Learning More from UV-Visible Spectroscopy & The Role of Defects in Selective Propane Ammoxidation

Gerry Zajac, Innovene USA LLC, Naperville, IL 60563

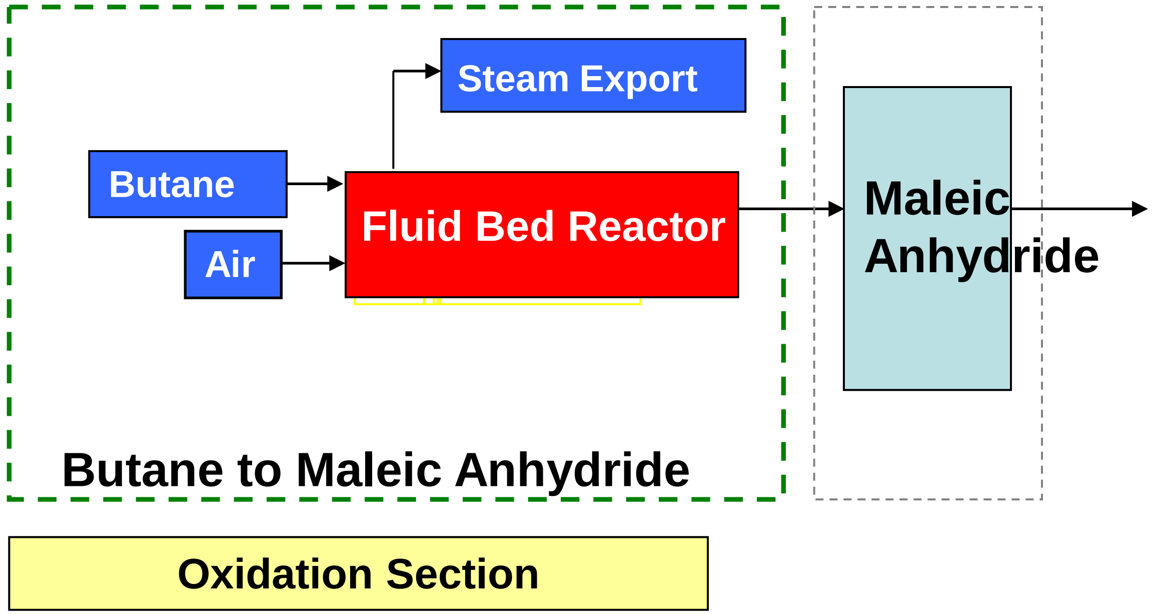
- **An intractable Problem made doable via SGI Altix : Modeling Defects in 104 Atom Unit Cell of Vanadyl Pyrophosphate**
- **Modeling the vibrational Spectra of Cation Defects in a Rutile Structure Catalyst***

G. Xiong, V. Sullivan, P. Stair, G. Zajac, S. Trail, J. Kaduk, J. Golab and J. Brazdil,
***J. of Catalysis*, 230 (2005) 317-326**

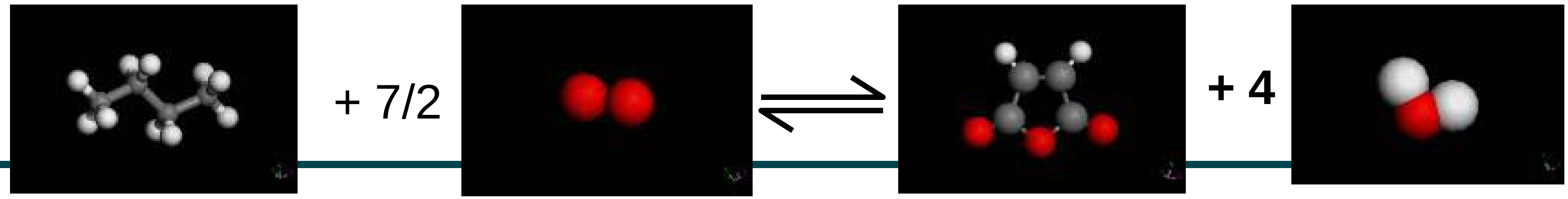
innovene

BP's MAN Technology and History

• <u>Simplified Process</u>

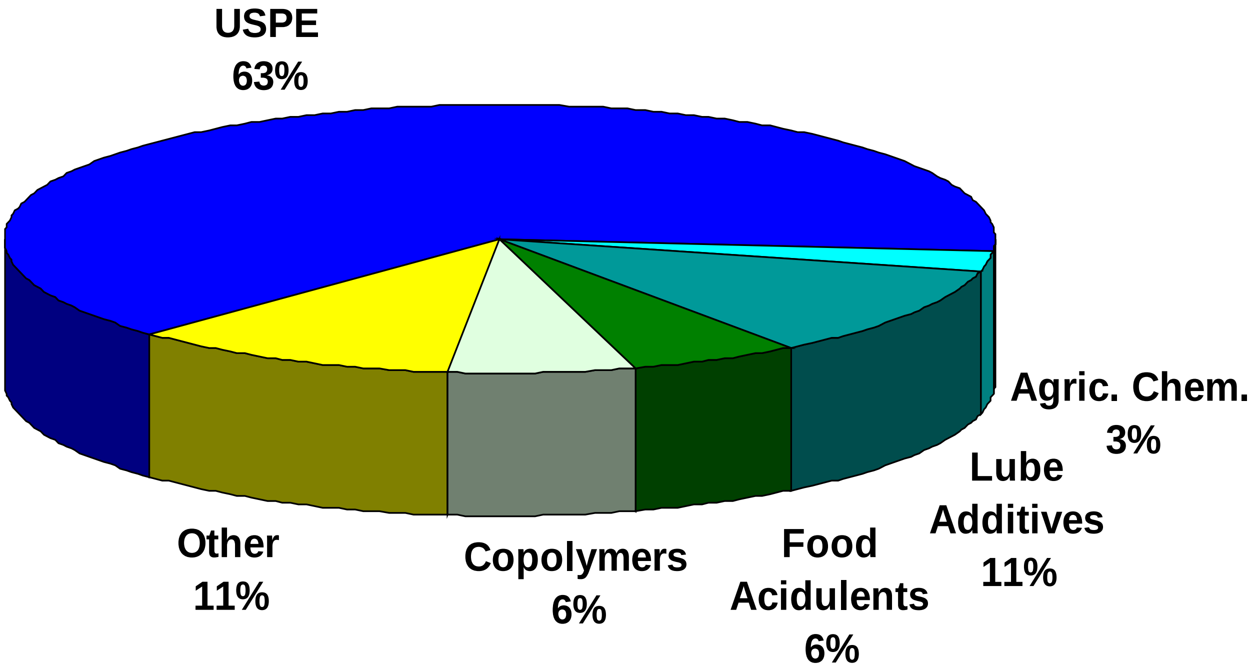


1970's: BP Research explores ways to upgrade alkanes
1976 : Amoco starts the first fixed bed reactor for maleic anhydride
1980's: Fluid-bed version of maleic anhydride (MAN) catalyst (Nitriles expertise) developed



innovene

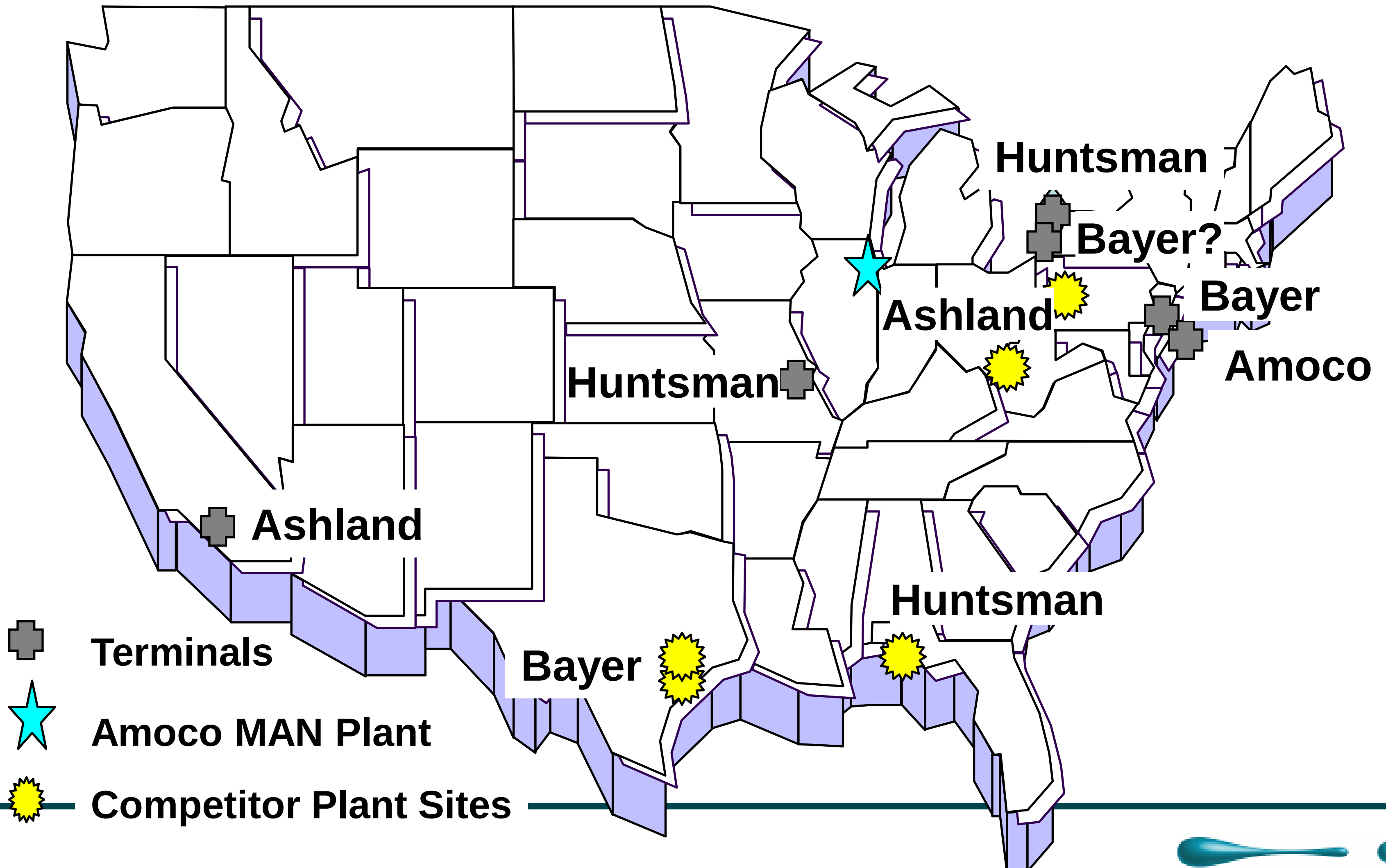
MAN End-Uses



Source: SRI, 1995

Total = 195 k MT

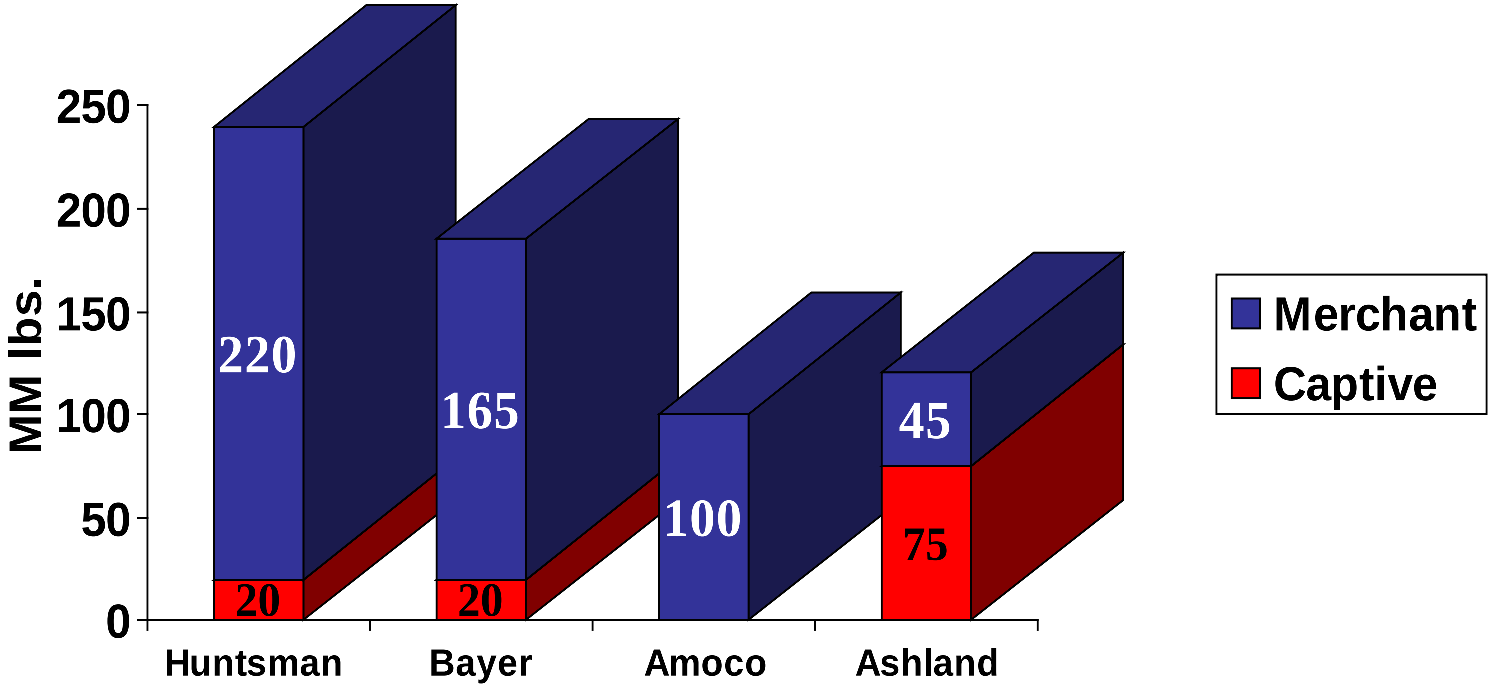
U.S. MAN Production Locations & Terminals



innovene

Maleic Anhydride
U.S. Nameplate Capacity - 1996

Total Nameplate Capacity: 645 MM lbs



Source: SRI International Report, 1993, 1995

MAN
Butane Oxidation Catalyst

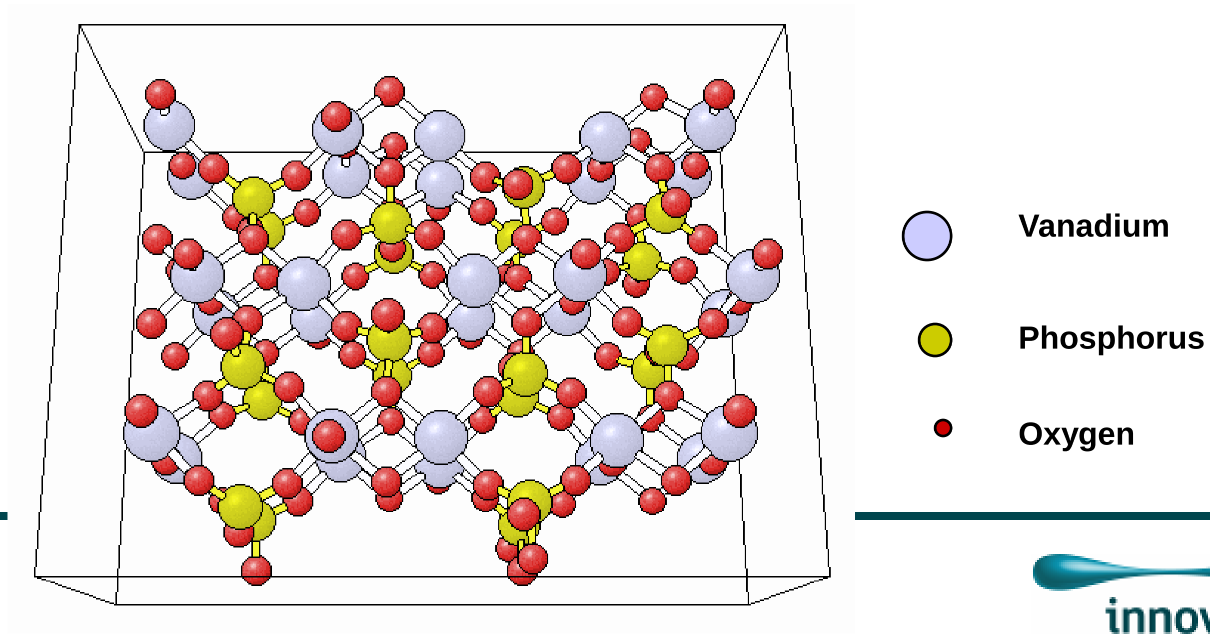
Fluid-Bed Catalyst

Single Phase Material

No Added Hardening Agent

100 % Vanadyl Pyrophosphate

$(VO)_2P_2O_7$



innovene

MAN Catalyst Manufacturing Process

Raw Material Reaction

Recipe:

(1) 1 part Vanadium as V_2O_5

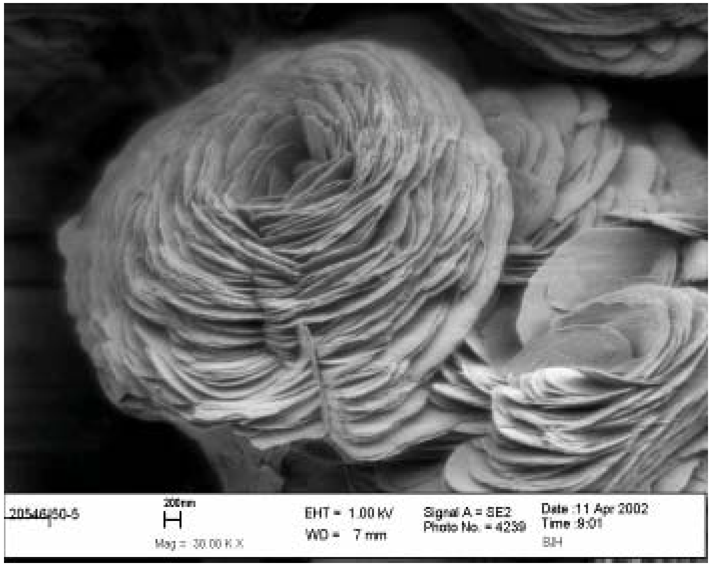
(2) 1.25 parts Phosphorus as 95 % H_3PO_4 (25 % xs phos acid)

(1) (3) excess isobutanol

Reaction Slurry Products

(1)VO(HPO$_4$) • ½ H$_2$O

5-15 micron "rosette" shaped particles



innovene

MAN Catalyst Composition Changes During Manufacture

Raw Material Reaction and Product:

$$V_2O_5 + 2\ H_3PO_4 \xrightarrow{\text{alcohol}} 2\ VOHPO_4 \cdot 1/2\ H_2O$$

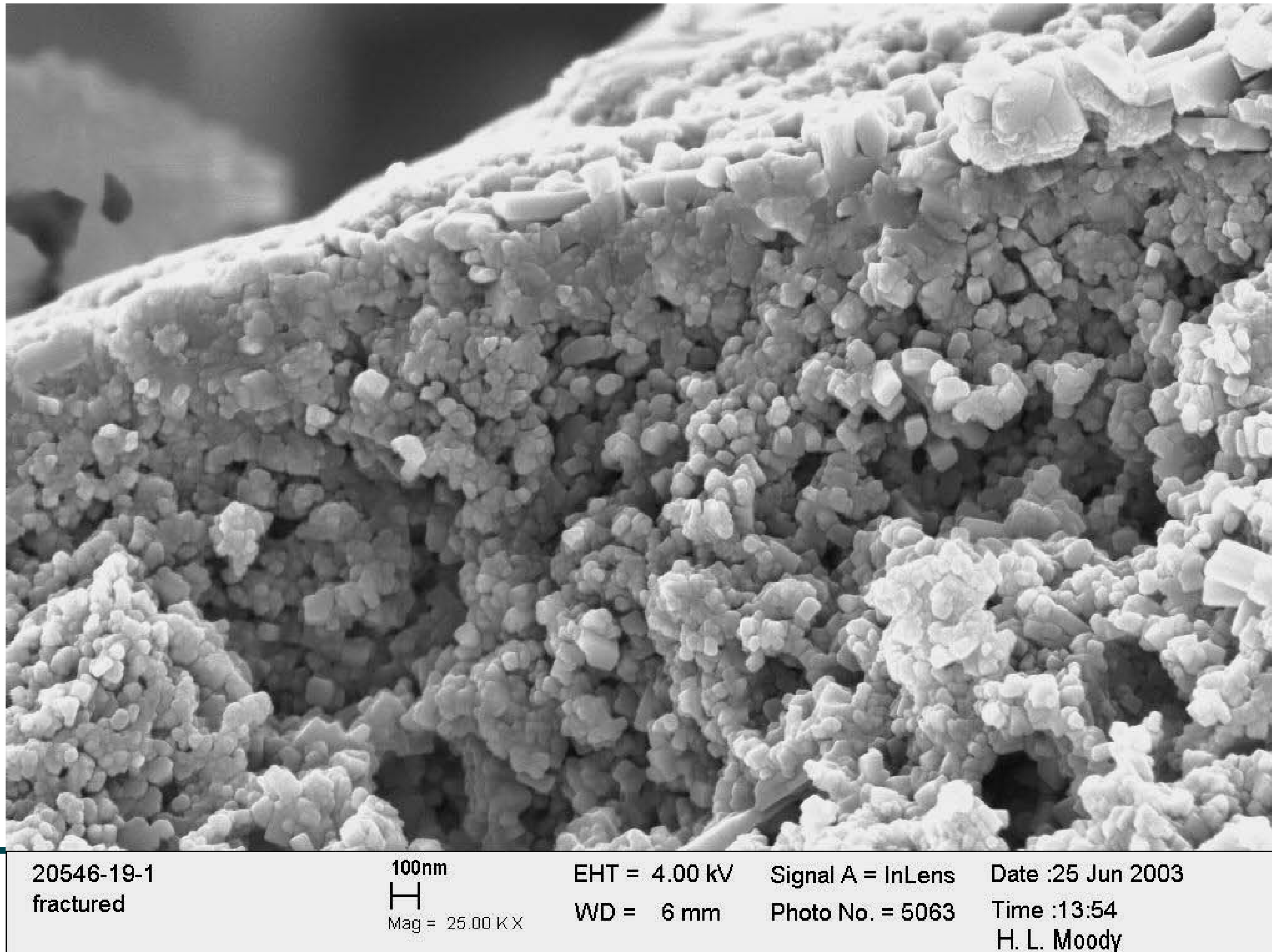
Critical Phase Transformations during <u>Catalyst Activation</u>:

$$2\ VOHPO_4 \cdot 1/2\ H_2O \xrightarrow{< 300\ ^{\circ}C} 2\ VOHPO_4 + H_2O$$

$$2\ VOHPO_4 \xrightarrow{< 350^{\circ}C} (VO)_2P_2O_7 + H_2O$$

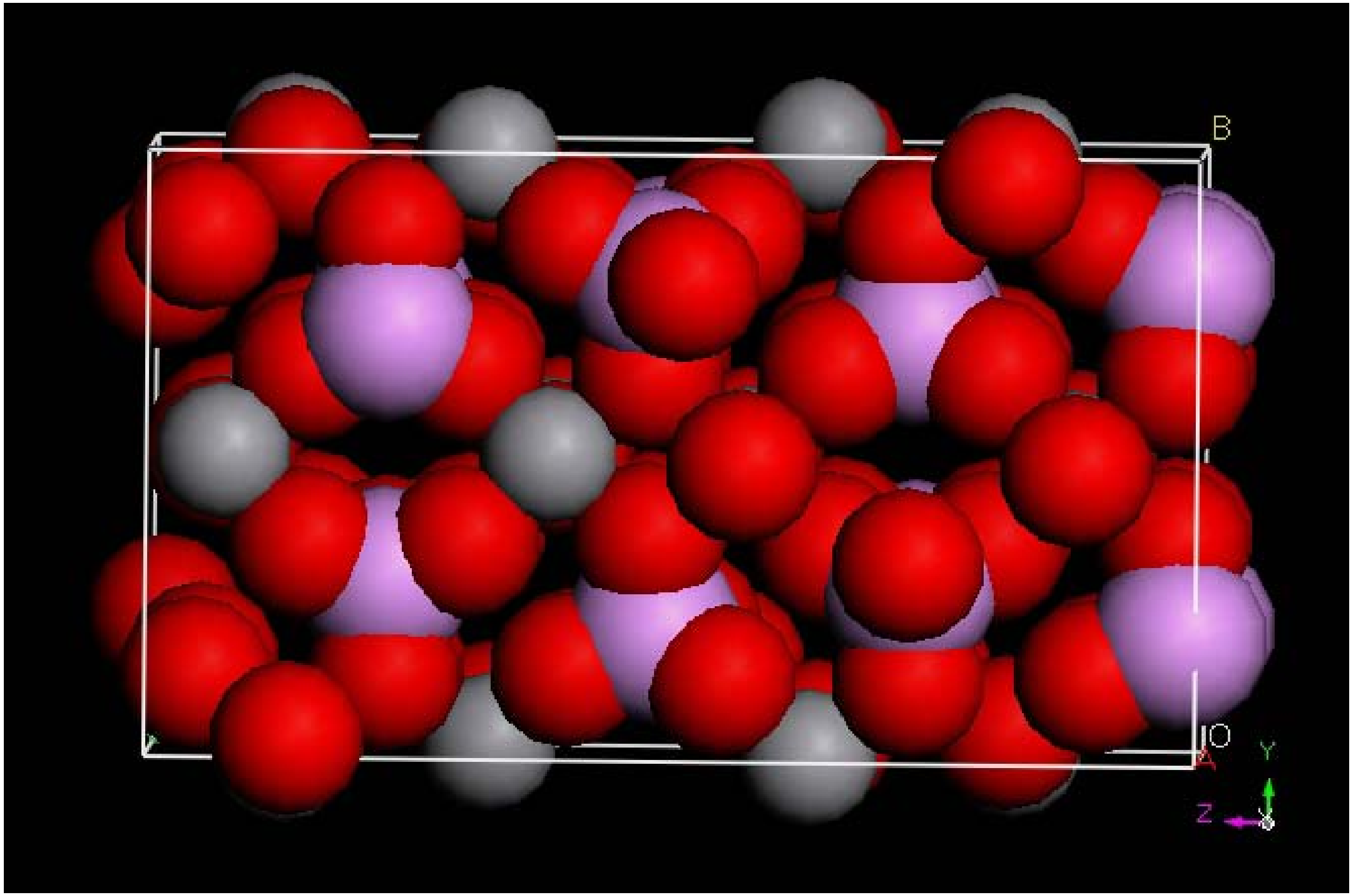
MAN Catalyst Morphology

11/30/00 Sample (Fractured Cross-section @ 25 K X)

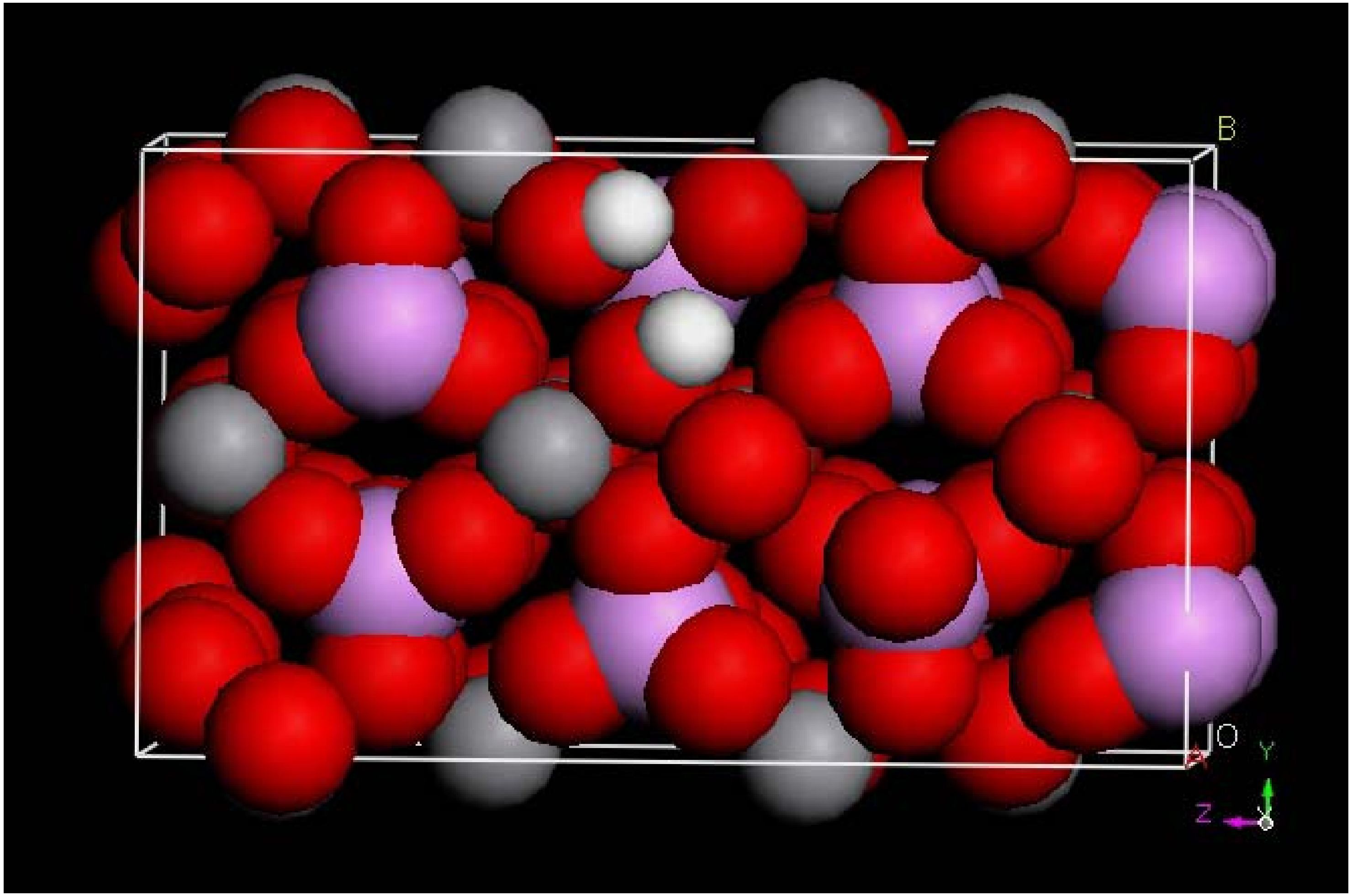


ovene

Vanadyl Pyrophosphate Unit Cell



Vacancy Model - Loss of PO_2^+ Unit

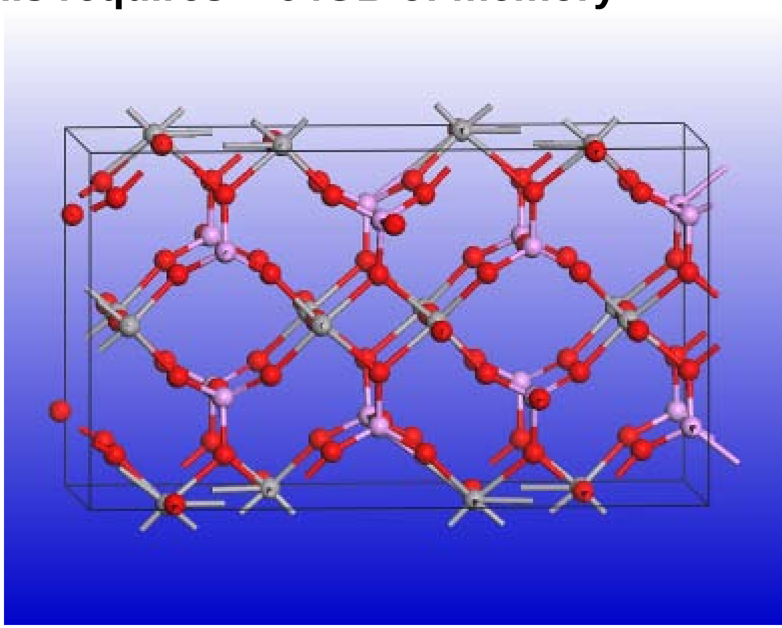


CASTEP Capability on Altix

Study of the aging of catalyst vanadyl pyrophosphate.

Need a 104 atoms unit cell and look at changes in optical properties with P vacancies.

This requires > 64GB of memory



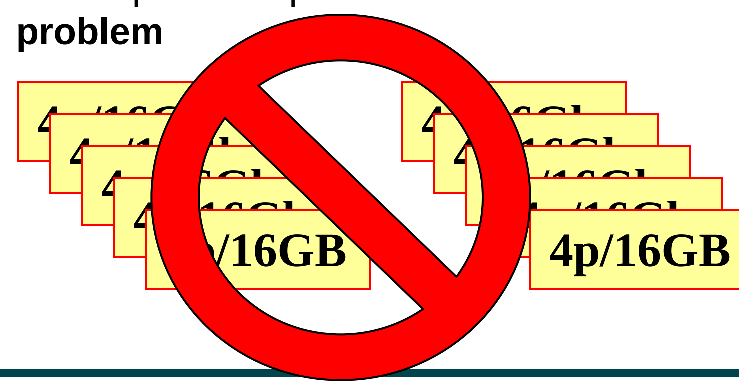
Dr. Gerry Zajac, Innovene, Inc. (2005)

SGI Altix with globally addressable memory has no problem at all

SGI Altix

32cpu/128GB

A heavy-duty standard 32-bit Linux cluster with 4cpu/16GB per node **cannot run this problem**



CASTEP Performance on Altix

A CASTEP job requires around 75 steps of a geometry optimization. Each step takes around 19 hours on 1 processor of an Altix 1.6GHz/9M and 48 min on 32 processors

SGI Altix

To complete on 1 processor:
~ 2 months

Su	Mo	Tue	We	Th	Fr	Sa
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

Su	Mo	Tue	We	Th	Fr	Sa
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

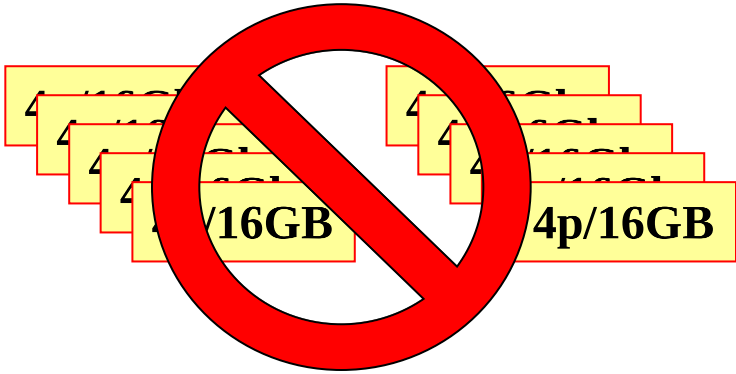
SGI Altix

To complete on 32 processors:
less than 2 days

Su	Mo	Tue	We	Th	Fr	Sa
		1	2	3	4	5
6	7	8	9	10	11	12
13	14	15	16	17	18	19
20	21	22	23	24	25	26
27	28	29	30	31		

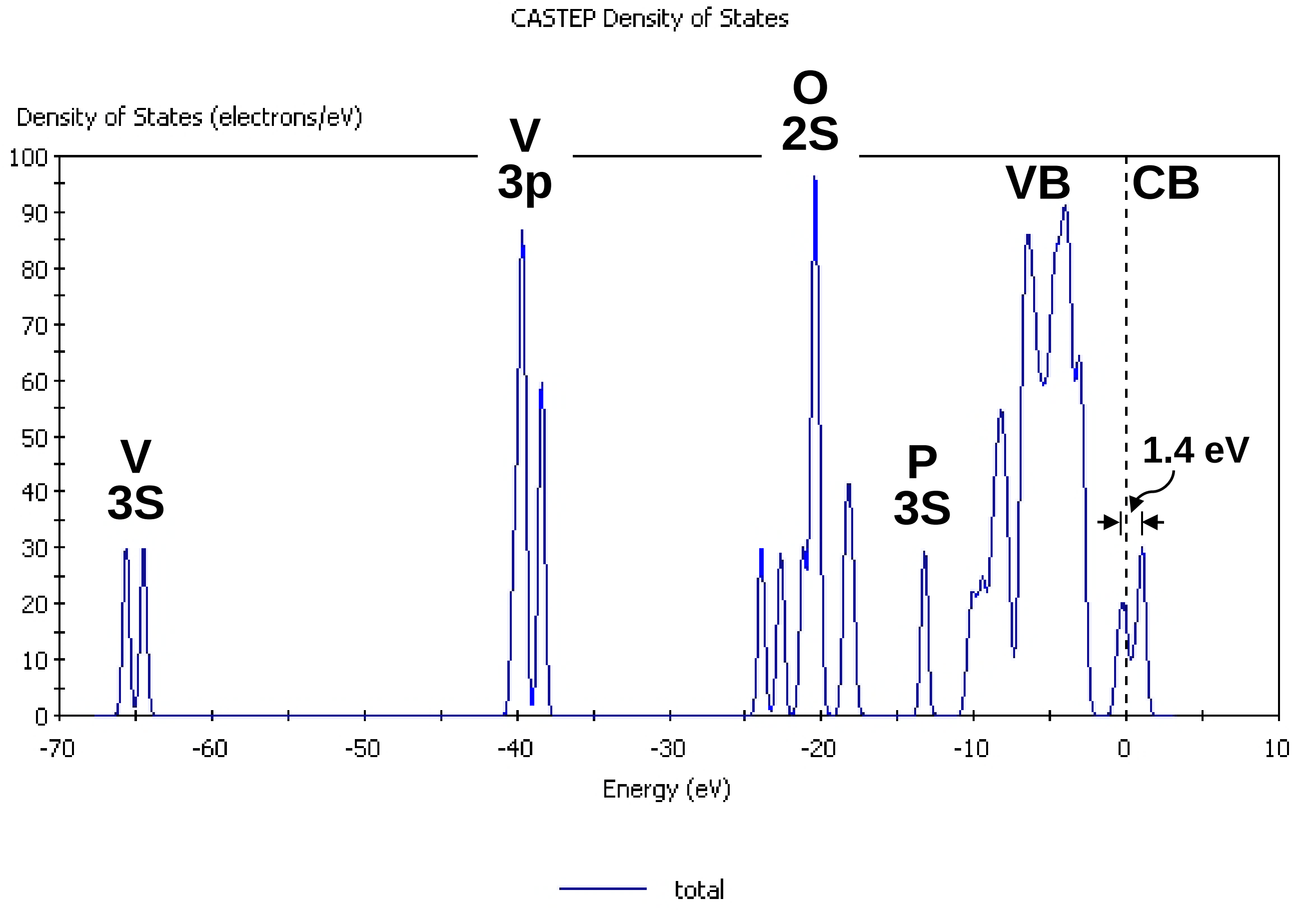
32-bit Linux Cluster

A heavy-duty standard 32-bit Linux cluster with 4cpu/16GB per node **cannot run this problem**

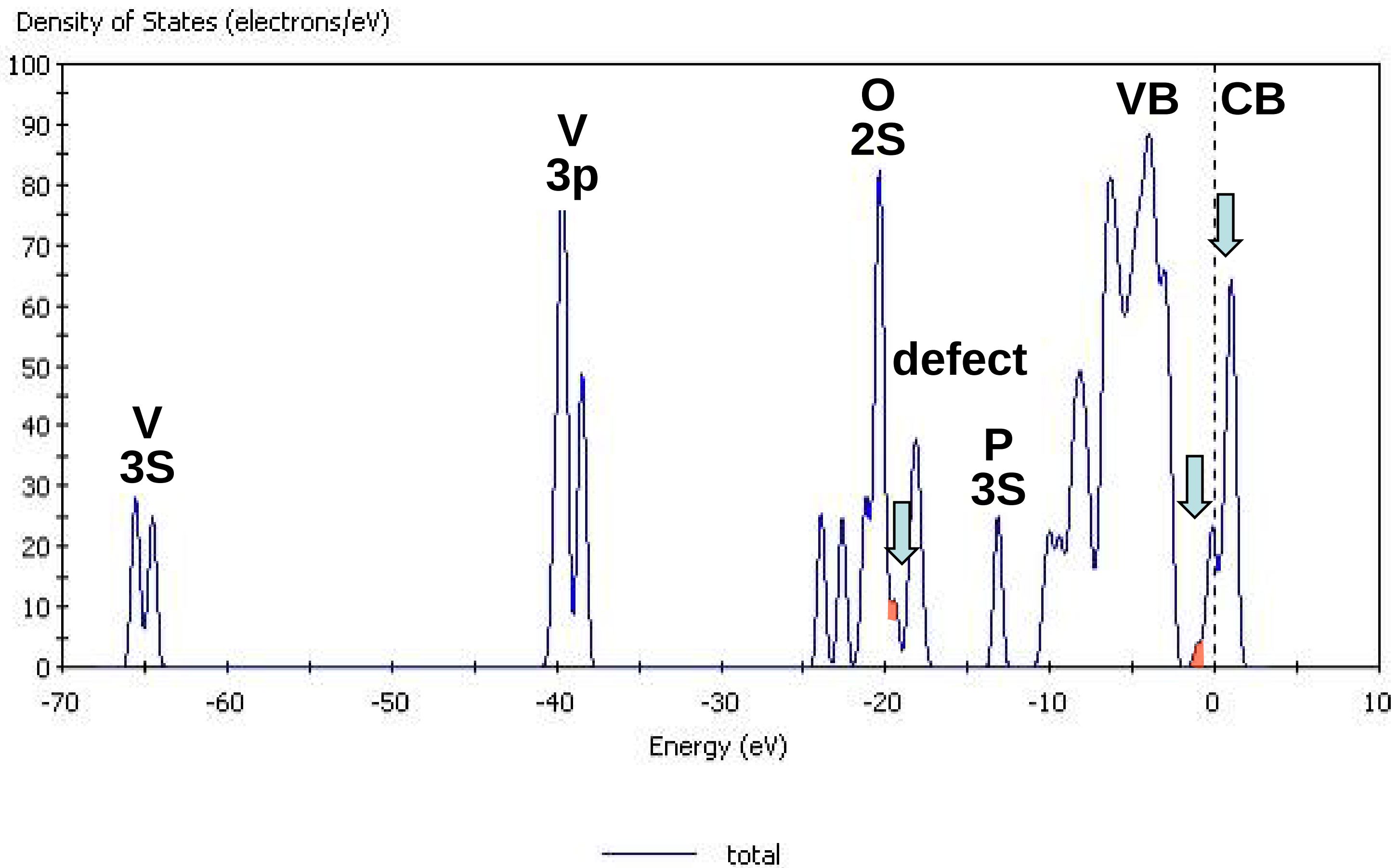


innovene

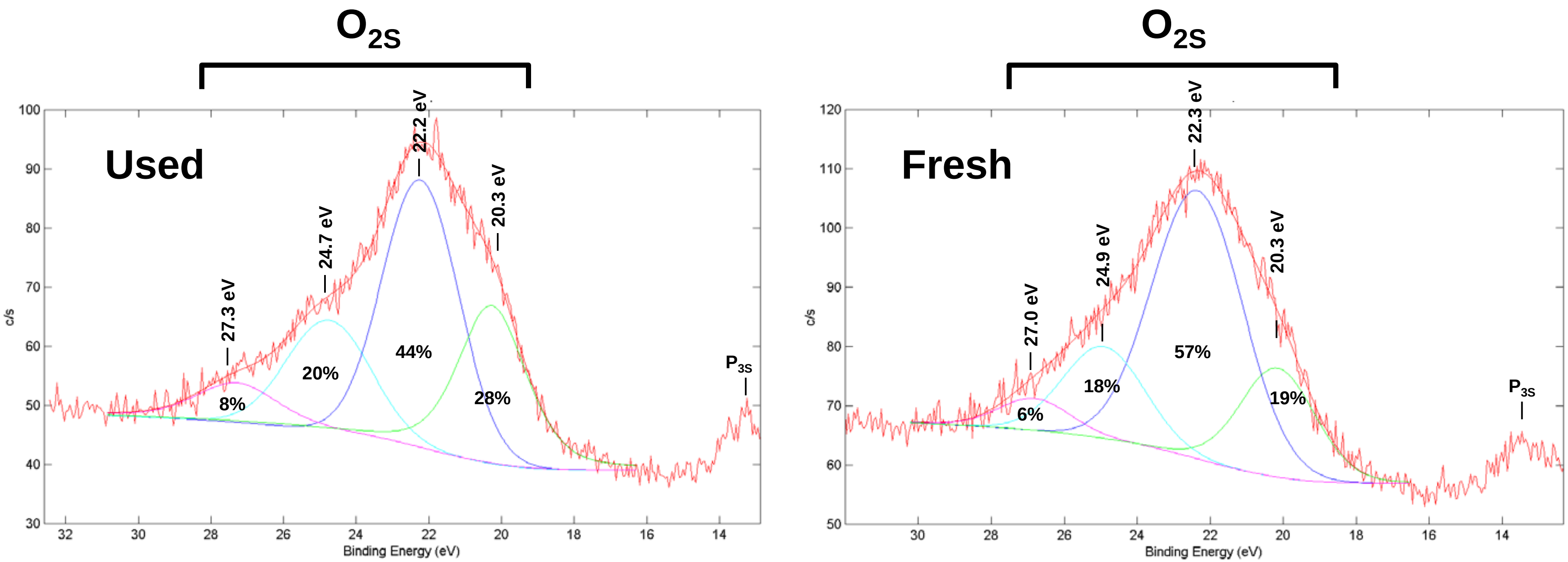
Total Density of States – $(VO)_2P_2O_7$



Total Density of States – Vacancy Model

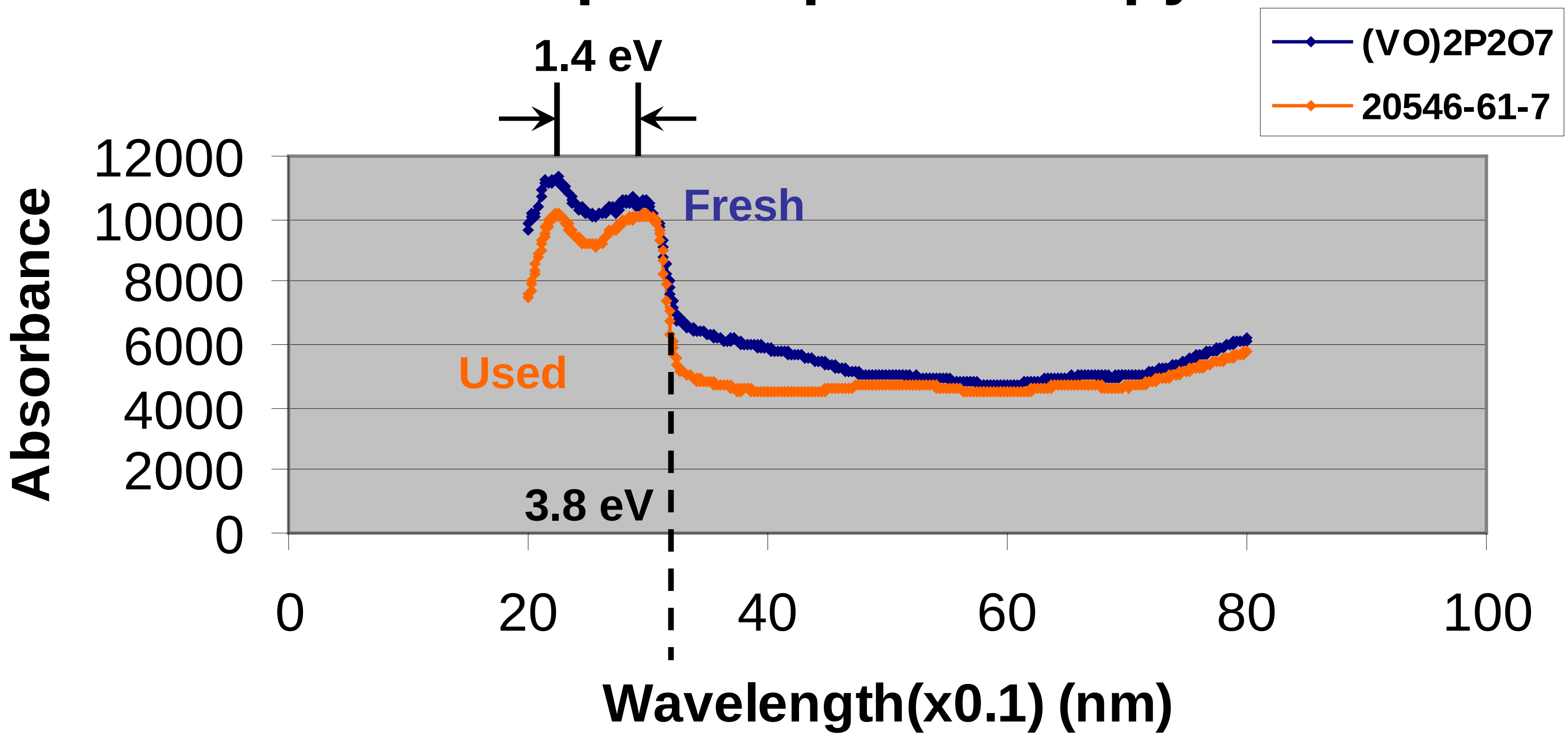


X-Ray Photoelectron Spectroscopy O_{2S} Region

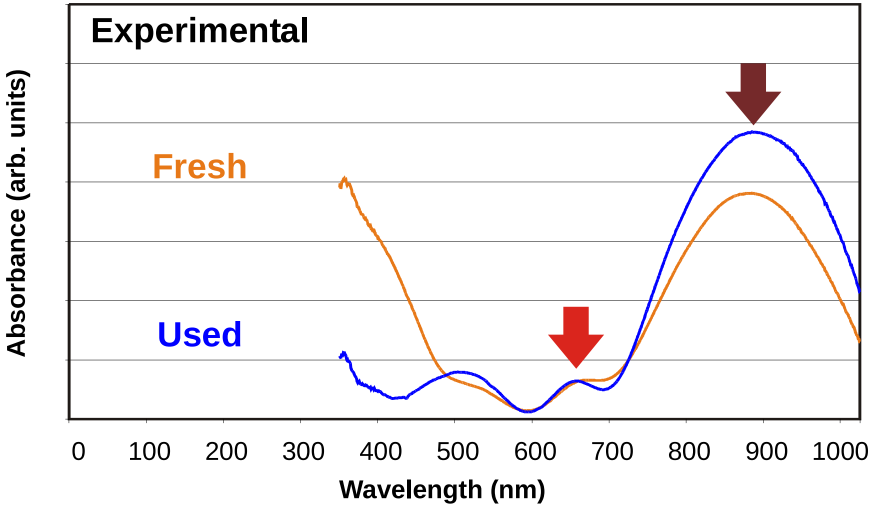


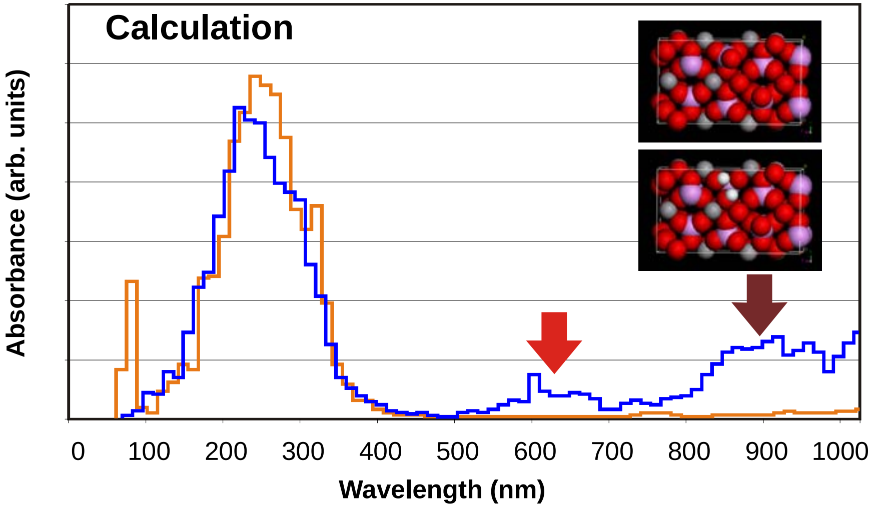
innovene

UV-Visible Absorption Spectroscopy



UV-VIS Absorption $(VO)_2P_2O_7$





Summary

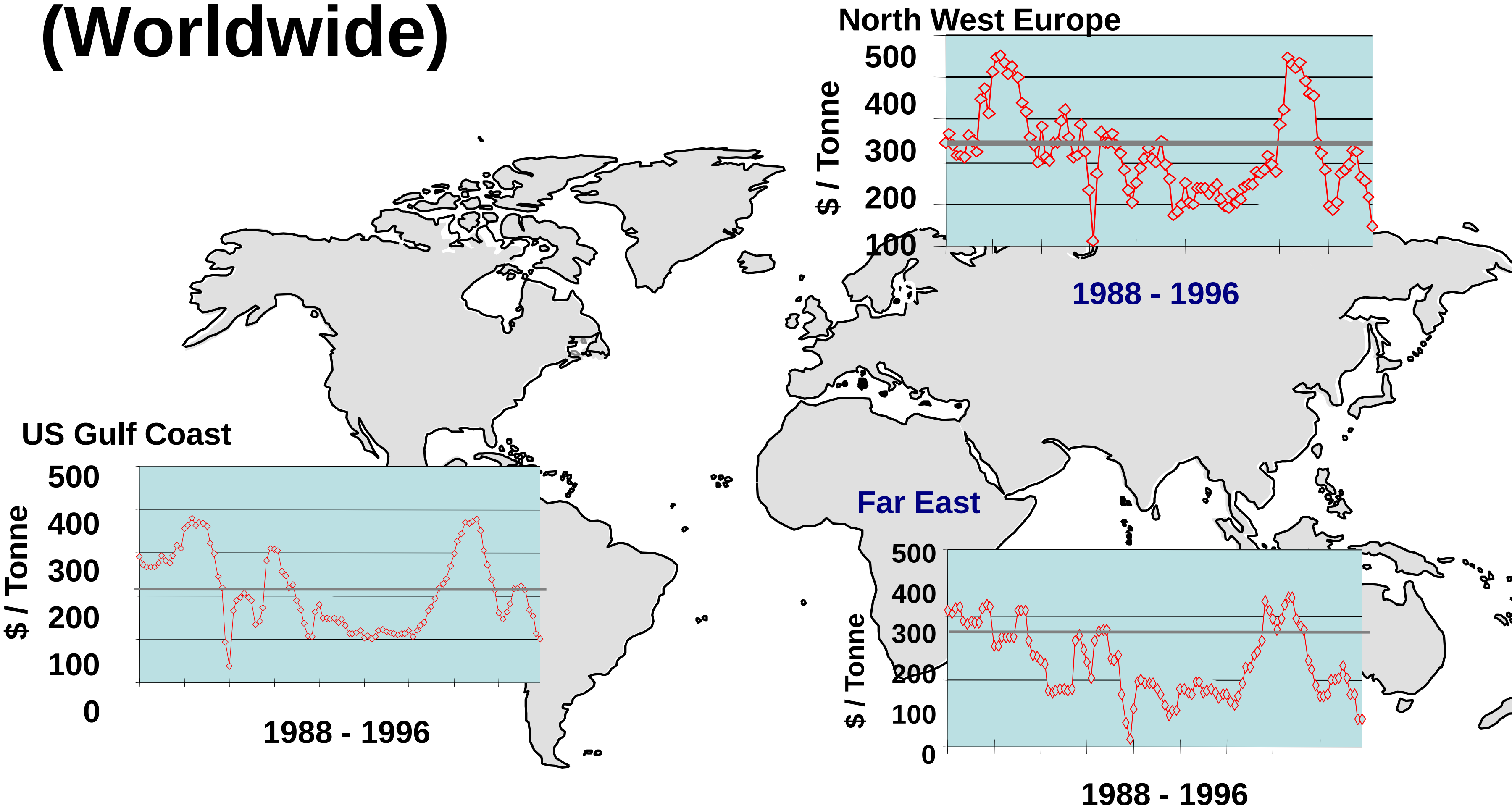
- DFT DOS calculations critical to identify PO_x Defects.
- Experimental evidence of these defects by XPS and uv-visible spectroscopy.
- SGI Altix – Accelrys collaboration critical to addressing this vanadyl pyrophosphate application.

Effect of Titanium Substitution on the Structure of $V_{8/9}Sb_{8/9}O_4$ Catalysts for Propane Ammoxidation*

Guang Xiong, Vivian S. Sullivan, Peter C. Stair
Center for Catalysis and Surface Science, Northwestern University
and
Gerry W. Zajac, Steven S. Trail, James A. Kaduk, Joseph T. Golab, James F. Brazdil
Innovene LLC USA, 150 W. Warrenville Rd., Naperville, IL 60563

* **Guang Xiong, et al, J. of Catalysis 230 (2005) 317-326**

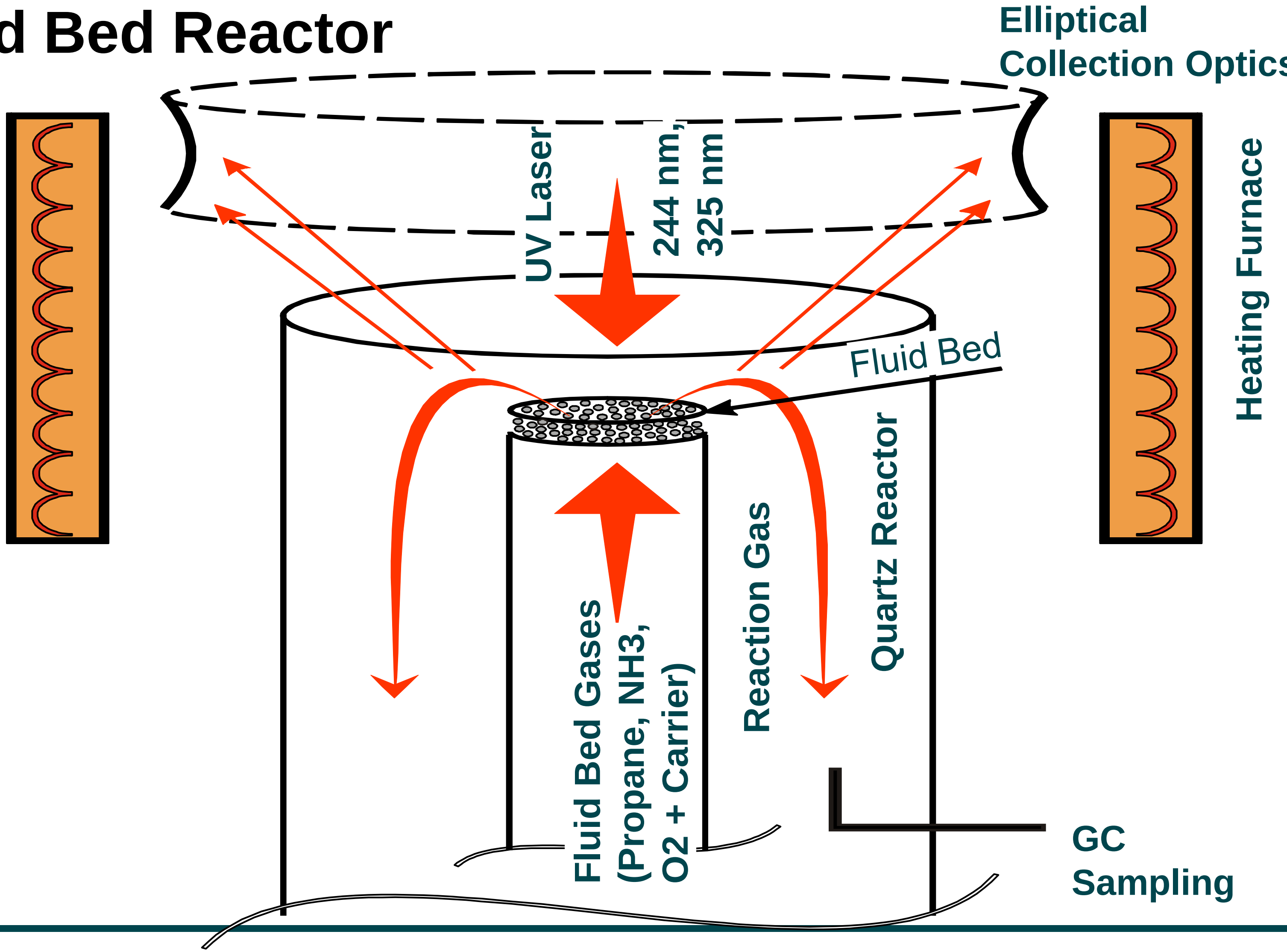
Propane Ammoxidation
Propylene/Propane Price Differentials (Worldwide)



innovene

Northwestern UV Raman

Fluid Bed Reactor

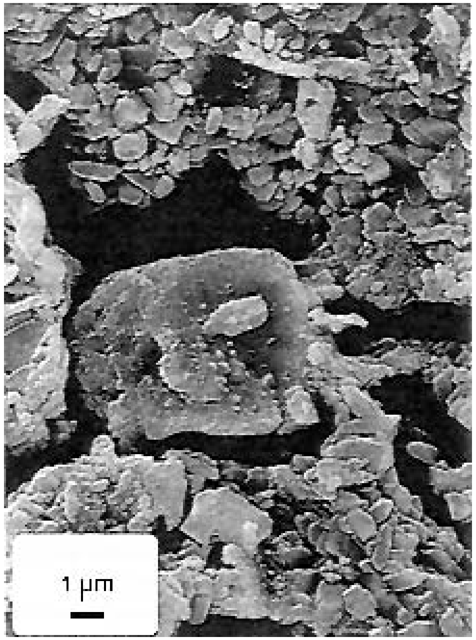


Conditions: ~ < 500°C, atmospheric pressure

innovene

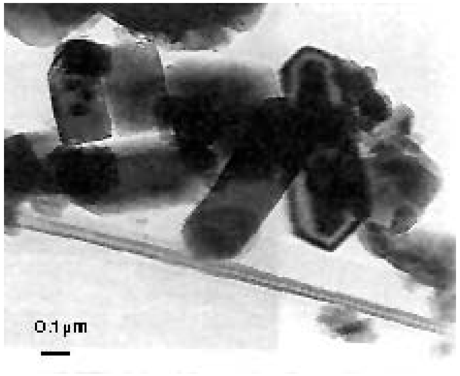
SEM/TEM Images of Vanadium Antimonate Crystals

SEM



Scanning electron micrograph of an $Sb_{0.9}V_{0.9}O_4$/a-Sb_2O_4 catalyst

TEM



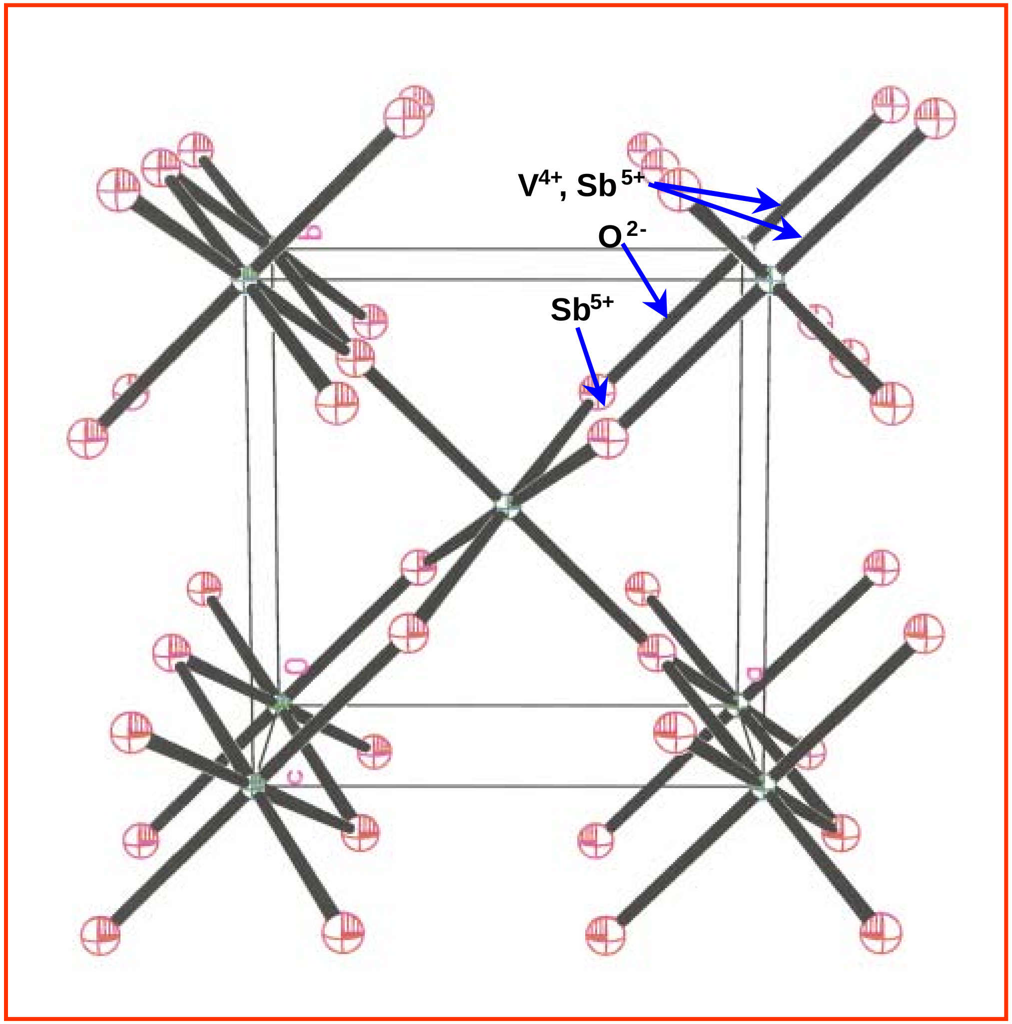
Low resolution transmission electron micrograph of typical $Sb_{0.9}V_{0.9}O_4$ crystals.

Small crystallites of vanadium antimonate similar to those of CX-200. [1]
Primary basal plane faces are (110) planes.

[1]Jerker Nilsson, PhD. Thesis, Dept. of Chemical Engineering II, Lund Unversity 1999.

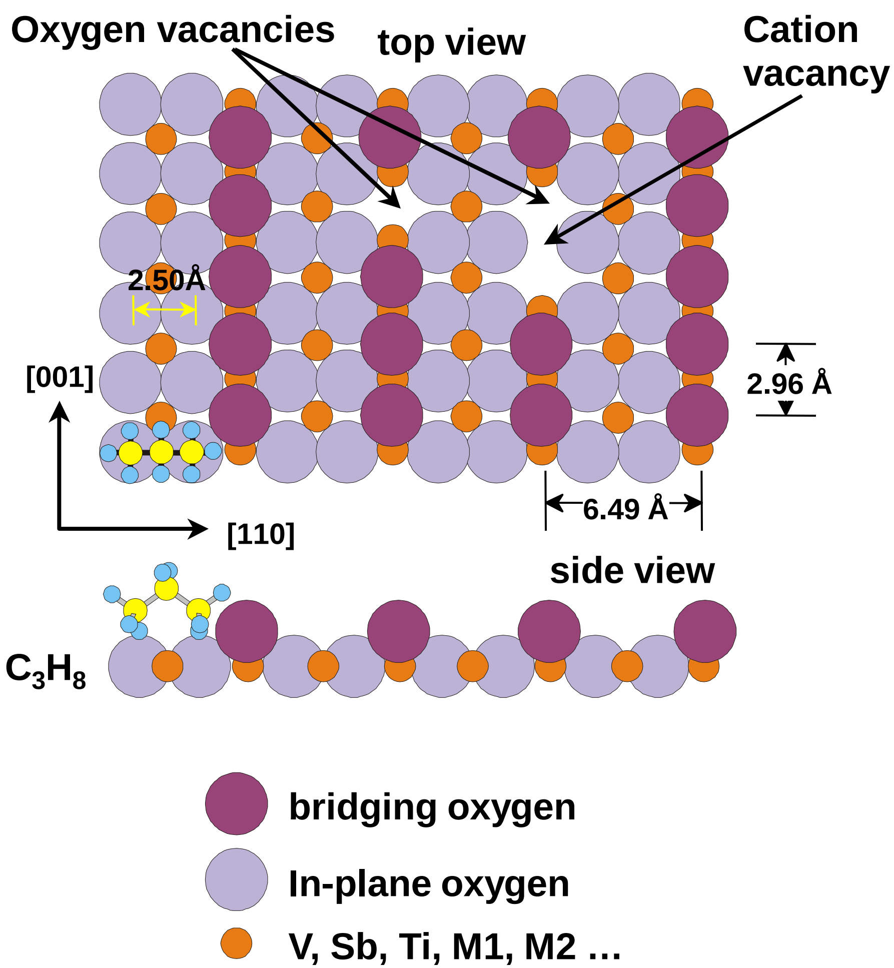
innovene

Rutile Unit Cell of VSbO4

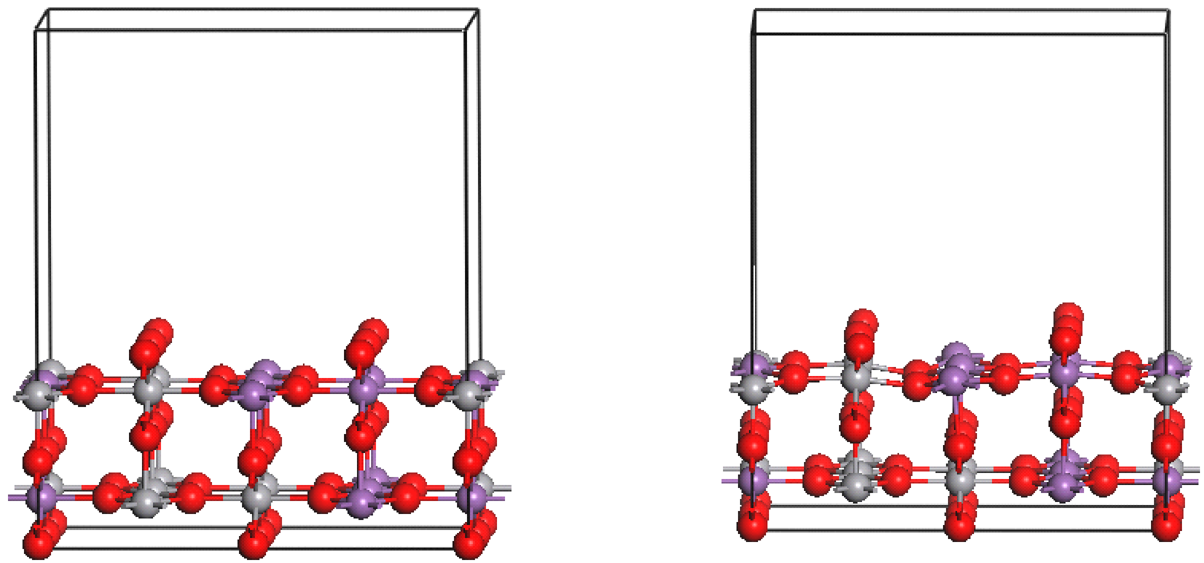


- The cations (V^{4+},$Sb^{3+,5+}$) are disordered
- There is only 1 equivalent site
- The oxygen anions are 3 coordinate, as $OVSb_2$ and OV_2Sb

Model of Rutile (110) Face with Proposed OMoVSb 3- coordinate O^{2-} Site

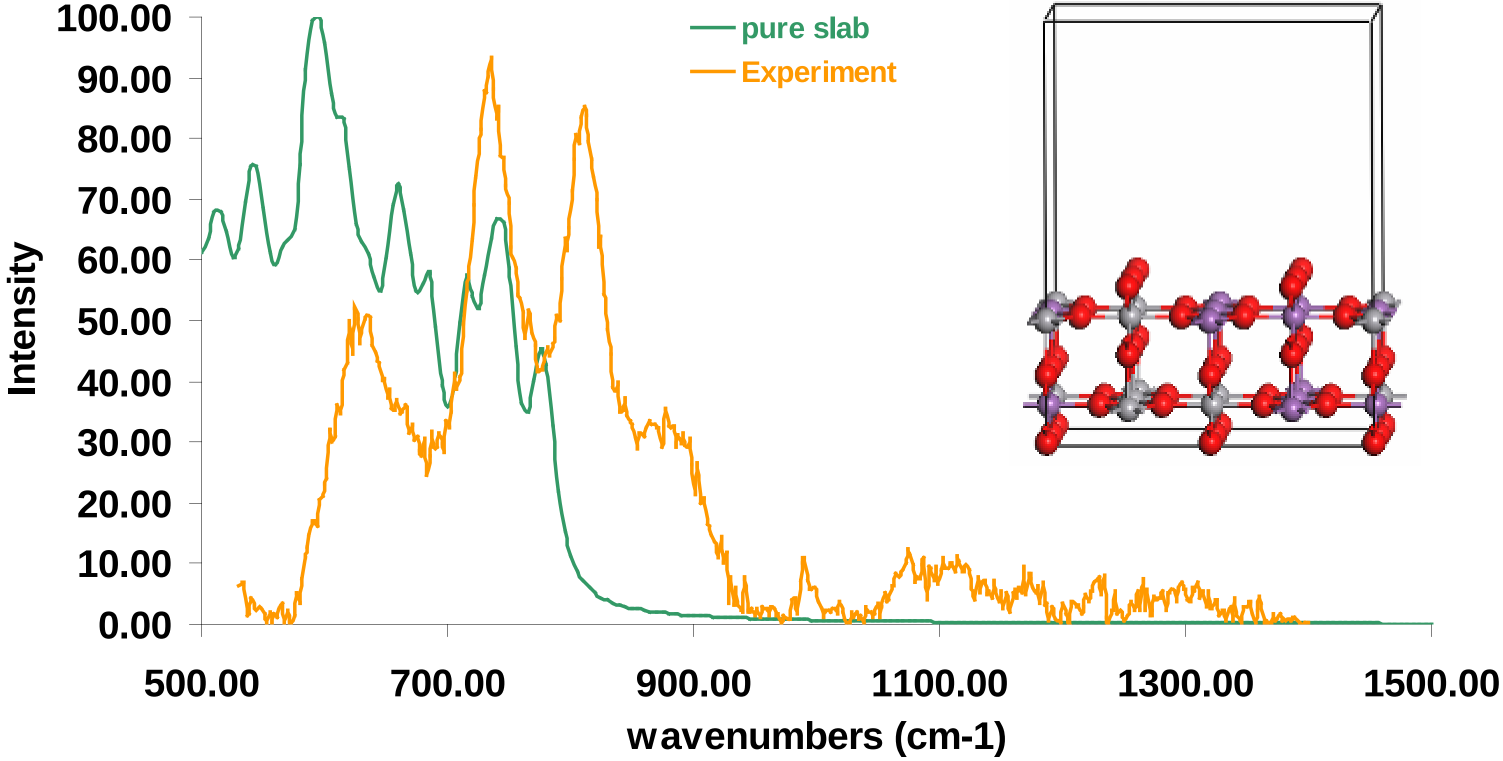


Calculations using CASTEP optimized slab models

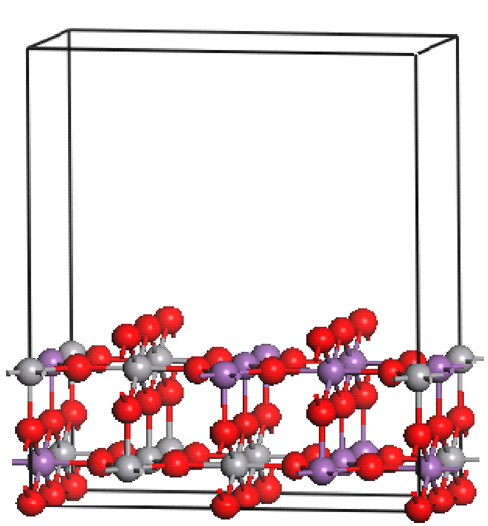


The initial VSbO4 110 structure (left) is compared to the CASTEP optimized structure.

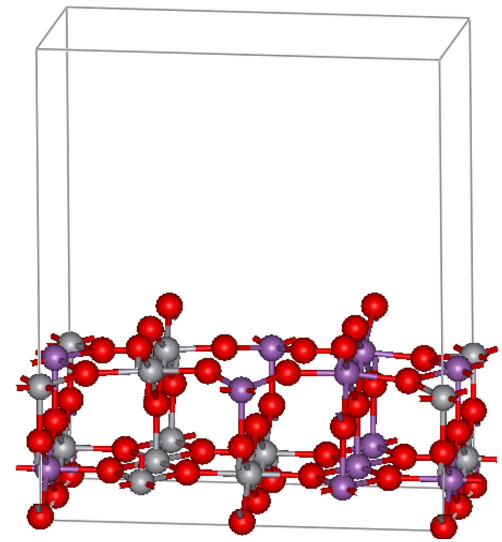
DMOL Simulated Infrared Spectra w/o Cation Defect



Calculations using CASTEP optimized slab models

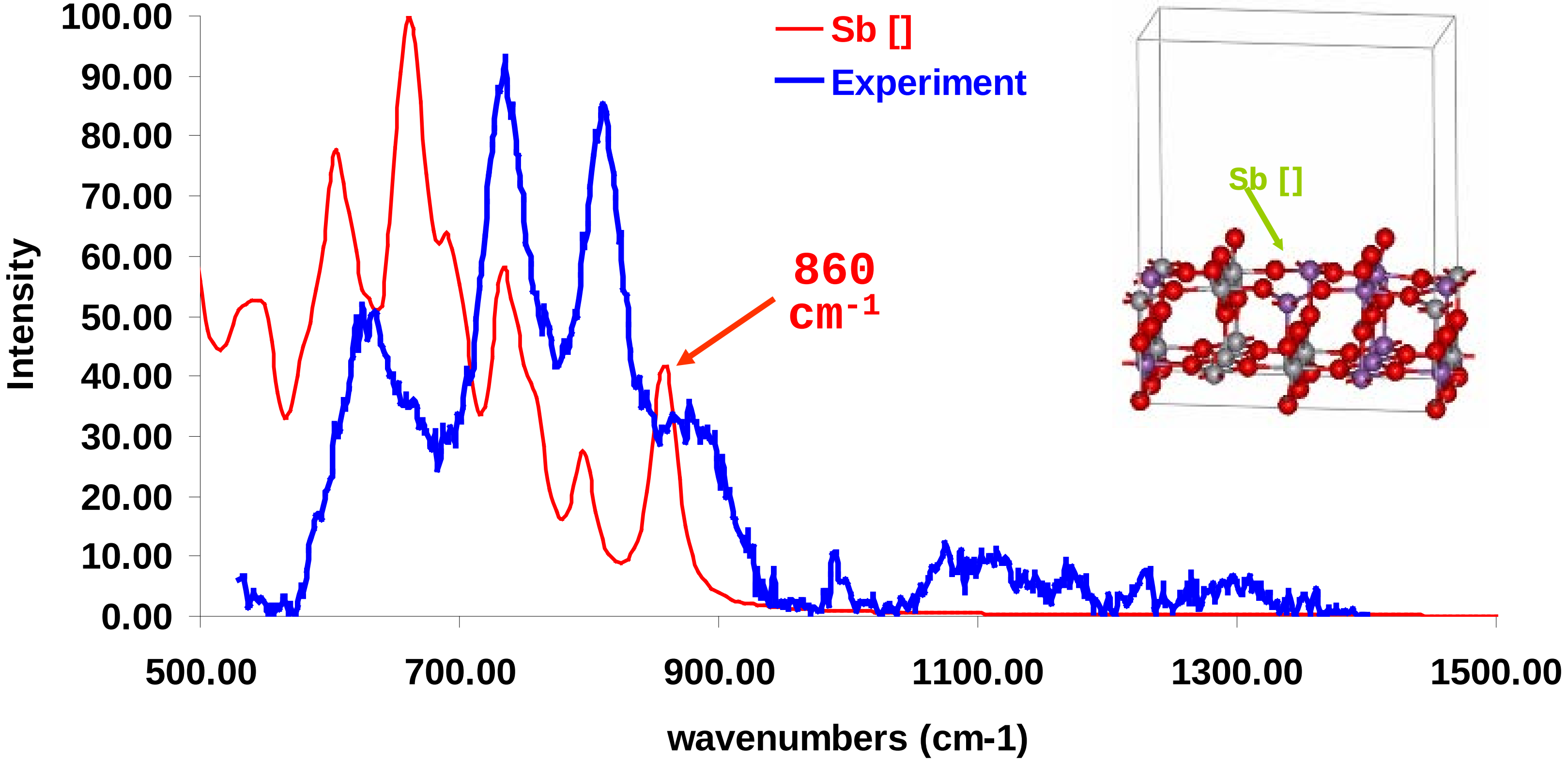


VSbO4 110 "slab" consisting of 48 atoms; 32 O (red), 8 V (grey), & 8 Sb (purple).
The overall dimensions of the slab are 6.1 Å x 13.1 Å x 15.8 Å with an additional 15 Angstroms of vacuum over the surface.

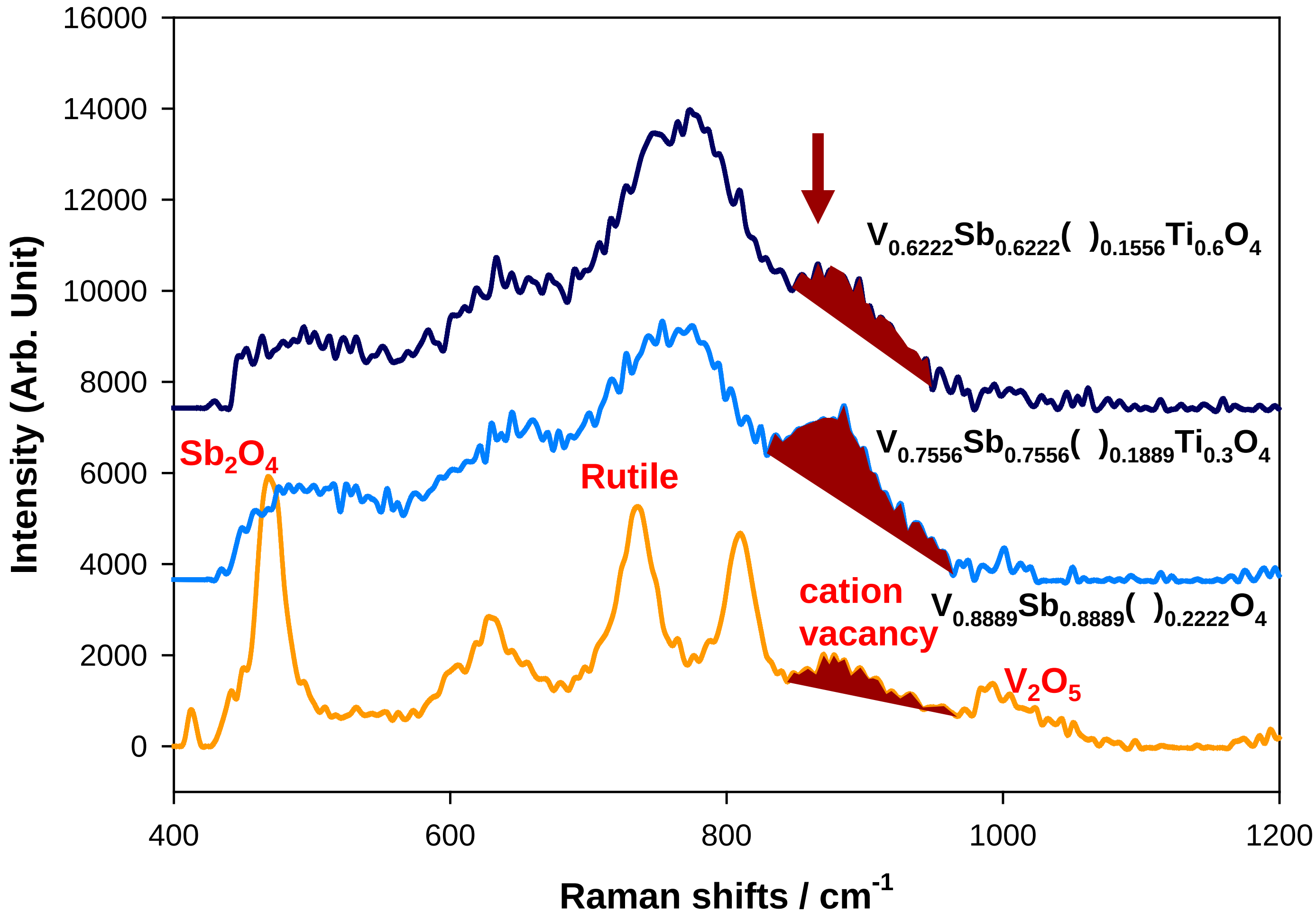


VSb[]O4 110 "slab" created from Model consisting of 47 atoms; 32 O (red), 8 V (grey), & 7 Sb (purple).
The missing antimony comes from a 5-fold site at the surface.

DMOL Simulated Infrared Spectra with Cation Vacancy

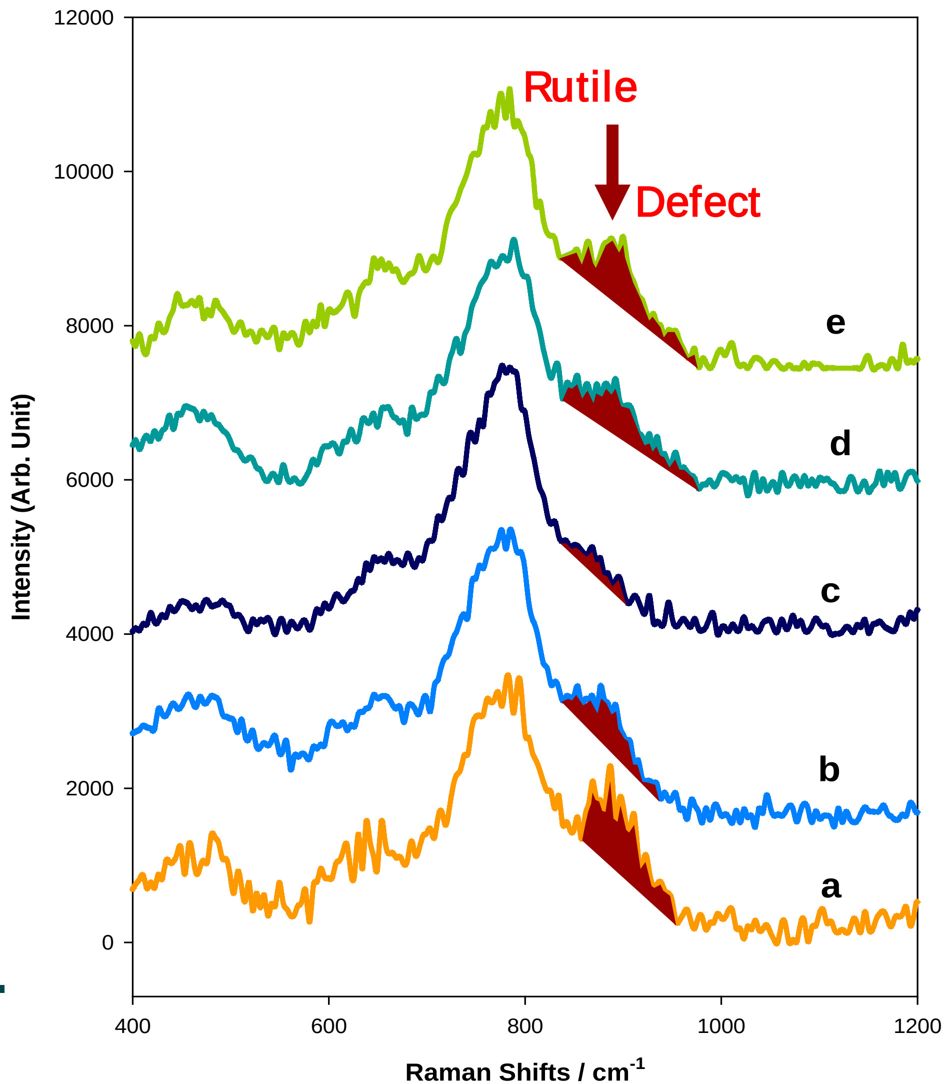


Raman Spectra of $VSbO_4$ and $VSbTiO_4$ Catalysts



innovene

UV Raman spectra of $V_{0.7556}Sb_{0.7556}()_{0.1889}Ti_{0.3}O_4$ under reducing and oxidizing atmosphere



e = oxidized in air for 22 hrs

d = oxidized in air for 3 hrs

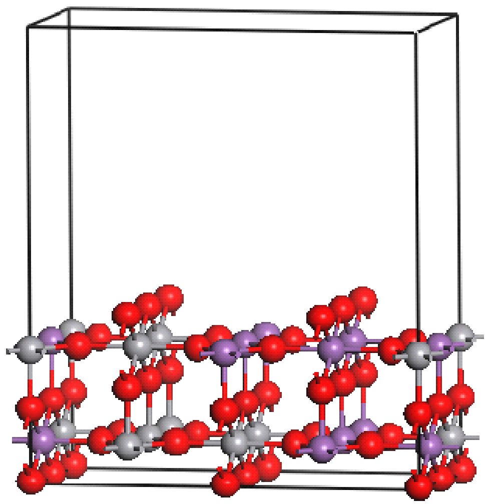
c = reduced in NH_3 for 10 min

b = reduced in NH_3 for 5 min

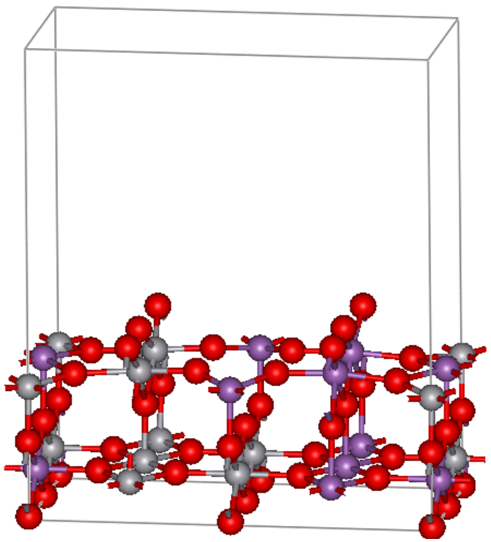
a = fresh catalyst

innovene

Calculations using CASTEP optimized slab models



VSbO4 110 “slab” consisting of 48 atoms; 32 O (red), 8 V (grey), & 8 Sb (purple).
The overall dimensions of the slab are 6.1 Å x 13.1 Å x 15.8 Å with an additional 15 Angstroms of vacuum over the surface.



VSb[]O4 110 “slab” created from Model consisting of 47 atoms; 32 O (red), 8 V (grey), & 7 Sb (purple).
The missing antimony comes from a 5-fold site at the surface.

Summary of Propane Ammox Study

- Identification of an unknown band in Raman spectroscopy made possible by DFT vibrational analysis.
- The cation defect leads to saturatively uncoordinate oxygen anions.
- The activation of the ammonia (& hydrocarbon) via hydrogen abstraction is due to these sites.

Acknowledgements

- Jim Brazdil, Innovene USA LLC
- Jeannine Crockford, HP
- George Fitzgerald, Accelrys
- Gary Goeden, Innovene USA LLC
- Joe Golab, Innovene USA LLC
- Roberto Gomperts, SGI
- Muin Haddad, Innovene USA LLC
- Jim Kaduk, Innovene USA LLC
- Thanh Nguyen, Innovene LLC
- Eric Renner, SGI
- Peter Stair, Northwestern Univ.
- Vivian Sullivan, Northwestern Univ.
- Steve Trail, Elgin Community College
- Guang Xiong, Argonne National Lab

innovene