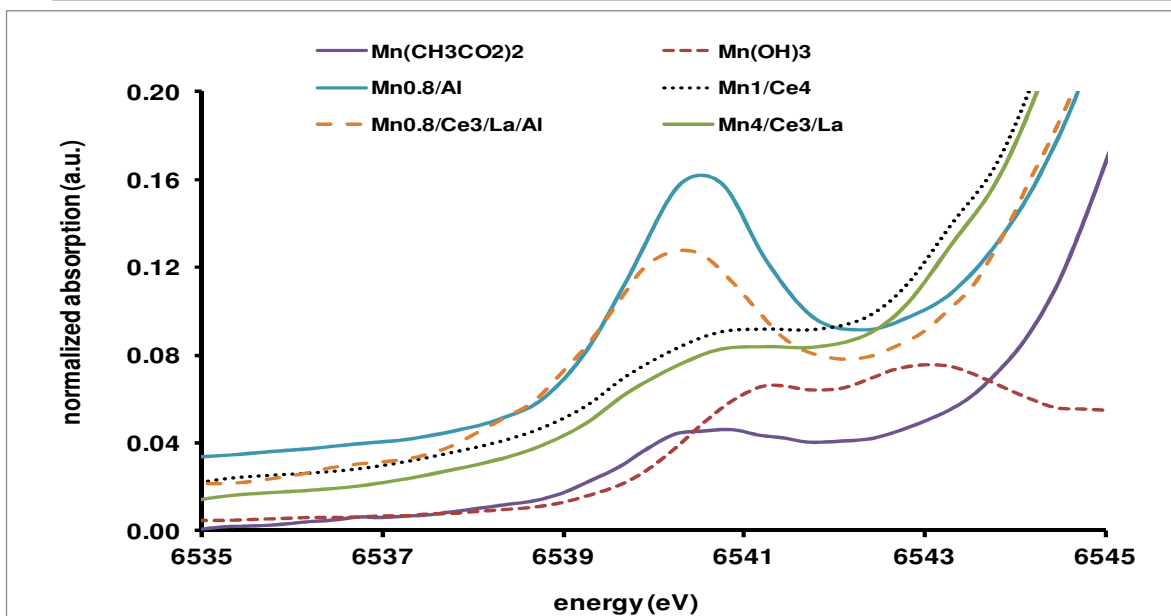# Key Issues in Syngas Cleanup

Kerry Dooley - Dept. of Chemical Engineering, Louisiana St. Univ., dooley@lsu.edu

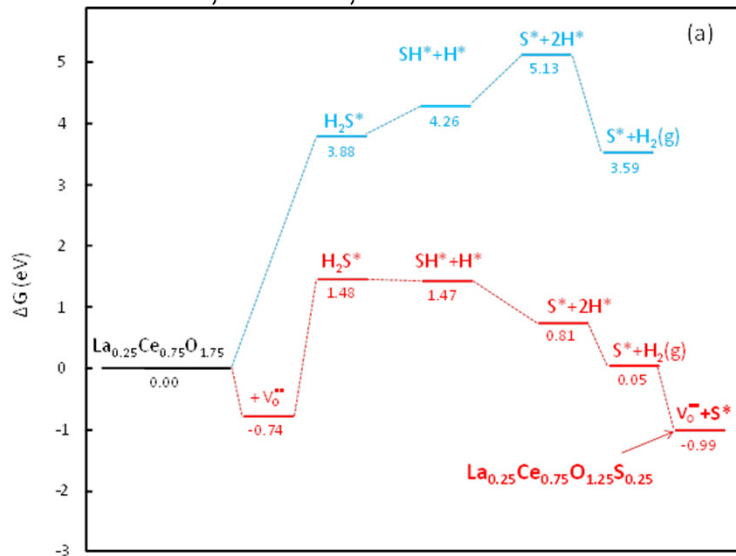**& Michael Janik -** Dept. of Chemical Engineering, Penn. St. U., mjanik@engr.psu.edu

Using XANES (Mn K) of Mn/Ce/La to determine mixed oxidation states in sulfur adsorbents

Mn^{2+} Tet.: Singlet
Mn^{2+} Oct.: Ill-defined doublet
Mn^{3+} Oct.: Well-defined doublet
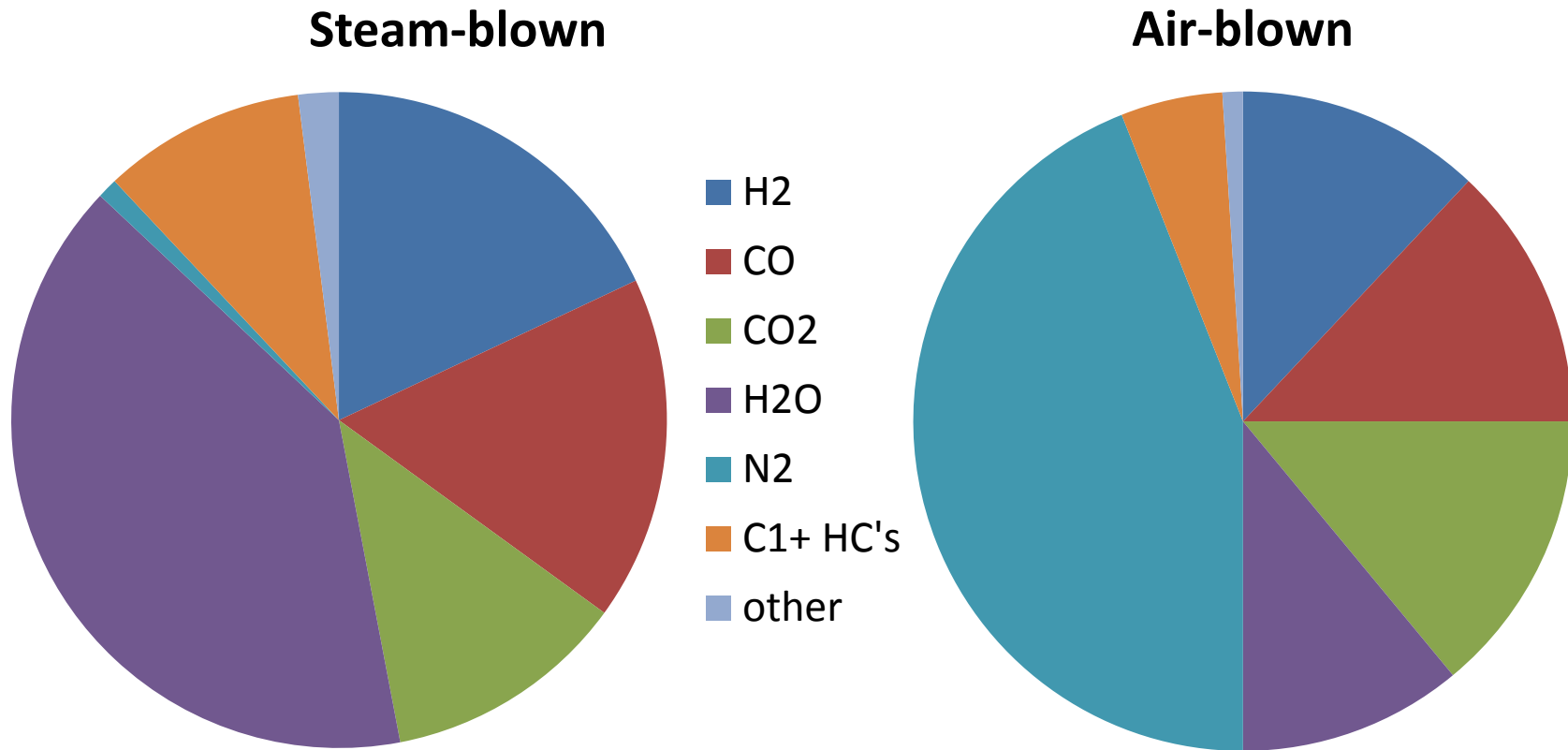- Mn dissolved in CeO_2 (~octahedral, +2/+3)

Our Research

- High temperature sulfur adsorbents and tar cracking / reforming catalysts for biomass/coal gasifier effluents - synthesis, testing.

- Design of adsorbents/catalysts from first principles - computational (DFT) methods, especially DFT + U

- Characterization of sulfur etc. adsorbents - XRD, XANES, porosimetry

- Characterization of tar cracking / reforming catalysts - above, plus XAFS, TPR, TPO, Raman.

DFT+ *U* determined (a) free energy of H_2S adsorption/dissociation on La_2O_3/CeO_2 (111) at 1100K; P_{H2} = 0.35 atm, P_{H2S} = 10^{-2} atm, and P_{H2O} = 0.03 atm.

Typical Gasifier Effluent Compositions

Steam-blown

Air-blown

Legend:
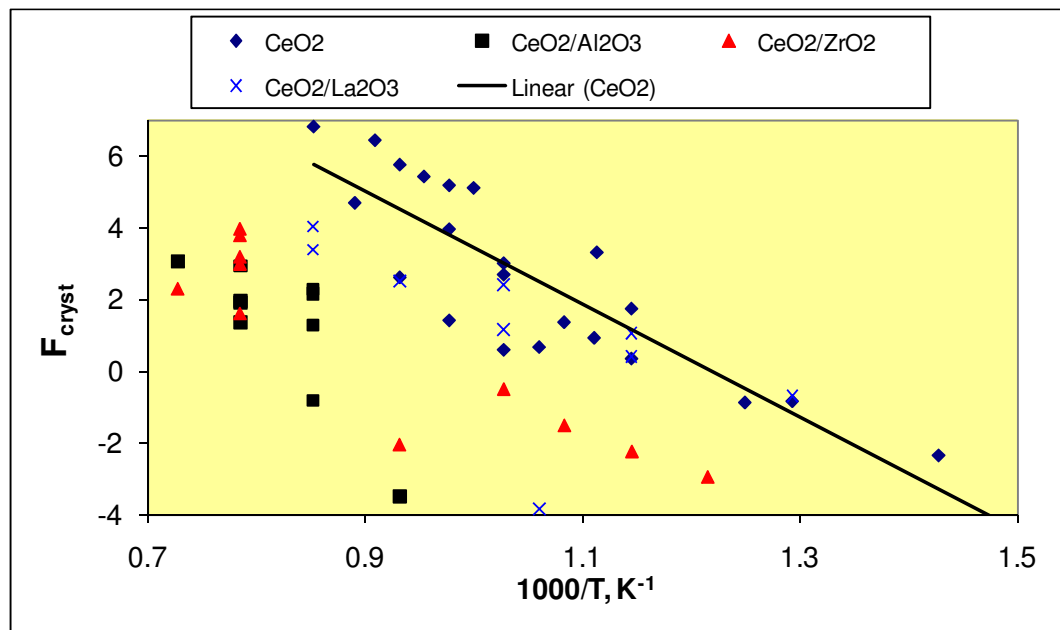- H2
- CO
- CO2
- H2O
- N2
- C1+ HC's
- other

- **Naïve to think that same adsorbents can be used on both, or same tar removal strategies.**
- **Good news: NH$_3$ less of a problem than sulfur (at least in high-T adsorption)[1-2]**

1. Yoon, Y. I. et al., *Chem. Eng. Sci. (*2003) 58, 2079-2087
2. Ohtsuka, Y. et al., *Fuel* (2004), 83, 685-692.

For high-T sulfur adsorbents, what are keys?

(1) The <u>active phase compositions are key</u> to thermal stability

E.G., Ce/LaO$_x$ -- Intimate mixtures to ~60 at% La in CeO$_2$ to 1200 K.[1-3] CeO$_x$/La$_2$O$_3$ more easily regenerated than single oxides.[4-5]

[1]M. Ozawa and C.K. Loong, *Catal. Today* (1999), 50, 329-342.
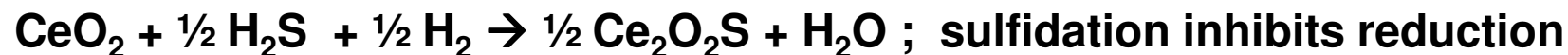[2]S. Bernal et al., *Catal. Lett.* (1998) 53, 51-57.
[3]M.F. Wilkes et al., *J. Catal.* (2003) 219, 286-294.
[4]M. Flytzani-Stephanopoulos et al., *Science* (2006) 312: 1508-1510.
[5]H. Hu et al., *J. Rare Earths* (2006) 24, 695-698.

$$F_{cryst} = \ln\left[\frac{d^3 - d_0^3}{d_0^3}\right]$$

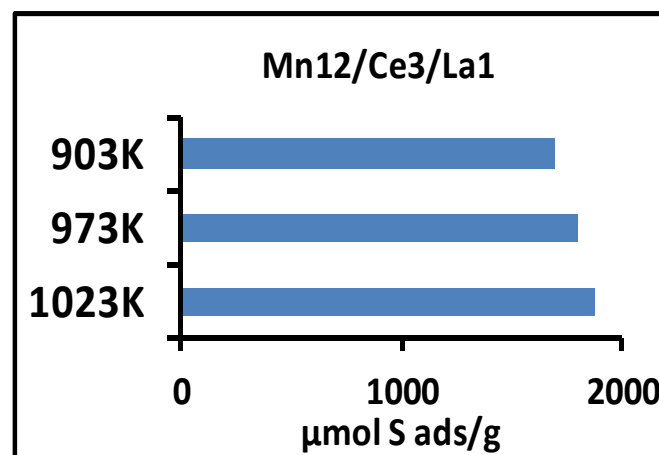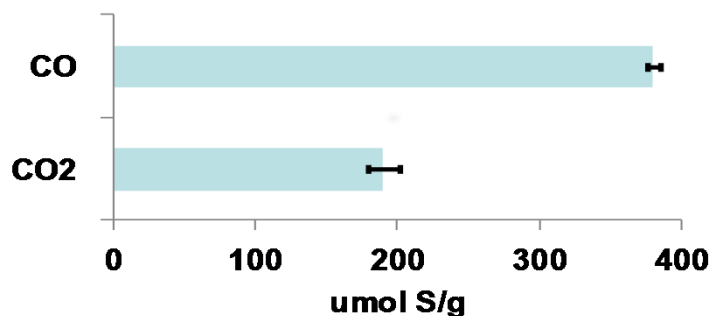**Are CeO$_2$, ZrO$_2$, TiO$_2$ or MgAl$_2$O$_4$ better supports for "sulfur getters" (MnO$_x$, Cu)? CeO$_2$: ~20 µmol/g S at 630 C; equil.: 1450-2900 µmol/g S. Why?**

CeO$_2$ + ½ H$_2$S + ½ H$_2$ → ½ Ce$_2$O$_2$S + H$_2$O ; sulfidation inhibits reduction

(2) Both gas + adsorbent compositions determine maximum capacity and pre-breakthrough concentrations

Designation, Molar Ratios (wt % Al_2O_3)	Surface area (m^2/g) as calcined used		Pre-breakthrough H_2S (ppm), 630°C	S-Capacity ($\mu mol/g$), 630°C
CeO_2	220	190	10	20
Mn12/Ce3/La	60	10	13	1700
Mn1.1/Ce3/La/Gd0.05	130	50	4.5	360
Mn0.8/Ce3/La/Al (89)	210	200	4.1	71
Mn0.8/Al (75)	150	120	25-50[1]	130

Adsorption capacity - 32% CO or CO_2 over $Mn_{1.1}/Gd_{0.05}/Ce_3/LaO_x$

903K, feed = 32% CO or CO_2, 23% H_2, 5% H_2O, 0.1% H_2S, bal. N_2, GHSV=15500

5

(3) High capacity ≠ regenerability

• Capacity test: 32% $CO(CO_2)$, 23% H_2, 5% H_2O, 0.1% H_2S, balance N_2, GHSV=15500, 903 K

32% CO in feed, 903 K

1700 μmol/g

Bar chart categories (top to bottom): Mn0.8/Al, Mn0.8/Ce3/La/Al, Mn1.4/Ce6/La/Gd0.10, Mn1.1/Ce3/La/Gd0.05, Mn1/Ce4, Mn1/Ce1, Mn4/Ce3/La, Mn12/Ce3/La

x-axis: μmol S ads/g (100, 300, 500, 700, 900)

> Sulfided MnO_x can form sulfates with air regeneration.
> MnO_x can react with Al_2O_3 to inactive $MnAl_2O_4$[1] but with no CO_2, H_2O, HCl and T's < 800ºC, nothing better[2-4]

Legend: MnS — S — MnSO4 — Ce6Tb — Mn1/Ce4 — Mn1.1/Ce3/La/Gd0.05

y-axis: normalized absorption (0, 0.5, 1, 1.5, 2, 2.5, 3)
x-axis: energy (eV) (2455, 2465, 2475, 2485, 2495, 2505, 2515)

Sulfate amounts :
Mn1.1/Ce3/La/Gd.05 < Mn1/Ce4 < Ce6/Tb

1. Bakker, W. J. W. et al. *Chem. Eng. J.* 2003, *96*, 223.
2. Westmoreland, P. R. & Harrison, D. P. *Environ. Sci. Technol.* 1976, *10*, 659.
3. Ko, T. H. et. al., *Chemosphere* 2005, *58*, 467.
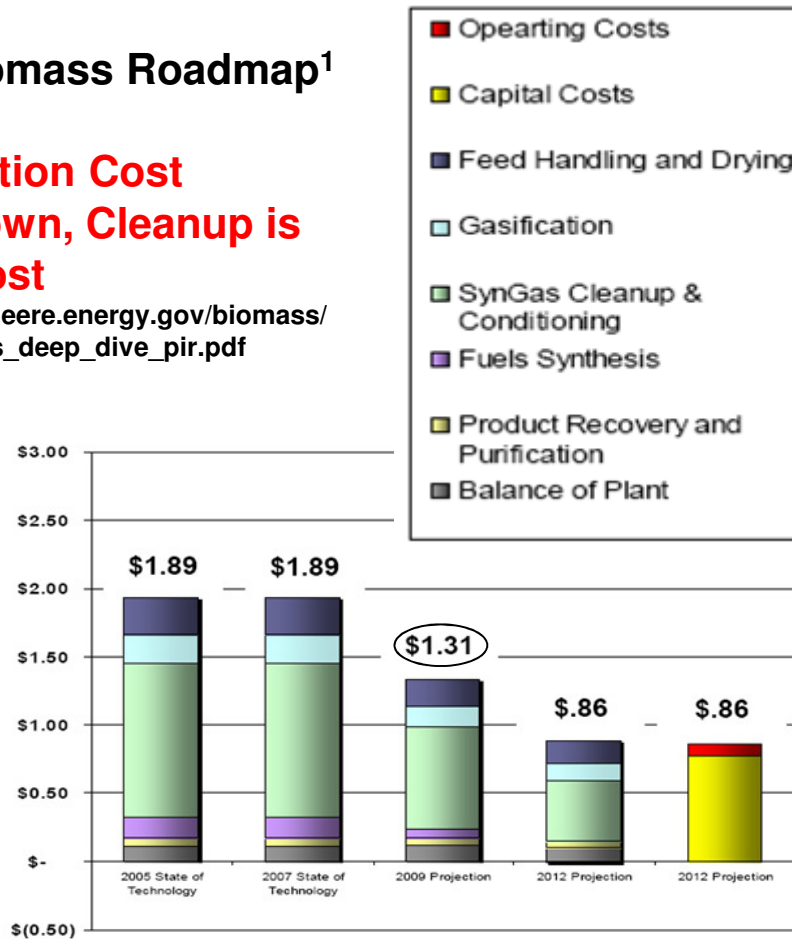4. Wakker, J. P. et al., *Ind. Eng. Chem. Res.* 1993, 32, 139-149.

Gasifier Cleanup / Conditioning

DOE Biomass Roadmap[1] (2009) –

Gasification Cost Breakdown, Cleanup is Chief Cost

[1]**http://www1.eere.energy.gov/biomass/ pdfs/biomass_deep_dive_pir.pdf**

Legend:
- ■ Opearting Costs
- ■ Capital Costs
- ■ Feed Handling and Drying
- ☐ Gasification
- ■ SynGas Cleanup & Conditioning
- ■ Fuels Synthesis
- ☐ Product Recovery and Purification
- ■ Balance of Plant

Minimum Conversion Processing Cost of Ethanol, $/gal ethanol (2007$s)

$1.89 $1.89 $1.31 $.86 $.86

2005 State of Technology | 2007 State of Technology | 2009 Projection | 2012 Projection | 2012 Projection

* Conversion costs represented in the figure above are based on conversion of woody feedstocks and equate to an Minimum Ethanol Selling Price $1.59 in 2012.
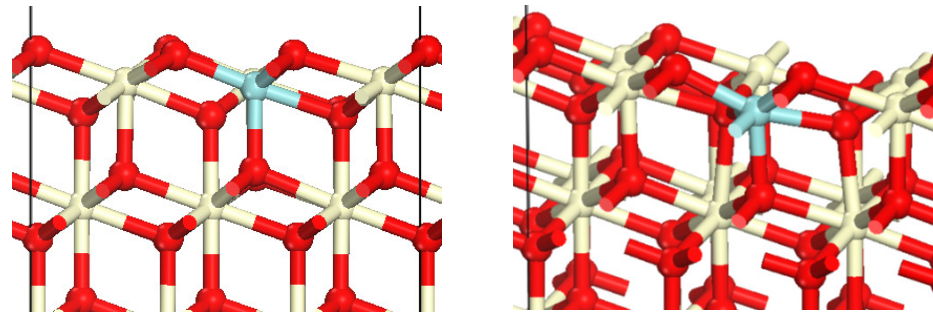
Critical if coal / biomass gasification is ever to be economically feasible!

- Effluents from gasifiers – up to 2% tars; H_2S, NO_x, NH_3, Cl, K also[1-9].
- O_2-blown coal gasifier 0.2-1% H_2S[10-11]
- Air-blown coal gasifier 0.08-0.5% H_2S[11-12]
- Biomass gasifiers 20-200 ppm H_2S[13-14]

- T's > 870 K for effluents; need adsorbents /catalysts that are stable at these T's, with water and CO_2 present.

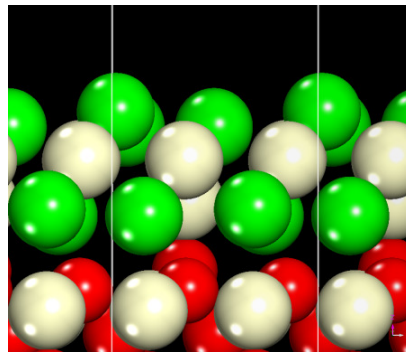- **Can we reform/crack tars at conditions similar to desulfurization?**

[1]R. Zhanga et al., *Fuel Proc. Technol.* (2005) 86, 861-874.
[2]W.Torres et al., *Catal. Rev.-Sci. Eng.* (2007) 49, 407-456.
[3]L. Pengmei et al., *Energy Conv. & Mgt.* (2007), 48, 1132-1139
[4]S. Juutilainen et al., *Appl. Catal. B: Env.* (2006) 62, 86-92.
[5]H. Kuramochi et al., *Fuel,* (2005) 84, 377-387.
[6]Kurkela, E. et al., *Biomass Bioenergy* (2000)18, 87-91.
[7]Anis, S. et al., *Ren. Sust. Energ. Rev.* (2011) 15, 2355-2377.
[8]Narvaez, I. et al., *Ind. Eng. Chem. Res.* (1997) 36, 317-327.
[9]Lu, M. et al., *Energy Fuels* (2013) 27, 2099–2106.
[10]Swisher, J. H., *Fuel Energy Abstracts* (1996) 37, 181.
[11]Stanczyk, K. et al., *Fuel* (2011) 90, 1953-1962.
[12]Khare, G. P. et al., *Environ. Prog.* (1995) 14, 146-150.
[13]Corella, J. et al., *Energy Fuels* (1999) 13, 1122-1127.
[14] Tijmensen, M. J. A. et al., *Biomass Bioenergy* (2002) 23, 129-152.

Questions in tar reforming/cracking

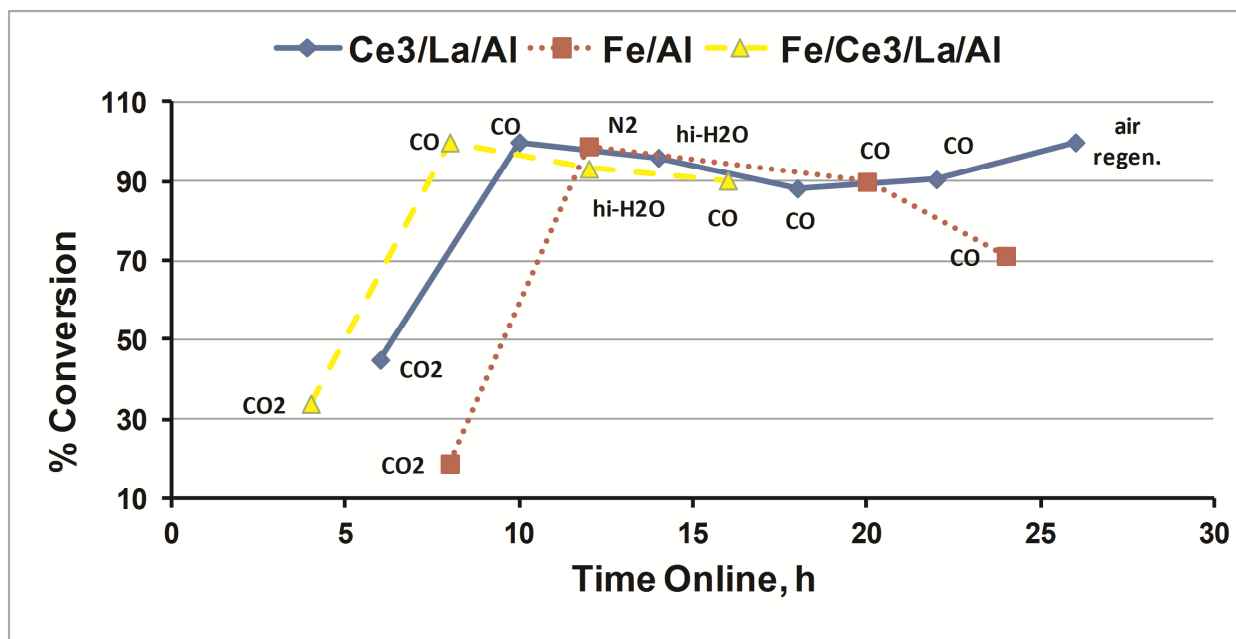- **What is the steady-state active form of the catalysts: oxidized, partially reduced, fully reduced?**

- **Are the surfaces primarily sulfided , carbided or neither?**

Ce is white, Metal dopant blue, O red, S green

- **Can we take the tars to CO + H_2? What is the pathway?**

Gas composition greatly affects tar reforming

Naphthalene reforming in synthetic gasifier effluent - metals partly reduced?

At >800ºC picture reversed, with H_2O and CO_2 as tar oxidants.[1-3]

1. Wu, W. et al., *Energy Fuels* 2011, 25, 5394–5406.

2. Simell, P. A. et al., *Fuel* 1997, 76, 1117-1127.

3. Nordgreen, T. et al., *Fuel* 2006, 85, 689-694.

4. Berguerand, N. et al., *Ind. Eng. Chem. Res.* 2012, 51, 16610-16616.
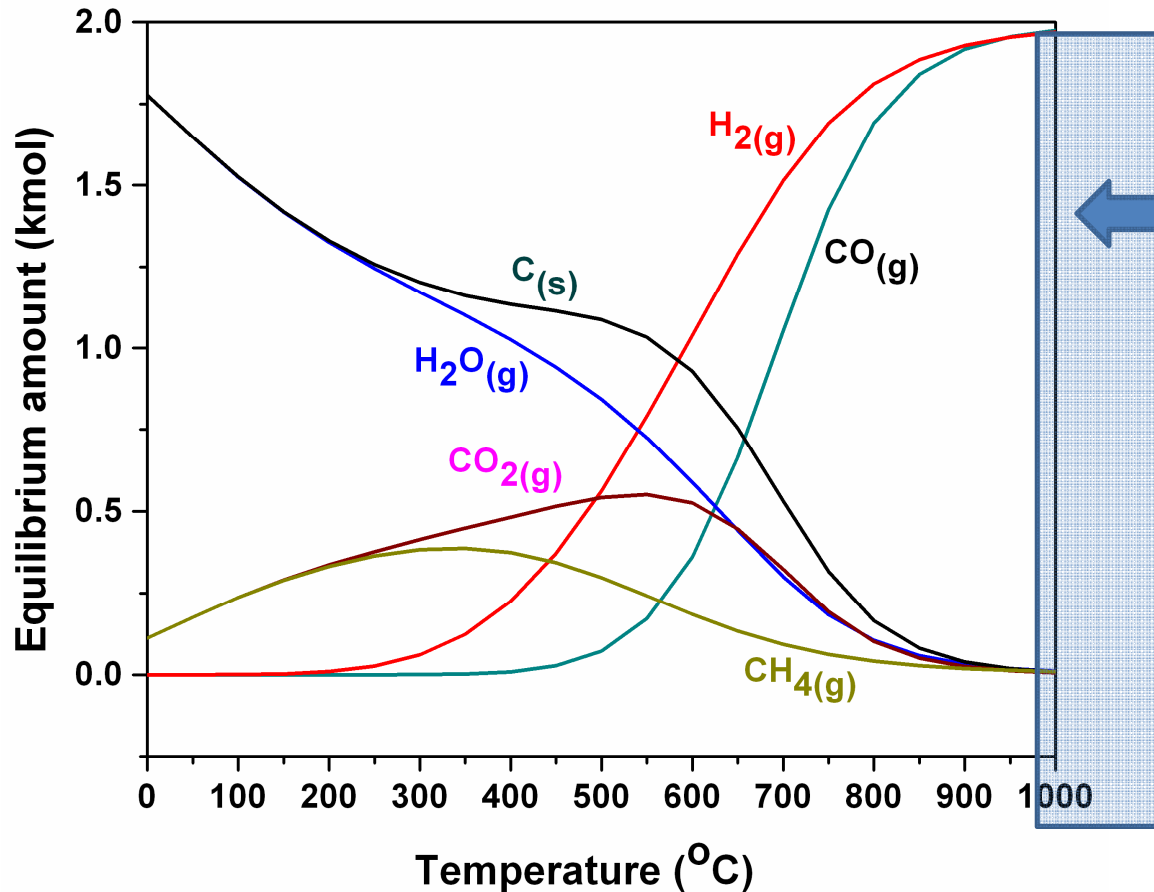
5. Caballero, M. A. et al., *Ind. Eng. Chem. Res.* 2000, 39, 1143-1154.

6. Bain, R. L. et al., *Ind. Eng. Chem. Res.* 2005, 44, 7945-7956.

7. Nitsch, X. et al., *Energy Fuels* 2013, 27, 5459–5465.

Feed – 32% H_2, 8% CH_4, 0.32% naphthalene, 3.1% water (5.5% for "hi"), balance CO, CO_2 or N_2; GHSV = 6000, 600-650ºC.

Detected products – CO, light HC's (tr.), C_6H_6 (tr.) – typical, showing that (hydro)cracking precedes reforming.[1-7]

T ~ 900°C for tar conversion?
EQUILIBRIUM DATA SAYS SO

T increase 600 → 950ºC, less tar production, better conversions to CO, H_2 [1-3]
Better thermo. efficiency for downstream operations (gas turbine).

[1]C. Kinoshita et al., *J. Anal. Appl. Pyrolysis* 1994, 29, 169-181.
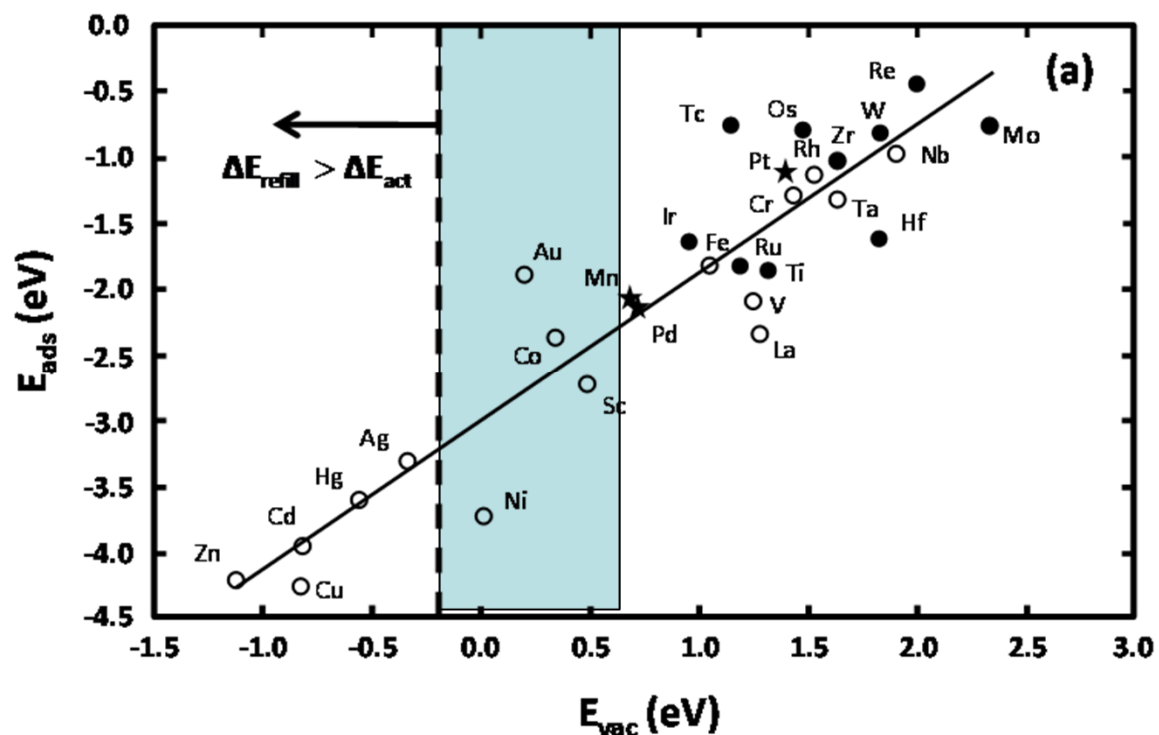[2] T. Milne et al., 2003, IEA/H2/TR-02/01.
[3]P. Ferreira-Aparicio et al., *Catal. Rev.-Sci. Eng.* 2005, 47, 491-588.

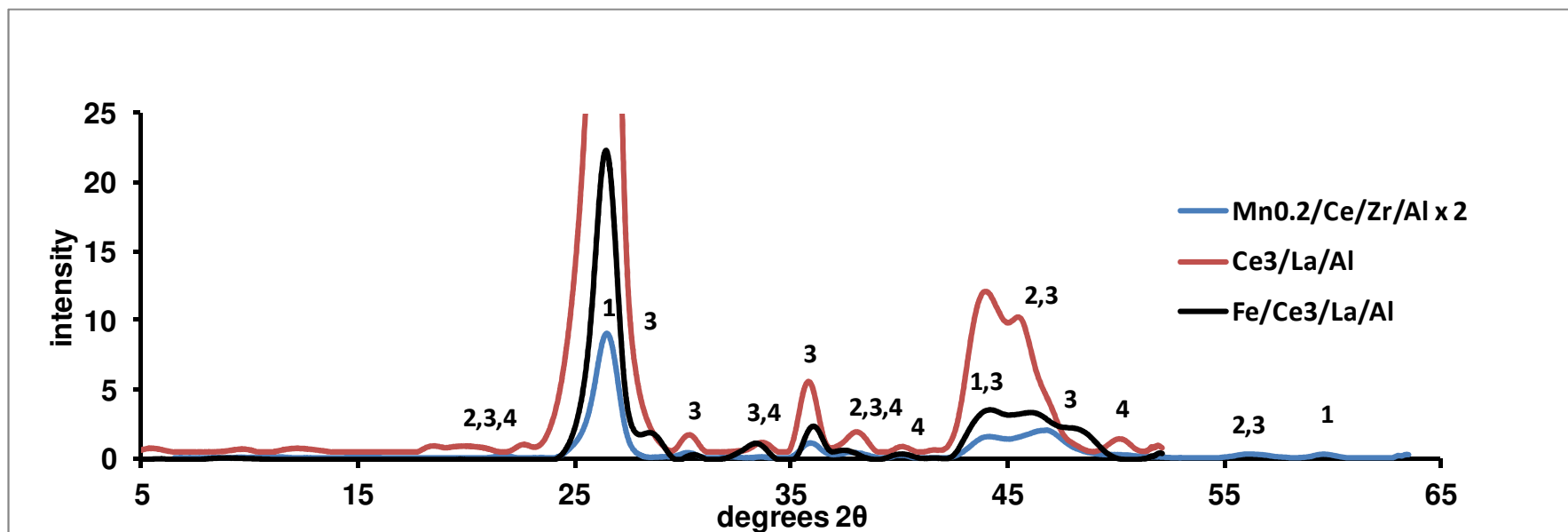# Computational Predictions for Hydrocarbon Conversion - Doped CeO$_2$

Expt: **Naphthalene reforming in synthetic gasifier effluent Mn and Fe addition to REOs leads to increased conversion; also La to CeO$_x$**

DFT+ *U*: **C-H bond activation correlates with surface reducibility in M-CeO$_2$, dopants**

Early TMs alter Ce reducibility; Late TMs are reduction centers

Tar Reforming Catalysts Highly Reduced/Carbonized

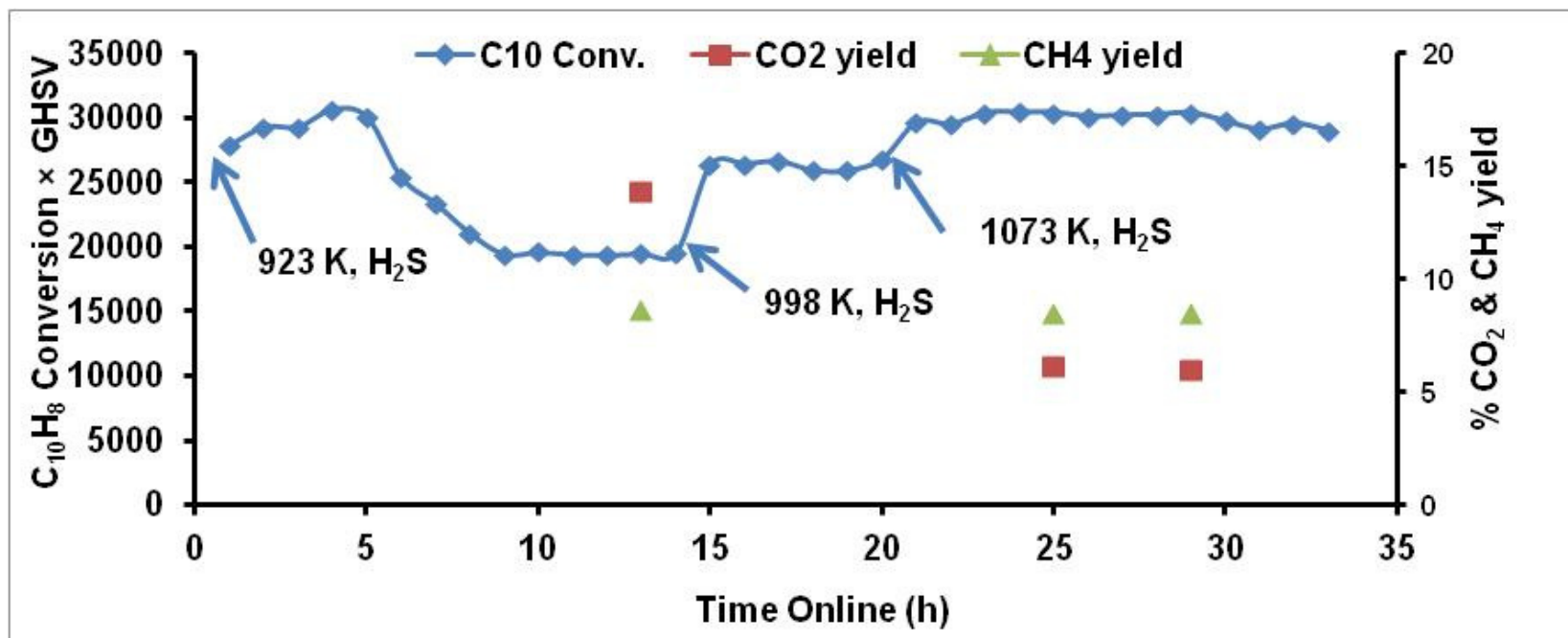**1 = C; 2 = γ-Al$_2$O$_3$; 3 = CeO$_x$/CeLaO$_x$; 4 = Ce$_2$O$_3$; fresh, CeO$_2$ only.**

C-amounts (mol/g): Mn0.2/Ce/Zr/Al = 0.040; Fe/Ce3/La/Al = 0.11; Ce3/La/Al = 0.52; Ni/K/Mg4/Al = 0.46

Coke deposition can be controlled by catalyst

But the sulfur dominates deactivation process

Cat. - Mn0.2/Ce/Zr/Al (82 wt% Al_2O_3)
Feed - H_2O 9.1%, CO 54.5%, CH_4 4.1%, H_2 30.9%, N_2 1.07%, $C_{10}H_8$ 0.33%, H_2S 40 ppm
Turnovers - 90 on naphthalene basis
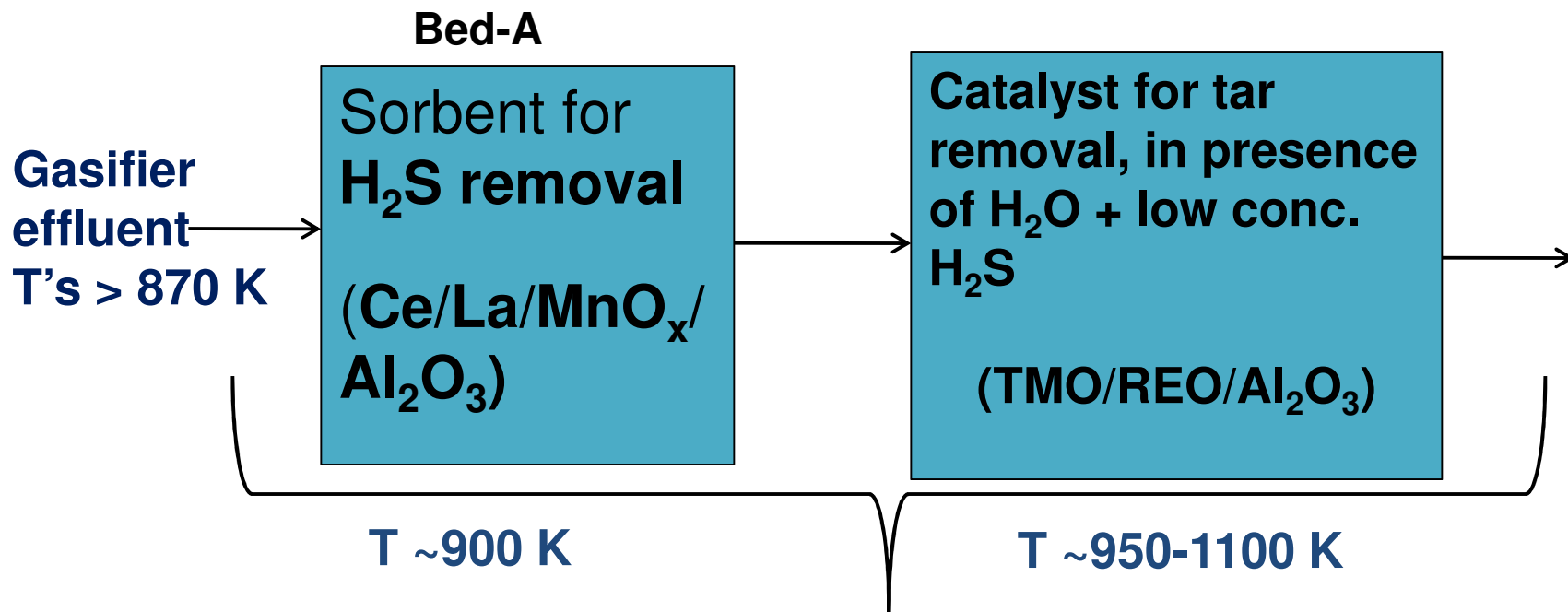ΔE = 62 kJ/mol (naphthalene)

Equally true for Ni-based catalysts

CO$_2$ and CH$_4$ yields after extended times online

	CO$_2$ % yield 650-700ºC	CH$_4$ % yield 650-700ºC	CO$_2$ % yield 800ºC	CH$_4$ % yield 800ºC
Fe/Ce3/La/Al	14	7.8	7.8	7.2
Mn0.2/Ce/Zr/Al	14	8.6	6.1	8.5
Ce3/La/Al	11	11	6.1	8.7
Ni2/Ca/Mg2/Al	13	14	6	18
Ni/K/Mg/Al[1]			36	10
Ni/Mg/Al[2]			38	3.3
Ni/Co/Mo[3]			15	~1
Ni/Al[4]	32	11	26	8.4
Ni/Al + CaO[5]			17	0.4
Fe/Ti[6]			42	13
THEORY (EQUIL.)	30	7.0	5.6	1.7

In general, can't go completely to CO, H$_2$ - methanation and WGS both problems

1. Bain, R. L. et al., *Ind. Eng. Chem. Res.* 2005, 44, 7945-7956
2. Aznar, M. P. et al., *Ind. Eng. Chem. Res.* 1993, 32, 1-10.
3. Lu, M. et al., *Energy Fuels* 2013, 27, 2099–2106.
4. Berguerand, N. et al., *Ind. Eng. Chem. Res.* 2012, 51, 16610-16616.
5. Caballero, M. A. et al., *Ind. Eng. Chem. Res.* 1997, 36, 5227-5239.
6. Lind, F. et al. , *Ind. Eng. Chem. Res.* 2011, 50, 11553-11562.

Overall Strategy?

Bed-A

Gasifier effluent T's > 870 K →

| Sorbent for H_2S removal $(Ce/La/MnO_x/Al_2O_3)$ | Catalyst for tar removal, in presence of H_2O + low conc. H_2S $(TMO/REO/Al_2O_3)$ |

T ~900 K   T ~950-1100 K

Publications (~15 presentations)

- K.M. Dooley, V. Kalakota, S. Adusumilli, "High-temperature desulfurization of gasifier effluents with rare earth and rare earth/transition metal oxides." *Energy Fuels*, 25 (2011), 1213–1220. [10.1021/ef101487v]

- A. D. Mayernick, R. Li, K. M. Dooley, M. J. Janik. "Energetics and Mechanism for H_2S Adsorption by Ceria-Lanthanide Mixed Oxides: Implications for the Desulfurization of Biomass Gasifier Effluents." *J. Phys. Chem. C* 115 (2011), 24178–24188 . [10.1021/jp206827n]

- M.D. Krcha, A.D. Mayernick, M.J. Janik, "Period   trends of oxygen vacancy formation and C–H bond activation over transition metal-doped CeO_2 (111) surfaces." *J. Catal.* 293 (2012) 103–115. [10.1016/j.jcat.2012.06.010]

- R. Li , M.D. Krcha, M.J. Janik, A.D. Roy and K.M. Dooley, "Ce-Mn Oxides for High-Temperature Gasifier Effluent Desulfurization", *Energy Fuels*, 26 (2012) 6765-6776. [10.1021/ef301386f]

- M.D. Krcha and M.J. Janik, "Examination of Oxygen Vacancy Formation in Mn-Doped CeO2 (111)
Using DFT+U and the Hybrid Functional HSE06," *Langmuir* 29 (2013) 10120–10131. [10.1021/la401747n]