SO_2 Oxidation model on Pt/Pd DOC

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Congratulations Huskies !!!

UConn 93, Louisville 60: Huskies win eighth national championship

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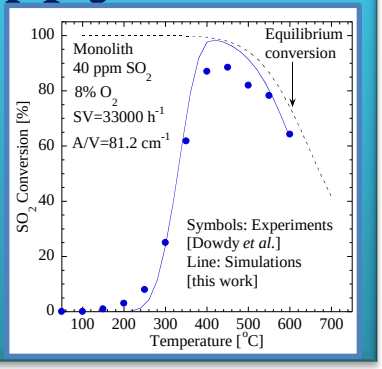
Outline

Background : SO_x impacts on DOC

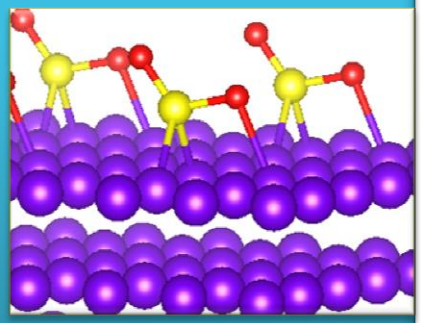
Microkinetic modeling : SO_2 oxidation on Pt

- Mechanism development
- Kinetics parameters
- Model performance



First Principles DFT study:

- SO_x Chemistry on Pt(111)/Pd(111)
- SO_2 Oxidation on Pt(111) /Pd(111)
  - Reaction pathways



Implementation of first principles into microkinetic modeling

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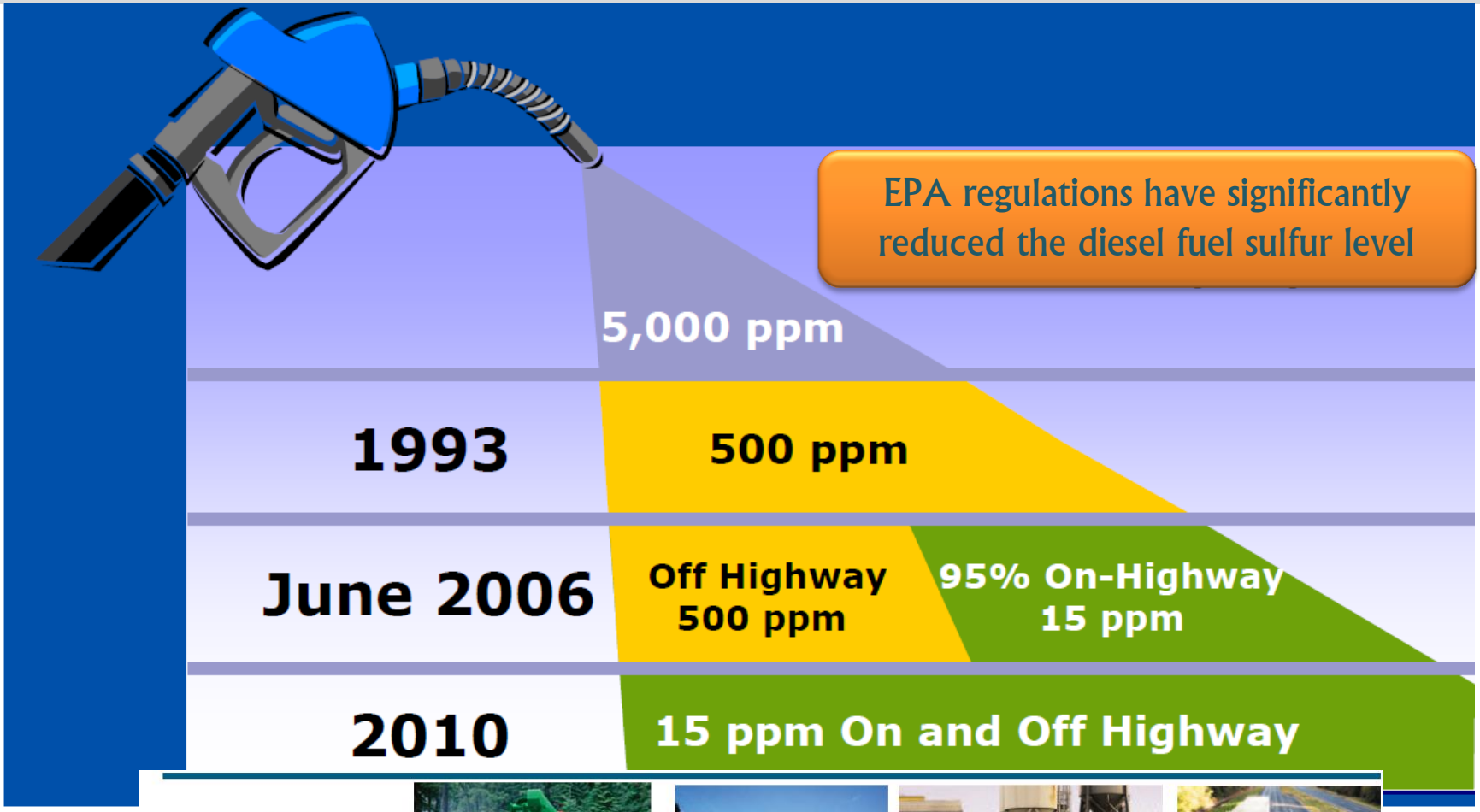
Sulfur in diesel fuel

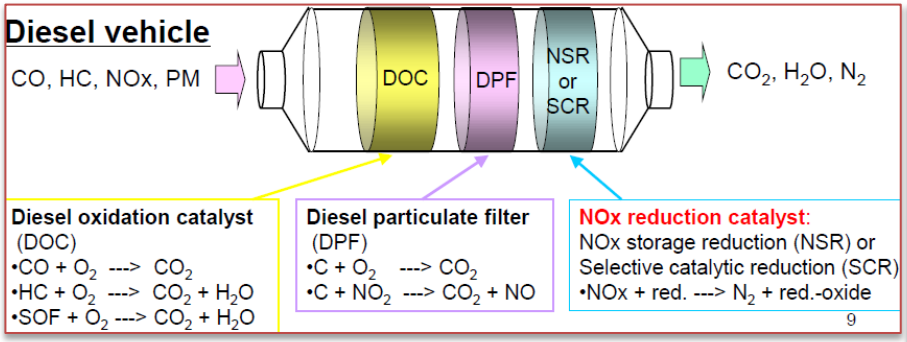




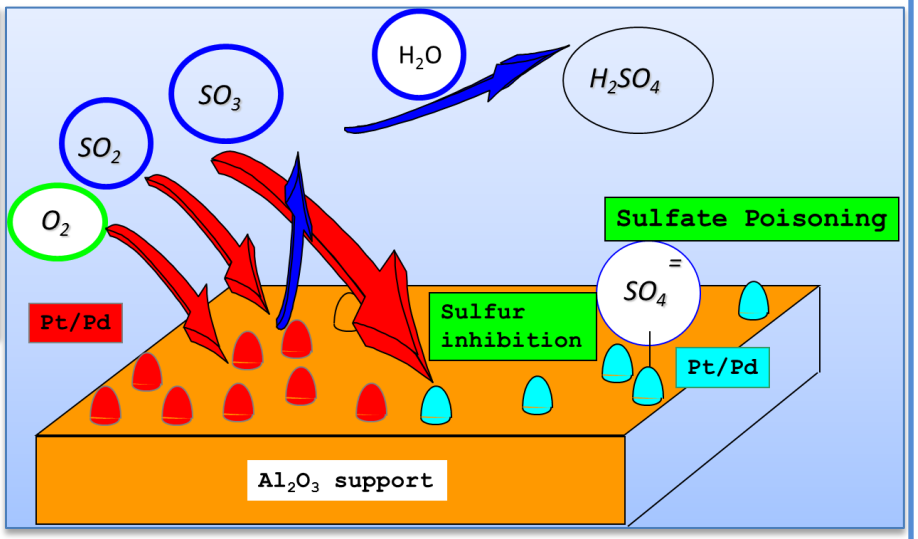


Sulfur impacts on diesel oxidation catalysts

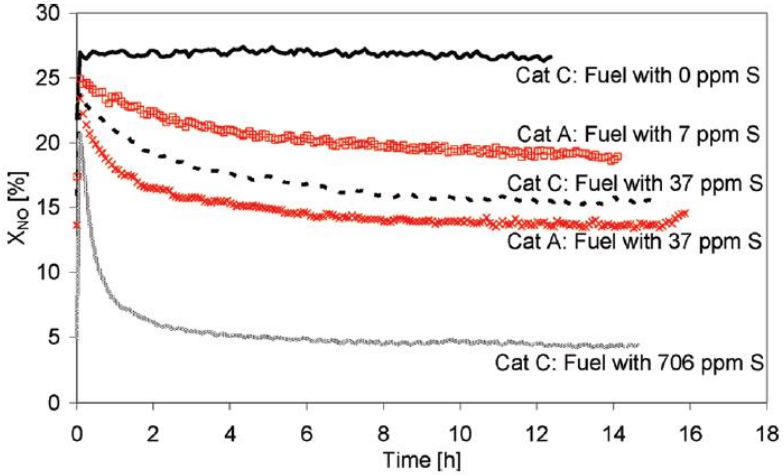
Aftertreatment system



Sulfur chemistry on DOC



Impact of Sulfur on DOC chemistry



SO_x chemistry	Sulfation chemistry
$SO_2 + * \leftrightarrow SO_2*$	$Al_2O_3 + 3SO_3* \leftrightarrow Al_2(SO_4)_3$
$SO_2* + O* \leftrightarrow SO_3* + *$	
$SO_3 + * \leftrightarrow SO_3*$	
$H_2O + * \leftrightarrow H_2O*$	$PdO + SO_3* \leftrightarrow PdSO_4$
$SO_3* + H_2O* \leftrightarrow H_2SO_4* + *$	
$H_2SO_4 + * \leftrightarrow H_2SO_4*$	

Krocher, O. et al., Ind. Eng. Chem. Res., 2009

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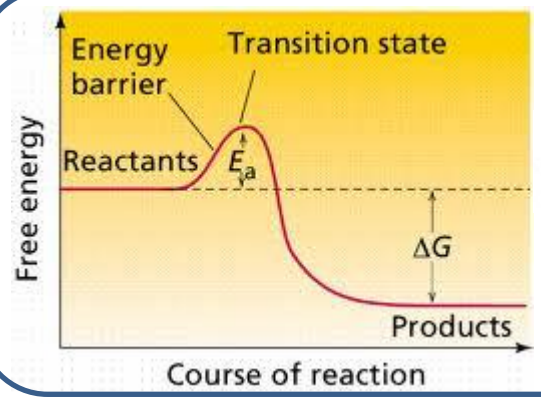
Key steps in microkinetic modeling

$SO_2(g) \rightarrow SO_2^* \rightarrow SO_3^* \rightarrow SO_3(g)$

$SO_3^* \rightarrow SO_2^* \rightarrow SO_2(g)$

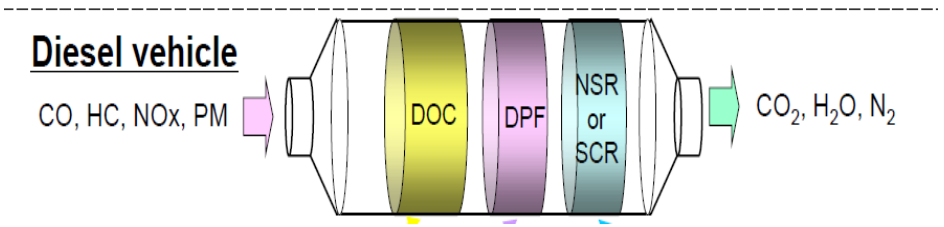
Mechanism development



$$K = Ae^{-Ea/RT}$$

A: Pre-exponential
E_a: Activation energy
Q: Binding energy
BI: Bond index

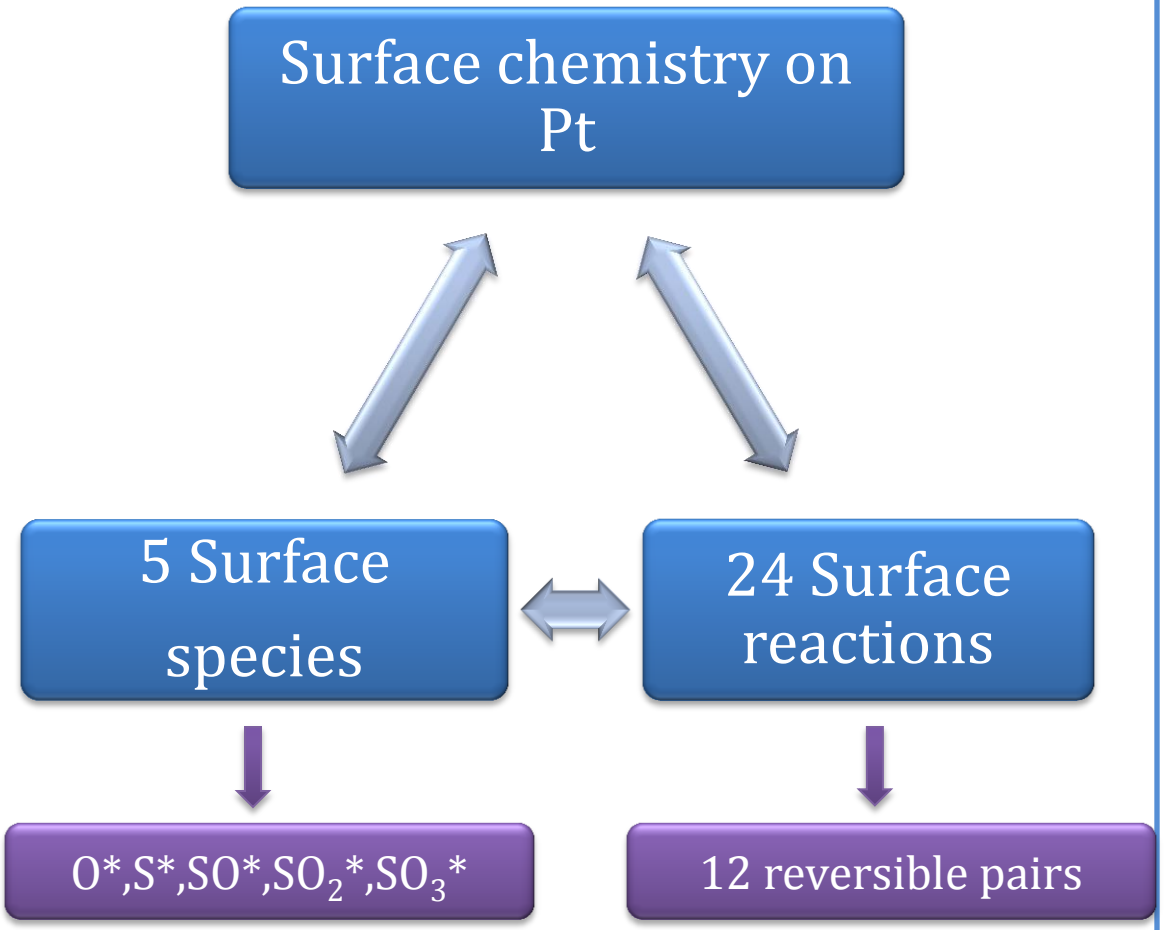
Parameter estimation



Model performance

Mechanism development

	Oxygen adsorption/desorption[171]
R_1	$O + * \rightarrow O^*$
R_2	$O^* \rightarrow O + *$
R_3	$O_2 + 2* \rightarrow 2O*$
R_4	$2O^* \rightarrow O_2 + 2*$
	SO_x adsorption/desorption
R_5	$S + * \rightarrow S^*$
R_6	$S^* \rightarrow S + *$
R_7	$SO + * \rightarrow SO^*$
R_8	$SO^* \rightarrow SO + *$
R_9	$SO_2 + * \rightarrow SO_2^*$
R_{10}	$SO_2^* \rightarrow SO_2 + *$
R_{11}	$SO_3 + * \rightarrow SO_3^*$
R_{12}	$SO_3^* \rightarrow SO_3 + *$
	SO_x oxidation/reduction
R_{13}	$SO_3^* + * \rightarrow SO_2^* + O^*$
R_{14}	$SO_2^* + O^* \rightarrow SO_3^* + *$
R_{15}	$SO_2^* + * \rightarrow SO^* + O^*$
R_{16}	$SO^* + O^* \rightarrow SO_2^* + *$
R_{17}	$SO^* + * \rightarrow S^* + O^*$
R_{18}	$S^* + O^* \rightarrow SO^* + *$
R_{19}	$2SO_2^* \rightarrow SO^* + SO_3^*$
R_{20}	$SO^* + SO_3^* \rightarrow 2SO_2^*$
R_{21}	$S^* + SO_2^* \rightarrow 2SO^*$
R_{22}	$2SO^* \rightarrow S^* + SO_2^*$
R_{23}	$SO^* + SO_2^* \rightarrow S^* + SO_3^*$
R_{24}	$S^* + SO_3^* \rightarrow SO^* + SO_2^*$



Sharma, H. N.; Suib, S. L.; Mhadeshwar, A. B.; Novel Materials for Catalysis and Fuels Processing, ACS, 2013, In press

Kinetic parameters

Pre-exponential factors

- A
  - TST[1]
    - Desorption: 10^{13} s^{-1}
    - Surface reaction: 10^{11} s^{-1}
  - Literature
    - Sticking coefficients

Binding energies

- Q
  - DFT
  - TPD

Activation energies

- E
  - UBI-QEP

Bond indices

- BI
  - UBI-QEP
    - 0.5

Adsorbate interactions

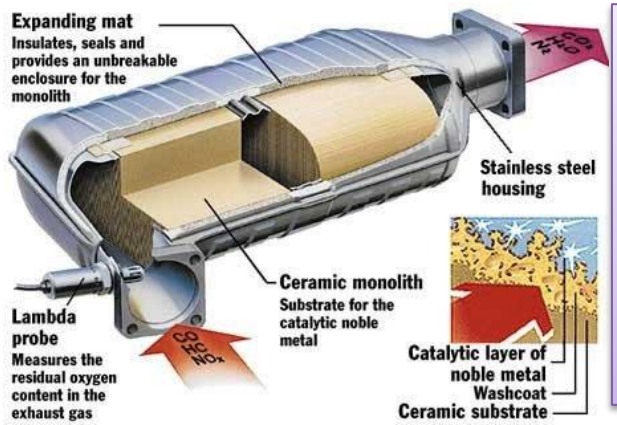
- α
  - TPD
  - DFT

1. Dumesic, J. *et al.*, The Microkinetics of Heterogeneous Catalysis,1998

Model validation

Why model validation is necessary ?

Kinetic parameters are extracted/taken from UHV TPD/R conditions and 0K DFT calculations



DOC operating conditions are significantly different:

- Atmospheric pressure
- High flow rates
- Low emissions concentrations (ppm)
- Monoliths
- Fixed beds (literature experiments)

- Mechanism/model performance should be tested under practically relevant conditions.
- Isothermal plug flow reactor modeling at steady state.

Model details

Fixed beds/ Monoliths (PFR)
Oxidation of SO_2

- Steady state
- Isothermal

Governing Equations for PFR:

Mass balance for gas species:

$$\frac{dY_k}{dz} = \frac{R_k M_k}{\rho u} + \left(\frac{A}{V}\right)\frac{S_k M_k}{\rho u}$$

Surface species rate:

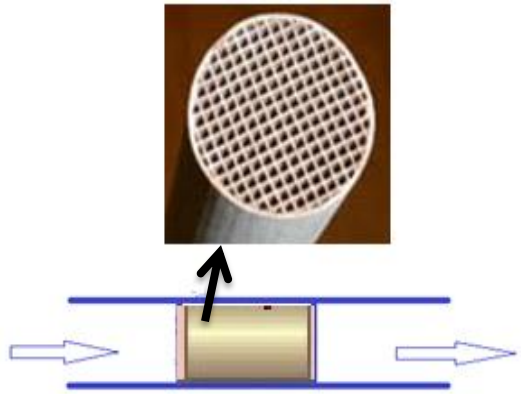
$$S_k = 0$$

Site balance:

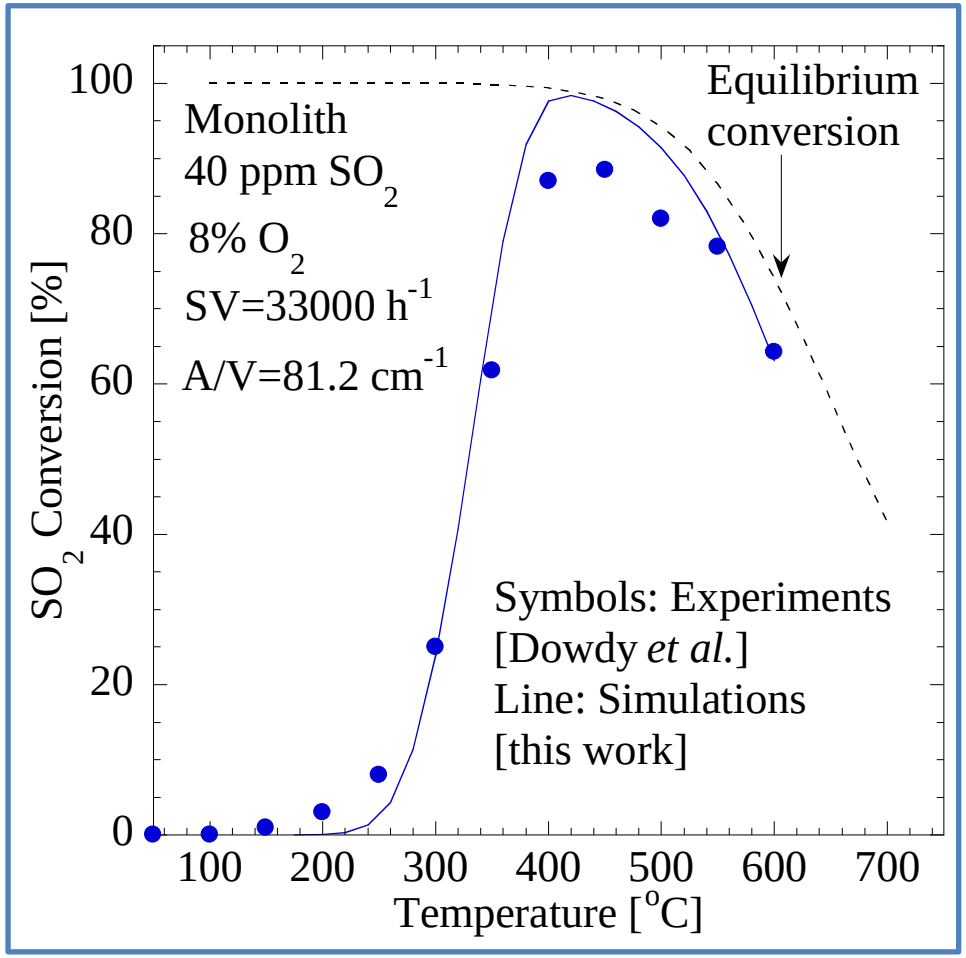
$$\sum \theta_k = 1$$

Fixed Bed

Monolith



Model performance: SO_2 oxidation on Pt



$SO_2^* + O^* \Leftrightarrow SO_3^* + *$

BI = 0.9

$A_{forward} = 2\times10^{12}\ s^{-1}$

Sharma, H. N.; Suib, S. L.; Mhadeshwar, A. B.; Novel Materials for Catalysis and Fuels Processing, ACS, 2013, In press;

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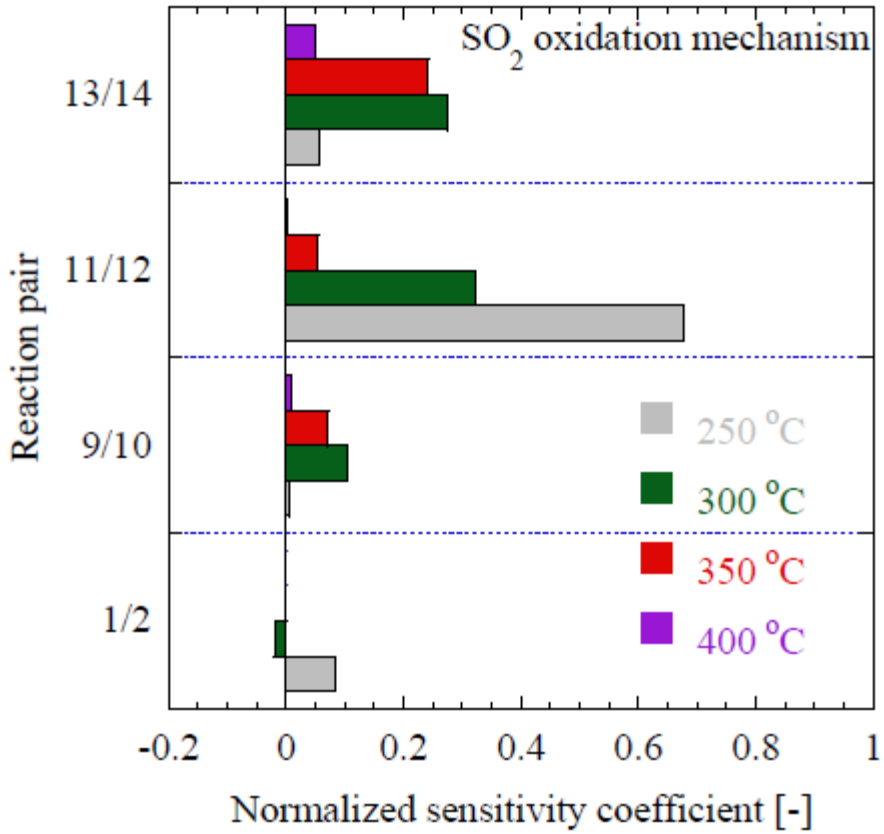
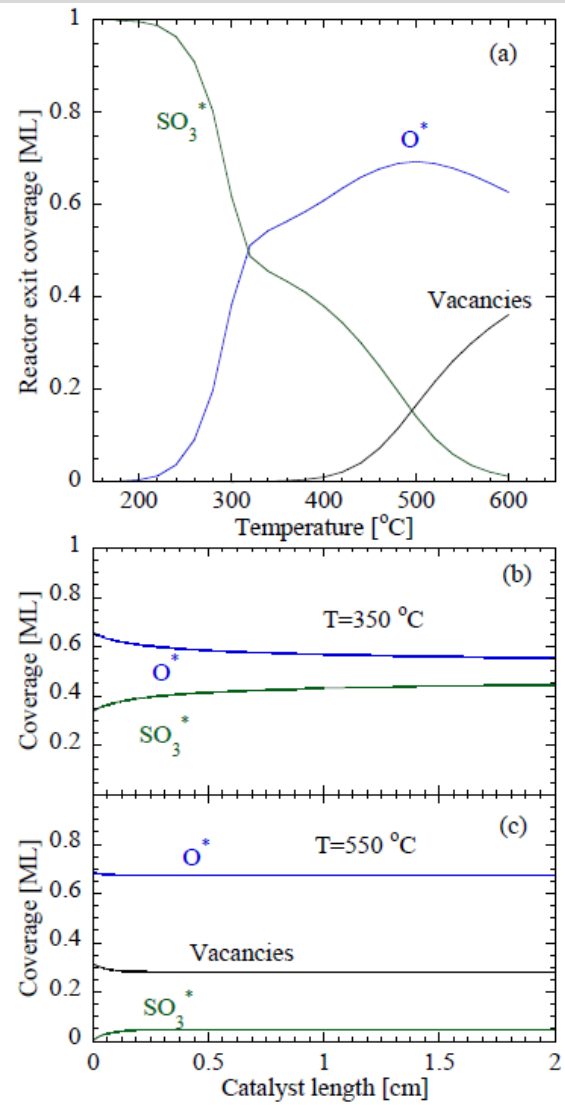
Sensitivity/Coverage analysis: SO_2 oxidation





11/12 $SO_3 + * \Longleftrightarrow SO_3*$

13/14 $SO_2* + O* \Longleftrightarrow SO_3* + *$

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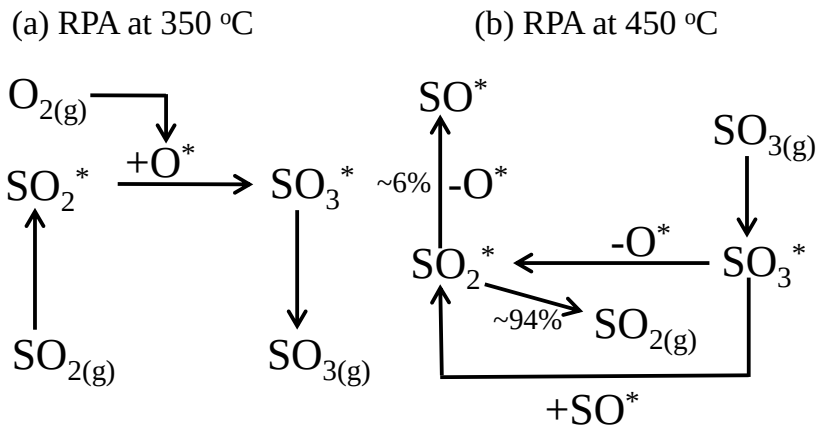
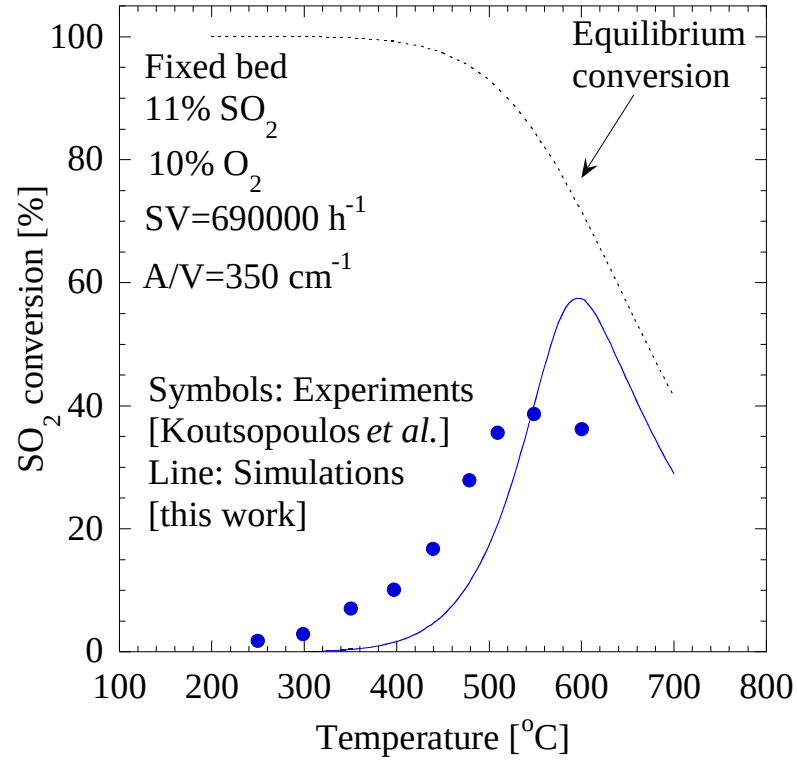
Reaction Pathways : SO_2 oxidation

Reaction Pathways



Model validation



High SO_2 concentration
High space velocity

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Model reduction: SO_2 oxidation

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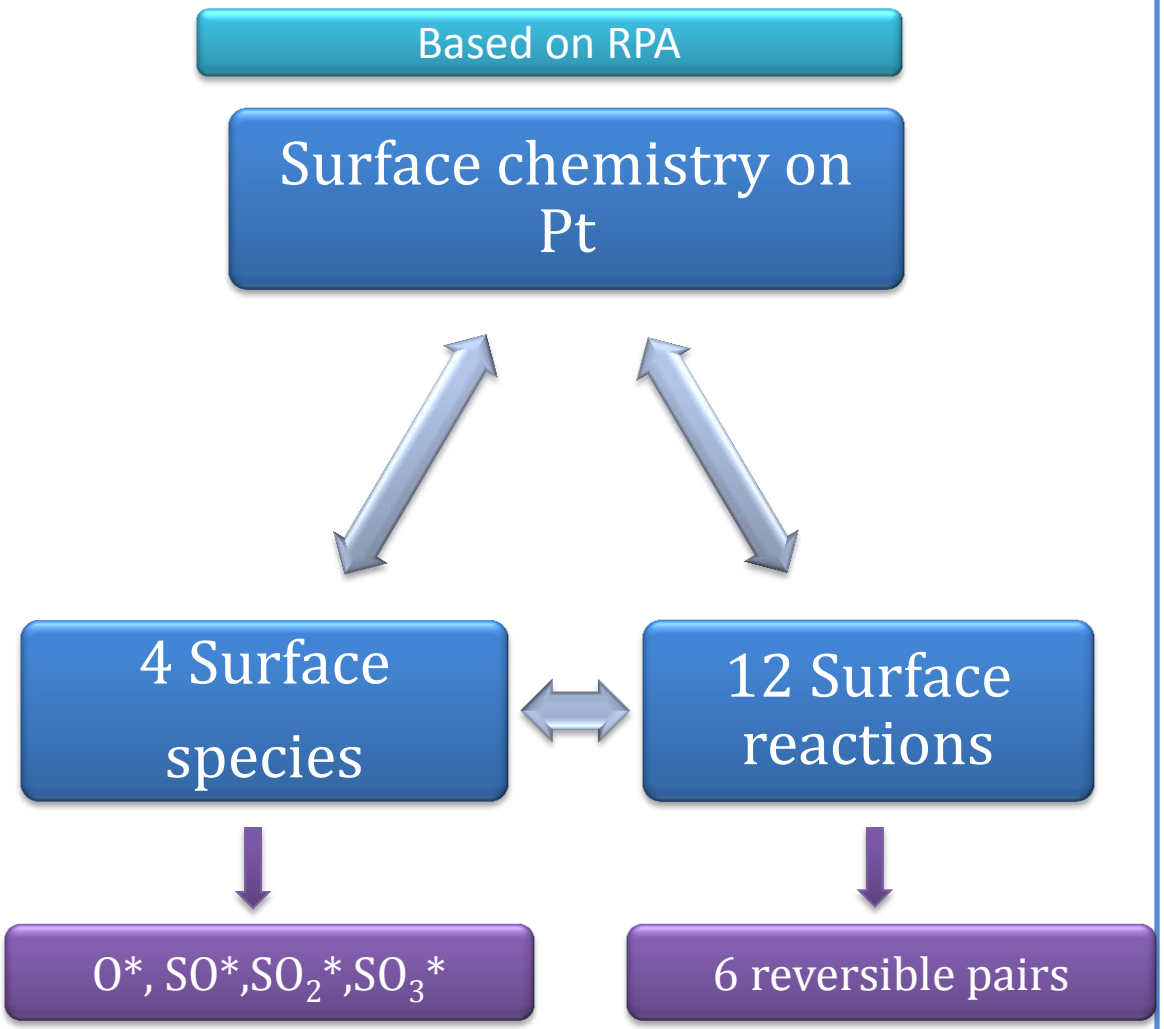

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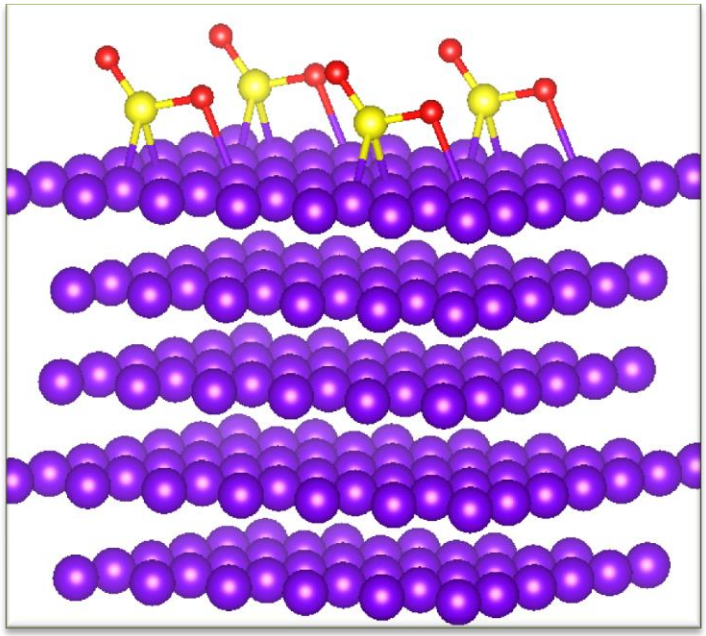
SO_x chemistry on Pt(111)/Pd(111) surfaces

- Density functional theory implemented in VASP[1]
- Perdew-Burke-Ernzerhof (PBE) functional[2]

Model Parameters

- (111) surface
- 3x3 supercell
- 5 layers (2 bottom layers frozen)
- 45 Pt/Pd Atoms
- 4x4x1 k-point mesh
- 12 Vacuum
- Plane-wave cut-off energy = 400 eV



[1]Kresse, G.; Furthmuller, J. Phys. Rev. B 1996, 54(16),11169.
[2]Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77(18), 3865-3868.

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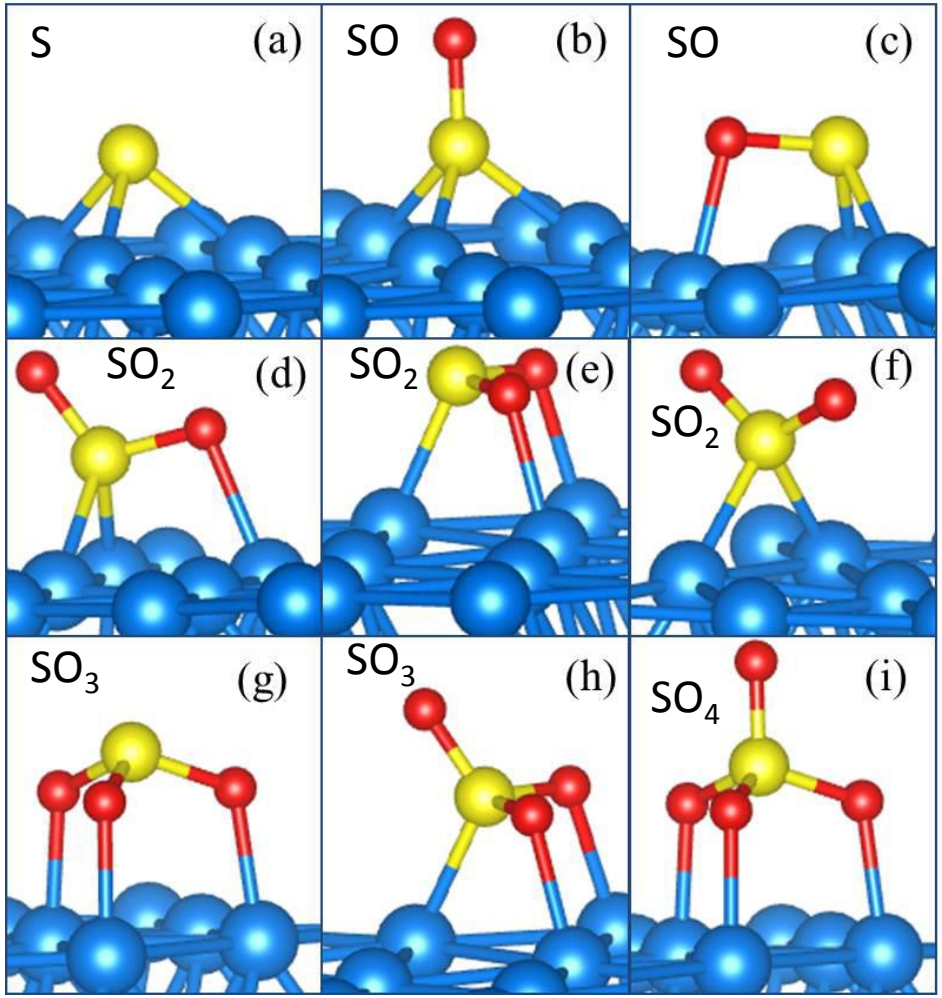
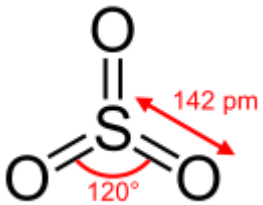
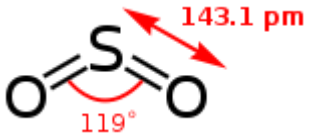
SO_x chemistry on Pt(111)/Pd(111) surfaces







<u>Molecular Orientation</u>

1. Upright standing
2. Parallel to the surface

Upright standing molecule are stable

Strong binding to fcc position

S-O bond length increases & ∠OSO angle decreases

SO_x chemistry on Pt(111)/Pd(111) surfaces

Binding energy (kcal/mol) [0.11ML]

Species	Pt(111)		Pd(111)	
	This work	Other DFT[1-2]	This work	Other DFT[1-3]
SO_4	87.2	86.5, 81.6	85.1	-
SO_3	30.3	27.5, 33.0	27.4	-
SO_2	27.2	24.4, 28.1	26.7	28.9
SO	69.5	68.1, 68.0	66.8	-
S	122.2	118.7	115.1	111.8
O	98.6	100.6	99.7	108.1

Binding Strength

$$S > O > SO > SO_4 > SO_3 > SO_2$$

[1]Happel, M.; Luckas, N.; Vines, F.; Sobota, M.; Laurin,M.; Gorling, A.; Libuda, J. J. Phys. Chem. C 2011, 115,479-491.
[2]Lin, X.; Schneider, W. F.; Trot, B. L. J. Phys. Chem. B 2004, 108(35), 13329{13340.
[3]Alfonso, D. R. Surface Science 2005, 596(1-3), 229{241.

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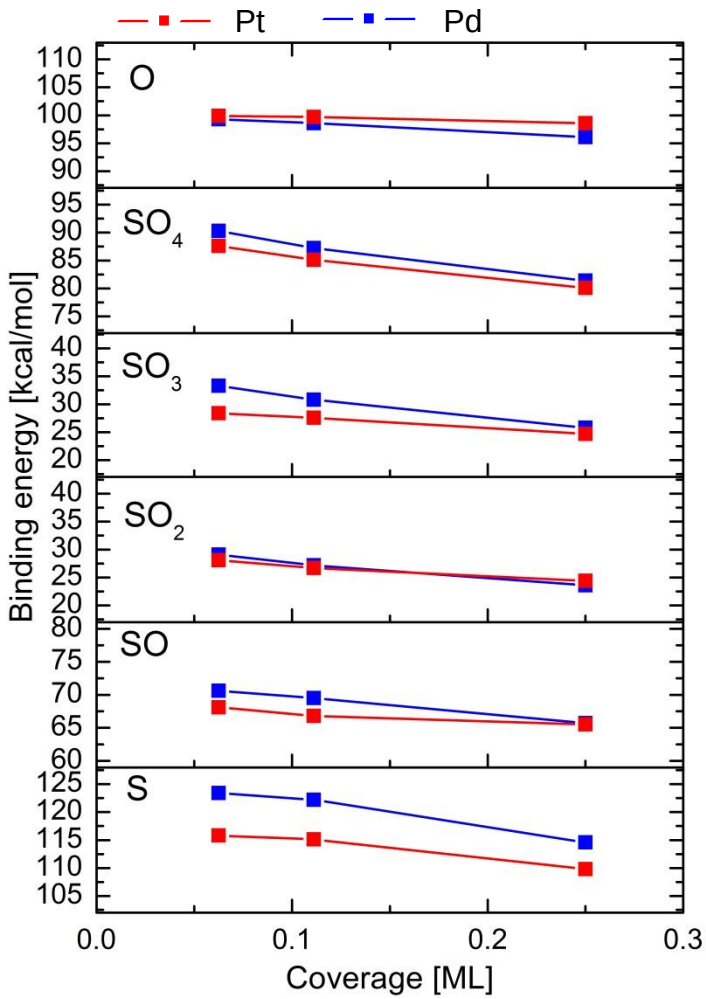
SO_x chemistry on Pt(111)/Pd(111) surfaces

Coverage dependent binding energy

$p(2\times2)$	$p(3\times3)$	$p(4\times4)$
0.25 ML	0.11 ML	0.06 ML



Coverage dependence

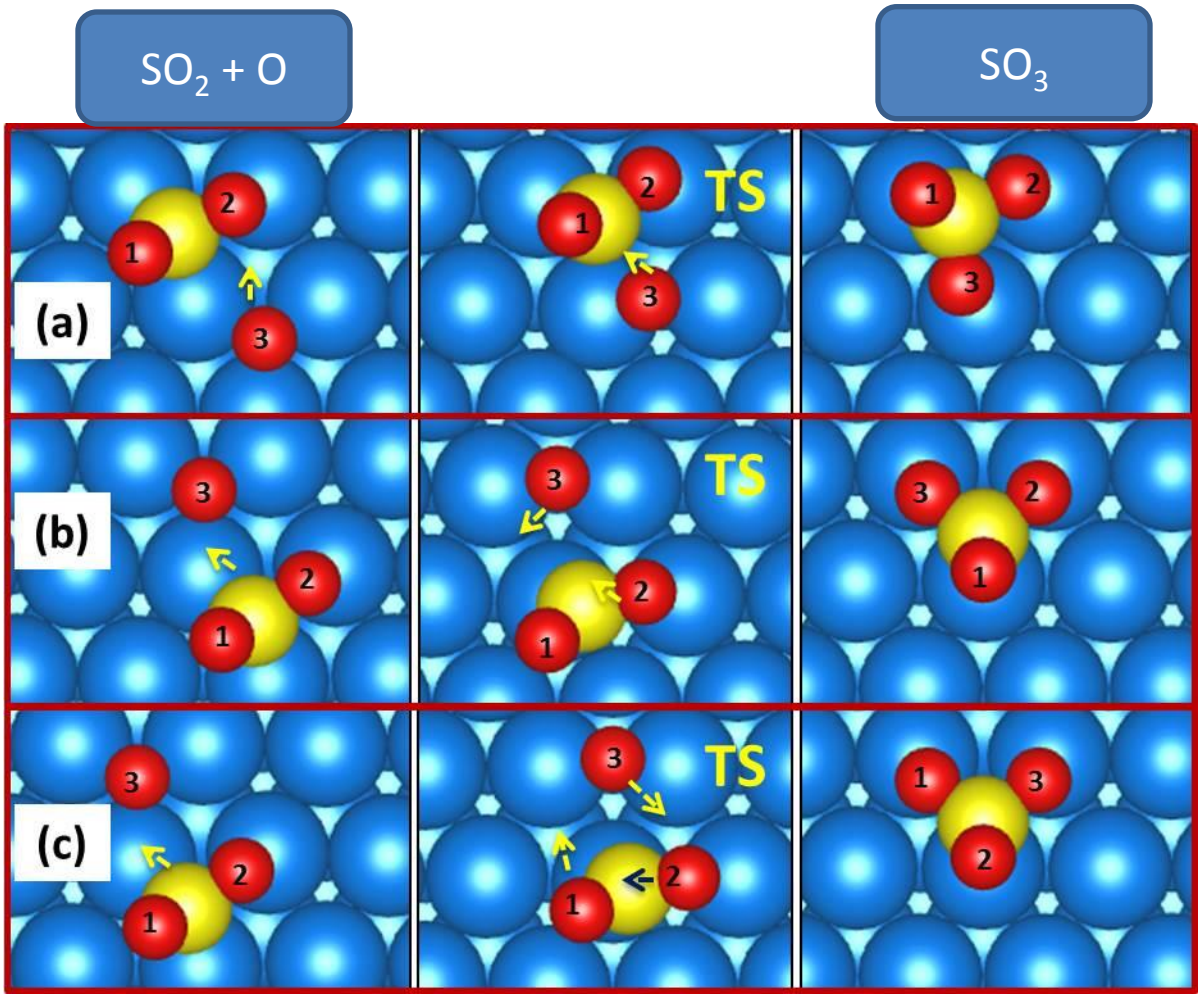
SO_4 largest
O smallest

SO_2 Oxidation on Pt(111)/Pd(111) surfaces

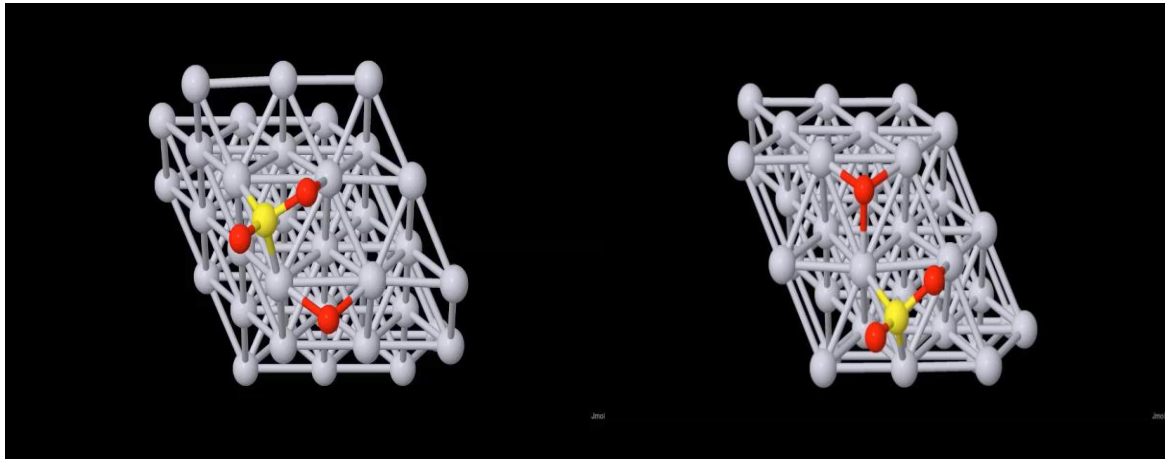
CI-NEB based analysis

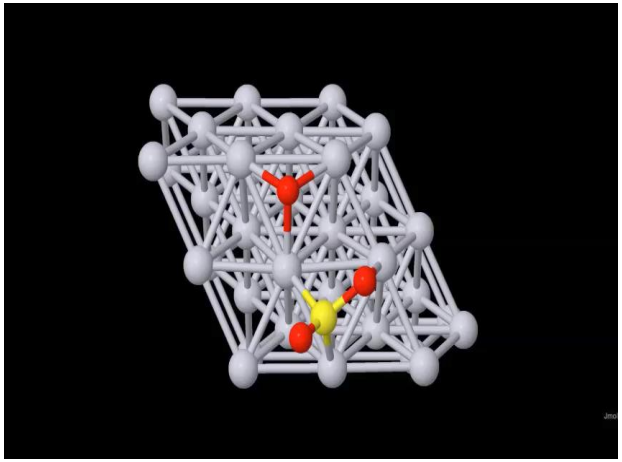
Path A- O diffusion

Path B &C – SO_2 diffusion



SO_2 Oxidation on Pt(111)/Pd(111) surfaces





Path A

Path B

Path C

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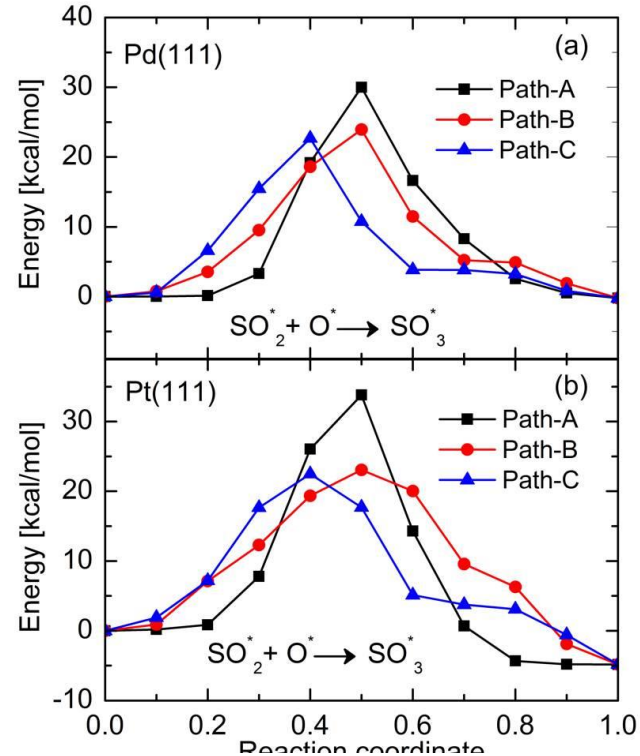
SO_2 oxidation on Pt(111)/Pd(111) surfaces

SO_2 Oxidation	Pt(111) E_a (Kcal/mol)	Pd(111) E_a (Kcal/mol)
This work	22.5-33.8	22.7-30
Experiment	~23[b-e]	
UBI-QEP	21.5[a]	22.3

Method	Path	Pt(111)		Pd(111)	
		E_a (kcal/mol)	A_o (s^{-1})	E_a (kcal/mol)	A_o (s^{-1})
CI-NEB	Path A	33.8	1.5×10^{11}	30.0	4.4×10^{12}
	Path B	23.1	1.1×10^{11}	23.9	6.1×10^{11}
	Path C	22.5	3.0×10^{11}	22.7	5.9×10^{11}



$$A_o = \frac{K_B T}{h} exp\left(\frac{\Delta S^o{}_f{}^{\ddagger}}{K_B}\right)$$

[a]Sharma, H. N.; Suib, S. L.; Mhadeshwar, A. B.; Novel Materials for Catalysis and Fuels Processing, ACS, 2013, In press;
[b]Nagoshi, H. A study of sulfur dioxide oxidation on platinum Master's thesis, 1972.
[c]Ertl, G.; Knzinger, H.; Schth, F.; Weitkam, J. Handbook of Heterogeneous Catalysis, Vol. 4; Wiley, 1997.
[d]Benzinger, W.; Wenka, A.; Dittmeyer, R. Appl. Catal., A 2011, 397(1-2), 209-217.
[e]Dupont, V.; Jones, J. M.; Zhang, S.-H.; Westwood, A.;Twigg, M. V. Chem. Eng. Sci. 2004, 59(1), 17-29.

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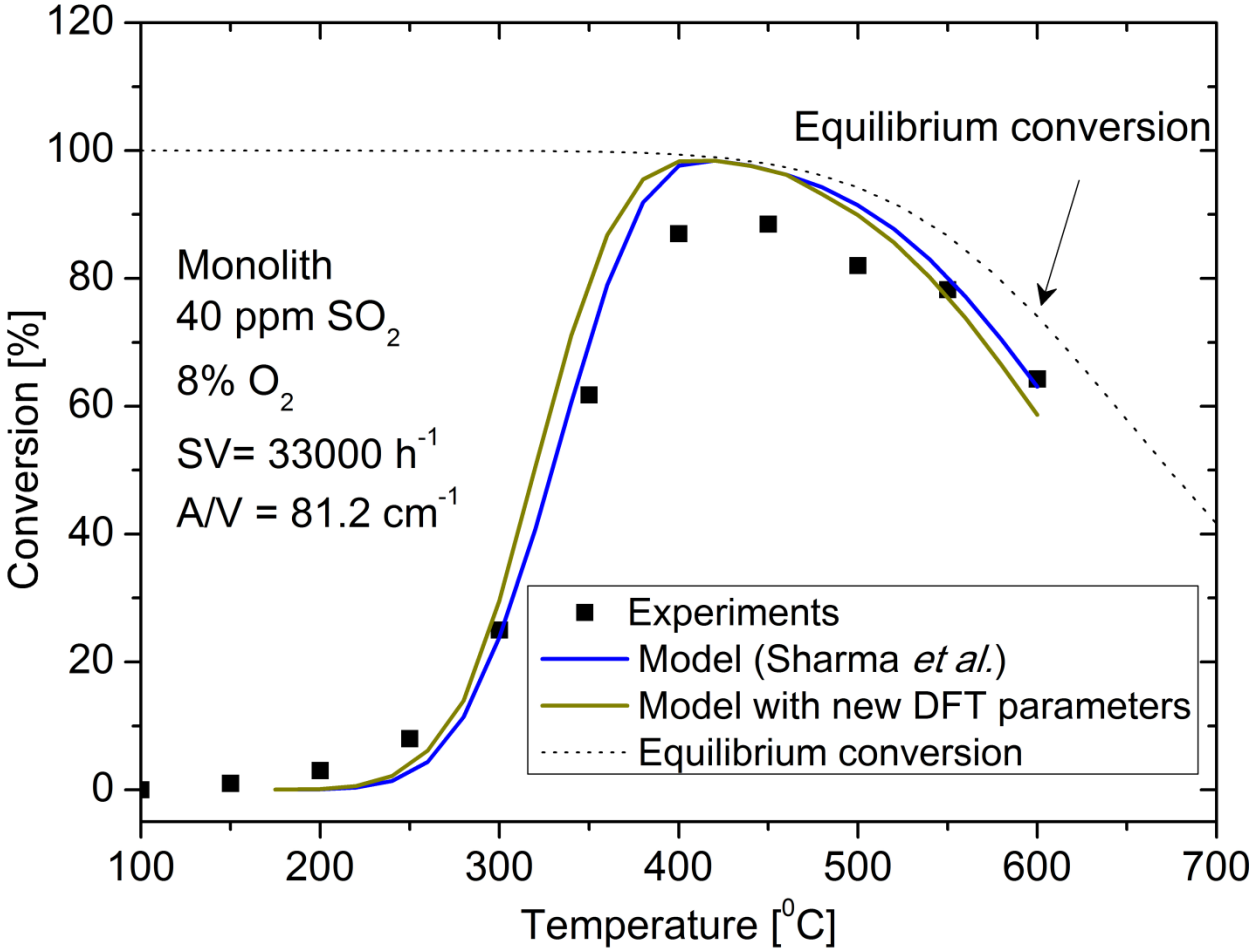
Validation of SO_2 model with DFT parameters

Utilizing Q and A from this work



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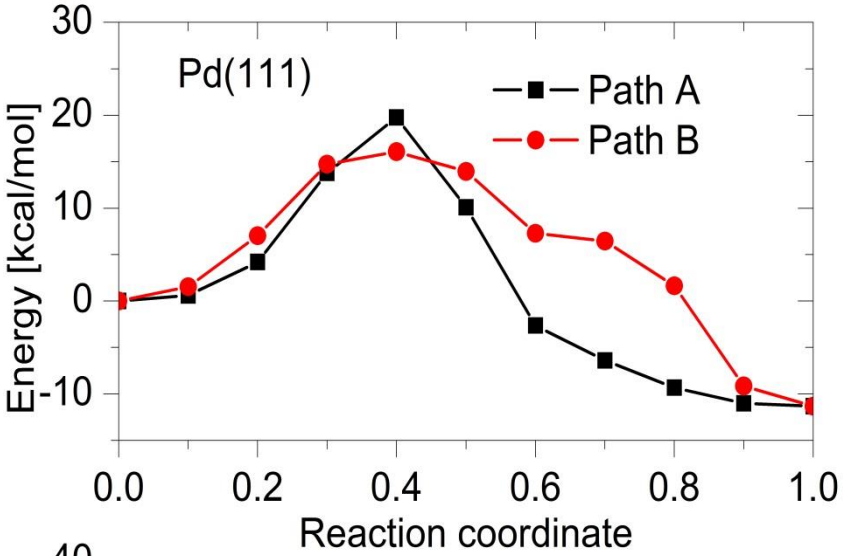
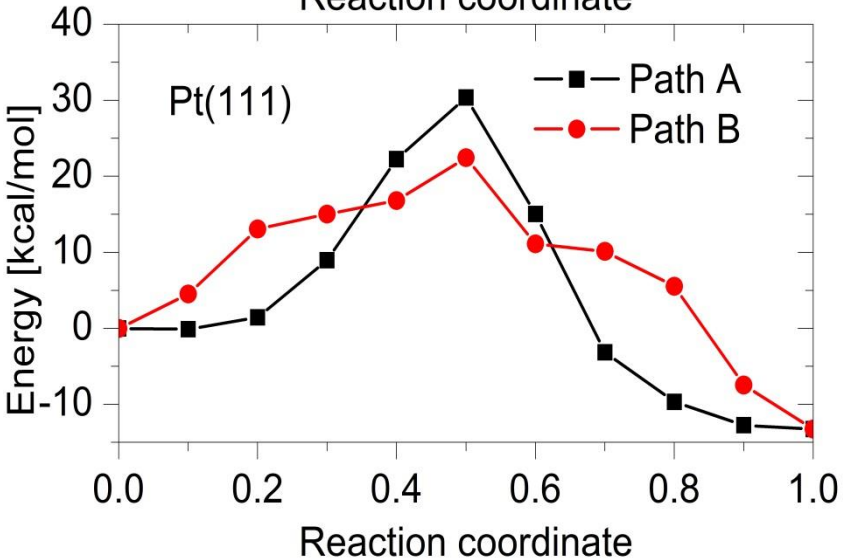
SO_3 Oxidation on Pt(111)/Pd(111) surfaces





$SO^*_3 + O^* \longrightarrow SO^*_4$

Path A- O diffusion

Path B – SO_3 diffusion

SO_3 Oxidation	Pt(111) E_a (Kcal/mol)	Pd(111) E_a (Kcal/mol)
Path-A	30.3	19.7
Path-B	22.4	16.0

Lower barrier for SO_4 formation on Pd(111) may indicate the possibility of sulfate formation on Pd catalysts as observed in experimental studies.

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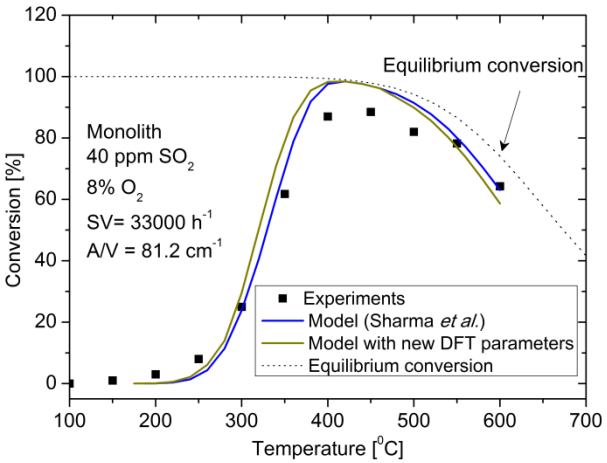
Summary

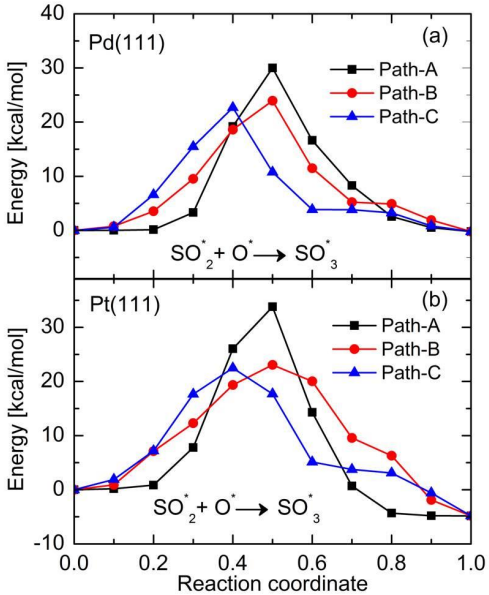
Microkinetic modeling

- SO_2 oxidation model was developed.
- Plug flow reactor model was used to test the SO_2 oxidation mechanism.
- Model performed well in DOC relevant conditions.



SO_x chemistry using DFT

- Various stable SO_x species were studied.
- Activation barriers and pre-exponential factors were computed and compared with experimental results.
- Microkinetic model was simulated using DFT computed parameters.



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Funding

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Group members

Postdocs

- **Dr. Clive Bealing**
- **Dr. Ghanshyam Pilania**
- **Dr. Vinit Sharma**

Graduate students

- **Satyesh, Venkatesh, Arun, Lihua, Chenchen, Yenny**

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