

Depth-dependent Characterization of (Ag,Cu)(In,Ga)Se₂ by X-ray Absorption Spectroscopy

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Cu(In,Ga)Se₂-based (CIGS) solar cells are high-performance thin-film photovoltaic devices renowned for their chemical stability and high light absorption coefficient. Alloying CIGS with silver to form (Ag,Cu)(In,Ga)Se₂ (ACIGS) can further improve the device by improving the crystal quality, increasing the optical bandgap and open-circuit voltage.^[1] While the role of Ag on the device performance and crystal structure has already been analyzed,^[2] important gaps in our understanding remain, especially with regard to the atomistic (short-range) structure. Specifically, recent studies by X-ray absorption spectroscopy (XAS) have shown that local atomic arrangements in Ag-free CIGS deviate from the long-range crystallographic structure deduced from X-ray diffraction (XRD) measurements.^[3] However, it remains to be found how these structural deviations evolve with Ag alloying, particularly in the presence of Ga depth gradient used in the actual absorber films. XAS is an element-specific technique that offers chemical sensitivity to probe local environment of elements. Angular resolved XAS allows for depth-profiling studies and measures sub-nanometer scale structure and compositional variations at varying depths within thin films, minimizing bulk contribution and enables high-sensitivity surface measurements (in grazing incidence mode).^[4]

In this work, we employ angle-resolved XAS to probe the local environment of the elements at different depths and at the film surface by varying the incidence angles between 0.05°, 0.5°, and 10°. We analyze several high-performance (~19%) ACIGS devices with overall [Ag]/([Ag]+[Cu]) ratios below 0.2 and a clear compositional Ga gradient. By complementing these results with XRD measurements for the long-range structures, glow discharge optical emission spectroscopy (GDOES) for the elemental profiles, and scanning transmission electron microscopy (STEM) for the morphologies, changes in element-specific bond lengths, cell parameters, and anion displacement depending on compositions of Group [I] (Cu, Ag) and Group [III] (In, Ga) within different depths of samples were mapped. The results suggest that the local atomic arrangement of the investigated (A)CIGS thin film solar cell samples is depth dependent and deviates from the long-range crystallographic structure. Possible reasons for this deviation including anion displacement, tetragonal distortion and/or the presence of other phases or off stoichiometry compounds will be discussed. These findings offer a better understanding of the atomic-scale properties of ACIGS in the actual thin-film solar cells containing in-depth composition variations.

[1] M. Edoff, et al. *IEEE J. Photovol.* 2017, 7, 1789.

[2] J. H. Boyle et al. *J. Appl. Phys.* 2014, 115, 223504.

[3] C. S. Schnohr et al. *Acta Materialia* 2018, 153, 8.

[4] J. Just, D. et al. *APL Mater.* 2017, 5, 126106.



Depth-dependent Characterization of $(\text{In,Ga})\text{Se}_2$ by X-ray Absorption Spectroscopy

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Why solar power?



Energy crisis & climate catastrophe
Developments in renewable energy is key importance to transition to net zero by 2050.
Si solar cells dominate the solar market (95%)
However; high material consumption & High energy payback time (years)

Motivation

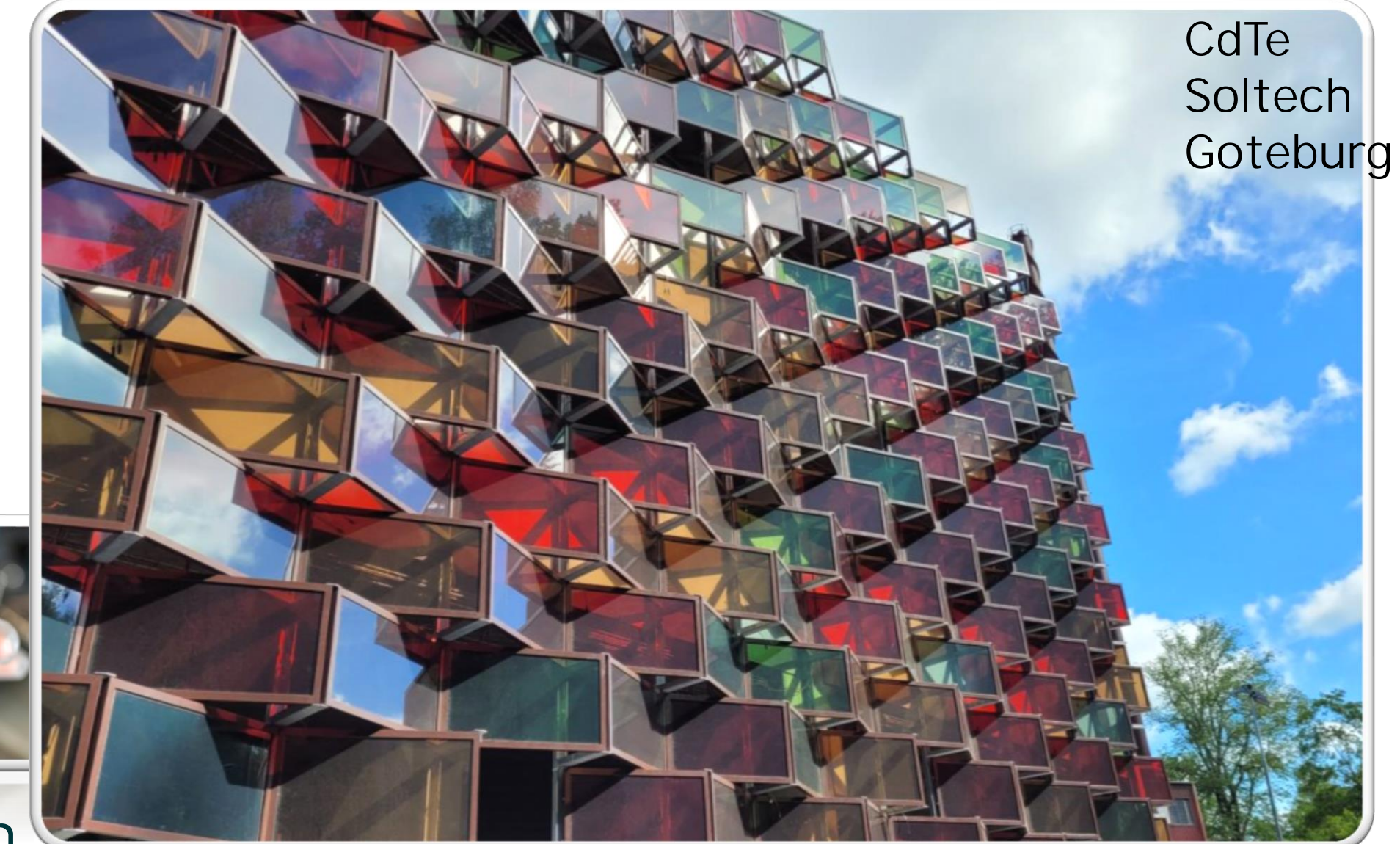
TFSCs cannot yet compete with fossil fuels due to high cost. For efficient solar cells, understanding their structure performance relationships at atomic level through advanced synchrotron techniques is crucial.



Aim

Investigation of structural deviations between local atomic arrangements in the TFSCs and long range crystallographic structure and how they evolve with alloying, which can pave way for high band gap applications such as tandem solar cells by increasing optical band gap and operating voltage.

Thin film solar cells



Low material consumption: cheaper
Flexible, semi-transparent, lightweight
Short energy payback time (10-15 months)
Commercially available
Good efficiency: a-Si: 14.0%, CdTe 22.1%, $(\text{In,Ga})\text{Se}_2$: 23.4%

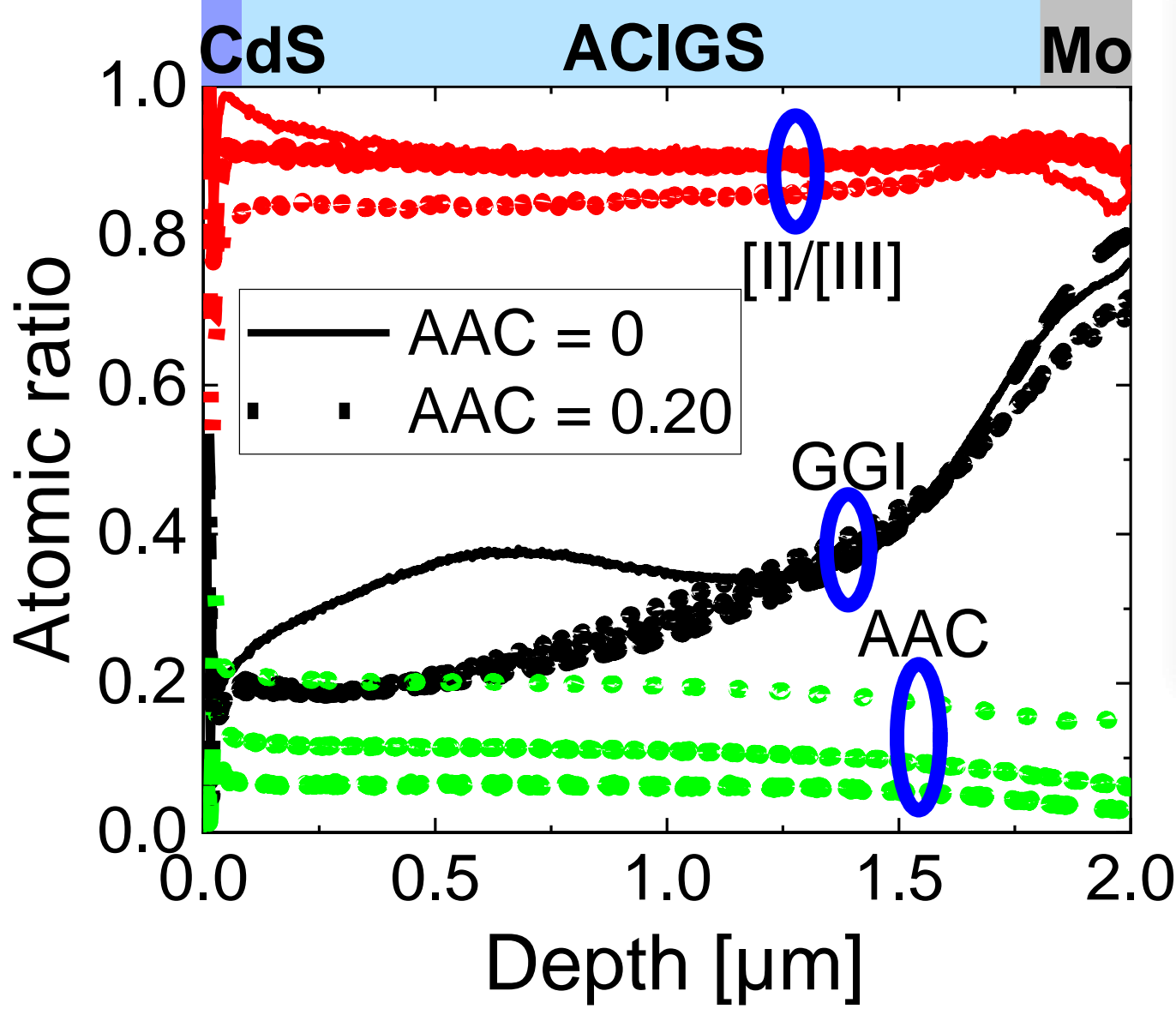
Devices synthesis & characterization

CuInGaSe_2 (CIGS) and $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ (ACIGS) devices with varying $\text{Ag}/(\text{Ag}+\text{Cu})$ (AAC) and $\text{Ga}/(\text{Ga}+\text{In})$ (GGI) ratios were synthesized by sputtering.
Deposited Ag replaces Cu atoms in the structure

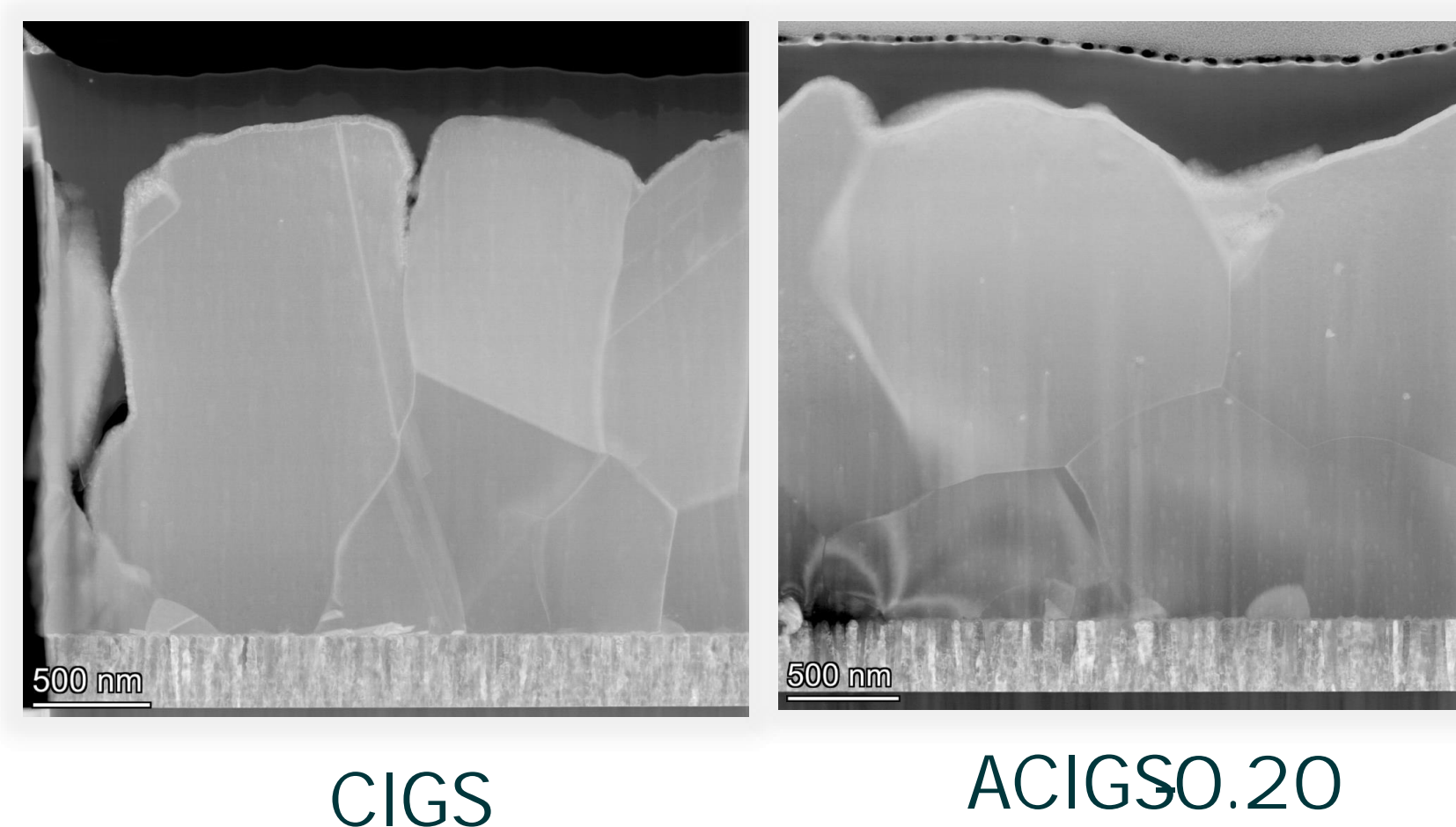
Sample compositions by XRF

Sample	Cu%	In%	Ga%	Se%	Ag%	I/III	Ga/III	Ag/(Ag+Cu)
CIGS	23.2	15.2	10.3	51.4	0	0.91	0.40	0
ACIGS0.05	21.4	16.3	8.8	52.3	1.3	0.90	0.35	0.05
ACIGS0.10	20.3	16.2	8.8	52.5	2.3	0.90	0.35	0.10
ACIGS0.20	17.8	16.6	8.9	52.7	4.1	0.86	0.35	0.19

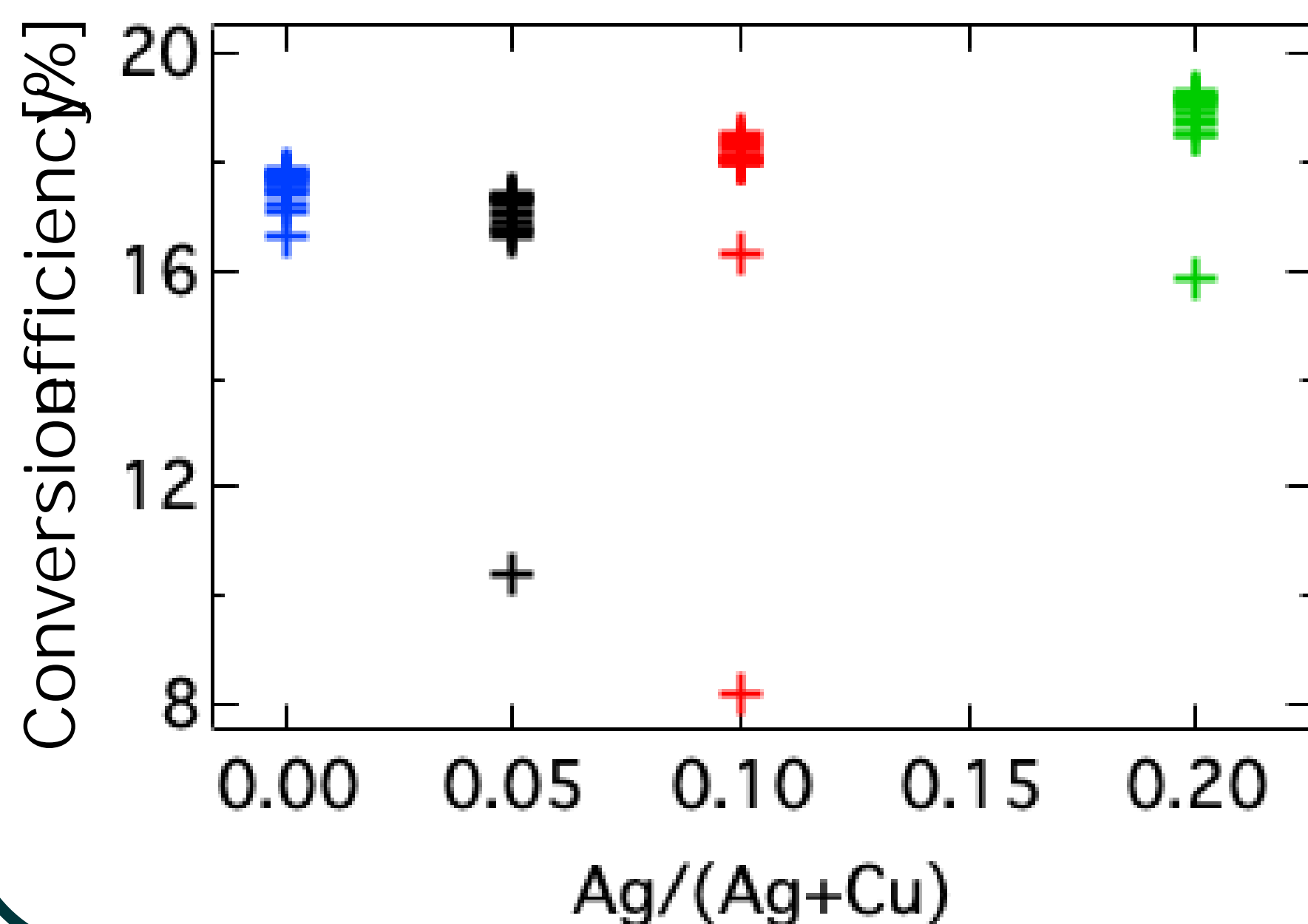
Glow discharge optical emission spectroscopy



STEM annular dark field images



Ga and Ag composition profile within the ACIGS absorbers vary: likely to influence the local atomic structure
Slightly larger grains in the samples containing Ag



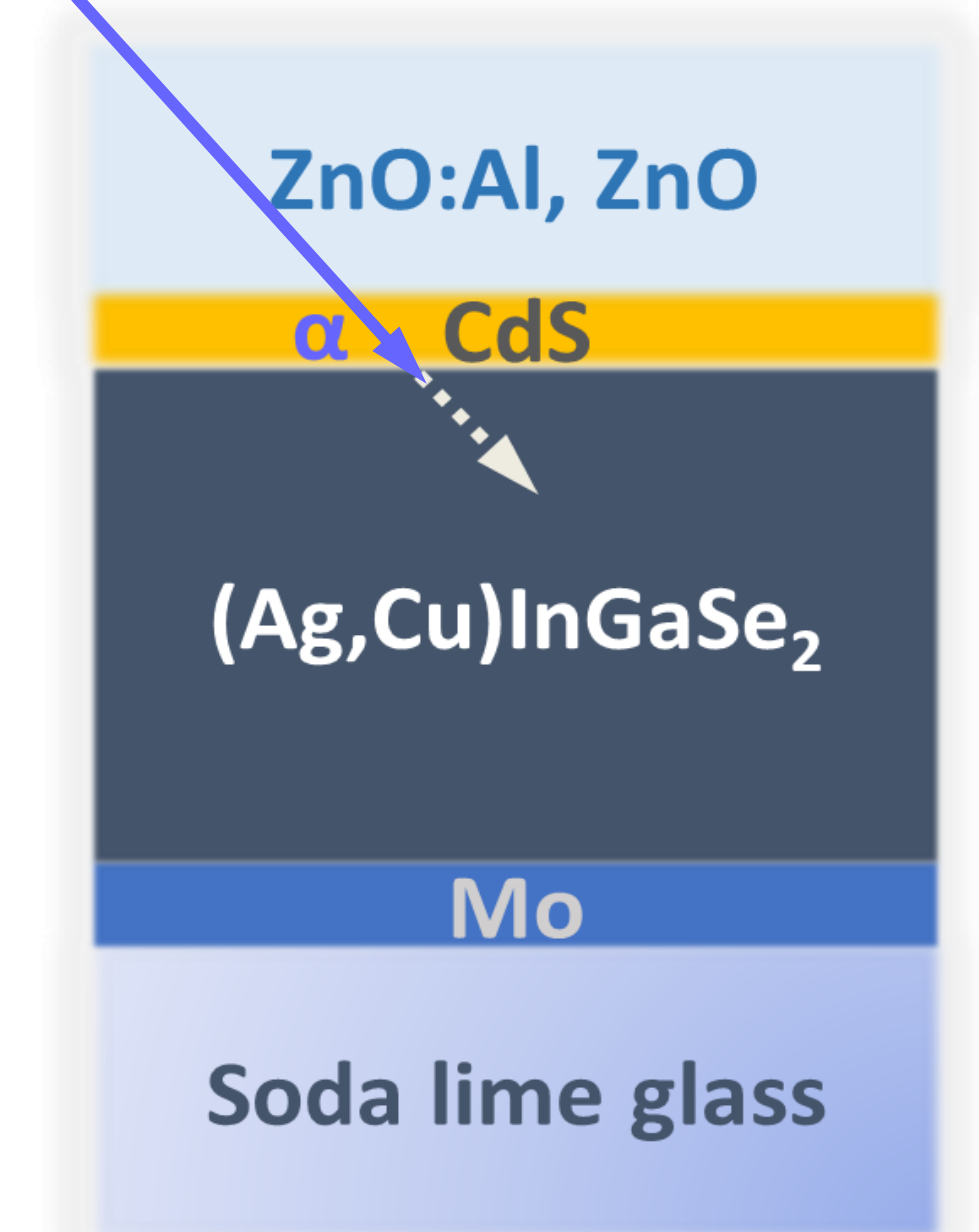
Device performance

Power conversion efficiency of CIGS thin film solar cells increase to ~20% with Ag alloying.

X-ray absorption spectroscopy experiments

Accurate probe of chemical, electronic and geometric structure
Compositional changes, bond distances, neighboring atom species, distances, and coordination numbers
Oxidation state, coordination chemistry, bond lengths

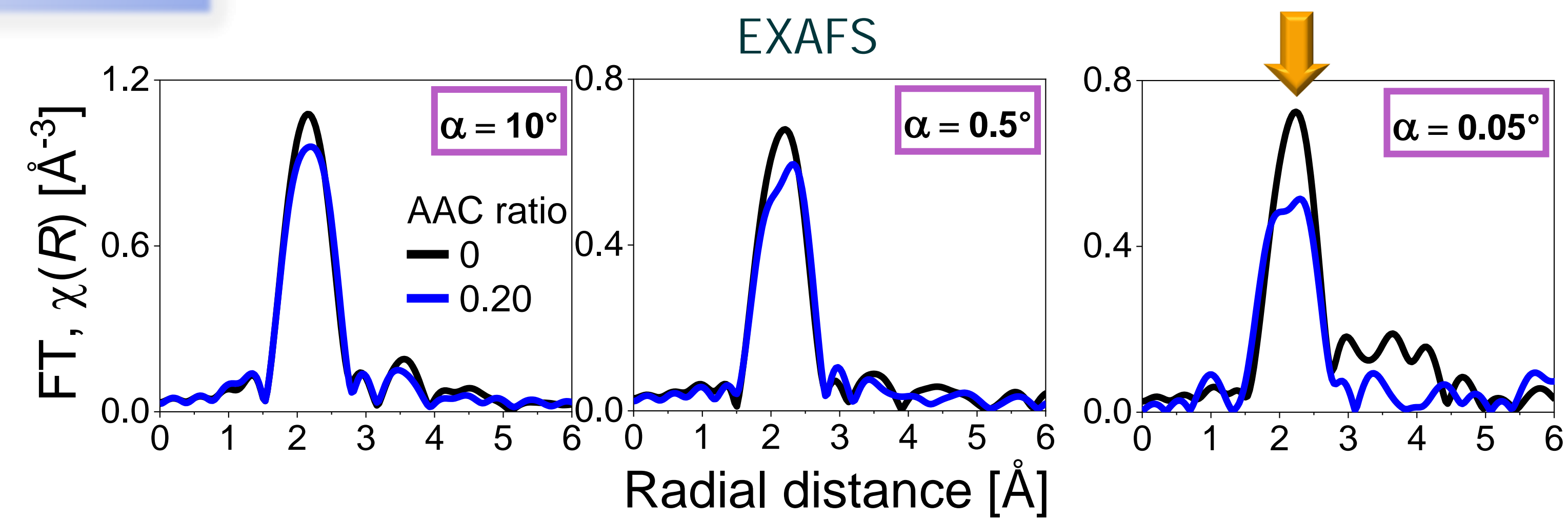
incident X-ray beam



Angle resolved XAS allows investigation of compositional and structural changes at different probing depths from the surface of films

- $\alpha = 10^\circ$ (~2000 Å)
- $\alpha = 0.5^\circ$ (~120130 Å)
- $\alpha = 0.05^\circ$ (~35 nm)

More pronounced effect of Ag alloying near the film surface

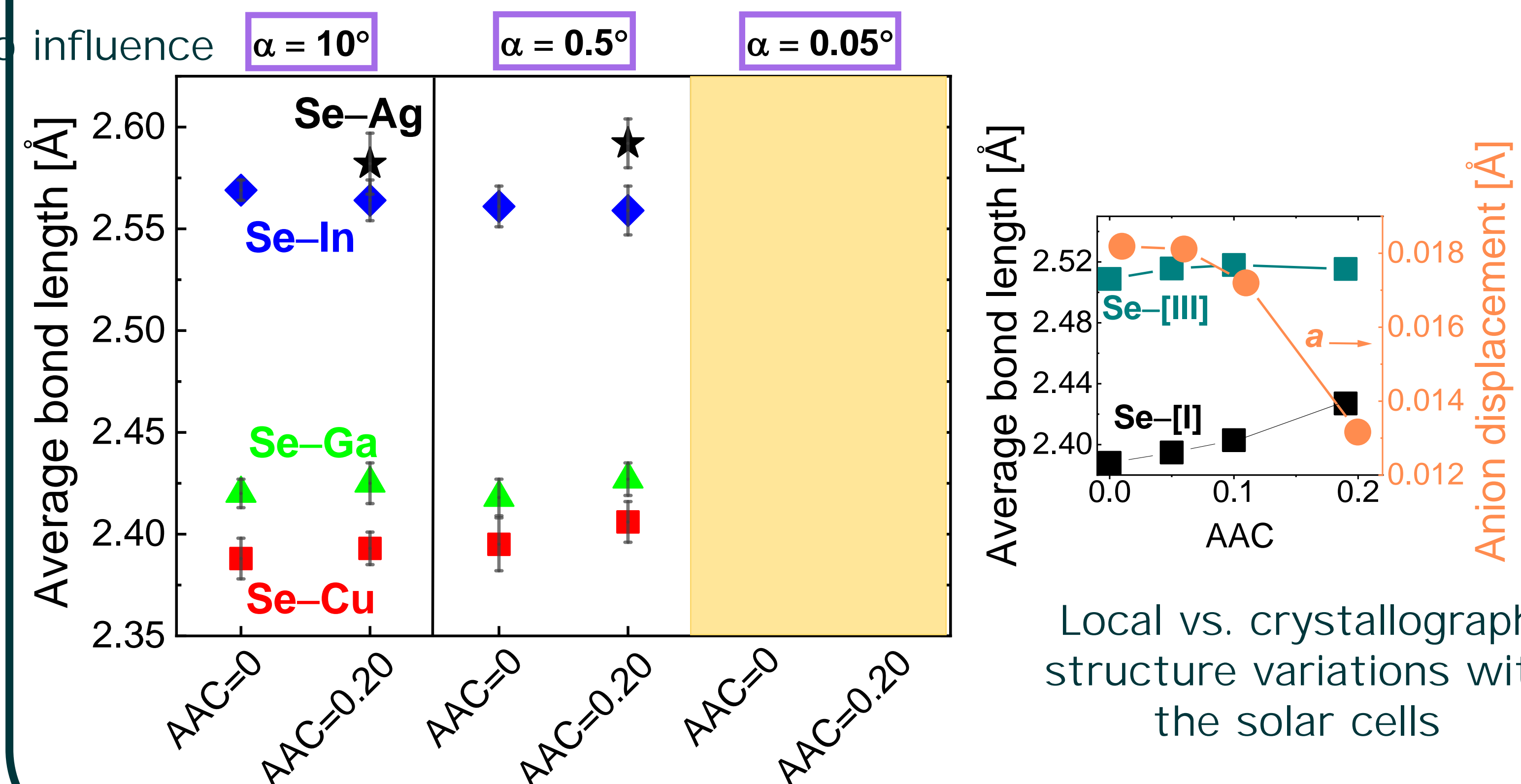


With increasing Ag content:

Non-

The anion position in the mixed ACIGS system is influenced by sublattices Ag and Cu, or In and Ga, thus strongly depends on charge compensation

A coexistence of many different anion configurations is expected



XAS spectra collected at Cu K, Ga K, and Se K edges at room temperature

Conclusions

Local atomic arrangement for the investigated ACIGS absorbers is depth dependent (due to compositional variations) and deviates from the long range crystallographic structure.

Investigation of TFSCs at atomic level through synchrotron techniques offers opportunities for rational design of solar cells with improved efficiencies.

References

- N. M. Martin et al. ACS Appl. Mater. Sci. 2022, 5, 461.
- J. D. Sachs et al. Nat. Sustain. 2019, 2, 805.

Acknowledgements



In-Situ X-ray Absorption Spectroscopic Characterization of Oxidized Iron Intermediates in the Catalytic Oxidation of CO with N₂O

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Elucidating relationships between active site speciation and catalytic function continues to remain a challenge in heterogeneous catalysis, although *in-situ* studies under reaction-relevant operating conditions can provide novel insight into the nature of active sites and aid in clarifying complex reaction mechanisms. *In-situ* x-ray absorption spectroscopy (XAS) measurements specifically have been widely used in the field of catalysis to reveal information regarding the oxidation state and local coordination environment of active species during reaction that can be key to identifying kinetically-relevant intermediates and determining reactivity-dependent catalyst changes.

Here, we describe for a metal-organic framework (MOF) catalyst, formed by the combination of Fe₃O inorganic nodes linked by organic trimesate molecules, the use of *in-situ* XAS measurements to identify short-lived reaction intermediates key to the redox activity for the reaction of CO with N₂O. Specifically, a microreactor assembly was employed for monitoring the catalyst in a plug-flow design using a capillary polyimide tube for supporting the catalyst to allow sufficient x-ray transmittance at the iron K-edge. Under steady state reaction conditions at 473 K, different equilibrated concentrations of oxidized iron intermediates were identified under varying partial pressures of the reactants. Through estimation of Fe-O bond lengths by analysis of the extended x-ray absorption fine structure combined with linear combination fitting of the absorption edge for characterizing the iron oxidation state, it was determined that the reaction of N₂O with Fe²⁺ active sites results in the formation of iron-oxyl (Fe³⁺-O⁻) intermediates. Results of this work provide novel insight into the transitory reactive species, aids in explaining their more radical character in comparison to iron-oxo (Fe⁴⁺=O²⁻) species characterized in other classes of synthetic catalysts,^[1] and may be applicable toward understanding structure-activity relationships in heterogeneous catalysts, more broadly.

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[1] Synder, B.E.R., *et al. Nature* 536 (2016) 317-321.

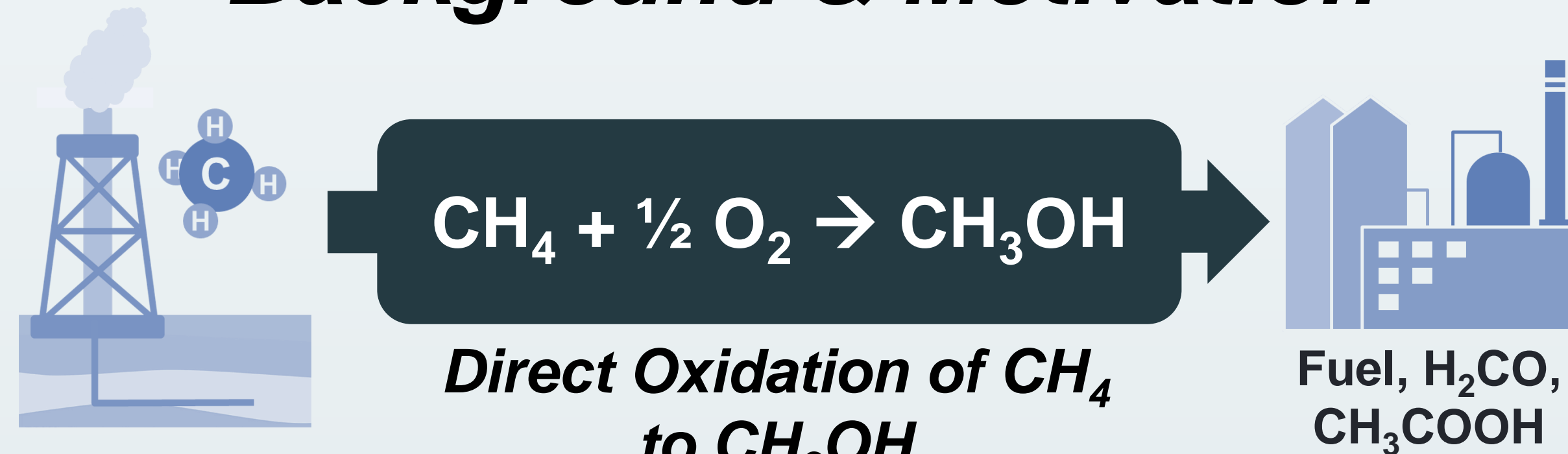
In-Situ X-ray Absorption Spectroscopic Characterization of Oxidized Iron Intermediates in the Catalytic Oxidation of CO with N₂O

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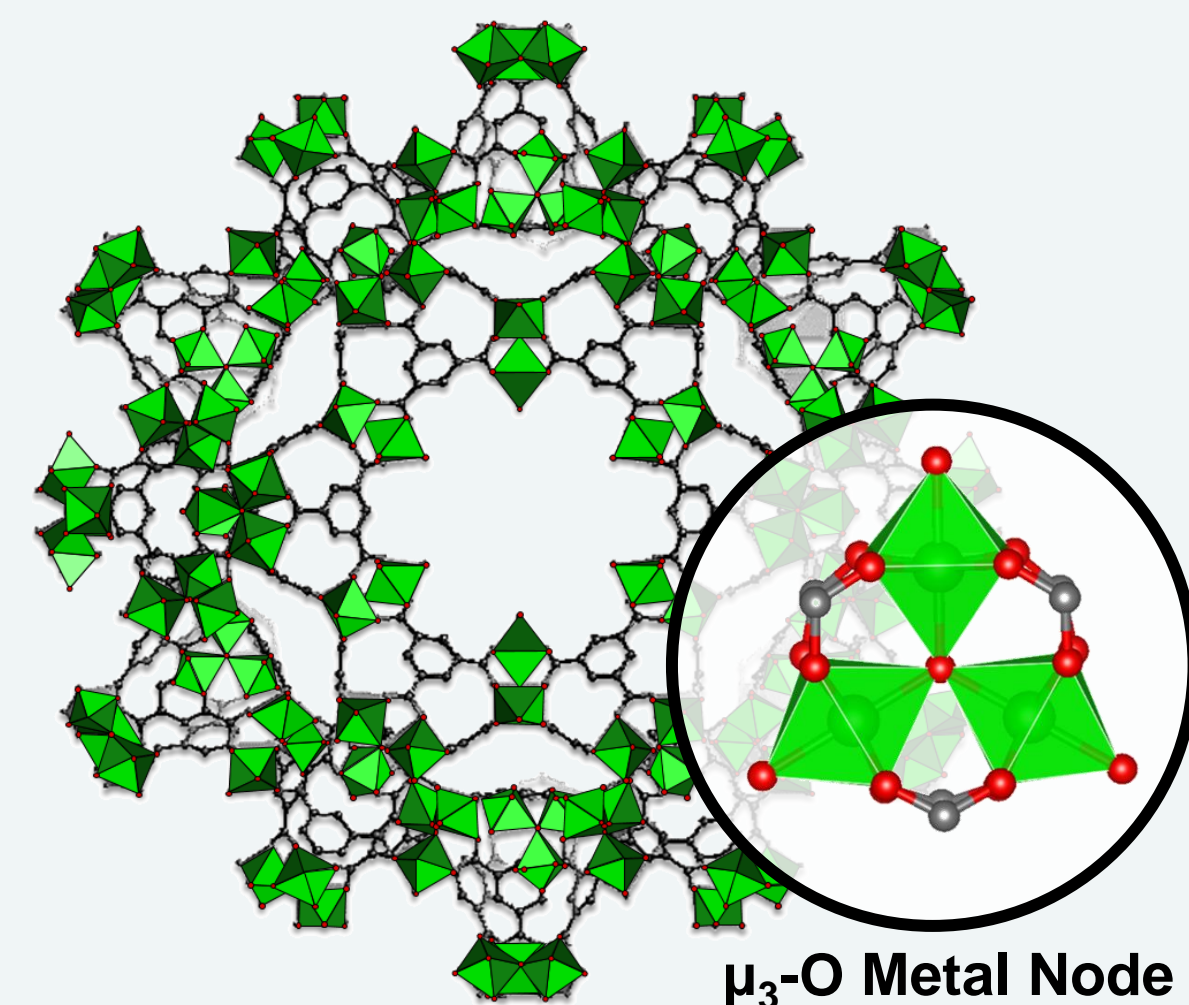
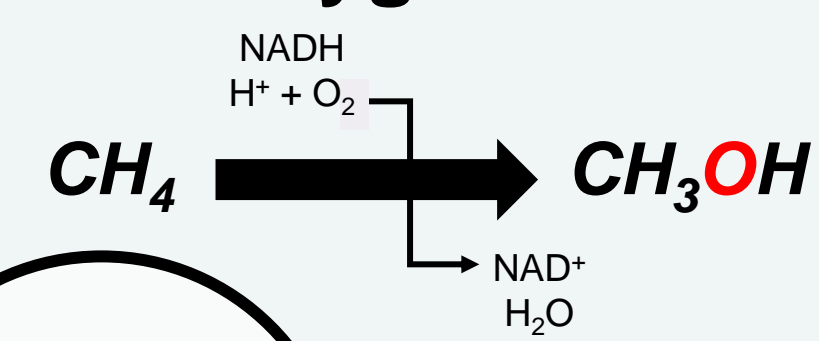
Background & Motivation



Bio-Inspired Metal-Organic Frameworks (MOFs)

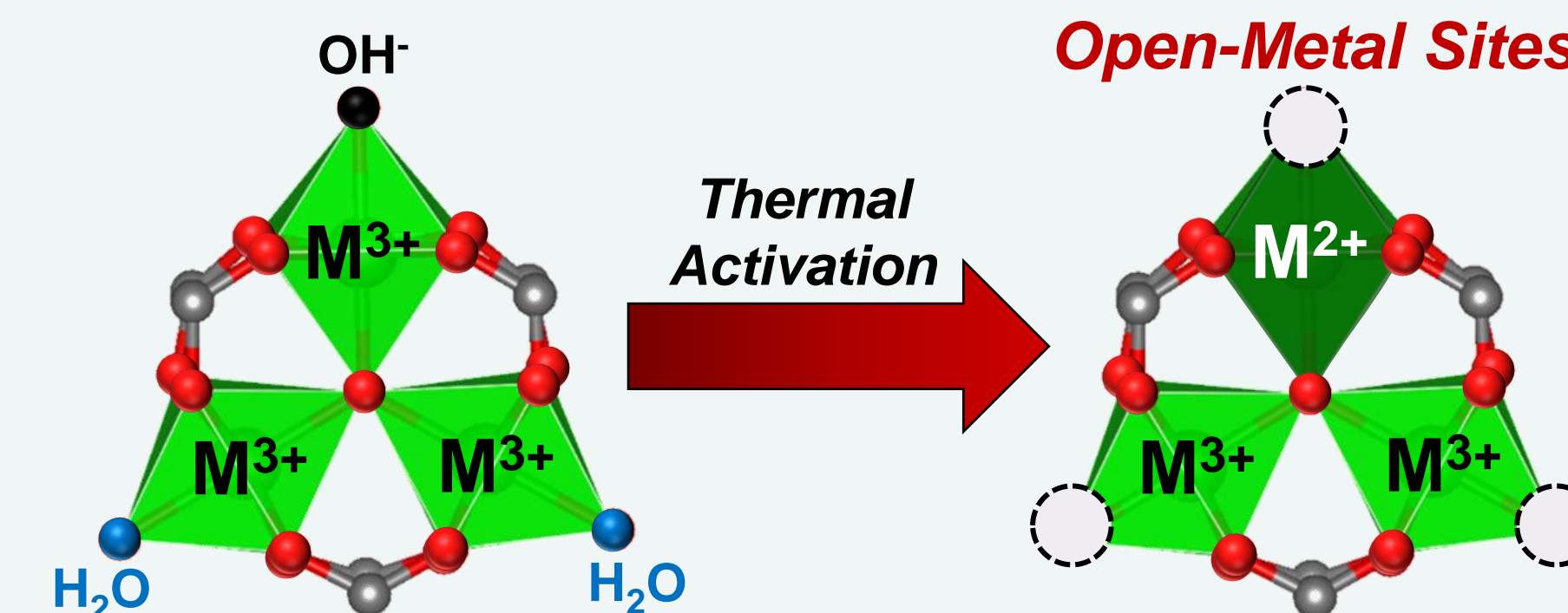
MIL-100^[1]

Methane Monooxygenase^[2]

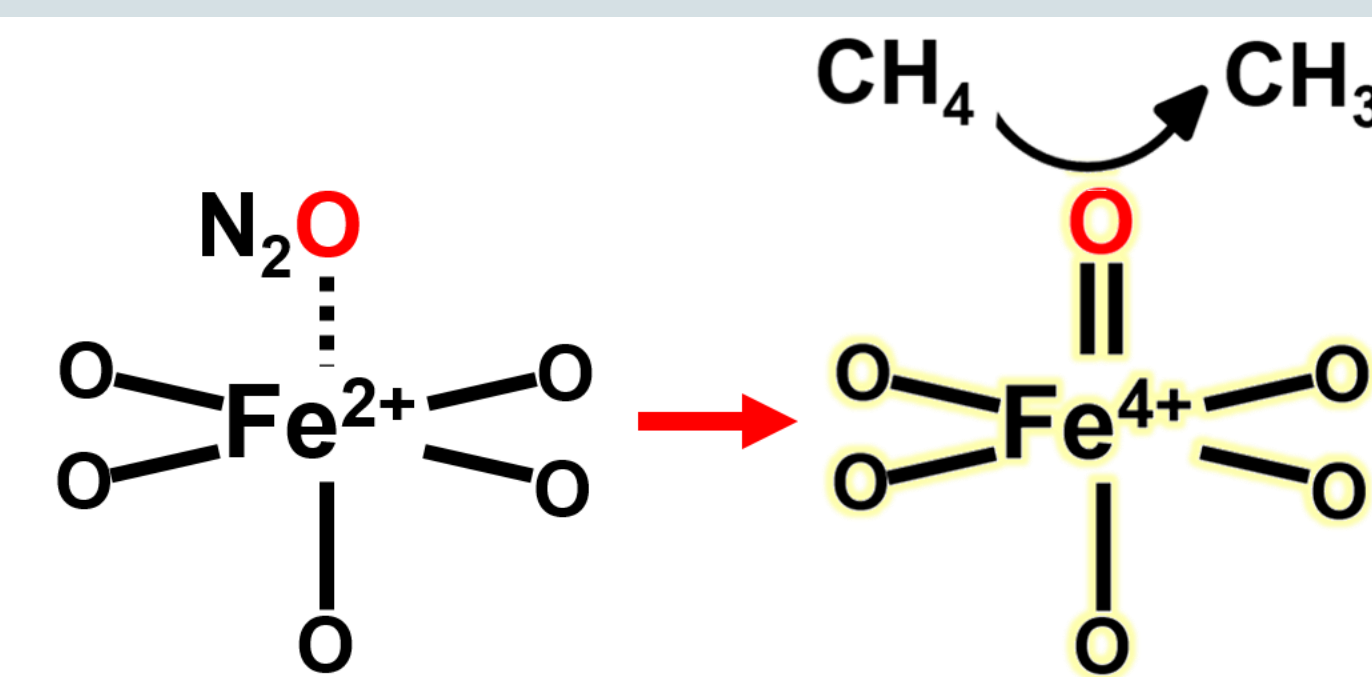


$\text{Fe}^{\text{IV}} \text{---} \text{O} \text{---} \text{Fe}^{\text{IV}}$

Active Site Formation



Oxo-Formation



DFT predicted Fe⁴⁺=O formation by the decomposition of N₂O on Fe²⁺ sites^[3]

RESEARCH GOAL: Elucidate reaction steps that mediate redox turnovers over MIL-100(Fe) with N₂O as an oxidant for the broad purpose of improving atomic-level efficiencies for light alkane conversion

Acknowledgements

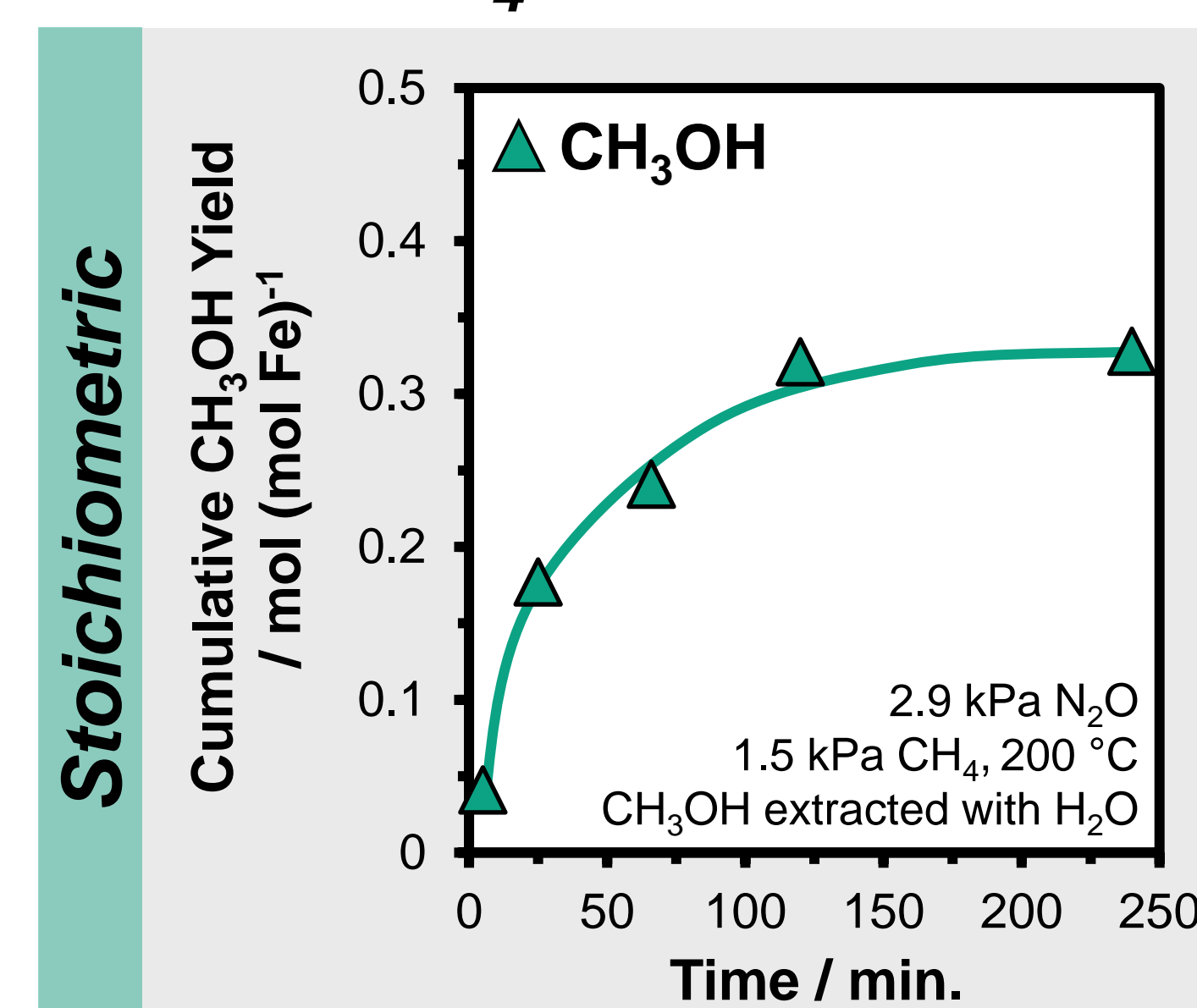
Financial support was provided through award # 61226-DN15 from the ACS Petroleum Research Fund (PRF). A portion of the work was supported by the U.S. DOE, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program. Work at Argonne National Laboratory was supported by the U.S. DOE, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, Catalysis Science Program under Contract No. DE-AC-02-06CH11357. Use of the Advanced Photon Source is supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DEAC02-06CH11357.

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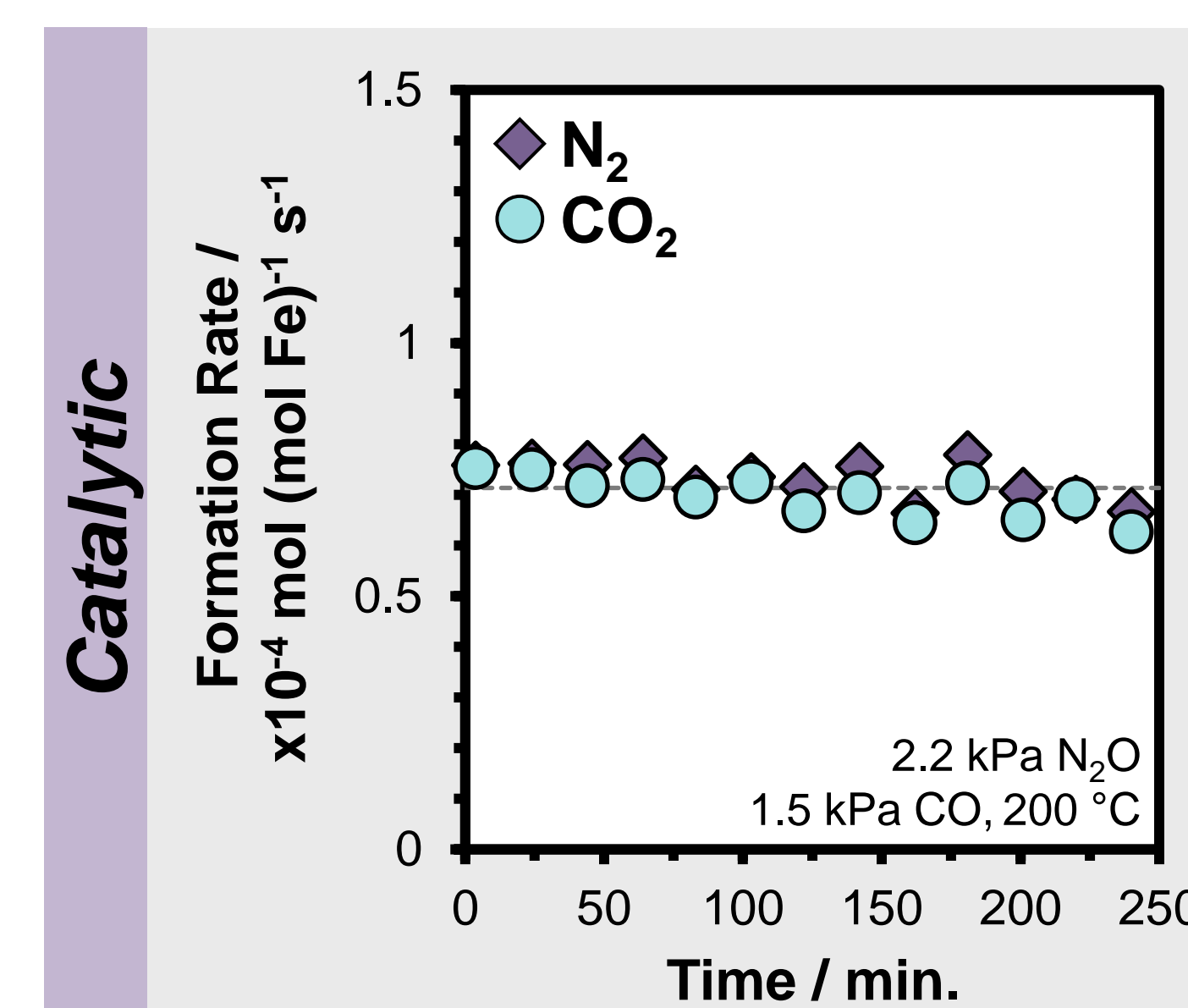
(1) Férey, G., et al., *Angew. Chem. Int. Ed.* 43 (2004) 6296. (2) Kopp, D.A., & Lippard, S.J., *Curr. Opin. Chem. Biol.* 6 (2002) 568-576. (3) Vitillo, J.G., et al., *ACS Catal.* 9 (2019) 2870-2879.

Oxidation of CO: Catalytic Probe

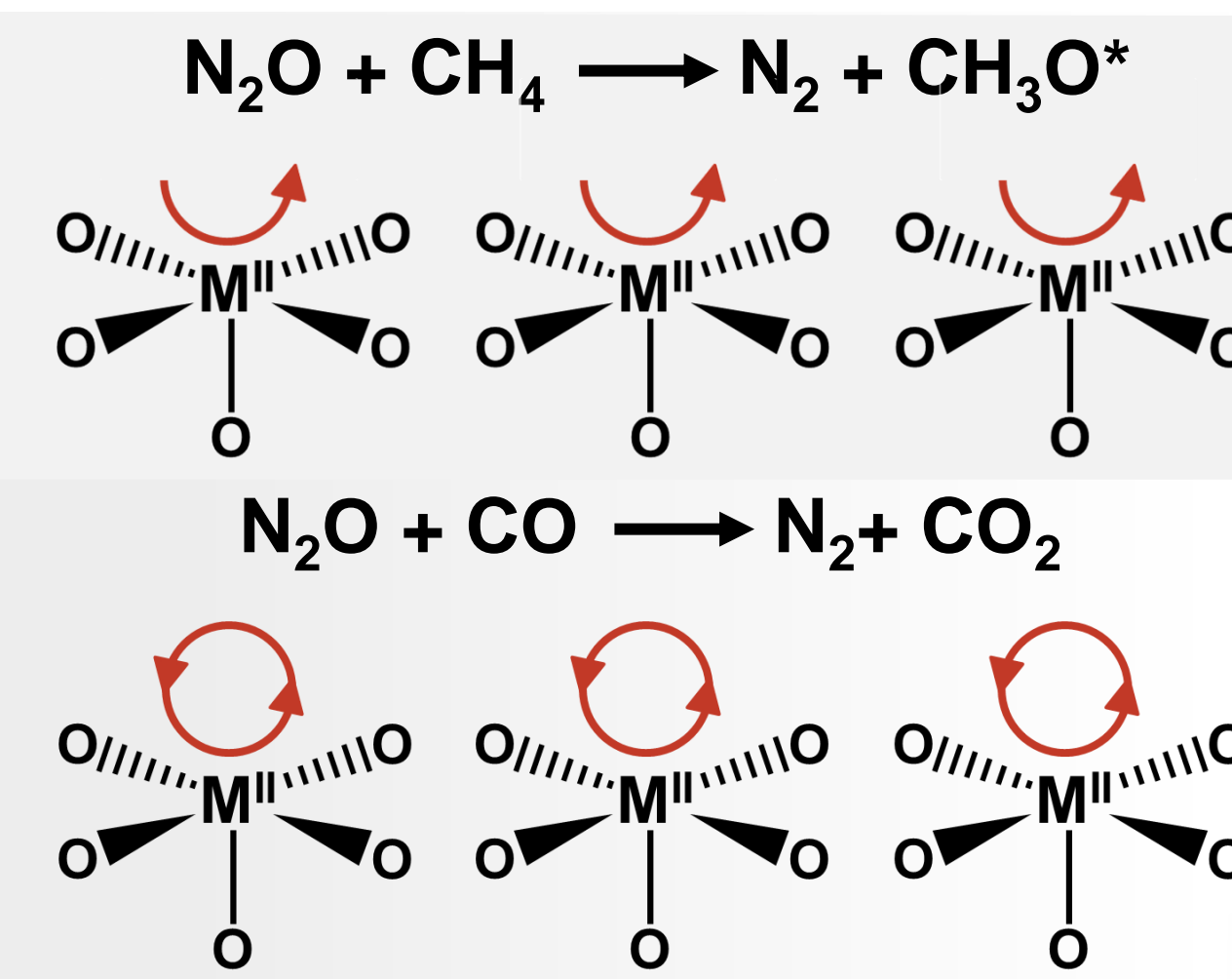
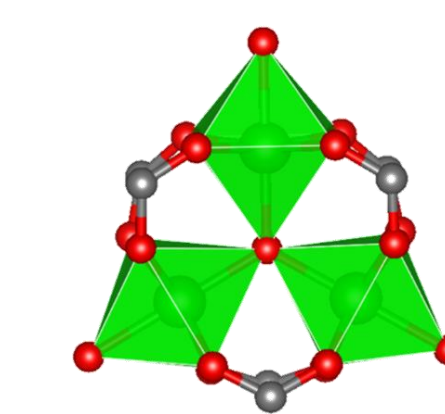
CH₄ Oxidation



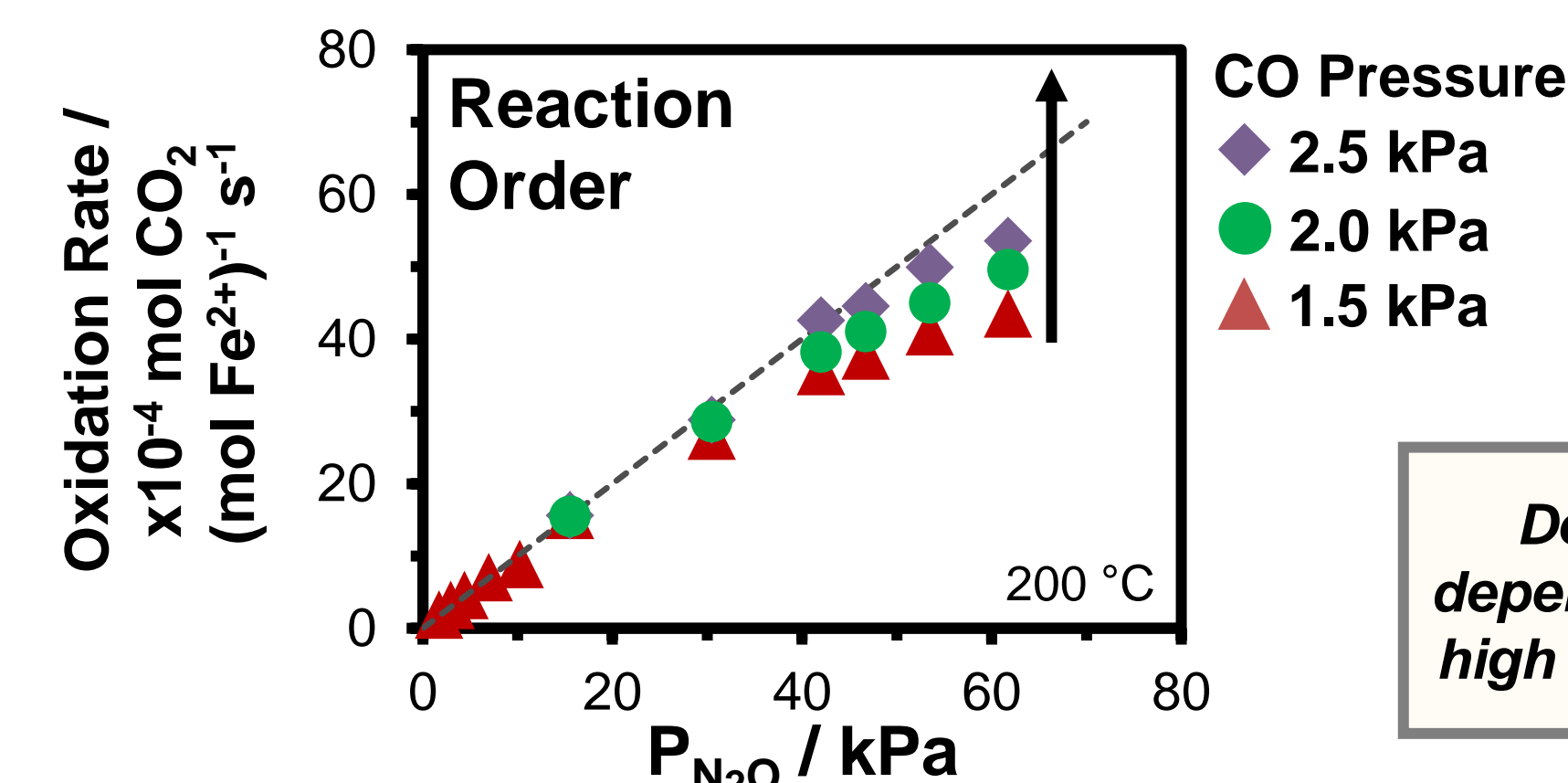
CO Oxidation



Utilizing catalytic CO oxidation to further understanding of N₂O-mediated redox cycles over trimeric nodes in MIL-100 catalysts



F-O Coverages during Steady-State Reaction



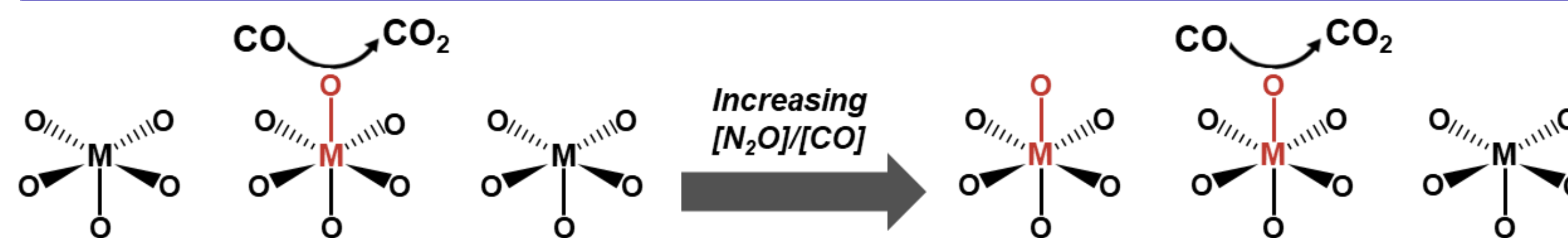
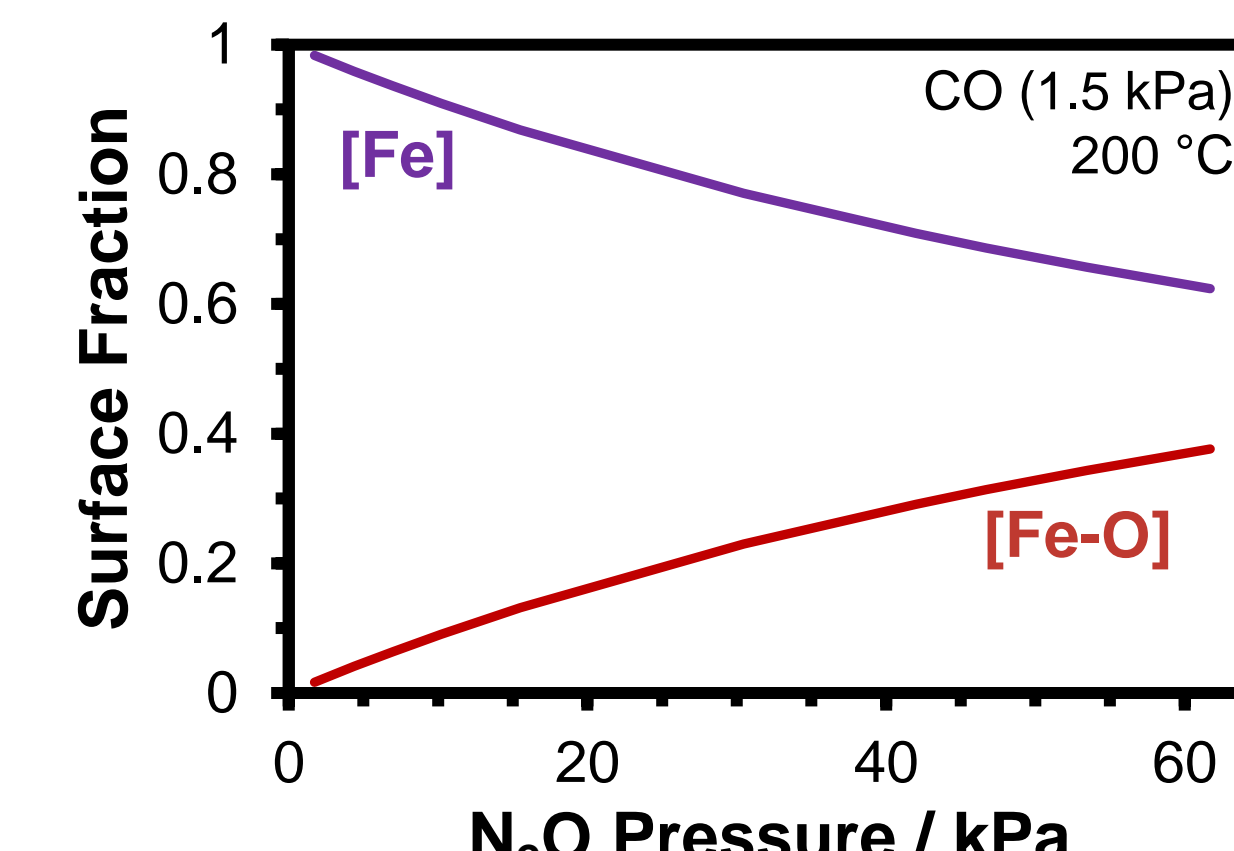
Reaction Kinetics

Deviation from first-order dependence on N₂O pressure at high N₂O/CO molar ratios (≥ 20)

Model Fitting

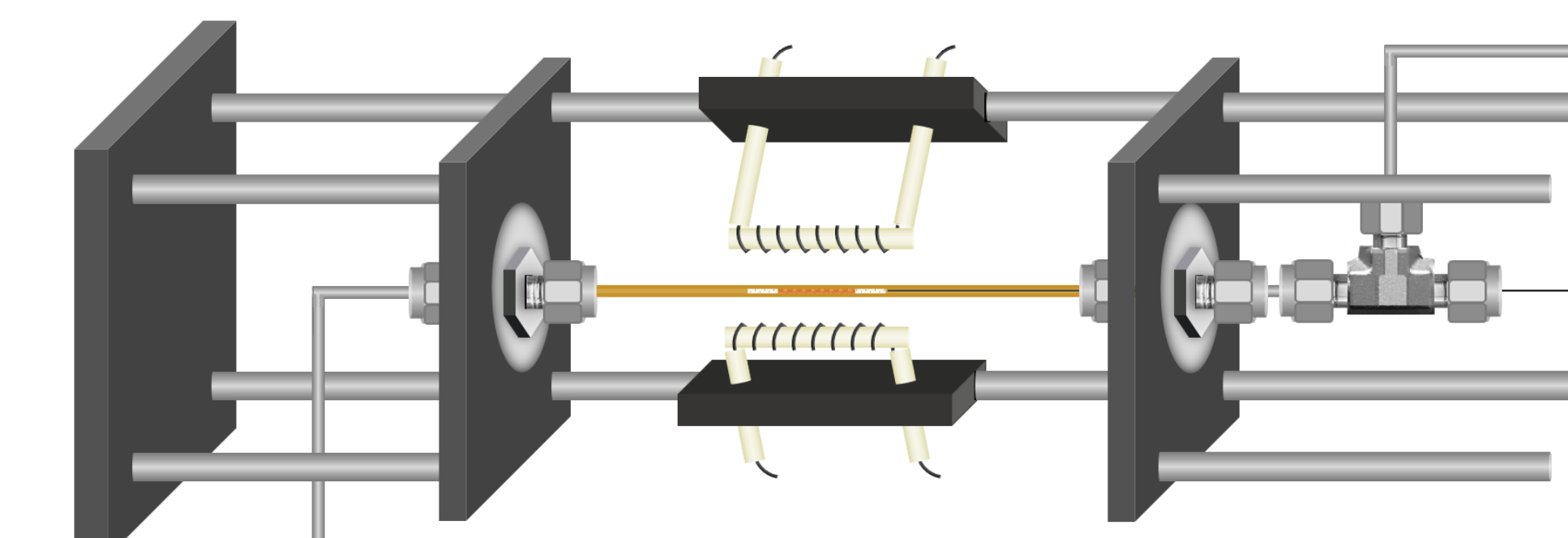
Simplified Rate Expression:

$$r = \frac{k_2 K_1 [\text{N}_2\text{O}]}{1 + \left(\frac{k_2 K_1 [\text{N}_2\text{O}]}{k_3 [\text{CO}] \left(1 - \frac{k_3}{k_3 + k_4} \right)} \right) [\text{Fe-O}]}$$

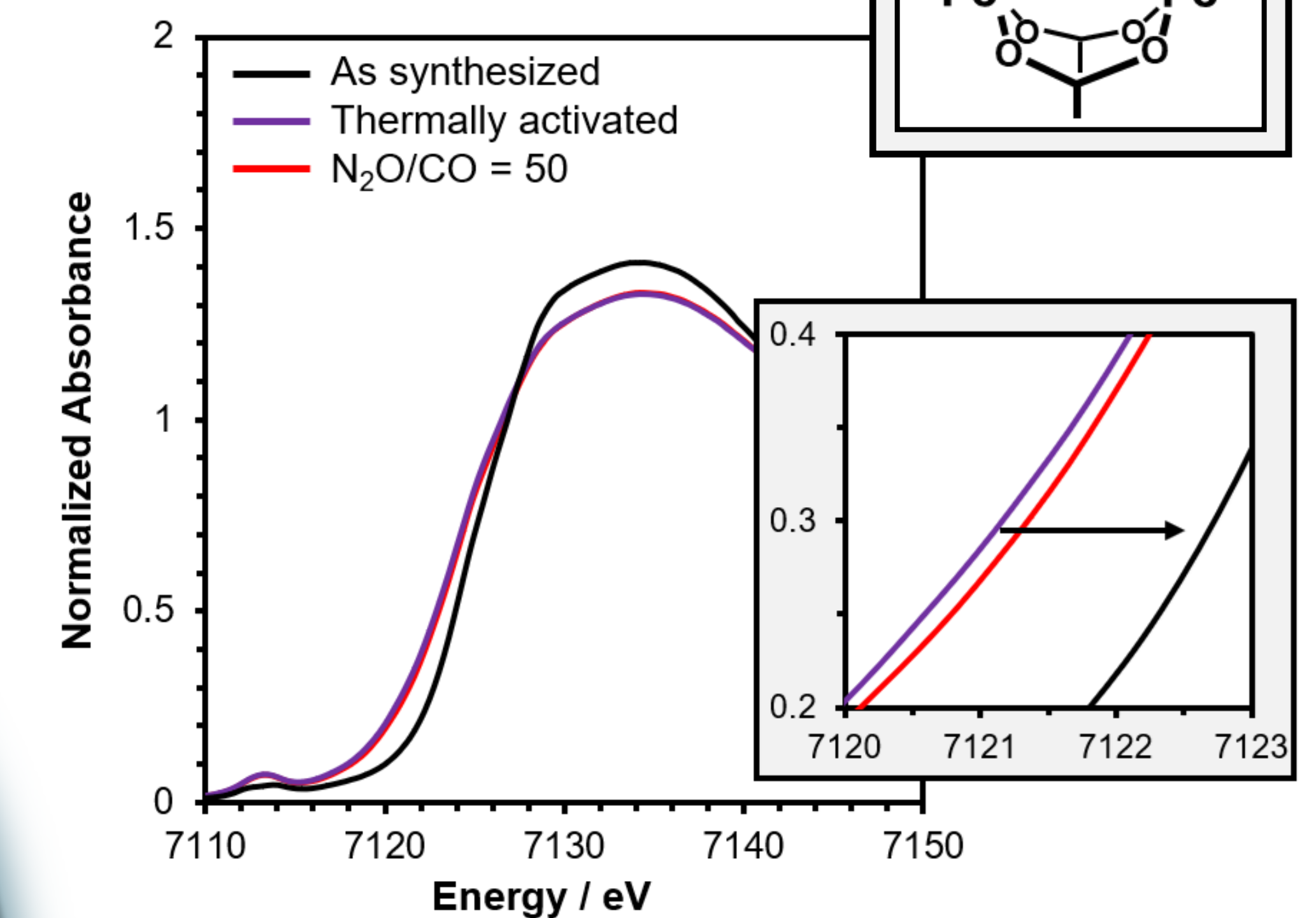
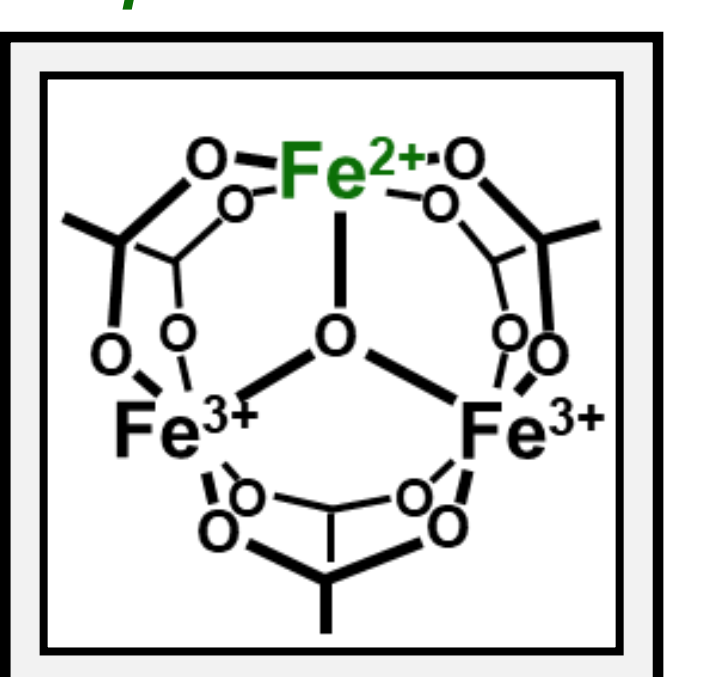


In-Situ XAS Characterization

X-ray Absorption Fine Structure (XAFS) Analysis



Proposed Active Site



Thermal Activation:

~ 30% of the total iron is reduced from Fe³⁺ to Fe²⁺

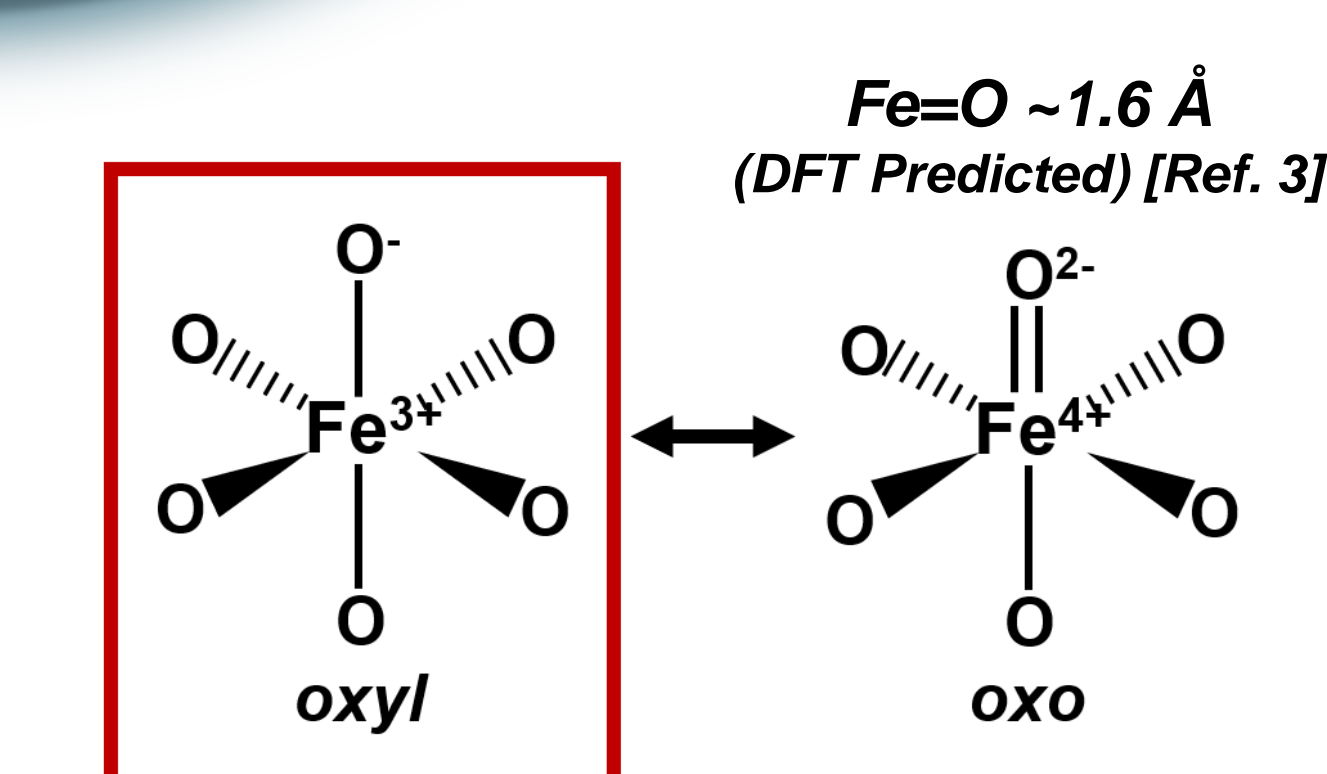
Under Reaction (N₂O/CO = 50):

Oxidation of iron observed in XANES spectra during reaction

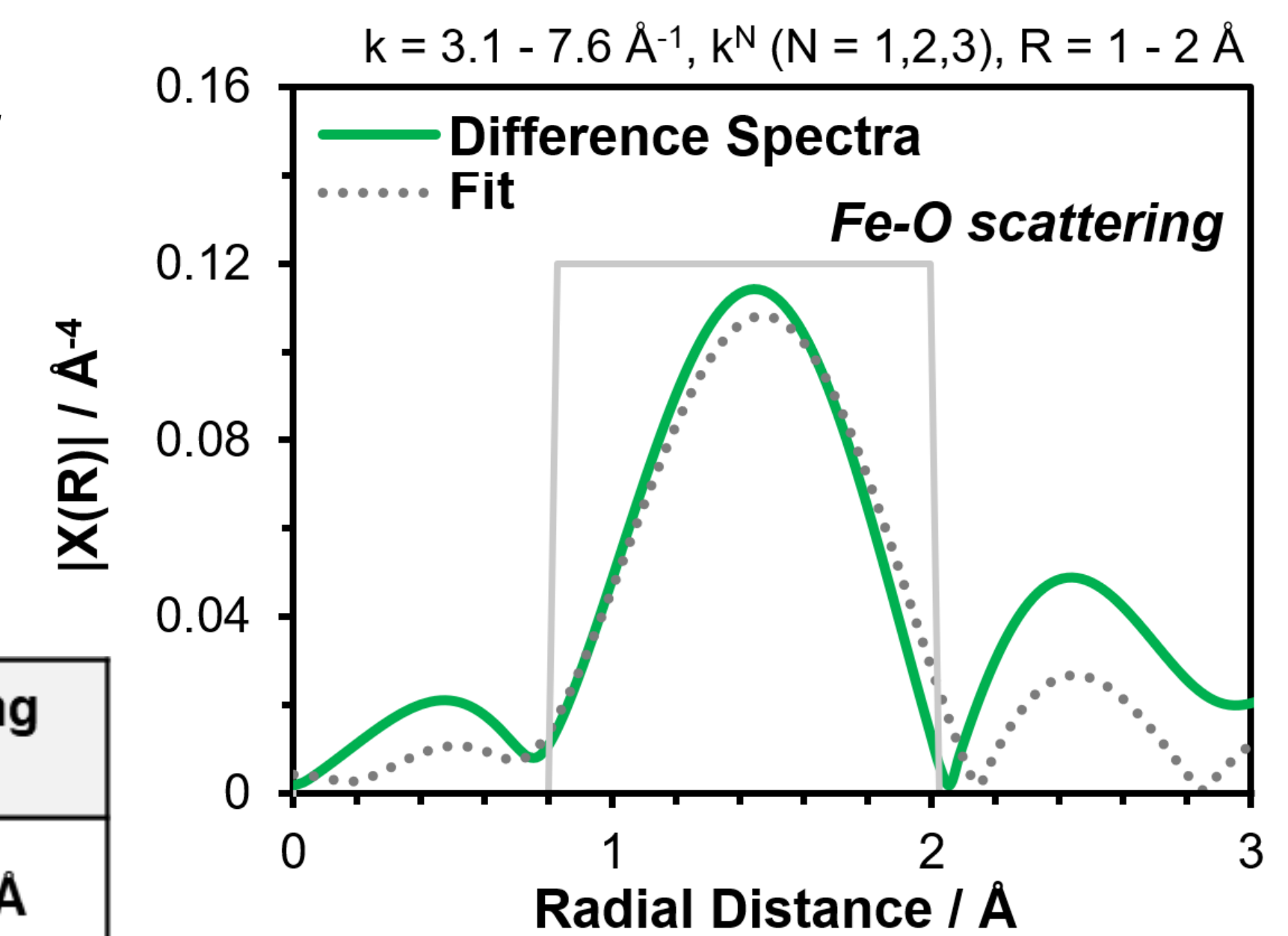
Characterizing Fe-O Intermediates

Difference Analysis

$$\left(\text{Sample Under } \text{N}_2\text{O/CO} \right) - \left(\text{Thermally Activated Sample} \right) = \left(\text{Difference Spectra} \right)$$



Fe-O Coordination Number	Fe-O Scattering Path Length
0.09 ± 0.03 mol (total mol Fe) ⁻¹	1.946 ± 0.026 Å



Fe-O intermediates exhibit oxyl character under steady-state reaction conditions and the fraction of oxidized iron (~ 9%) corresponds closely with estimates from kinetic measurements (~13%)