Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Supporting Information

First principle and experimental studies on $[ZrO(OH)]^+$ or $ZrO(OH)_2$ for enhancing $CO_2$ desorption kinetics – imperative to significant reduction of $CO_2$ capture energy consumption

*Ye Wu[a,b]†, Tianyi Cai [c]†, Wenwen Zhao[a, b], Xiaoping Chen [c]*, Hongyan Liu[d], Yujun Wang[e], Armistead G. Russell[f], Maohong Fan[f,g]*, Dong Liu [a, b]*

[a]*MIIT Key Laboratory of Thermal Control of Electronic Equipment, School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China.*

[b]*Advanced Combustion Laboratory, School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China.*

[c]*Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy & Environment, Southeast University, Nanjing 210096, People's Republic of China.*

[d]*Departments of Chemical and Petroleum Engineering, University of Wyoming, 1000 E University Avenue, Laramie, WY 82071, USA.*

[e]*State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*

[f]*School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA.*

[g]*Departments of Chemical and Petroleum Engineering, University of Wyoming, 1000 E University Avenue, Laramie, WY 82071, USA.*

†*: Ye Wu and Tianyi Cai are co-first authors because they contributed equally to the work.*

**: Maohong Fan and Xiaoping Chen are co-corresponding authors because both of them supervised this work*

Table S1 the calculated and experimental lattice constants of bulk $ZrO_2$

| | crystal parameter(°) | cell volume(Å$^3$) | lattice parameter(Å) |
|---|---|---|---|
| before geom. opt. | α=γ=90, β=99.23 | 140.456 | a=5.145, b=5.208, c=5.311 |
| after geom. opt. | α=γ=90, β=99.03 | 141.881 | a=5.130, b=5.235, c=5.349 |
| experiment value[38] | α=γ=90, β=99.15 | 140.635 | a=5.145, b=5.202, c=5.322 |
| relative error | 0.10% | 0.88% | 0.29%, 0.63%, 0.51% |

The definition of surface energy ($\gamma$, J/m$^2$), adsorption energy ( $E_{ads}$, eV), and interaction energy ( $E_{inter}$, eV) are described as bellow:

$$\gamma = (E_{slab} - n \times E_{bulk})/2A \quad \text{ES1}$$

$$E_{ads} = E_{slab} + E_{molecule} - E_{molecule/slab} \quad \text{ES2}$$

$$E_{inter} = E_{CO_2+H_2O+slab} + E_{slab} - E_{CO_2+slab} - E_{H_2O+slab} \quad \text{ES3}$$

In equation ES1 and ES2, $E_{slab}$, $E_{bulk}$, $E_{molecule/slab}$ and $E_{molecule}$ is the energy of the clean surface slab, the bulk crystal unit, the surface slab together with the adsorbed molecules, the free molecules in the vacuum respectively, and n is the multiple value which the number of atoms containing in slab divided by bulk crystal, A is the total area including both top and bottom surfaces of the periodic surface slab. With this definition, the bigger positive value of adsorption energy implies more advantageous adsorption. In equation ES3, $E_{CO_2+H_2O+slab}$, $E_{CO_2+slab}$ and $E_{H_2O+slab}$ is the total energy of the surface slab together with the two adsorbed molecules $H_2O$ and $CO_2$, the slab system for single $CO_2$ adsorption, the slab system for single $H_2O$ adsorption, respectively. With this definition, the negative and positive value of the interaction energy implies it is advantageous and disadvantageous to the two molecules co-adsorption on the surface plane, respectively.

For the reaction the molecules adsorbed on the surface slab, the molecule was decomposed to one and another species which can be expressed as $AB \rightarrow A + B$

adsorbed on plane surface. The reaction energy ($\Delta E_r$, eV) and activation barrier energy ($\Delta E_a$, eV) are calculated on the basis of the following formulas:

$$\Delta E_r = E_{A+B/slab} - E_{AB/slab} \quad \text{ES4}$$

$$\Delta E_a = E_{TS/slab} - E_{AB/slab} \quad \text{ES5}$$

Where $E_{AB/slab}$ is the total energy of the adsorbed AB, $E_{A+B/slab}$ is the total energy of the co-adsorbed A and B on slab surface, and $E_{TS/slab}$ is the total energy of transition state on slab surface.

Table S2 the surface energy of different low index surfaces and terminations of $ZrO_2$

| | (010) | (111) | (-111) | (001)t1 | (001)t2 | (001)t3 | (001)t4 | (001)t5 | (001)t6 |
|---|---|---|---|---|---|---|---|---|---|
| $\gamma$ ($J/m^2$) | 0.126 | 0.088 | 0.076 | 0.070 | 0.177 | 0.258 | 0.142 | 0.296 | 0.178 |

Note: The t1-t6 in the table refers to the termination 1- 6.

Figure S1 the side view of different low index surfaces and terminations of $ZrO_2$