layers} (layer thickness) and $z_{Ca\text{-}O}$ (superficial average Ca-O distance). The chemical property included E_{ads} (adsorption energy of As^0), which could reflect CaO's property of capturing As_2O_3.

The Δz_{layers}, $\Delta z_{Ca\text{-}O}$ and E_{ads_mean} was defined as follows:

$$\Delta z_{layers} = | z_{layers\_relaxed} - z_{layers\_fixed} | \quad (1)$$

$$\Delta z_{Ca\text{-}O} = | z_{Ca\text{-}O\_relaxed} - z_{Ca\text{-}O\_fixed} | \quad (2)$$

$$\Delta E_{ads} = | E_{ads} - E_{ads\_mean} | \quad (3)$$

The suffix of 'fixed' represented that the surface layer of slab models was fixed, while 'relaxed' represented the opposite. The suffix of 'mean' represented the mean adsorption energy.

Table S1: Changes in physical and chemical properties of different surface size.

surface size	Δz_{layers}, Å	$\Delta z_{Ca\text{-}O}$, Å	ΔE_{ads}, kJ/mol
1×1	7.9×10^{-2}	7.0×10^{-5}	62.2
2×2	7.9×10^{-2}	6.0×10^{-5}	10.3
3×3	7.8×10^{-2}	6.0×10^{-5}	4.5
4×4	7.7×10^{-2}	6.0×10^{-5}	5.8

The *a*×*a*-surface (*a*=1, 2, 3 and 4) slab models (layer is fixed as 4 layers) were constructed and optimized. The changes in physical and chemical properties are shown in Table 2. Among the models, the 3×3-surface model has the second lowest Δz_{layers} (7.8×10^{-2} Å), the lowest $\Delta z_{Ca\text{-}O}$ (6.0×10^{-5} Å) and the lowest ΔE_{ads} (4.5 kJ/mol). The model surface size was therefore optimized as 3×3. The average adsorption energy E_{ads_mean} did not include the 1×1-surface model due to the obvious large difference (62.2 kJ/mol).

Table S2: Changes in physical and chemical properties of different layers.

layers	Δz_{layers}, Å	$\Delta z_{Ca\text{-}O}$, Å	ΔE_{ads}, kJ/mol
2	7.3×10^{-2}	1.0×10^{-4}	1.1
3	7.1×10^{-2}	9.2×10^{-5}	0.7
4	5.0×10^{-2}	9.0×10^{-5}	0.3
5	7.2×10^{-2}	1.0×10^{-4}	0.9
6	7.3×10^{-2}	1.0×10^{-4}	0.7

The layer thickness was then optimized based on the 3×3-surface size. As shown in Table 3, the 4-layer model has demonstrated acceptable physical and chemistry properties (lowest Δz_{layers}, lowest $\Delta z_{Ca\text{-}O}$, lowest ΔE_{ads}). As the consequent, the 4-layer 3×3-surface slab model was selected to simulate the adsorption of As_2O_3 on CaO surface in this study.

Initial adsorbate structures

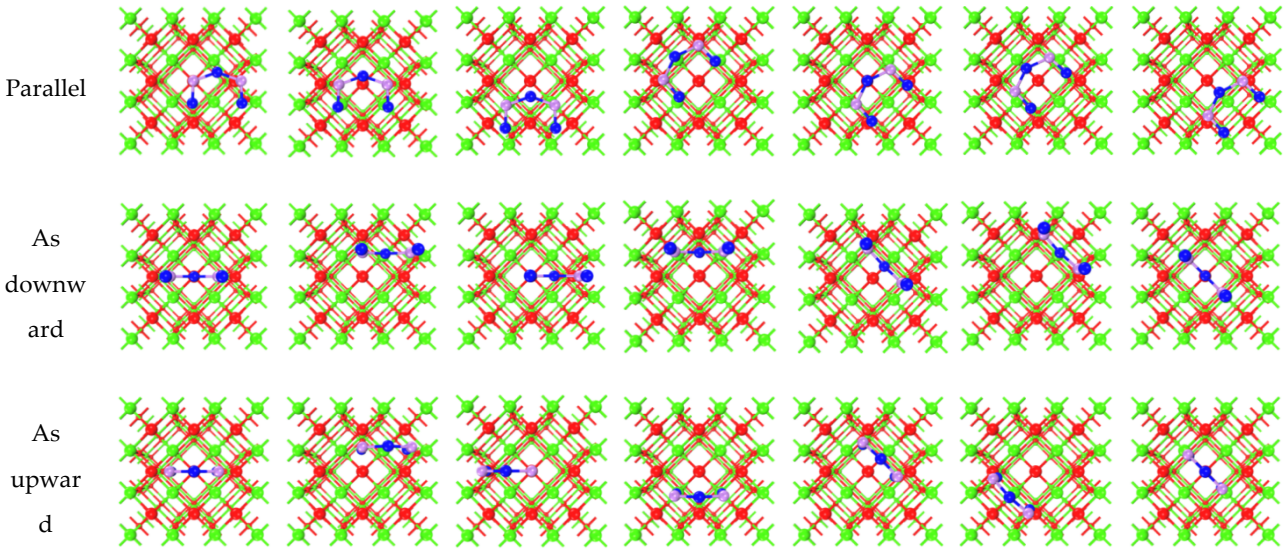

Figure S1: Initial adsorbate structures.

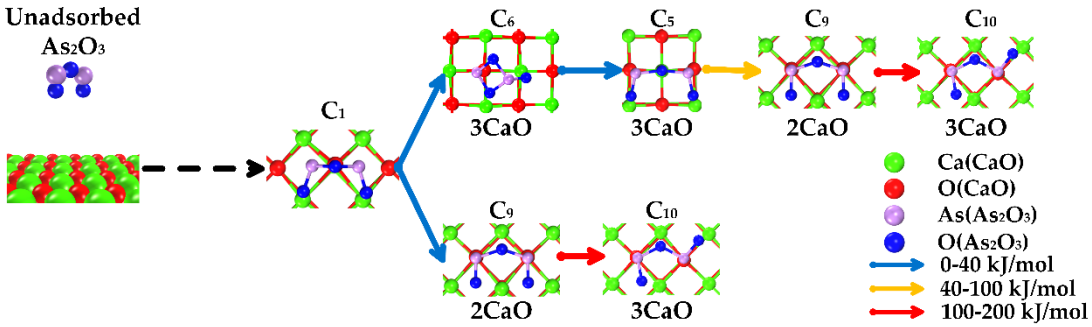

Figure S2: Paths and structures of the physisorption and chemisorption reaction from chemisorption structure 1.

PDOS Analysis

PDOS (Partial Density of States) was calculated to describe the electronic structure changes of As_2O_3 and CaO slab model surface during adsorption. Both the PDOS of physisorption structures and chemisorption structures are selected for discussion here.

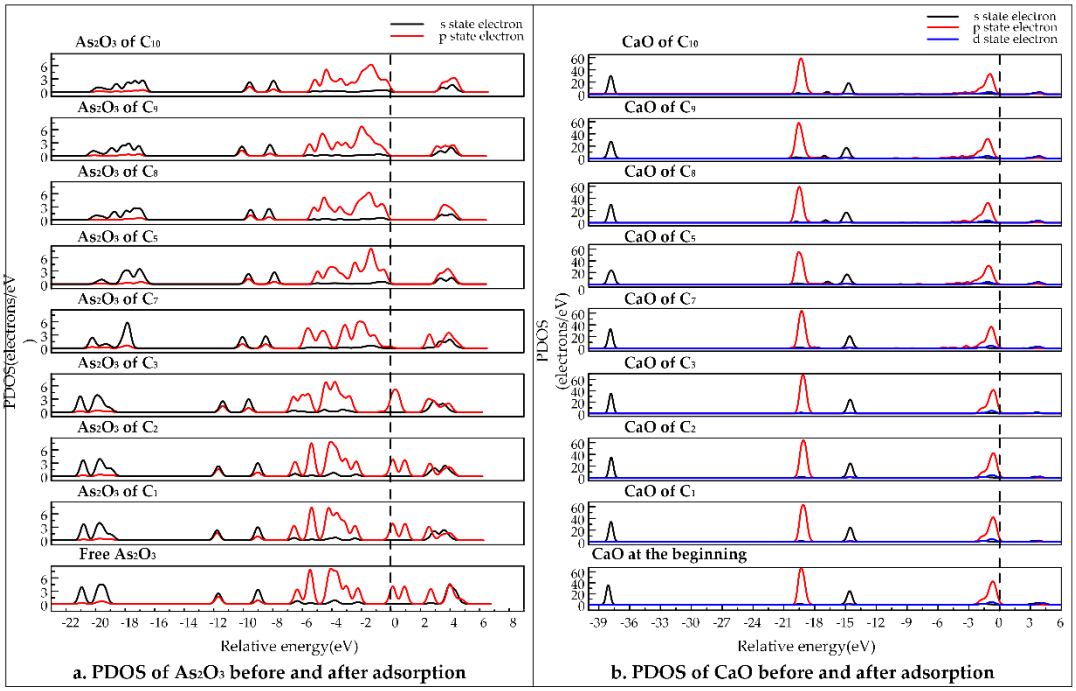

Figure S3: PDOS of As_2O_3 and CaO surface during physisorption and chemisorption (a. PDOS of As_2O_3 molecule; and b. PDOS of CaO surface).

Reference

1. Di Valentin, C.; Pacchioni, G.; Bernasconi, M. Ab initio molecular dynamics simulation of NO reactivity on the CaO (001) surface. *J. Phys. Chem. B* **2006**, *110*, 8357-8362.

2. Xin, G.; Zhao, P.; Zheng, C., Theoretical study of different speciation of mercury adsorption on CaO (001) surface. *Proc. Combust. Inst.* **2009**, *32*, 2693-2699.