Quantitative Chemical Imaging of Atomic-Scale Chemistry Changes at Interfaces

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Purpose

- Understand quantitatively how structures evolve under different operating conditions, using new generation of aberration-corrected microscopes and in situ stages.
- Develop robust method to quantify atomic-scale changes in structure, composition, and bonding occurring at interfaces

Key Successes

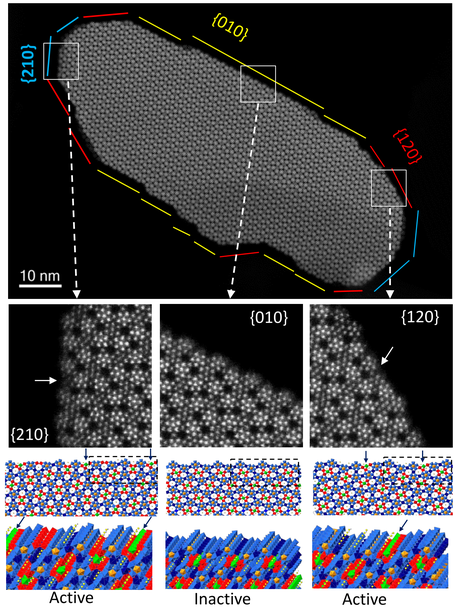
7 invited presentations at conferences and research institutions, 9 papers published in top journals, as exemplified by:

- JD Kistler, N Chotigkrai, P Xu, B Enderle, P Praserthdam, CY Chen, ND Browning, and BC Gates. 2014. Accepted in *Angewandte Chemie*
- P Xu, M Sanchez-Sanchez, D Hartmann, ND Browning, and J Lercher. 2014. Submitted to *Angewandte Chemie*
- SC Chambers, M Cu, P Sushko, H Yang, CM Wang, and ND Browning 2013. *Advanced Materials* **29**, 4001-4005.

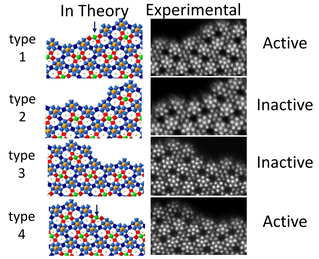
Research Accomplishments

Assessing the active sites for complex oxide MoVTeNbO catalysts

Direct Imaging of Crystal Termination



Predict Steps along Crystal Termination and Their Activity



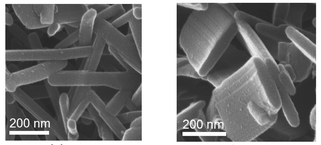
Statistical Analysis of Active Sites Exposure: From Atomic to Macroscopic Level

Sample	A	B
Morphology	Round rods	Flattened rods
Average cross-section [001] (nm^2) [a]	6637	26672
Average particle length (nm)[a]	2500	718
Frequency of lateral facet (%)[b]	{010}: 23.4 {120}: 43.5 {210}: 31.5 {001}: 1.6	{010}: 38.7 {120}: 32.5 {210}: 18.5 {001}: 10.3
Concentration of active centers (sites/nm^2) [c]	0.359	0.279
Activity in ethane ODH (μmol/g_{M1} s)[d]	190.6	144.5

Analyze many images to determine statistical prevalence of the active sites concentrated in a particular sample

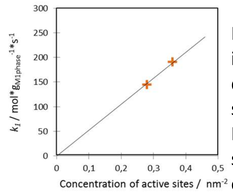
Morphology-Activity Relationship

Predict sample activity from its particle morphology



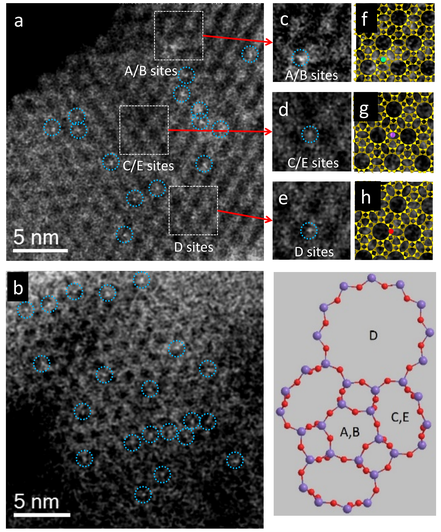
Highly Active Not {010} Rich

Poorly Active {010} Rich



Direct correlation between activity in ethane oxidative dehydrogenation (ODH) of the samples (normalized per gram of M1 phase) and density of active sites can be clearly observed. Xu P et al. 2014, *Submitted*

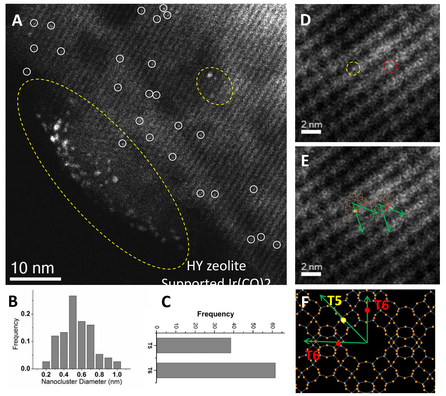
Determining interfaces between single-atom Pt species and zeolite supports



Site-isolated Pt atoms in KLTL zeolite in (a) as-prepared and (b) oxidized samples. Before oxidation: 66% D, 23% A/B, 11% C/E; After oxidation: 56% D, 24% A/B, 20% C/E.

- Indicated one of the best-defined supported platinum catalysts and first site-isolated platinum catalyst with defined locations of the Pt atoms.
- Demonstrated opportunities for tailoring stable single-site catalysts. Kistler J et al. 2014, *Accepted*

Where does metal go?



First evidence that zeolite crystalline region stabilizes mononuclear metal complexes more effectively than amorphous materials. Martinez MC et al. 2014, *Submitted*

Next Steps

- Apply in-situ methods and developments of new capabilities to these systems
- Apply DTEM for dynamics of nanoscale heterogeneous catalysis
- Develop DOE-BES proposal