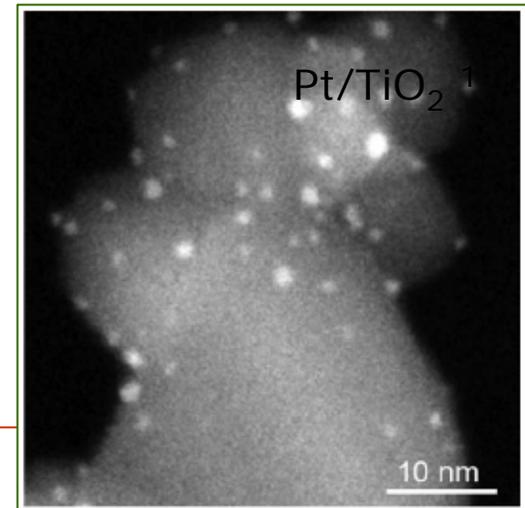


Solid Catalysts

Challenge to understand nature of
typical catalytically active species:

- small
- non-uniform
- minority
- on non-uniform support
- in sea of red herrings



Catalytic Species on Supports: Approaches to Fundamental Understanding

Identify and characterize catalytically active species in typical (non-uniform) catalysts

fish out active species and characterize them

under catalytic reaction conditions

Synthesize structurally simple and uniform (model) catalysts
on porous supports

use reactive molecular precursors for uniform supported species
(virtually molecular) on uniform (crystalline) supports

Characterize by complementary methods

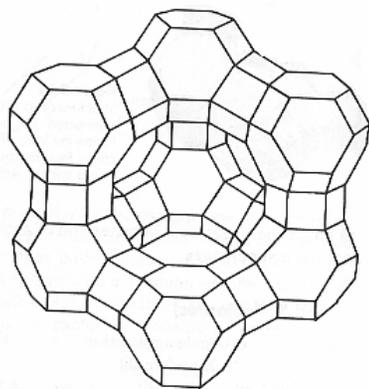
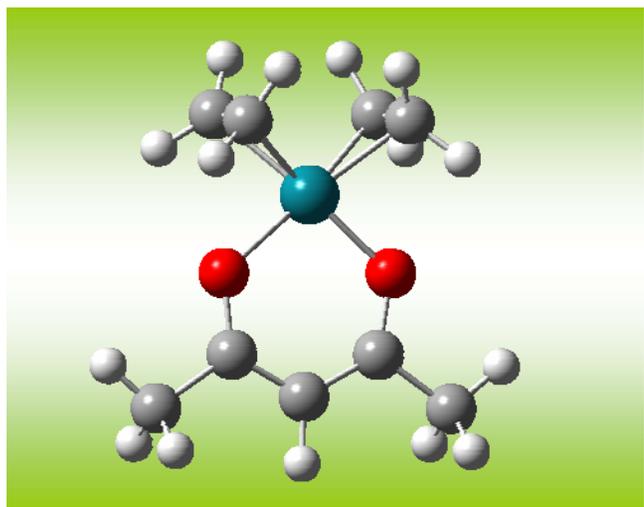
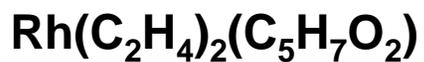
-imaging

-spectroscopy

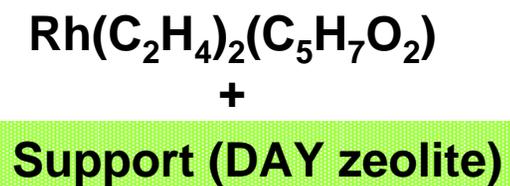
-theory

under catalytic reaction conditions

Supported Rhodium Complex



Dealuminated zeolite Y
Si/Al ratio: 30



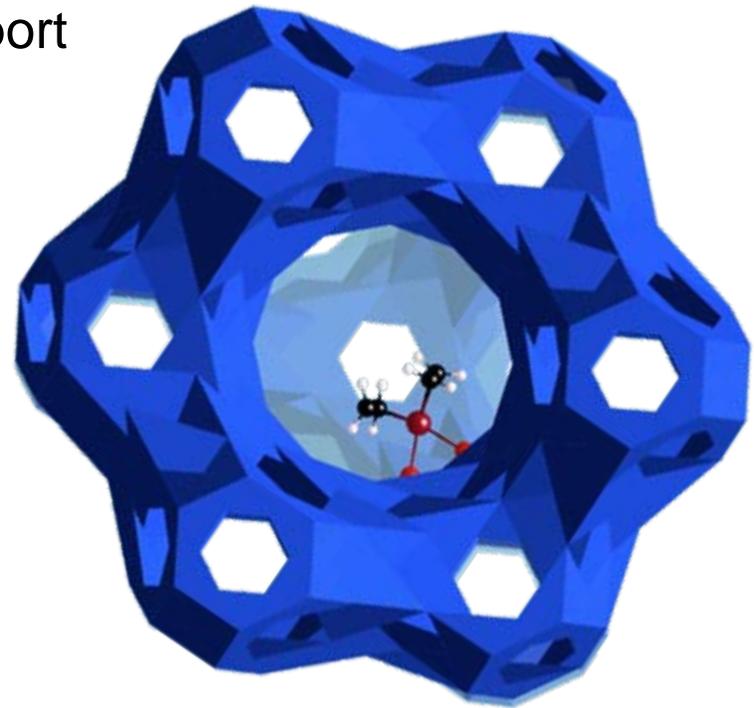
n -pentane slurry, 200 K



Support

Mononuclear metal complex, crystalline support

- Precise synthesis:
uniform supported species on nearly uniform support (zeolite)
- Realistic metal loadings (1 wt% metal):
approaching saturation of sites on support
- Reactive ligands
 - easily removed or converted
 - ready entry into catalytic cycle



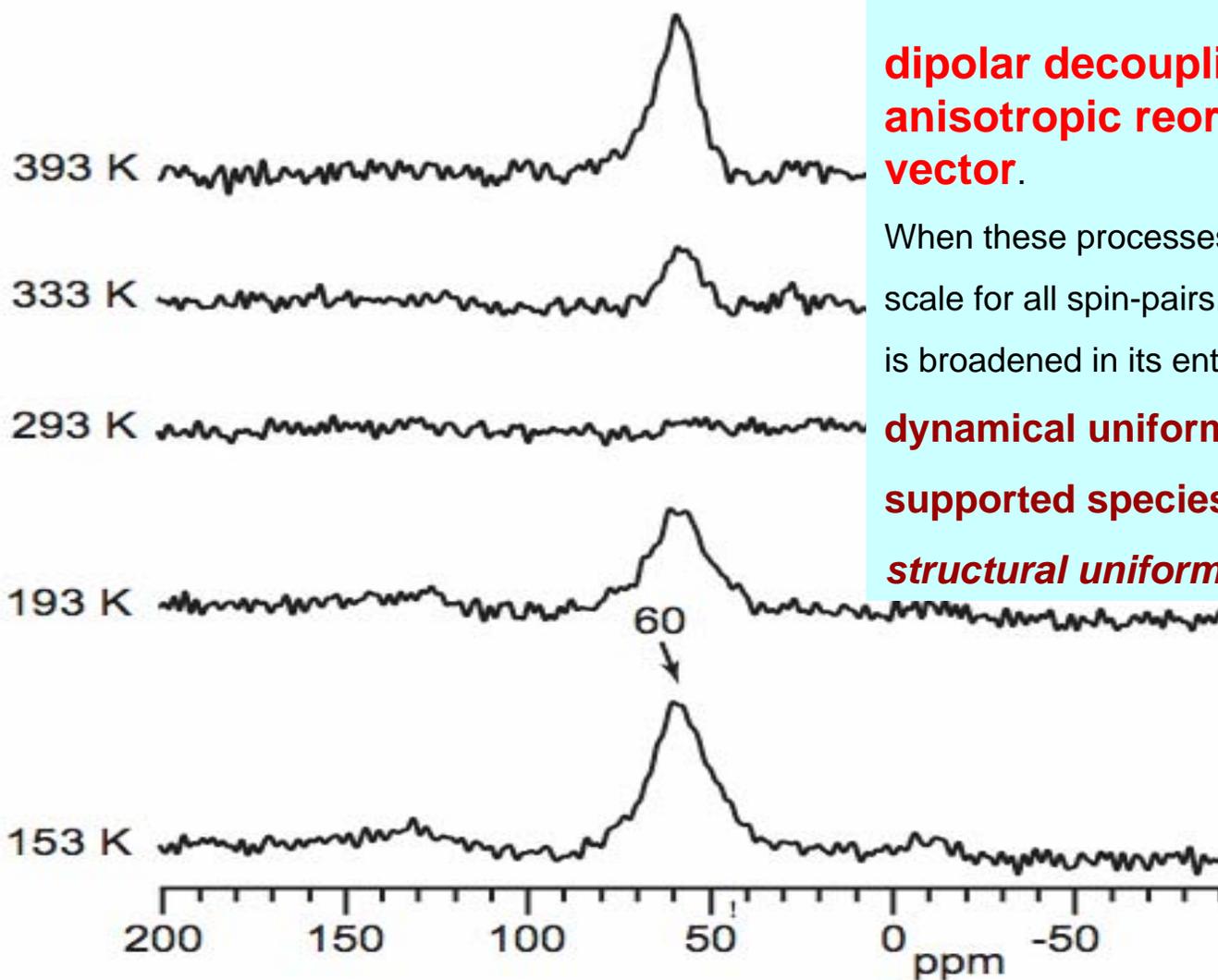
^{13}C resonance of π -bonded ethylene

broadened as result of **conflict of ^1H - ^{13}C**

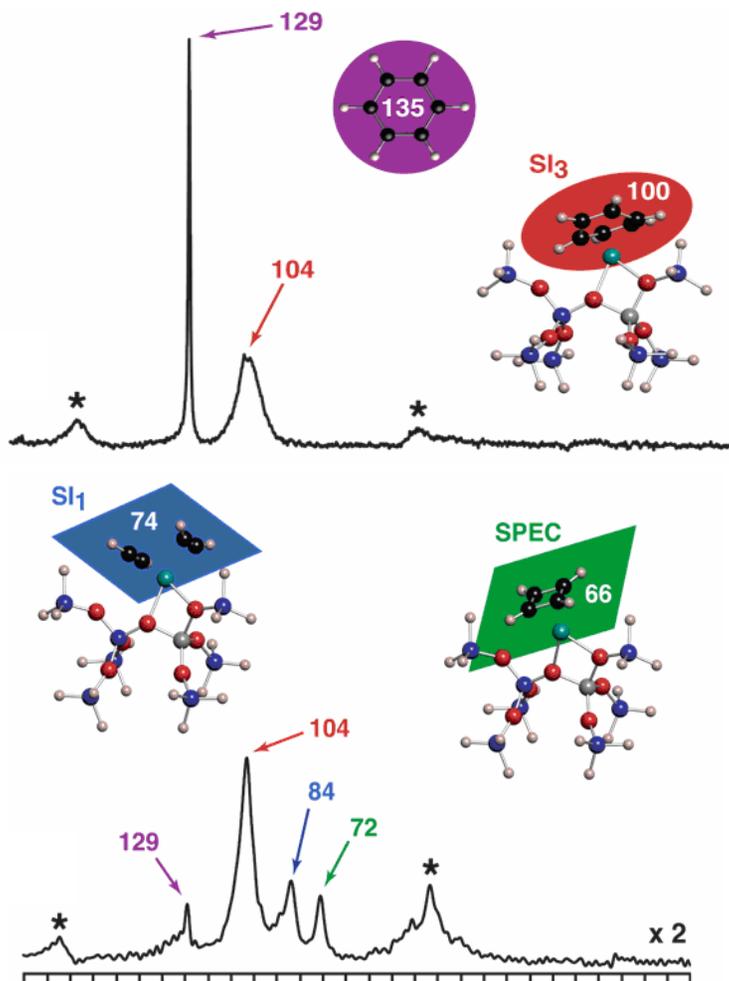
dipolar decoupling & random anisotropic reorientation of ^1H - ^{13}C bond vector.

When these processes occur on same time scale for all spin-pairs, carbon resonance is broadened in its entirety & indicates

dynamical uniformity of supported species, hence evidence of **structural uniformity.**



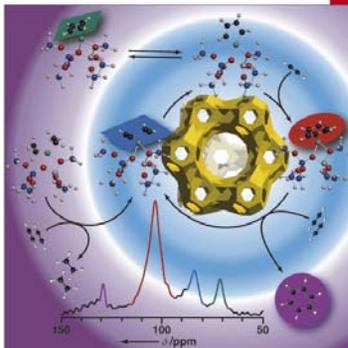
^{13}C NMR Characterization of Acetylene Cyclotrimerization



- Benzene formation in gas phase
- Benzene chemically bonded to supported Rh^+ complex
- Reaction intermediates:
 - Bis-acetylene complex
 - Cyclobutadiene complex

Catalytic Cycle for Acetylene Trimerization

anchor points by spectroscopy; fill in gaps with DFT



Concept
Enantioselective Radical Cyclizations:
A New Approach to Stereocentral of Cascade Reactions
H. Miyabe and Y. Takemoto



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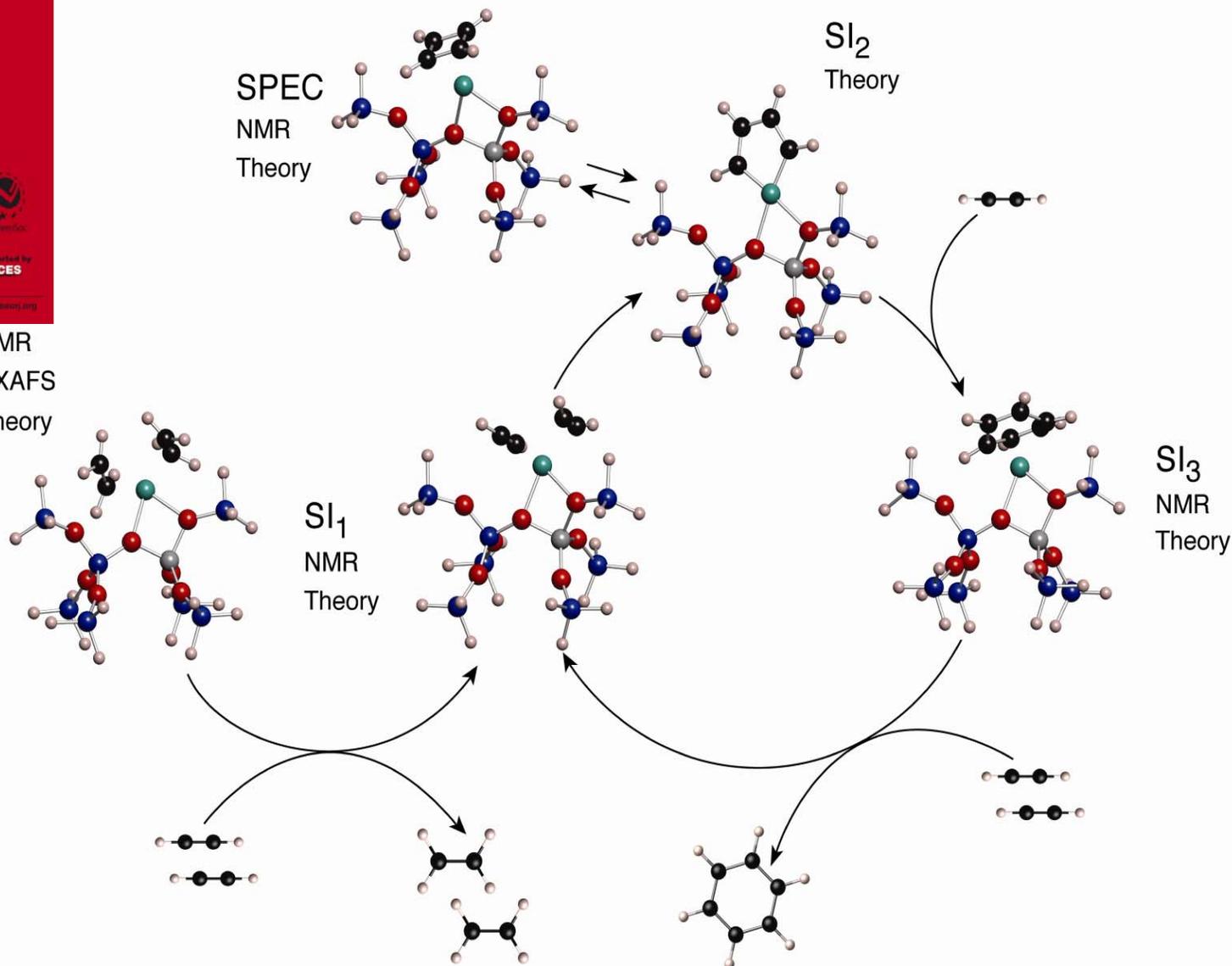
NMR
EXAFS
Theory

SPEC
NMR
Theory

SI₂
Theory

SI₃
NMR
Theory

SI₁
NMR
Theory



IRIDIUM ETHYLENE COMPLEX ON DAY ZEOLITE

1/2

PRECURSOR:



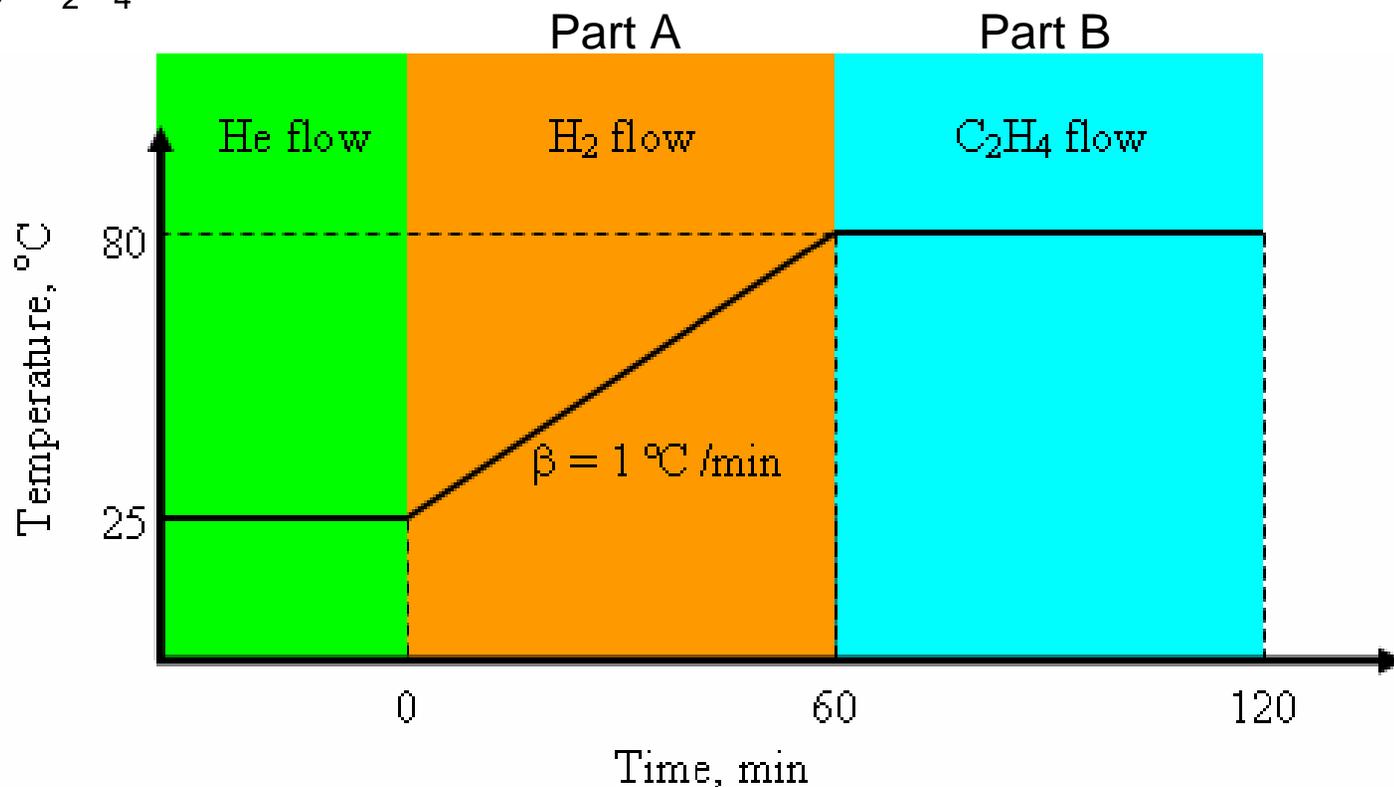
reactive precursor, gives iridium
ethylene complex on support
**ISOSTRUCTURAL WITH RHODIUM
ETHYLENE COMPLEX**

**GOALS: CHARACTERIZE CLUSTER FORMATION
IN TRANSIENT EXPERIMENTS**

Transient flow reactor experiments with measurement of EXAFS at Ir L_{III} edge, XANES, & IR spectra

Experiment #1 – H₂ treatment of as-prepared sample at room temperature for 2 h

Experiment #2 – H₂ treatment of as-prepared sample during temperature ramp, followed by C₂H₄ flow



Part A – Temperature ramp to 80 °C in H₂ flow in 1 h

Part B – C₂H₄ flow at 80 °C

EXAFS after 2 h in H₂ flow at room temperature

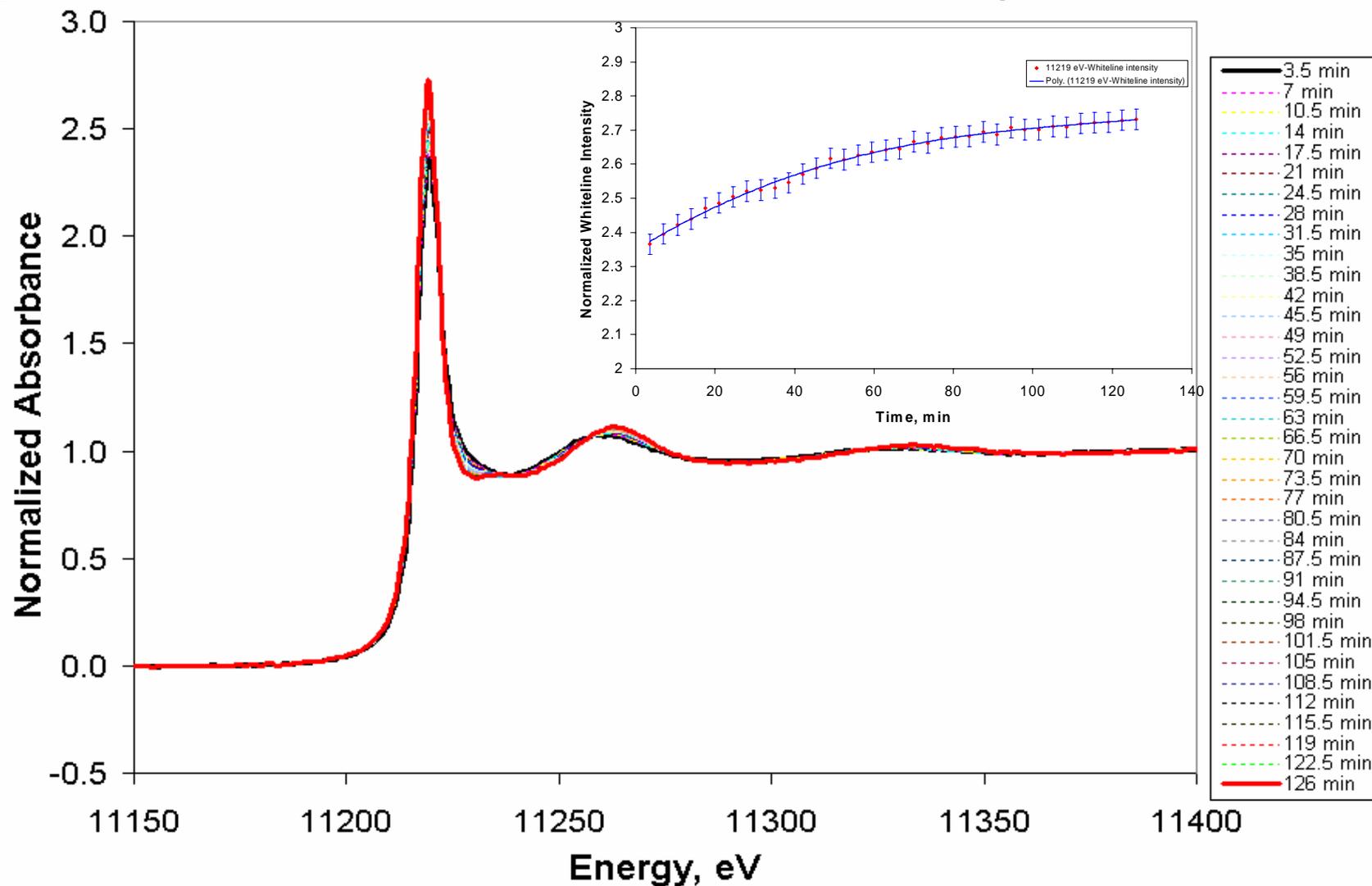
Shell	N	$R, \text{Å}$
Ir–O	1.9	1.99
Ir–C	2.7	2.11
Ir–C _l	3.5	3.14
Ir–Al	1.1	3.12

Errors: N , $\pm 20\%$, R , $\pm 0.02 \text{ Å}$, except for Ir–C_l and Ir–Al.

Ir–C_l: long Ir–C contribution

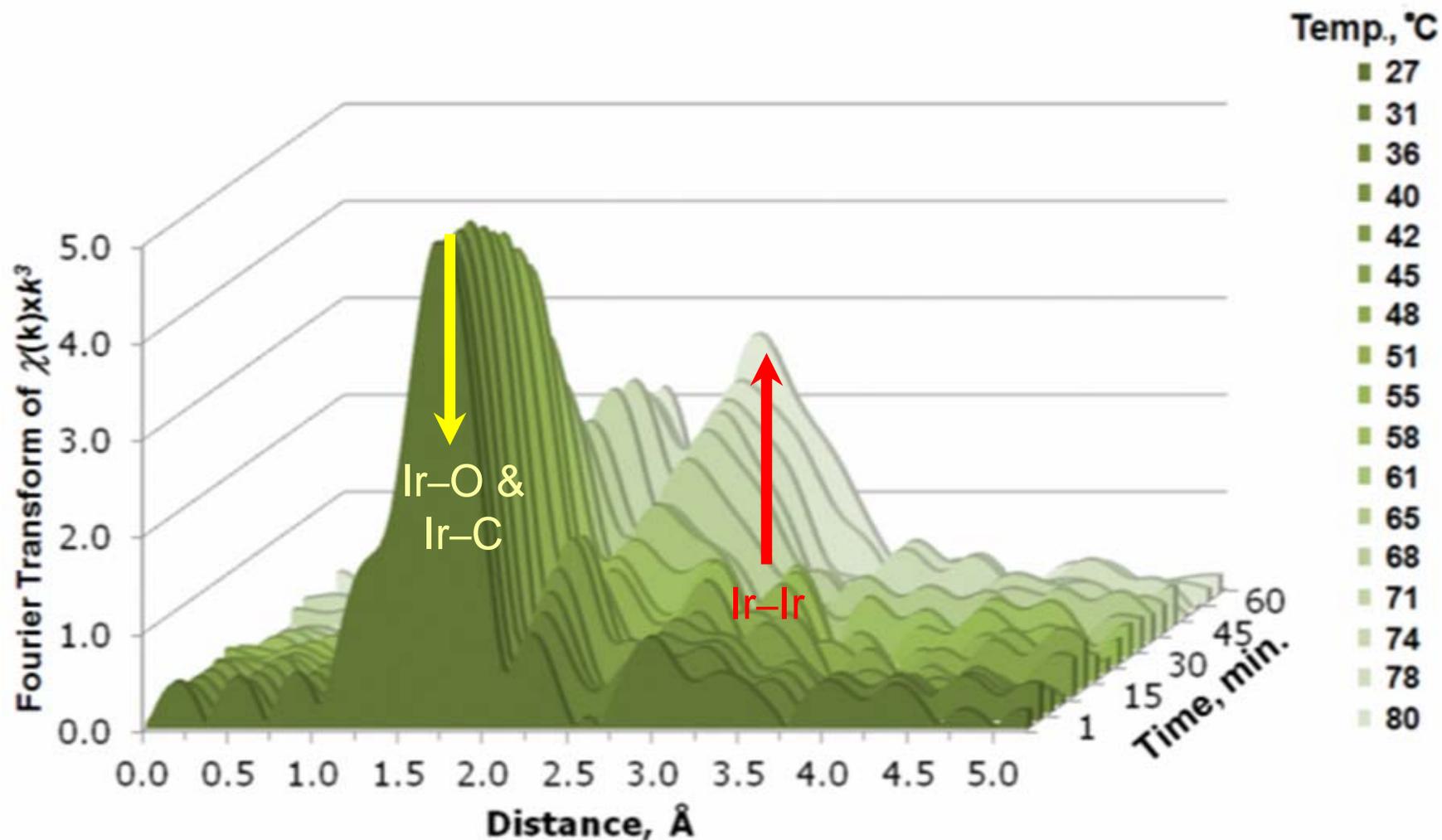
- No Ir–Ir shell detected (within error)
- Complex still mononuclear after 2 h of H₂ treatment at room temperature
- Ethylene ligands converted
- Ethyl ligands formed [tentative hypothesis]

H₂ treatment at room temperature for 2 h – XANES region



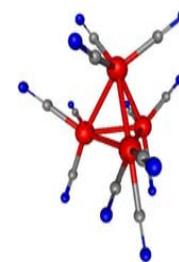
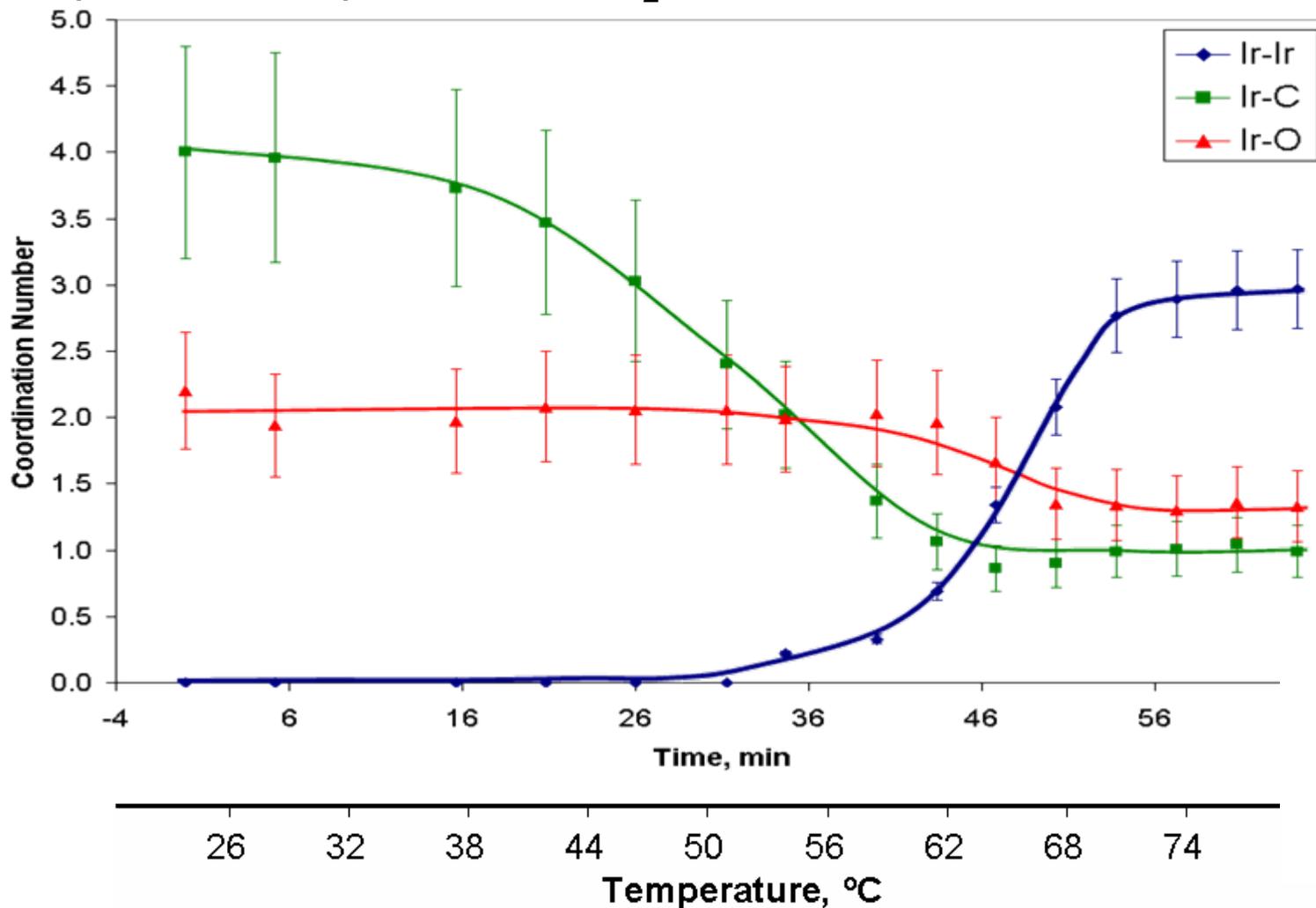
- Isosbestic points: evidence confirming structural changes: 1 species to another
- Increase in white line intensity with time at room temperature

Temperature ramp to 80 °C in H₂ flow in 1 h – EXAFS in *R* space



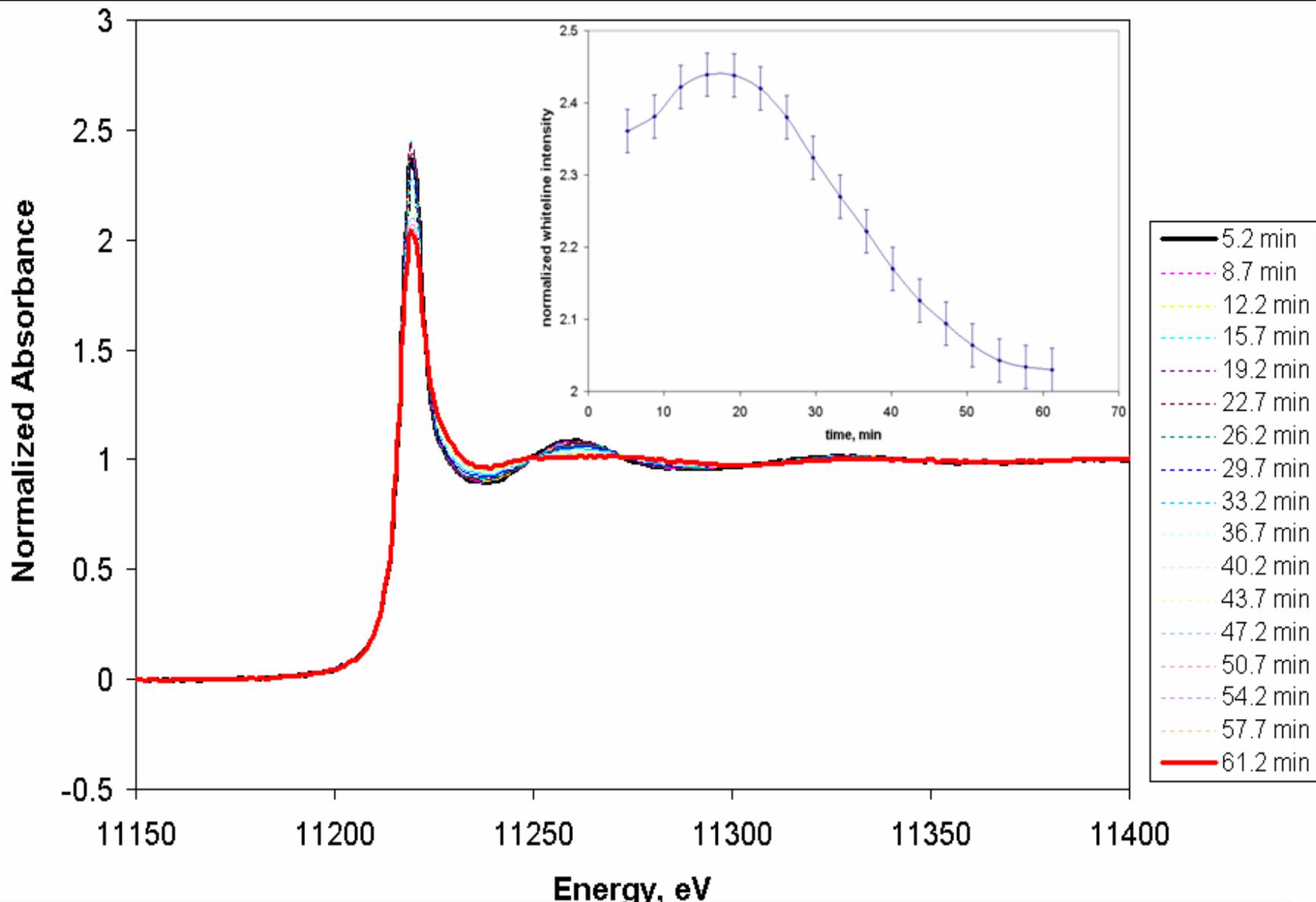
- Ir-Ir contribution increases—**clusters formed**
- Ir-C & Ir-O contributions decrease concomitantly
- Cluster formation begins in H₂ flow at elevated temperature

Temperature ramp to 80 °C in H₂ flow in 1 h – EXAFS



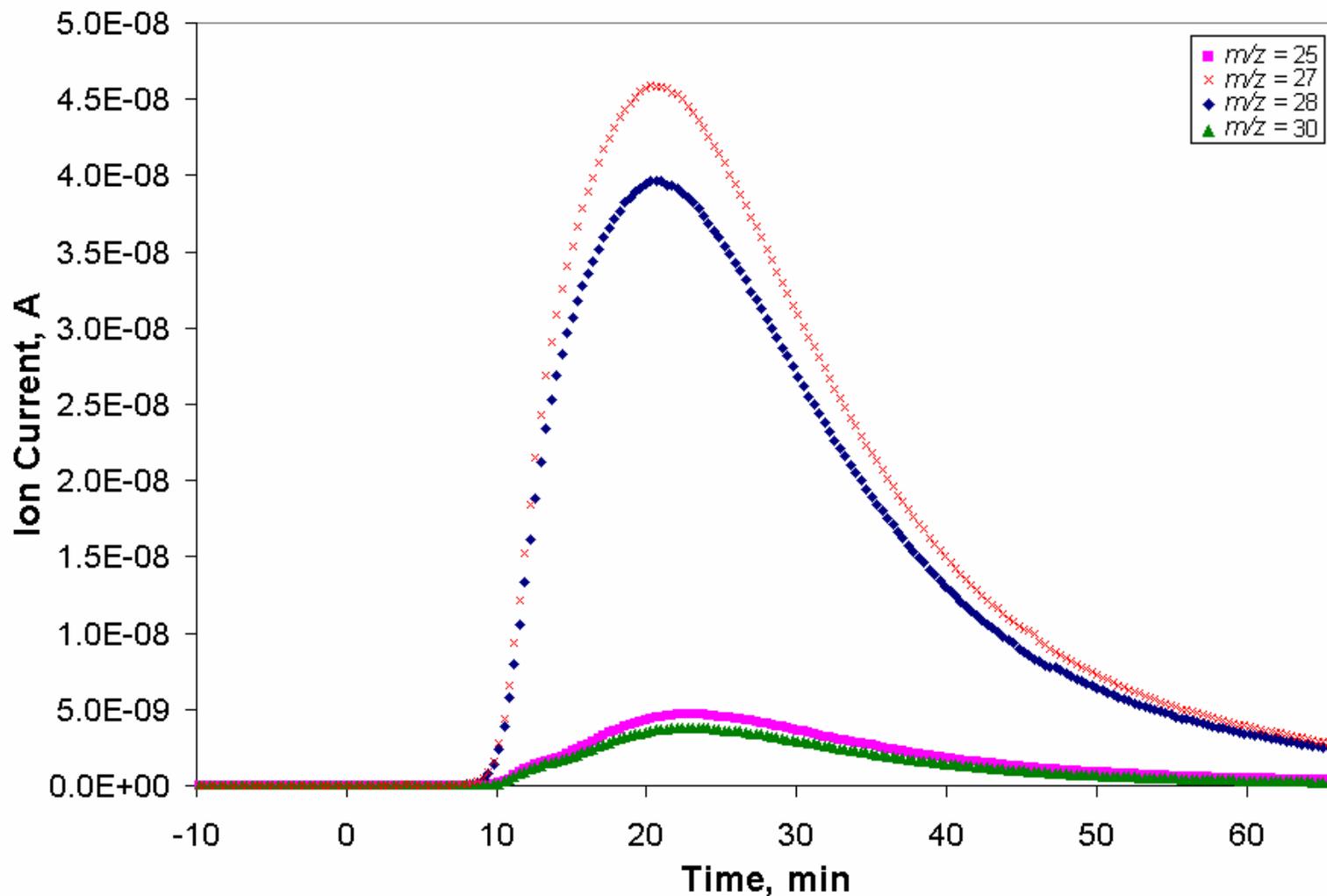
- Cluster formation begins at about 50 °C
- Clusters (data indicate Ir₄) form; rate increases as clusters form
- Ir–C coordination number decreases from 4 to 1, evidence of a carbon ligand

Temperature ramp to 80 °C in H₂ flow in 1 h – XANES



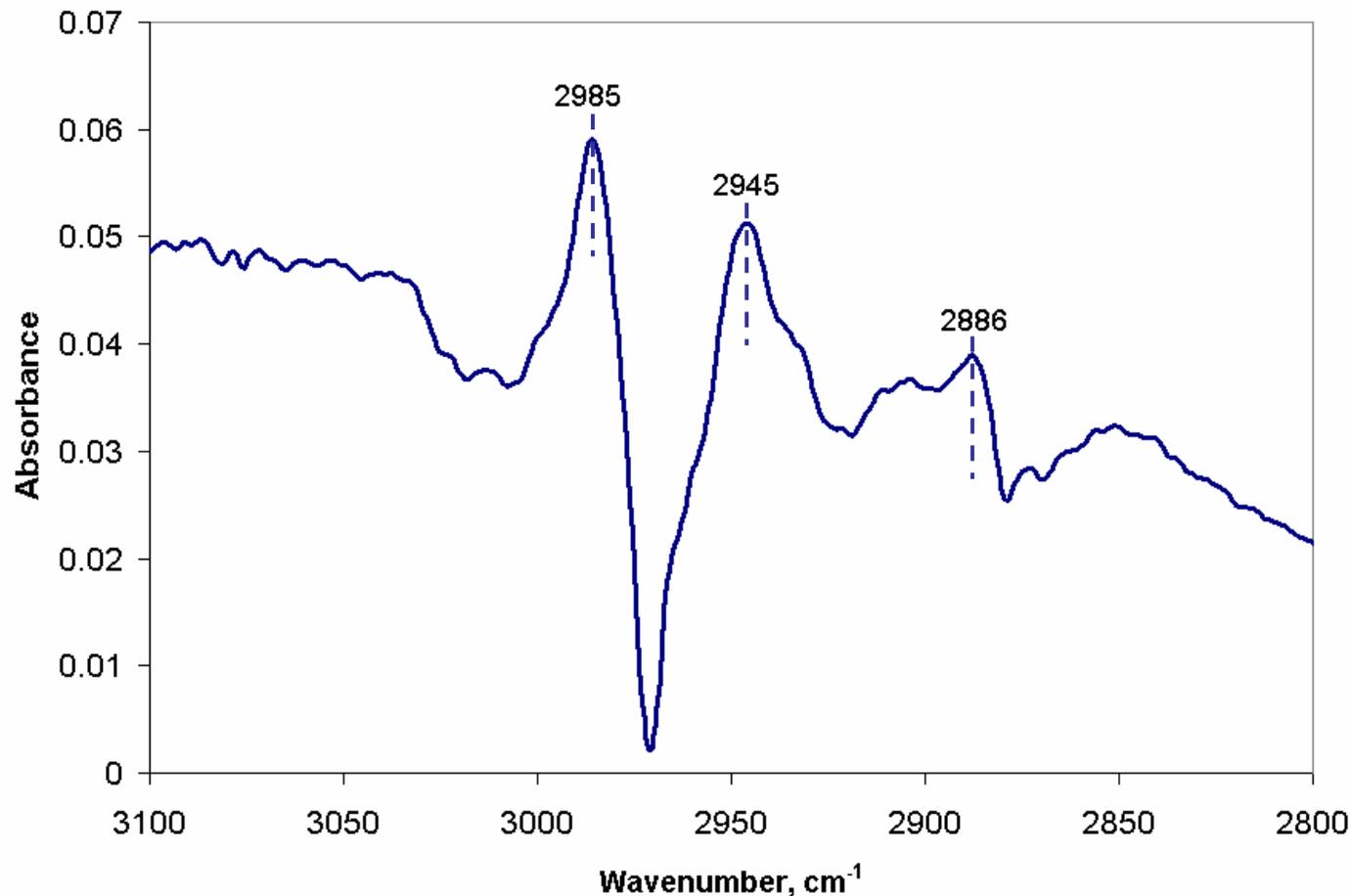
Isosbestic points: evidence of structural changes as mononuclear complex converted to clusters

Temperature ramp to 80 °C in H₂ flow in 1 h – GC & mass spectrometry data



MS & GC: Ethane is produced—presumably related to catalysis although one reactant missing from gas phase (but still present on surface)

Temperature ramp to 80 °C in H₂ flow in 1 h – IR results (difference spectra:
spectra at 80 °C in H₂ flow [end of ramp] – spectra at RT in H₂ flow [initial])



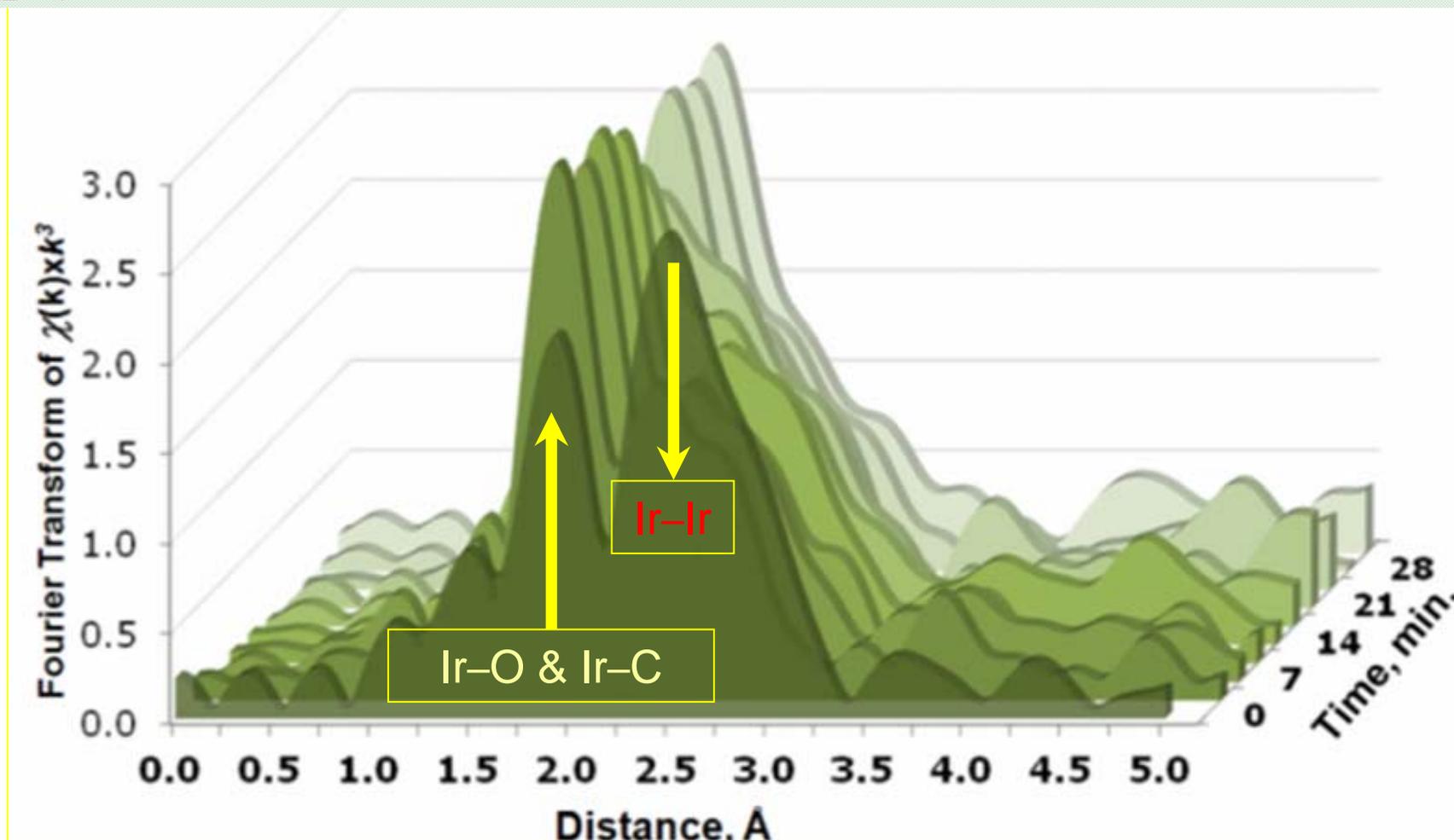
For comparison: CH₃CH₂Cl bands:¹ 2983, 2946, 2890 cm⁻¹

Confirm formation of ethyl ligands during H₂ treatment—suggested catalytic intermediate

¹Shimanouchi, T. In Tables of Molecular Vibration Frequencies; National Standard Reference. Data Series; National Bureau of Standard Washington, DC, 1967.

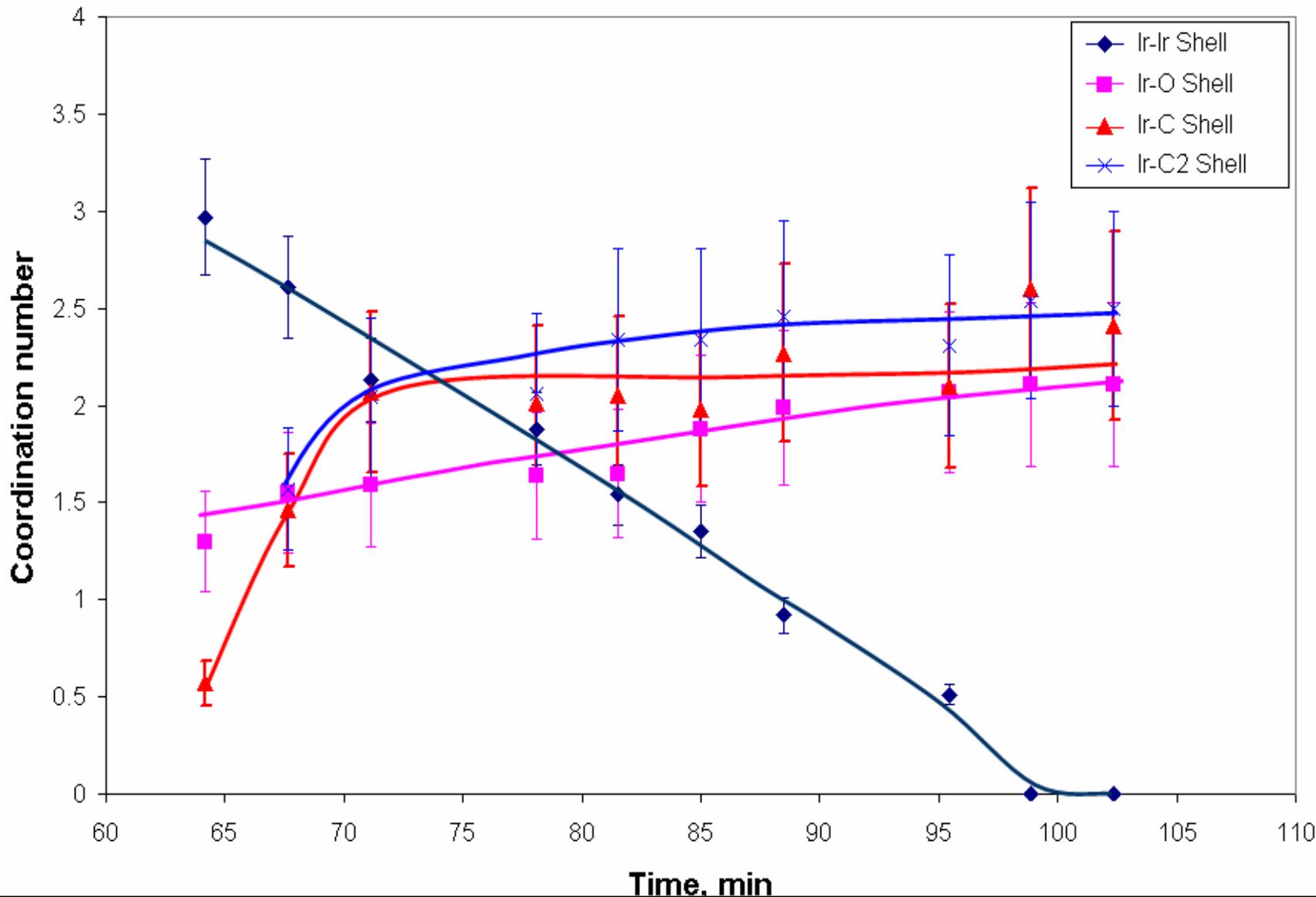
NEXT SET OF EXPERIMENTS:

C_2H_4 flow at 80 °C – EXAFS in R space



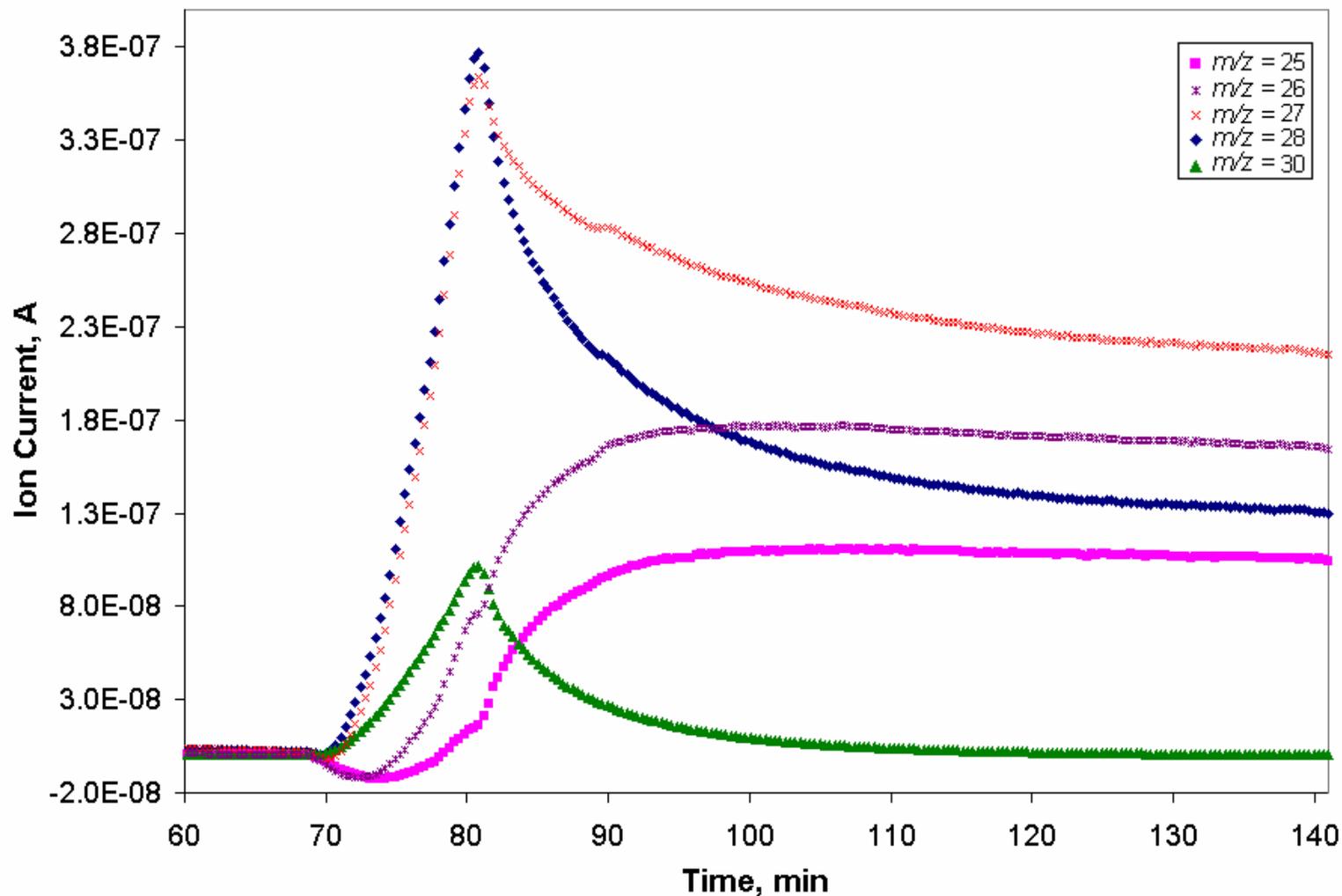
- Ir-C & Ir-O contributions increase
- Ir-Ir contribution decreases
- Clusters break up in ethylene (CLUSTER FORMATION REVERSED)

C_2H_4 flow at 80 °C – EXAFS results



Ir–Ir coordination number decreases from 3 to undetectable: Break-up of clusters (tentatively, Ir_4) in flowing C_2H_4 at 80 °C. **Reconstruction of mononuclear complexes.** Postulate coordination of ethylene ligands.

Sample in flowing C_2H_4 at $80\text{ }^\circ C$ – mass spectrometry data



Ethane produced until all remaining surface hydrogen consumed
Presumably related to catalytic hydrogenation

CLUSTERS ON SUPPORTS

EXAFS and STEM: Synergy

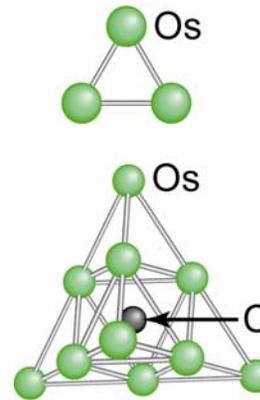
MgO-supported $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$

MgO-supported $\text{Os}_3(\text{CO})_{12}$ treated in He and CO at 548 K

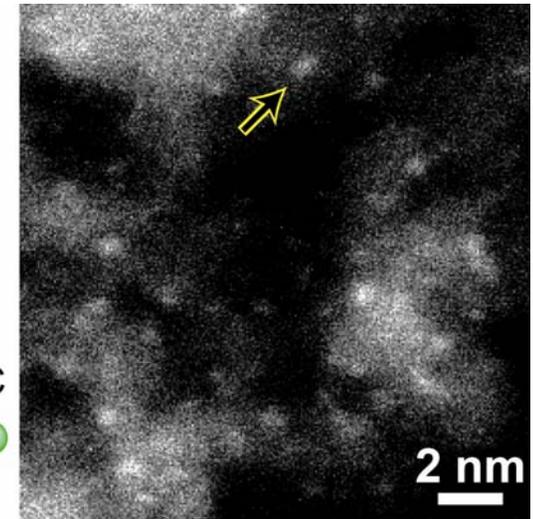
EXAFS

	<i>N</i>	<i>R, A</i>
Os-Os	2.5	2.89
Os-Os	2.3	2.73

EXAFS and STEM results agree with crystallographic data characterizing $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$



TEM



Uniform metal species on non-uniform support

Capability for characterization of decarbonylated clusters during catalysis by both techniques at very low pressures

Where next?

Focus X-ray beam at individual cluster or complex

Combine imaging & structural determination

match conditions (pressure, temperature, reactive atmosphere)

Real-time structural changes by complementary techniques recorded simultaneously

- XAS
- IR
- XRD
-

Make measurements on time scale of chemical bond breaking & formation

Extend to increasingly nonuniform catalysts

Acknowledgments

U.S. Department of Energy, Basic Energy Sciences
NSF, Chemical & Transport Systems



National Synchrotron Light Source



Advanced Photon Source

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Alper Uzun
Apoorva Kulkarni
Jim Haw & research group
Dave Dixon & research group
Nigel Browning