



UNIVERSITY *of* DELAWARE

In-situ characterization of Pt-Ni and Mo₂C

In-situ Methods of X-ray Absorption Spectroscopy

Session I. Operando Experiments: Techniques, Data Analysis and Modeling

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Introduction to the Chen Group

- Expertise in surface science and supported catalysis for energy applications
 - Specialize in developing trends to correlate structure and electronic properties to catalytic properties
 - Correlating d-band center, hydrogen binding energy, and coordination number to activity and selectivity
 - Bridging the “pressure gap” and “materials gap”

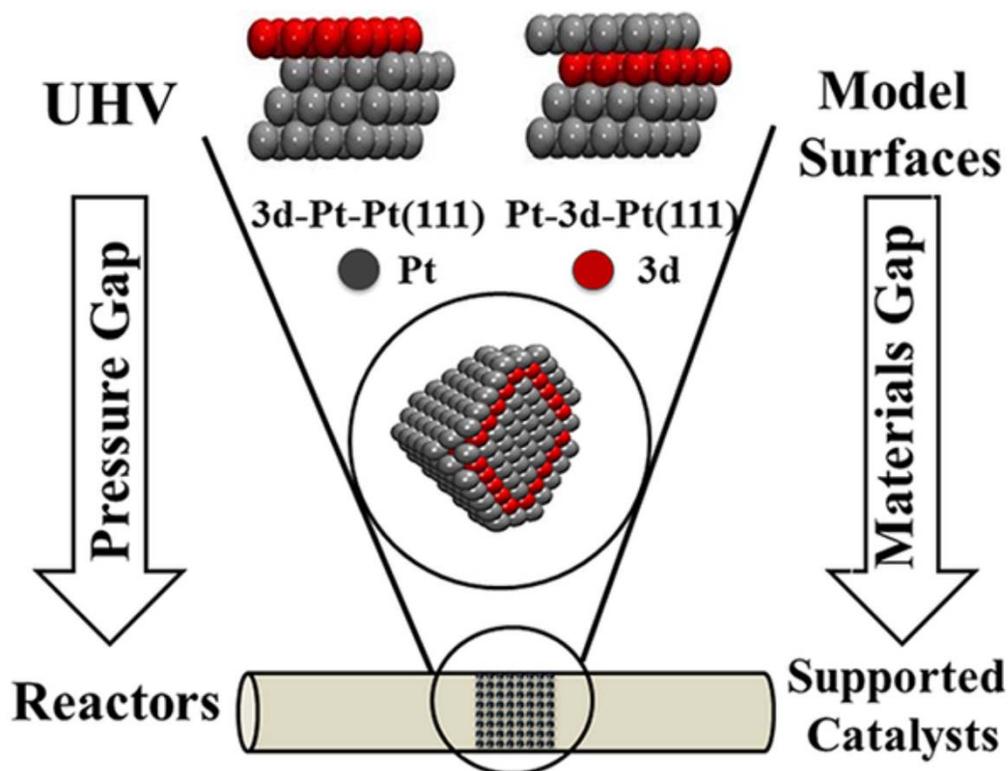
Analytical Techniques:

DFT, TPD, HREELS, FTIR,
CO Chemisorption, TEM, GC, XAFS





Correlating Model Surfaces to Supported Catalysts





Lesson Outline

Common Theme: Discovering trends to identify desirable catalysts

- 1) **Hydrogenation of propanal:** a successful correlation with PtNi
- 2) **Activation of CO₂:** a system that is not yet fully characterized or understood



Lesson Outline

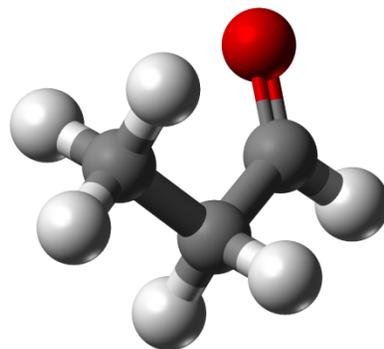
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- 1) **Hydrogenation of propanal:** a successful correlation with PtNi
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Propanal as a Probe Molecule

- Hydrogenation of C=O bonds is important for organic synthesis
 - Also an important step during biomass conversion (Cellulose → Polyols)

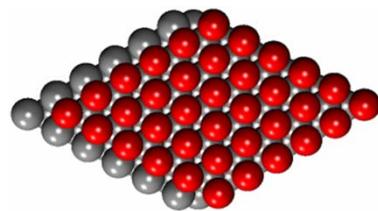


- Propanal is a very simple hydrocarbon with only one C=O bond
 - Bimetallic surfaces have previously been shown to be active for hydrogenation



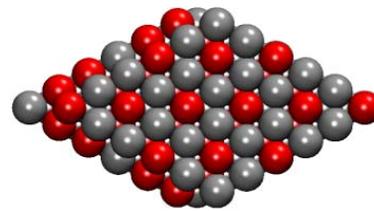
Structure of Bimetallic Surfaces

- Pt–3d bimetallic surfaces are capable of forming three configurations



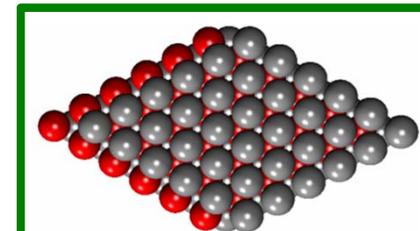
Surface

3d-Pt-Pt(111)



Intermixed

Pt-3d-Pt(111)



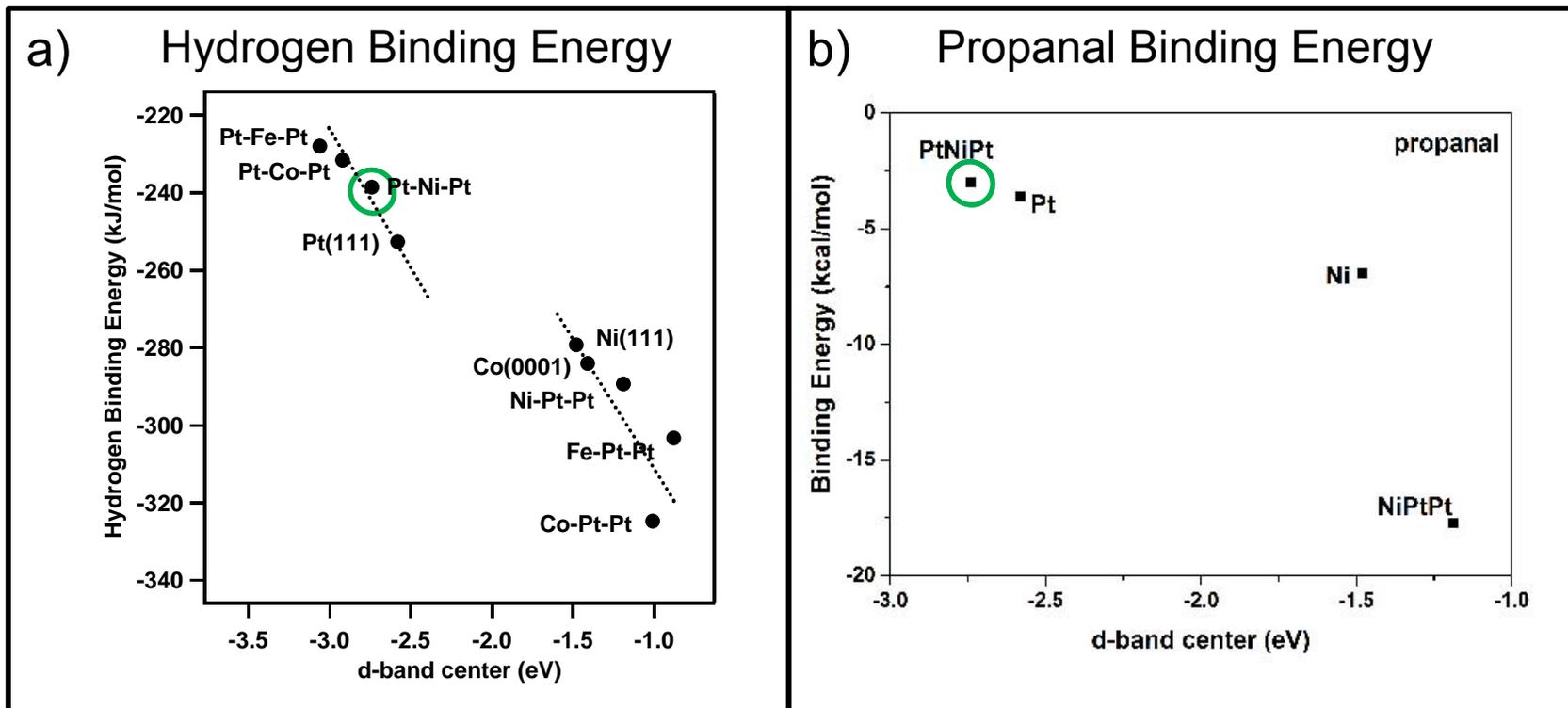
Subsurface

Pt-3d-Pt(111)

- Pt-3d-Pt lowers H_2 binding energy and dissociates hydrogen more easily than Pt(111)
 - Enhanced hydrogenation activity over either of its parent metals



DFT Identification of Active Surfaces



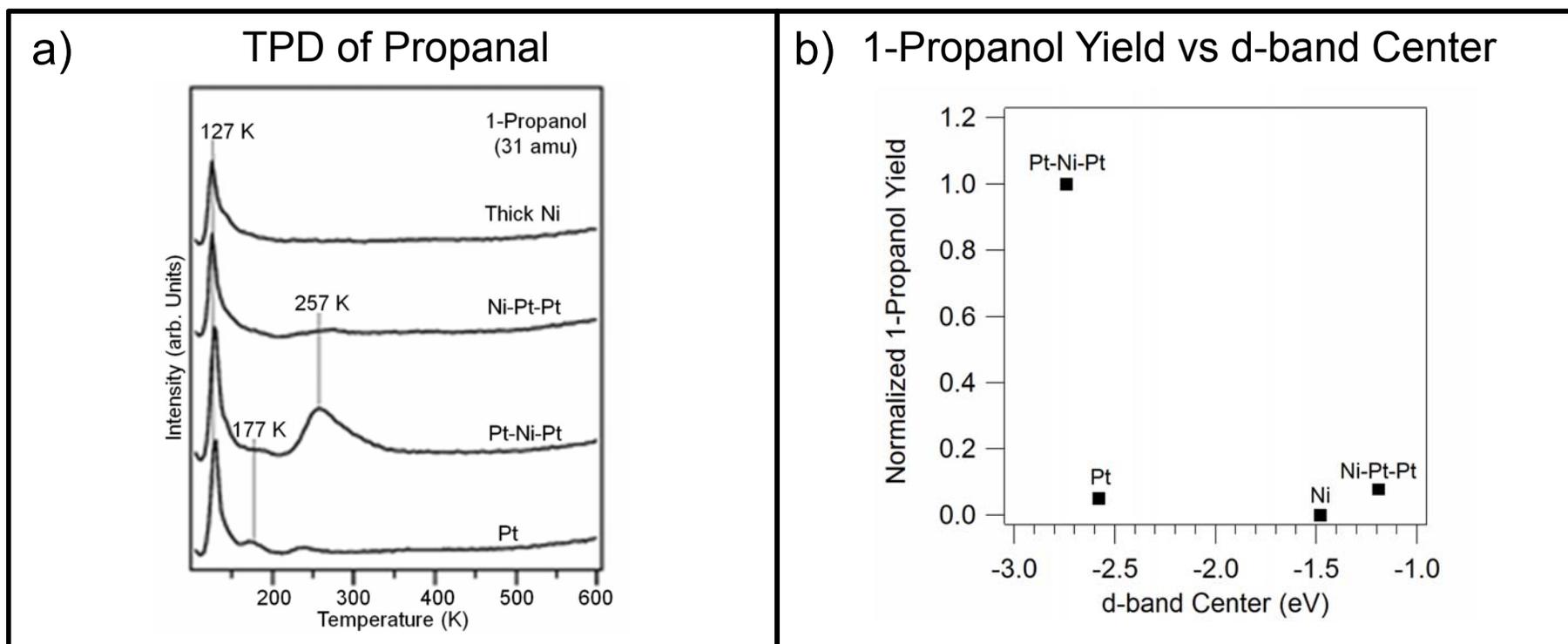
- Surfaces that bind H_2 and propanal more weakly should be more active for hydrogenation
 - Pt-Ni-Pt subsurface binds propanal and H_2 more weakly than both Pt and Ni

[1] M.D. Porosoff, W. Yu, J.G. Chen, J. Catal. (2013).

[2] R.Y. Zheng, M.P. Humbert, Y.X. Zhu, J.G. Chen, Catal. Sci. Technol. 1 (2011) 638-643.



Temperature Programmed Desorption (TPD)

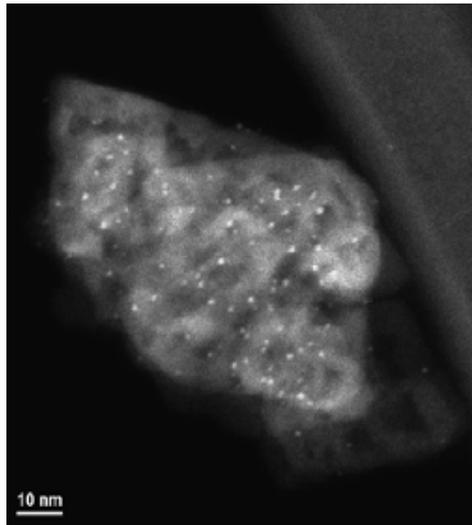


- TPD studies *in UHV conditions* indicate Pt-Ni-Pt is more active than Pt and Ni
- Using d-band center as a predictor could save significant time to identify supported catalysts for reactor experiments

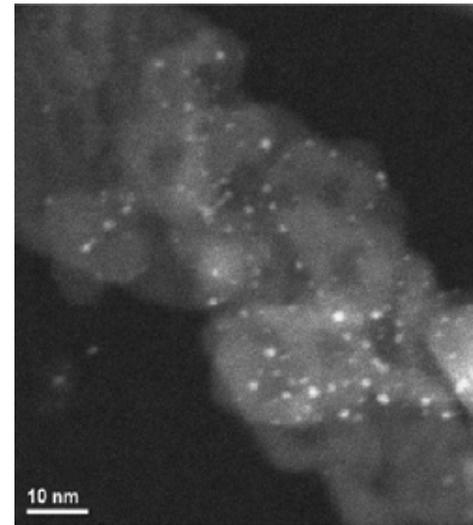


Ex-situ Characterization of PtNi/ γ -Al₂O₃

- Catalysts are synthesized using incipient wetness impregnation
- TEM measurements indicate there are well-distributed, metallic particles, ~1.5 nm



Pt/ γ -Al₂O₃



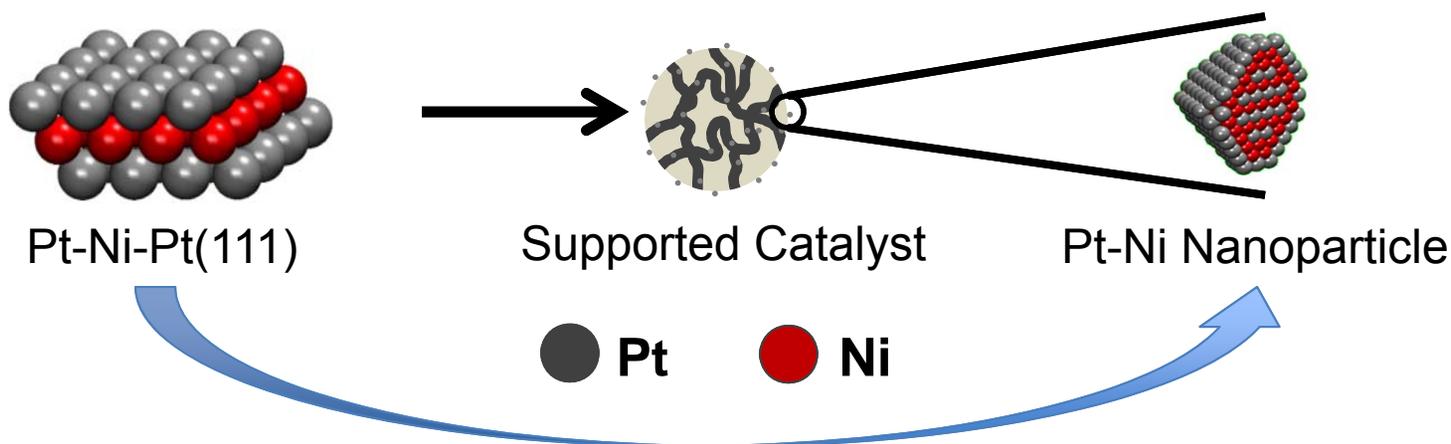
PtNi/ γ -Al₂O₃

Can you tell which is bimetallic?



Why are we interested in XAFS?

- DFT and UHV studies indicate that the Pt-Ni-Pt surface is very active for propanal hydrogenation
 - Necessary to replicate an analogous surface in supported catalysts

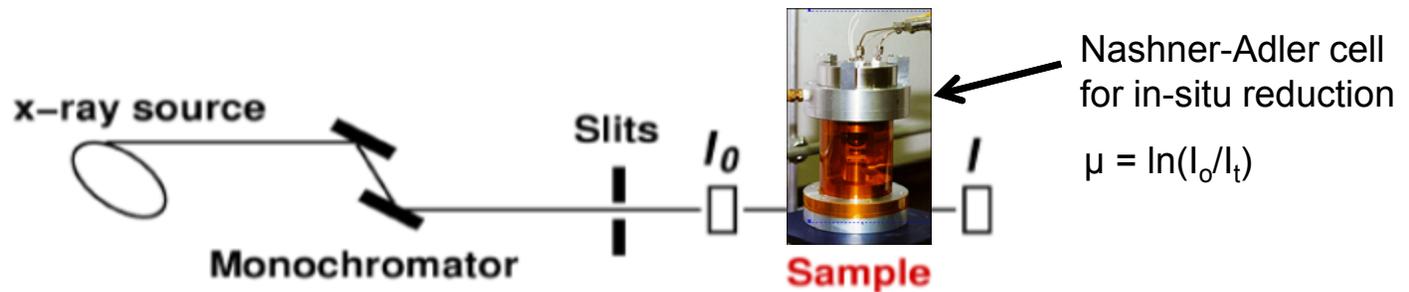


Do we have bimetallic particles?
Can we compare these systems?



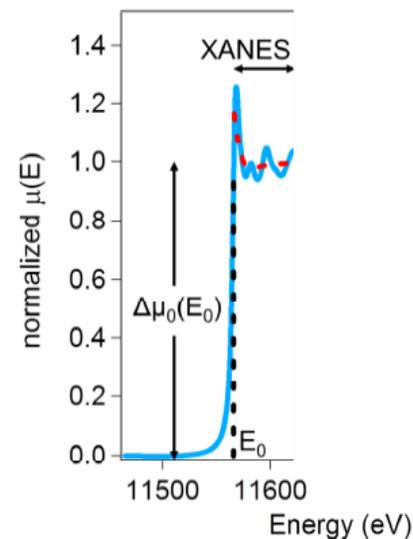
X-ray Absorption Fine Structure (XAFS)

- Used to measure bond distances, coordination number, and nearest neighbors of metal atoms to confirm existence of bimetallics



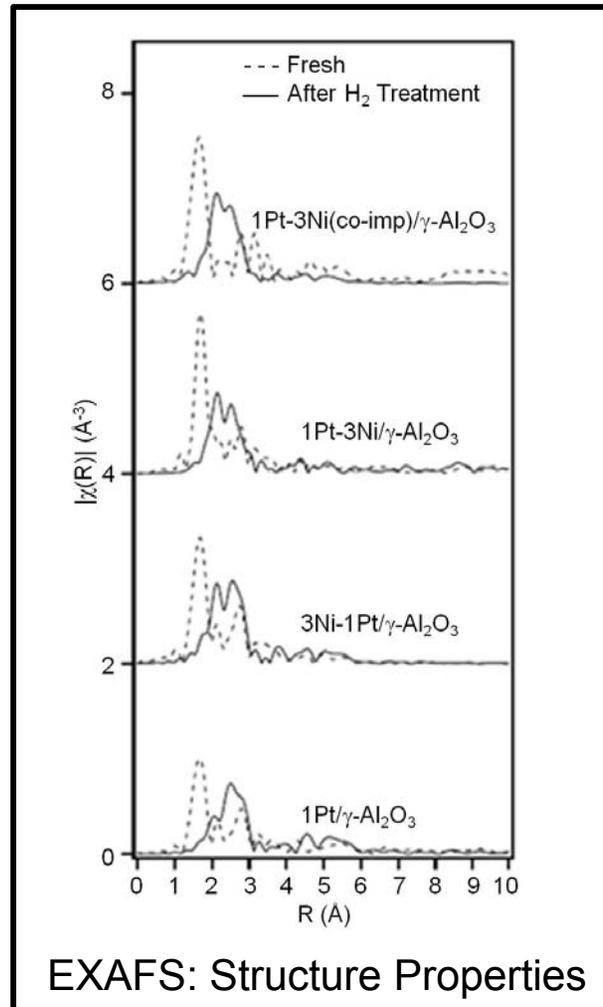
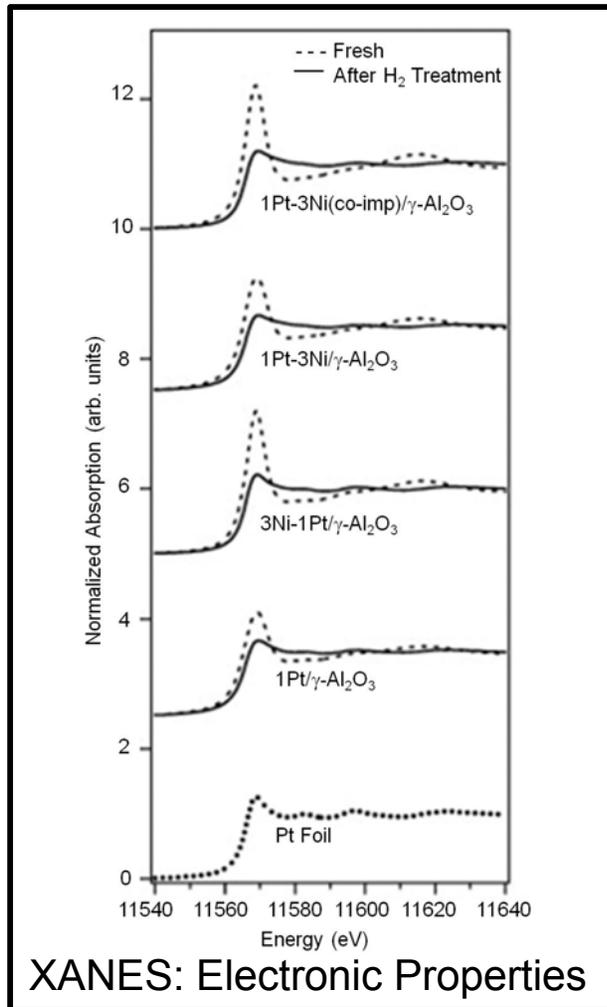
- XANES: Near edge region of absorbance spectrum, contains *electronic information*
 - Oxidation states

- EXAFS: Extended edge region of absorbance spectrum, contains *structure information*
 - Bond distances, nearest neighbors and coordination numbers





Pt-Based XAFS Data



- Samples were reduced in-situ in 5% H₂ and appear similar to Pt foil after reduction
- All data sets consist of 5 scans that are pre-processed, aligned and merged in Athena
- Decrease in M-O bonds and increase in M-M bonds upon reduction

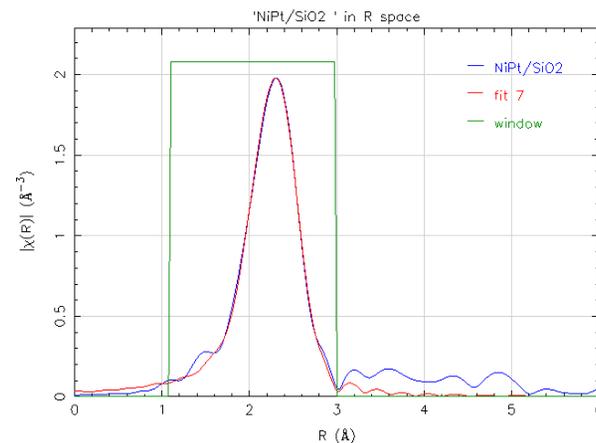


First Shell Fitting of EXAFS Data in Artemis

- Data was fit *after reduction* in 5% H₂/He with 7 parameters

#		Name	Math Expression
1	g	NPt	6
2	g	enot	0
3	g	delrPt	-0.1
4	g	ssPt	0.005
5	g	NNi	6
6	g	delrNi	-0.2
7	g	ssNi	0.005

Guess, Def, Set



R-Space Data

label: _____
N: 1 S02: NPt*0.8
delE0: enot
delR: delrPt
sigma2: abs(ssPt)
Et: _____
3rd: _____
4th: _____

Pt FEFF Path

label: _____
N: 1 S02: NNi*0.8
delE0: enot
delR: delrNi
sigma2: abs(ssNi)
Et: _____
3rd: _____
4th: _____

Ni FEFF Path



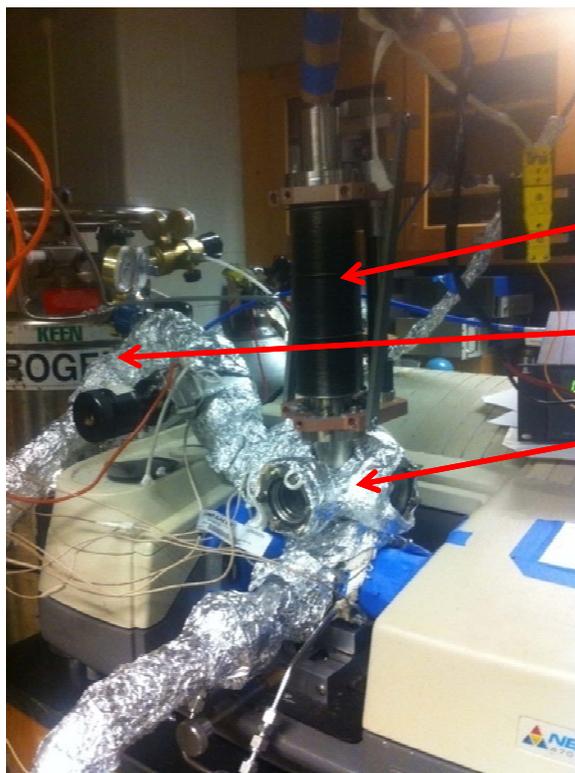
EXAFS Fitting Results

Catalysts	N(Pt-Pt)	N(Pt-Ni)	d(Pt-Pt)	d(Pt-Ni)	σ^2 (Pt-Pt)	σ^2 (Pt-Ni)
Pt/ γ -Al ₂ O ₃	6.2 ± 0.4	--	2.75 ± 0.01	--	0.006 ± 0.001	--
1Pt-3Ni/ γ -Al ₂ O ₃	4.4 ± 0.7	2.6 ± 0.6	2.72 ± 0.01	2.57 ± 0.01	0.007 ± 0.001	0.010 ± 0.002
3Ni-1Pt/ γ -Al ₂ O ₃	7.3 ± 0.9	1.4 ± 0.5	2.74 ± 0.01	2.58 ± 0.01	0.007 ± 0.001	0.008 ± 0.002
1Pt-3Ni/ γ -Al ₂ O ₃ co-imp	5.7 ± 0.9	3.2 ± 0.5	2.72 ± 0.01	2.58 ± 0.01	0.007 ± 0.001	0.010 ± 0.001

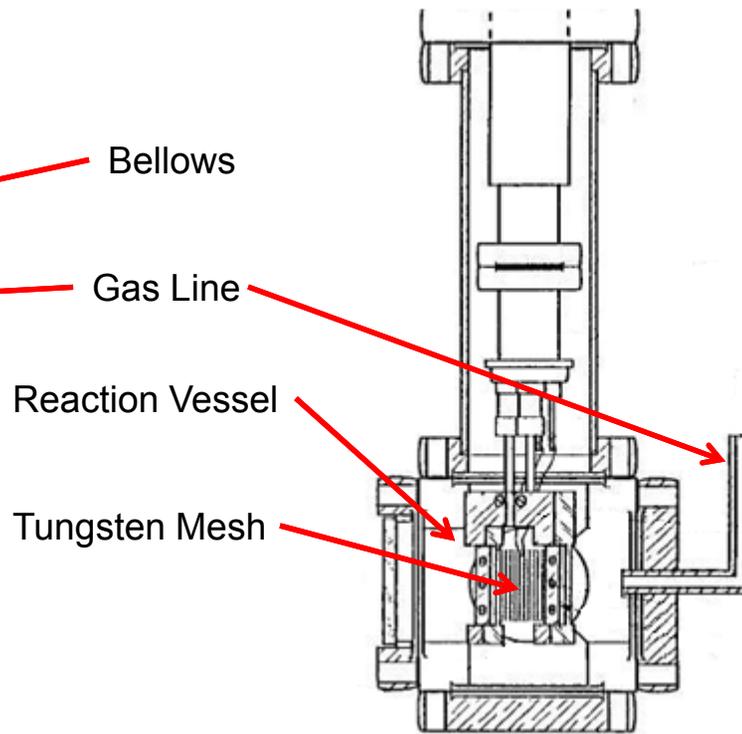
- In all cases, Pt-Pt distances are smaller than bulk Pt-Pt (**2.77 Å**), while Pt-Ni distances are larger than bulk Ni-Ni (**2.49 Å**), suggesting bimetallic bonds
- Small goodness of fit parameter ($\sigma^2 < 0.01$) indicates excellent fit
- Bimetallic coordination number is largest on the co-impregnated catalyst
- Can we infer the structure of the bimetallic particles?



Batch Reactor with In-situ Fourier Transform Infrared Spectrometer



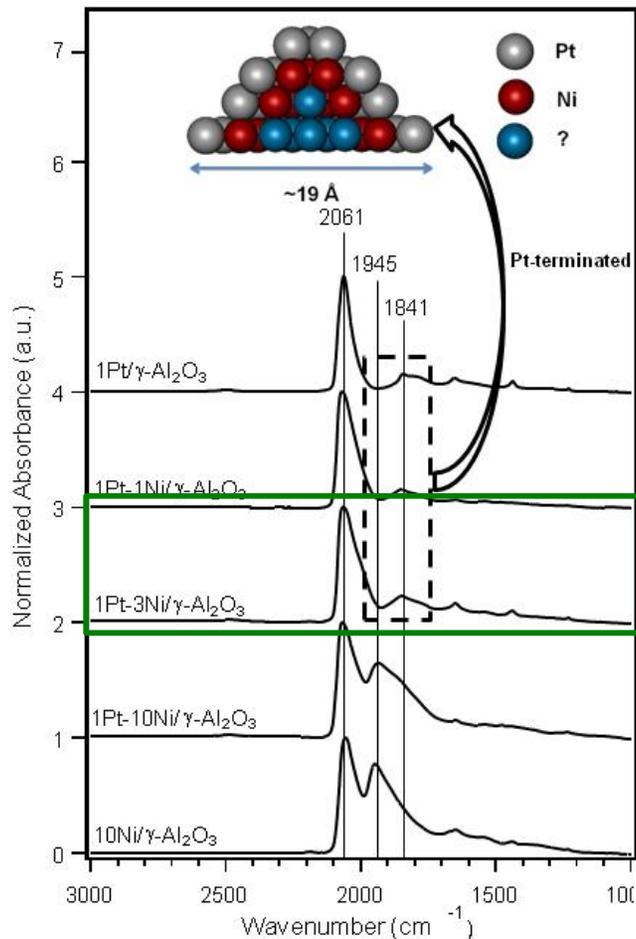
Exterior View



Interior View



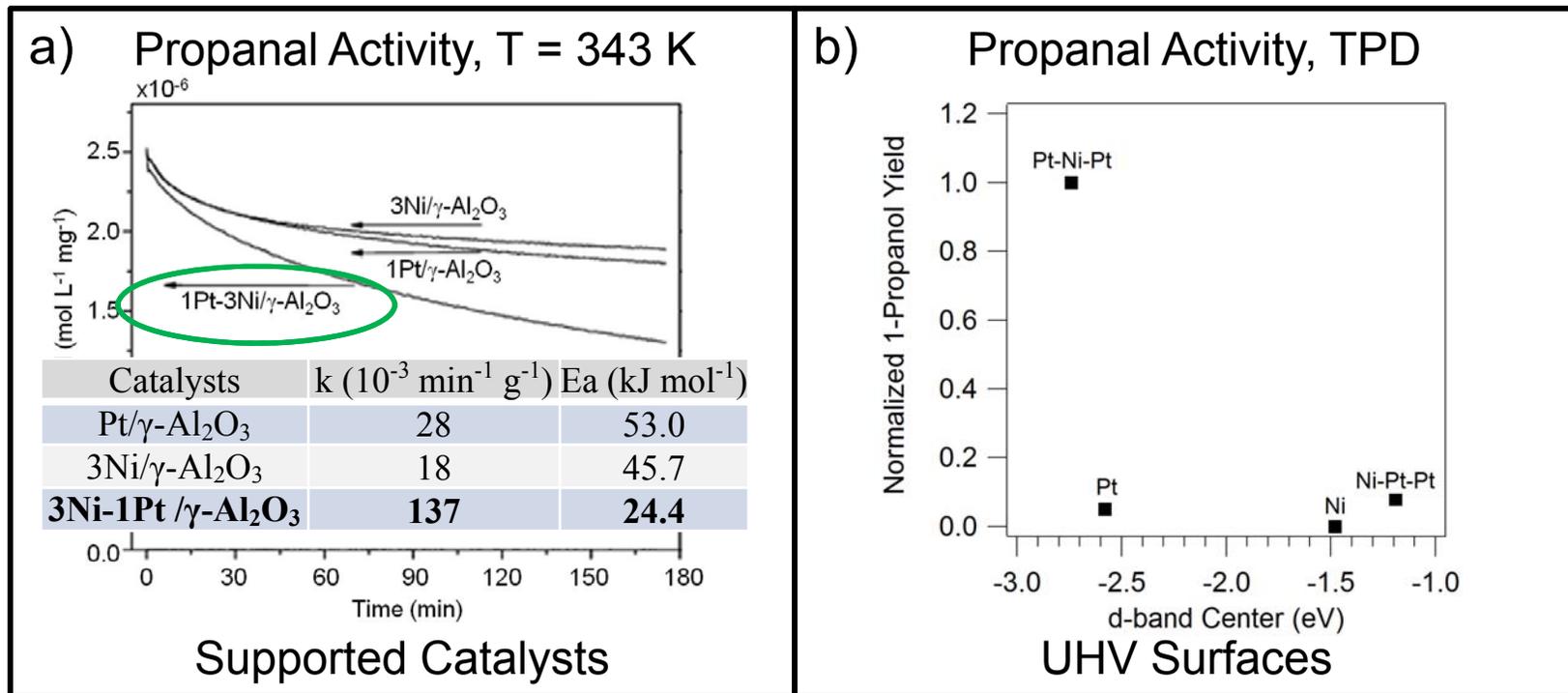
Bimetallic Catalyst Structure by CO Adsorption with FTIR



- Figure shows CO binding signatures in FTIR on Pt/Ni catalysts on $\gamma\text{-Al}_2\text{O}_3$
- 2061 cm^{-1} for atop sites
- 1945 cm^{-1} for bridge on Ni
- 1841 cm^{-1} for bridge on Pt
- Bimetallic Pt-Ni are similar to monometallic Pt, suggesting bimetallic supported catalysts are ***Pt-terminated***



Batch Reactor Activity for Hydrogenation



- PtNi/ γ -Al₂O₃ is more active for propanal hydrogenation than either of its parent metals
- Recall: Pt-Ni-Pt subsurface was most active in UHV experiments

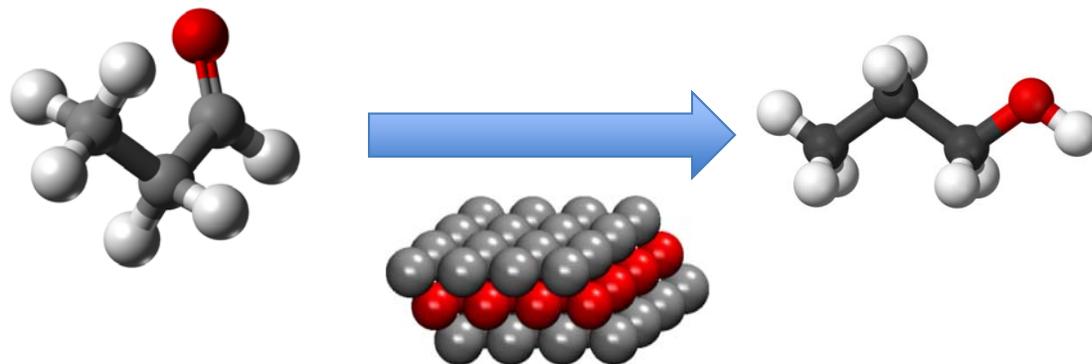
[1] W.W. Lonergan, D.G. Vlachos, J.G. Chen, J. Catal. 271 (2010) 239-250.

[2] R.Y. Zheng, M.P. Humbert, Y.X. Zhu, J.G. Chen, Catal. Sci. Technol. 1 (2011) 638-643.



Summary of Hydrogenation of Propanal

- DFT and UHV studies indicated that Pt-Ni-Pt surface would be active for propanal hydrogenation
- Bimetallic structure of supported catalysts confirmed with TEM, EXAFS and CO FTIR
- Extent of bimetallic formation is critical for high activity during hydrogenation reactions
- EXAFS can be used to confirm the active phase of the bimetallic particles





Lesson Outline

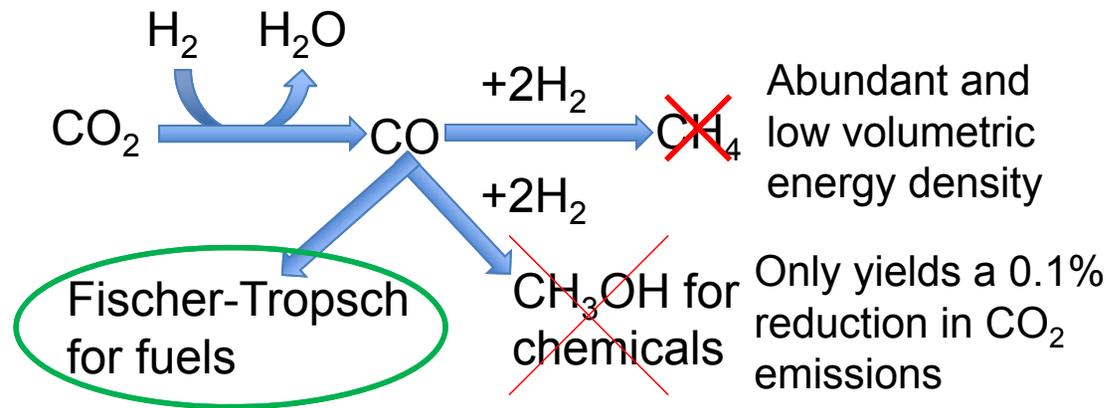
Common Theme: Discovering trends to identify desirable catalysts

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Introduction to CO₂ Activation

- Significant cuts in emissions are required to stabilize CO₂ levels
- Sequestration is costly (~\$50-100/ton CO₂) with unknown effects
 - Convert CO₂ into a useful chemical



- CO from CO₂ has a potential for a 40% reduction in CO₂ emissions by utilizing CO in Fischer-Tropsch
- CO₂ is highly stable and unreactive → activate with a catalyst

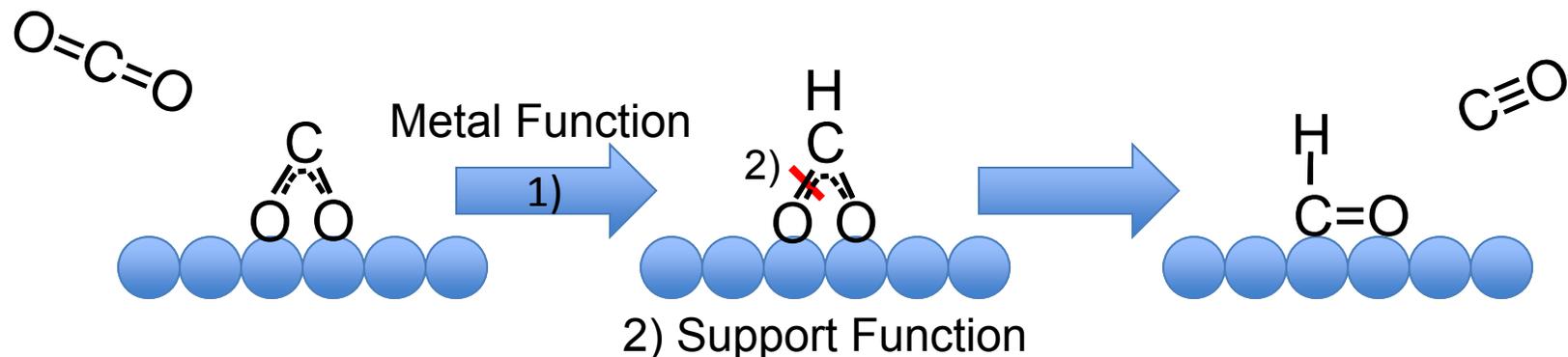
[1] <http://www.netl.doe.gov/publications/factsheets/program/Prog065.pdf>

[2] C.S. Chen, W.H. Cheng, S.S. Lin, Appl. Catal. A-Gen. 257 (2004) 97-106. [3] L. Fan, K. Fujimoto, J. Catal. 150 (1994) 217-220



Supported Catalyst Selection for CO₂ Activation

- CO₂ activation requires a dual-functional catalyst with high hydrogenation and C=O bond breaking activity
 1. Hydrogenation of CO₂ (metal) → formate intermediate
 2. Scission of C=O bond (support) → aldehyde intermediate
- Active metal and oxide support both must play a role

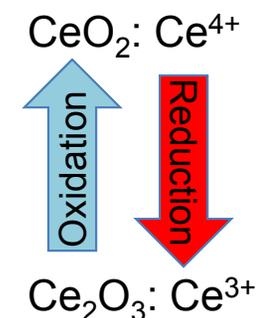




Supported Catalyst Identification

- Supported catalyst: Active Metal + Support
- Active Metal: Nano-sized metallic particles provide adsorption sites and aid dissociation of reactants
 - PtNi was active for C=O hydrogenation in acetone and propanal
- Support: Metal oxides provide stability and increase active metal dispersion
 - Irreducible: γ -Al₂O₃, **Reducible: CeO₂**
 - Lattice oxygen vacancies in CeO₂ can accept oxygen from CO₂ to contribute to its activation
 - CeO₂ cannot activate CO₂ alone

Co	Ni	Cu
Rh	Pd	Ag
Ir	Pt	Au



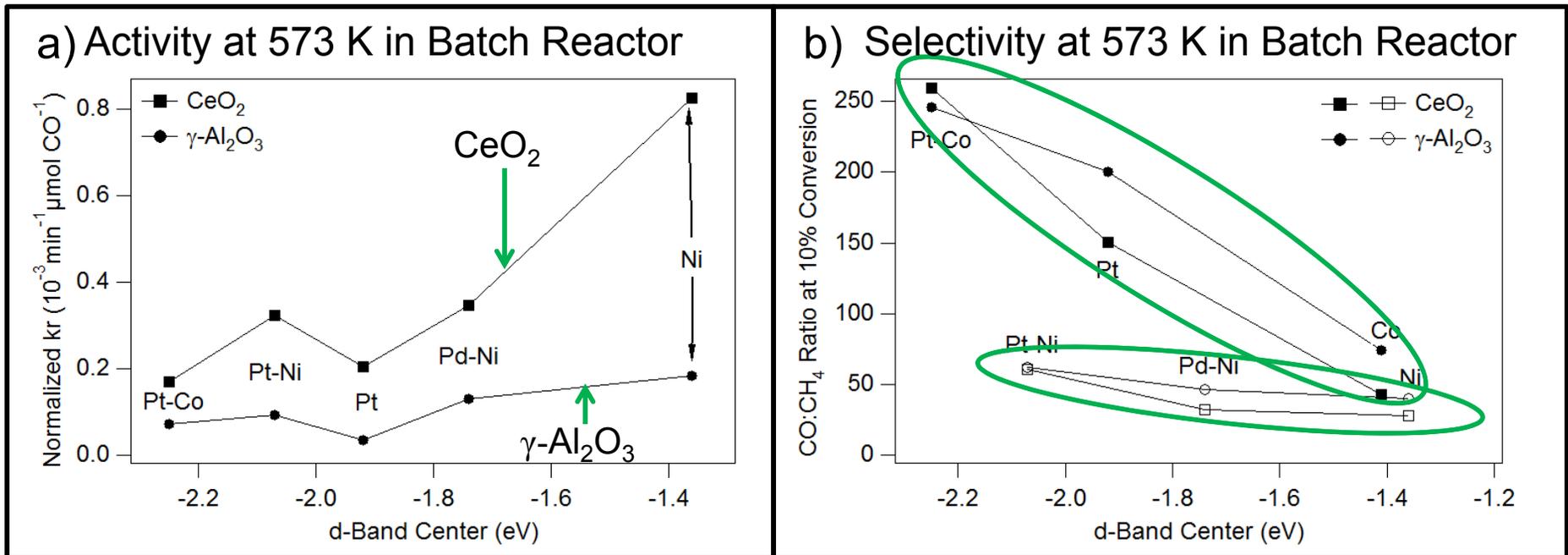
[1] S.T. Qi, et al, Appl. Catal. A-Gen. 393 (2011) 44-49.

[2] R.Y. Zheng et al, Catal. Sci. Technol. 1 (2011) 638-643.

[3] T. Jin, et al, ACS. 87 (1987) 5931-5937.



Determining Trends in Activity and Selectivity

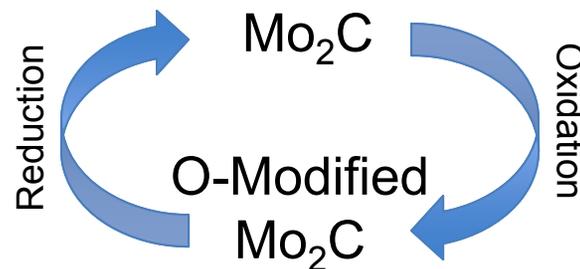


- The support dominates the activity and metals control selectivity
 - Support effect: The activity is higher on each CeO₂ based catalyst
 - Metallic effect: Decreasing CO:CH₄ with increasing values of d-band center
- Investigate other catalysts that exhibit dual-functionality and oxidation-reduction cycles



Mo₂C as a Catalyst for CO₂ Activation

- Metal carbides show catalytic properties similar to precious metals in many reactions: reforming, hydrogenation, isomerization
 - Mo₂C is a dual functional catalyst with high hydrogenation and C=O bond breaking activity
- High Mo₂C activity and selectivity for CO₂ activation could be from an oxidation-re carburization cycle
 - Mirrors the oxygen storage capacity seen in ceria



[1] C. Shi, A.J. Zhang, X.S. Li, S.H. Zhang, A.M. Zhu, Y.F. Ma, C.T. Au, Appl. Catal. A-Gen. 431 (2012) 164-170.

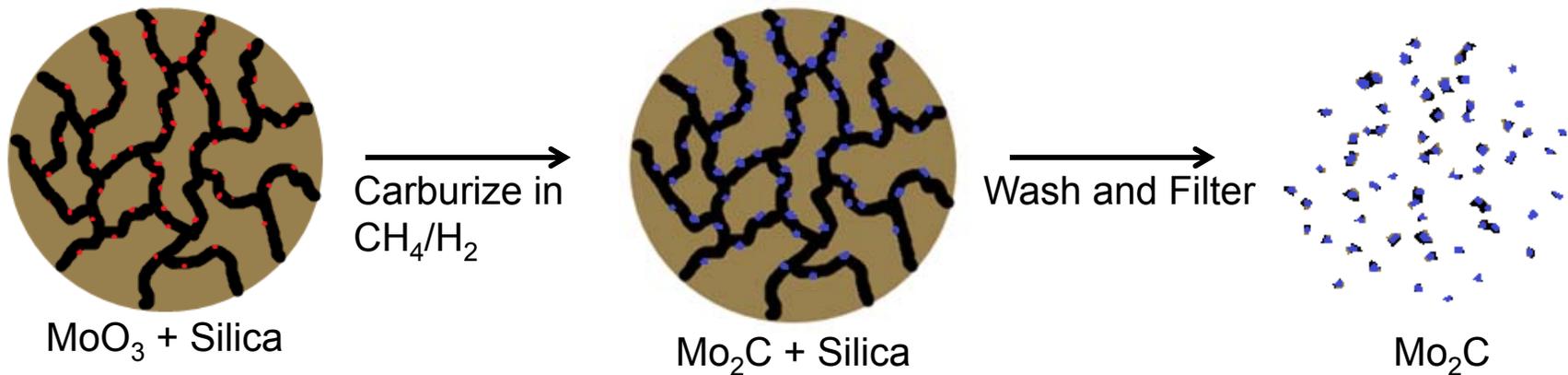
[2] J.L. Dubois, K. Sayama, H. Arakawa, Chem. Lett. (1992) 5-8.

[3] J. Sehested, C.J.H. Jacobsen, S. Rokni, J.R. Rostrup-Nielsen, J. Catal. 201 (2001) 206-212.



Mo₂C Synthesis

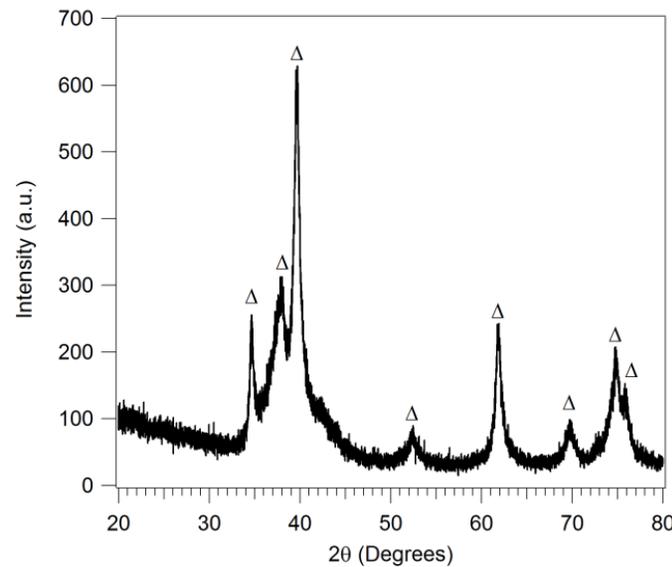
1. Impregnate ammonium molybdate tetrahydrate into silica support (S.A ~ 1000 m²/g, 2.1 – 2.7 nm pore size)
2. Calcine, then carburize catalyst
3. Wash away silica with NaOH, then filter and fully dry Mo₂C





Characterization of Mo₂C

- Mo₂C is a new compound for the group and the synthesis is a new procedure → must verify the compound is pure Mo₂C
 - XRD indicates β -Mo₂C (more stable phase)
- Compare with a reference Mo₂C using **EXAFS**

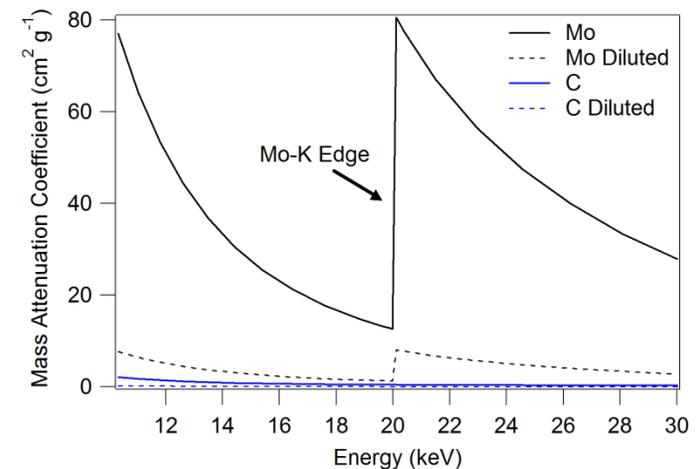


Δ : Peaks associated with β -Mo₂C



Calculations Prior to EXAFS of Mo₂C

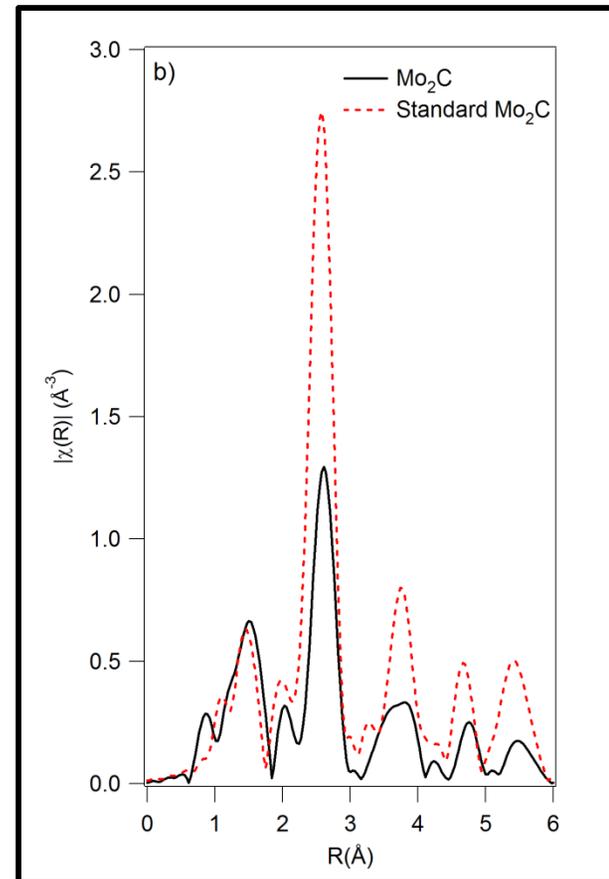
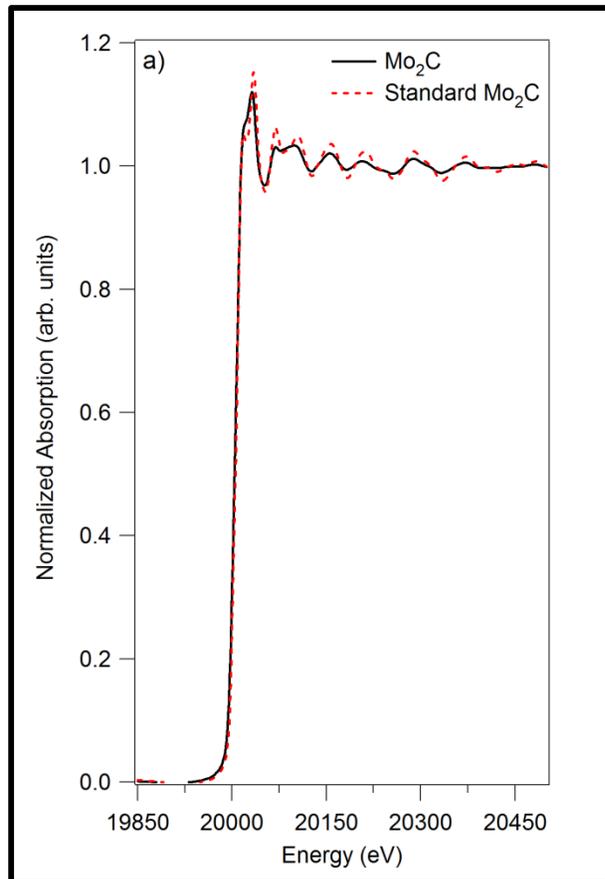
- Mo₂C is a pure compound: sufficient X-ray transmittance is a challenge
 - PtNi/ γ -Al₂O₃ is 1.67 wt% Pt and 1.5 wt% Ni on a relatively X-ray transparent support
 - Sample must be diluted: mass attenuation data on NIST can be very helpful



- Dilution must be great enough to allow transmission, but small enough to see an edge jump
 - $\mu = \ln(I_o/I_t) \rightarrow 0.1 < \mu < 1.2$
 - Sample diluted ~1:20 with boron nitride



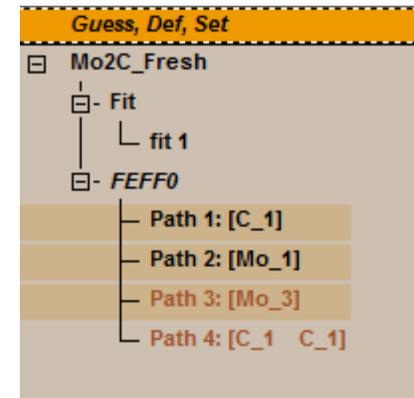
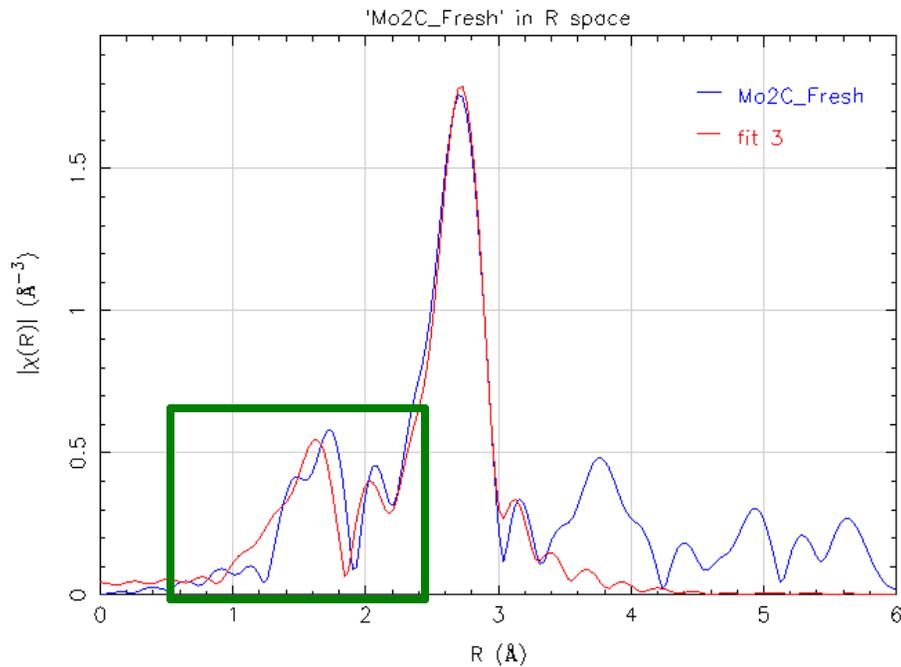
Ex-situ EXAFS of Mo₂C



- Comparison with Alfa-Aesar standard shows similar structure
 - Requires a .inp file to fit the data in Artemis



Mo₂C EXAFS Fits

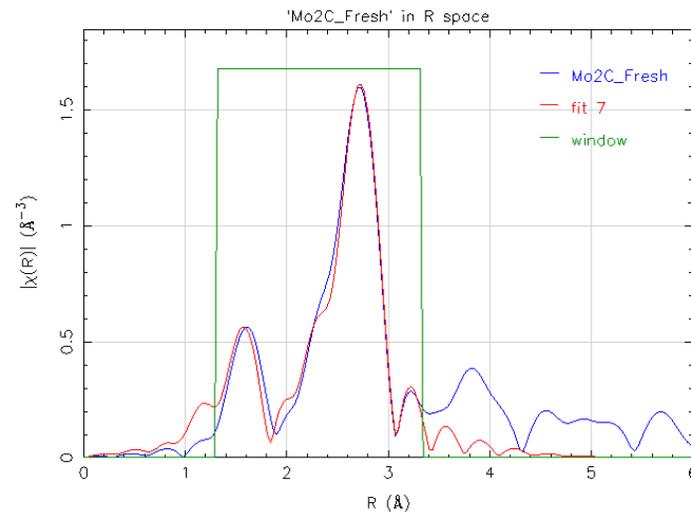
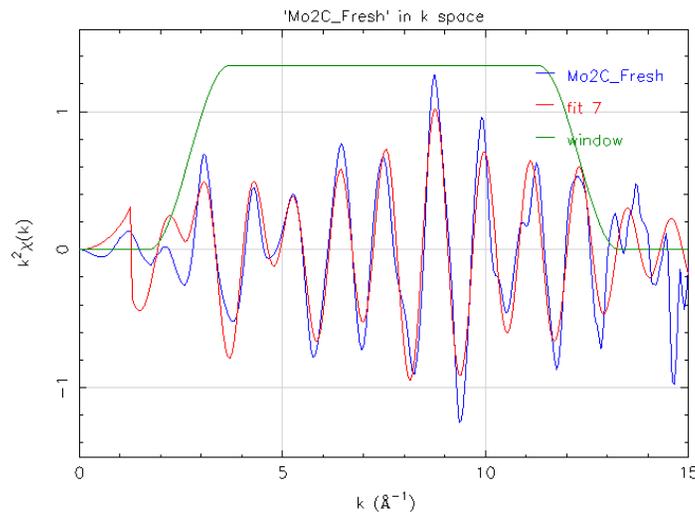


- Lack of fit at low values of R
 - Poor model or are fit parameters inadequate?

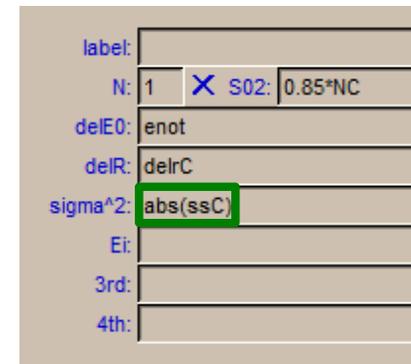
#	Name	Math Expression
1	g: NMo	4
2	g: NC	4
3	g: delrMo	0
4	g: delrC	0
5	g: ssMo	0.005
6	g: ssC	0.005
7	g: enot	0



Troubleshooting Mo₂C EXAFS Fits



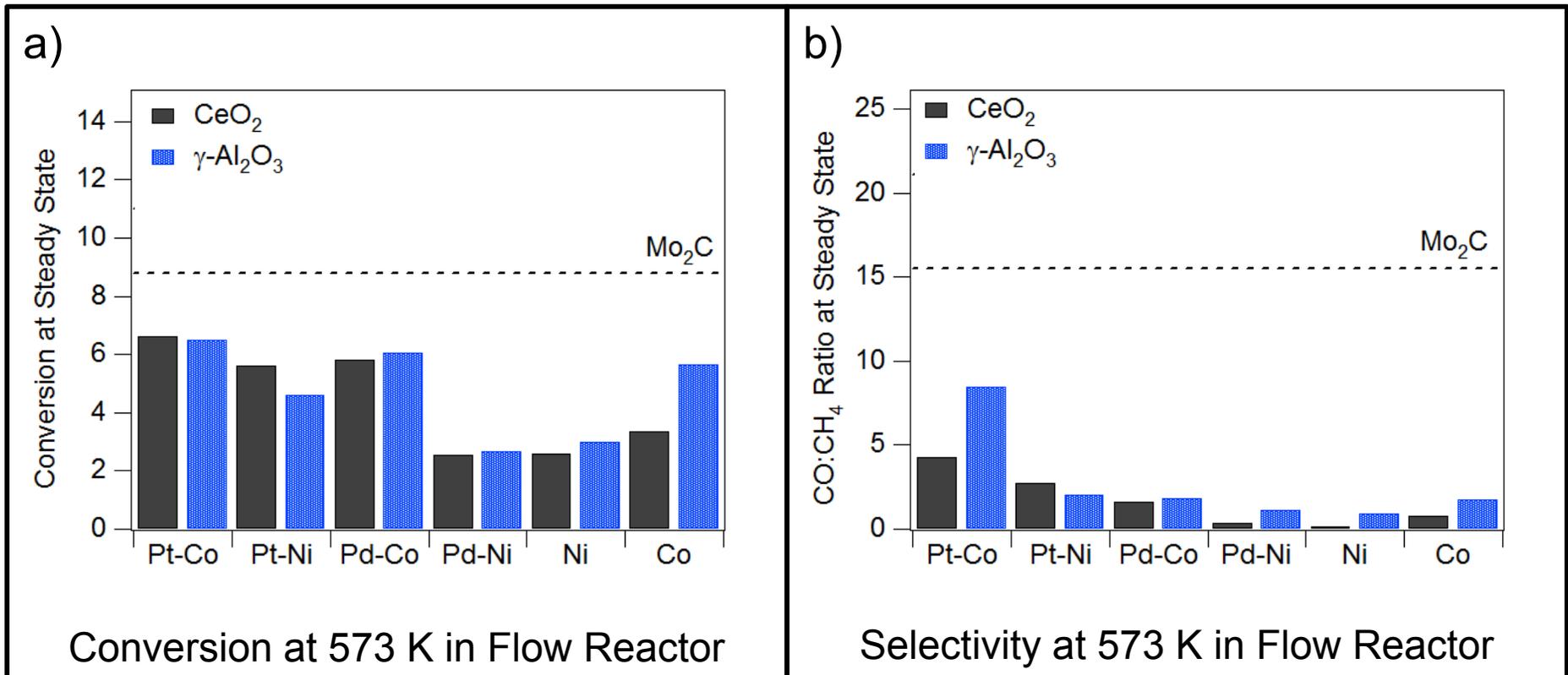
- Modify fit window to exclude low and high values of K (alternate representation of energy)
 - Also add absolute value to σ^2 parameters



- Mo₂C has been successfully synthesized, but is it active for CO₂ activation?



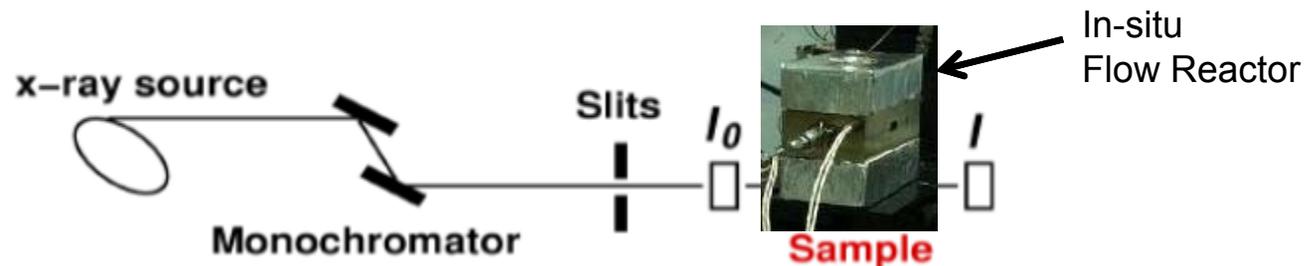
Mo₂C Activity and Selectivity



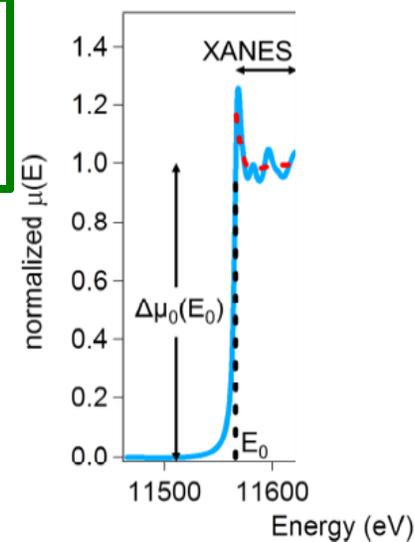
- Mo₂C shows similar conversion as bimetals, but higher selectivity
- High activity from oxidation-re carburization? → Good candidate for in-situ XANES



X-Ray Absorption Near Edge Structure (XANES)



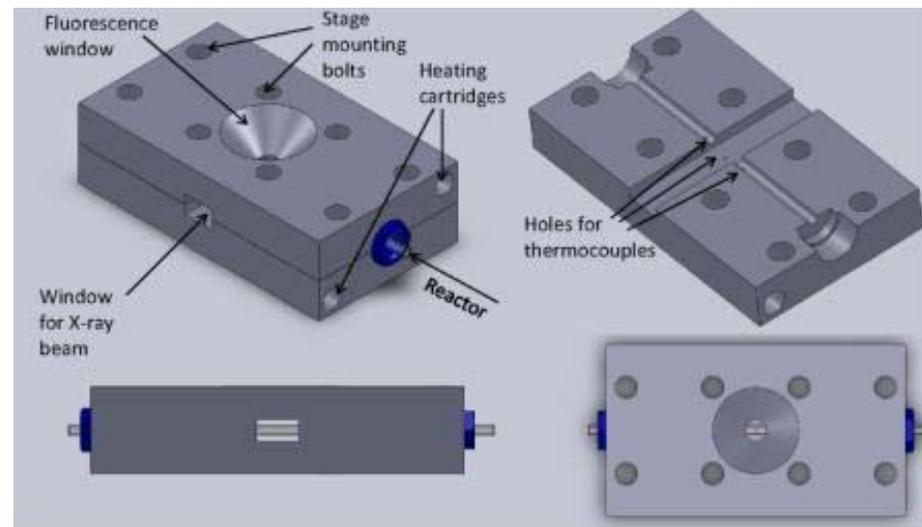
- XANES: Near edge region of absorbance spectrum, contains *electronic information*
 - Oxidation states
- EXAFS: Extended edge region of absorbance spectrum, contains *structure information*
 - Bond distances, nearest neighbors and coordination numbers





In-situ Flow Reactor (Ayman's Cell)

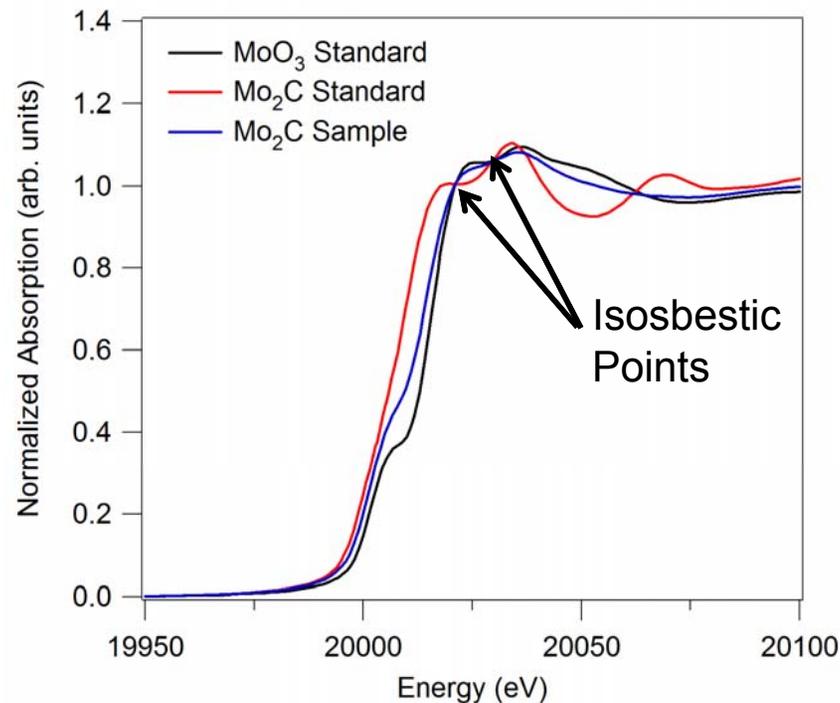
- Flow reactor used with glassy carbon tubes for in-situ XAFS measurements
 - Glassy carbon tubes allow high transmittance of X-rays
- Can measure products and reactants with in-line RGA (Residual Gas Analyzer)





Isosbestic Points in XANES Data

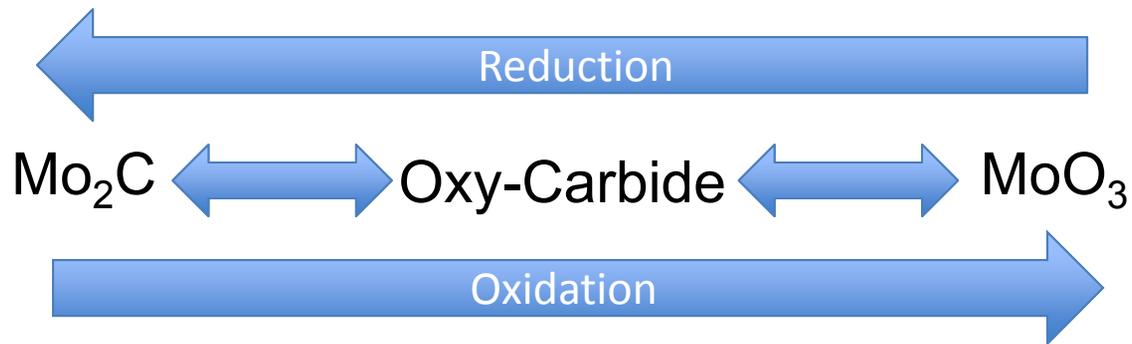
- Occur when a compound is composed of a combination of two parent species: $x\text{A} + y\text{B} = \text{C}$, $x + y = 1$
 - Signature indicator for Linear Combination Analysis (LCF)





Linear Combination Fitting (LCF)

- Recall: High Mo_2C activity in CO_2 activation could be from an oxidation-re carburization cycle
 - It appears that Mo_2C cycles between an oxidized and reduced state
 - Can we prove this? Yes, Linear Combination Fitting of XANES data



- LCF requires standards at both sides of the spectrum (Reduced and oxidized)
 - Standards cannot be arbitrary Mo compounds



Linear Combination Fitting in Athena

The screenshot shows the Athena software interface with the 'Linear combination fitting' dialog box open. The dialog box is titled 'Linear combination fitting' and has a menu bar with 'File', 'Edit', 'Group', 'Values', 'Plot', 'Mark', 'Data', 'Merge', 'Analysis', 'Settings', and 'Help'. The 'Unknown' is set to 'Mo2C_Fresh'. The 'Fitting range' is set to '-20' to '100'. The 'Fitting space' includes 'norm(E)', 'deriv(E)', and 'chi(k)'. The 'Standards spectra' tab is active, showing a table of standards with their weights and fit parameters.

Standards	weight	e0	fit?	req.
1: MoO3_STD	0.500	0.384	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
2: Mo2C_STD	0.500	-1.647	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
3: 0: None	0	0	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
4: 0: None	0		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
5: 0: None	0		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>

The 'Options' section includes checkboxes for 'Add a linear term after e0', 'Weights between 0 & 1', 'Force weights to sum to 1', and 'All standards use same e0'. The 'Operations' section includes 'Fit this group', 'Fit all combinations', 'Fit marked groups', 'Write a report', 'Marked fits report', 'Plot data + sum', 'Plot data + sum in R', 'Make fit group', and 'Make difference group'. The 'Plotting options' section includes checkboxes for 'mu(E)', 'background', 'pre-edge line', 'post-edge line', 'Normalized', and 'Derivative'. The 'Emin' is set to -40 and 'Emax' is set to 70.

HINT: Athena is highly configurable -- see the Preferences dialog in the Setting menu.

Document section: Linear combination fitting

Return to the main window

plotting in energy from group 'H2_XANES' ... done!



Summary of CO₂ Activation

- Mo₂C is bifunctional and highly active for CO₂ activation
- Structure of Mo₂C confirmed using XRD and EXAFS
- Linear combination fitting analysis indicates that Mo₂C undergoes oxidation-reduction
- In-situ XRD and e-TEM for future studies to investigate long-range order of Mo₂C

