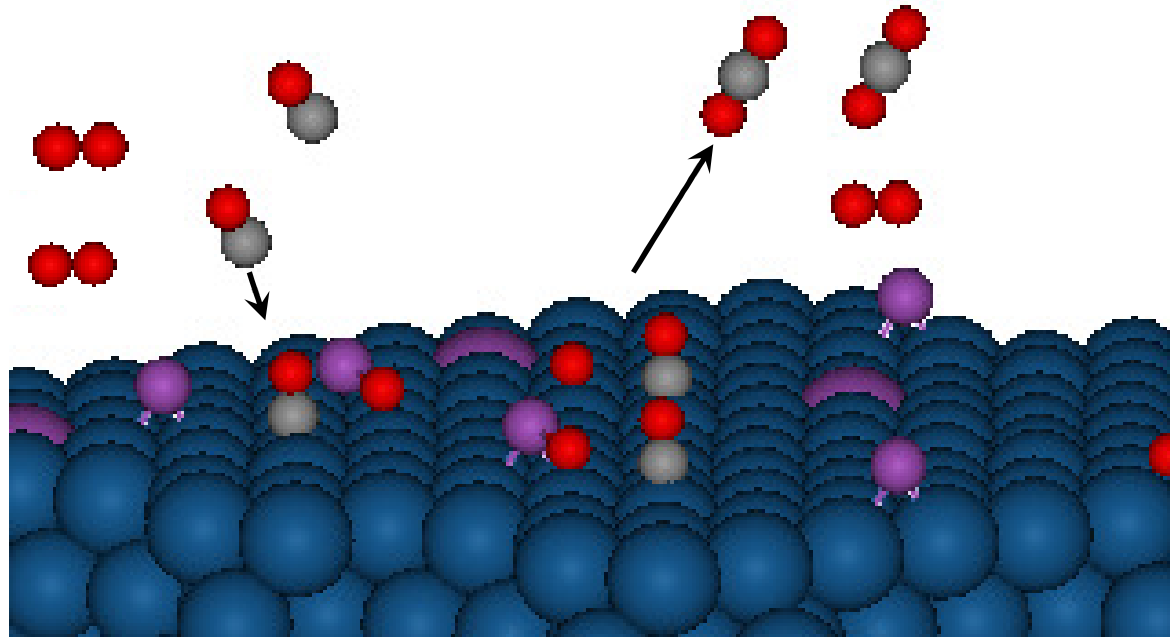


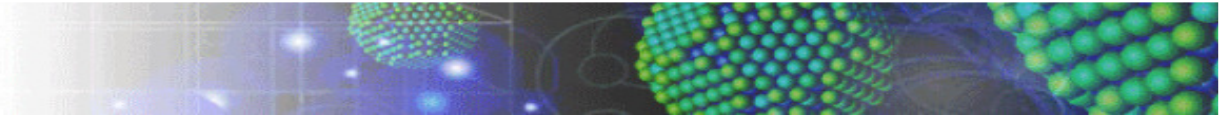
# Ab Initio Insights into Improved CO Oxidation on Bi doped Pt(111)

Neeti Kapur<sup>1</sup>, Bin Shan<sup>1</sup>, Jangsuk Hyun<sup>1</sup>, Ligen Wang<sup>1</sup>, Sang Yang<sup>1</sup>,  
John B. Nicholas<sup>1</sup> and Kyeongjae Cho<sup>2</sup>

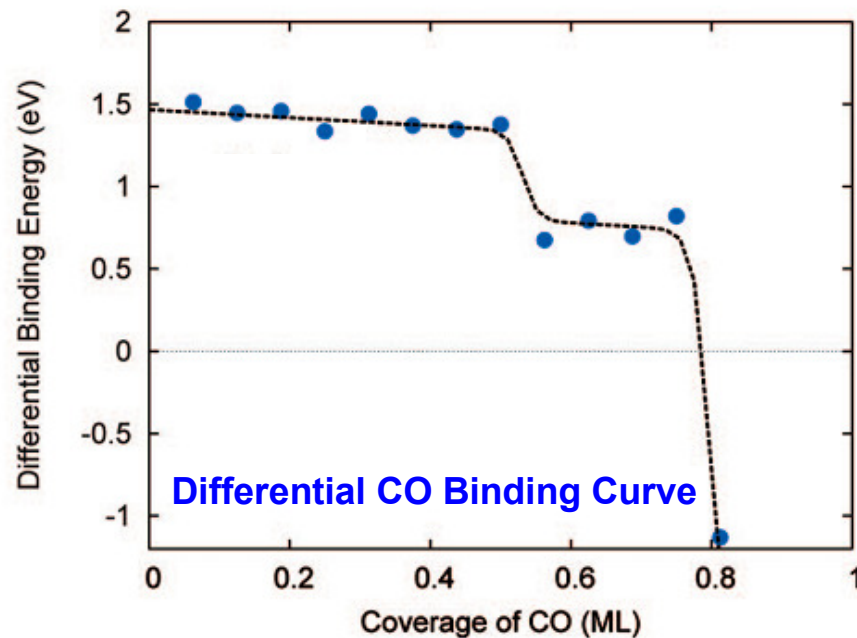
<sup>1</sup>*Nanostellar Inc., 3696 Haven Avenue, Redwood City, CA*

<sup>2</sup>*Department of Material Science and Engineering and Department of Physics, University of Texas at Dallas, Richardson, TX*

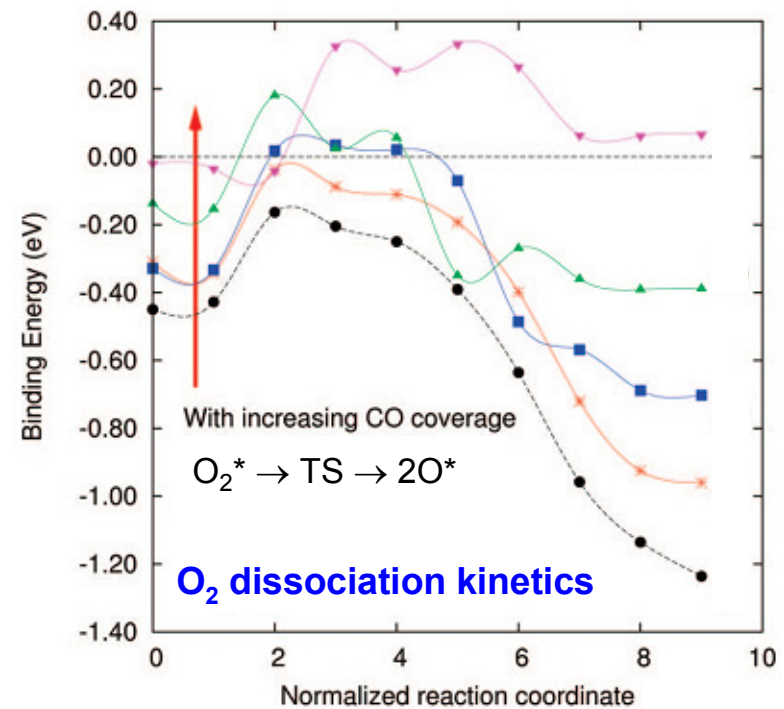




## CO Oxidation Mechanism on Pt(111)

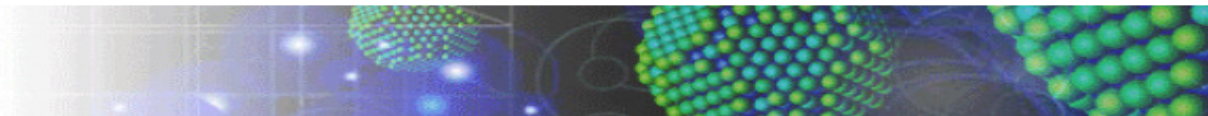


B. Shan et al, JPC C (2009) 113, 6088

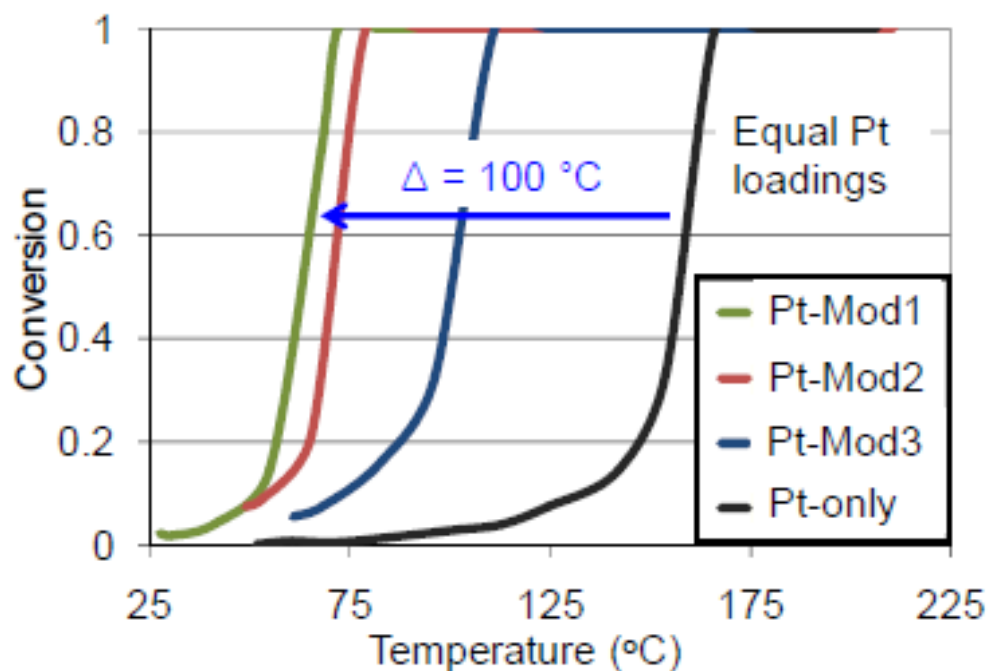


B. Shan et al, JPC C (2009) 113, 710

- Langmuir Hinshelwood mechanism for CO oxidation widely accepted on Pt
- CO oxidation on Pt based surfaces can be improved with **dopants which**
  - **Promote CO desorption** to alleviate surface poisoning
  - **Reduce  $O_2$  activation barrier**  $\rightarrow O^*$  readily available for surface reaction with  $CO^*$



## CO Light-off Characteristics on Pt and Bi Doped Pt

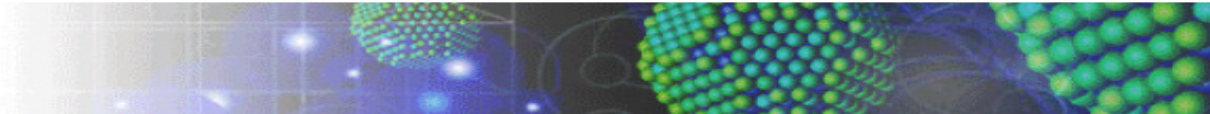


- Bi doping/Pt suppresses CO poisoning in direct alcohol fuel cells (Oana et al, Surf. Sci. (2005) 574, 1) (Blasini et al, Surf. Sci. (2006) 600, 2670)
- CO light-off temperature depends on Bi/Pt loading ratio

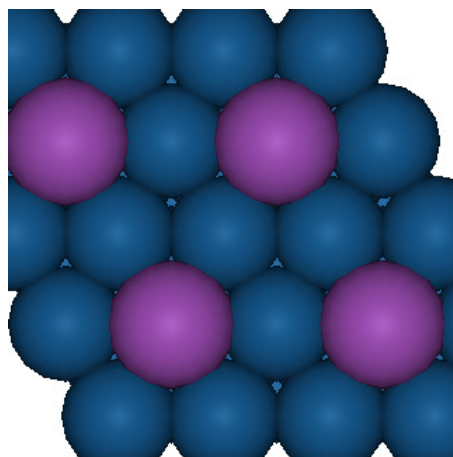
Nanostellar Inc. US Patent 7,605,109 B1  
SAE Paper 2008-01-0070

### **Objective: Understand role of Bismuth in promoting CO oxidation on Pt surfaces**

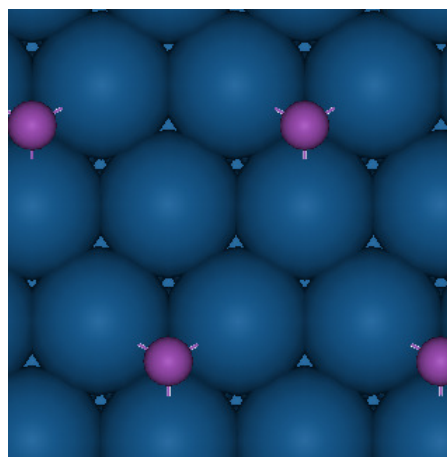
- Examine Bi as “site blocker” and its electronic effect on CO and O adsorption
- Investigate reaction kinetics for O<sub>2</sub> dissociation and CO oxidation on Bi promoted Pt
  - Bi can exist in both reduced (XAS) and partially oxidized suboxide (XPS) under O<sub>2</sub> rich conditions (Keresszegi et al, J. Catal (2004) 225, 138 & Taylor et al. Surf. Sci. (1983) 134, 529)



## Computational Methodology



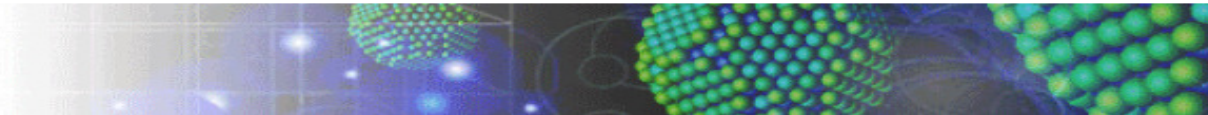
PtBi surface alloy



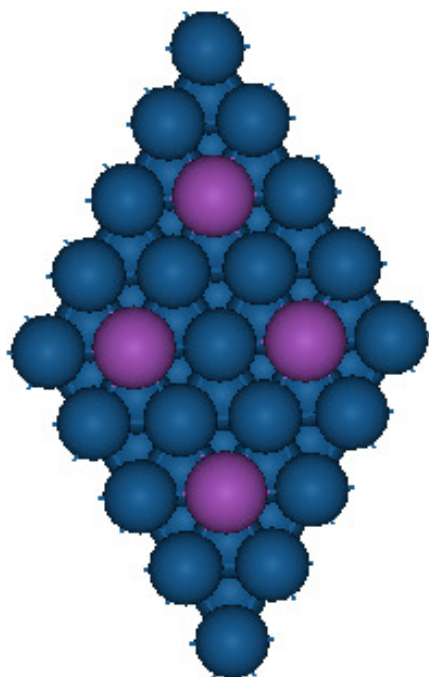
Bi adatom

### Density functional theory calculations in VASP

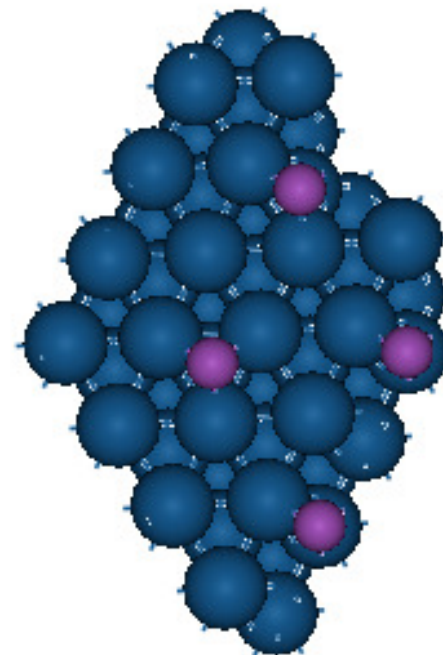
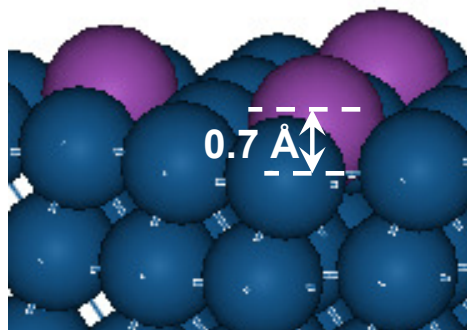
- Three-layered Pt(111) metal slab, top two layers allowed to relax
- Bi atom modeled as both **surface dopant** and as **adatom**
- (2x2) and (4x4) unit cell
- (4x4x1) and (2x2x1) Monkhorst-Pack scheme for k-points sampling
- RPBE exchange-functional, PAW pseudopotentials, Cutoff energy 400eV
- Transition states calculated by dimer method



## Favorable Configurations for Bi Promoter/Pt(111)

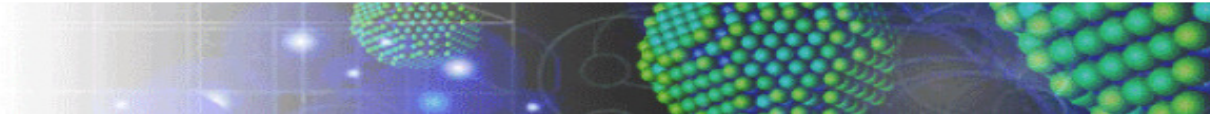


PtBi Surface Alloy  
(Pt<sub>3</sub>Bi/Pt(111))



Bi<sub>ad</sub>/ Pt(111)

- Bi surface dopant induces strain in Pt substrate since Bi (3.09 Å) has larger atomic radii than Pt (111) lattice (2.78 Å)
- Bi adatom favors binding on three-fold hcp site (-383 kJ/mol (0.25 ML) & -393 kJ/mol (0.0625 ML))
- **Bi adatom/Pt surface is energetically more stable than Bi surface dopant configuration by 52 kJ/mol**
  - Bi adatom/Pt (111) vs (PtBi surface alloy + bulk Pt atom)

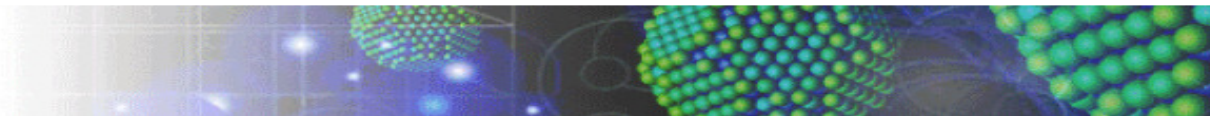


## CO Adsorption on Pt<sub>3</sub>Bi/Pt(111) Surface Alloy & Bi<sub>ad</sub>/Pt(111)

Site	Binding Energy (kJ/mol)		
	Pt(111)	PtBi surface alloy	Bi <sub>ad</sub> /Pt(111)
Atop Pt	-132	-81	-67
Atop Bi	/	-2	Desorbs
Bridge Pt-Bi	/	atop Pt	bridge Pt-Pt
Bridge Pt-Pt	-137	-89	-49
FCC Pt-Pt-Pt	-133	-92	-78
HCP Pt-Pt-Pt	-134	-93	-70
FCC Pt-Pt-Bi	/	bridge Pt-Pt	atop Pt
HCP Pt-Pt-Bi	/	bridge Pt-Pt	/

- CO binding is significantly weakened (~ 50-70 kJ/mol) on Bi doped Pt(111) substrate
  - d-band center for Bi doped Pt (-2.27 eV) is lower than that for Pt (-2.14 eV)
  - CO easier to desorb from Bi adatom configuration due to increase in interatomic repulsions

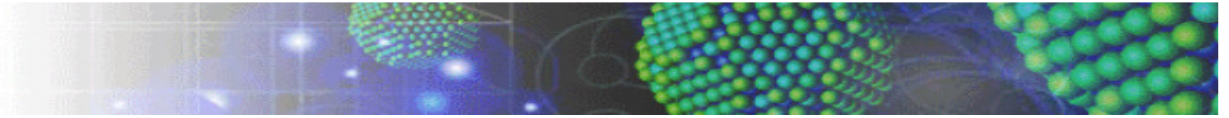




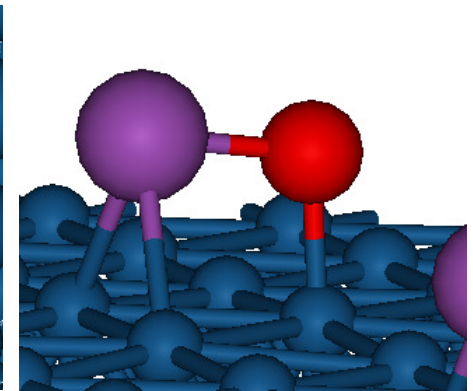
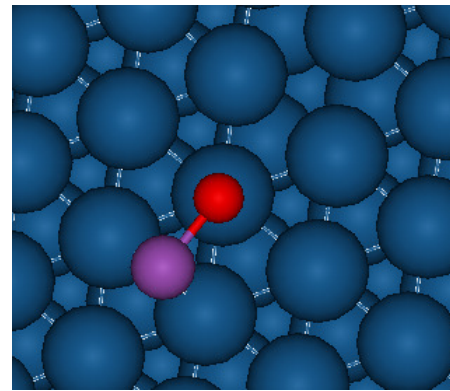
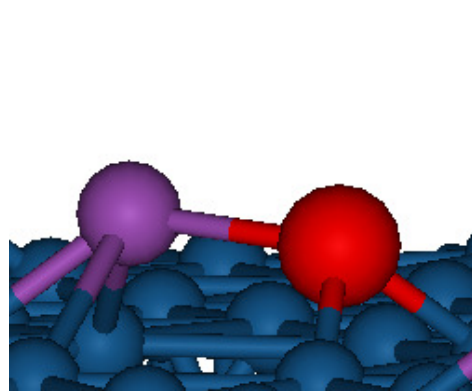
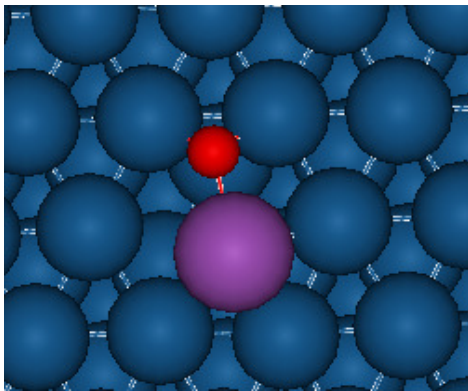
## O\* Binding on Pt<sub>3</sub>Bi/Pt(111) Surface Alloy & Bi<sub>ad</sub>/Pt(111)

Site	Binding Energy (kJ/mol)		
	Pt(111)	PtBi surface alloy	Bi <sub>ad</sub> /Pt(111)
Atop Pt	26	71	-10
Atop Bi	/	51	69
Bridge Pt-Bi	/	BiO*	fcc Pt-Pt-Pt
Bridge Pt-Pt	fcc Pt-Pt-Pt	BiO*	BiO*
FCC Pt-Pt-Pt	-106	-54	9
HCP Pt-Pt-Pt	-49	-20	BiO*
FCC Pt-Pt-Bi	/	BiO*	BiO*
HCP Pt-Pt-Bi	/	BiO*	/

- Similar to CO\*, O\* is weakly bound on both configurations of Bi promoted Pt(111)
- **O\* adsorption is favorable in the vicinity of the dopant atom where CO adsorption is prohibited**
  - O\* easily pulls Bi out of the strained surface alloy structure to form oxide-like structure when O\* is in the CO-free zone
  - Bi adatom is thermodynamically favored to form BiO suboxide when in close contact with O\*



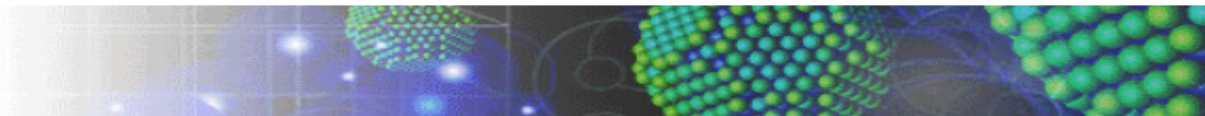
## O\* Binding on Pt<sub>3</sub>Bi/Pt(111) Surface Alloy & Bi<sub>ad</sub>/Pt(111)



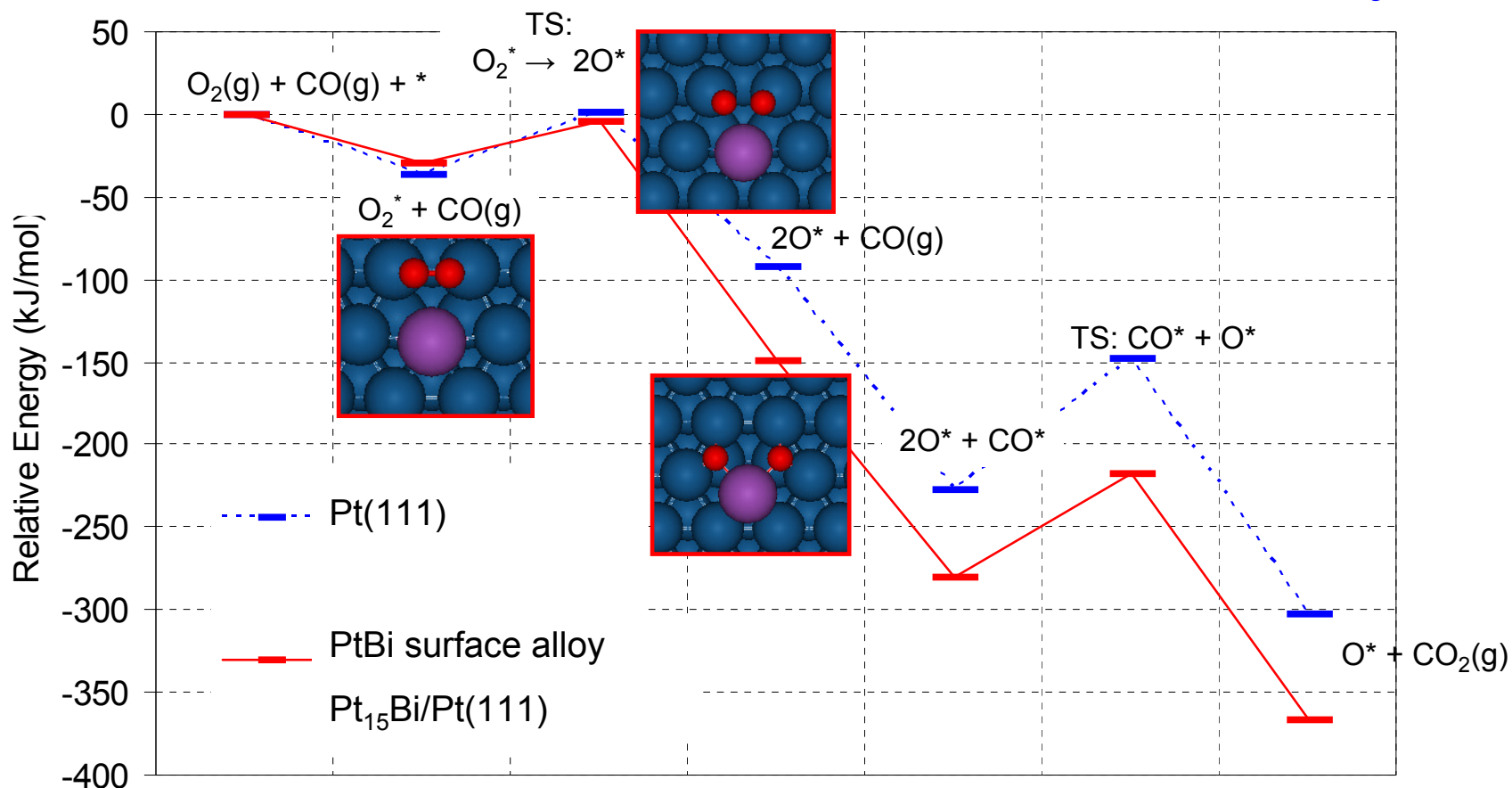
**PtBi Surface Alloy  
Pt<sub>3</sub>Bi/Pt(111)**

**Bi<sub>ad</sub>/ Pt(111)**

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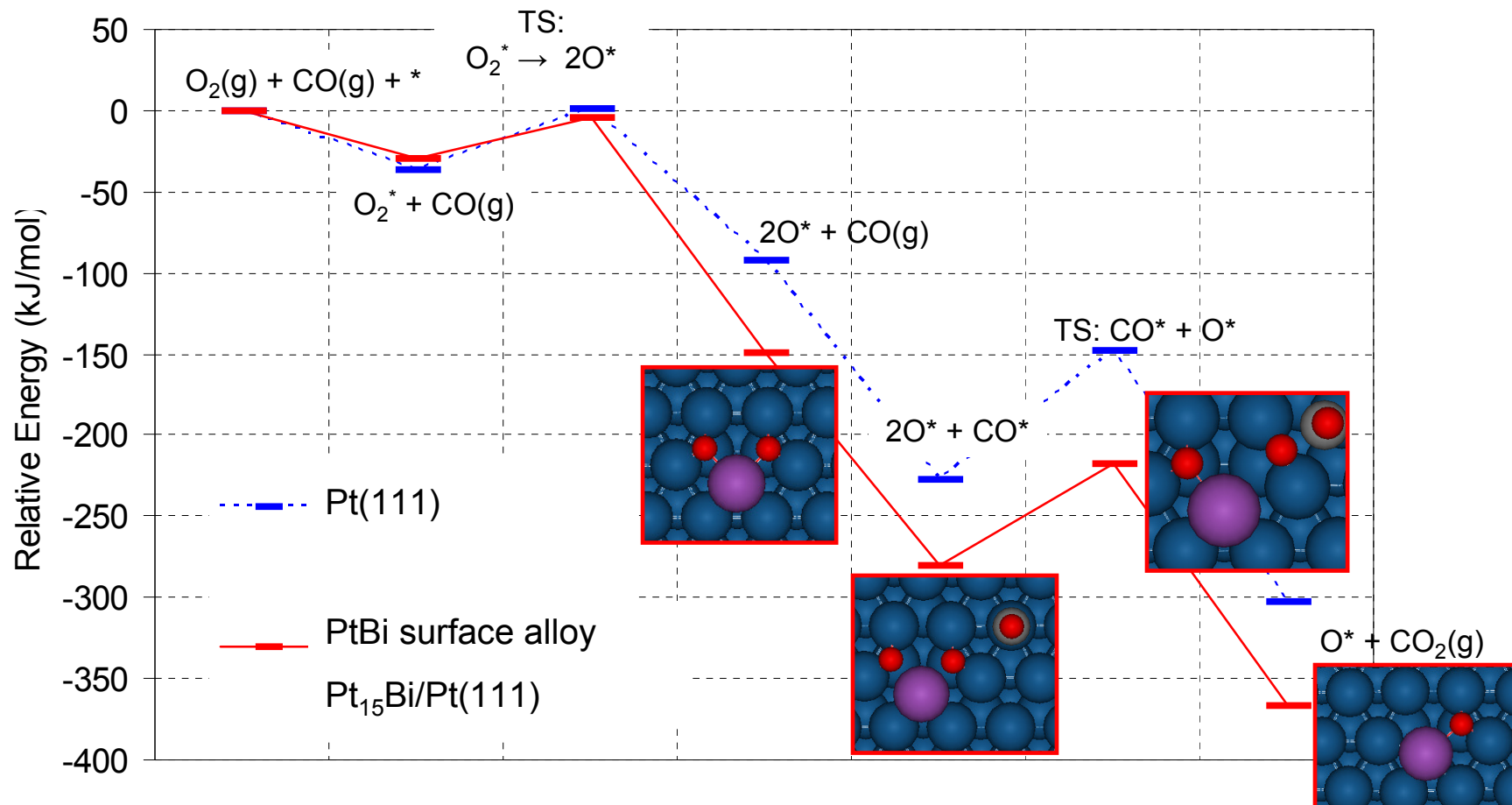


## CO Oxidation Kinetics on PtBi Surface Alloy

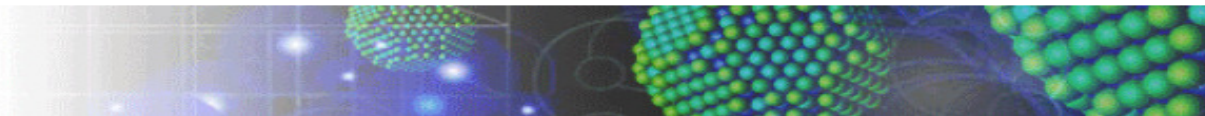


- O-O scission is exothermic on PtBi surface alloy due to BiO\* formation
  - Early TS structure and barrier equals 24 kJ/mol (38 kJ/mol on Pt(111))
- CO oxidation proceeds via late TS on PtBi surface alloy (barrier of 64 kJ/mol while 80 kJ/mol on Pt(111))
- **CO oxidation proceeds readily on PtBi surface alloy via lower energy states**

## CO Oxidation Kinetics on PtBi Surface Alloy



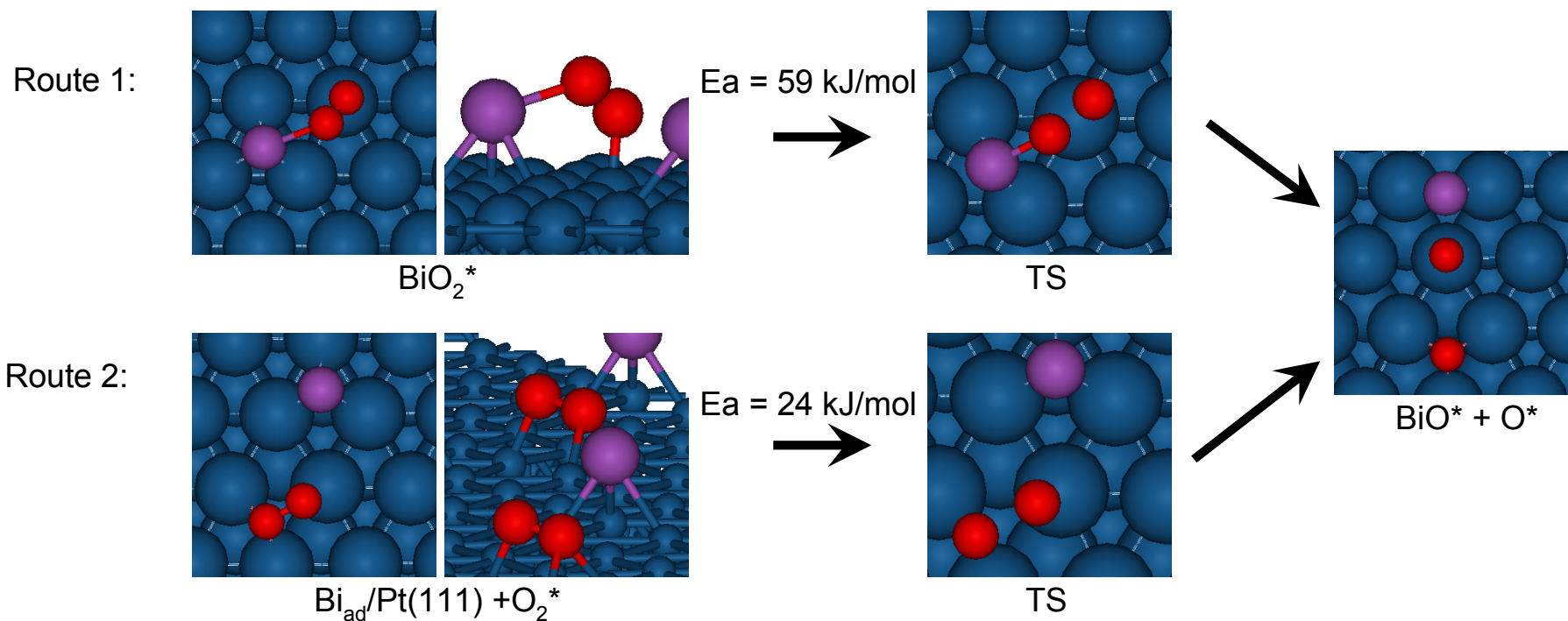
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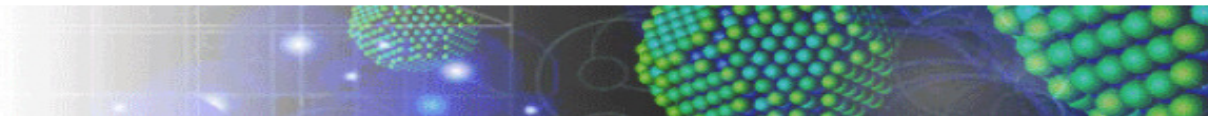
## O<sub>2</sub> Dissociation on Bi<sub>ad</sub>/Pt(111) Configuration

Two potential routes

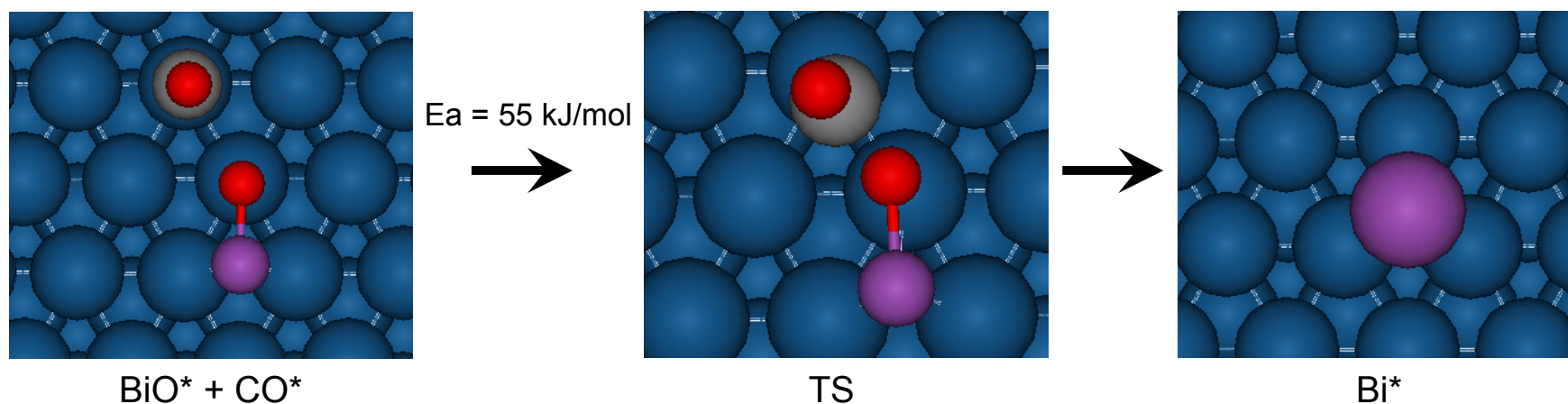
- 1) Bi<sub>ad</sub> → BiO<sub>2</sub>\* → BiO\* + O\*
- 2) Molecular O<sub>2</sub> precursor → BiO\* + O\*



- BiO<sub>2</sub> formation is exothermic by 12 kJ/mol while O<sub>2</sub> binding energy equals 31 kJ/mol
- ***Molecular O<sub>2</sub> precursor route is favored energetically and kinetically for O\* and BiO\* formation in Bi adatom configuration***

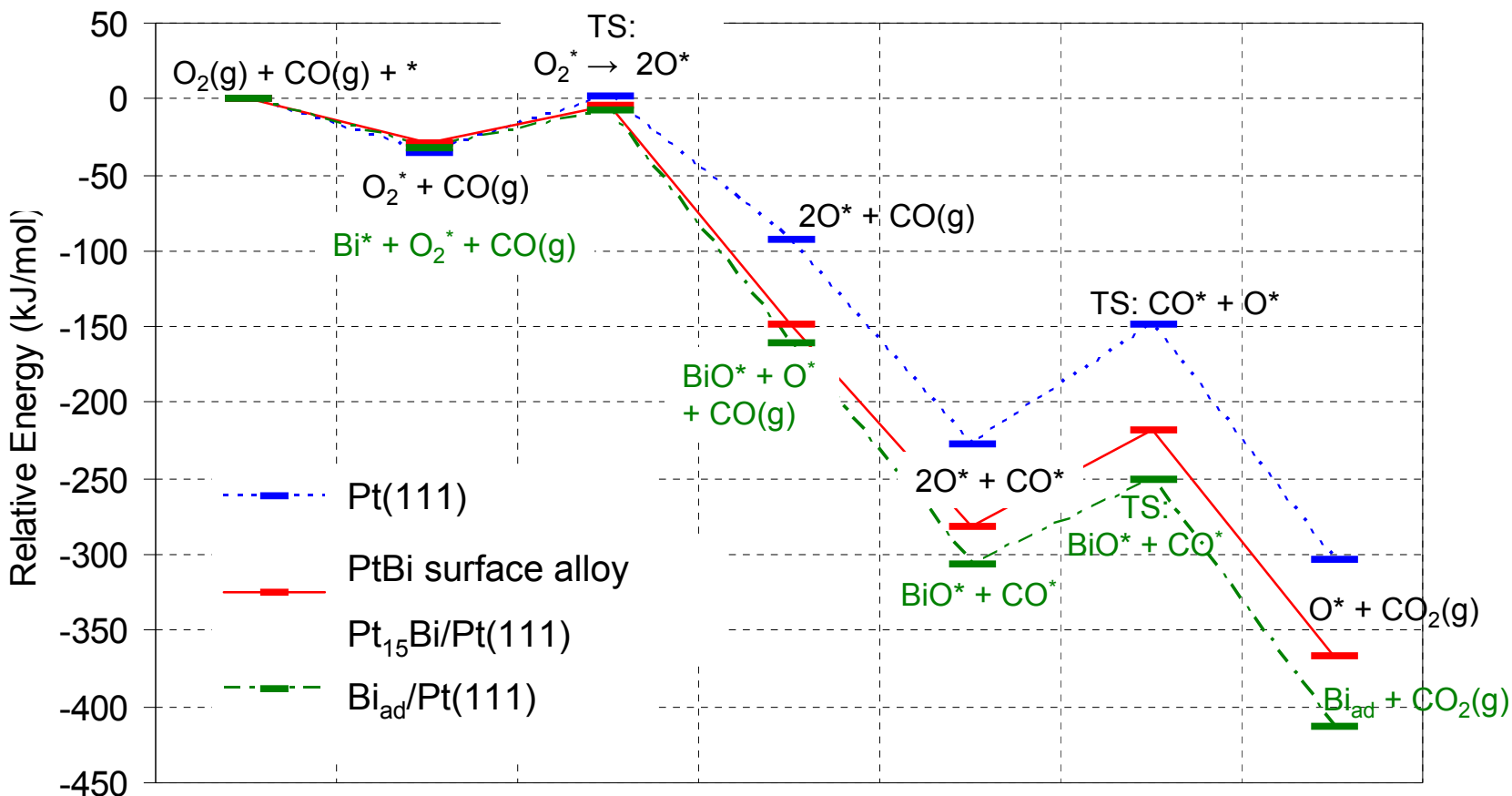


## CO Oxidation Kinetics on Bi<sub>ad</sub>/Pt(111) Configuration

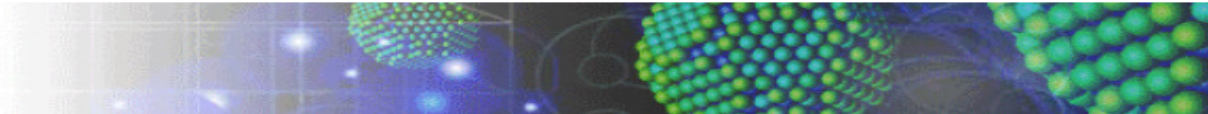


- O\* extraction from BiO\* is kinetically favored for CO oxidation rather than CO\* + O\* surface reaction (Ea equals 80 kJ/mol)
- **Overall reaction pathway for CO oxidation on this dopant configuration energetically lower than Pt and comparable to PtBi surface alloy**

## CO Oxidation Kinetics on Bi<sub>ad</sub>/Pt(111) Configuration



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- **Overall reaction pathway for CO oxidation on this dopant configuration energetically lower than Pt and comparable to PtBi surface alloy**



## Summary: Bi Doped Pt Promotes CO oxidation

- CO oxidation on Bi doped Pt proceeds via states lower in energy than those on Pt(111), for both dopant configuration considered
- Bi dopant promotes elementary reactions involved in the CO oxidation mechanism by affecting electronic and geometric characteristics of Pt substrate
- Reduced CO poisoning on Bi doped Pt substrate
  - Blocks Pt adsorption sites
  - Repels CO from Pt sites in the vicinity of dopant atom to create a CO-free zone
  - Lowers CO desorption barrier on doped substrate
- Enhanced O<sub>2</sub> dissociation and CO oxidation to CO<sub>2</sub> in the presence of Bi dopant
  - O<sub>2</sub> adsorption and dissociation allowed in the CO-free zone around Bi dopant
  - O<sub>2</sub> dissociation promoted kinetically and thermodynamically due to BiO (suboxide) formation
  - Reduced CO oxidation barrier due to surface reaction between CO\* and BiO\*

*Catalytic properties for Bi modified Pt(111) controlled by simultaneous weakening of CO adsorption and preferential oxygen adsorption near dopant atoms*