The Material Development of Ethanol Reformers and Solid Oxide Fuel Cells in the Green Energy Research

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Outline

- **Introduction:**
- **Methodology**
  - **Hybrid experimental/computational method**
- **Current results:**
  - **Ethanol reformers**
  - **Hydrogen solid oxide fuel cells**
- **Future work**
  - **How if we nanoize the materials**

Introduction: Alternative energy resources

Problem: The recent soaring oil price and the appreciation of the green house effect have led to the general public's awareness of the detrimental outcome from the world's addiction to fossil fuels

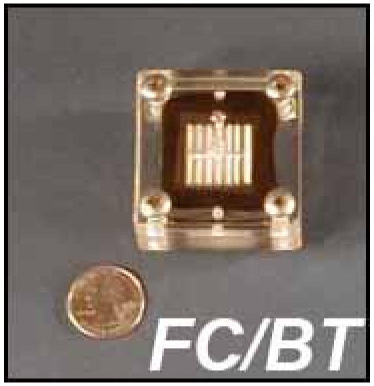
Solution: fuel cells are considered as the cleanest, most efficient and versatile system for chemical to electrical energy conversion

Applications: in various scales

large ⟷ small

Power station

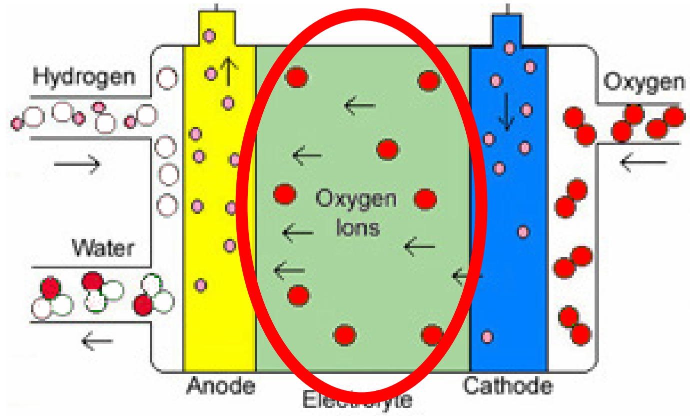
Low emission vehicle



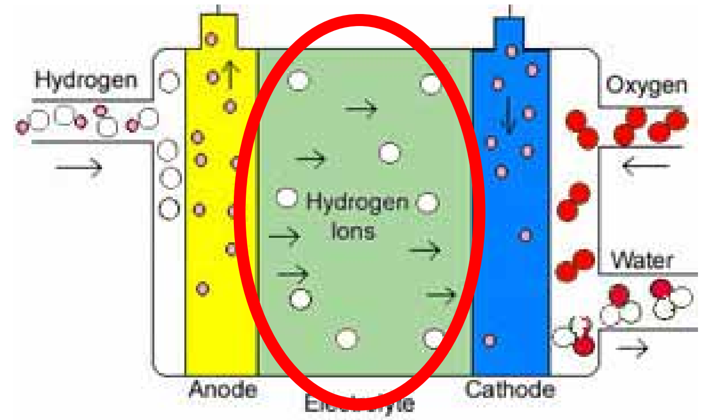
Portable devices

Introduction: Alternative energy resources

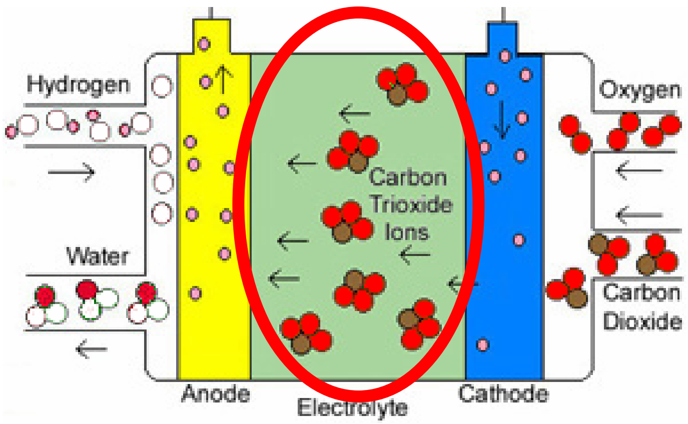
Types of Fuel cells: Conductive ions of O^{2-}, CO_3^{2-}, H^+ and OH^-



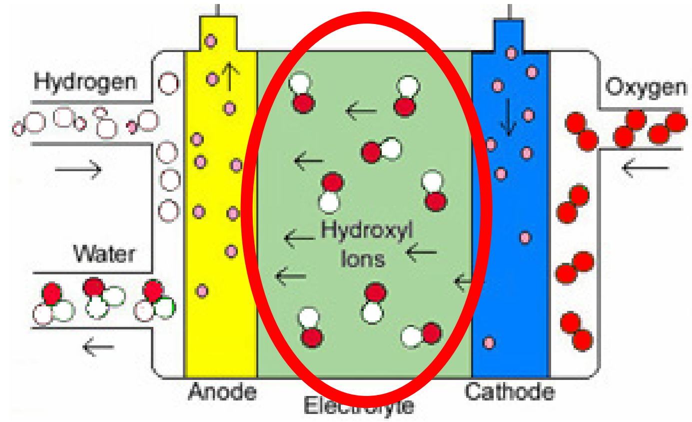
Solid oxide (SOFC): 500 ~ 1000 ^oC



Polymeric electrolyte membrane (PEMFC)
Phosphoric acid (PAFC): ~ 200 ^oC



Molten carbonate (MCFC): ~650 ^oC



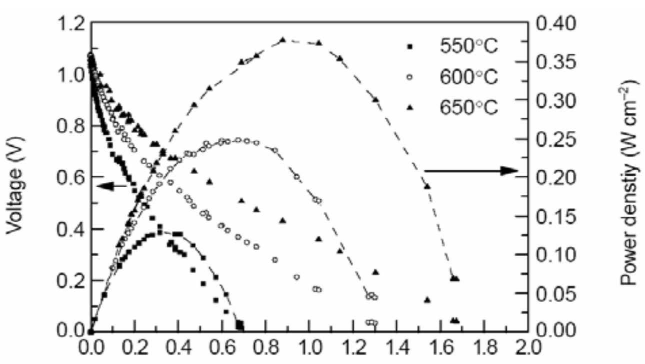
Alkaline (AFC): ~ 70 ^oC

Steele, B. C.; Helnzel, A.; *Nature*, **414**, 345 (2001)

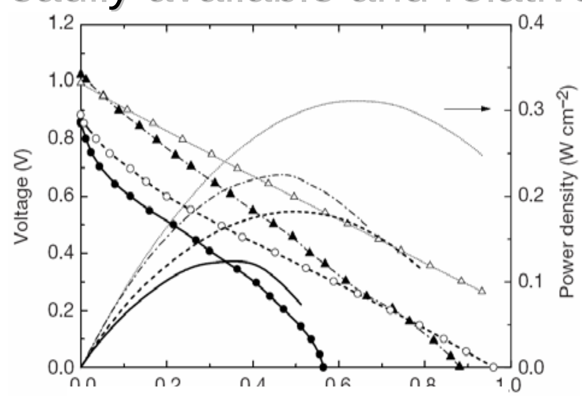
Introduction: Alternative energy resources

SOFC with hydrocarbon fuel:

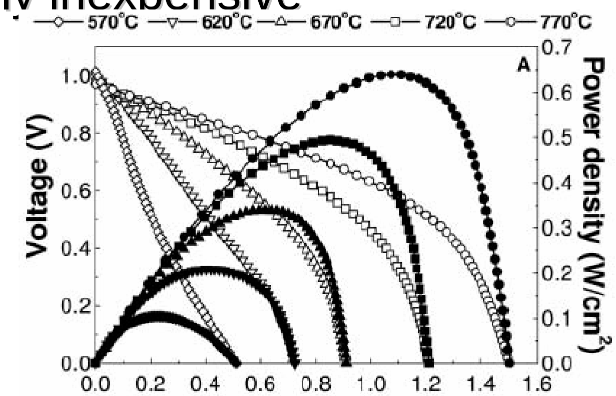
- **SOFC** can operate at high temperature and has excellent fuel flexibility;
- **Hydrocarbon fuels** are readily available and relatively inexpensive



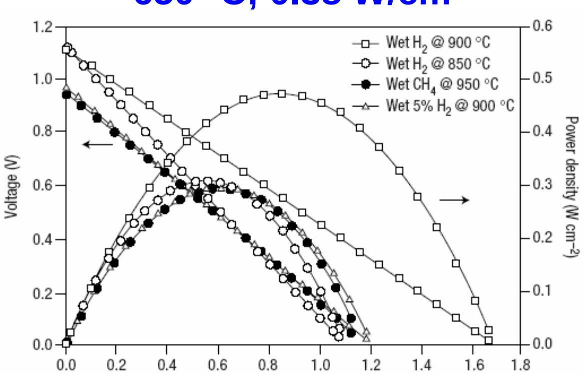
Y-CeO_2 ; methane[1]
650 °C; 0.38 W/cm²



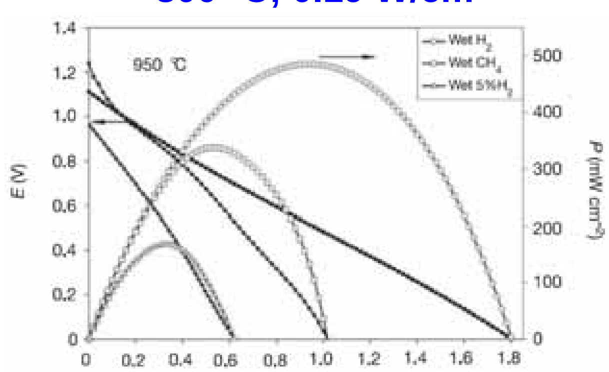
(Cu,Sm)-CeO_2; butane[2]
800 °C; 0.19 W/cm²



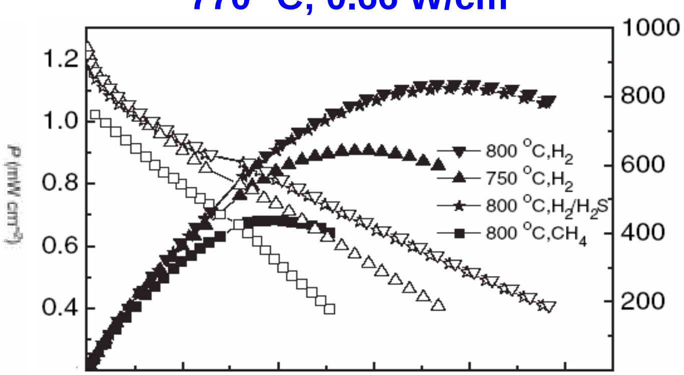
Ru-CeO_2; octane[3]
770 °C; 0.66 W/cm²



(La,Sr)(Cr,Mn)O_{3-d}; methane[4]
950 °C; 0.3 W/cm⁻¹



(La,Sr)(Ti,Mn,Ga)O_{3-d}; methane [5]
950 °C; 0.5 W/cm²



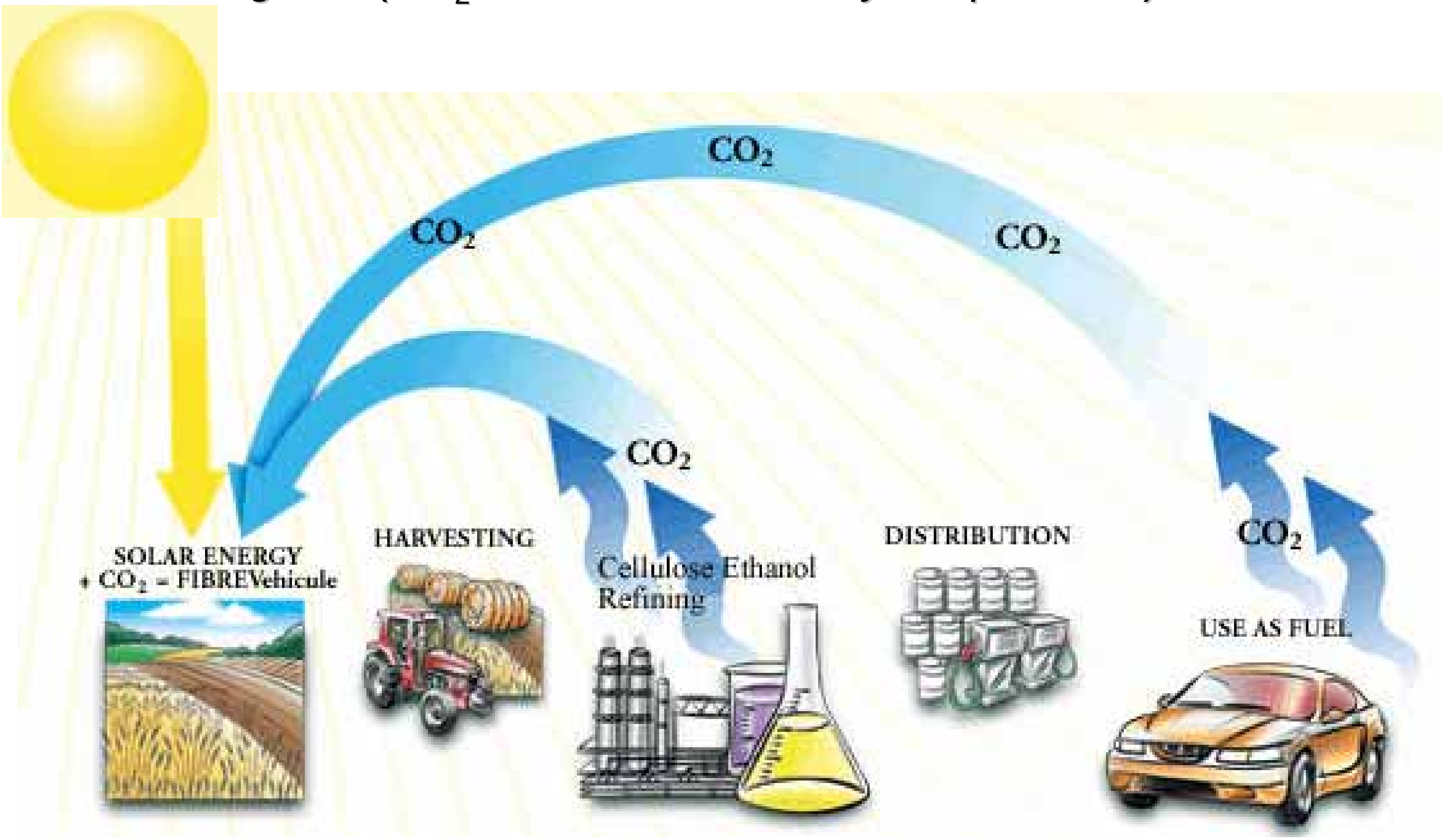
Sr(MgMo)O_{3-d}; methane[6]
800 °C; 0.4 W/cm²

[1] Murry, E. P.; Tsai, T.; Barnett, S. A.; *Nature*, **400**, 649 (1999)
[2] Park, S.; Vohs, J. M.; Gorte, R. J.; *Nature*, **404**, 265 (2000)
[3] Zhan, Z.; Barnett, S. A.; *Science*, **308**, 844 (2005)
[4] Tao, S.; Irvine, J. T. S; *Nature Materials*, **2**, 320 (2003)
[5] Ruiz-Morales, J. C.; Canales-Vazquez, J.; Savaniu, C.; Marrero-Lopez, D.; Zhou, W. Irvine, J. T. S.; *Nature*, **439**, 568 (2006)
[6] Huang, Y. H.; Dass, R. I.; Xing, Z. L.; Goodenough, J. B.; *Science* **312**, 254 (2006)

Introduction: The green energy

SOFC with ethanol:

- Ethanol is green (CO_2 will be consumed by the producer)

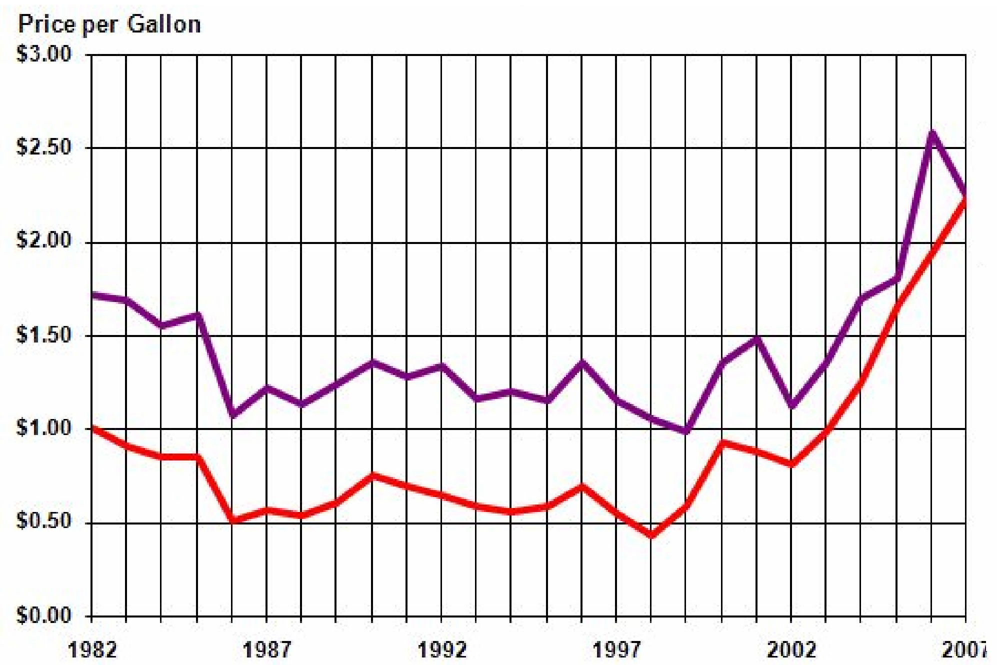


Wang, M.; The Debate on Energy and Greenhouse Gas Emissions Impacts of Fuel Ethanol. http://www.transportation.anl.gov/
Center for Transportation Research Energy Systems Division, Argonne National Laboratory (2005)

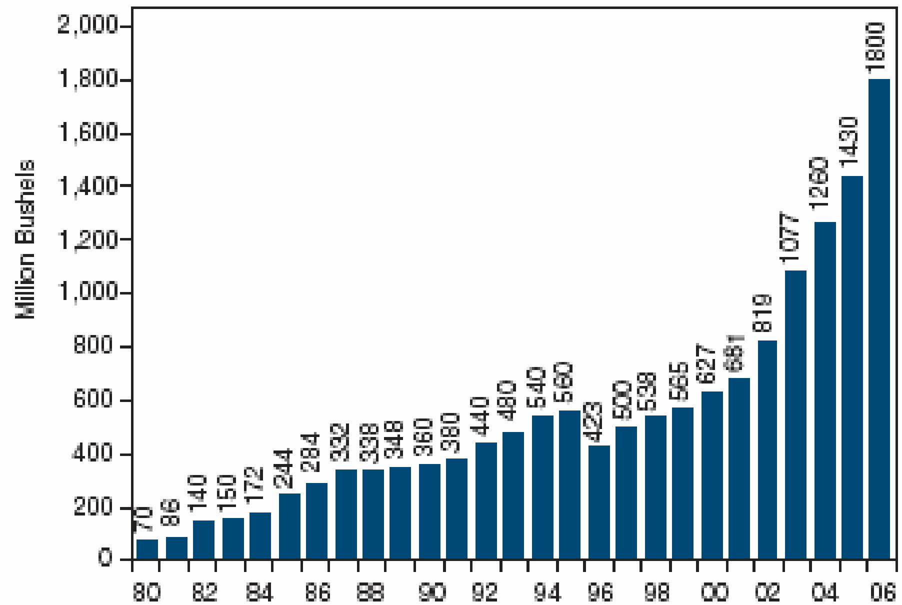
Introduction: The green energy

SOFC with ethanol

- It is readily available from industrial processes
- The cost for production will be even cheaper than gasoline



Costs of ethanol and gasoline



Ethanol production

Wang, M.; The Debate on Energy and Greenhouse Gas Emissions Impacts of Fuel Ethanol. http://www.transportation.anl.gov/
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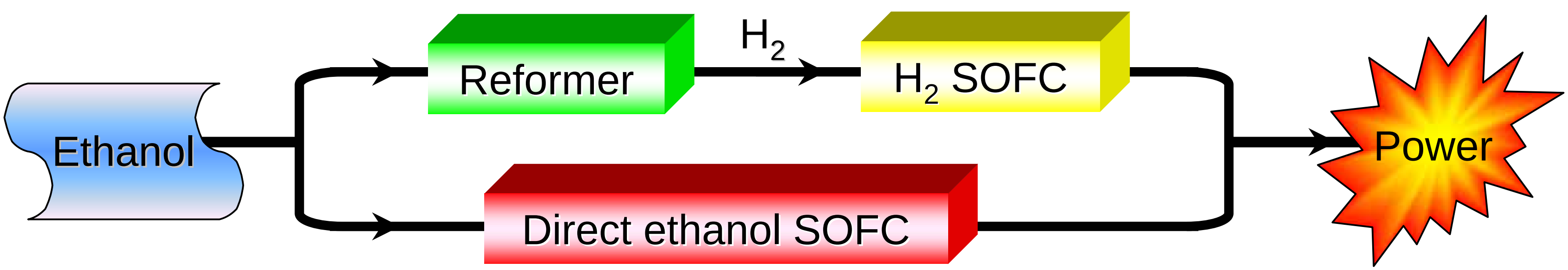
Introduction: Green power generators

➔ Challenge: The development of materials with better conversion efficiency, longer chemical stability and lower fabrication cost

WTW efficiency[1] =	WTT efficiency ×	TTW efficiency
C_xH_y fuels < 22%	< 84%	Combustion engine < 16%[2]
H_2 fuel < 29 %	< 58%	H_2-SOFC < 50%
Biomass fuels	< 75% (ethanol)	Hydrocarbon-SOFC < 25%[3]

Our research:

- Ethanol Reformer: improve WTT efficiency of **H_2 fuel**
- Direct ethanol SOFC: improve TTW efficiency of fuel cells



1. Well-to-Wheel Energy Use and Greenhouse Gas Emissions of Advanced Fuel/Vehicle Systems. General Motors, Argonne National Laboratory, BP, Exxon Mobile and Shell, 2001.
2. "Toyota Fuel Cell Hybrid Vehicle"; (2004) http://www.toyota.co.jp/en/tech/environment/fchv/fchv11.html.
3. Z. Zhan, S. A. Barnett: "An Octane-Fueled Solid Oxide Fuel Cell"; Science 308 (2005) 844.

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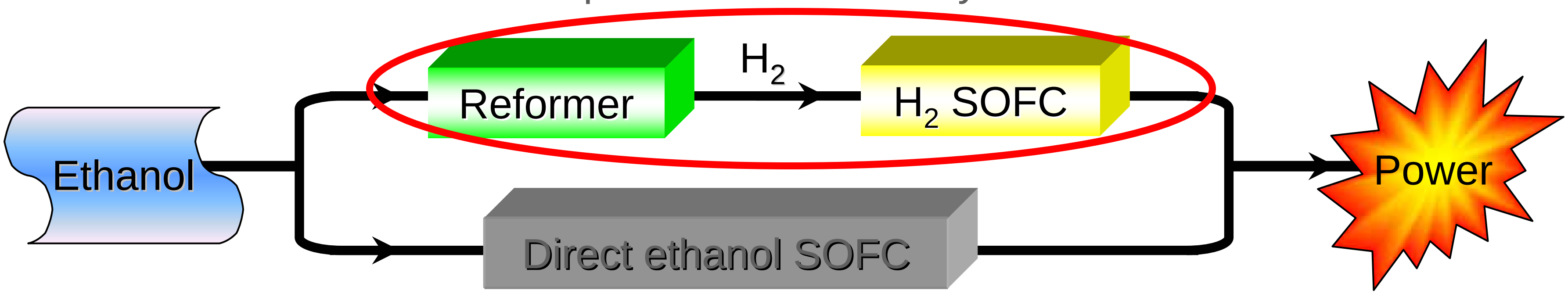


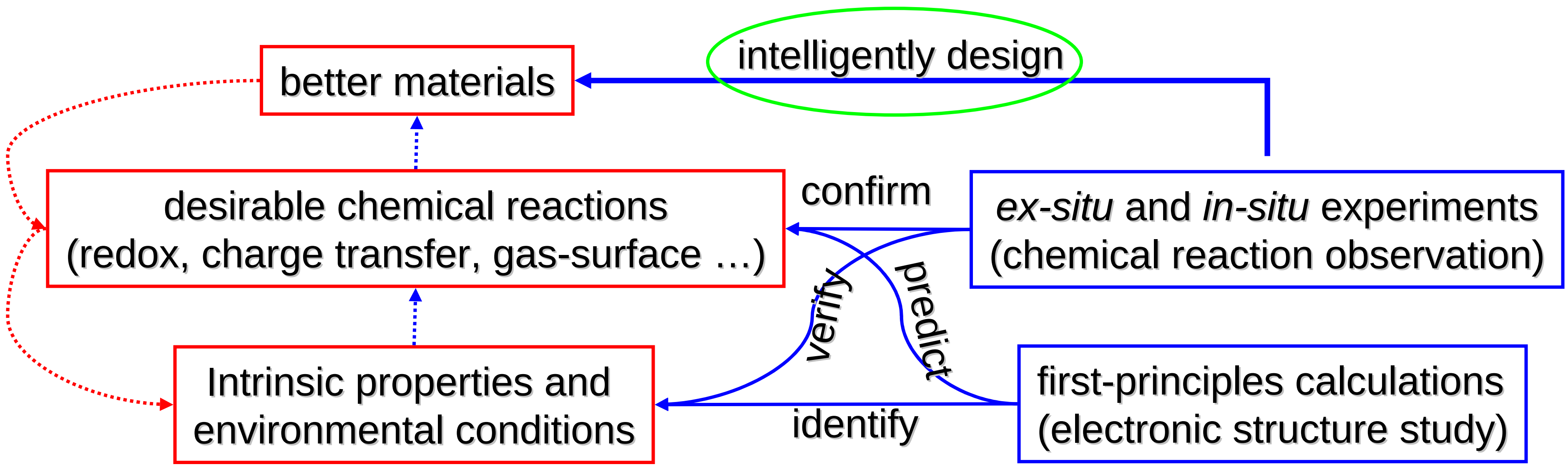
1. Well-to-Wheel Energy Use and Greenhouse Gas Emissions of Advanced Fuel/Vehicle Systems. General Motors, Argonne National Laboratory, BP, Exxon Mobile and Shell, 2001.
2. "Toyota Fuel Cell Hybrid Vehicle"; (2004) http://www.toyota.co.jp/en/tech/environment/fchv/fchv11.html.
3. Z. Zhan, S. A. Barnett: "An Octane-Fueled Solid Oxide Fuel Cell"; Science 308 (2005) 844.

Methodology: Hybrid experiments & computation

Techniques

- Experiments: *ex-situ* and *in-situ* experiments
  - *Ex-situ* characterization: XRD, SEM , EDX, TEM
  - *In-situ* performance testing

- Computation: first-principles calculations
  - Density function theory (DFT) for the "larger system"
  - Periodic boundary condition for heterogeneous catalytic reactions



Methodology: Density functional theory

- Kohn-Sham equation (DFT)

$$\hat{H}_{KS}\rho(r) = E_{KS}\rho(r)$$

$$\hat{H}_{KS}[\rho] = -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0}\int\frac{\rho(r')}{|r-r'|}dr' + \frac{\delta V_{xc}[\rho]}{\delta\rho}$$

$$\rho(r) = \varphi^*(r)\varphi(r)$$

- Periodic boundary condition (PBC)

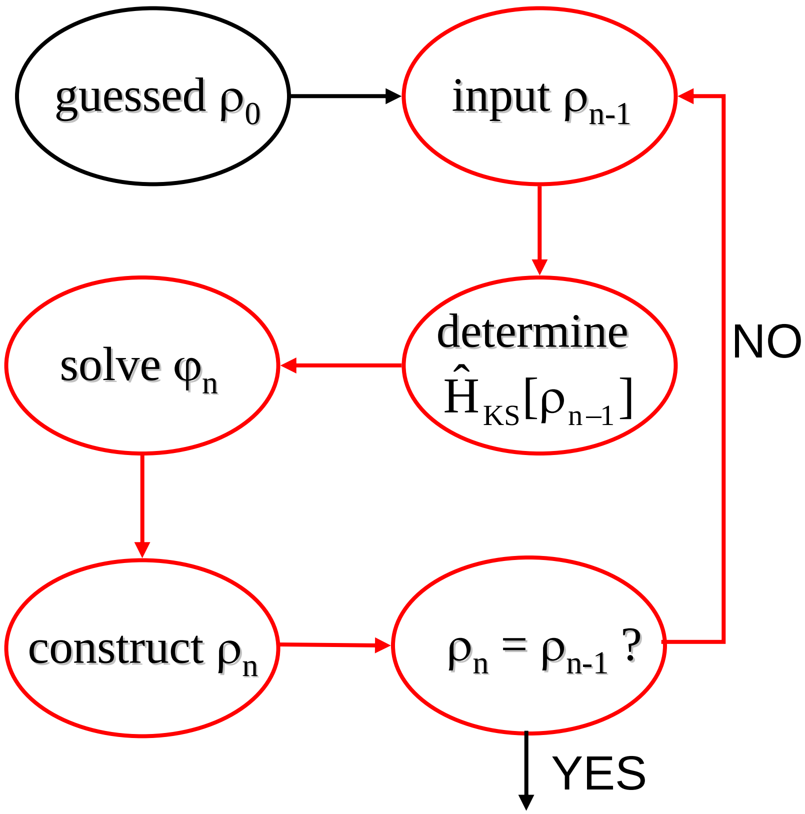
$$\varphi_k^n(r) = u_k^n(r)e^{ikr} = u_k^n(r+R)e^{ik(r+R)} = \varphi_k^n(r+R)$$

$$\rho(r+R) = \rho(r)$$

$$\hat{H}_{KS}(r+R) = \hat{H}_{KS}(r)$$

$$E_{KS}(r+R) = E_{KS}(r)$$

- Self-consistent iterations

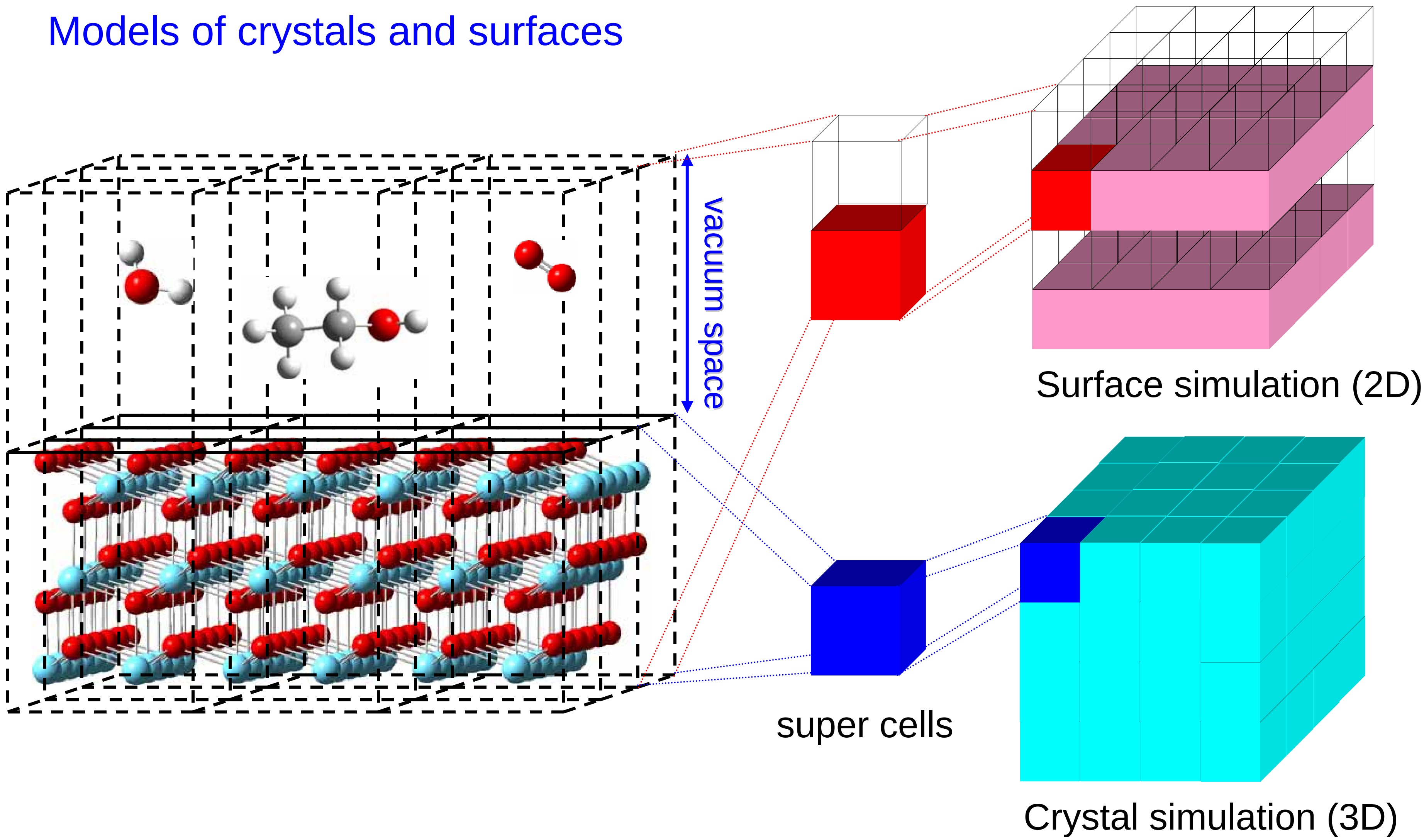


self-consistent density ρ_0 obtained
and ground state energy obtained

Parr, R. G.; Yang, W.; *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989
Slater, J. S. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4

Methodology: Periodic boundary condition

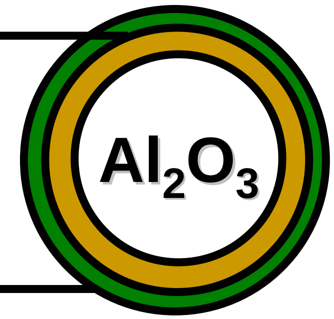
Models of crystals and surfaces



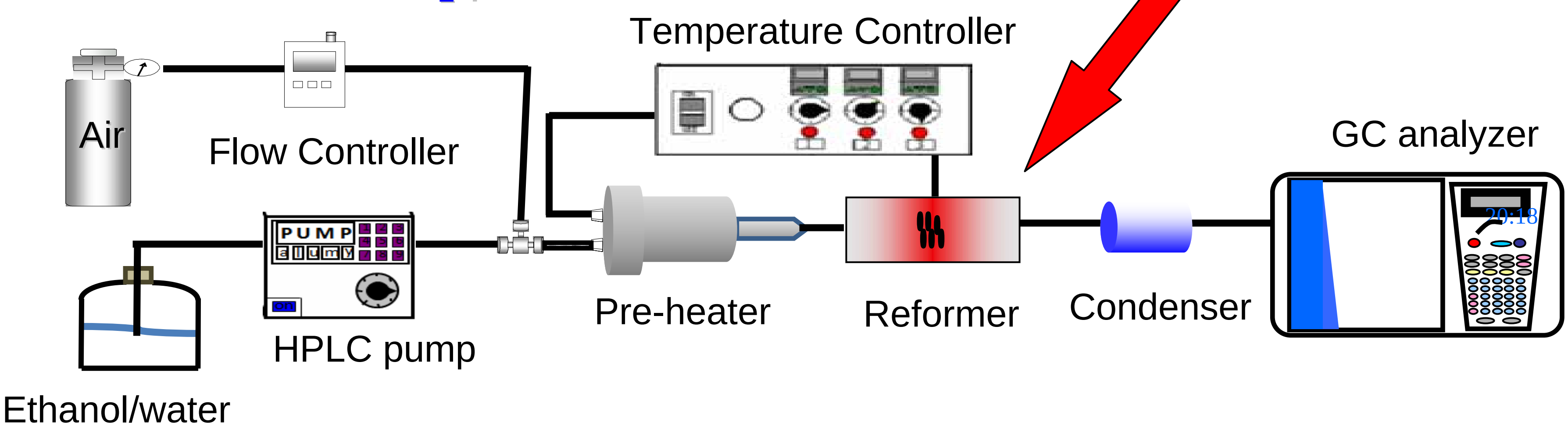
Current results: Ethanol reformers (expt.)

Reformer preparation

- Metal oxide supporter (M1)
  - Impregnate $M1(NO_3)_x$ solution on Al_2O_3
  - Vaporize water solvent
  - Fire at 600 °C to form metal oxide
- Metal/metal oxide reformer ($M2/M1O_x/Al_2O_3$)
  - Impregnate $M2(NO_3)_x$ solution on $M1O_x/Al_2O_3$
  - Vaporize water solvent
  - Reduce to M2 in H_2 at high temperature

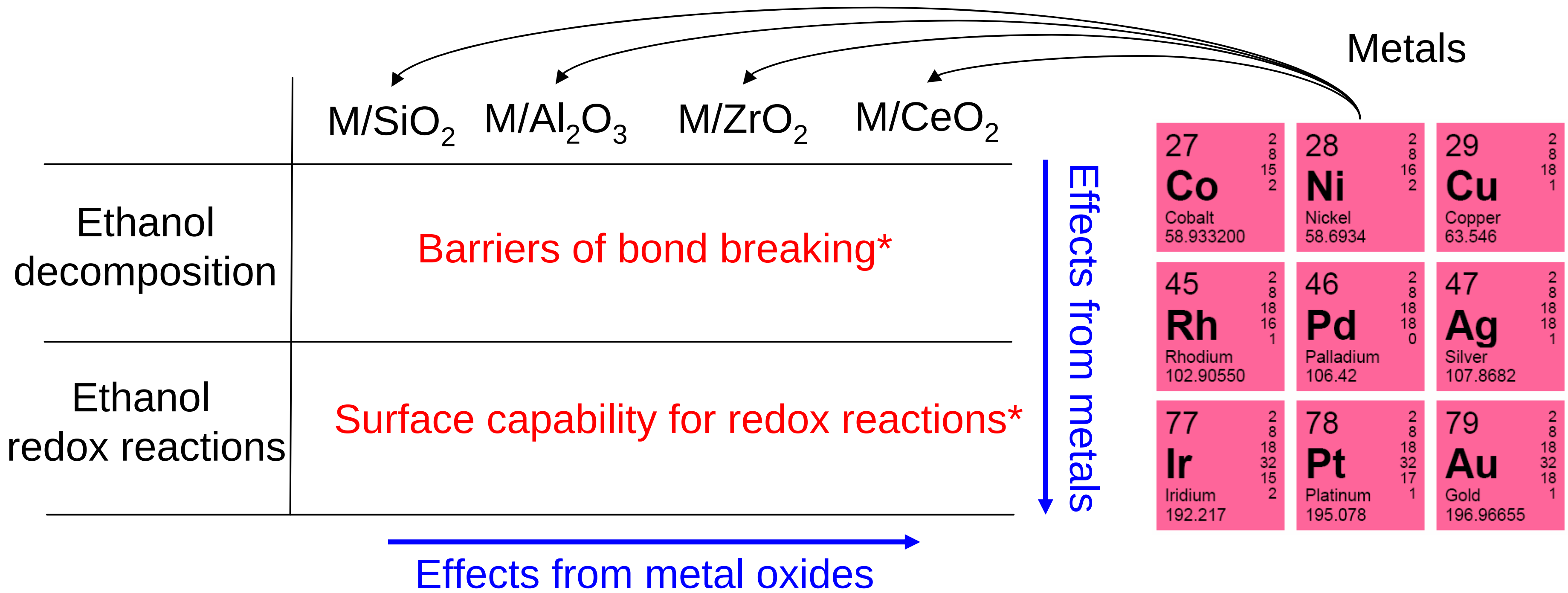


Measurement of H_2 production



Current results: Ethanol reformers (expt.)

To systematically study the reforming mechanism and establish design rules



Selected combinations

- SiO_2 and Al_2O_3: less active metal oxides
- ZrO_2: corresponding to the common SOFC electrolyte, Y-doped ZrO_2 (YSZ)
- CeO_2: corresponding to the common SOFC electrolyte, Gd-doped CeO_2 (GDC)
- Metals: All metals have the same crystal structures and no geometrical effects

Navarro, R. M.; Peña, M. A.;Fierro, J. L. G; *Chem. Rev.* **107** 3952 (2007)

Current results: Ethanol reformers (expt.)

Results: H_2 production on different reformers (%)

27 Co Cobalt 58.933200 (2 8 15 2)	28 Ni Nickel 58.6934 (2 8 16 2)	29 Cu Copper 63.546 (2 8 18 1)
45 Rh Rhodium 102.90550 (2 8 18 16 1)	46 Pd Palladium 106.42 (2 8 18 18 0)	47 Ag Silver 107.8682 (2 8 18 18 1)
77 Ir Iridium 192.217 (2 8 18 32 15 2)	78 Pt Platinum 195.078 (2 8 18 32 17 1)	79 Au Gold 196.96655 (2 8 18 32 18 1)

M/SiO_2

1.6	0.2	0.2
49.6	0.3	0.3

M/Al_2O_3

2.6	1.7	5.5
50.0	12.8	2.7
	20.8	

M/ZrO_2

2.8	0.3	9.7
41.0	12.5	5.1
	15.1	

M/CeO_2

20.2	27.3	20.3
90.5	26.9	15.0
97.3	53.7	17.6

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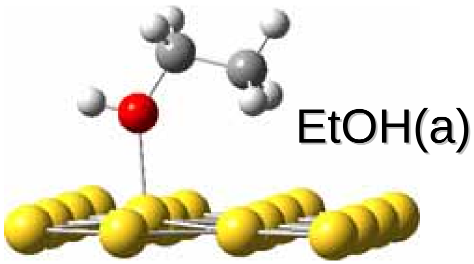
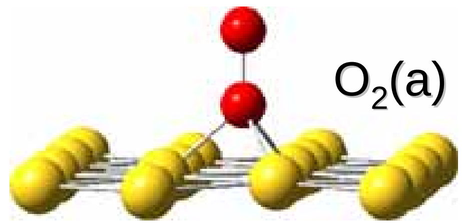
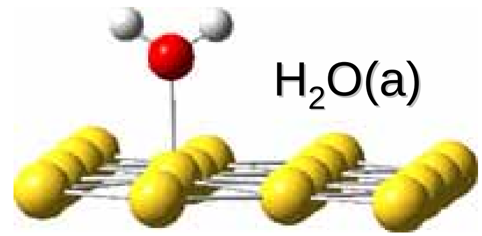
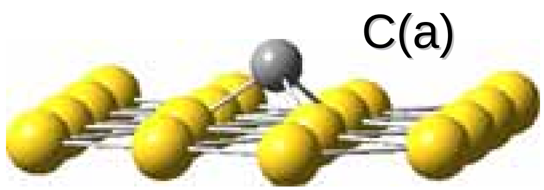
Current results: Ethanol reformers (compt.)

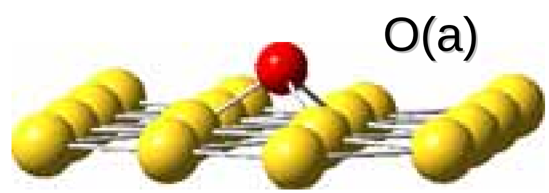
Adsorptions energies (kcal/mole)







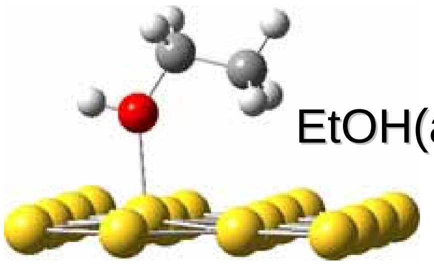


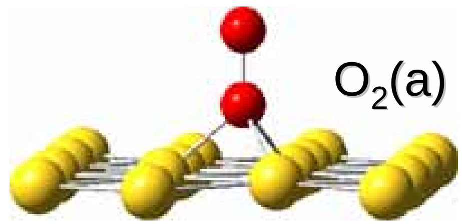


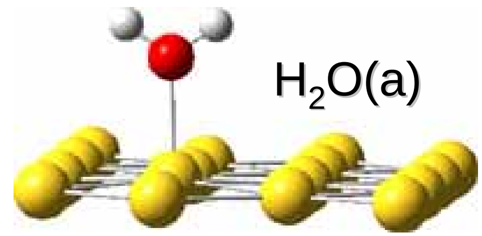
	Co	Ni	Cu	Rh	Pd	Ag	Ir	Pt	Au
EtOH(a)	-7.1	-7.5	-4.9	-7.6	-6.4	-2.8	-5.8	-5.4	-2.0
O_2(a)	-26.2	-22.9	-11.7	-42.7	-23.7	-16.7	-36.4	-24.4	-16.1
H_2O(a)	-6.9	-6.5	-5.4	-6.9	-5.3	-3.8	-6.2	-4.3	-1.2
C(a)	-174.6	-166.2	-118.8	-170.8	-163.1	-85.0	-170.9	-171.6	-111.4
O(a)	-141.2	-135.2	-122.1	-128.5	-109.1	-93.0	-123.0	-107.7	-84.8

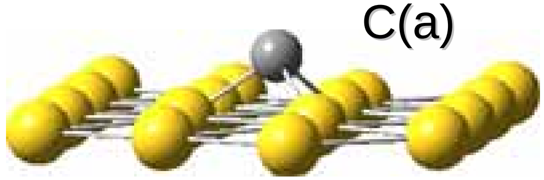
Current results: Ethanol reformers (compt.)

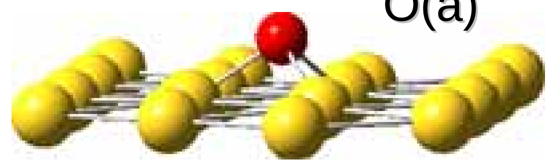
Cu, Ag and Au have lower adsorption energies











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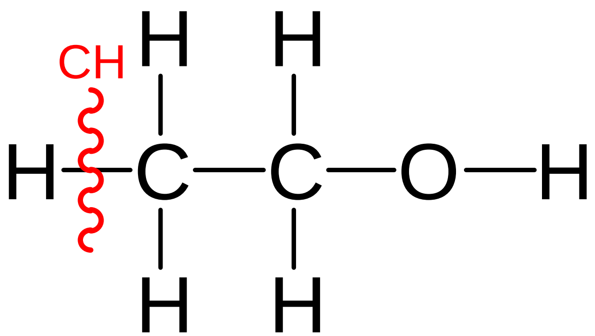
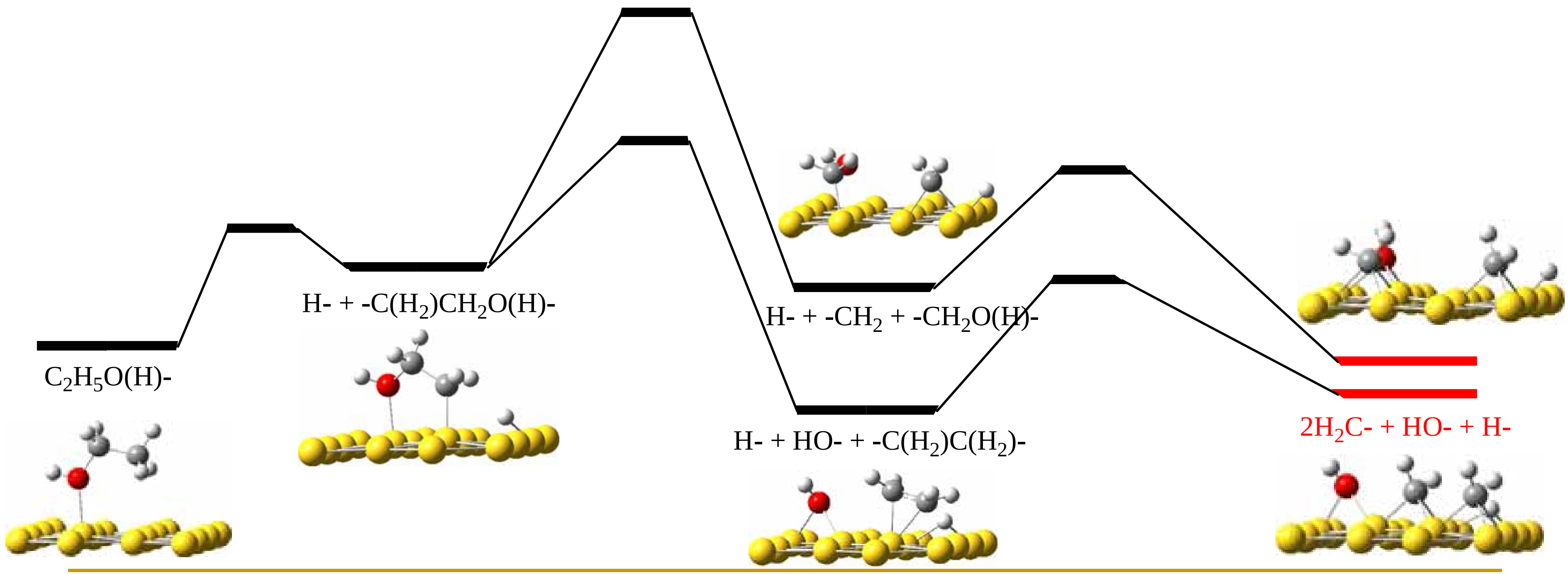
Reaction mechanism: initial C-H breaking reaction



$C_2H_5O(H)$- → H- + -$C(H_2)CH_2O(H)$- (C-H)
→H- + H_2C- + -$CH_2O(H)$- (C-C) → H- + $2H_2C$- + HO- (C-O)

→H- + HO- + -$CH_2C(H_2)$- (C-O) → H- + $2H_2C$- + HO- (C-O)



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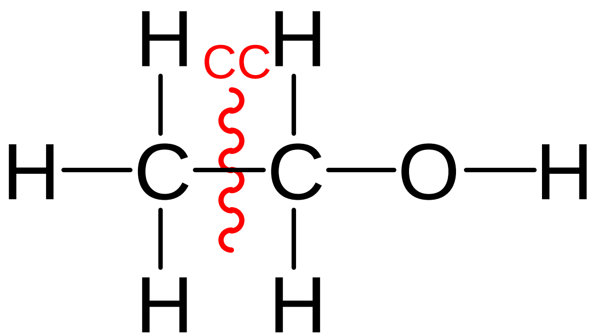
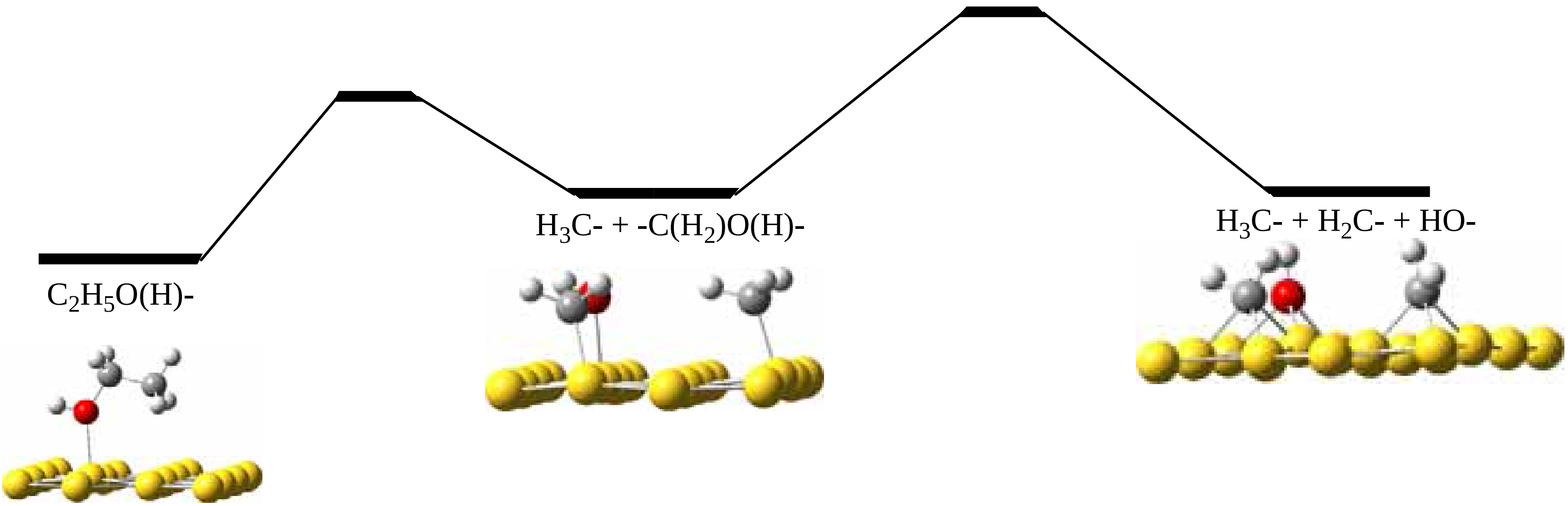
Reaction mechanism: initial C-C breaking reaction



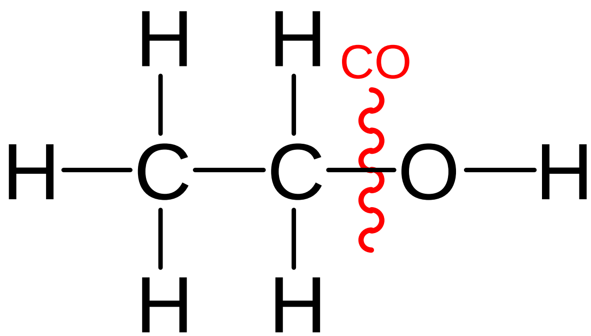
$C_2H_5O(H)- \rightarrow H_3C- + -C(H_2)O(H)-$ (C-C)

$\rightarrow H_3C- + H_2C- + HO-$ (C-O)



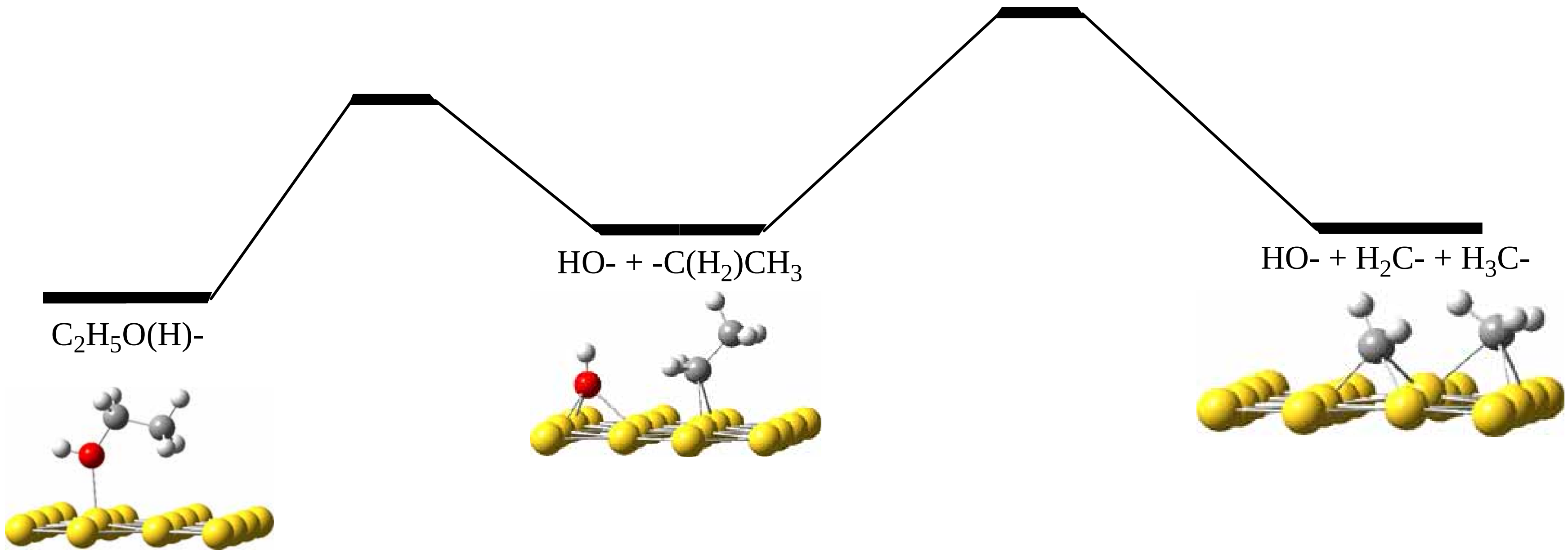
Current results: Ethanol reformers (compt.)

Reaction mechanism: initial C-O breaking reaction



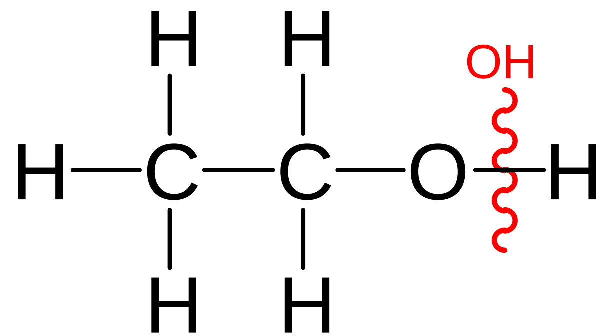
$C_2H_5O(H)- \rightarrow HO- + -C(H_2)CH_3$ (C-O)

$\rightarrow HO- + H_2C- + H_3C-$ (C-C)

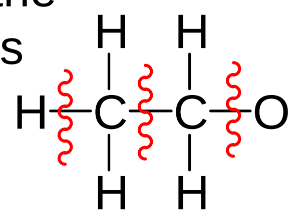


Current results: Ethanol reformers (compt.)

Reaction mechanism: initial O-H breaking reaction

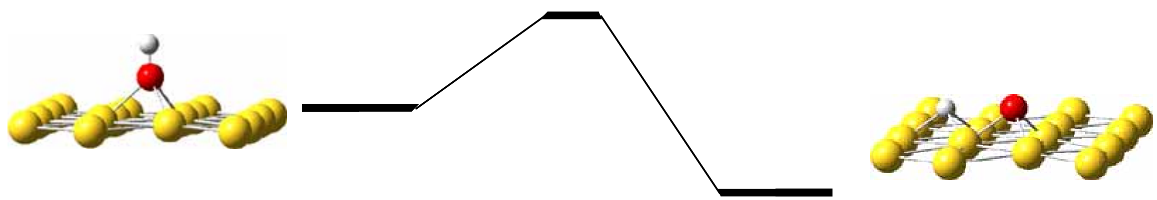


Starting from C_2H_5O– and following the C-H, C-C and C-O breaking reactions

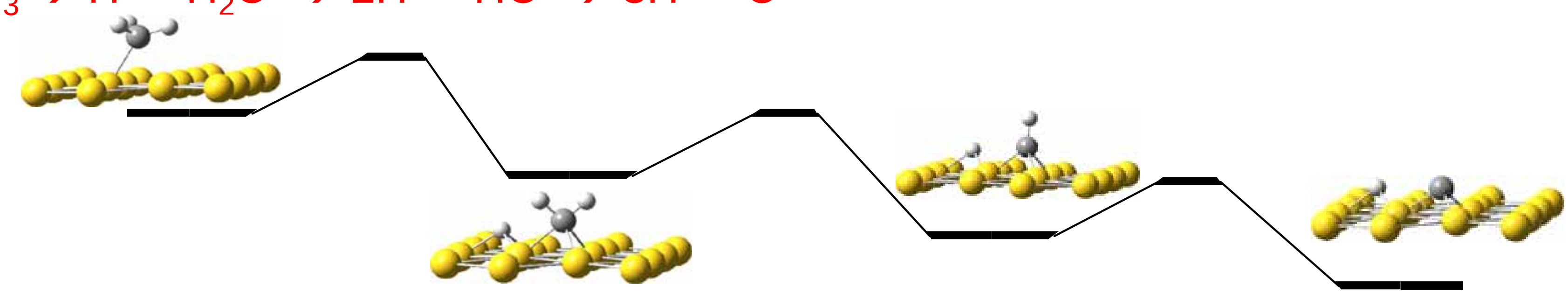


Fragments CH_3 and OH dissociation:

-OH → O- + H-



$-CH_3$ → H- + H_2C- → 2H- + HC- → 3H- + C-



Current results: Ethanol reformers (compt.)

TS barrier (heat of reaction) in eV

	Co	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au
$C_2H_5O(H)- \xrightarrow{TS(CC1)} H_3C- + -C(H_2)O(H)- \xrightarrow{TS(CO1)} H_3C- + H_2C- + HO-$									
TS(CC1)	2.66(1.01)	2.65(0.50)	2.02(0.39)	2.24(0.88)	2.70(0.71)	2.35(0.14)	3.34(1.48)	3.36(2.22)	4.04(1.50)
TS(CO1)	0.64(-0.77)	1.07(0.01)	0.87(0.00)	1.20(-0.43)	1.32(0.69)	0.94(0.87)	1.45(0.17)	1.84(1.15)	2.14(1.62)
$C_2H_5O(H)- \xrightarrow{TS(CO2)} H_3C(H_2)C- + HO- \xrightarrow{TS(CC2)} H_3C- + H_2C- + HO-$									
TS(CO2)	1.02(-0.16)	1.76(0.20)	1.71(0.37)	1.46(0.10)	2.23(0.59)	1.93(0.36)	1.78(0.45)	2.16(1.35)	2.48(1.50)
TS(CC2)	1.30(0.17)	1.20 (0.38)	0.78(0.18)	1.30(0.45)	1.43 (1.09)	0.93(0.56)	1.87(1.41)	2.66(2.00)	2.06(1.63)
$C_2H_5O(H)- \xrightarrow{TS(CH1)} -C(H_2)C(H_2)O(H)- + H- \rightarrow \begin{cases} \xrightarrow{TS(CC3)} H_2C- + -C(H_2)O(H)- + H- \xrightarrow{TS(CO3)} 2H_2C- + HO- + H- \\ \xrightarrow{TS(CO4)} -C(H_2)C(H_2)- + HO- + H- \xrightarrow{TS(CO3)} 2H_2C- + HO- + H- \end{cases}$									
TS(CH1)	1.34(0.46)	0.52(0.45)	0.48(0.41)	1.46(0.51)	1.38(0.55)	0.91(0.40)	2.03(1.09)	3.09(1.90)	2.90(1.33)
TS(CC3)	0.63(0.32)	1.02(-0.03)	0.60(-0.17)	0.86(0.17)	0.87(0.35)	1.14(0.28)	2.08(1.24)	2.71(2.09)	2.33(1.63)
TS(CO3)	0.34(-1.03)	1.00(-0.11)	0.94(0.45)	0.27(-0.43)	1.24(0.64)	1.28(0.87)	1.16(0.06)	1.83(1.13)	2.12(1.54)
TS(CO4)	0.03(-0.88)	0.42(-0.69)	0.54(-0.42)	0.14(-0.73)	0.68(-0.27)	0.78(0.27)	1.59(-0.43)	2.13(-0.27)	1.91(0.65)
TS(CC4)	0.88(0.86)	0.99(0.82)	1.28(0.33)	1.04(1.02)	1.66(1.48)	2.01(0.33)	2.76(1.99)	3.45(2.92)	2.70(2.52)
$C_2H_5O(H)- \xrightarrow{TS(OH1)} C_2H_5O- + H-$									
TS(OH1)	0.44(-0.74)	0.58(-0.19)	0.69(0.21)	0.67(-0.58)	0.70(0.25)	0.99(0.55)	1.10(-0.10)	1.94(0.84)	1.45(1.32)

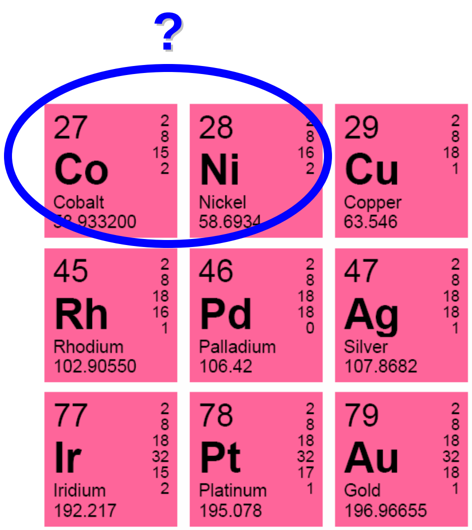
Current results: Ethanol reformers (compt.)

TS barrier (heat of reaction) in eV

	Co	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au
$C_2H_5O- \xrightarrow{TS(CC5)} H_3C- + -C(H_2)O- \xrightarrow{TS(CO5)} H_3C- + H_2C- + O-$									
TS(CC5)	1.52(0.78)	1.41(0.65)	1.85(0.37)	1.62(1.26)	1.93(0.53)	2.08(1.04)	2.27(1.87)	2.79(1.66)	3.45(0.88)
TS(CO5)	0.78(-0.10)	1.12(-0.23)	1.01(-0.13)	1.13(-0.49)	1.63(0.75)	1.50(0.42)	1.70(1.48)	2.65(2.60)	2.86(2.32)
$C_2H_5O- \xrightarrow{TS(CO6)} H_3C(H_2)C- + O- \xrightarrow{TS(CC6)} H_3C- + H_2C- + O-$									
TS(CO6)	0.86(0.12)	1.27(-0.07)	1.20(-0.13)	0.90(0.26)	0.77(0.42)	1.37(0.03)	1.83(1.03)	2.13(1.13)	1.57(1.40)
TS(CC6)	1.15(0.25)	1.43(0.36)	0.97(-0.01)	1.28(0.45)	1.13(0.82)	1.65(0.10)	1.86(1.20)	3.05(2.02)	1.71(1.64)
$C_2H_5O- \xrightarrow{TS(CH2)} -C(H_2)C(H_2)O- + H- \rightarrow \begin{cases} \xrightarrow{TS(CC7)} H_2C- + -C(H_2)O- + H- \xrightarrow{TS(CO7)} 2H_2C- + O- + H- \\ \xrightarrow{TS(CO8)} -C(H_2)C(H_2)- + O- + H- \xrightarrow{TS(CO8)} 2H_2C- + O- + H- \end{cases}$									
TS(CH2)	1.28(1.08)	0.55(0.52)	0.44(0.04)	1.47(1.15)	1.03(0.55)	0.75(-0.27)	1.67(1.11)	3.12(1.35)	1.68(1.34)
TS(CC7)	0.19(-0.18)	0.45(-0.24)	0.72(-0.03)	0.30(-0.19)	0.60(-0.06)	0.73(0.18)	2.20(1.96)	2.30(1.02)	1.60(0.74)
TS(CO7)	0.10(-0.57)	0.07(-0.48)	0.50(-0.73)	0.12(-0.69)	0.71(-0.78)	1.14(0.43)	1.25(0.48)	3.55(2.55)	3.60(2.28)
TS(CO8)	0.05(-1.51)	0.05(-1.10)	0.21(-0.60)	0.10(-1.33)	0.18(-0.62)	1.02(0.24)	1.13(0.09)	1.08(-0.12)	1.24(0.36)
TS(CC8)	0.92(0.90)	0.97(0.84)	1.44(0.32)	1.05(1.01)	1.78(1.52)	1.40(0.48)	2.27(2.00)	4.10(3.81)	3.02(2.96)
$H_3C- \xrightarrow{TS(CH3)} H_2C- + H- \xrightarrow{TS(CH4)} HC- + 2H- \xrightarrow{TS(CH5)} C- + 3H-$									
TS(CH3)	0.11(-0.17)	0.18(-0.25)	0.28(0.04)	0.32(-0.20)	0.56(-0.07)	0.64(-0.01)	1.25(0.78)	2.03(1.69)	1.67(1.39)
TS(CH4)	0.15(-0.33)	0.11(-0.51)	0.31(-1.14)	0.17(-0.34)	0.33(-0.46)	0.54(-0.50)	1.05(0.61)	1.66(1.32)	1.21(0.77)
TS(CH5)	1.08(0.50)	1.07(0.42)	1.11(0.76)	1.24(0.60)	1.31(0.40)	1.16(0.61)	1.56(1.37)	2.27(1.90)	2.16(1.63)
$HO- \xrightarrow{TS(OH2)} O- + H-$									
TS(OH2)	0.99(-0.16)	0.65(-0.21)	0.45(-0.16)	1.00(-0.13)	1.26(0.15)	0.57(0.01)	1.82(0.71)	2.60(1.74)	2.06(1.40)

Recall: Ethanol reformers (expt.)

Reactivity: Ir > Rh > Pt > Pd*



M/SiO_2

1.6	0.2	0.2
49.6	0.3	0.3

M/Al_2O_3

2.6	1.7	5.5
50.0	12.8	2.7
	20.8	

M/ZrO_2

2.8	0.3	9.7
41.0	12.5	5.1
	15.1	

M/CeO_2

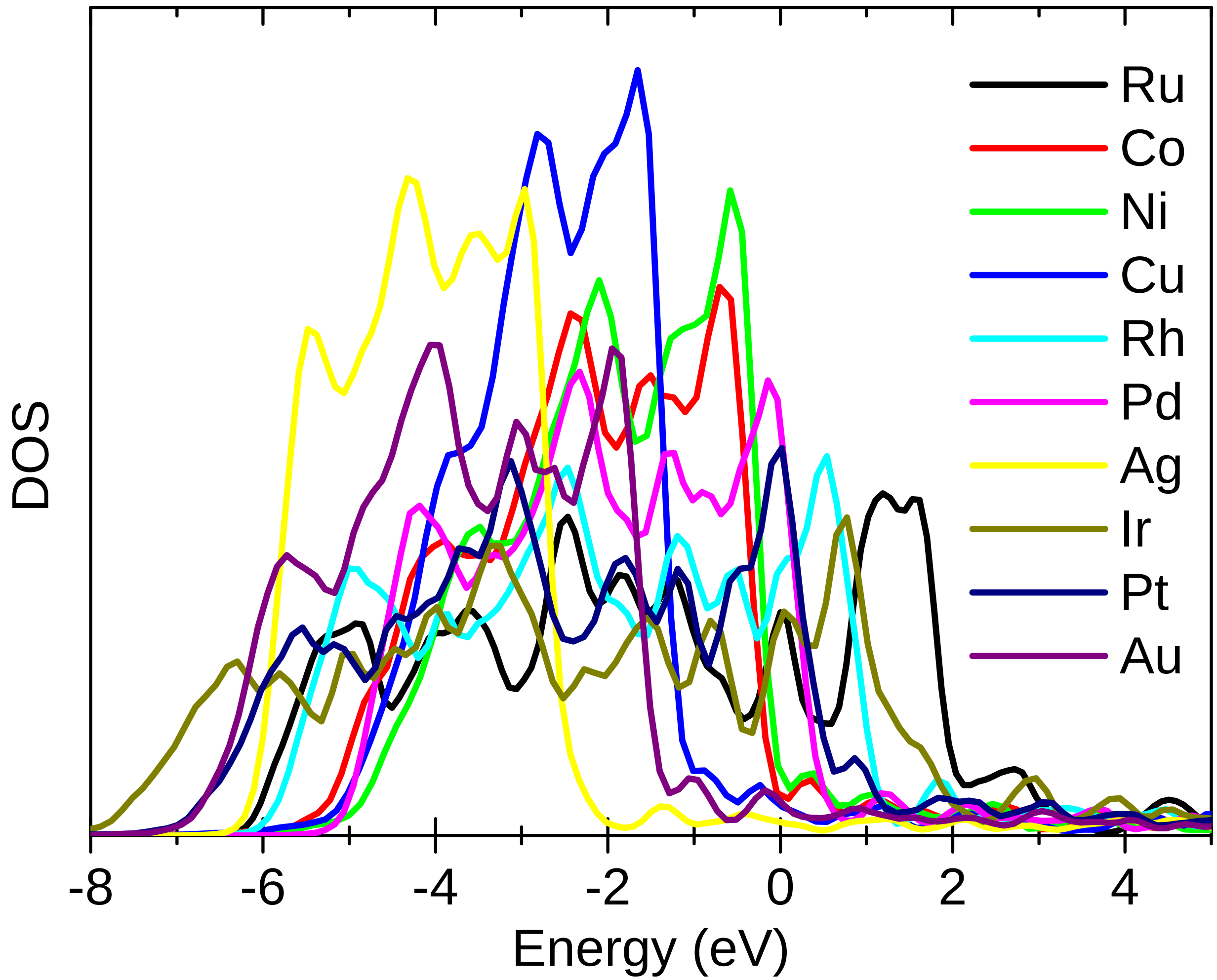
20.2	27.3	20.3
90.5	26.9	15.0
97.3	53.7	17.6

➔ No clear correlation between decomposition barriers and reactivity

Rh > Pd > Ni = Pt/γ-Al_2O_3: Llorca, J.; Homs, N.; Sales, J.; de la Piscina, P. R. *J. Catal.* **209**, 306 (2002)
Rh > Pd > Pt > Ru /γ-Al_2O_3 : Auprête, G.; Descorme, C.; Duprez, D. *Catal. Commun.* **3**, 263 (2002)

Current results: Ethanol reformers (compt.)

Electronic structure: DOS analysis



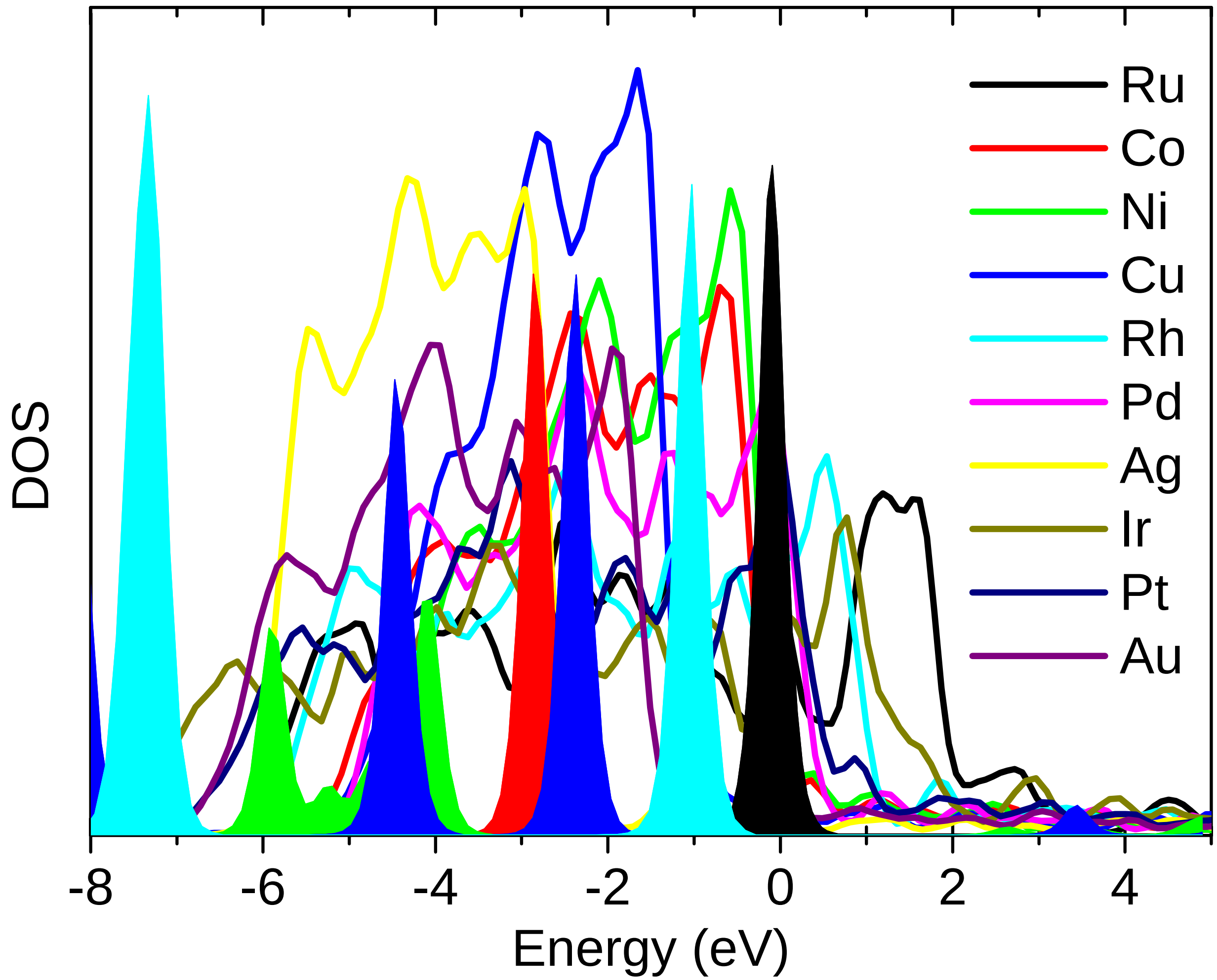
d-band centers*

Ru*	-1.41
Co	-1.17
Ni	-1.29
Cu	-2.67
Rh	-1.73
Pd	-1.83
Ag	-4.30
Ir	-2.11
Pt	-2.25
Au	-3.56

95% Ru/CeO_2: Deluga, G. A.; Salge, J. R.; Schmidt, L. D.; Verykios, X. E.; *Science* **303** 933 (2004)
Hammer, B; Norskov, J. K.: *Adv. Catal.* **43**, 71 (2000)

Current results: Ethanol reformers (compt.)

Electronic structure: DOS analysis



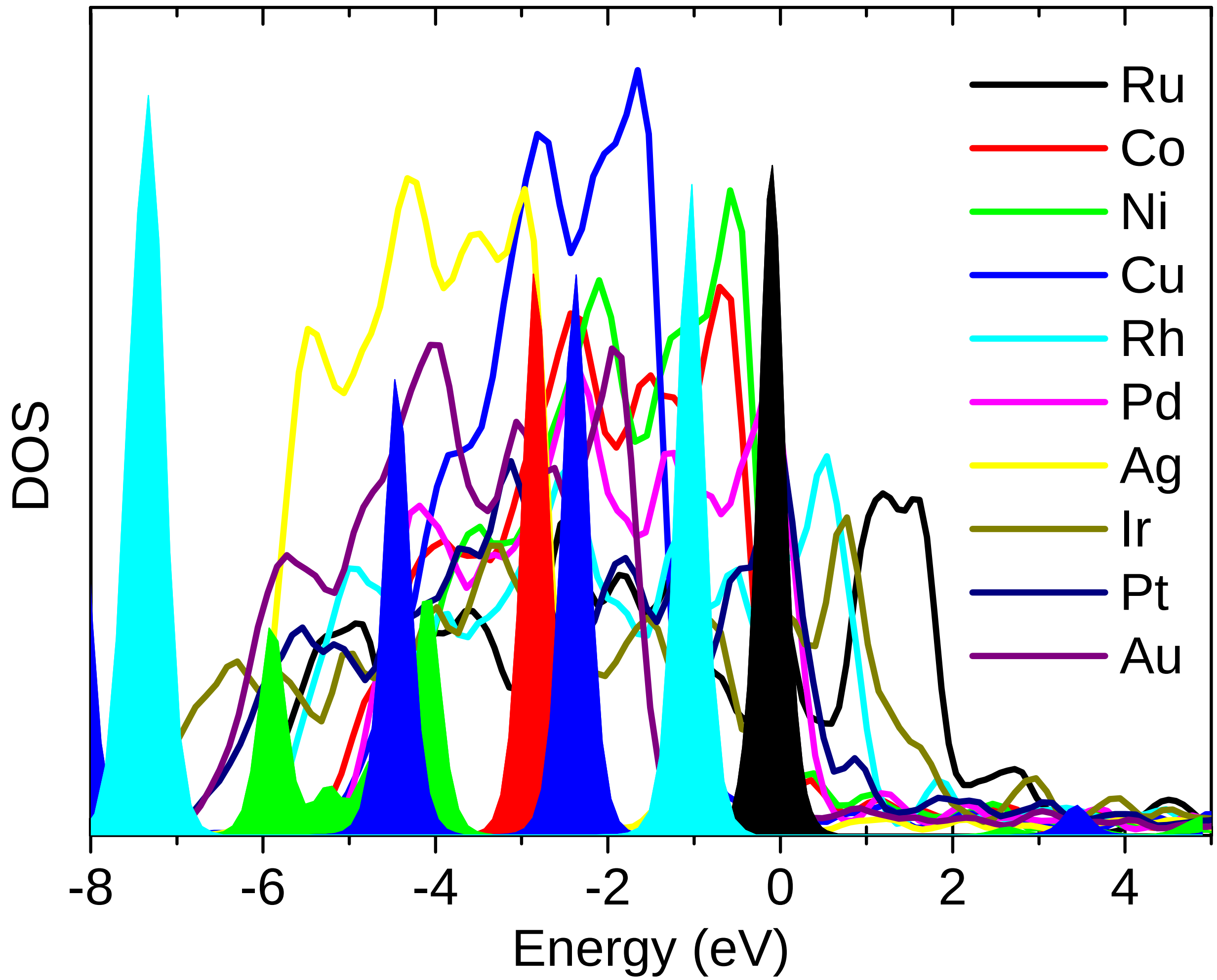
Δ Bader charges

	C	O_2	H_2O	O	EtOH
Co	.25	.27	.26	.33	.25
Ni	.28	.29	.27	.36	.22
Cu	.25	.24	.23	.31	.22
Rh	.35	.26	.23	.36	.26
Pd	.31	.25	.28	.34	.18
Ag	.18	.19	.16	.29	.16
Ir	.39	.29	.28	.39	.25
Pt	.34	.22	.20	.37	.18
Au	.18	.14	.17	.26	.13

C O_2 H_2O O EtOH

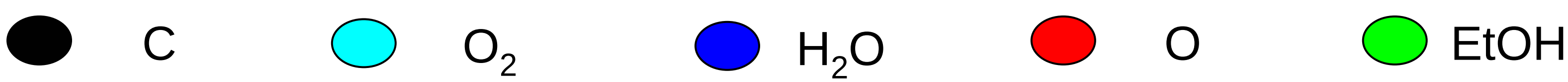
Current results: Ethanol reformers (compt.)

Electronic structure: DOS analysis



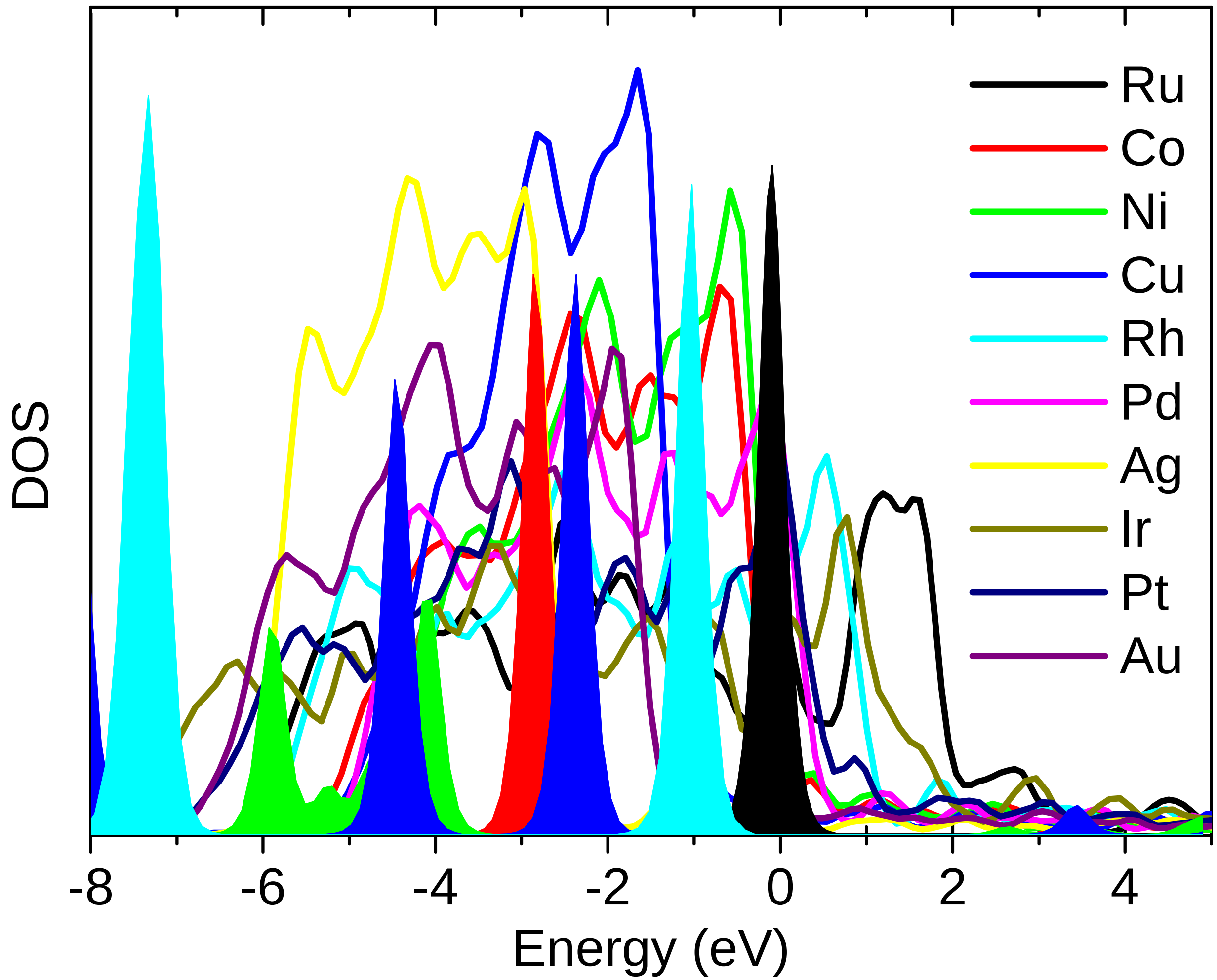
Δ Bader charges

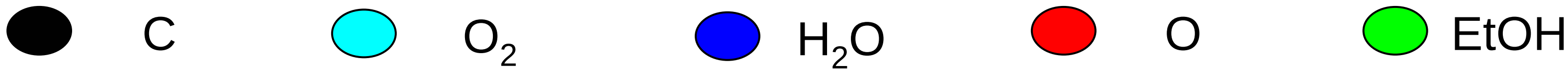
	C	O_2	H_2O	O	EtOH
Co	.25	.27	.26	.33	.25
Ni	.28	.29	.27	.36	.22
Cu	.25	.24	.23	.31	.22
Rh	.35	.26	.23	.36	.26
Pd	.31	.25	.28	.34	.18
Ag	.18	.19	.16	.29	.16
Ir	.39	.29	.28	.39	.25
Pt	.34	.22	.20	.37	.18
Au	.18	.14	.17	.26	.13



Current results: Ethanol reformers (compt.)

Electronic structure: DOS analysis

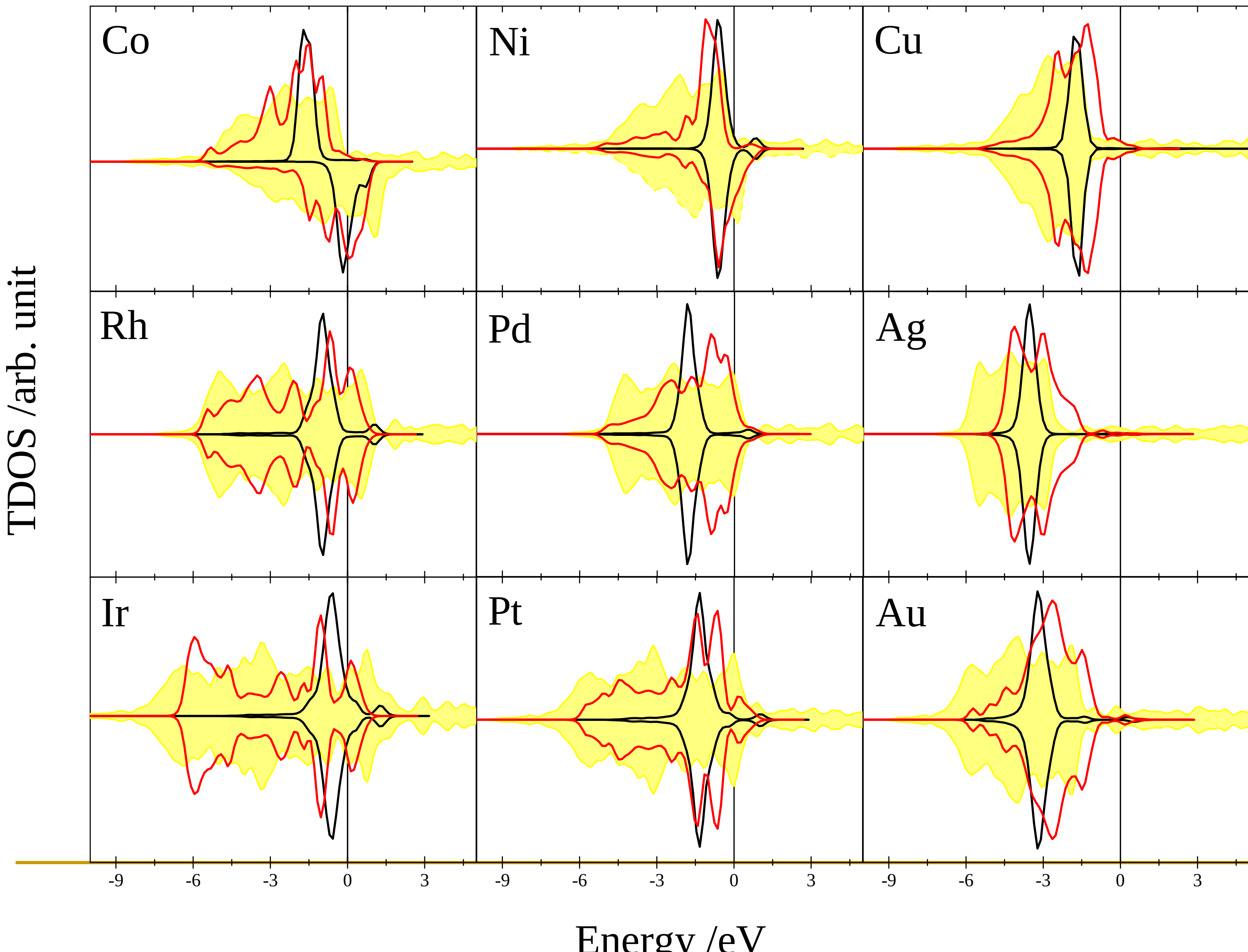




- Ru, Ir, Rh has better reactivity with broader DOS
- Rh, Ir, Pd and Pt has larger DOS overlap with C (fast e-transfer)
- Ag and Au has smaller DOS overlap with O_2 (slow e-transfer)

Current results: Ethanol reformers (compt.)

Electronic structure: DOS analysis of M/CeO_2



Current results: Ethanol reformers

Ethanol reforming related two major factors:

decomposition and redox reaction*

- Decomposition reaction: Cu, Ag and Au have ***higher*** decomposition barriers (compt.) and ***low*** reforming efficiency (expt.). Rh and Ir have ***lower*** decomposition barriers and ***higher*** reforming efficiency.

  However, Co and Ni showed the ***low*** barriers, but with the ***low*** efficiency.

- Redox capability: Ru, Rh, Ir, Pd and Pt have ***broader*** d-band distribution and good overlap with all the reactants of ethanol, O_2 and H_2O, which promote the electron transfer between metal surface and adsorbates and enhance the redox reaction in the ethanol reforming process.

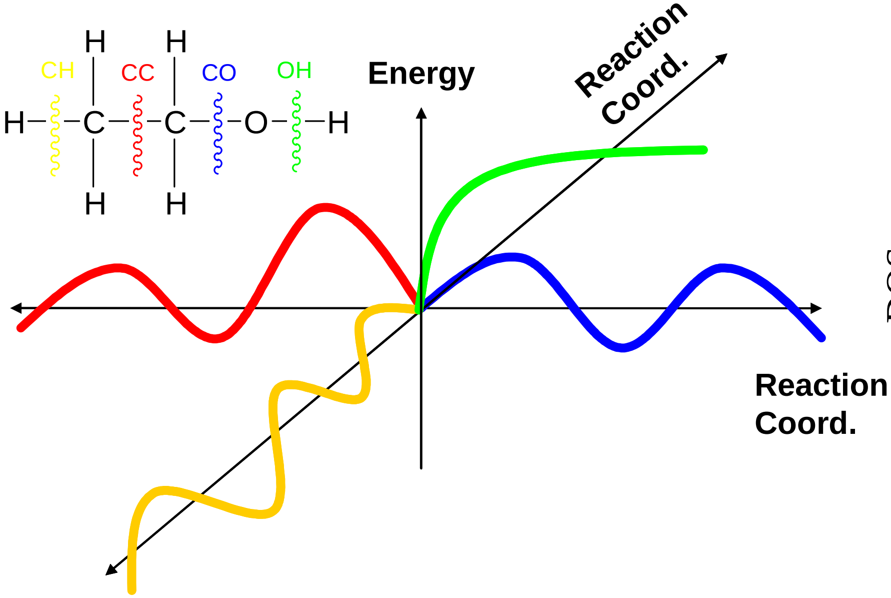
➔ Lower decomposition barrier is NOT necessary to assist the ethanol reforming process. The decomposed C(a) might cause surface poisoning if it can not be removed by the redox reaction.

Navarro, R. M.; Peña, M. A.;Fierro, J. L. G; *Chem. Rev.* **107** 3952 (2007)

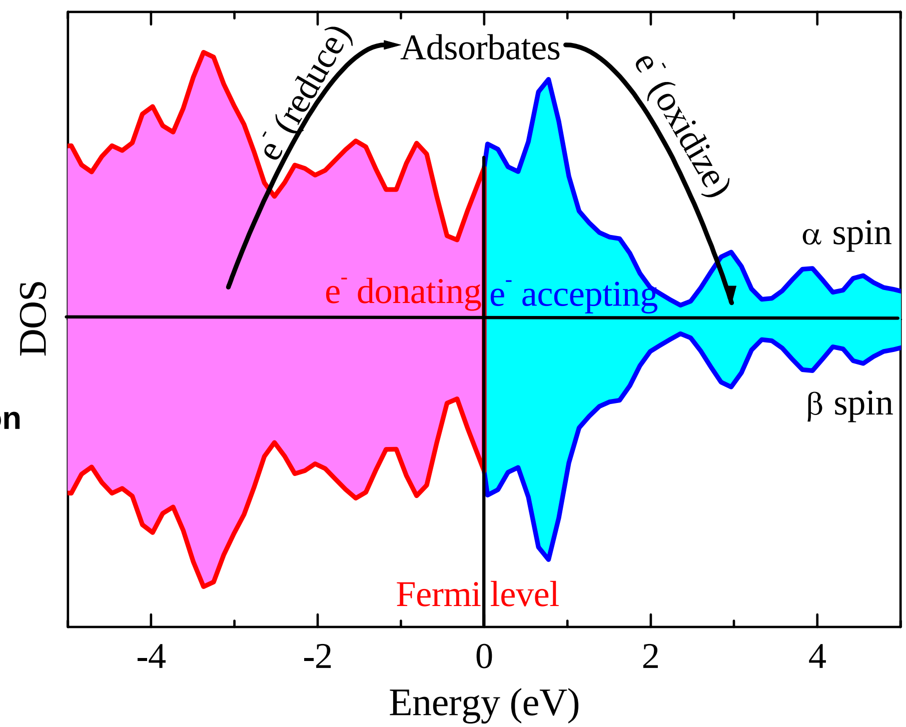
Current results: Ethanol reformers

Ethanol reforming: $C_2H_5OH+0.5O_2+2H_2O \rightarrow 2CO_2+5H_2$

ethanol decomposition
(PES calculation)



redox capability
(DOS analysis)



Current results: H_2 SOFC (expt.)

Powder preparation: Glycine nitrade process (GNP)

Mix metal nitrade solution with glycine (NH_2CH_2COOH)

Ni anode:

$Ni(NO_3)_2\text{-}6H_2O + 2NH_2CH_2COOH$

$Zr_{0.92}Y_{0.08}O_{2-\delta}$ (YSZ) electroyte:

$0.92ZrO(NO_3)_2 + 0.08Y(NO_3)_3 + 2.32NH_2CH_2COOH$

$La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) cathode:

$0.8\ La(NO_3)_3.6H_2O + 0.2\ Sr(NO_3)_2 + Mn(NO_3)_2.4H_2O + 4.4\ NH_2CH_2COOH$

- Heat up the solution to vaporize the water (convert to gel), to auto-ignite to flame and to result fine ashes

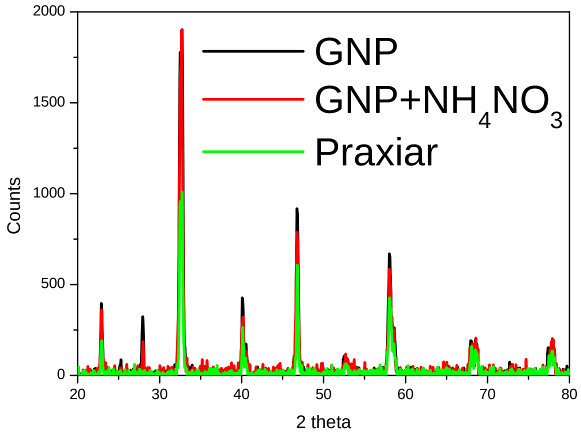
- Fire ashes in furnace at 800 ^oC for 3 hours

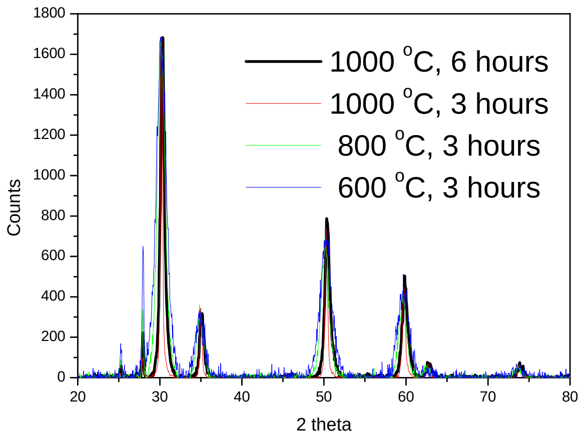
➔ **NO_3^{2-}/glycine = 1 : 1**

Insufficient glycine leds to less vigorous auto-ignition and extra amout of glycine hinders formation of the desired phase due to the residual carbon

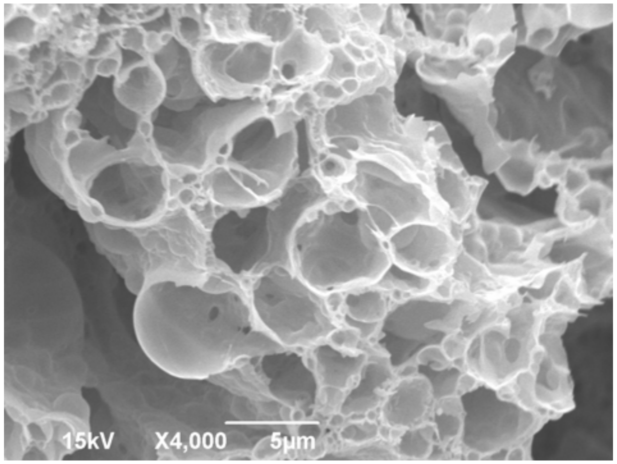
Current results: H_2 SOFC (expt.)

XRD: NH_4NO_3 has limited effect in GNP and higer temperature results narrower peak.

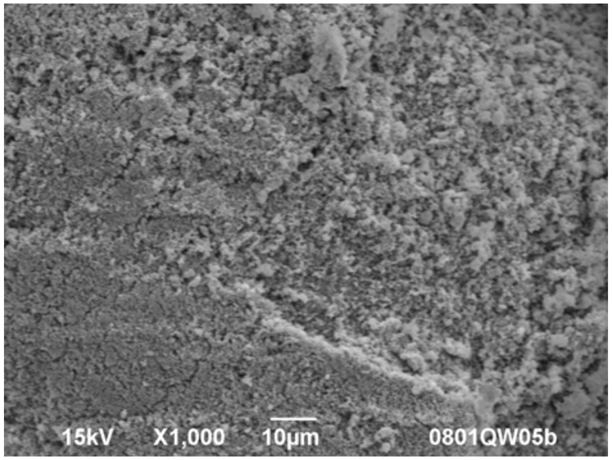




SEM: **GNP** shows better microstructure (than solid state reaction (SSR) does)



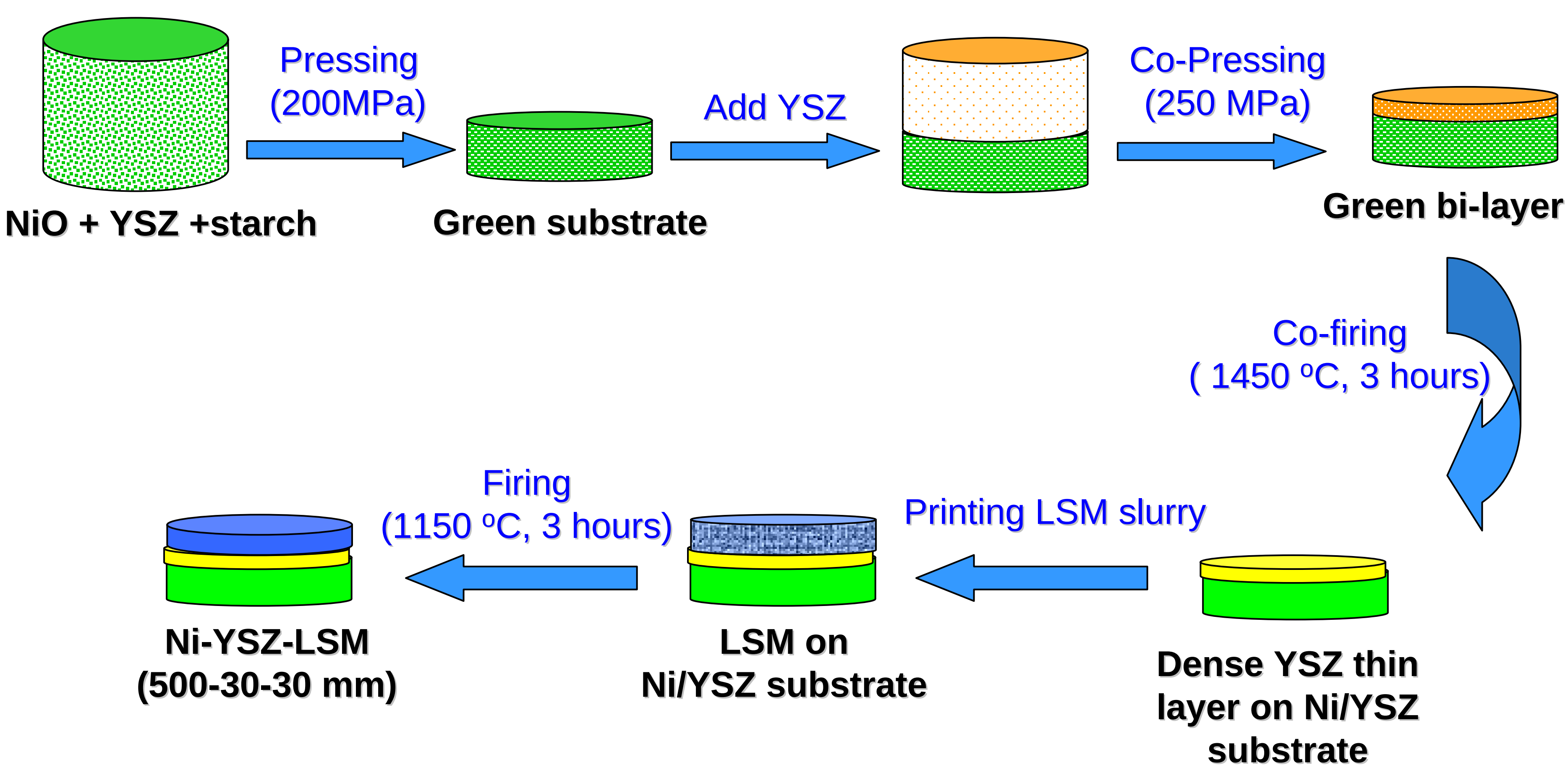
GNP



SSR

Current results: H_2 SOFC (expt.)

Cell assembling: Dry-pressing process (a simple and cost-effective method)



Current results: H_2 SOFC (expt.)

Ni/YSZ/LSM: Single cell fabrication

Nitrade solution

Fire

Metal oxide powder

Co-press

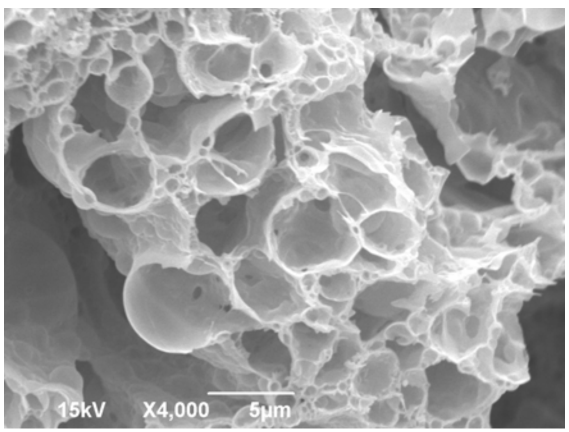
Co-fire

NiO/YSZ half cell

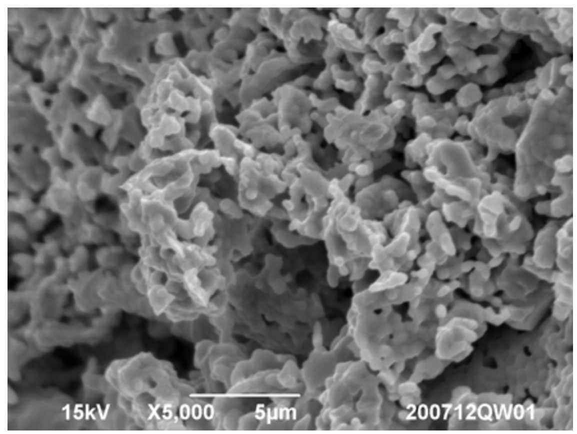
Print LSM

Fire

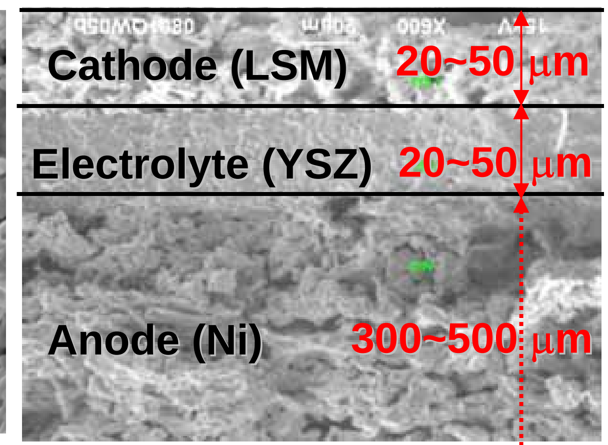
NiO/YSZ/LSM single cell



Foam-like structure



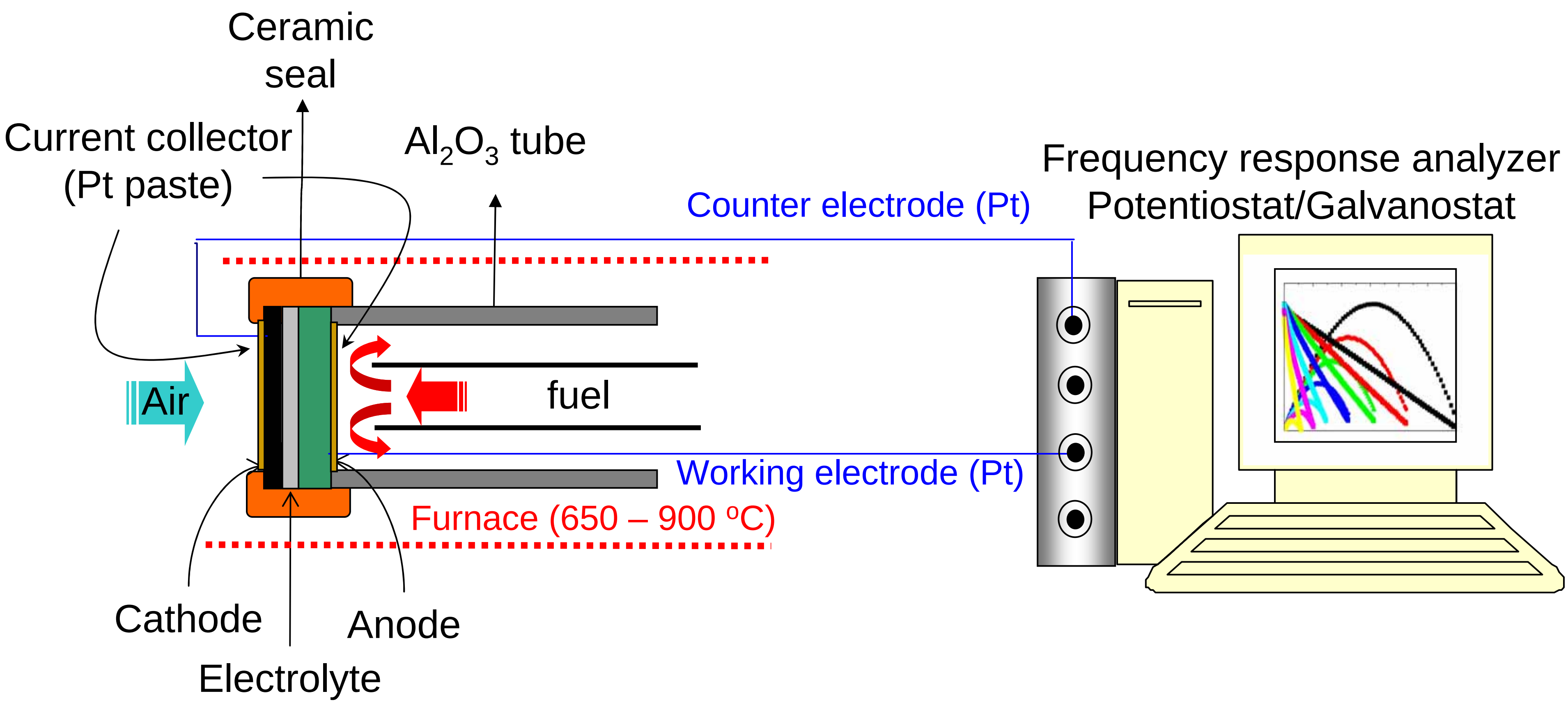
Porous anode surface



Cross section

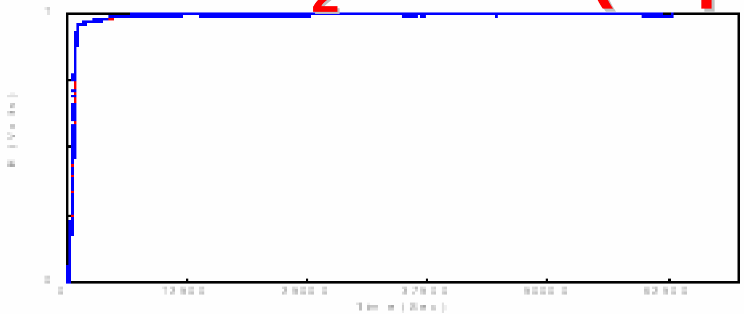
Current results: H_2 SOFC (expt.)

Schematic diagram of SOFC performance testing

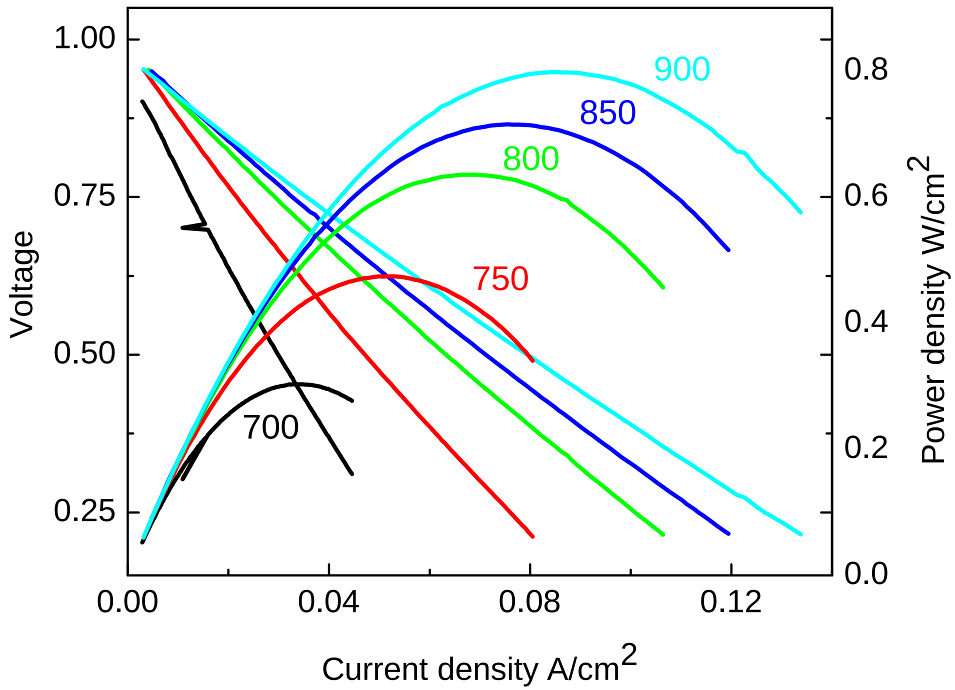


Current results: H_2 SOFC (expt.)

OCV (stabilize), 1.0 V

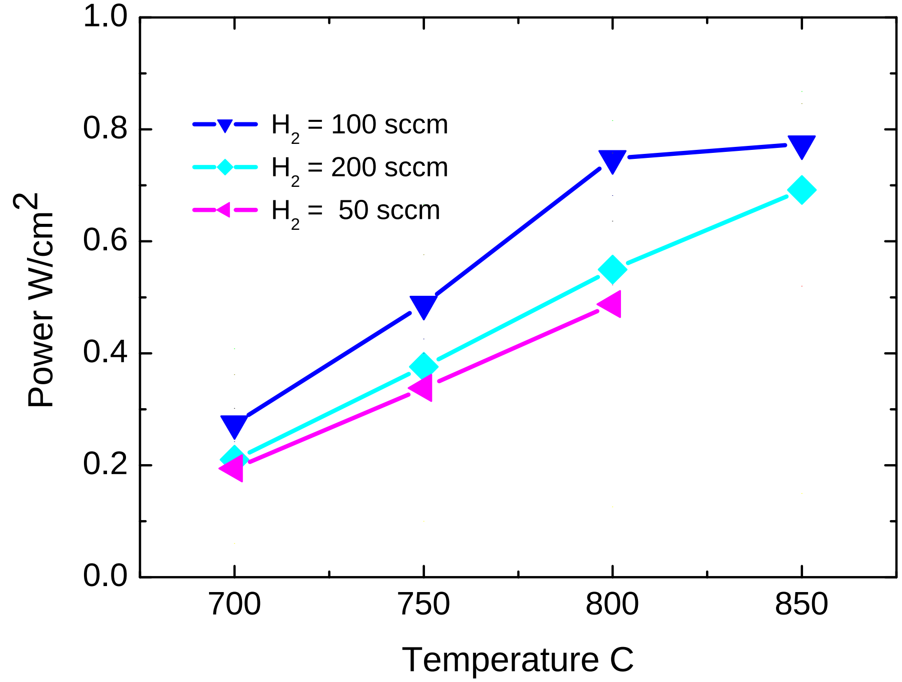


Temperature effect, 0.8 W/cm²



H_2 effect, 50, 100, 200 sccm

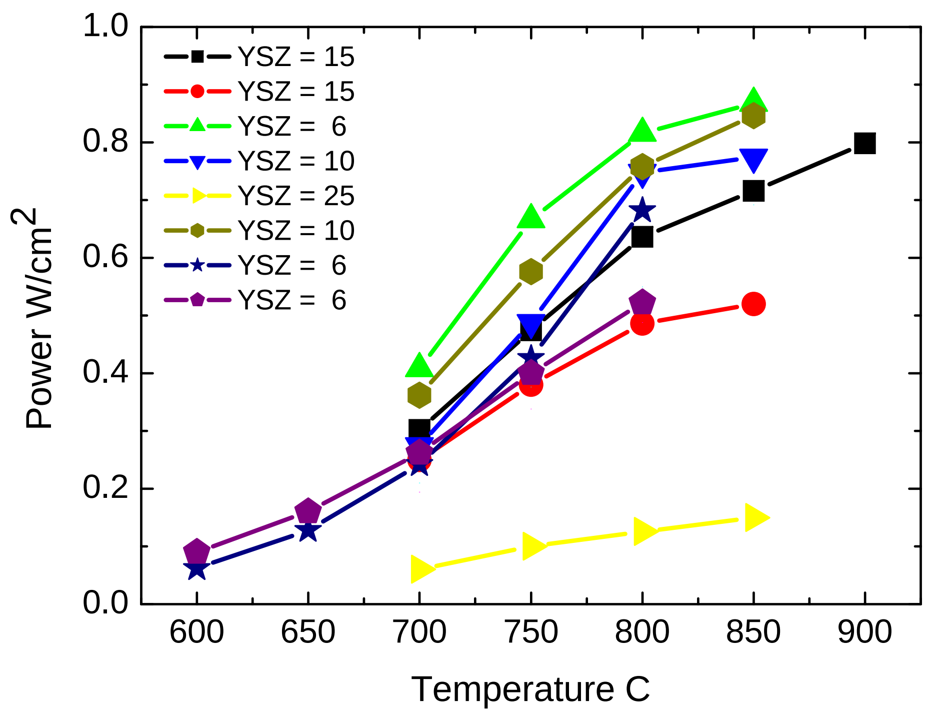
→ 50 sccm H_2 flow is still high enough



Current results: H_2 SOFC (expt.)

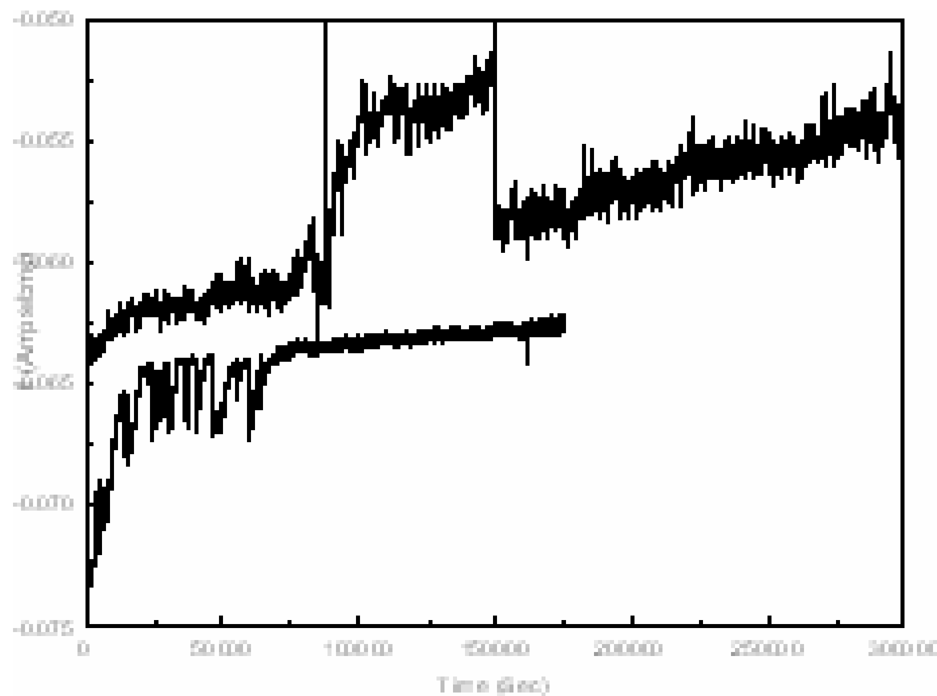
YSZ thickness, 6, 10, 15, 25 mg

Thinner YSZ → lower resistant
6, 10 and 15 have similar performance



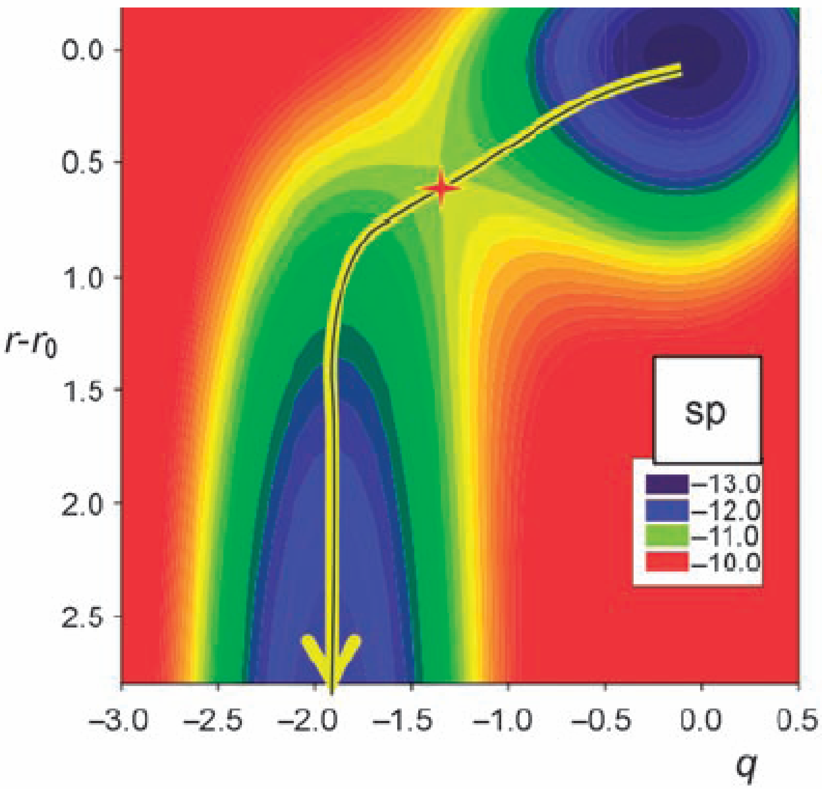
Long term stability, 55 and 83 hours

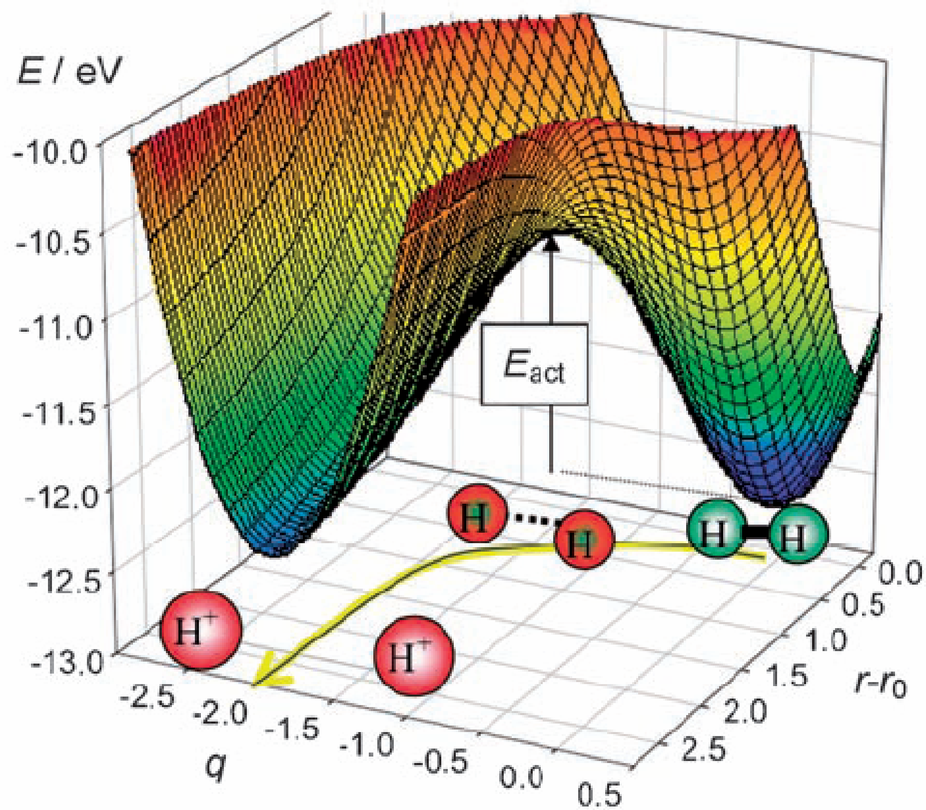
55 hours, power reduce < 1%
86 hours, power reduce < 5% (damage)



Current results: H_2 SOFC (compt.)

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$



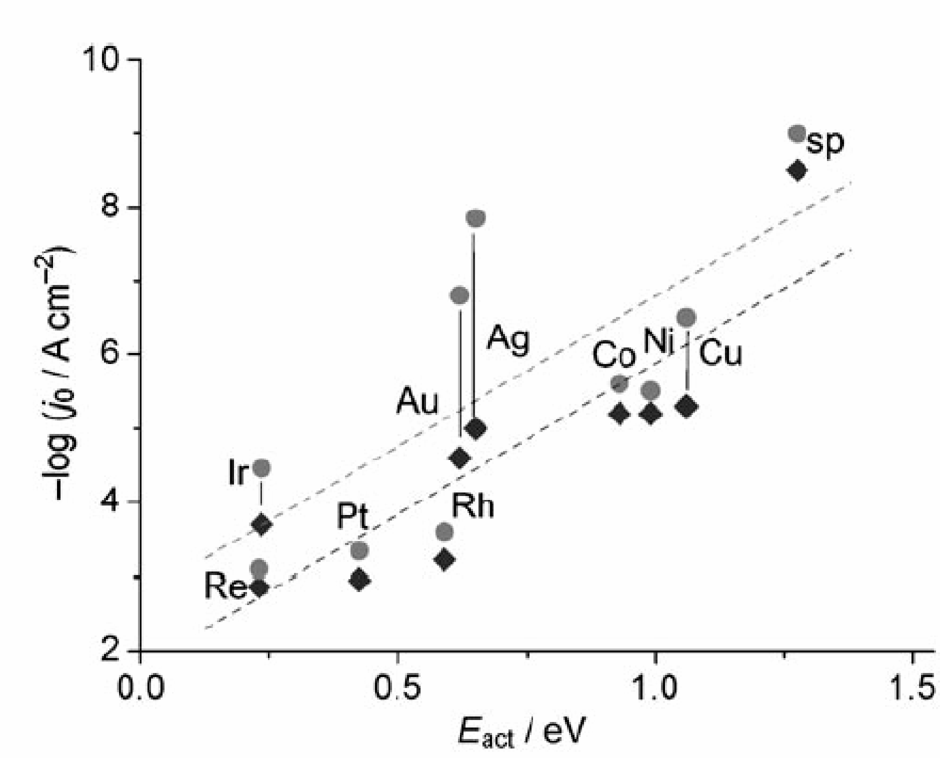


Elizabeth Santos and Wolfgang Schmickler; Angew. Chem. Int. Ed. 2007, 46, 8262 –8265

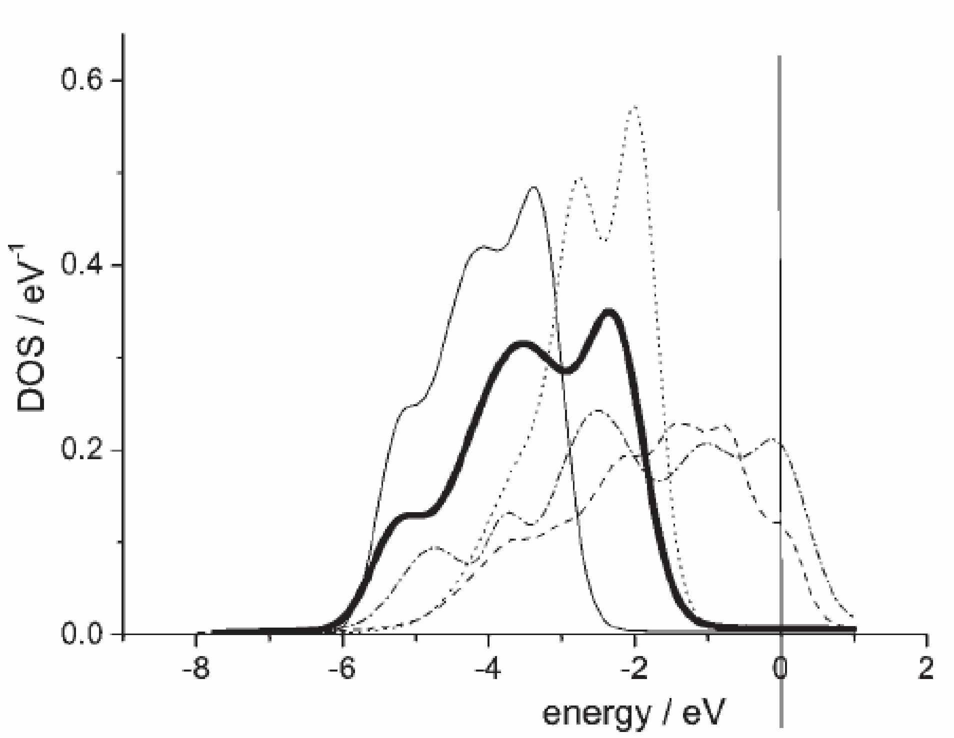
Current results: H_2 SOFC (compt.)

For metal surfaces, the performance is related to d-band centers

Performance --- H_2 dissociation



Dissociation barriers --- d-band structure

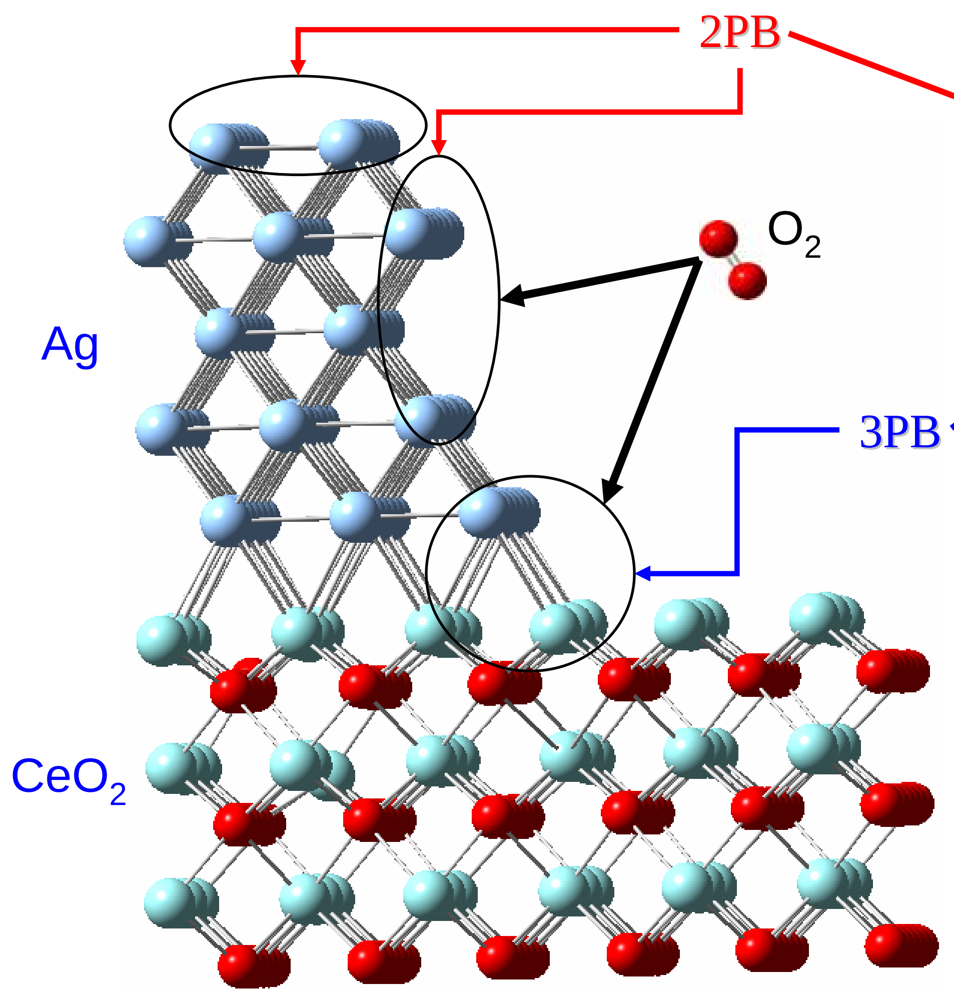


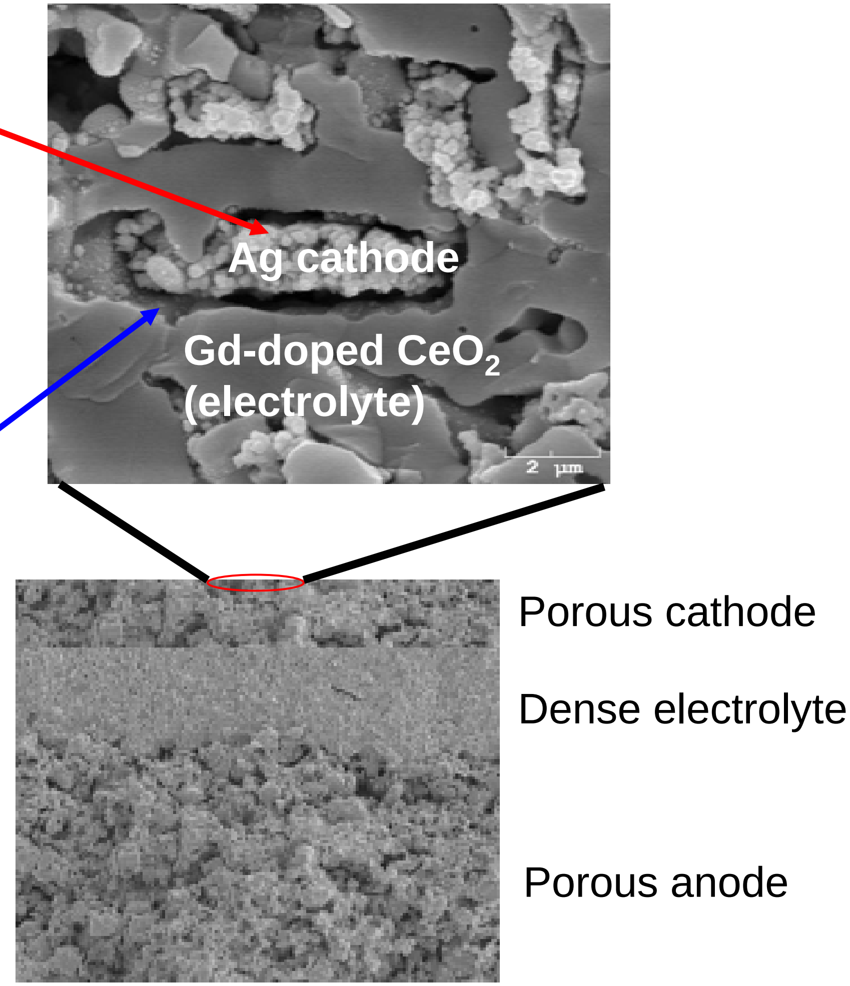
Elizabeth Santos and Wolfgang Schmickler; Angew. Chem. Int. Ed. 2007, 46, 8262 –8265

Hammer, B.; Norskov, J. K.; *Adv. Catal.*, **45**, 71 (2000)

Current results: H_2 SOFC (compt.)

PES of O_2 dissociation on Ag/CeO_2 (3PB) and Ag (2PB) surfaces





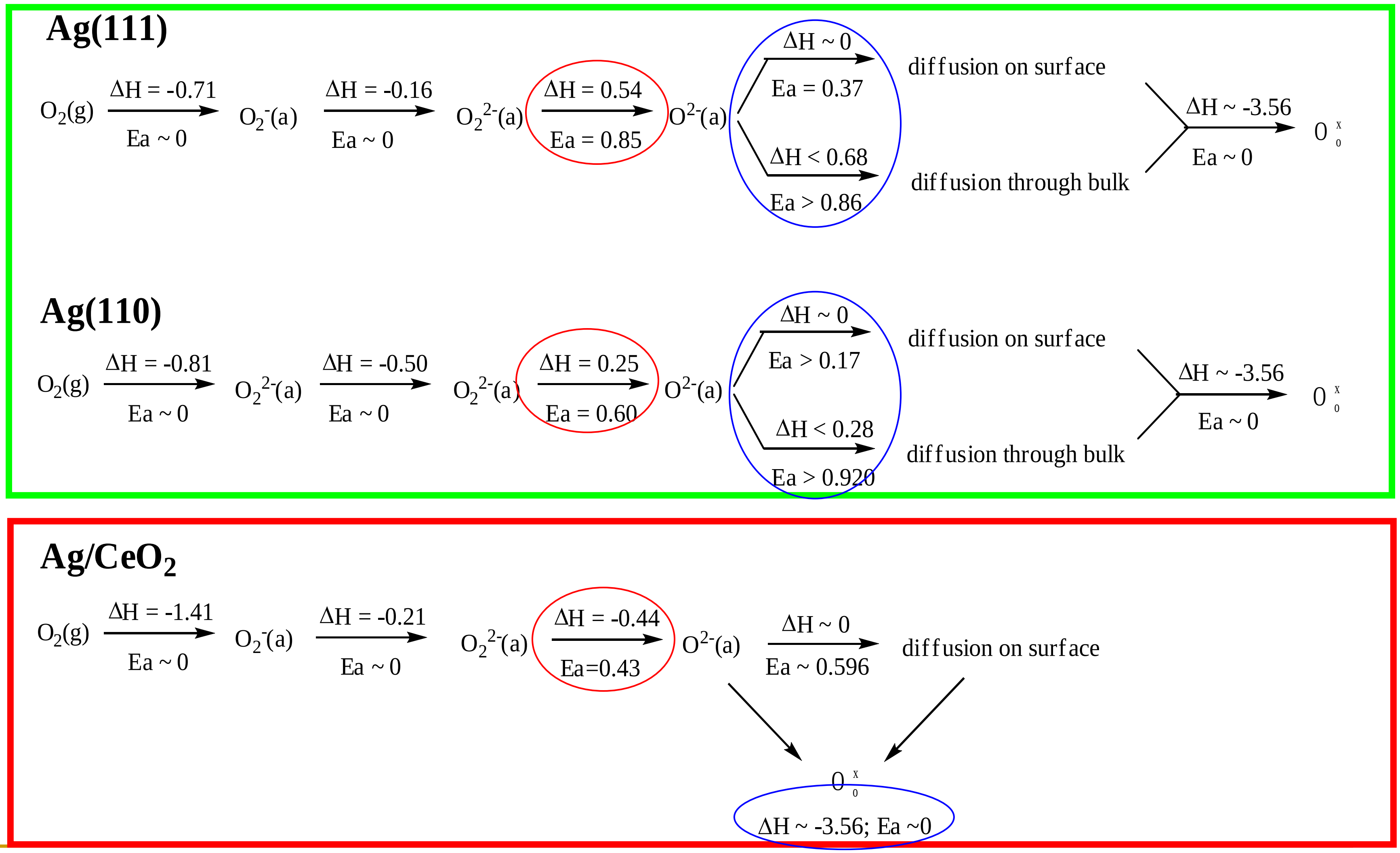
Wang, J. H.; Liu, M.; DOE SECA FY 2006 annual report

Current results: H_2 SOFC (compt.)

The O_2 reduction prefers to occur at 3PB

2PB

3PB

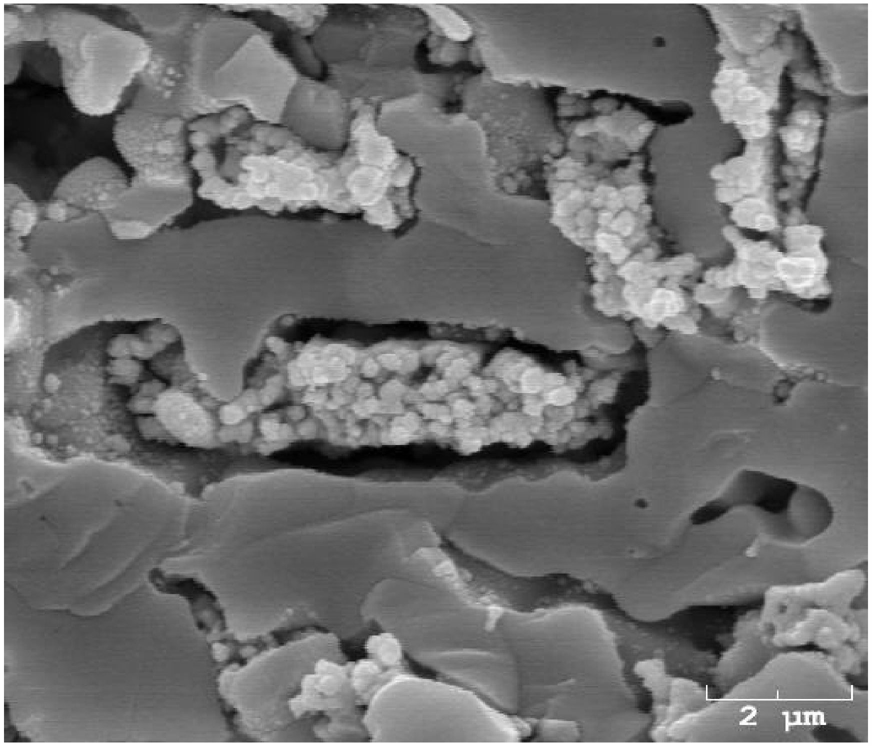


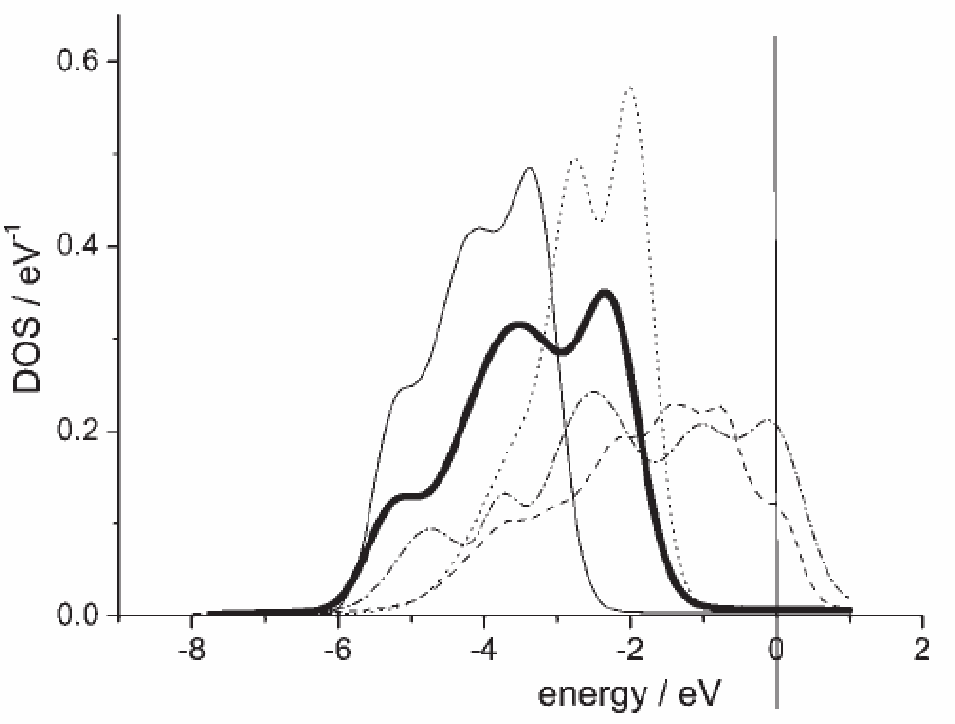
Wang, J. H.; Liu, M.; Solid State Ionics **177** 939 (2007)

Future work: how if we nanoize the materials

The changes of physical and chemical properties

Increase reaction sites, 3PB (physical) **Band structure changes, redox, (chemical)**





Elizabeth Santos and Wolfgang Schmickler; Angew. Chem. Int. Ed. 2007, 46, 8262 –8265
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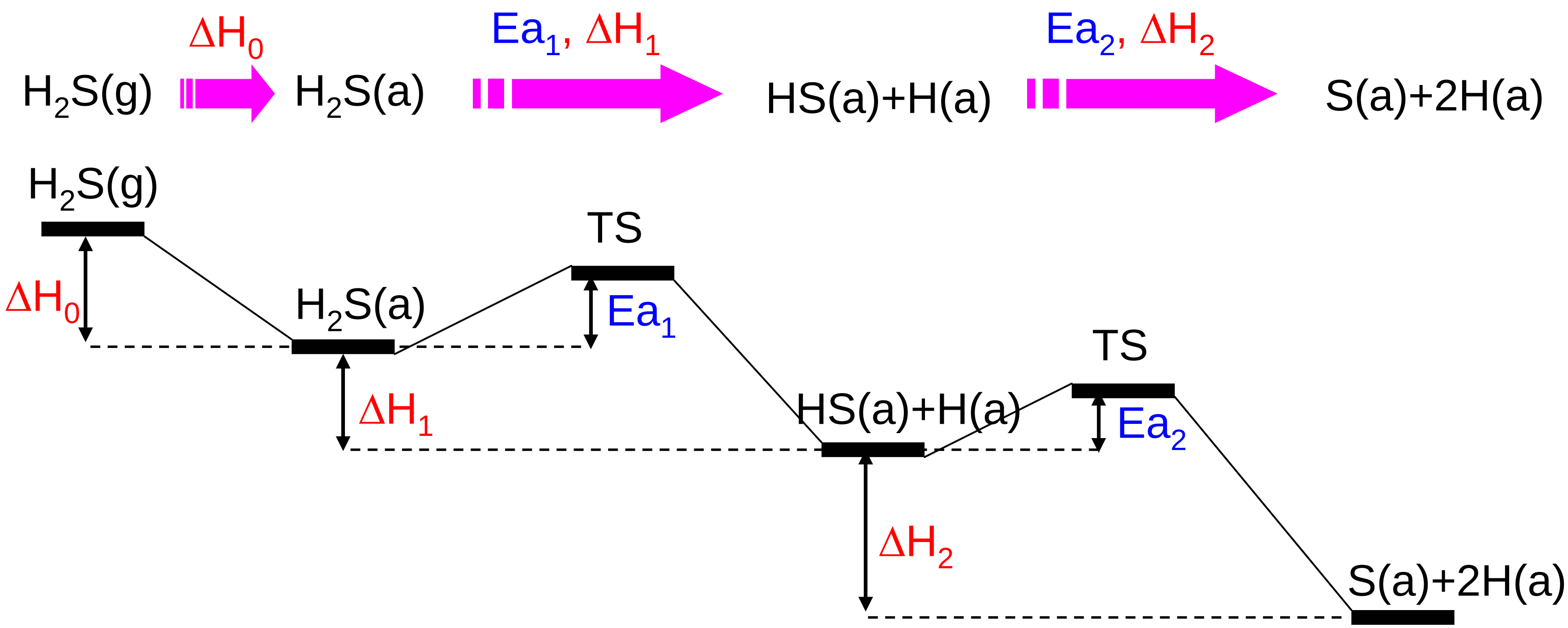
Future work: how if we nanoize the materials

Surface orientation (physical)

	Ni(100)	Ni(111)	Fe(110)	Fe(100)
$H_2S(g) \rightarrow H_2S(a)$ (ΔH_0)	-0.83	-0.67	-1.20	-0.50
$H_2S \rightarrow HS+S$ (Ea_1)	0.29	0.15	0.10	0.25
$H_2S \rightarrow HS+S$ (ΔH_1)	-1.56	-0.98	-1.50	-1.30
$HS \rightarrow H + S$ (Ea_2)	0.45	0.11	0.11	0.28
$HS \rightarrow H + S$ (ΔH_2)	-1.05	-0.86	-1.35	-1.30

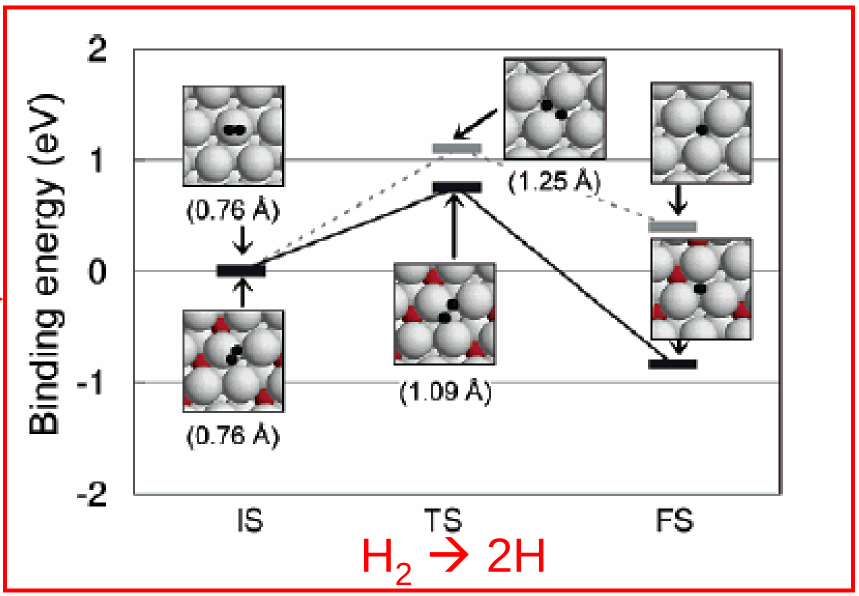


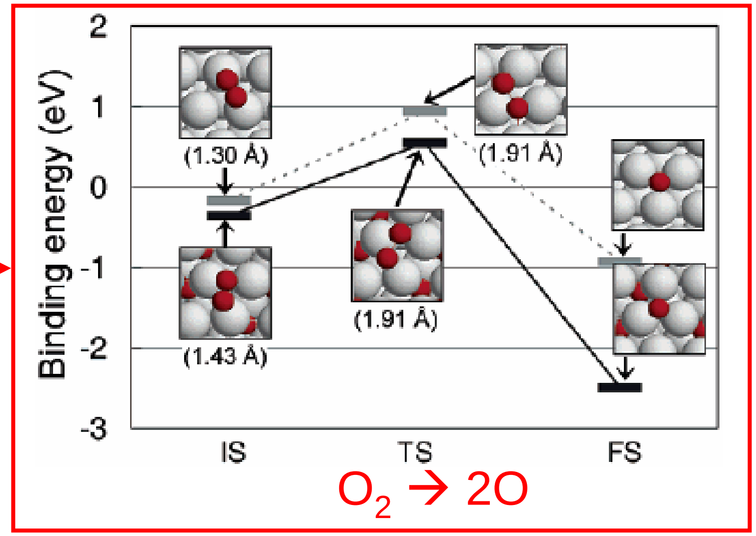
Pt(111): A. Michaelides and P. Hu, J. Chem. Phys. **115**, 8570 (2001)
Pd(111): D. R. Alfonso, et. Al., Catal. Today **99**, 315 (2005)
Rh(111): B. McAllister and P. Hu, J. Chem. Phys. **122**, 84709 (2005)
Fe(110): D. E. Jiang and E. A. Carter, Surf. Sci. **583**, 60 (2005)
Fe(100): D. E. Jiang and E. A. Carter, J. Phys. Chem. B **108**, 19140 (2004)

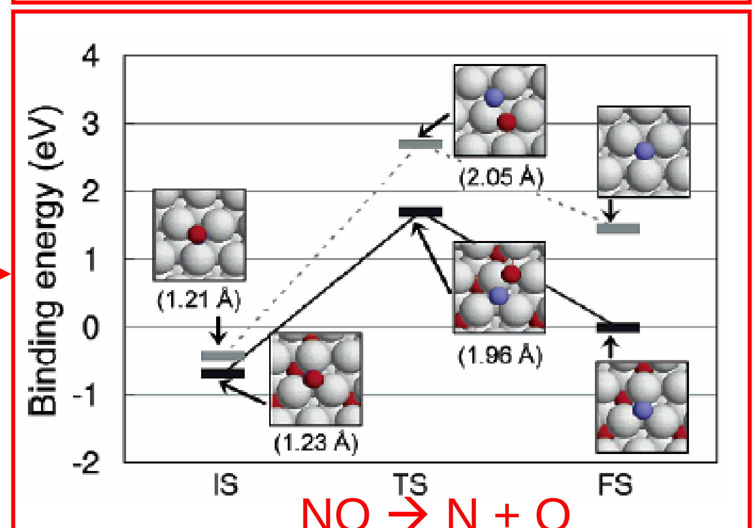
Future work: how if we nanoize the materials

Catalytic activity (chemical)

reaction	$O_{(ads)}$ coverage	E_a (eV)	ZPE-corrected E_a^{ZPE} (eV)
$H_2 \rightarrow 2H$	0	1.11	1.04
	1/2	0.74	0.72
$O_2 \rightarrow 2O$	0	1.11	1.06
	1/2	0.90	0.86
$NO \rightarrow N + O$	0	3.12	3.08
	1/2	2.38	2.33







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行政院原子能委員會核能研究所 Institute of Nuclear Energy Research AEC ROC

Thank you !