## **Supporting Information**

# $SO_x$ Oxidation Kinetics on Pt(111) and Pd(111): First Principles Computations Meet Microkinetic Modeling

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#### S.1 Structural details

The calculated bulk lattice constant of Pt and Pd were 3.97 Å and 3.95 Å respectively, which are in good agreement with previous theoretical calculations (Pt,  $a_o = 3.96$  Å–4.0 Å<sup>S1–S3</sup> and Pd,  $a_o = 3.94$  Å– 3.97 Å<sup>S3–S5</sup> as well as experimental (Pt,  $a_o = 3.92$  Å<sup>S3,S6</sup> and Pd,  $a_o = 3.89$ Å<sup>S3,S7</sup>) results. The calculated cohesive energies were 5.6 eV/atom (experimental E<sub>cohesive</sub> = 5.8 eV/atom<sup>S8</sup>) and 3.7 eV/atom (experimental E<sub>cohesive</sub> = 3.89 eV/atom<sup>S7</sup>) for Pt and Pd respectively.

Surface work function ( $\varphi$ ) calculated for Pt and Pd slabs were 5.78 eV and 5.05 eV, respectively, which are consistent with the corresponding experimental values of 5.8 eV<sup>S8</sup> and 5.0 eV<sup>S9</sup>, respectively. Furthermore, the calculated surface energies were 97.9 meV/Å<sup>2</sup> and 82.4 meV/Å<sup>2</sup> for Pt(111) and Pd(111), which are in agreement with previous DFT studies.<sup>S10</sup> Our DFT calculations are in close agreement with experimental values for bond angles and bond lengths for gas phase SO<sub>x</sub> species available in Computational Chemistry Comparison and Benchmark Data-Base by National Institute of Standards and Technology (NIST).<sup>S11</sup>

The binding energy,  $E_b$ , of an atom or a molecule on the slab is defined as.

$$E_b = -[E_{slab+adsorbate} - E_{slab} - E_{adsorbate}] \tag{1}$$

where  $E_{slab+adsorbate}$ ,  $E_{slab}$ , and  $E_{adsorbate}$  represent the energy of the slab with the atom/molecule, energy of the clean slab, and the energy of an isolated atom/molecule, respectively. The  $E_b$ values are positive numbers, where the increase in positive number indicates the strong binding to the surface.

For each minimum energy path (MEP) from the CI-NEB<sup>S12</sup>, we calculated the activation energy barrier,  $E_{act}$  as.

$$E_{act} = E_{TS} - E_{IS} \tag{2}$$

where  $E_{TS}$  and  $E_{IS}$  represent the energy of the transition state, and energy of initial state (reactants) respectively.

#### S.2 Binding energy and adsorption geometry

Table S1: Bond lengths (Pt/Pd-S, Pt/Pd-O, S-O), bond angles (OSO), and binding energies of the stable configurations of oxygen (O), and sulfur oxides (SO<sub>x</sub>) adsorbed on Pt(111) and Pd(111) Surfaces. Total number of identical bond lengths and bond angles of that particular configuration are reported in parentheses, which arises from the symmetry of the adsorbed molecule.

Molecule	Conformation	Pt(111) surface Pd(111) surface									
		Bond leng	th(Å)		Bond $angle(^{o})$	Binding energy	Bond leng	th(Å)		Bond $angle(^{o})$	Binding energy
		Pt–O	Pt–S	S–O	∠OSO	$(\rm kcal/mol)$	Pd–O	Pd-S	S–O	∠OSO	$(\rm kcal/mol)$
$SO_4$	$(fcc)\eta^3 - O_a O_a O_a$	$2.09(\times 3)$		1.43	$108.6(\times 3)$	87.2	$2.09(\times 3)$		1.44	$108.6(\times 3)$	85.1
				$1.53(\times 3)$	$110.3(\times 3)$				$1.53(\times 3)$	$110.3(\times 3)$	
$SO_4$	$(hcp)\eta^3 - O_a O_a O_a$	$2.10(\times 3)$		1.43	$108.5(\times 3)$	87.2	$2.09(\times 3)$		1.43	108.5	85.1
				$1.53(\times 3)$	$110.3(\times 3)$				$1.53(\times 3)$	$110.4(\times 3)$	
$SO_3$	$(fcc)\eta^3 - S_aO_aO_a$	$2.13(\times 2)$	2.28	1.44	106.6	30.8	2.18	2.25	1.45	109.3	27.6
				$1.54(\times 2)$	111.0				$1.52(\times 2)$	112.7	
$SO_3$	$(hcp)\eta^3 - S_aO_aO_a$	$2.13(\times 2)$	2.27	1.44	107.0	30.3	$2.19(\times 2)$	2.25	1.45	109.5	27.4
				$1.55(\times 2)$	111.1				$1.52(\times 2)$	112.6	
$SO_3$	$(fcc)\eta^3$ – $O_aO_aO_a$	$2.11(\times 3)$		$1.55(\times 3)$	$107.1(\times 3)$	27.0	$2.11(\times 3)$		$1.54(\times 3)$	$107.4(\times 3)$	26.9
$SO_3$	$(hcp)\eta^3 - O_a O_a O_a$	$2.11(\times 3)$		$1.55(\times 3)$	$107.0(\times 3)$	27.0	$2.11(\times 3)$		$1.54(\times 3)$	$107.5(\times 3)$	26.8
$SO_2$	$(fcc)\eta^2 - S_aO_a$	2.32	2.27	1.45	114.5	27.2	2.32	2.28	1.46	113.6	26.7
				1.51					1.50		
$SO_2$	$(hcp)\eta^2 - S_aO_a$	2.33	2.28	1.45	114.6	25.2	2.33	2.27	1.46	114.5	26.1
				1.51					1.52		
$SO_2$	$(bridge)\eta^1 - S \perp$		2.29	$1.46(\times 2)$	117.3	24.6		2.26	$1.47(\times 2)$	116.7	26.2
$SO_2$	$(fcc)\eta^3 - S_aO_aO_a$	$2.16(\times 2)$	2.30	$1.54(\times 2)$	108.1	23.7	$2.22(\times 2)$	2.28	$1.52(\times 2)$	111.2	23.9
$SO_2$	$(hcp)\eta^3-S_aO_aO_a$	$2.17(\times 2)$	2.30	$1.54(\times 2)$	108.5	23.1	$2.22(\times 2)$	2.28	$1.51(\times 2)$	111.2	23.8
SO	$(fcc)\eta^1-S_f$		$2.24(\times 3)$	1.46		69.5		$2.20(\times 3)$	1.47		66.8
SO	$(hcp)\eta^1 - S_h$		$2.24(\times 3)$	1.46		66.8		$2.20(\times 3)$	1.47		66.2
SO	$(fcc)\eta^2 - S_bO_a$	2.15	$2.27(\times 2)$	1.56		64.6	2.19	$2.22(\times 2)$			60.2
SO	$(hcp)\eta^2 - S_bO_a$	2.16	$2.27(\times 2)$	1.57		63.5	2.20	$2.23(\times 2)$			59.5
S	$(fcc)\eta^1 - S_f$		$2.27(\times 3)$			122.2		$2.23(\times 3)$			115.1
S	$(hcp)\eta^1 - S_h$		$2.27(\times 3)$			117.7		$2.24(\times 3)$			107.6
0	$(fcc)\eta^1-O_f$	$2.05(\times 3)$				98.6	$2.00(\times 3)$				99.7
0	$(hcp)\eta^1 - O_h$	$2.04(\times 3)$				90.2	$2.00(\times 3)$				95.3
0	$({\rm atop})\eta^1 – {\rm O}_a$	$1.82(\times 3)$				69.7	$1.81(\times 3)$				64.3

Table S1 contains the computed structural parameters of SO<sub>x</sub> (x = 0-4) species on both surfaces. In the conformation notation, the number super-scripted to  $\eta$  represents the number of atoms in a molecule coordinated to the metal (111) surface, and the subscripts a, b, f, and h stand for the atoms on atop sites, bridge sites, fcc hollow sites, and hcp hollow sites, respectively. The  $\eta^1$ -S $\perp$  notation represents the S atom in SO<sub>2</sub> molecule with 2 O atoms attached only with S atom (unbound to the metal surface). From Table S1, it has been observed that the metal to sulfur (M-S) bond lengths were relatively shorter in for the Pd(111) surface. However, no such pattern was observed for metal to oxygen (M-O) and sulfur to oxygen (S-O) bonds. The increase in interatomic bond length was quite large when both atoms directly attached to the surface compared to the case when one atom is attached. The shortest metal sulfur bond (2.20 Å) was for SO molecule where S is attached to 3 metal atoms in fcc position. The S-O bond (O unbound to the metal) increased slightly (1.43 Å

Molecule	Conformation	Pt(1)	11) surface	Pd(111) surface		
		This work	Other DFT	This work	Other DFT	
$SO_4$	$(fcc)\eta^3 - O_a O_a O_a$	87.2	$86.5^{S13}, 81.6^{S14}$	85.1	_	
$SO_3$	$(fcc)\eta^3 - S_a O_a O_a$	30.3	$27.5^{S13},33.0^{S14}$	27.4	_	
$SO_2$	$(fcc)\eta^2 - S_a O_a$	27.2	$24.4^{S13}, 28.1^{S14}$	26.7	$28.9^{S15}$	
SO	$({ m fcc})\eta^1$ –S <sub>f</sub>	69.5	$68.1^{S13},  68.0^{S14}$	66.8	_	
S	$({ m fcc})\eta^1$ –S <sub>f</sub>	122.2	$118.7^{S13}$	115.1	$111.84^{S5}$	
0	$({\rm fcc})\eta^1$ –O <sub>f</sub>	98.6	$100.6^{S13}$	99.7	$108.1^{S16}$	

Table S2: Comparison of binding energies (kcal/mol) for the most stable configurations of  $SO_x$  species on Pt(111) and Pd(111) surfaces. Surface coverage of 0.11 ML is considered for the comparison.

- 1.46 Å) from the gas phase bond length of 1.42 Å; however, the bond length increased tremendously (1.51 Å – 1.55 Å) in the case when both S and O atoms are attached. The bond angle ( $\angle OSO$ ) decreased from the gas phase values ( $SO_2(\angle OSO) = 119.5^{\circ}$  and  $SO_3(\angle OSO) =$  $120^{\circ}$ )). An interesting configuration,  $SO_2(\text{bridge})\eta^1-S\perp$ , has both oxygen atoms unbounded to the metal surface, showed the minimal decrease in bond length ( $\angle OSO$ ) =  $117^{\circ}$ ) from the gas phase  $\angle OSO$  bond angle. Furthermore, the computed binding energies of various  $SO_x$ species are compared with the available DFT based results (see **Table S2**).

Typically, the increase in surface coverage of an adsorbate decreases the binding strength of that adsorbate on the metal surface. In this work, we explored the effect of coverage on binding energies of  $SO_x$  and O on both surfaces. The computed binding energies of the most stable species of  $SO_x$  are given for the coverage range from 0.25 ML to zero coverage (see **Table S3**). The zero coverage binding energies are estimated from linear interpolation of the DFT-computed binding energies.

#### S.3 Bader charge analysis

Bader charge analysis, purely based on the electronic charge density, was performed to calculate the net charge transfer from/to molecules to/from catalysts surface. The Bader analysis results are presented in **Table S4**, where we report the net charge transfer to the molecule from the slab  $(Q_{mol})$ , the net charge acquired by the metal atoms  $(Q_{Pt} \text{ or } Q_{Pd})$ 

Molecule	Conformation	Pt(111) surface				Pd(111) surface			
		$p(2 \times 2)$	$p(3 \times 3)$	$p(4 \times 4)$	estimated	$p(2 \times 2)$	$p(3 \times 3)$	$p(4 \times 4)$	estimated
		$0.25~\mathrm{ML}$	$0.11~\mathrm{ML}$	$0.06~\mathrm{ML}$	$0 {\rm ML}$	$0.25~\mathrm{ML}$	$0.11~\mathrm{ML}$	$0.06~\mathrm{ML}$	$0 {\rm ML}$
$SO_4$	$(fcc)\eta^3$ – $O_aO_aO_a$	81.4	87.2	90.3	92.8	80.1	85.1	87.6	89.8
$SO_3$	$(fcc)\eta^3$ –S <sub>a</sub> O <sub>a</sub> O <sub>a</sub>	25.8	30.8	33.3	35.6	24.7	27.6	28.4	29.8
$SO_2$	$(fcc)\eta^2 - S_aO_a$	23.6	27.2	29.1	30.8	24.4	26.7	28.1	29.1
SO	$(fcc)\eta^1 - S_f$	65.7	69.5	70.6	72.4	65.5	66.8	68.1	68.7
S	$({\rm fcc})\eta^1 - {\rm S}_f$	114.6	122.2	123.4	126.9	109.8	115.1	115.8	118.3
0	$(fcc)\eta^1 - O_f$	96.1	98.6	99.3	100.4	98.6	99.6	99.9	100.5

Table S3: Coverage dependent binding energy (kcal/mol) of the most stable  $SO_x$  species and O atom adsorbed on Pt(111) and Pd(111) surfaces.

directly attached to the atom/molecule, and the net charge acquired by the sulfur atom  $(Q_S)$ in the molecule.

Among the different configurations of a molecule, the one with higher number of O atoms attached directly to the metal rendered larger negative charge on the molecule and larger positive charge on attached Pt atoms; however, it exhibited decrease in the net charge on S atom. For example, the  $Q_{mol}$ ,  $Q_{Pd}$ , and the  $Q_S$  of SO<sub>3</sub> (fcc) $\eta^3$ –S<sub>a</sub>O<sub>a</sub>O<sub>a</sub> on Pd(111) were -0.696, +0.424, and +4.714 respectively; however, those for SO<sub>3</sub> (fcc) $\eta^3$ –O<sub>a</sub>O<sub>a</sub>O<sub>a</sub> changed to -0.957, +0.585, and +4.316 respectively producing ~27% difference in charge transfer between two configurations of a molecules. An interesting behaviour was observed for SO<sub>2</sub>(bridge) $\eta^1$ – S $\perp$  molecule, where  $Q_{mol}$  and  $Q_{Pt}$  (or  $Q_{Pd}$ ) were remarkably low but the  $Q_S$  was higher compared to other SO<sub>2</sub> configurations.

### S.4 Density of states analysis

Here, we decomposed the electron density and wave function into contributions from atomic orbitals, i.e. s, p and d orbitals centered on each atom. **Figure S1** shows the p-DOS of various SO<sub>x</sub> molecules on Pd(111) and Pt(111) surfaces. In **Figure S1**, each panel (a-h) shows the projected atomic DOS of atom/molecule in a isolated state along with the pure slab surface in the lower part and the adsorbed states of those in the upper part. Further, comparison of DOS of S adsorption on Pd(111) and Pt(111) surfaces is given in **Figure S1**(i). We observed the shifting of active metal d band to lower energy after adsorption

Molecule	Molecule Conformation		(111) sur	face	Pd(111) surface		
		$Q_{mol}$	$Q_{Pt}$	$\mathbf{Q}_S$	$\mathbf{Q}_{mol}$	$\mathbf{Q}_{Pd}$	$\mathbf{Q}_S$
$SO_4$	$(\mathrm{fcc})\eta^3$ – $\mathrm{O}_a\mathrm{O}_a\mathrm{O}_a$	-1.010	+0.700	+6.000	-1.070	+0.670	+6.000
$SO_4$	$(\mathrm{hcp})\eta^3 - \mathrm{O}_a\mathrm{O}_a\mathrm{O}_a$	-1.000	+0.690	+6.000	-1.070	+0.671	+6.000
$SO_3$	$(fcc)\eta^3$ –S <sub>a</sub> O <sub>a</sub> O <sub>a</sub>	-0.656	+0.412	+4.60	-0.696	+0.424	+4.714
$SO_3$	$(\rm hcp)\eta^3{-}S_aO_aO_a$	-0.652	+0.414	+4.614	-0.694	+0.411	+4.697
$SO_3$	$(fcc)\eta^3$ – $O_aO_aO_a$	-0.891	+0.646	+4.280	-0.957	+0.585	+4.316
$SO_3$	$(\mathrm{hcp})\eta^3 - \mathrm{O}_a\mathrm{O}_a\mathrm{O}_a$	-0.920	+0.685	+4.263	-0.937	+0.466	+4.313
$SO_2$	$({ m fcc})\eta^2$ –S $_a{ m O}_a$	-0.330	+0.189	+3.325	-0.369	+0.258	+3.334
$SO_2$	$(\rm hcp)\eta^2{-}S_aO_a$	-0.327	+0.157	+3.336	-0.373	+0.201	+3.361
$SO_2$	$(bridge)\eta^1 - S \perp$	-0.272	+0.023	+3.475	-0.353	+0.114	+3.403
$SO_2$	$(fcc)\eta^3$ –S <sub>a</sub> O <sub>a</sub> O <sub>a</sub>	-0.443	+0.341	+2.997	-0.471	+0.362	+3.095
$SO_2$	$(hcp)\eta^3 - S_a O_a O_a$	-0.439	+0.317	+2.999	-0.469	+0.343	+3.098
SO	$({ m fcc})\eta^1 - { m S}_f$	-0.196	+0.152	+1.693	-0.195	+0.152	+1.693
SO	$(hcp)\eta^1 - S_h$	-0.163	+0.142	+1.700	-0.151	+0.202	+1.701
SO	$(\mathrm{fcc})\eta^2 - \mathrm{S}_b \mathrm{O}_a$	-0.236	+0.057	+1.434	-0.267	+0.165	+1.469
SO	$(\mathrm{hcp})\eta^2 – \mathrm{S}_b \mathrm{O}_a$	-0.232	+0.056	+1.451	-0.303	+0.163	+1.146
S	$({\rm fcc})\eta^1 – {\rm S}_f$	-0.125	+0.076	-0.125	-0.256	+0.244	-0.256
S	$(\mathrm{hcp})\eta^1 - \mathrm{S}_h$	-0.081	+0.060	-0.081	-0.256	+0.228	-0.256
0	$({\rm fcc})\eta^1\!\!-\!\!{\rm O}_f$	-0.772	+0.622		-0.773	+0.752	
0	$(\mathrm{hcp})\eta^1$ – $\mathrm{O}_h$	-0.757	+0.633		-0.764	+0.714	
0	$(\mathrm{atop})\eta^1$ –O $_a$	-0.599	+0.484		-0.604	+0.386	

Table S4: Bader charge analysis of O and  $SO_x$  adsorption on Pt(111) and Pd(111) surfaces. Charge (au) in the molecule  $(Q_{mol})$ , surface metal atoms  $(Q_{Pt})$ , and sulfur atom  $(Q_S)$  represents the total charge acquired after adsorption.

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Figure S1: Projected density of states (*P*-DOS) analysis of adsorbed SO<sub>x</sub> species on metal surface and comparison to the atomic components in isolated states: (a) S (fcc) $\eta^1$ –S<sub>f</sub>, (b) SO (fcc) $\eta^1$ –S<sub>f</sub>, (c) SO (fcc) $\eta^2$ –S<sub>b</sub>O<sub>a</sub>, (d) SO<sub>2</sub> (fcc) $\eta^2$ –S<sub>a</sub>O<sub>a</sub>, (e) SO<sub>2</sub> (fcc) $\eta^3$ –S<sub>a</sub>O<sub>a</sub>O<sub>a</sub>, (f) SO<sub>3</sub> (fcc) $\eta^3$ –O<sub>a</sub>O<sub>a</sub>O<sub>a</sub>, (g) SO<sub>3</sub> (fcc) $\eta^3$ –O<sub>a</sub>O<sub>a</sub>O<sub>a</sub>, and (h) SO<sub>4</sub> (fcc) $\eta^3$ –O<sub>a</sub>O<sub>a</sub>O<sub>a</sub> on Pd(111) surface and (i) S (fcc) $\eta^1$ –S<sub>f</sub> on Pt(111) and Pd(111) surfaces. The lower part each panel (a-h) represents the projected DOS of Pt, S and O atomic orbitals in isolated atomic/molecular/pure slab state and the upper part represents the same in adsorbed state. The O-1 and O-2 represent the oxygen atom attached to Pt (with S) and S atom only. Similarly, Pd-1 and Pd-2 represent the Pd atom attached to S atom and O atom respectively. The Fermi energy (E<sub>Fermi</sub>) is adjusted to zero in the plot.

of atom/molecule in all cases. The d band shifting was larger in the case of sulfur metal interaction compared to oxygen metal interaction. Panel c, d, e, and f (in Figure S1) show the difference in d band shifting, where Pd-1 shows larger shift (M-S interaction) then Pd-2 (M-O interaction). Along the same line, we found very similar characteristics of DOS in the case of Pt(111) surface. Nonetheless, we showed the DOS of S adsorption (see **Figure** S1(i) on both surfaces for the comparison. We note that the oxygen 2p orbitals attached to metal and sulfur atom (denoted as O-1 in **Figure S1**) showed more broadening with a spike at -7 eV, whereas the oxygen 2p orbitals attached only with sulfur atom (denoted as O-2 in **Figure S1**) showed relatively smaller broadening with a spike at -6eV. Furthermore, we observed strong interactions of p orbitals of S and O with each other and with metal d band in this reason (-5 to -8 eV) We note that the d band was larger and extend to lower energy in Pt(111) along with broadening and larger separation of bonding and antibonding states of p orbitals, which can be assigned to comparatively stronger  $SO_x$  binding to Pt(111) surface observed in this study. Finally, we also observed diffused metal s orbitals and provided some contribution to total DOS (not shown here); however, the contribution was negligible compared to metal d orbitals.<sup>S17</sup>.

#### S.5 Functional dependence of activation energy

To calculate activation energies using the UBI-QEP<sup>S18</sup> method, a thermodynamic loop with gas phase and surface reactions is considered. *Figure S2* shows the schematics of the reaction loop for UBI-QEP calculations.

Here, SO<sub>2</sub> oxidation reaction is written as a surface species dissociation in endothermic direction. i.e.  $SO_3^* + * \xleftarrow{E_f}{E_b} SO_2^* + O^*$ . For the reaction loop considered, heat of surface reaction can be calculated as:

$$\Delta H_{surf} = D_{gas} + Q_{SO_3} - Q_{SO_2} - Q_O \tag{S3}$$

Here, Q represents the binding energy of the species (different from the Q used in the Bader analysis). The binding energy is temperature dependent based on the calculations



Figure S2: Schematic of a reaction loop with gas phase and surface reactions.

for degrees of freedom lost/gained upon adsorption, as described by Mhadeshwar et al.<sup>S19</sup> and described later. Q can also be species coverage dependent, as described in **Table II**. This makes the heat of surface reaction coverage and temperature dependent. The gas phase bond dissociation energy  $D_{gas}$  is calculated from enthalpies of the reactants and the products as:

$$D_{gas} = H_{products} - H_{reactants} \tag{S4}$$

Here, the standard state molar enthalpy is temperature dependent and it is given by,

$$H^o = \int\limits_0^T C_p^o dT \tag{S5}$$

The specific heat  $C_p$  can be calculated using the polynomial coefficients for each species from thermodynamic databases (e.g., GRI-Mech 3.0 thermodynamic database).<sup>S20</sup>

$$\frac{C_p^o}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$
(S6)

Here, T is the temperature (K) and  $a_1$  to  $a_5$  are the polynomial coefficients. The UBI-QEP formalism is then used to compute the forward ( $E_f$ ) and backward ( $E_b$ ) activation energies for the reactions which is automatically a function of temperature and coverage as explained above. The forward activation energy is given by,

$$E_f = w[\Delta H_{surf} \frac{Q_{SO_2} Q_O}{Q_{SO_2} + Q_O}]$$
(S7)

Where w is the bond index. The range of bond index is from 0 to 1 (with a typical value of 0.5). Then, backward activation energy is calculated as:

$$E_b = E_f - \Delta H_{surf} \tag{S8}$$

In the case of non-activated dissociative adsorption (eg.  $O_2 + 2^* \leftrightarrow 2O^*$ ), the forward activation energy  $(E_f)$  is zero. However, the bond dissociation energy is non-zero. So,

$$\Delta H_{surf} = D_{gas} - 2Q_O \tag{S9}$$

and the backward activation energy is calculated as,

$$E_b = -\Delta H_{surf} \tag{S10}$$

Next, we discuss the generalized assumptions to calculate the temperature dependence to the binding energy of a molecule due to degrees of freedom lost/gained during adsorption: (a) Each translational, rotational, and vibrational degree of freedom (DOF) corresponds to  $0.5R_gT$ ,  $0.5R_gT$ , and  $R_gT$ , respectively. (b) Upon adsorption, all translational and rotational DOF are converted into vibrational DOF. For SO<sub>2</sub> and SO<sub>3</sub> molecules, with a vertical axis through the adsorbed atom, one of the gained vibrational DOF is assumed to be a free internal rotor (rigid rotor (RR) approximation) and counts as  $0.5R_gT$ .<sup>S23</sup> So, the total change in degrees of freedom (2.5R<sub>g</sub>T) of SO<sub>2</sub> and SO<sub>3</sub> for the temperature dependence can be calculated as:

$$-3F_T - 3F_R + F_{RR} + 4F_V \tag{S11}$$

Here  $F_T$ ,  $F_R$ , and  $F_V$  represent the translational, rotational, and vibrational degrees of freedom.  $F_{RR}$  represents that the vibrational DOF is assumed to be a free internal rotor. The "+" and "-" signs indicate gain and loss of DOF, respectively.

#### S.6 Pre-exponential factors

Pre-exponential factors are important kinetics parameters for the study of various catalytic process, which can be calculated rigorously using DFT. For an example, the elementary step surface reaction of  $SO_2$  oxidation on the Pt/Pd surfaces, the reaction rate constant k is given as:

$$k_i = A_o exp(\frac{-E_{a,i}}{K_B T}) \tag{S12}$$

Where  $A_o$ ,  $E_{a,i}$ ,  $K_B$ , and T represent the pre-exponential factor, reaction activation energy, Boltzman's constant, and temperature respectively. The pre-exponential factor  $A_o$  can be given as:

$$A_o = \frac{K_B T}{h} exp(\frac{\Delta S_i^{\circ}}{K_B})$$
(S13)

Where h is the Planck's constant and  $\Delta S_i^{\circ}^{\dagger}$  represents the standard state entropy change accompanying the formation of transition state and calculated as:

$$\Delta S^{o}{}_{i}{}^{\dagger} = S^{o}{}_{TS}{}^{\dagger} - S^{o}{}_{IS} \tag{S14}$$

Where  $S_{TS}^{\circ}^{\dagger}$  and  $S_{IS}^{\circ}$  represent the transition state entropy and the initial state entropy. The entropies can be calculated from the analysis of vibrational modes of the species as follows  $S^{221,S22}$ ,

$$S_{vib} = K_B \sum_{i}^{no.ofmodes} \left(\frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i})\right)$$
(S15)

Where  $x_i$  represents the each vibrational mode and calculated from the vibrational frequency  $\nu_i$  as:

$$x_i = \frac{h\nu_i}{K_B T} \tag{S16}$$

The lowest possible energy at ground state, zero-point energy (ZPE) accounts for the energy at zero Kelvin. The difference in zero-point energy, i.e.  $\Delta$ ZPE can be calculated as: <sup>S22</sup>

$$\Delta ZPE = \left(\sum_{i}^{no.ofmodes} \frac{h\nu_i}{2}\right)_{TS} - \left(\sum_{i}^{no.ofmodes} \frac{h\nu_i}{2}\right)_{IS}$$
(S17)

The vibrational frequencies, except the single imaginary mode in each transition state, are utilized to compute the pre-exponential factors and zero-point energy. The frequencies are listed in *Table S5*.

Table S5: List of the vibrational frequencies  $(cm^{-1})$  of initial state and transition state of SO<sub>2</sub> oxidation  $(SO_2^* + O^* \rightarrow SO_3^*)$  and SO<sub>3</sub> oxidation  $(SO_3^* + O^* \rightarrow SO_4^*)$  on Pt(111) and Pd(111) surfaces.

			Frequencies $(cm^{-1})$				
Reaction	Path	Pt(1	11)	Pd(111)			
		Initial state	Transition state	Initial state	Transition state		
$\overline{\mathrm{SO}_2{}^* + \mathrm{O}{}^* \to \mathrm{SO}_3{}^*}$	Path A	1173, 957, 491, 434, 404, 347	1197, 889, 496, 479, 312, 268	1167, 953, 482, 414, 365	1202, 962, 483, 441, 325, 279		
		306, 149, 87, 81, 44, 21	194, 156, 153, 87, 50	361, 175, 120, 96, 81, 63, 27	165, 153, 131, 71, 30		
	Path B		1220, 1017, 486, 476, 370, 197		1224, 1006, 490, 443, 384, 163		
			180, 108, 95, 62, 58		154, 144, 92, 60, 53		
	Path C		1261, 1063, 505, 482, 365, 200		1247, 1053, 495, 448, 400, 165		
			183, 127, 100, 53, 41		162, 150, 125, 46, 42		
$\mathrm{SO}_3{}^* + \mathrm{O}^* \to \mathrm{SO}_4{}^*$	Path A	1219, 871, 802, 582, 504, 457, 439	1213, 876, 741, 502, 485, 440, 416	1196, 914, 823, 561, 488, 439, 434	1240, 1051, 856, 484, 472, 426		
		410,  360,  285,  259,  217,  148,  103,  92	329, 232, 183, 166, 153, 127, 112	401, 352, 258, 228, 150, 127, 82, 53	390, 323, 227, 144, 130, 95, 90, 78		
	Path B		1307, 1190, 951, 500, 498, 404, 336		1307, 1256, 970, 494, 490, 422, 372		
			323,183,163,149,94,66		361,328,147,117,101,86,67		

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