SUPPORTING INFORMATION

Effects of oxygen chemical potential on the anisotropy of adsorption properties of Zr surfaces

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Zr(0001) surface

Zr(11Error!0) surface

Table S1 The adsorption energy (E_{ad} , in eV/atom) of O on Zr(0001) computed by the MLAM method. We use monolayer, i.e., ML, to denote the coverage.

	Adsorption sites	E_b
0.5ML	fcc+oc1:2	-9.07
	fcc+oc2:3	-9.25
	fcc+oc3:4	-9.20
	oc1:2+oc2:3	-8.65
	oc1:2+oc3:4	-8.84
	oc2:3+oc3:4	-8.88
0.75ML	fcc+oc1:2+oc2:3	-8.99
	fcc+oc1:2+oc3:4	-9.07
	fcc+oc2:3+oc3:4	-9.05
	oc1:2+oc2:3+oc3:4	-8.67
1.0ML	$f_{cc+oc1} + 2 + oc2 + 3 + oc3 + 4$	-8 89

Table S2 The adsorption energy (E_{ad} , in eV/atom) of O on

Zr(11Error!0) computed by the MLAM method.

	Adsorption sites	E_b
0.5 ML	bri2+oc1:3	-8.59
	bri2+oc2:4	-8.67
	bri2+oc3:5	-8.69
	bri2+oc4:6	-8.69
	oc1:3+oc1:3	-8.66
	oc1:3+oc2:4	-8.88
	oc1:3+oc3:5	-9.01
	oc1:3+oc4:6	-9.06
	oc2:4+oc3:5	-8.93
	oc2:4+oc4:6	-8.98
	oc3:5+oc3:5	-8.58
	oc3:5+oc4:6	-8.98
0.75 ML	bri2+oc1:3+oc2:4	-8.67
	bri2+oc1:3+oc3:5	-8.71
	bri2+oc2:4+oc3:5	-8.73
	bri2+oc2:4+oc4:6	-8.77
	oc1:3+oc1:3+oc2:4	-8.71
	oc1:3+oc1:3+oc3:5	-8.79
	oc1:3+oc3:5+oc3:5	-8.78
	oc1:3+oc2:4+oc3:5	-8.83
	oc1:3+oc2:4+oc4:6	-8.93
	oc1:3+oc3:5+oc4:6	-8.97
	oc2:4+oc3:5+oc4:6	-8.87
1.0 ML	bri2+oc2:4+oc4:6+oc6:8	-8.78
	oc1:3+oc1:3+oc3:5+oc3:5	-8.60
	oc1:3+oc1:3+oc4:6+oc4:6	-8.69
	oc1:3+oc2:4+oc3:5+oc4:6	-8.83
	oc1:3+oc2:4+oc4:6+oc6:8	-8.94
	oc2:4+oc3:5+oc4:6+oc6:8	-8.91
	oc2:4+oc4:6+oc5:7+oc6:8	-8.91
	oc3:5+oc4:6+oc5:7+oc6:8	-8.90

As shown in Fig. S1, we select 7 inequivalent high symmetry sites on Zr(10Error!0) surface to investigate the adsorption properties. These high symmetry sites include: two on-top sites (top1, top2), three bridge sites (bri1, bri2 and bri3), and three three-fold-hollow sites (t1 and t2). The adsorption energies of O at different sites on Zr(10Error!0) are listed in Table S3. We find the adsorption of O on T2 site of the surface is the most favourable, and the adsorption of O at top site is the most unstable.



Fig. S1 The top view of Zr(10**Error!**0) surface with possible O adsorption sites. The blue and pink balls denote Zr atoms in the first and second layers respectively.

Table S3 Adsorption energies (in eV) at different sites on Zr(10**Error!**0)

site	top1	top2	bri1	bri2	T1	T2
E_b	-6.919	-6.680	-8.650	-8.901	-9.025	-9.108



Fig. S2 The side view of Zr(10**Error!**0) surface. The octahedron and tetrahedron adsorption sites in subsurface are marked by square and diamond respectively.

Fig. S2 illustrates the side view of atomic structures and high symmetry sites in the outmost four sites with different depth, and Fig. S3 shows the adsorption energies of O adsorption at these high symmetry sites. The adsorption energies of O at octahedron sites are lower than that of O at tetrahedron sites, indicating that the penetration of single O atom into oc sites of subsurface is more energy favourable. Furthermore, the adsorption energies of O at sites in deep layers are lower than these of O at sites in shallow layers, which leads that O atom penetrates more deeply into subsurface layers. We notice that, on the contrary, O in deep layer of Zr(0001) surface is less favourable than that of Zr(10**Error!**0) surface. Therefore, we can infer that O on Zr(10**Error!**0) surface can penetrate into subsurface more easily than O on Zr(0001) surface does.



Fig. S3 Adsorption energies of oxygen at different adsorption sites of Zr(10 Error !0) surface as a function of the distance from the surface.

Then, we calculate the O adsorption at different coverage using the MALM method, and the results are shown in Table S4. For the 0.5 ML coverage, the adsorption on the combination of oc3:6 and oc7:10 is the most favourable. For the 0.75 ML coverage, the adsorption on the combination of oc3:6, oc5:8 and oc7:10 is the most favourable. For the 1 ML coverage, the adsorption on the combination of oc1:4, oc3:6, oc5:8 and oc7:10 is the most favourable. The behaviour of adsorption of O on Zr(10Error!0) is very similar to that of O on Zr(11Error!0) surface. For the 0.25, 0.50 and 0.75ML, the adsorption energy of O on Zr(0001) is lower than that of O on Zr(10Error!0) is lower than that of O on Zr(0001).

Finally, we calculate the Gibbs free surface energy of the surface with O adsorption to investigate the surface stability. Fig. S4 shows Gibbs free surface energies of Zr(10Error!0) surface with O adsorption as functions of O chemical potential. Like Zr(0001) and Zr(11Error!0), the surface with one O atom is the most stable configuration under the strong

O-reducing condition, while the surface with 4 O atoms is the most stable configuration under the weak O-reducing or the O-rich condition. The surface with 1 O atom at oc7:10 site is most stable under the strong O-reducing. In contrast, the surface with 4 O atoms on the combination of oc1:4, oc3:6, oc5:8 and oc7:10 sites is the most stable under weak O-reducing or the O-rich condition.

As shown in Fig. S5, we also can compare the Gibbs free surface energy variation and Gibbs free surface energy of Zr(10Error!0) with Zr(0001) and Zr(11Error!0). The Zr(10Error!0) and Zr(11Error!0) have similar properties when we consider the relative stability compared to (0001) in environment with different chemical potential.

Table S4 The adsorption energy (E_{ad} , in eV/atom) of O on Zr(10**Error!**0) computed by the MLAM method.

	Adsorption sites	E_{h}
0.5 ML	T1+oc1:4	-7.854
	T1+oc3:6	-7.952
	T1+oc5:8	-7.949
	T1+oc7:10	-7.961
	oc1:4+oc3:6	-8.964
	oc1:4+oc5:8	-9.015
	oc1:4+oc7:10	-9.014
	oc3:6+oc5:8	-9.038
	oc3:6+ oc3:6	-8.951
	oc3:6+oc7:10	-9.092
	oc7:10+oc7:10	-9.076
	oc5:8+oc7:10	-9.045
0.75 ML	T1+oc1:4+oc3:6	-8.233
	T1+oc1:4+oc5:8	-8.266
	T1+oc1:4+oc7:10	-8.264
	T1+oc3:6+oc5:8	-8.295
	T1+oc3:6+oc7:10	-8.335
	T1+oc5:8+oc7:10	-8.302
	oc1:4+oc3:6+oc5:8	-8.976
	oc1:4+oc3:6+oc7:10	-9.006
	oc1:4+oc5:8+oc7:10	-9.008
	oc3:6+ oc3:6+oc7:10	-9.003
	oc3:6+oc5:8+oc7:10	-9.034
1.0 ML	T1+oc1:4+oc3:6+oc5:8	-8.42
	T1+oc1:4+oc5:8+oc7:10	-8.451
	T1+oc3:6+oc5:8+oc7:10	-8.479
	oc1:4+ oc1:4+oc5:8+ oc5:8	-9.042
	oc3:6+oc3:6+oc7:10+oc7:10	-9.021
	oc1:4+oc3:6+oc5:8+oc7:10	-9.059



Fig. S4 The Gibbs free surface energies of Zr(10**Error!**0) surface with O adsorption.



Fig. S5 (a) The variation of Gibbs free surface energies when the O atom is adsorbed on the surface. (b) The Gibbs free surface energies of surfaces with O adsorption.



Fig. S6 The dependence of difference between adsorption energies of O at fcc and hcp sites on (0001) sites (E_{fcc} and E_{hcp}) on kinetic energy cutoff

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To check the effect of the kinetic energy on our calculation, we compute the adsorption energies of O at fcc and hcp sites on Zr(0001)-(1×1) surface by using different kinetic energies. Since the relative stability of O in different sites is the key issue in the calculations, we present the tests about the difference in O at two different sites. As shown in Fig. S6, we plot the dependence of the difference in the adsorption energy of O at fcc and hcp sites on the kinetic energy. It indicates that these values have converged in the calculation at a precision of 0.01 eV/atom when the kinetic energy is more than 270 eV.