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First-principles comparison of NO_x and SO_x storage mechanisms on alkaline earth oxides

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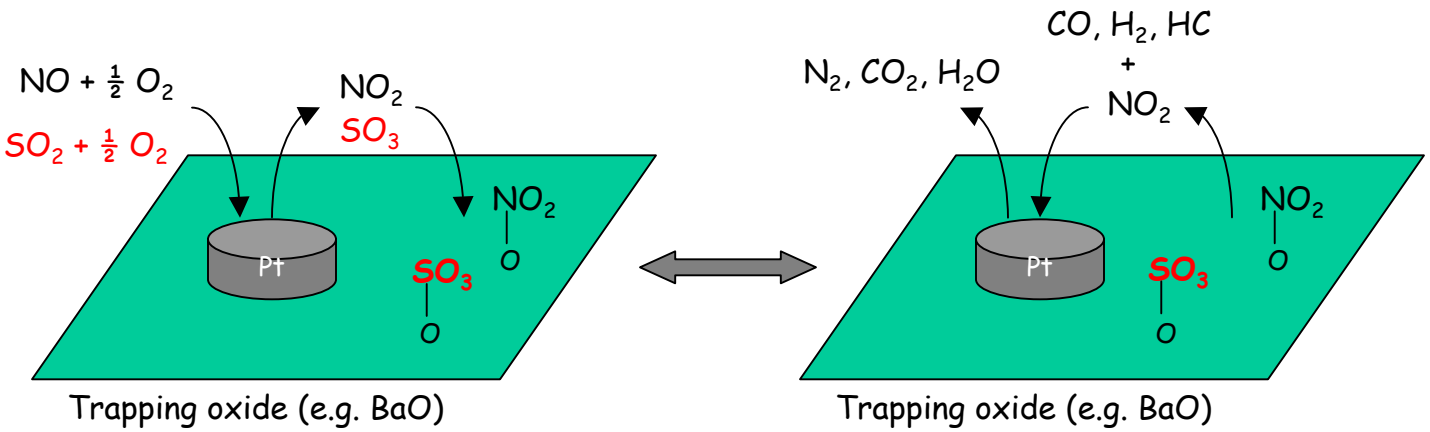
Molecular mechanism of NO_x trapping on oxides



Lean Conditions

NO_x and SO_x oxidized & trapped

Rich Conditions

NO_x decomposed and reduced, SO_x recalcitrant

Key Questions:

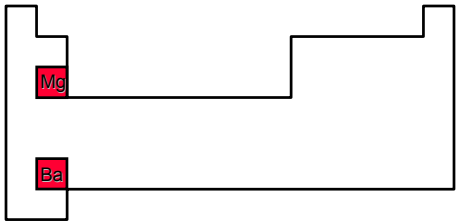
- ★ How does NO_x get oxidized and adsorbed on a trapping material?
- ★ How does the SO_x chemistry compare to NO_x?
- ★ How can we select trap materials to optimize selectivity for NO_x over SO_x?

- ★ Is this accepted NO_x trap picture valid?

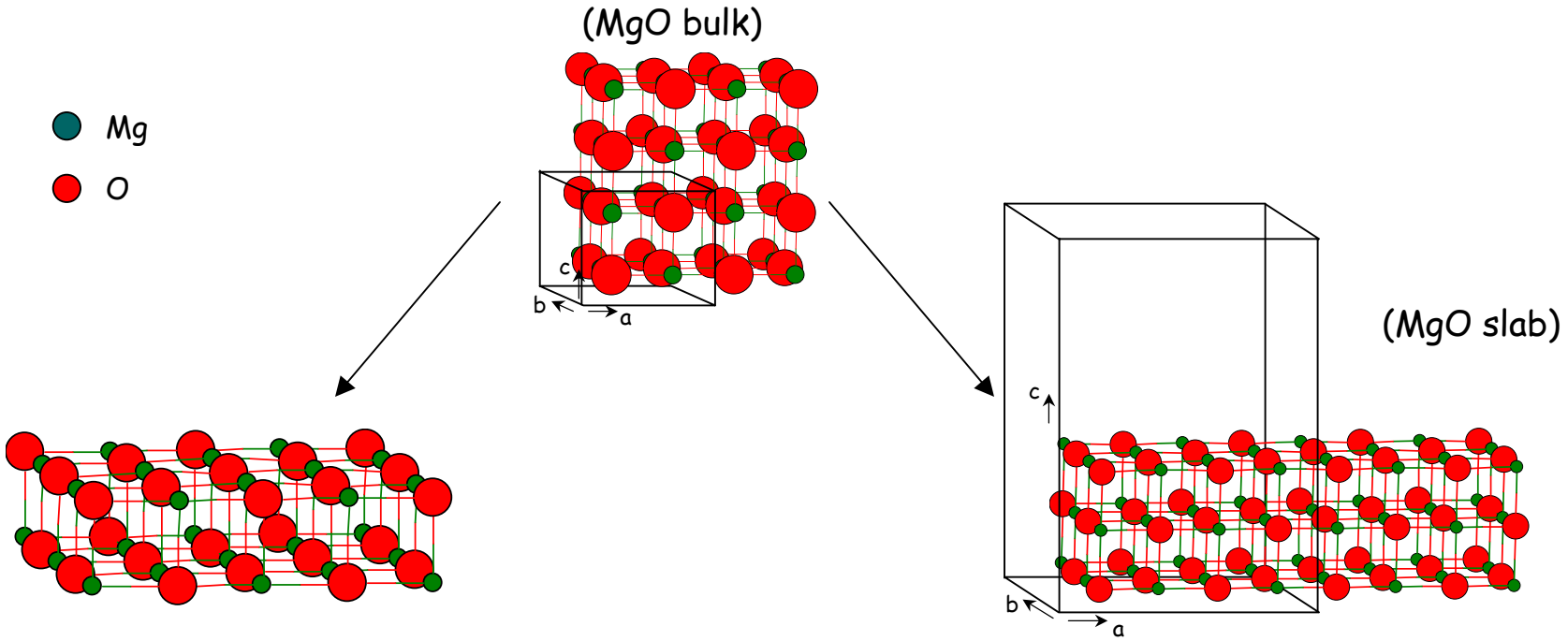
Alkaline Earth Oxide Adsorbents for NO_x Aftertreatment

- ★ Overall objectives
  - o To understand the intermediates, the thermodynamics, and the kinetics of adsorption, oxidation, and storage of NO_x and SO_x on metal oxides
  - o To use this information to help guide the selection of NO_x trap materials and the development of kinetic models of NO_x trap function

- ★ This work
  - o Use first-principles methods to simulate adsorption chemistry
    - o Atomic-level models provide detailed understanding of adsorption phenomena
  - o Focus on SO_x and NO_x on MgO
    - o Prototypical alkaline earth oxide
    - o Component of proposed low temperature NO_x traps
    - o Computationally convenient
    - o Easy to obtain controlled materials for experiments
    - o Numerous experimental results available



MgO Cluster and Supercell Models



"cluster" models
$(MgO)_n$ isolated clusters

DMol code
GGA xc-potential
All-electron
Atomic-like basis functions

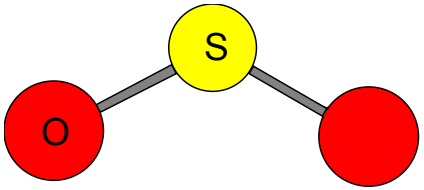
"supercell" models
$(MgO)_n$ periodic slab

Vasp code
GGA xc-potentials
"Ultrasoft" pseudopotentials
Plane-wave basis functions

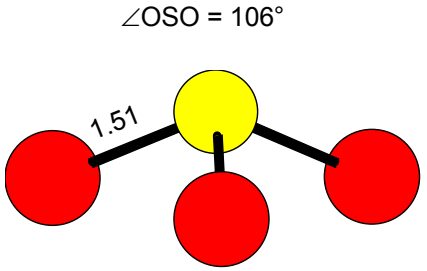
Sulfur Oxides-Lewis Acids

SO_2

	S-O	∠OSO
Exp't	1.43	118.9
LDA	1.448	119.4
GGA	1.466	119.2



O^{2-}

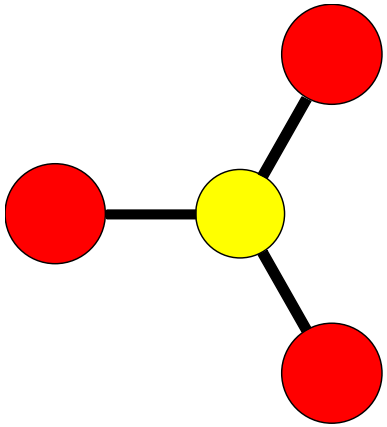


SO_3^{2-}
(sulfite)

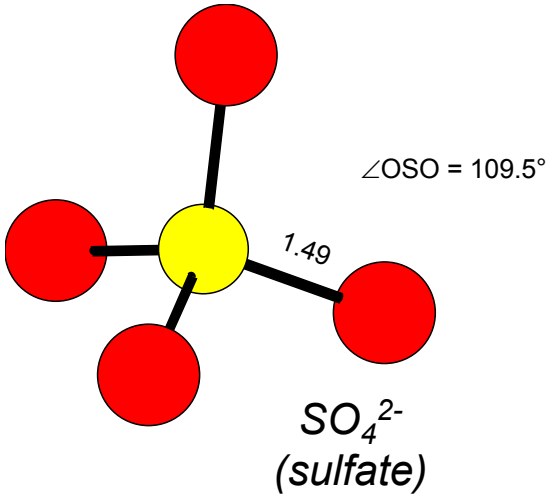
½ O_2

SO_3

	S-O
Exp't	1.42
LDA	1.439
GGA	1.456



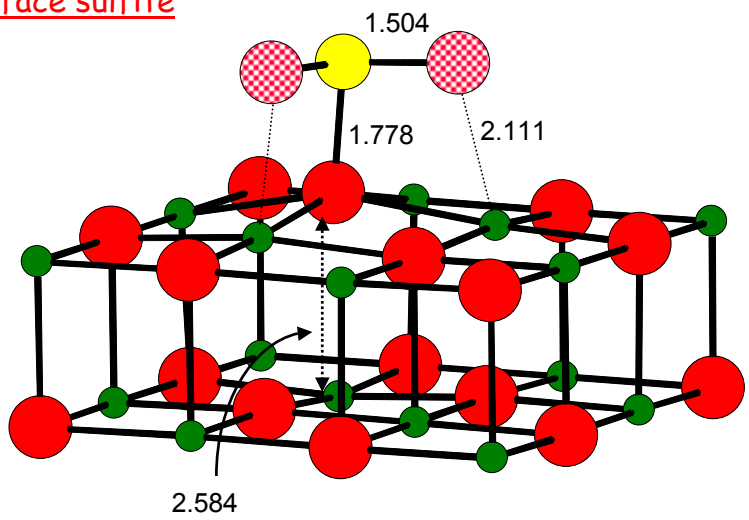
O^{2-}



SO_4^{2-}
(sulfate)

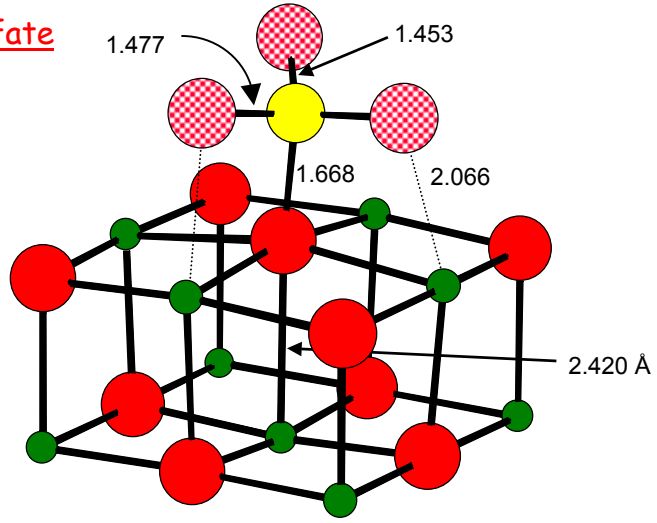
SO_x Chemisorption on MgO Terrace

Surface sulfite



MgO(001) + SO_2
-25 kcal mol^{-1}

Surface sulfate



MgO (001) + SO_3
-54 kcal mol^{-1}

- ★ SO_2 and SO_3 chemisorb at Lewis base oxygen anions
  - o Form surface "sulfites" and "sulfates," respectively
  - o Pronounced local distortions of oxide surface
  - o Weak coverage dependence on adsorption energy
- ★ Adsorption enhanced 20 – 30 kcal mol^{-1} at step edges
- ★ Similar results on BaO surface

$MgO + SO_x$ Vibrational Spectroscopy

	calc'd (LDA, CPMD, cm^{-1})			exp't (cm^{-1})		
	ν_{asym}	ν_{sym}		ν_{asym}	ν_{sym}	
SO_2	1318	1119		1361	1151	
$MgO(100) + SO_2$						
physisorbed	1251	1075		1339	1132	
chemisorbed	1096	1017		1030-1050	950-960	
$MgO(103) + SO_2$	1041	962		"	"	
	$\nu_{e'}$	$\nu_{e'}$	$\nu_{a'}$	$\nu_{e'}$	$\nu_{e'}$	$\nu_{a'}$
SO_3	1345	1345	1026	1330	1330	1069
$MgO(100) + SO_3$	1239	1204	999	1260	1100	930
$MgO(103) + SO_3$	1274	1094	955	"	"	"

Schneider, Li, and Hass, *JPC B* **2001**, *105*, 6972

- ★ *MgO* powder + SO_2
  - o Observed "surface sulfite" consistent with calculated SO_2 chemisorption
  - o Observed physisorption NOT consistent with calculation—likely an SO_2 overlayer on chemisorbed SO_2
- ★ *MgO* powder + SO_2 + O_2
  - o "Surface sulfite" observed at low temperatures
  - o Higher temperature "surface sulfate" consistent with calculated SO_3 chemisorption

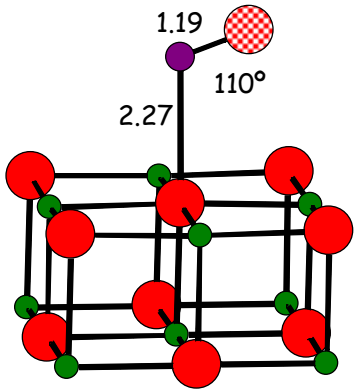
How does NO_x adsorb on MgO?
(First-order guess)

Common nitrogen oxides: NO, NO_2, NO_3

NO_x as Lewis acid	NO_x as Lewis base	
O_s-NO	Mg_s-ONO	"nitrite"
O_s-NO_2	Mg_s-ONO_2	"nitrate"

$NO\cdot/NO_2\cdot$ Physisorption on MgO Terrace

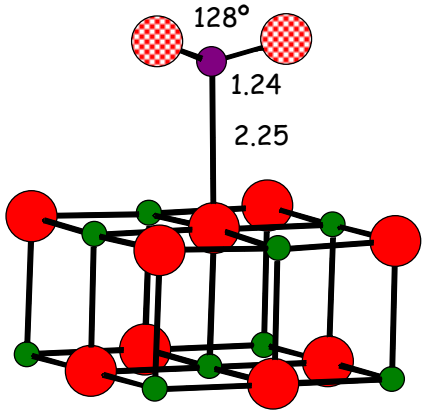
Physisorbed NO



MgO(001) + NO:

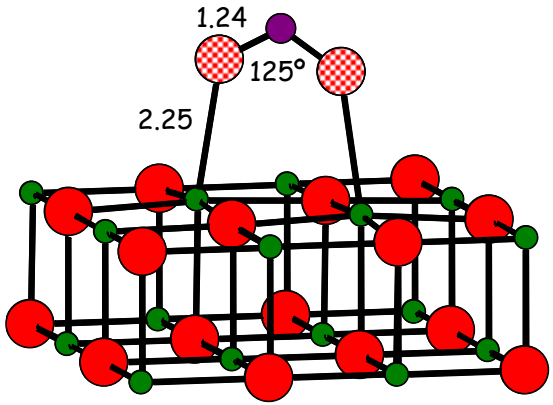
-6 kcal mol^{-1}

Physisorbed NO_2



MgO(001) +NO_2 N-down

-5 kcal mol^{-1}

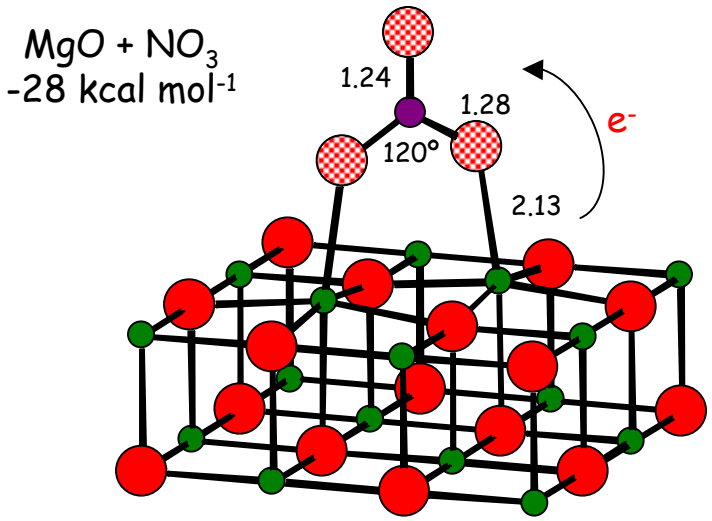


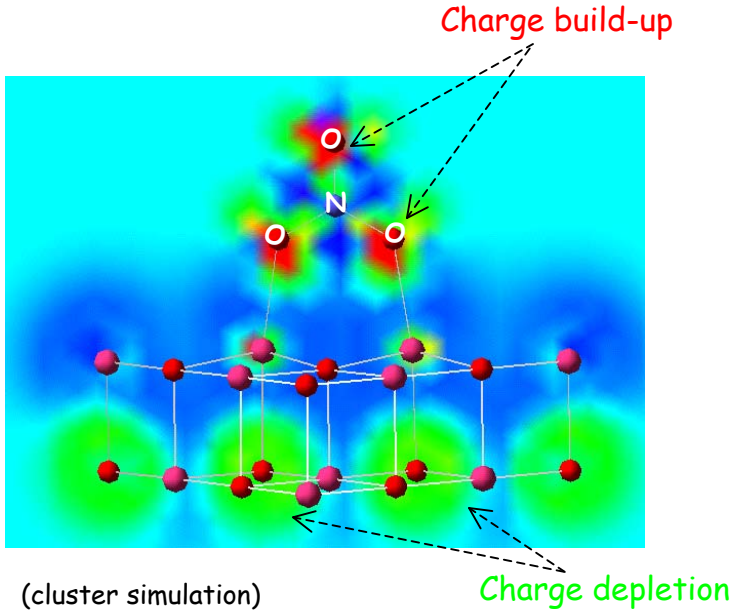
MgO(001) +NO_2 O-down

-10 kcal mol^{-1}

- ★ NO and NO_2 physisorb on MgO terraces
  - o Low NO_x Lewis basicity produces weak adsorbate-surface interactions
    - o Charge-dipole interaction with weak charge transfer to adsorbate
- ★ Not consistent with observations of "nitrite" and "nitrate" upon exposure of MgO to NO_x!

NO_3· Adsorption on MgO Terrace



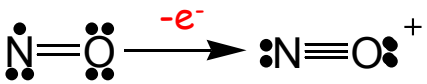


(cluster simulation)

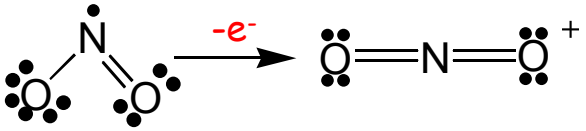
- ★ NO_3 binds more strongly than NO/NO_2 to MgO terraces
  - o NOT via Lewis acid-base interaction through surface O^{2-}, rather…
  - o Strongly oxidizing NO_3 draws nearly 1 electron from MgO
  - o Product "NO_3^-" coordinates to surface Mg^{2+}
  - o Multiple adsorbates strongly repel one another
- ★ Is this the correct model for nitration of MgO by NO_2?

Lewis Acid/Base Chemistry of NO_x

Lewis acids

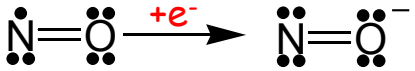


+9.26 eV

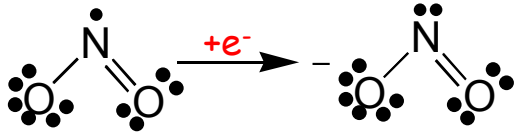


+9.59 eV

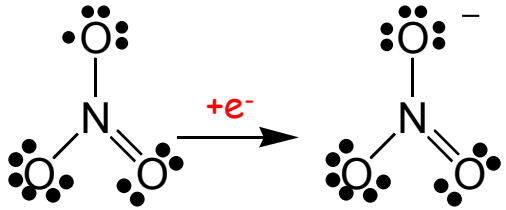
Lewis bases



-0.03 eV



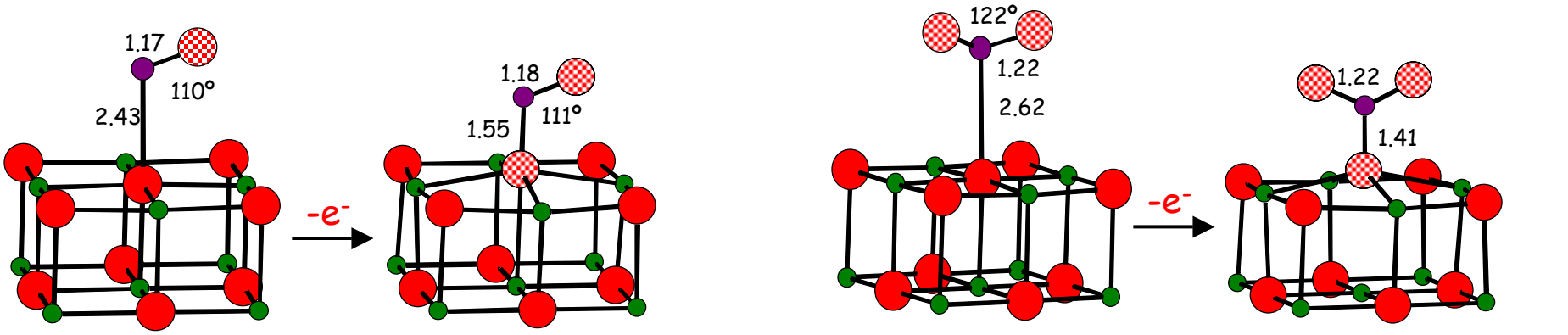
-2.27 eV



-3.91 eV

- ★ Lewis acid and base forms of NO_x generated by reduction and oxidation by one electron
- ★ Key questions:
  - o Do ionic NO_x forms bind more strongly to MgO than neutral ones?
  - o Can two NO_x molecules exchange an electron to produce complementary Lewis acid and base pairs?

NO_x^+ as Powerful Lewis Acids

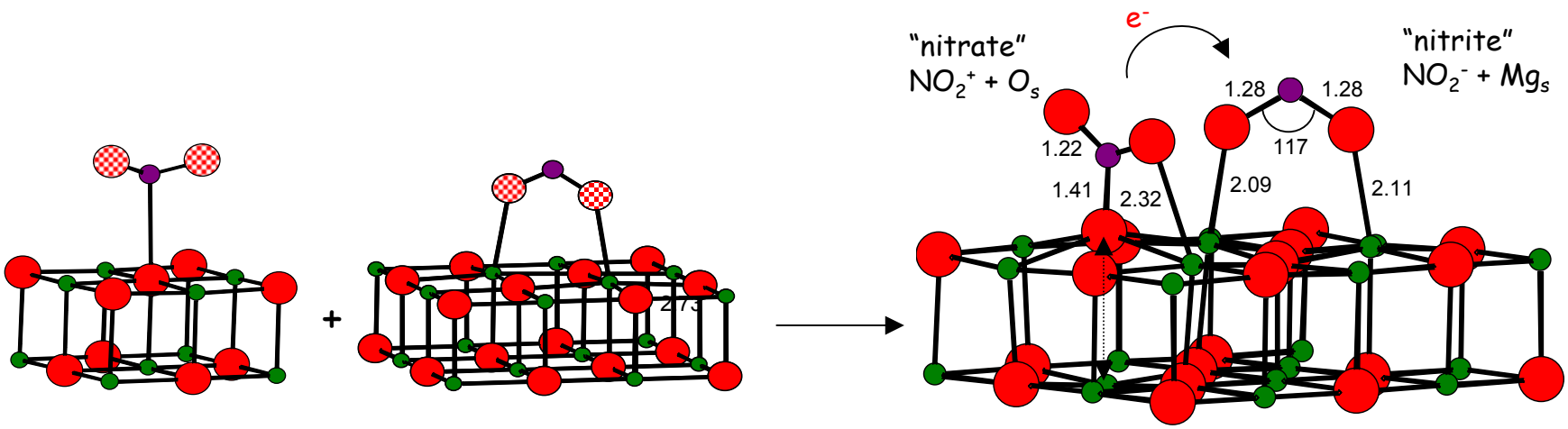


NO + MgO	NO^+ + $MgO \rightarrow Mg\text{-}ONO^-$	NO_2 + MgO	NO_2^+ + $MgO \rightarrow Mg\text{-}ONO_2^-$
-11 kcal/mol	-108 kcal/mol	-15 kcal/mol	-106 kcal/mol
Physisorbed NO	*Chemisorbed "nitrite"*	*Physisorbed NO_2*	*Chemisorbed "nitrate"*

★ NO^+/NO_2^+ strongly chemisorb on surface oxygen sites
- Geometric changes consistent with chemisorption
- Pronounced adsorption energy enhancement over neutrals

★ Somewhat less pronounced differences between NO_2^-/NO_3^- and NO_2/NO_3

Cooperative NO_2 Adsorption on MgO(001)

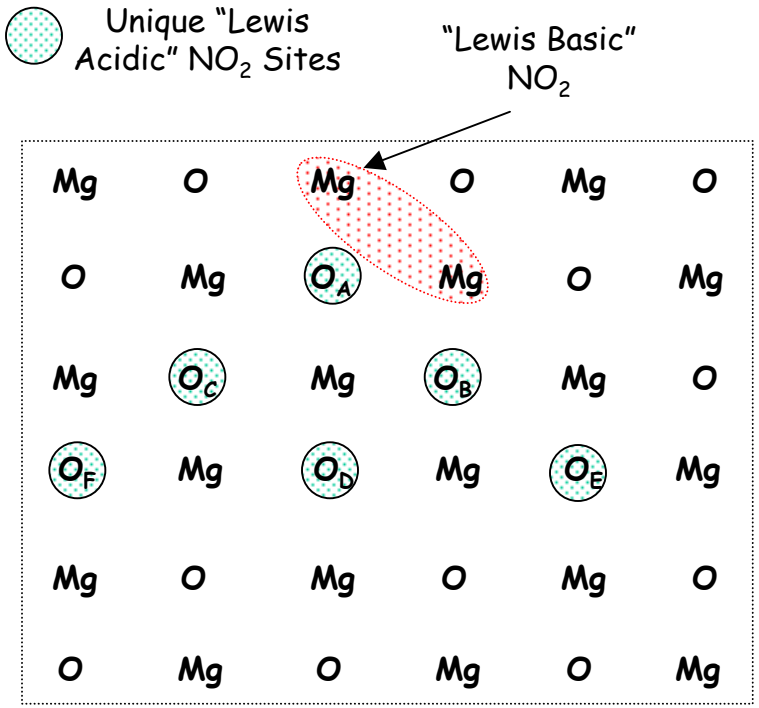


Isolated physisorbed NO_2

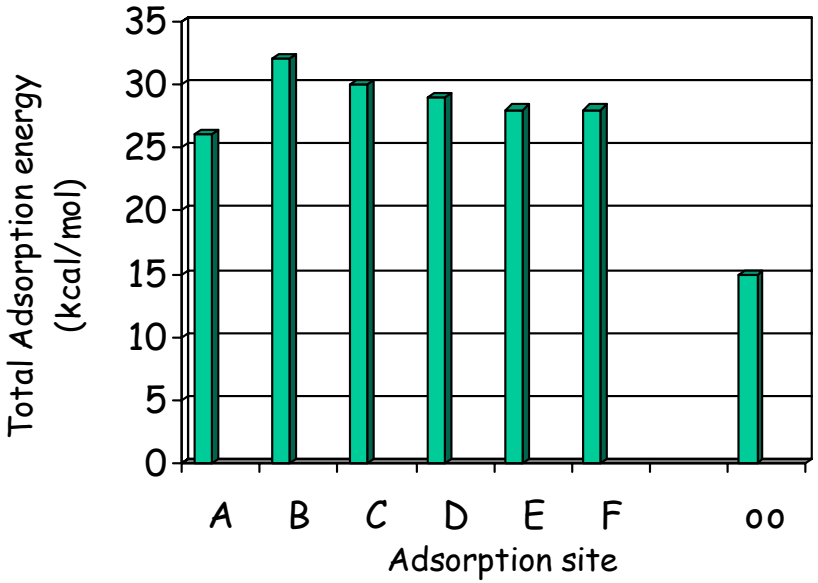
-15 kcal mol^{-1}
"cooperative" chemisorption

- ★ Two NO_2 form a cooperatively bound Lewis acid and base pair
  - o Charge transfer enhances binding of both adsorbates
  - o Structural/charge modifications consistent with chemisorption
  - o Binding energy enhanced by 15 kcal mol^{-1} (100%) over two separated NO_2!
- ★ Mixed nitrite/nitrate consistent with experimental observation for NO_2-exposed MgO

Distance Dependence of NO_2 Cooperative Adsorption

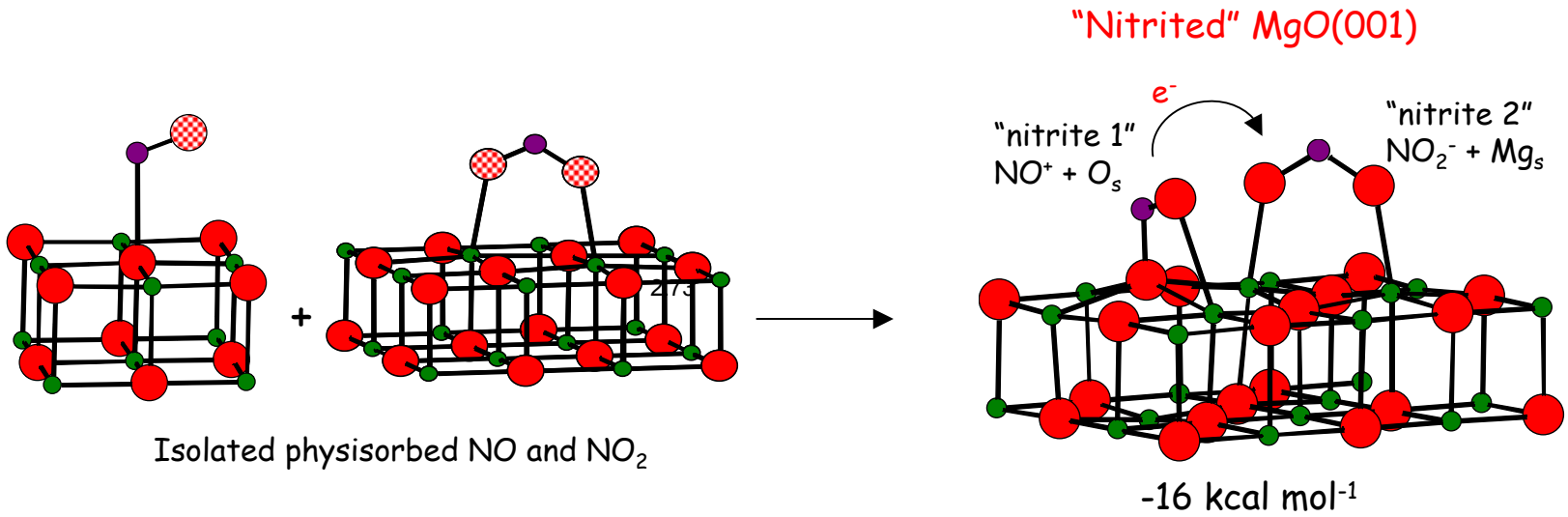


"3x3" MgO supercell



★ Cooperative effect decreases slowly with adsorbate separation
- o e^- transfer can occur over several Angstroms

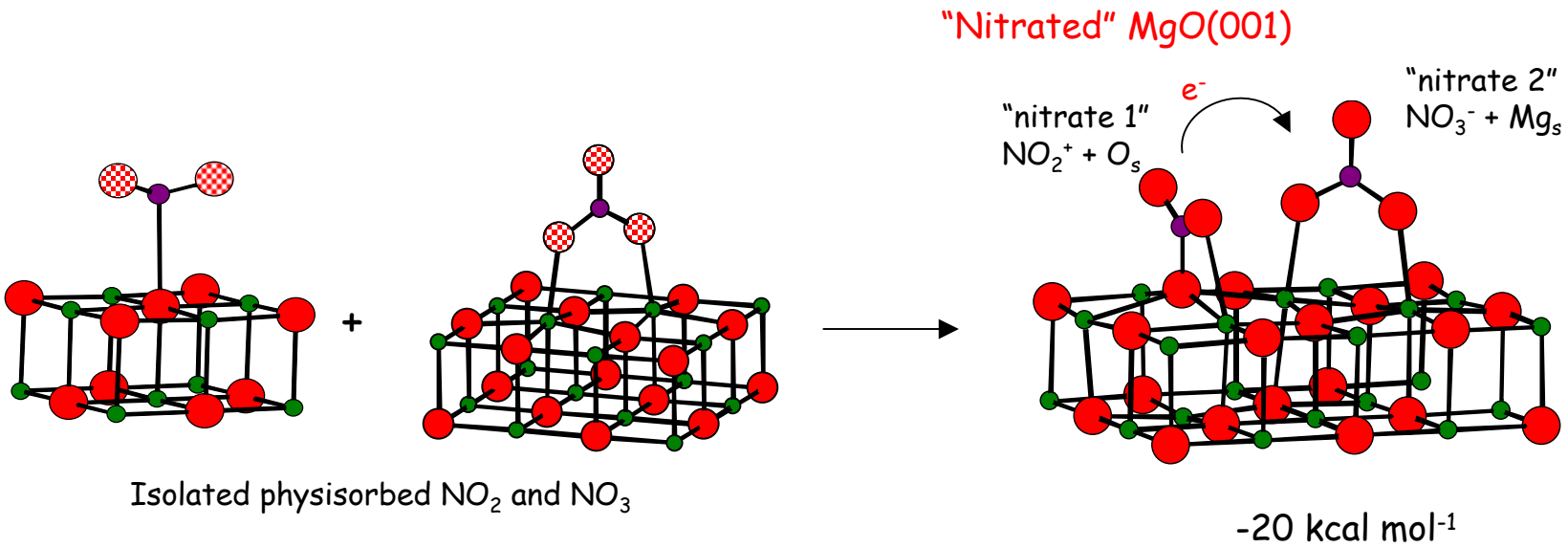
Cooperative NO + NO_2 Adsorption



- ★ NO + NO_2 cooperatively chemisorb as Lewis acid/base pairs
  - o Form two distinct types of surface nitrite
  - o Binding energy enhanced by 16 kcal mol^{-1} (factor of two!) over isolated adsorbates
- ★ Surface nitrite formation energetically competetive with sulfite (?)

$MgO(001) + 2\ NO + \frac{1}{2}\ O_2 \rightarrow Mg(NO_2)_2$	-60 kcal mol^{-1}
$2\{MgO(001) + SO_2 \rightarrow Mg(SO_3)\}$	~ -50 kcal mol^{-1}

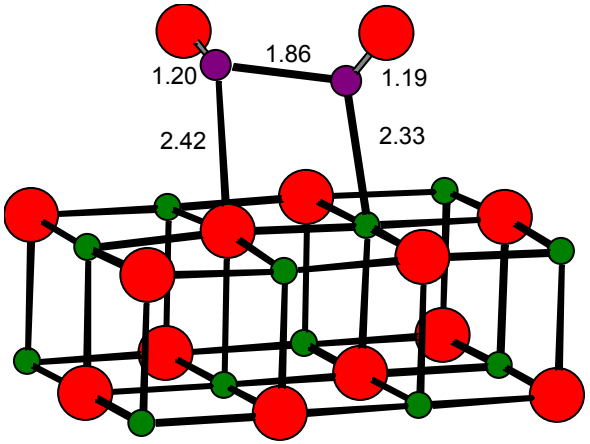
Cooperative NO_2 + NO_3 Adsorption



- ★ NO_2 + NO_3 cooperatively chemisorb as Lewis acid/base pairs
  - o Form two distinct types of surface nitrate
  - o Binding energy enhanced by 20 kcal mol^{-1} over isolated adsorbates
- ★ Sulfation strongly preferred over nitration (?)

$MgO(001) + 2\ NO_2 + \frac{1}{2}\ O_2 \rightarrow Mg(NO_3)_2$	-59 kcal mol^{-1}
$2\ \{MgO(001) + SO_2 + \frac{1}{2}\ O_2 \rightarrow Mg(SO_4)\}$	~ -144 kcal mol^{-1}

Cooperative NO + NO Adsorption?



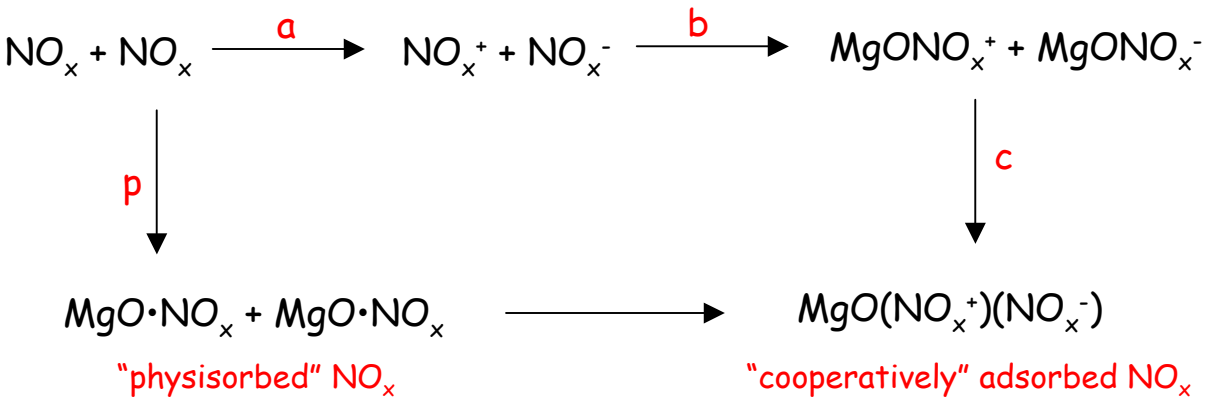
MgO(001) + NO: -5 kcal mol^{-1} *GGA*

MgO(001) + 2 NO: -15 kcal mol^{-1} *GGA*

★ NO adsorption generates physisorbed NO dimers
- o No cooperative adsorption effect
- o NO + NO → NO^+ + NO^- = 9.23 eV ionization penalty > other NO_x pairs

Thermodynamics of Cooperative Adsorption

Thermodynamic cycle for NO_x adsorption



Reaction energies (eV)

Step p	NO_x/NO_x	Step a	Step b	Step c	Total a + b + c
-0.52	NO/NO	9.23	?	---	---
-0.86	NO_2/NO_2	7.32	-6.25	-2.42	-1.35
-0.69	NO/NO_2	6.99	-6.34	-2.08	-1.43
-1.63	NO_2/NO_3	5.68	-5.88	-2.27	-2.47

b + c ~ -8.5 eV

Implications

- ★ NO_x chemisorption requires presence of both Lewis acid and base sites
  - o Novel "cooperative" chemisorption phenomenon consistent with available experiment
  - o Computational tests underway to extend to other oxides
  - o Provides more physically realistic representations for NO_x trap kinetic models

- ★ Differences with SO_x provide handle that could be exploited to design materials selective for NO_x storage
  - o Computationally screen simple oxides and oxide mixtures for NO_x vs. SO_x adsorption tendency