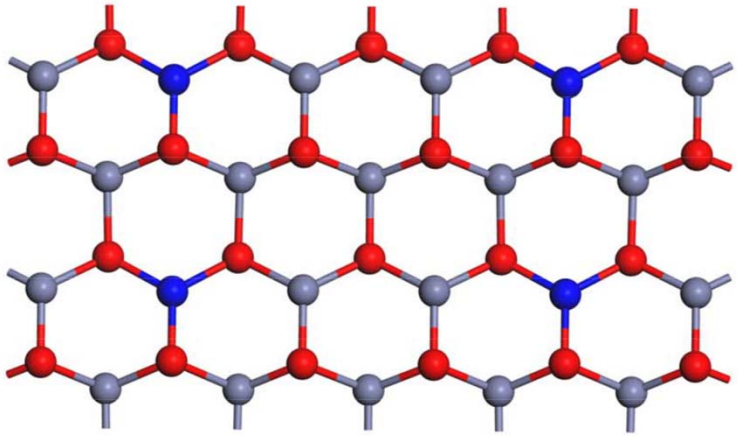
A DFT Study of the Low Temperature Water Gas Shift Reaction on Transition Metal Doped ZnO($10\bar{1}0$) Surface

Bryan Goldsmith

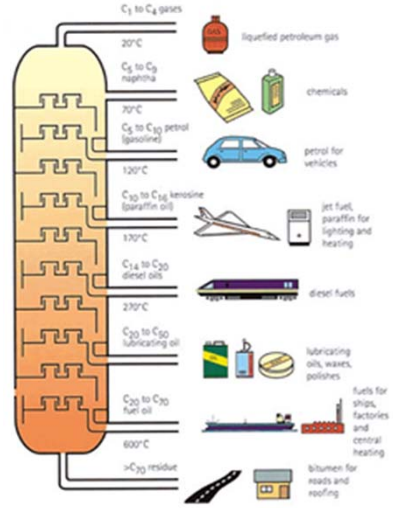
10/4/12



$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Motivation

Petrochemical industry

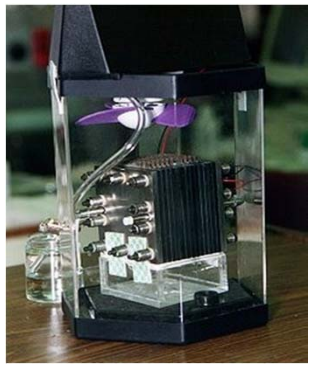


Agriculture

$$Fe/Al_2O_3/K$$

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$$

Fuel cells



$$H_2 \rightarrow 2\ H^+ + 2\ e^-$$

$$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$$

Desulfurization

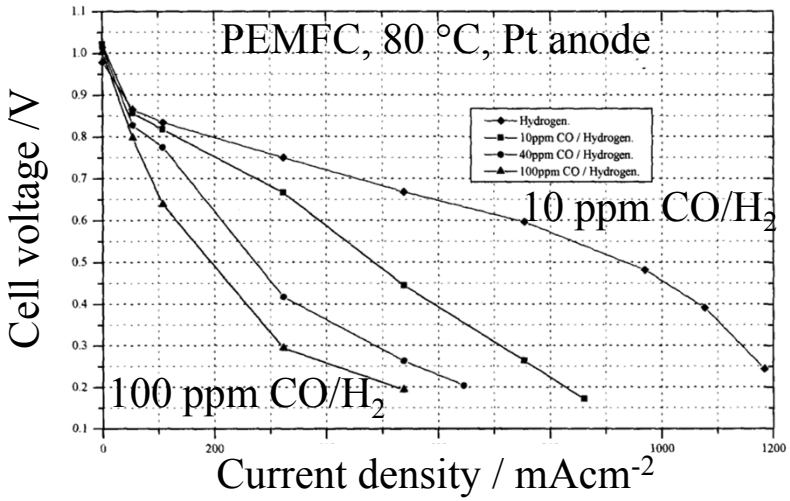
$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$$

Methanol production

$$CO_2 + 3\ H_2 \xleftrightarrow[200\text{–}300\ ^\circ C]{Cu/ZnO} CH_3OH + H_2O$$

Steam reforming

$$C_mH_n + mH_2O \rightleftharpoons mCO + (m + 1/2n)H_2$$



Acres et. al. *Catal. Today 1997, 38, 393-400*

Low Temperature Water Gas Shift Reaction

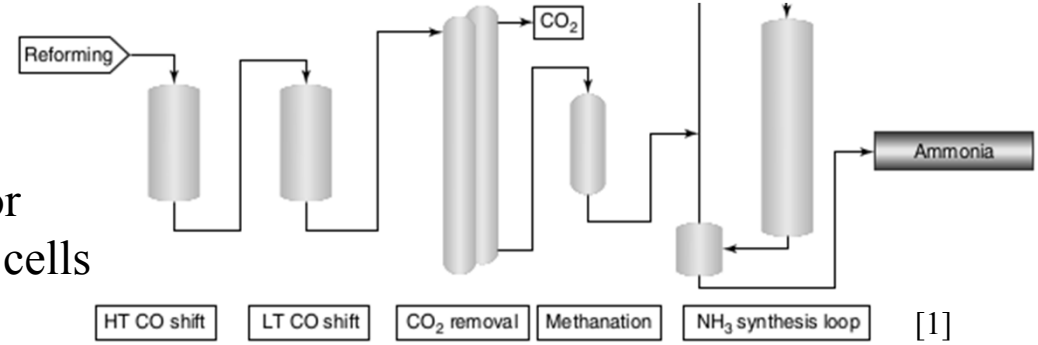
$CO + H_2O \rightleftharpoons CO_2 + H_2$ Exothermic (~40 kJ/mol), reversible

Low T push equilibrium toward H_2 production

High T provide faster kinetics

Industrial plants use two-step WGS reactor

Not viable for small-scale, e.g. fuel cells

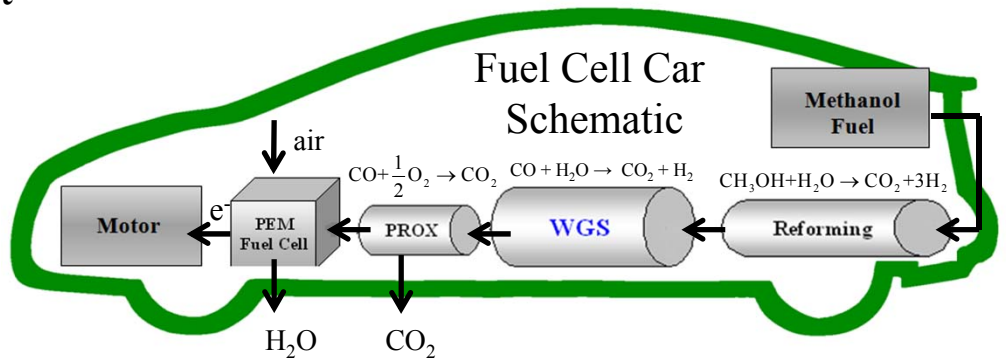


[1]

Community goal: Develop active, stable, and cheap LTWGS catalysts

Reduce volume/weight

Retain activity



"Idealized"

[1] Handbook of Fuel Cells – Fundamentals, Technology and Applications, Volume 3: Fuel Cell Technology and Applications.

LTWGSR catalysts

Conventional Catalyst

$Cu/ZnO/Al_2O_3$

Pro: stable*, selective

Con: activation, slow kinetics

Alternative Catalysts

Cu/CeO_2, Pt/CeO_2, Ni/CeO_2

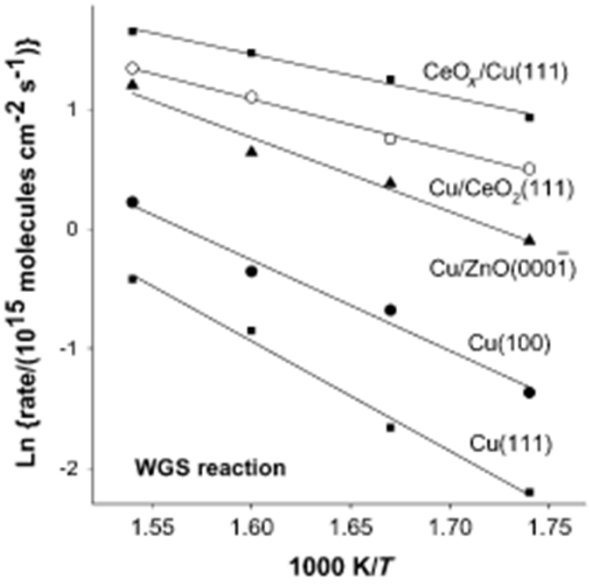
Inverse $CeO_x/Cu(111)$[1]

Pt-alkali-Ox(OH)y/Silica[2]

Nonmetallic Au on Ceria[3]

Au NP on CeO_2, TiO_2 or Fe_2O_3[4]

and others…



[1]

Pro: non pyrophoric, no activation

Con: $, sintering, poisoning

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad \Delta H_{rxn} = -217 \text{ kJ/mol}$$

[1] Rodriguez et. al. *Angew. Chem. Int. Ed.* 2009, 48, 8047

[2] Zhai et. al. *Science* 2010, 329, 1633-1636

[3] Fu et. al. *Science* 2003, 301, 935-938

[4] Deng et. al. *Top. Catal.* 2007, 44, 199-208

Two Mechanisms

Regenerative mechanism

$$CO + * \rightarrow CO*$$
$$H_2O + * \rightarrow O* + H_2$$
$$CO* + O* \rightarrow CO_2 + 2*$$

Fe_2O_3/Cr_2O_3[1]
Pt in $Ce_{1-x}Zr_xO_2$[2]
Au/TiO_2 [3]
Pd/CeO_2[4]

Associative mechanism

$$CO + * \rightarrow CO*$$
$$H_2O + 2* \rightarrow H* + OH*$$
$$OH* + CO* \rightarrow HCO_x* + *$$
$$HCO_x* + * \rightarrow CO_2* + H*$$
$$CO_2* \rightarrow CO_2 + *$$
$$2H* \rightarrow H_2 + 2*$$

$CeO_x/Au(111)$[5]
$Cu(111)$[6]
Pt-promoted thoria[7]
$TiO_{2-x}/Au(111)$[8]

[1] Rhodes et. al. *Catal. Today 1995, 23, 43-58*
[2] Deshpande et. al. *Appl. Catal., B 2010, 96, 83-93*
[3] Boccuzzi et. Al. *Surface Science 2000, 454-456*
[4] Hilaire et. al. J. *Appl. Catal., A 2001, 215, 271-278*
[5] Senanayake *J. Catal. 2010, 271, 392-400*
[6] Gokhale et. al. *J. Am. Chem. Soc.* 2008, *130*, 1402-1414
[7] Jacobs et. al. *J. Catal.* 2005, *235*, 79-91
[8] Rodriguez et. al. *Science* 2007, *318, 1757-1760*

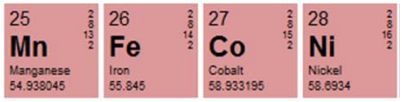
Theoretical study of catalytic role of dispersed metal on ZnO($10\bar{1}0$)

Questions:
Do highly dispersed metal species catalyze the WGSR?
What is the active site and catalytic cycle?

Host support: ZnO

Industrially used
Stable, cheap (~$1000-2000/ton)

Dopants selected:



Abundant, inexpensive
Could be atomically dispersed on ZnO

[1] Fu, Q et. al. *Science* 2003, *301*, 935-938
[2] Fu, Q et. al. *Catal. Lett.* 2001, *77*, 87-95
[3] Andreeva et. al. *Catal. Today* 2010, *158*, 69-77
[4] Deshpande et. al. *Appl. Catal., B* 2010, *96*, 83-93
[5] Li et. al. *Appl. Catal., A 2008, 334, 321-329*
[6] Qiao, B. et al. *Nat Chem* 2011, *3*, 634

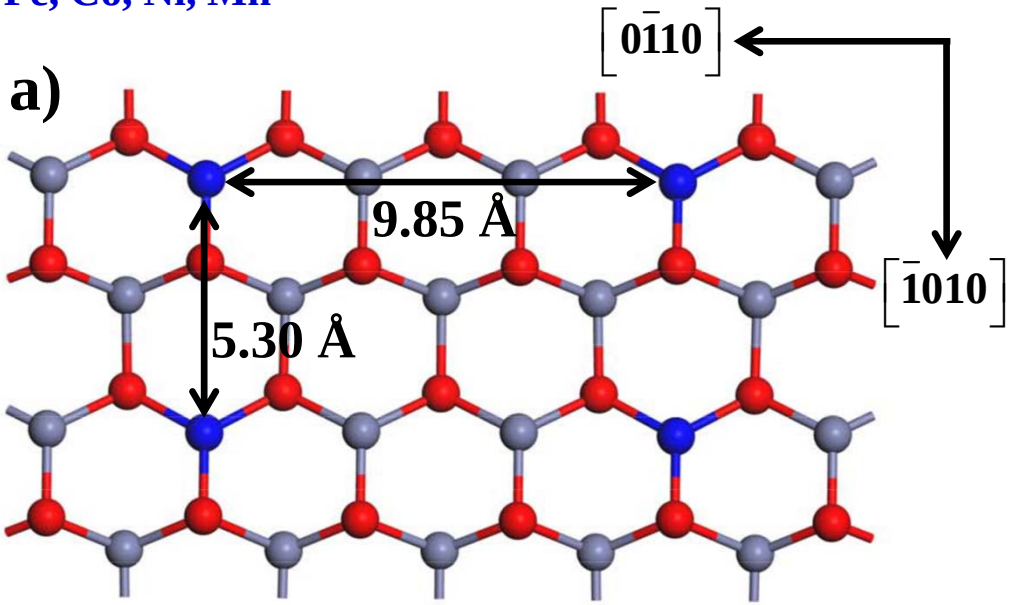
Modeling procedure

b-initio VASP ienna imulation ackage

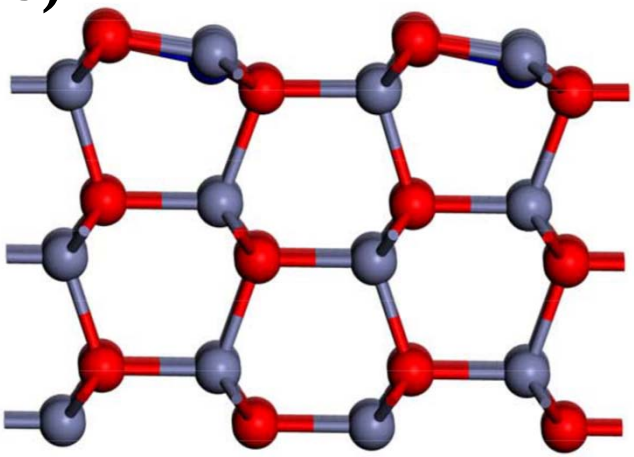
ZnO($10\bar{1}0$)
- nonpolar facet
- most energetically favorable surface

GGA-PW91[1], spin-polarized
6 layer slab model, 3x1 unit cell
4x4x1 k-point, 12 Å vacuum
Defect free
Bottom four layers fixed

Zn
O
TM = Fe, Co, Ni, Mn



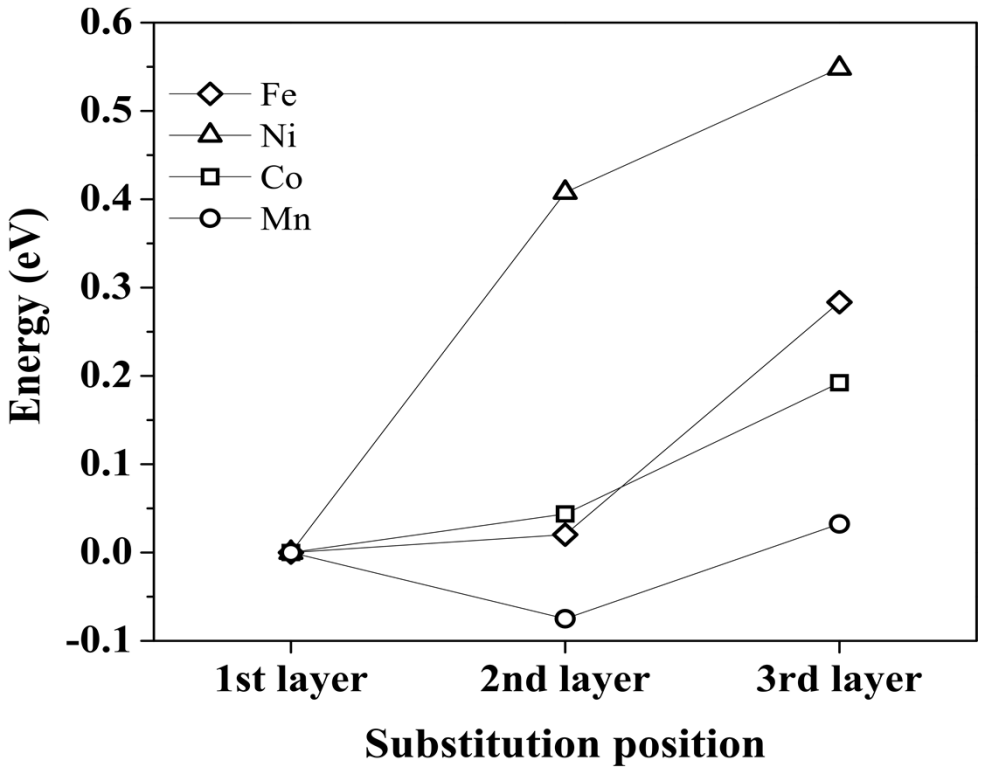
Top view



Side view

[1] J.P. Perdew, *et. al.* Phys. Rev. B 46, 6671 1992

Relative energies for Fe, Ni, Co, and Mn substituted in the 2nd and 3rd layer Zn lattice of the ZnO($10\bar{1}0$)



Pala et. al. found similar trend.
[1] Pala, R. G. S.; Metiu, H. J. Phys. Chem. C 2007, *111*, 8617

	TM-O distance (Å)	E_V (eV)	Bader charge	
			TM	O
Fe/ZnO	1.89	3.73	1.35	-1.23
Ni/ZnO	1.88	3.14	1.07	-1.21
Co/ZnO	1.87	3.58	1.13	-1.21
ZnO	1.92	2.96	1.23	-1.23

Large E_v
Exclude regenerative mechanism

TM = Fe, Co, or Ni

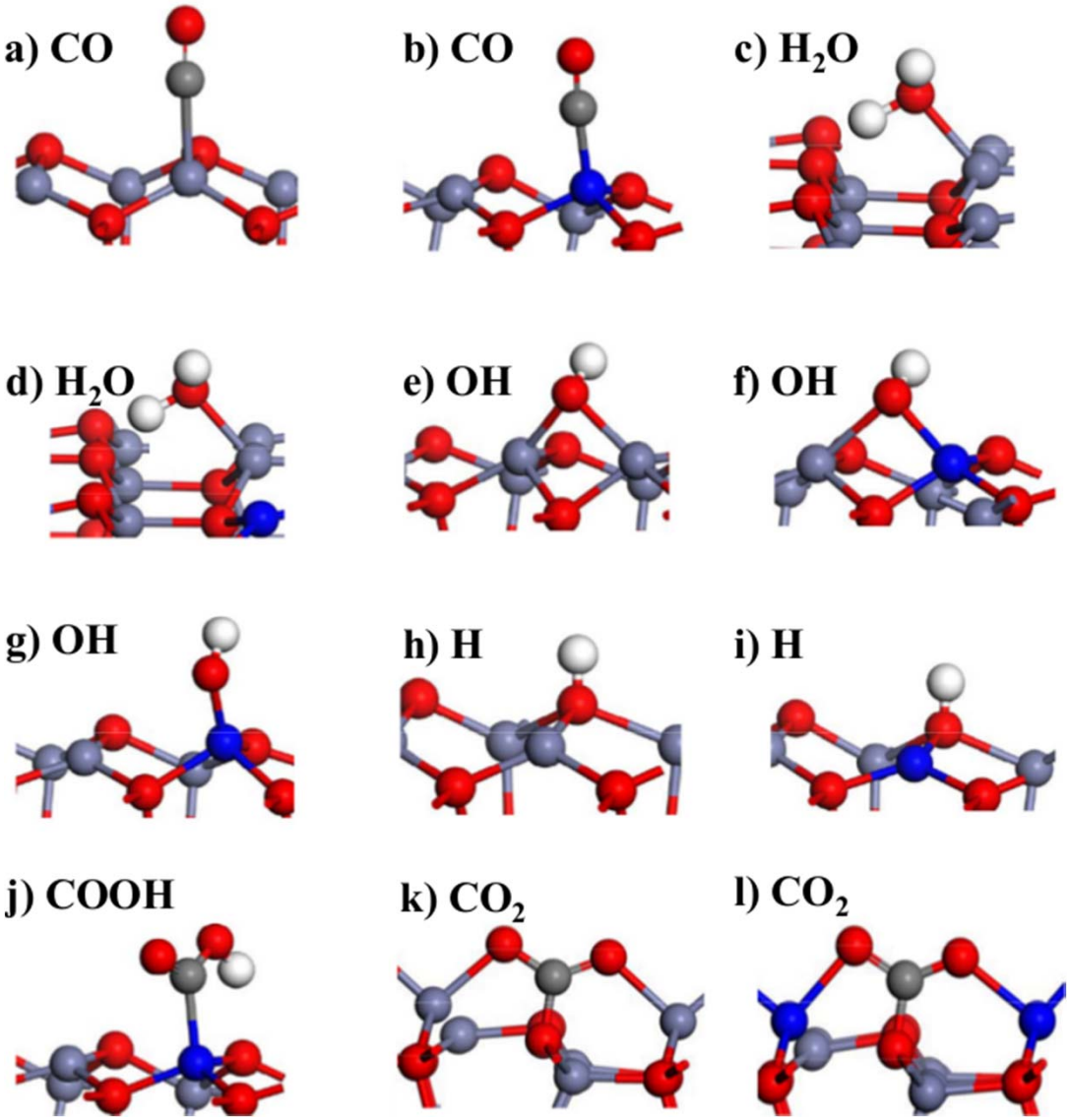
Adsorption of reactants and intermediates

Species	Site	Adsorption energy (eV)			
		Fe	Ni	Co	ZnO
CO	TM/Zn	-0.41	-0.43	-1.15	-0.32
H_2O	Zn	-1.09	-1.08	-1.09	-1.07
	TM	-0.76	-0.71	-0.84	-
OH	TM-Zn	-3.30	-2.61	-2.91	-1.86
	TM	-3.41	-2.45	-2.96	-
H	O	-2.22	-2.97	-2.62	-2.36
	TM/Zn	-1.72	-1.65	-1.75	-0.66
COOH	TM	-1.84	-1.72	-2.12	-
CO_2	TM-O-TM	-0.65	-0.59	-0.72	-0.83

TM = Fe, Co, or Ni

Most stable configurations found

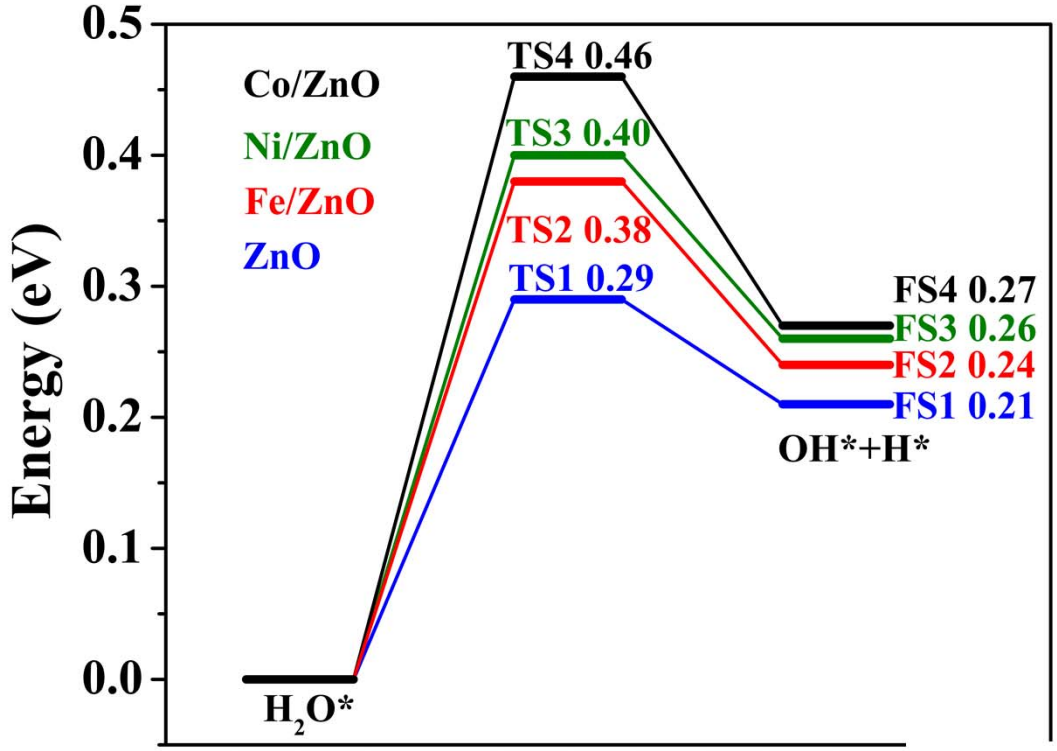
Zn
O
C
H
TM



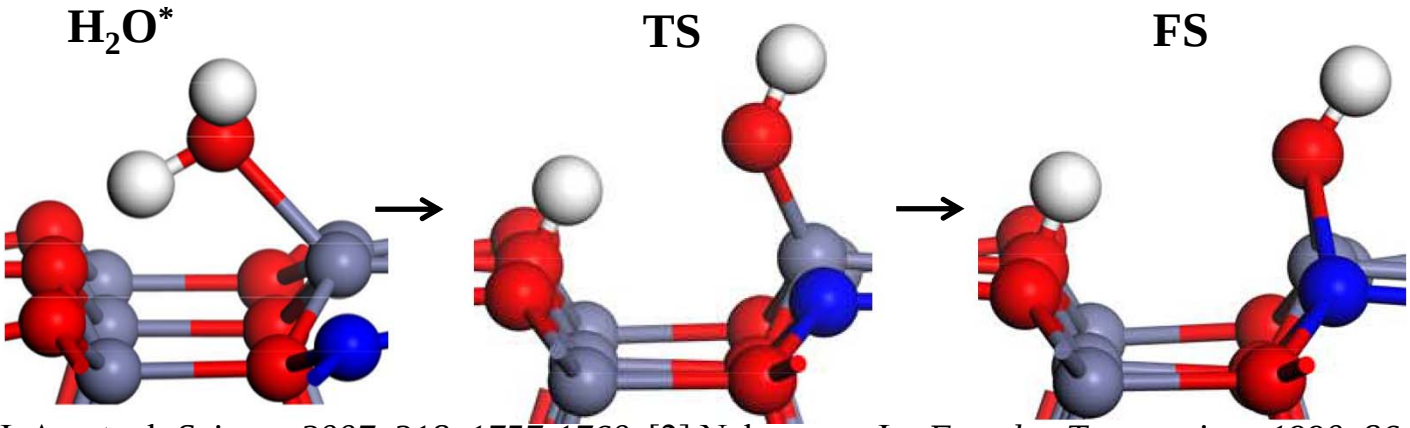
COOH only stable on TM dopants (not Ni)

f) is the OH on Ni/ZnO and **g)** is that on Fe/ZnO and Co/ZnO

Water dissociation

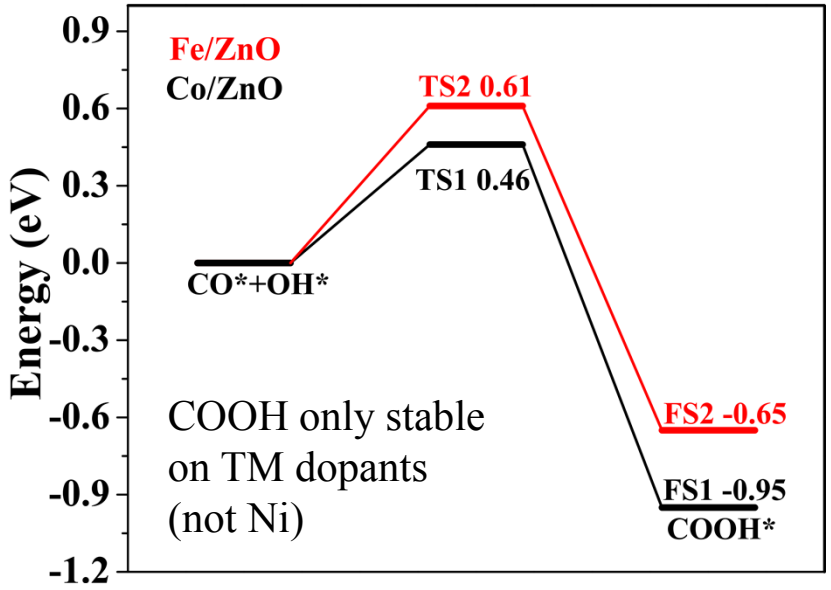


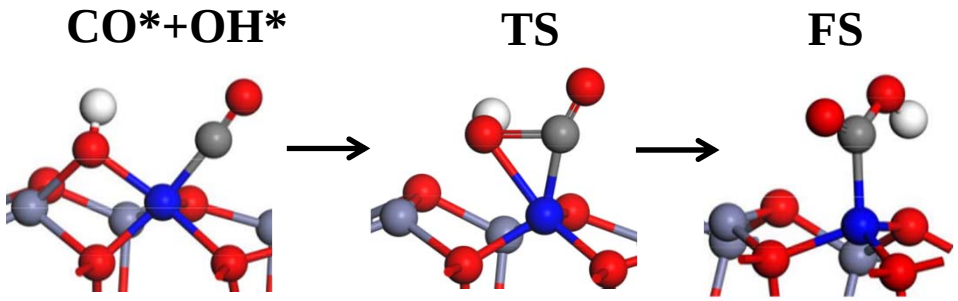
Theory:
TiO_2/Au(111) ~ 0.6 eV[1]
Expt:
Cu(110) ~0 .36 eV[2]
Cu(111) ~0.62 eV[2]

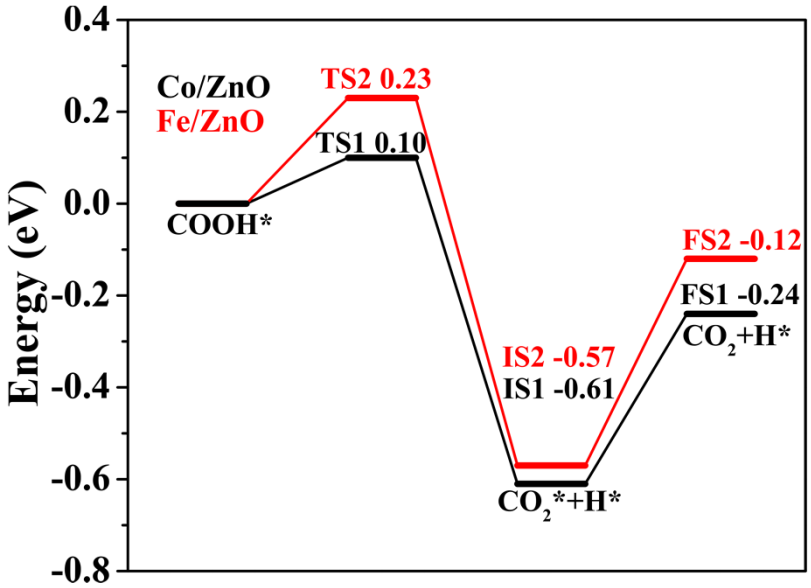


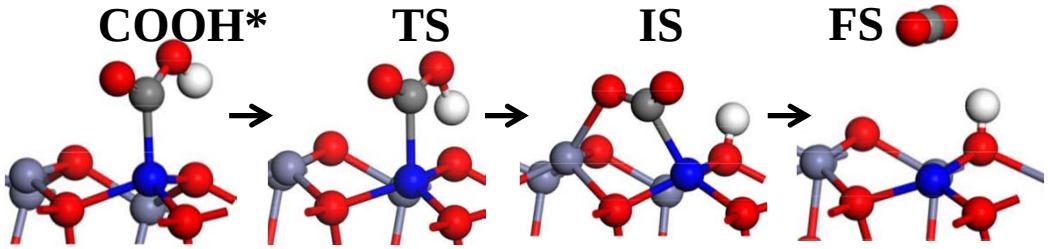
[1] Rodriguez, J. A.; et. al. *Science 2007, 318, 1757-1760,* [2] Nakamura, J.; *Faraday Transactions 1990, 86*

COOH formation and dissociation for Co and Fe

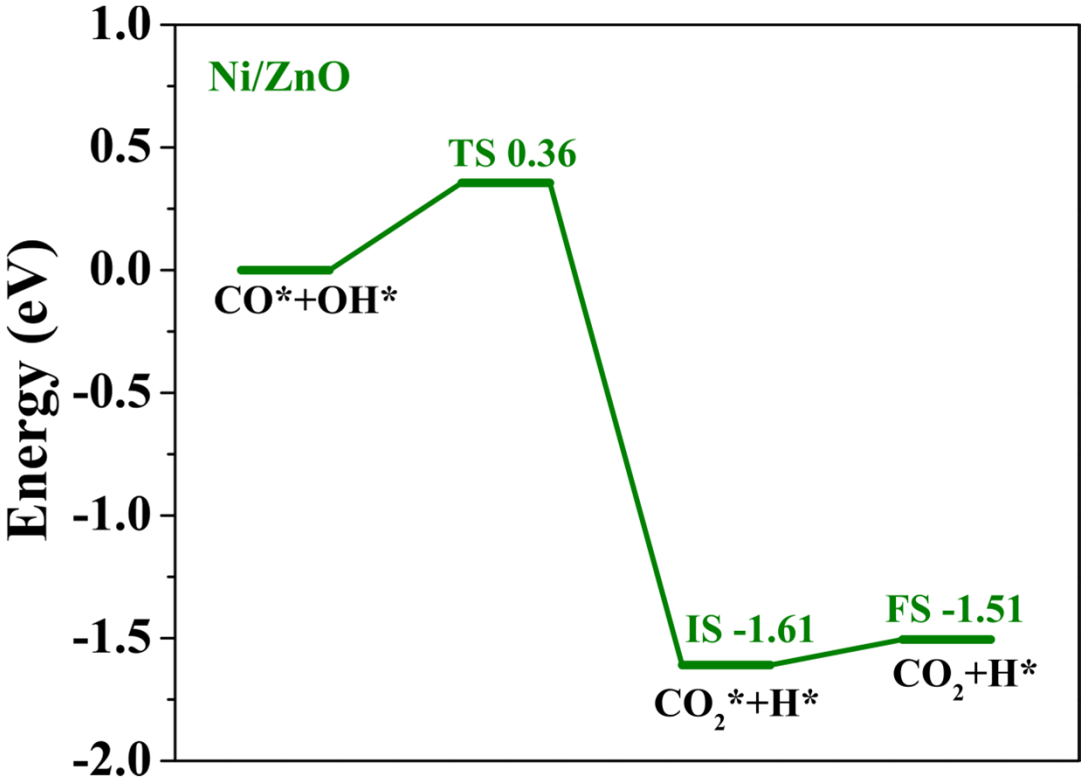


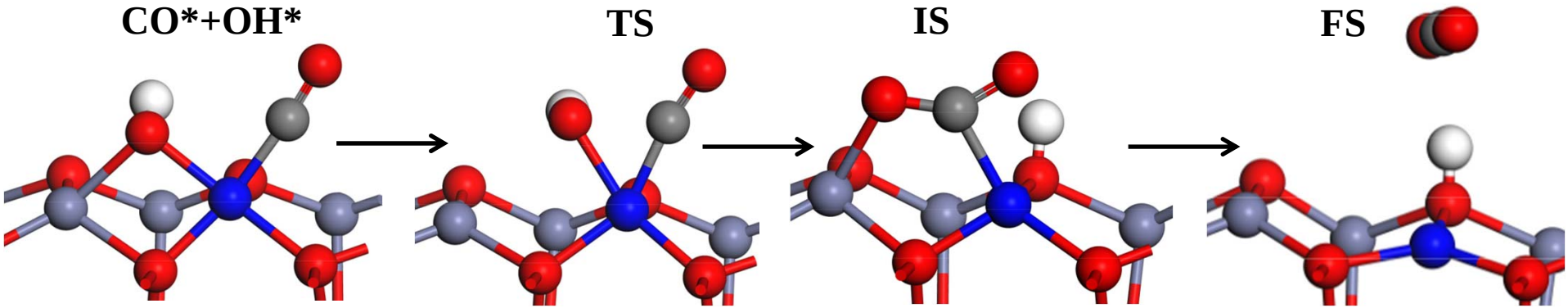




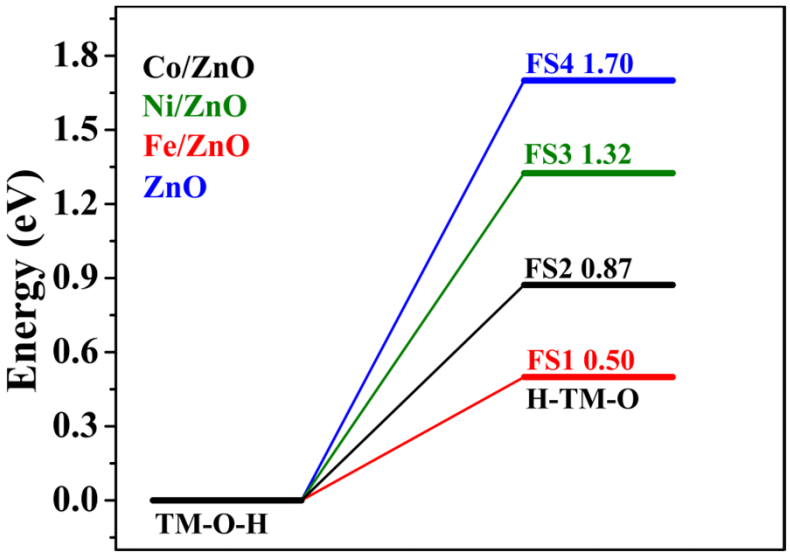


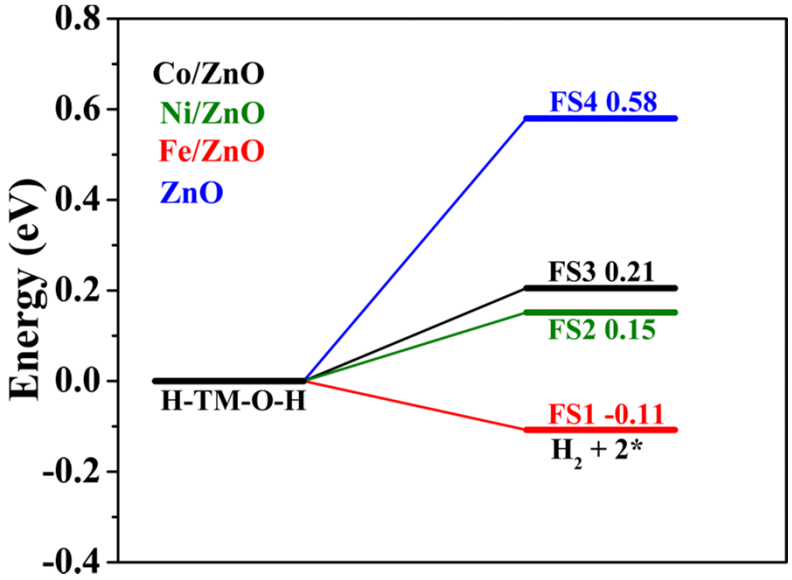
CO+OH to CO_2 + H^* dissociation on Ni and ZnO





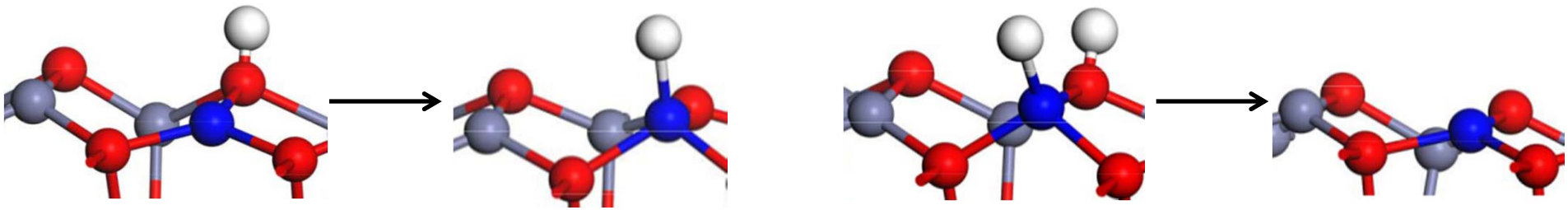
H_2 formation



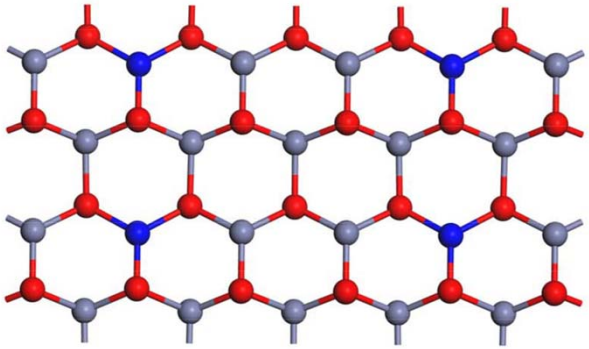


-TS = -0.76 eV/H_2
@ 1 atm, 500 K

TM-O-H **H-TM-O** **H-TM-O-H** **FS**



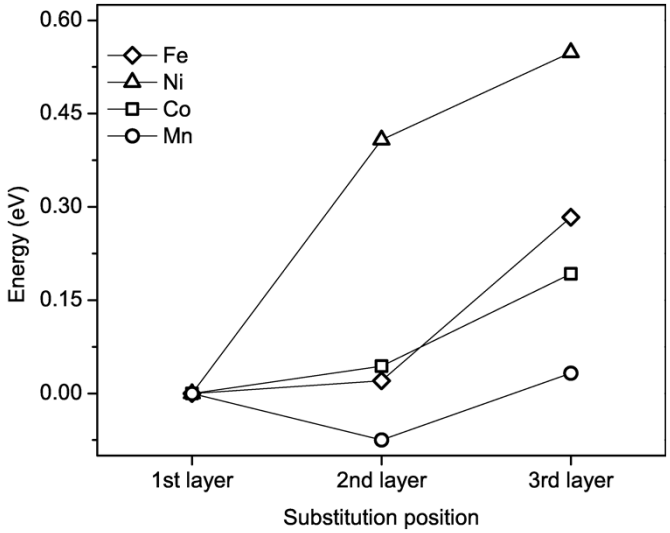
What we learned so far



Doping changes surface energetics

Water dissociation not facilitated by TM dopant

COOH only stable on TM dopants



Fe, Ni, Co appear stable in surface layer
Dope Fe, Ni, Co increases E_v locally

WGSR could proceed
via associative mechanism

$$CO + * \rightarrow CO*$$

$$H_2O + 2* \rightarrow H* + OH*$$

$$OH* + CO* \rightarrow HCO_x* + *$$

$$HCO_x* + * \rightarrow CO_2* + H*$$

$$CO_2* \rightarrow CO_2 + *$$

$$2H* \rightarrow H_2 + 2*$$

Acknowledgements

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