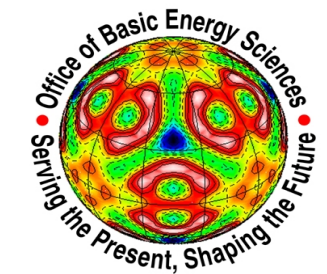


# Studies of Au Catalysts on Various Supports by EXAFS and XANES

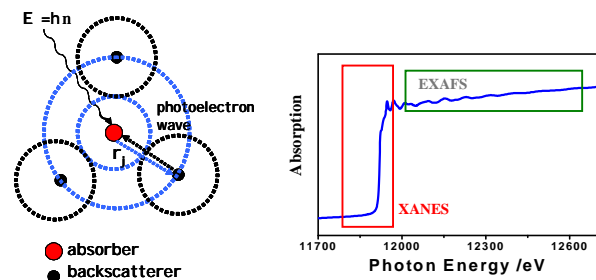
Viviane Schwartz, David Mullins, Wenfu Yan, Haoguo Zhu, Sheng Dai, and Steve Overbury  
Chemical Sciences Division, Oak Ridge National Laboratory  
Oak Ridge, TN 37831



FWP KCC053 Fundamentals of Heterogeneous Catalysis on Surfaces and Nanostructures

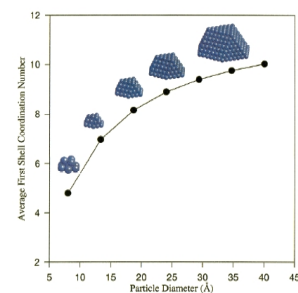
**Synopsis:** The combination of EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near-edge Structure) has been extremely useful for analysis and study of amorphous and highly dispersed solid structures. The near edge structure provides information about oxidation state and coordination environment of a specific type of absorbing atom. EXAFS yields information about bond distances and coordination to neighboring atoms. Most importantly, for catalytic applications, these studies can be performed while in the presence of reactant gases and while monitoring reaction products, providing means of acquiring structural information under *in-situ* and/or *operando* conditions. For this reason, X-ray absorption spectroscopy has been the tool of choice to investigate both the Au particle size/oxidation state on a functionalized amorphous silica support and titanium oxide, and the coordination of TiO<sub>2</sub> in the support phase.

## EXAFS and XANES of Au L<sub>111</sub>-edge

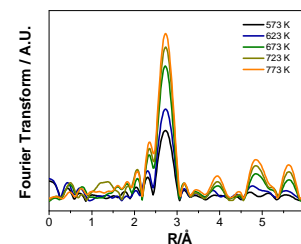


- EXAFS**
- Bond lengths, coordination number, and Debye-Waller factor.
  - Coordination number relates to particle size
  - In-situ* studies: particle size changes with variable temperatures, support type, loading, etc
- XANES**
- Local electronic structure
  - Au L<sub>111</sub>-edge density of unoccupied d states
  - p to d transition
  - Changes of oxidation state

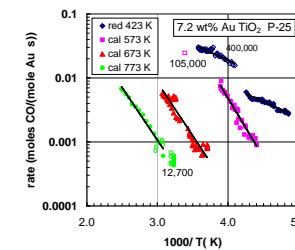
A. I. Frenkel, C. W. Hills and R. G. Nuzzo, *J. Phys Chem.* 105 (2001), 12689



The Au EXAFS intensity is related to the number of nearest neighbors around the Au scatterer (CN). Assuming a particle shape, the coordination number can be related to the particle size

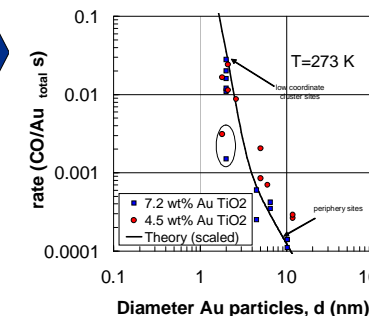


7.2 wt% Au / P25 following sequential reduction (at 425 K) and calcination at increasing temperatures: reactivity measured for various F/W ratio - rates measured at F/W = 40,000 mL CO/g<sub>cat</sub>h (open symbols) or otherwise indicated



Reactor data and EXAFS data are combined: Plotting below the measured atomic reaction rate AR as a function of particle size derived by EXAFS.

Atomic rates:  
7.2 wt% Au → d<sup>-3.0 ± 0.3</sup>  
4.5 wt% Au → d<sup>-2.4 ± 0.2</sup>



Both catalysts exhibit a trend toward decreasing rate rapidly with increasing Au particle size. The decrease is much faster than can be explained by loss of surface area. The size sensitivity was modeled by DFT calculations showing the rate dependency with low coordination sites.

DFT modeling curve from S. N. Rashkeev, A. R. Lupini, S. H. Overbury, S. J. Pennycook, S. T. Pantelides, *Physical Reviews B*, 76, 035438, (2007).

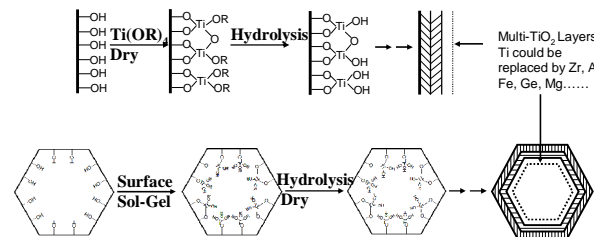
## Mixed and layered TiO<sub>2</sub>-SiO<sub>2</sub> Supports

Interaction between Au and Si is weak: Utilization of Mixed SiO<sub>2</sub>/TiO<sub>2</sub> and Functionalized Silica

Mixed (Si:Ti)O<sub>x</sub>

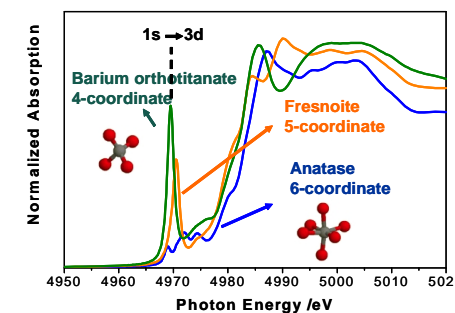
Layered TiO<sub>2</sub> on SiO<sub>2</sub>

Co-synthesis of mesoporous SiO<sub>2</sub> and TiO<sub>2</sub>, with varying metal ratio Si:Ti = 10, 5.5, and 2.7; and varying calcination temperatures



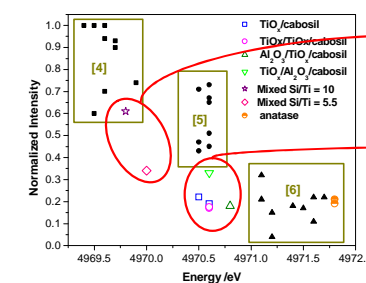
The titania can be deposited layer-by-layer and can be controlled so that it will coat internal or external surfaces. Small Au nanoparticles can be deposited by D-P methods.

**Ti XANES - Local coordination structure**  
Symmetry around Ti atom strongly affects the XANES. Ability to differentiate 4, 5, 6-fold coordination environment of Ti based on the pre-edge position and intensity



## Titania Support Structure by EXAFS

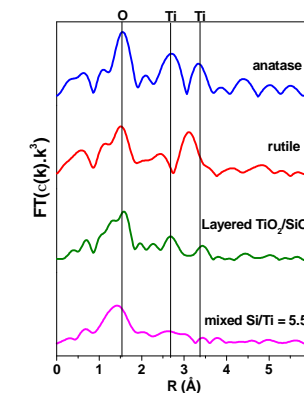
From pre-edge position and intensity...



Comparison of data from X. Gao et al. *J. Phys Chem B* 1998, 102, 5653.102 and our catalysts after dehydration

Mixed Oxides: As the Si:Ti ratio increases, Ti becomes 4-coordinated

Layered TiO<sub>2</sub>: Not fully 6-coordinated. Indication of mixture of several coordinations



**Layered TiO<sub>2</sub>/SiO<sub>2</sub>:** Pre-edge indicates a mixture of five- and sixfold coordinate environments. EXAFS Ti-O and Ti-Ti positions correlates well with an anatase crystal structure, however Ti-Ti coordination is greatly reduced. Decreasing of CN indicates presence of layered anatase-like species instead of thick crystallites.

**Mixed (Ti-Si)O<sub>x</sub>:** Intensity and energy of pre-edge features support presence of four-coordinated Ti species. EXAFS Ti-O distances are shorter than anatase and rutile and neighboring Ti shells are not observable indicating that Ti atoms should be highly dispersed on the silica structure.

	Ti-O		Ti-Ti		Ti-Ti	
	N	R (Å)	N	R (Å)	N	R (Å)
Anatase	4	1.93	4	3.04	4	3.79
Layered TiO <sub>2</sub> /SiO <sub>2</sub>	5.9	1.93	2.7	3.04	1.1	3.81
Mixed (Si/Ti = 5.5)	4.7	1.87				

where N is the coordination number around the Ti atom and R is the distance