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Some Thoughts About Surface Hydroxyl Groups and Catalysis

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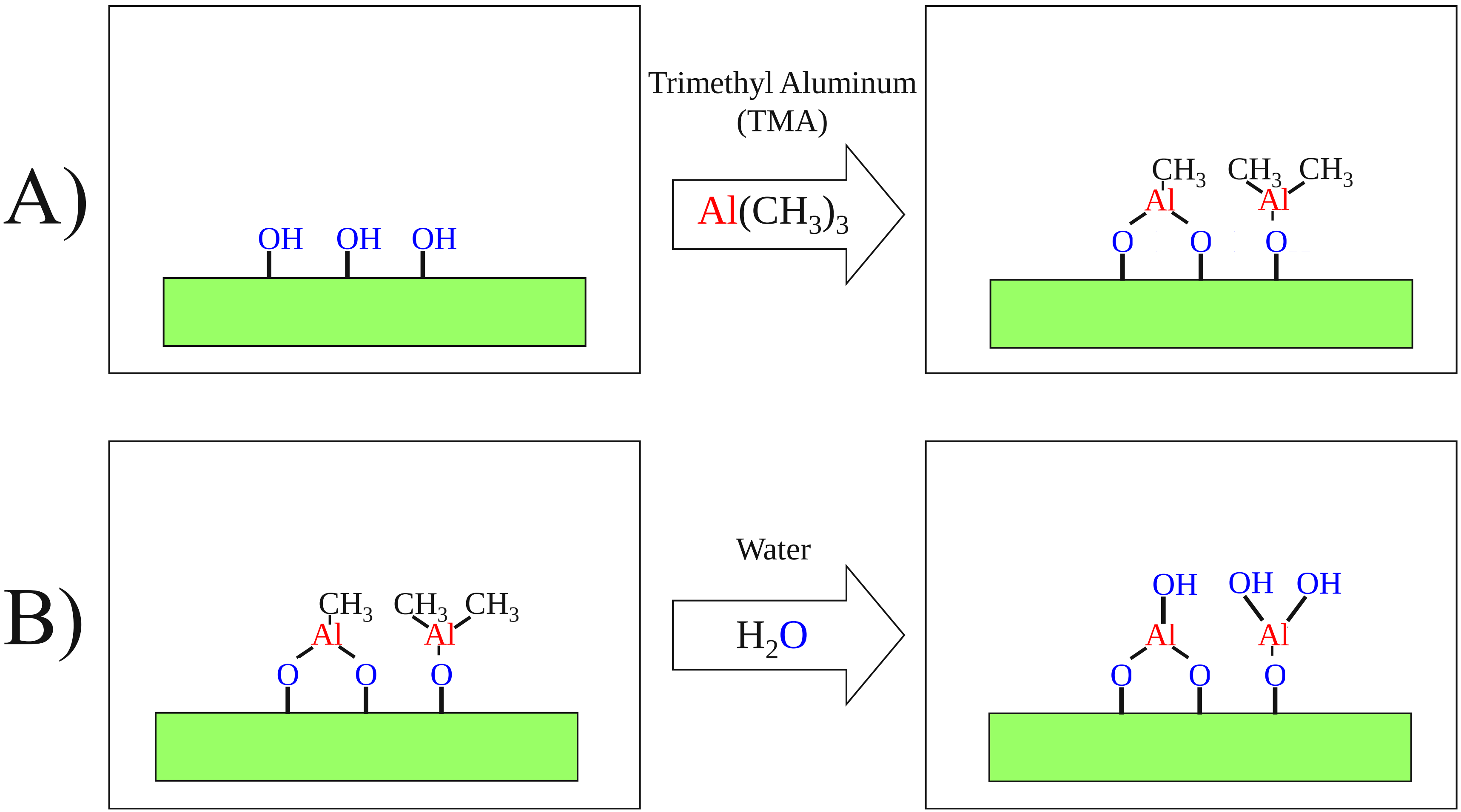
Atomic Layer Deposition: Support Synthesis

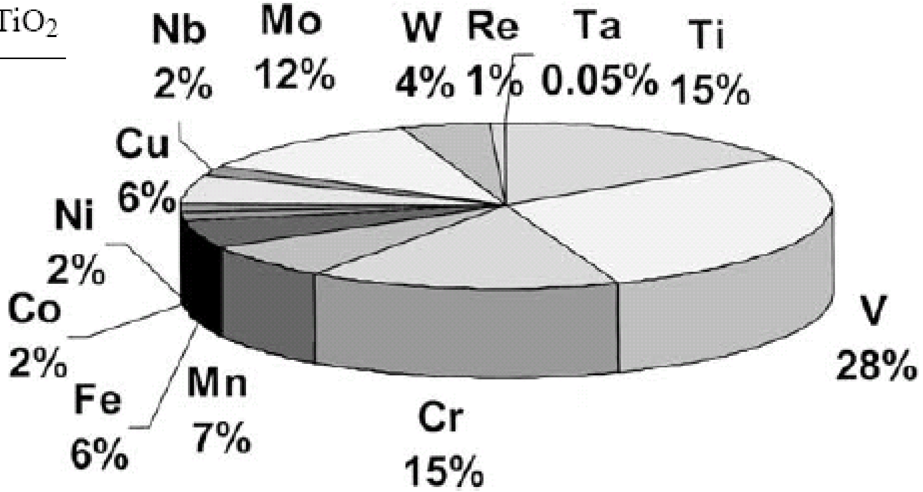


Significance of Vanadium Oxide

Industrial Processes

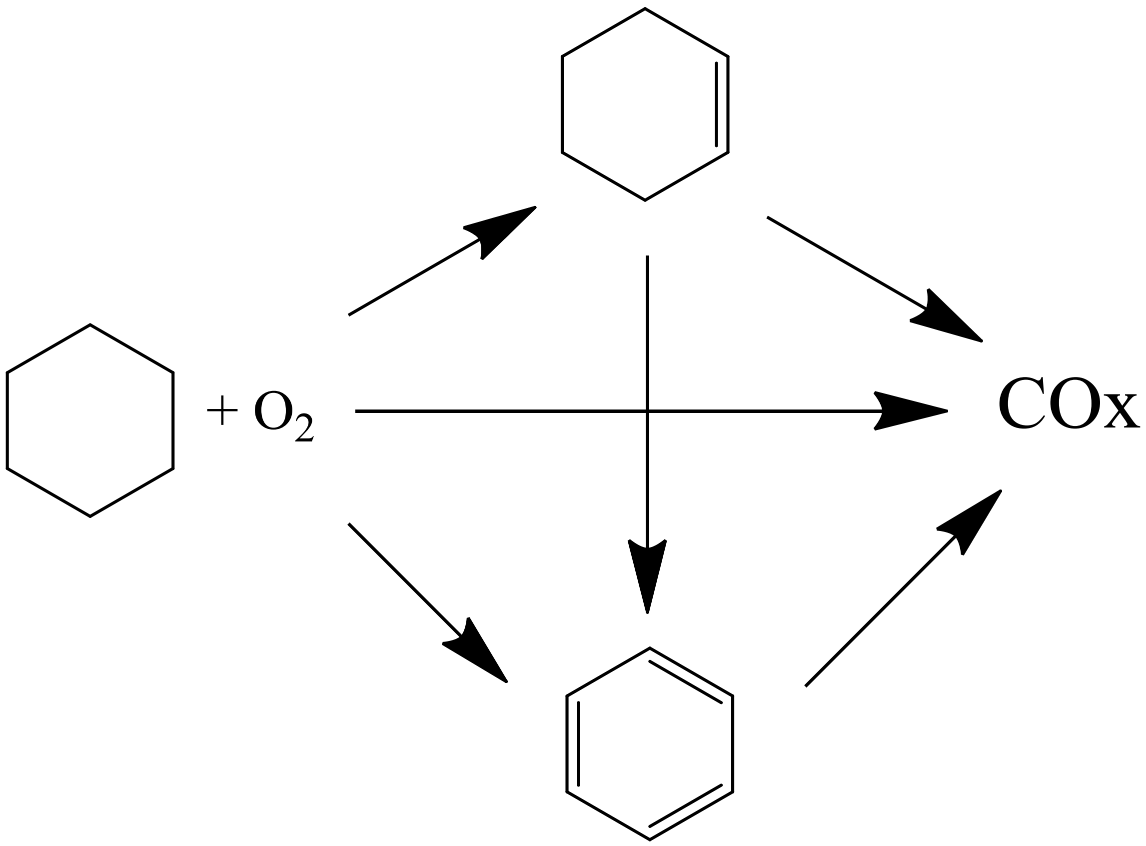
Industrial process	Catalyst material
Oxidation of SO_2 to SO_3 in the production of sulfuric acid	V_2O_5
Oxidation of benzene to maleic anhydride	V_2O_5
Oxidation of naphthalene to phthalic anhydride	V, Mo oxides
Oxidation of butene to phthalic anhydride	V, P oxides
Oxidation of *o*-xylene to phthalic anhydride	V, Ti oxides
Selective reduction of NO_x with NH_3	$V_2O_5/WO_3/TiO_2$

Literature

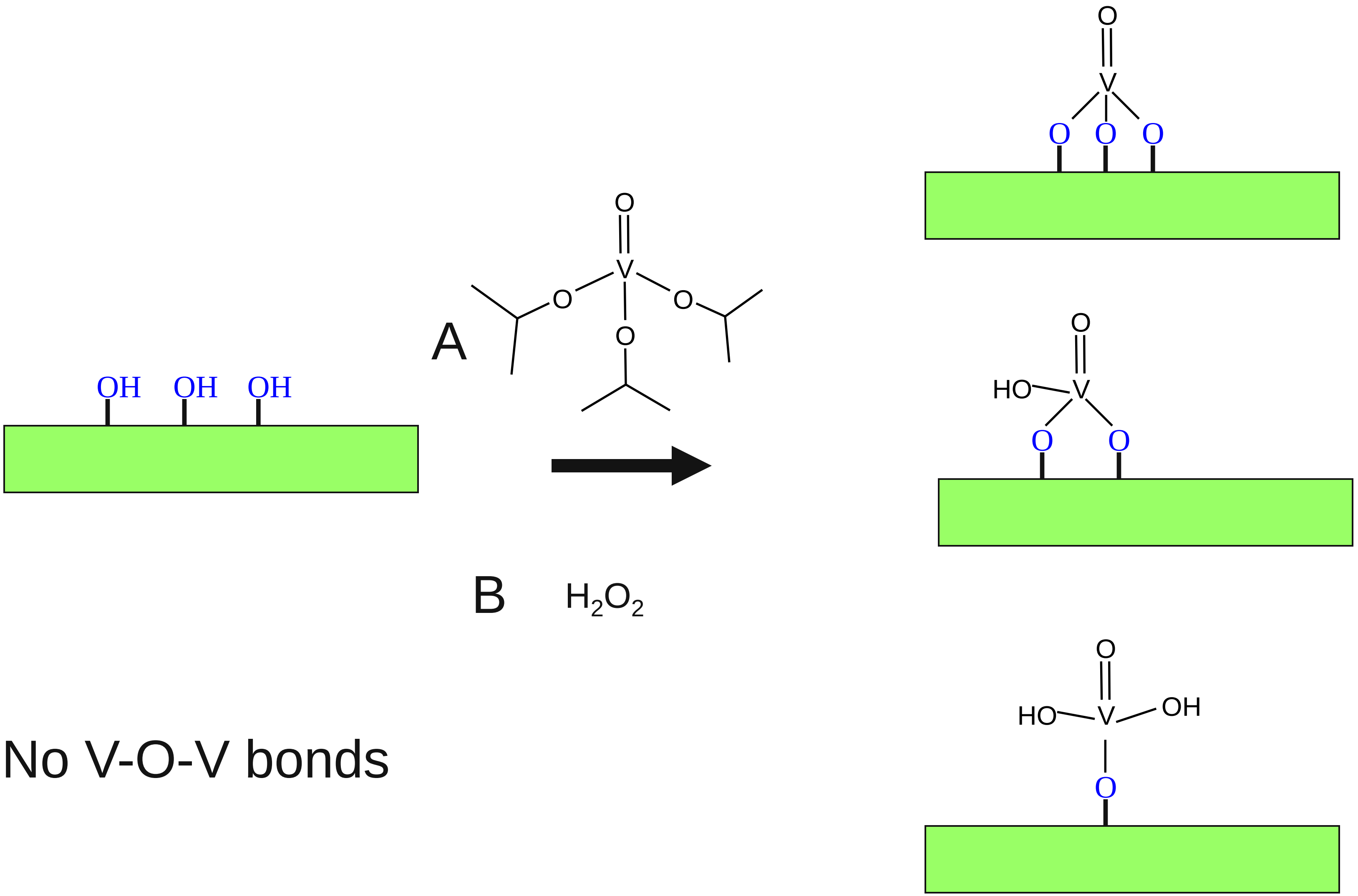


B.M. Weckhuysen, D.E. Keller / Catalysis Today 78 (2003) 25–46

Oxidative Dehydrogenation of Cyclohexane

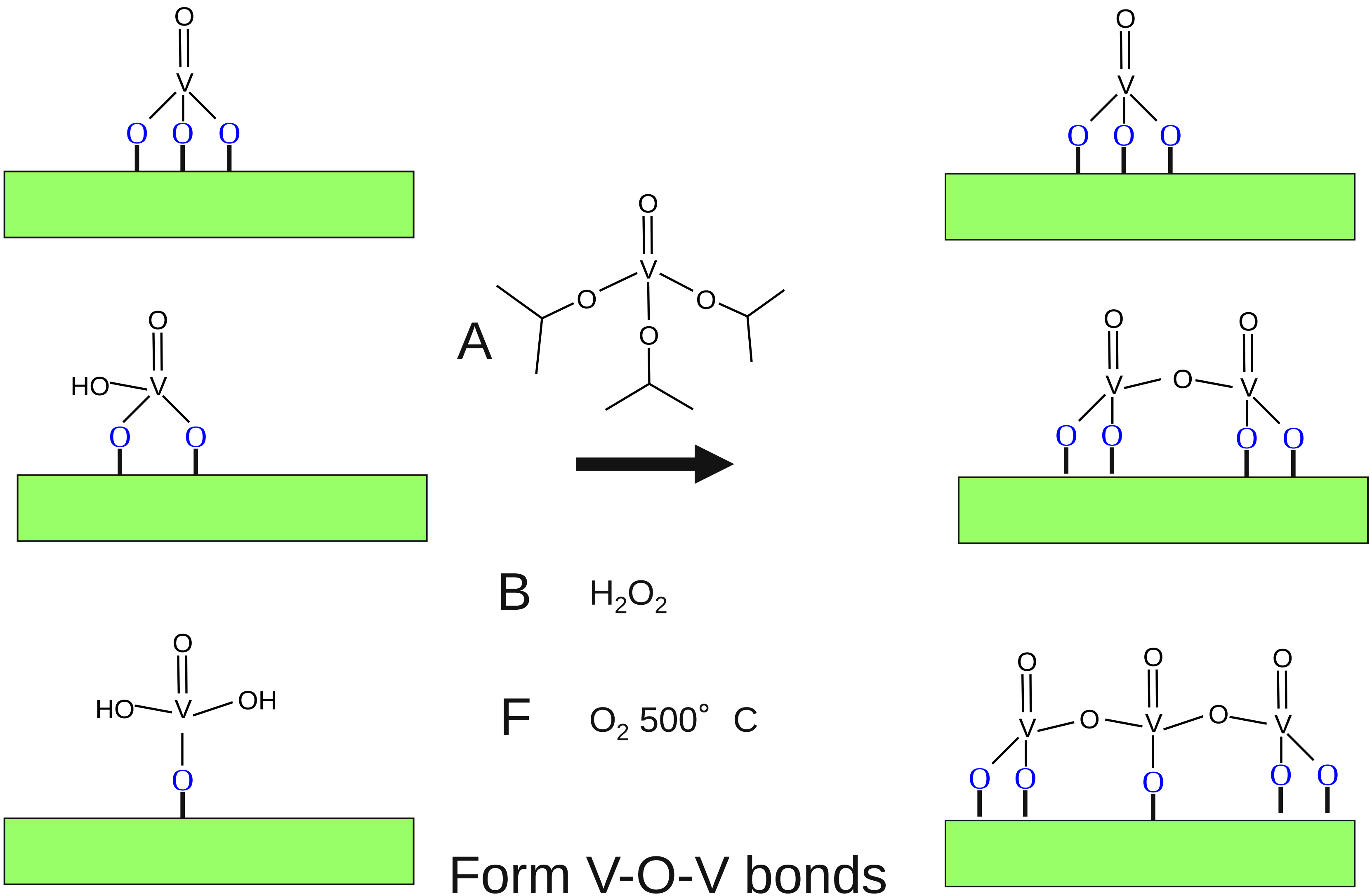


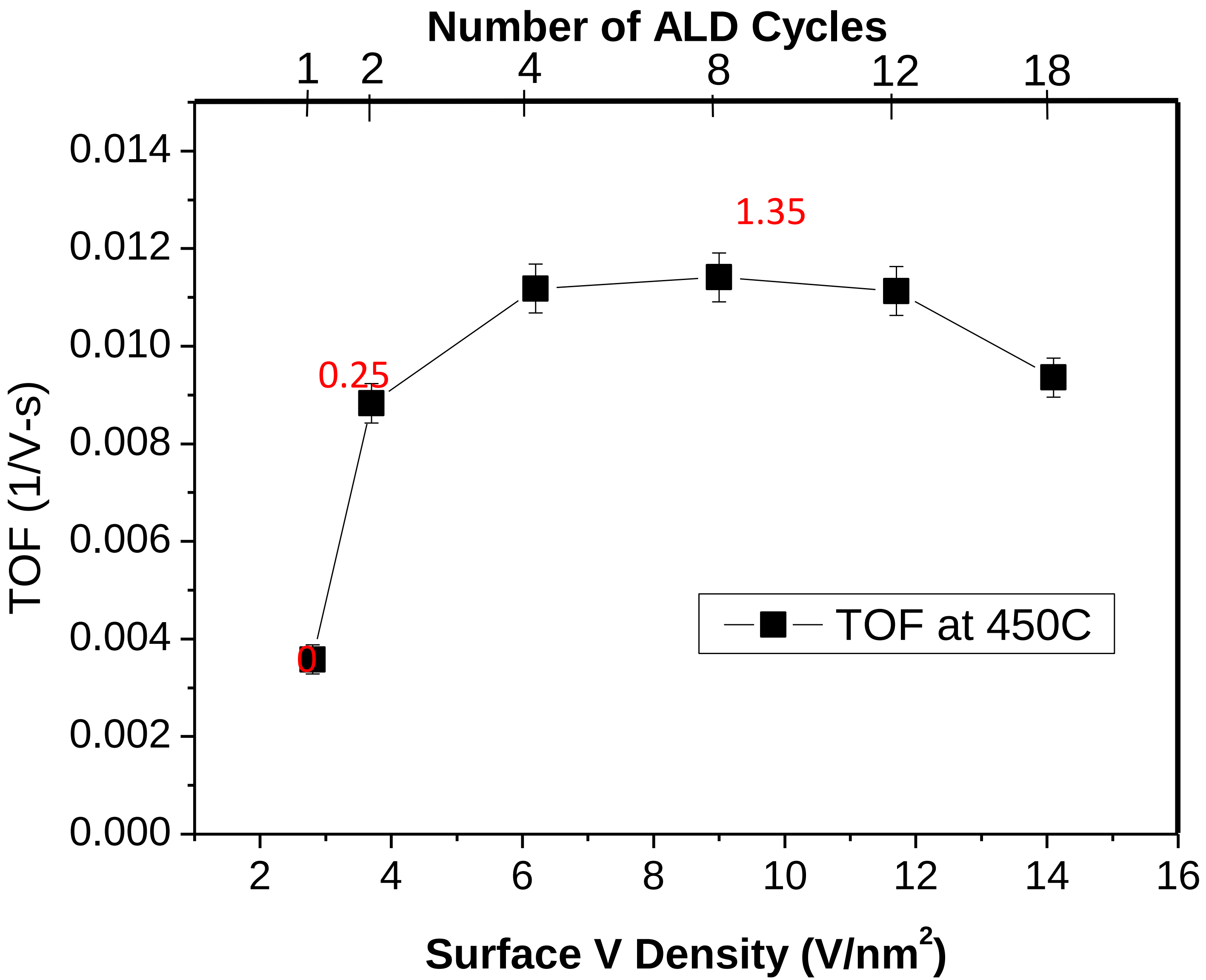
Vanadium ALD: First Cycle



No V-O-V bonds

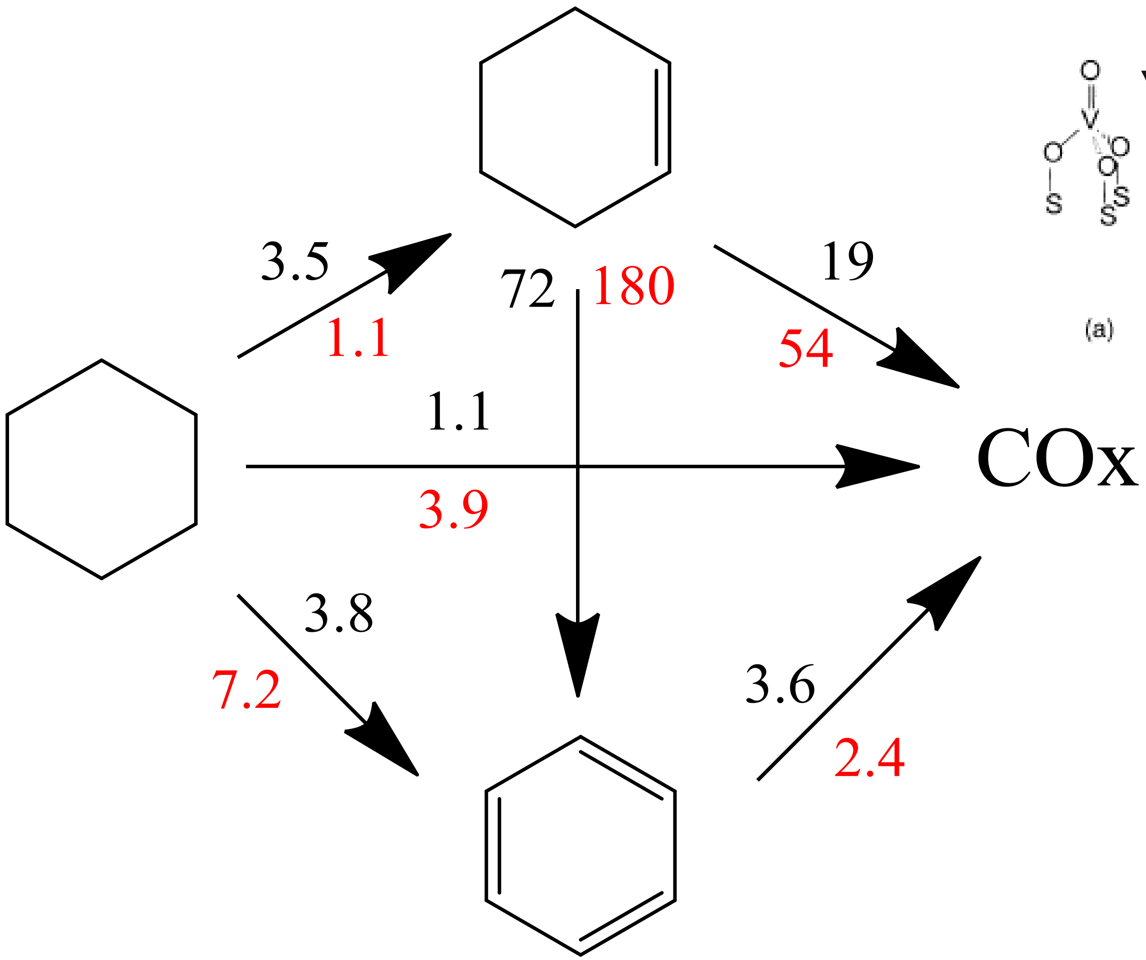
Vanadium ALD: Two Cycles

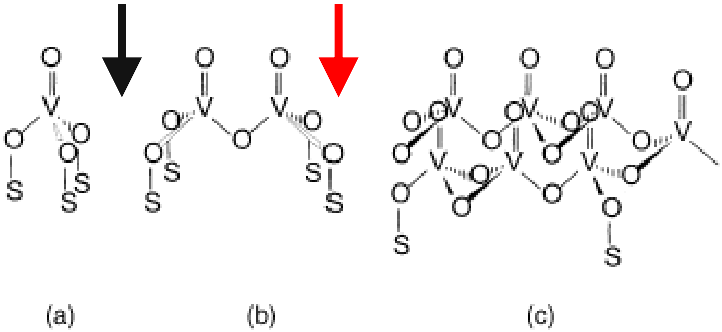




Number of ALD Cycles
1
2
4
8
12
18
TOF (1/V-s)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
1.35
0.25
0
TOF at 450C
2
4
6
8
10
12
14
16
Surface V Density (V/nm^2)

ODH TOFx1000: 450 °C

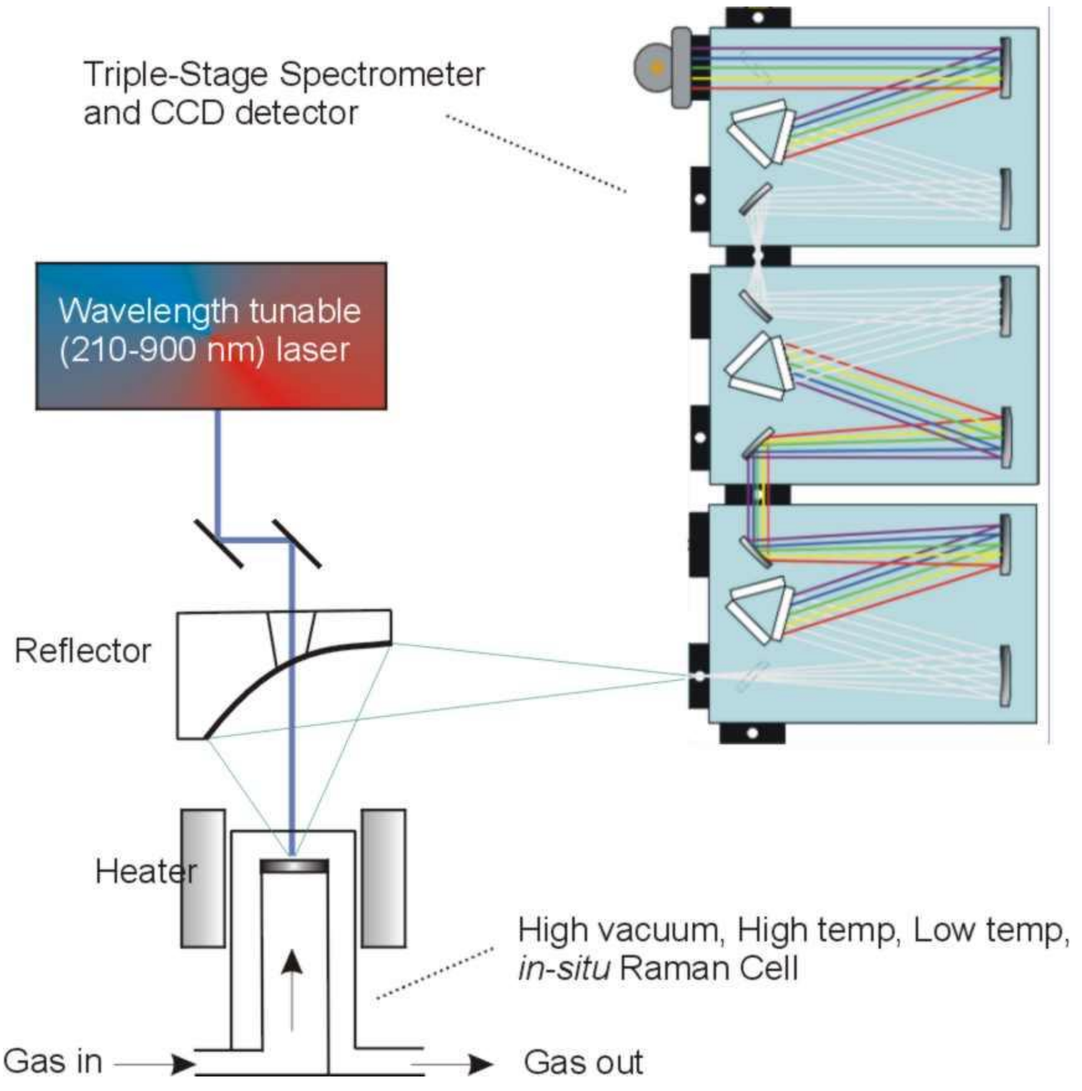




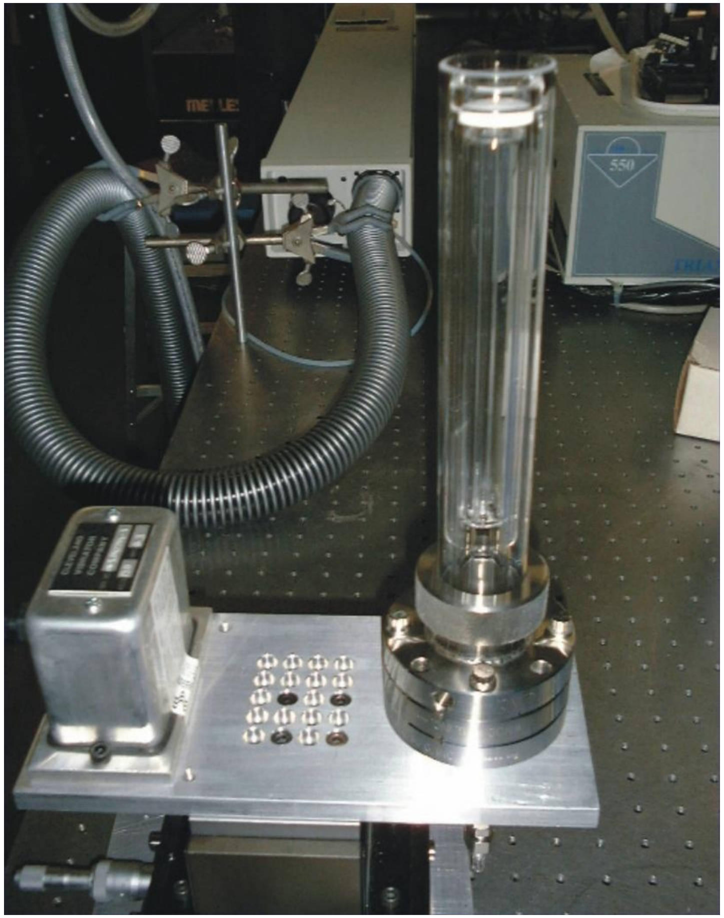
Black = 0.46 ML => Mostly VOx monomers

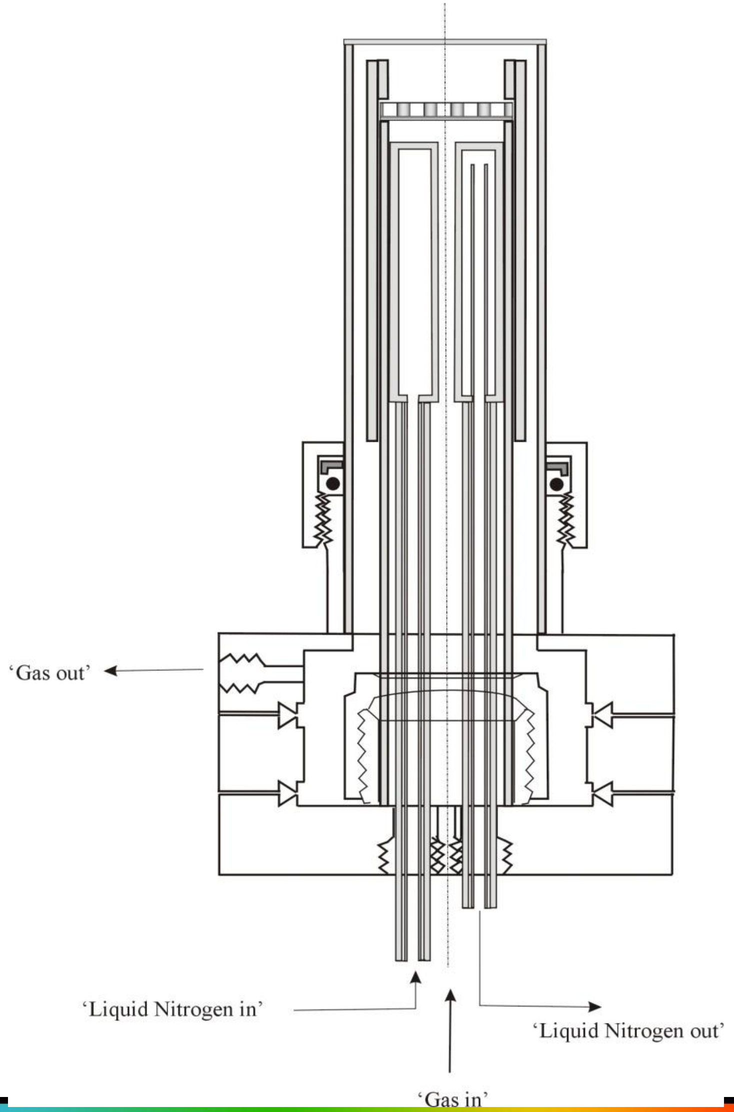
Red = 1.1 => More, larger VOx polymers

Tunable Raman Spectrometer

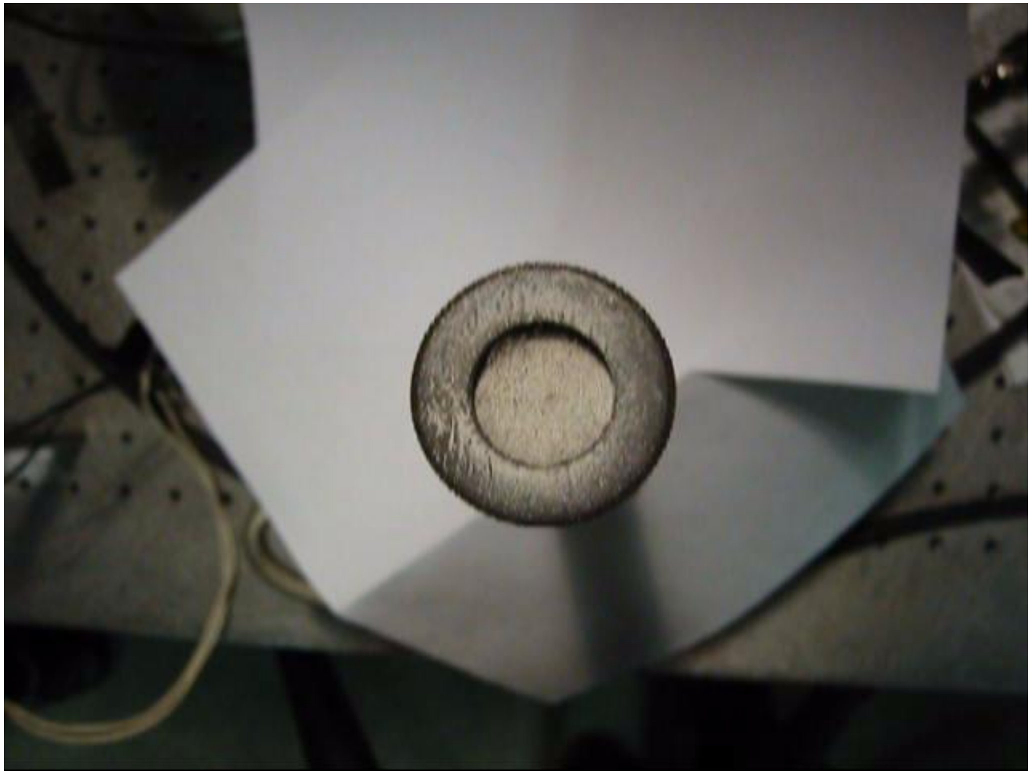


Low-T Fluidized Bed Cell





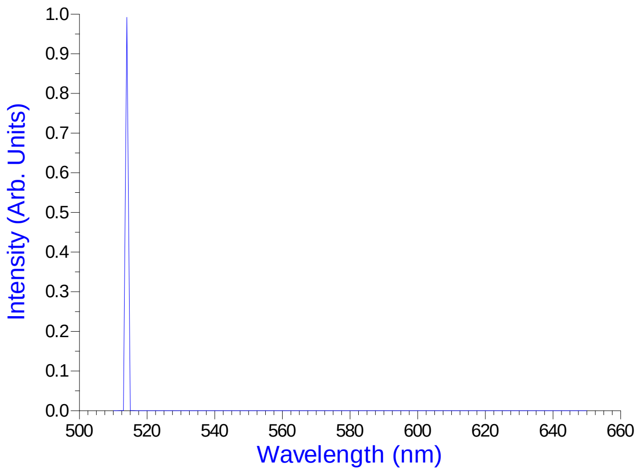
Fluidized Bed Action

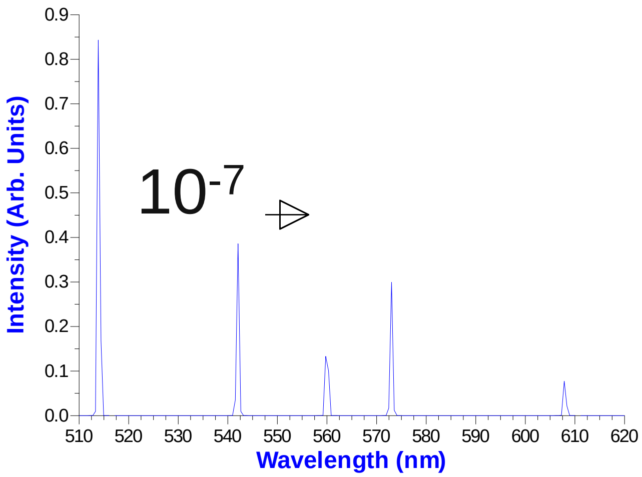


Features of Raman Spectroscopy

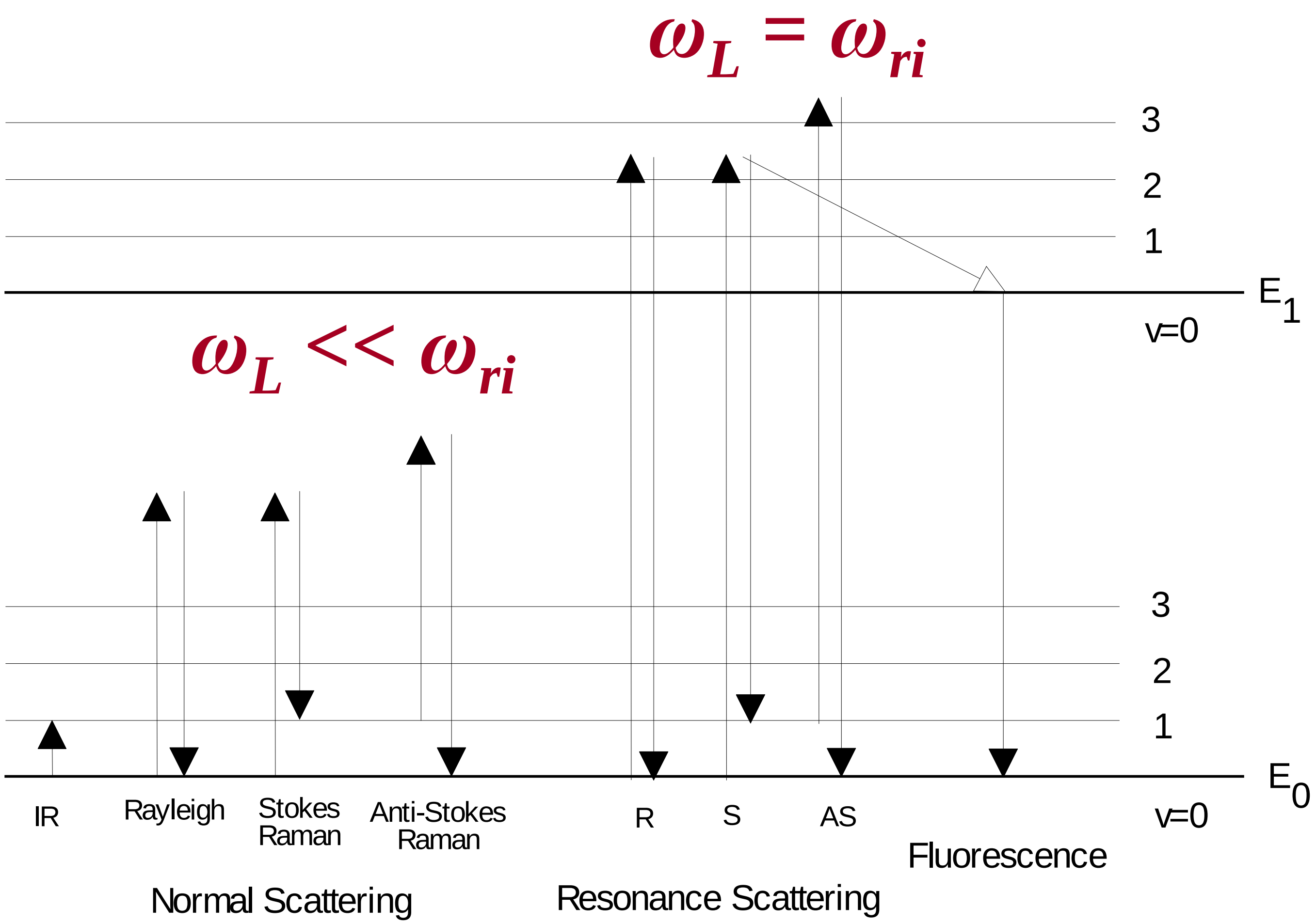
- **Advantages**
  - **Chemical and Structural Identification**
  - **Vibrations from 50 to 4000 cm^{-1}**
  - **Monitor Catalyst and Reagent**
  - **In-situ Measurements**
  - **Real Catalysts**

- **Disadvantages**
  - **Weak Signals (10^{-7} IR)**
  - **Fluorescence Interference**
  - **Quantification Difficulties**





Energy Levels



Raman Scattering Equation

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- Raman Scattering Intensity

$$I(\omega_L - \omega_{fi}) = N\, I_0(\omega_L)\, \frac{4\pi(\omega_L - \omega_{fi})^4}{3c^4} \sum_{\rho\sigma} (\alpha'_{\rho\sigma})^2$$

Raman Cross Section

- Polarizability Derivative

$\alpha'_{\rho\sigma}$ = polarizability derivative

$$\alpha'_{\rho\sigma} = \sum_r \left[\frac{(\mu_\rho)_{fr}(\mu_\sigma)_{ri}}{\hbar(\omega_{ri} - \omega_L) + i\Gamma_r} + \frac{(\mu_\sigma)_{fr}(\mu_\rho)_{ri}}{\hbar(\omega_{fr} + \omega_L) + i\Gamma_r} \right]$$

- When $\omega_L = \omega_{ri}$, α' is large => resonance enhancement

Vanadia/alumina Samples

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- Samples: V/α-, θ-, γ-Al2O3 with different loadings (0.01 – 34.2 V/nm^2), prepared by incipient wetness impregnation method.

- NH_4VO_3 solution, Dry in air at RT and 150°C, Calcine in O_2 at 500°C for 5 hrs

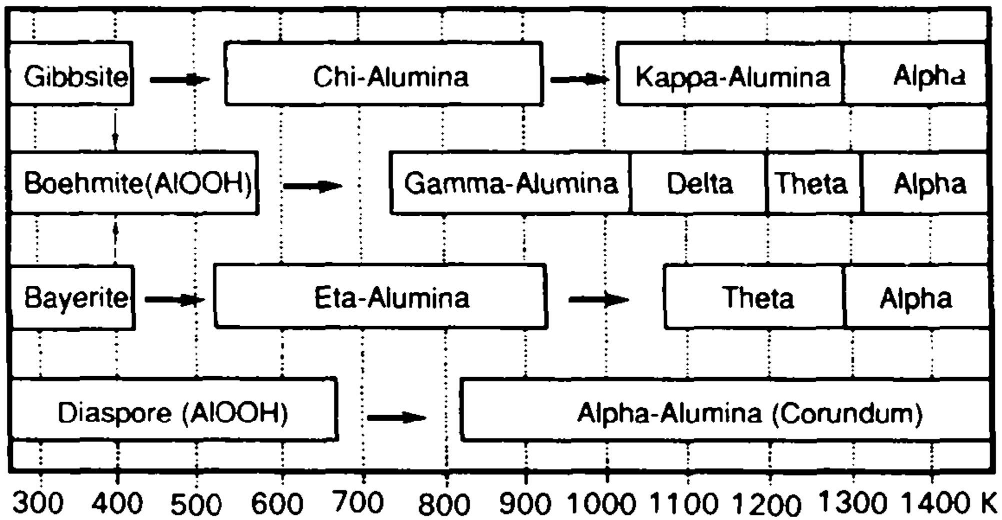

Fig. 1. Thermal diagram of the transition aluminas (after Wefers & Misra, 1987).

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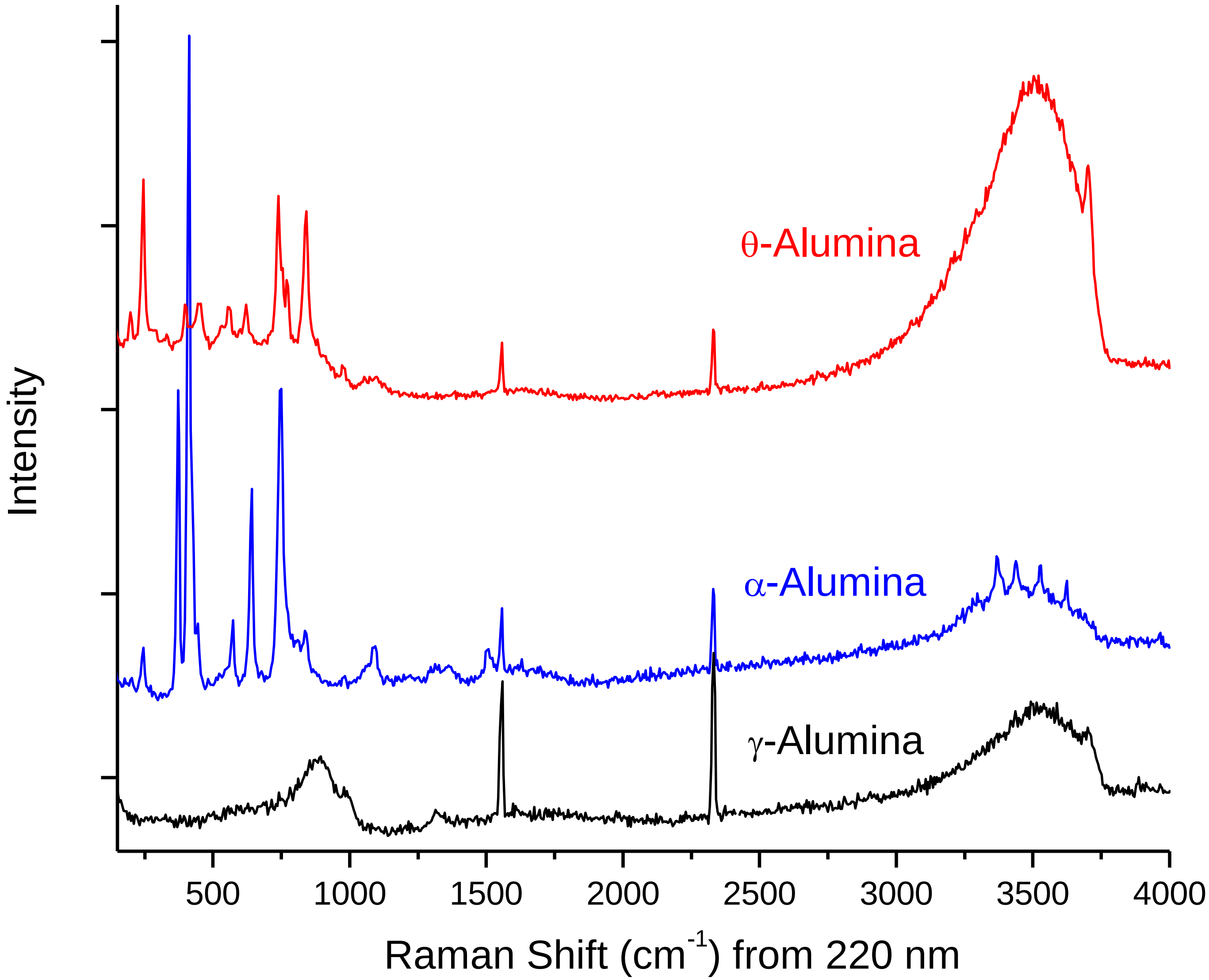
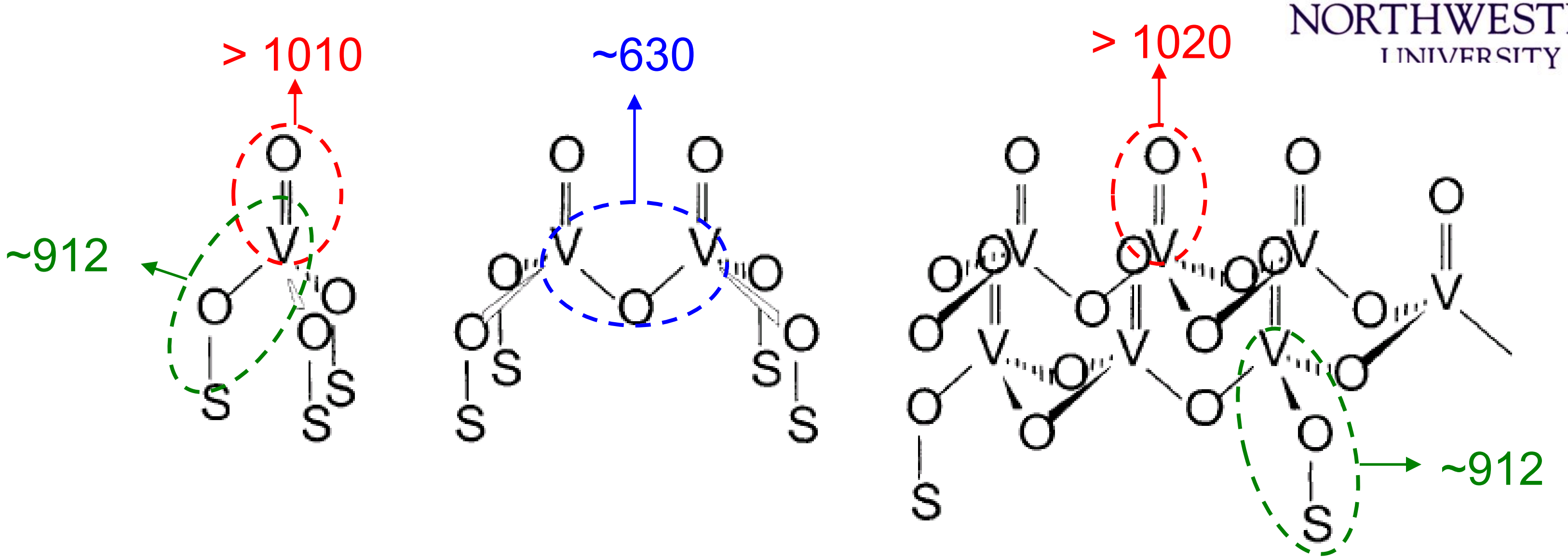
deep UV Raman: Alumina, Hydrated, RT



Incipient Wetness Impregnation

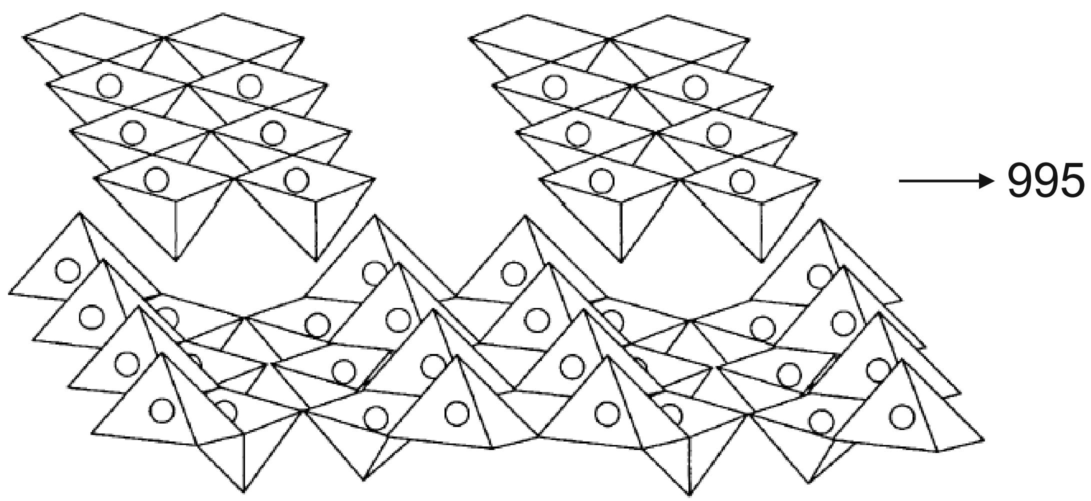
- Measure alumina surface area by BET
- Determine volume of H_2O needed for incipient wetness
- Dissolve weight of NH_4VO_3 for desired surface density
- Wet alumina with solution
- Dry at room temperature in air, then 120°C for 12 hours
- Dry at 550°C for 6 hours



monomeric dimeric polymeric

0.01 – 0.16 V/nm²

1.2 – 14.2 V/nm²

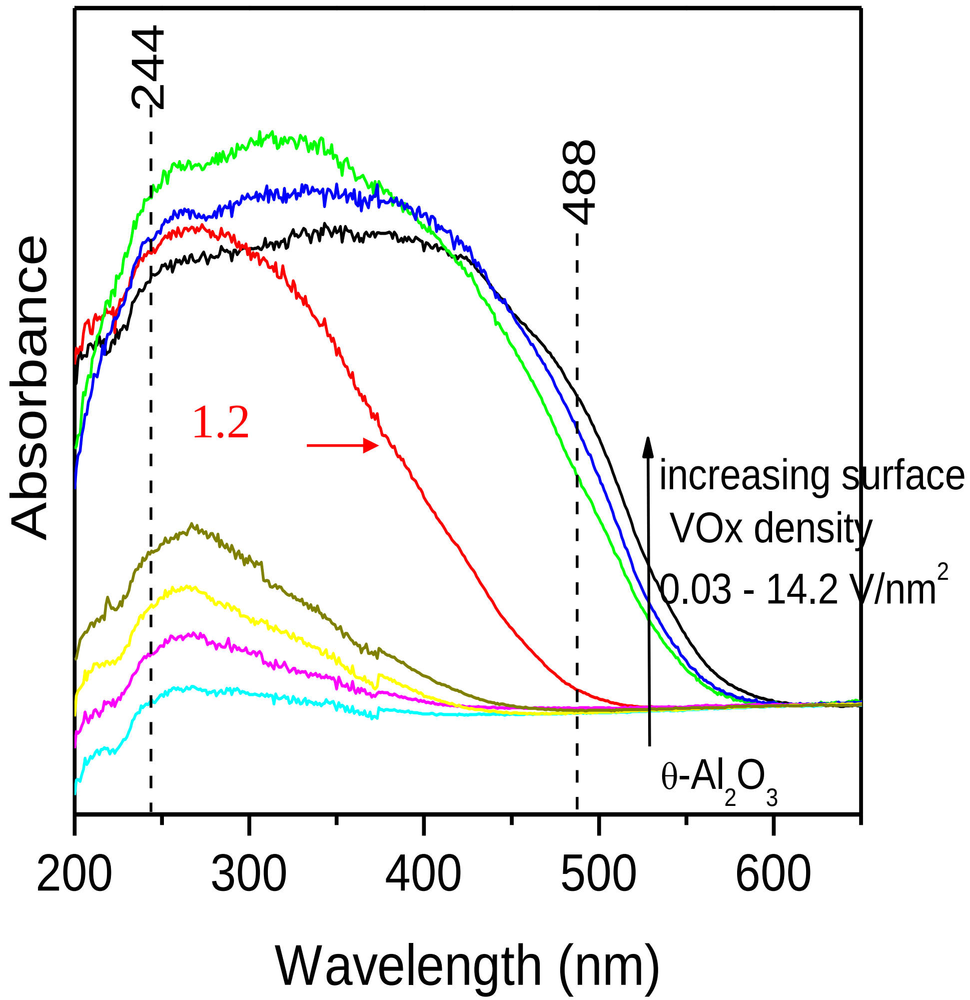


crystalline V_2O_5

4.4 – 14.2 V/nm²

Wu et al., J. Phys. Chem. B 109(2005)2793

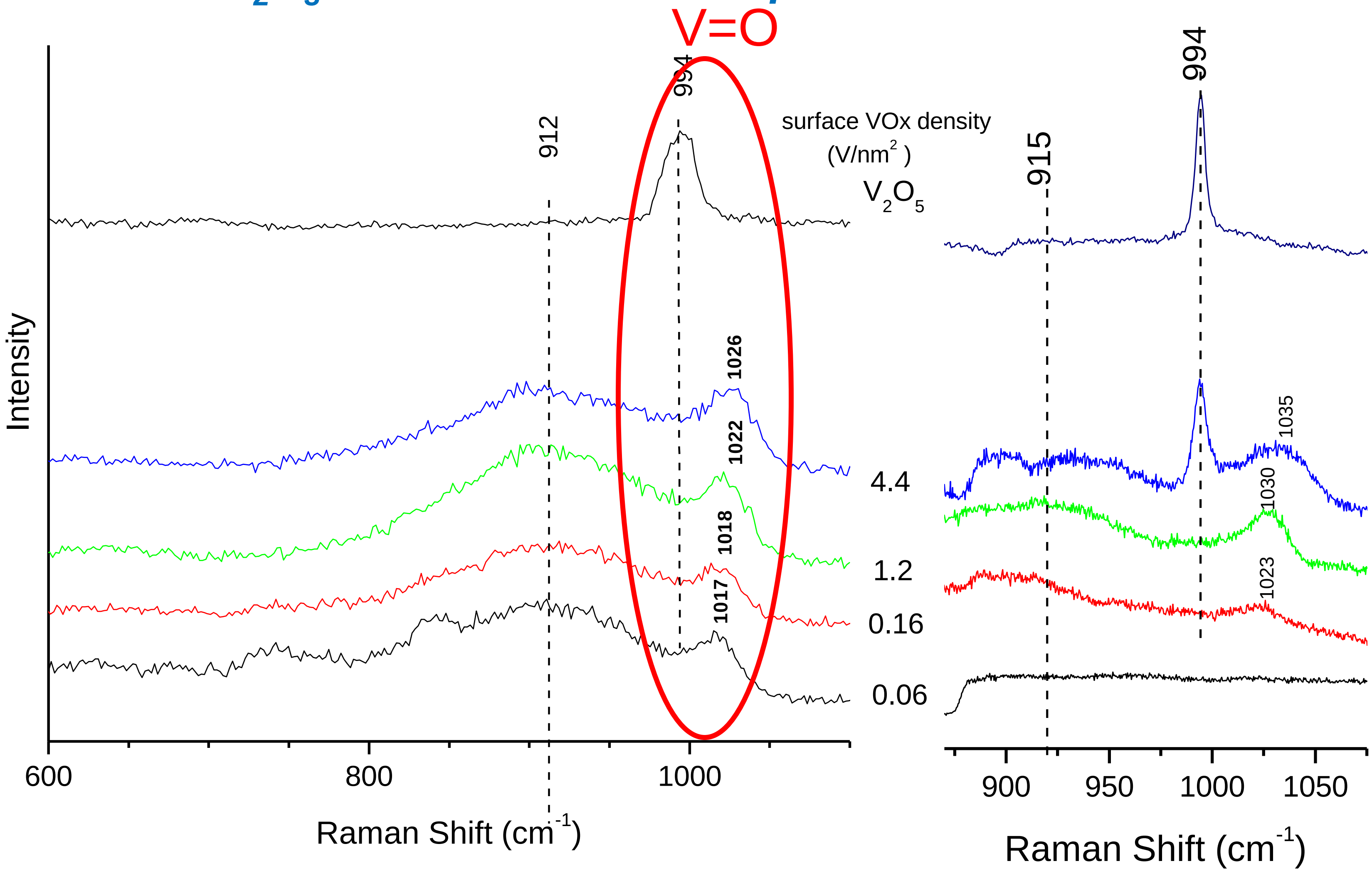
VOx/θ-Al_2O_3 UV-Vis Absorption



Monomeric VOx in resonance with UV (244 nm) excitation

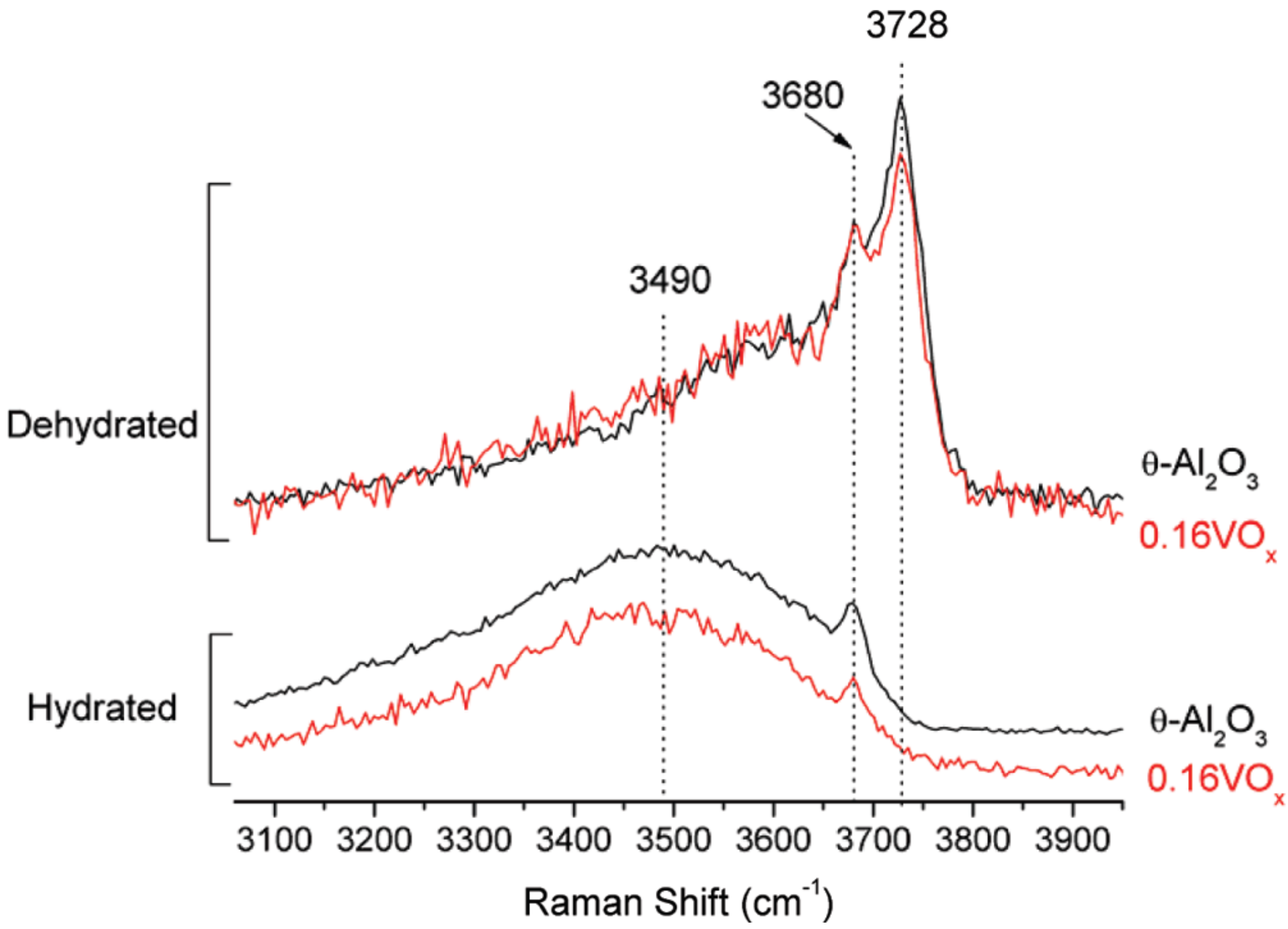
Polymeric VOx in resonance with Vis (488 nm) excitation

VOx/θ-Al_2O_3: UV/Vis Raman Comparison



λ = 244 nm **λ = 488 nm**

0.16 VO_x on θ-Al_2O_3



0.02 ML on θ-alumina : Raman

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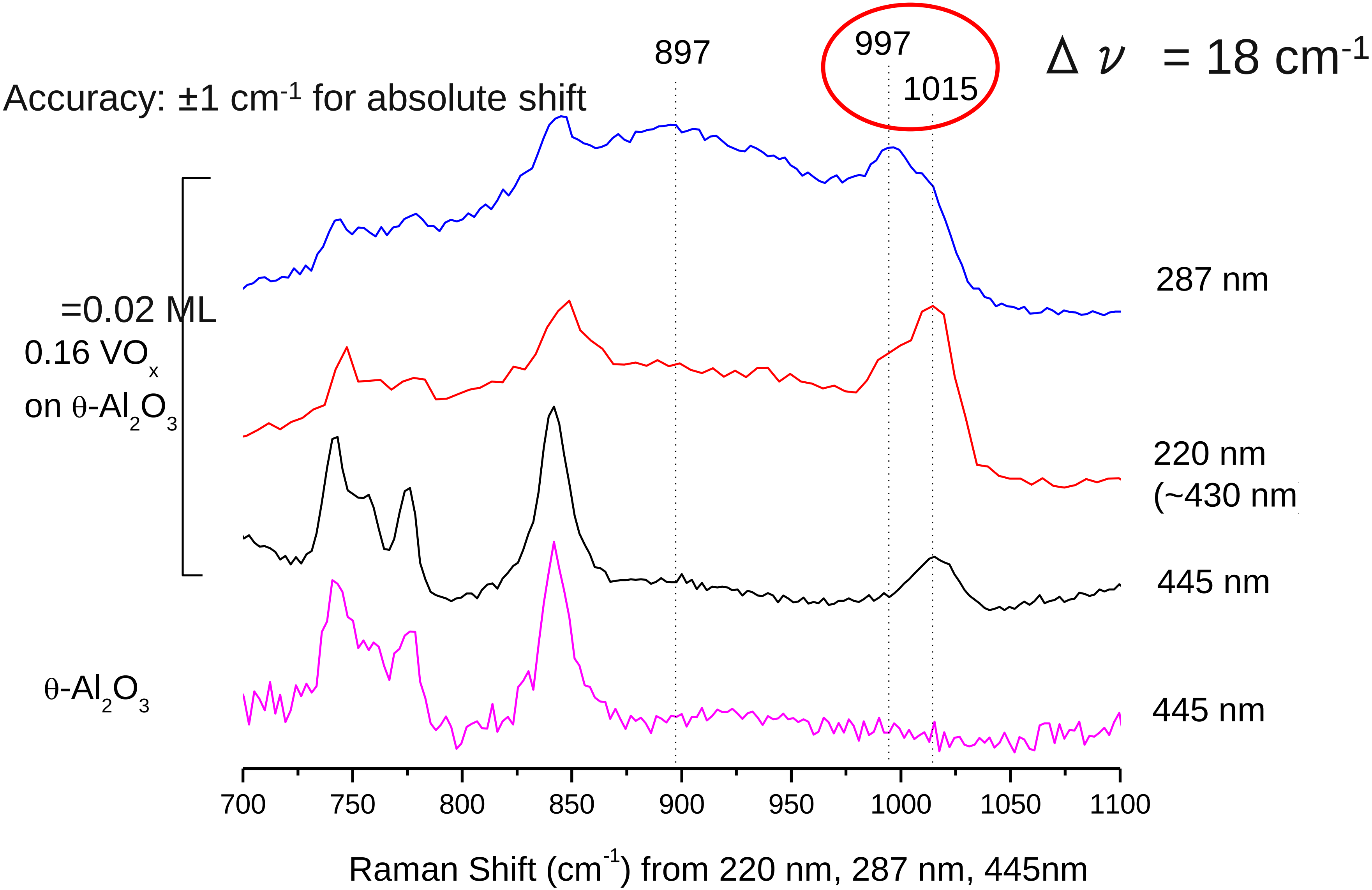
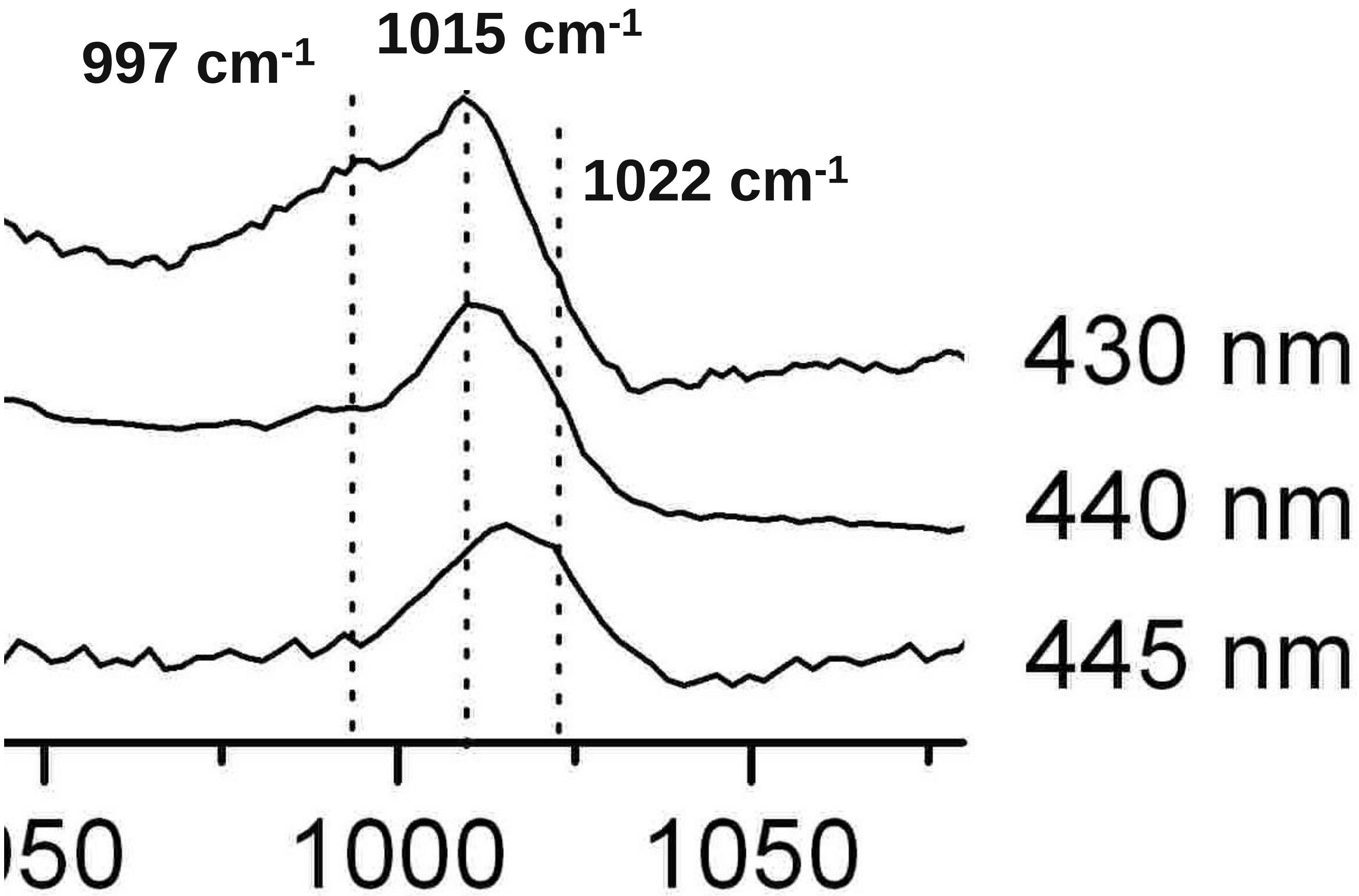
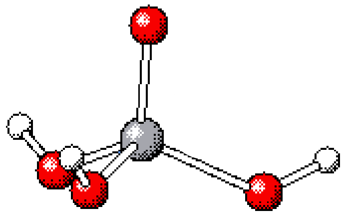


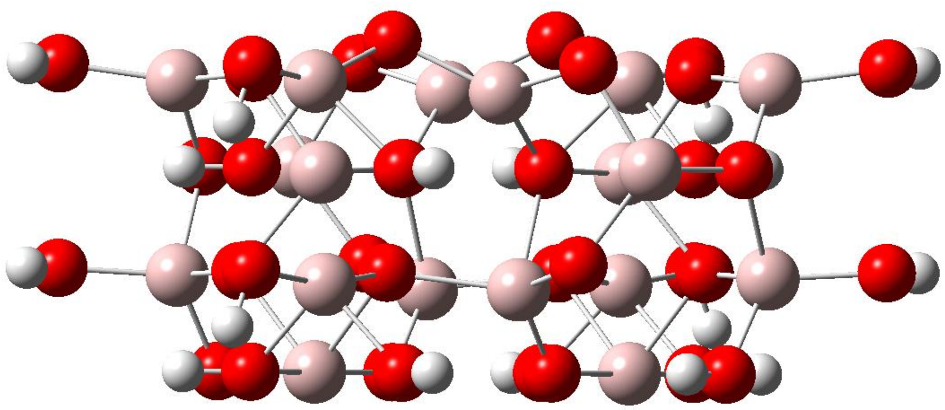
Three VOx Monomers



Density functional modeling of VOx monomers on (010) θ-Alumina



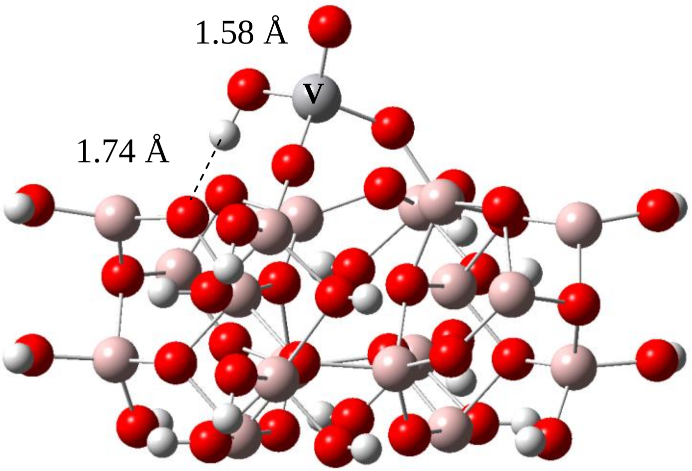
VO_4H_3



Cluster model for θ-Al_2O_3

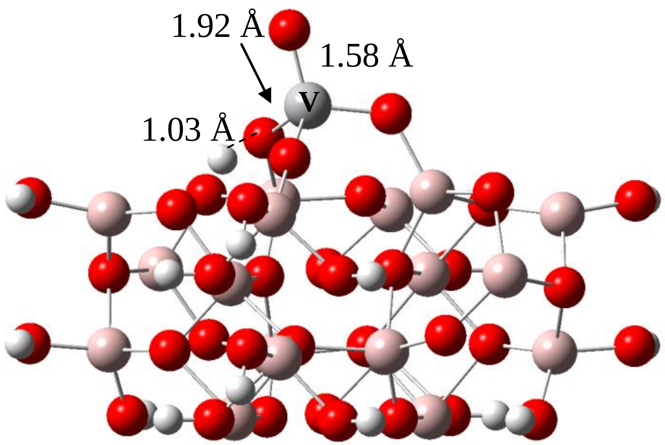
- B3LYP/6-31G* calculations using cluster model for alumina
- Full relaxation with perimeter atoms held fixed in crystal structure

VOx Monomer Structures



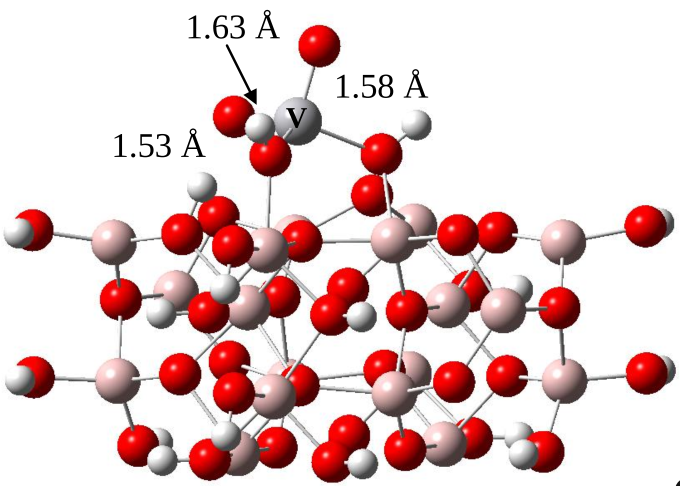
Dehydrated Bidentate

1022 cm^{-1}



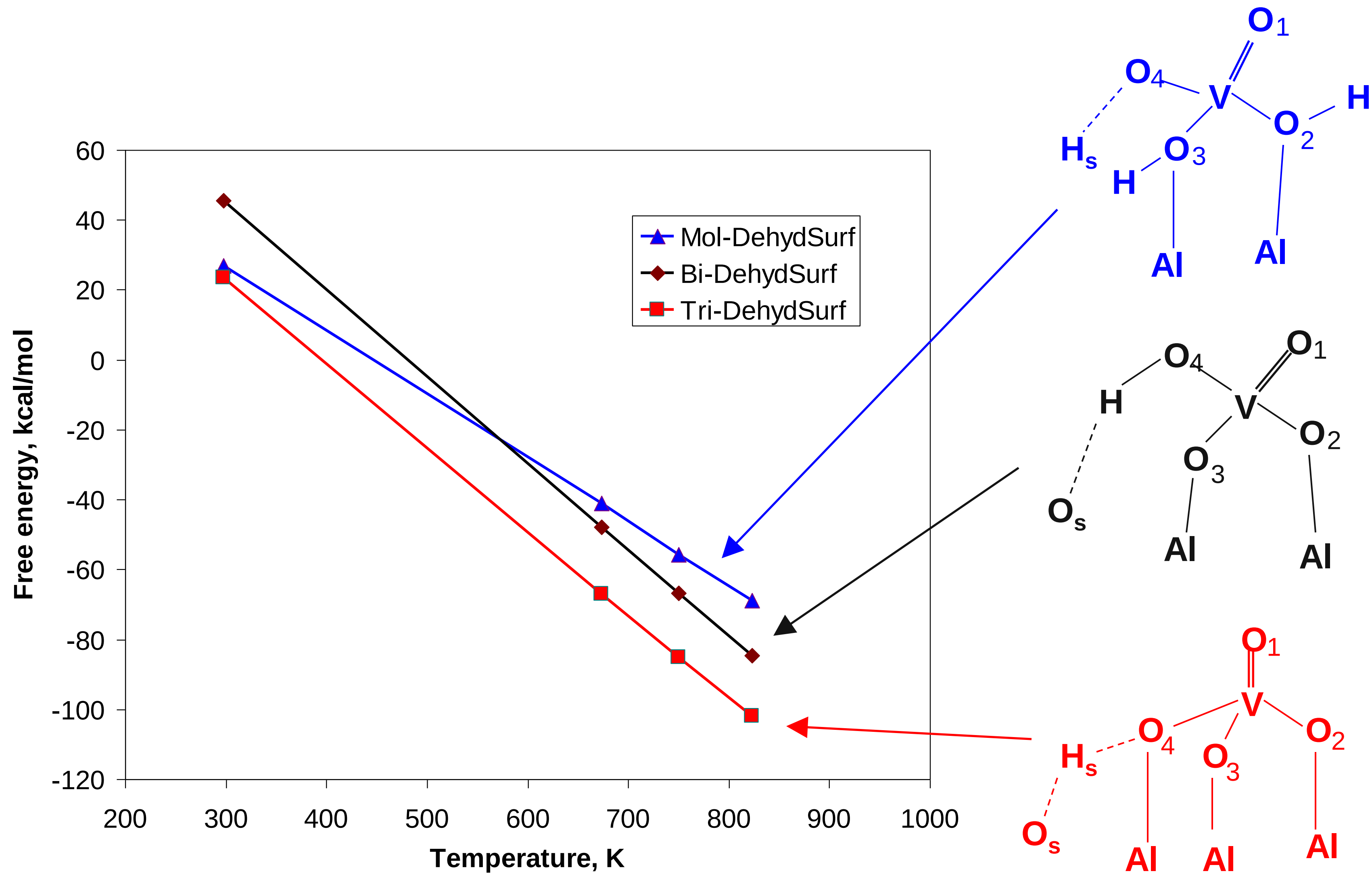
Dehydrated Tridentate

1015 cm^{-1}



Dehydrated Molecular

997 cm^{-1}

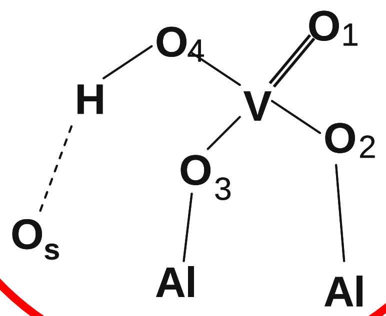


Mol-DehydSurf
Bi-DehydSurf
Tri-DehydSurf
Free energy, kcal/mol
Temperature, K
60
40
20
0
-20
-40
-60
-80
-100
-120
200
300
400
500
600
700
800
900
1000

Hydrogen Reduction: 0.16 V

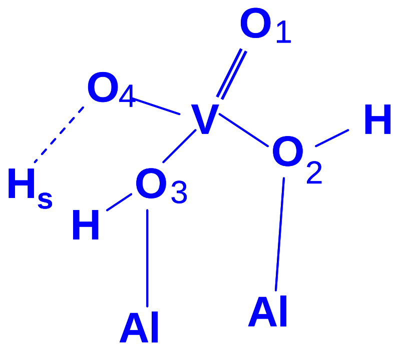
1. Hold in hydrogen for one hour
2. Measure Raman spectrum

Bidentate



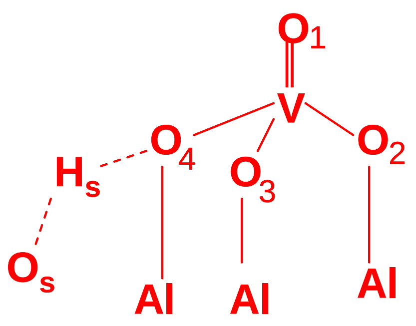
450 C

Molecular



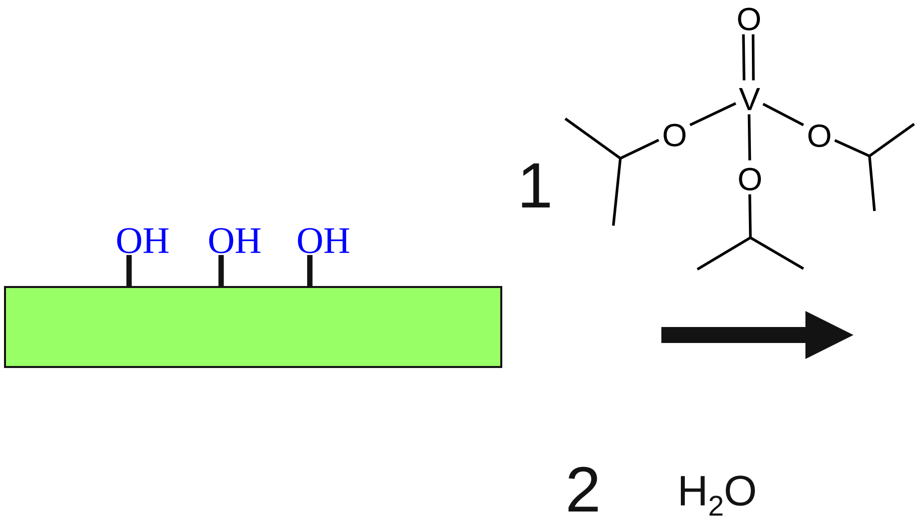
550 C

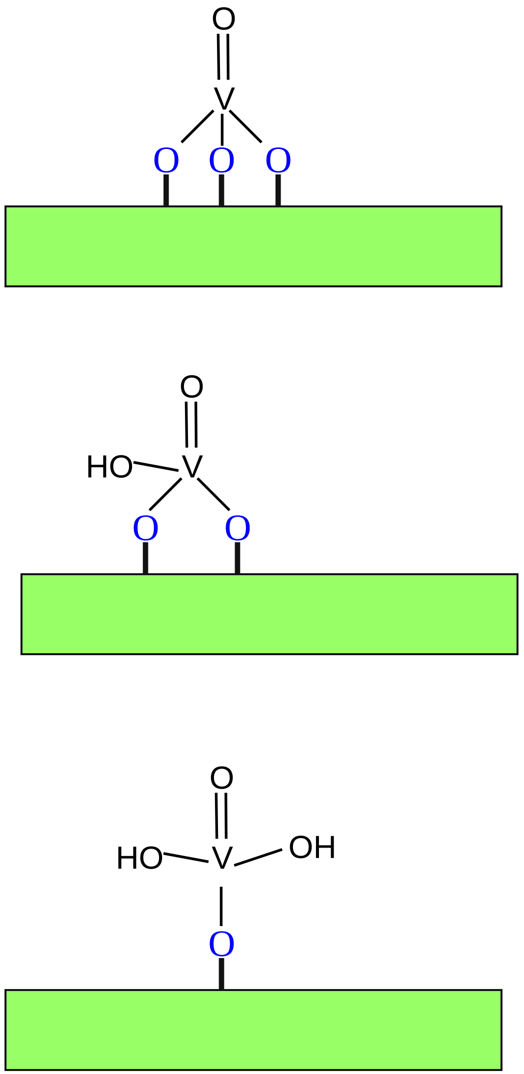
Tridentate



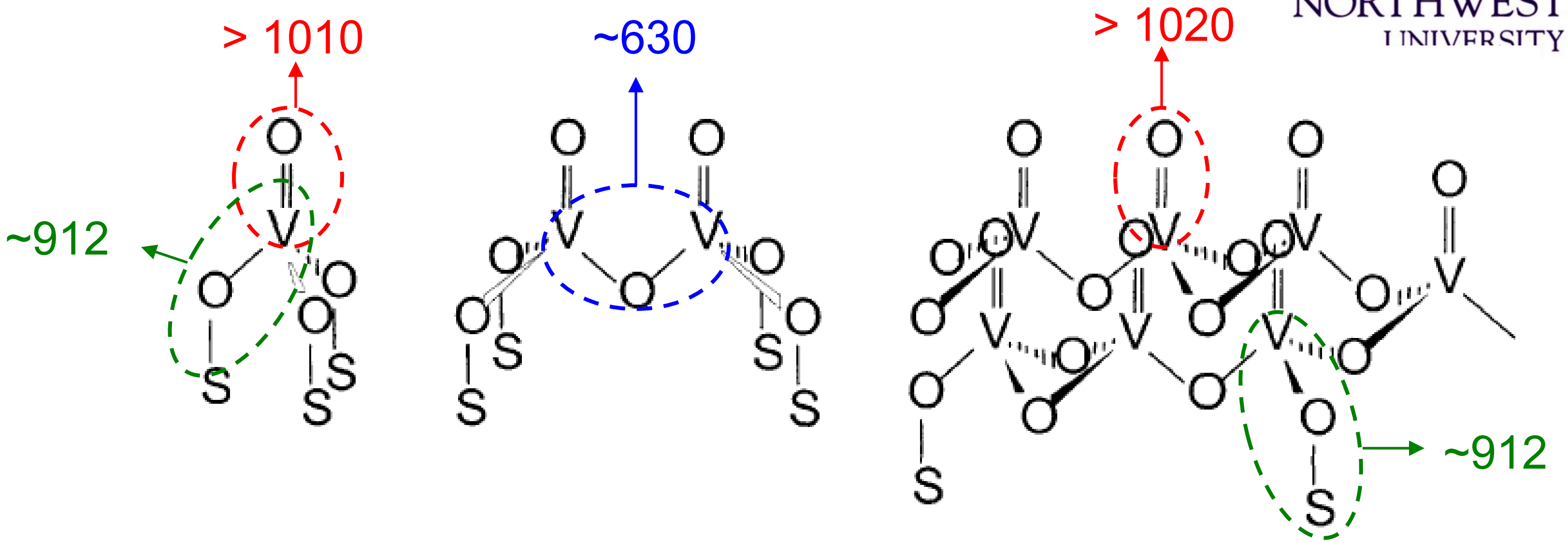
650 C

Vanadium ALD: First Cycle





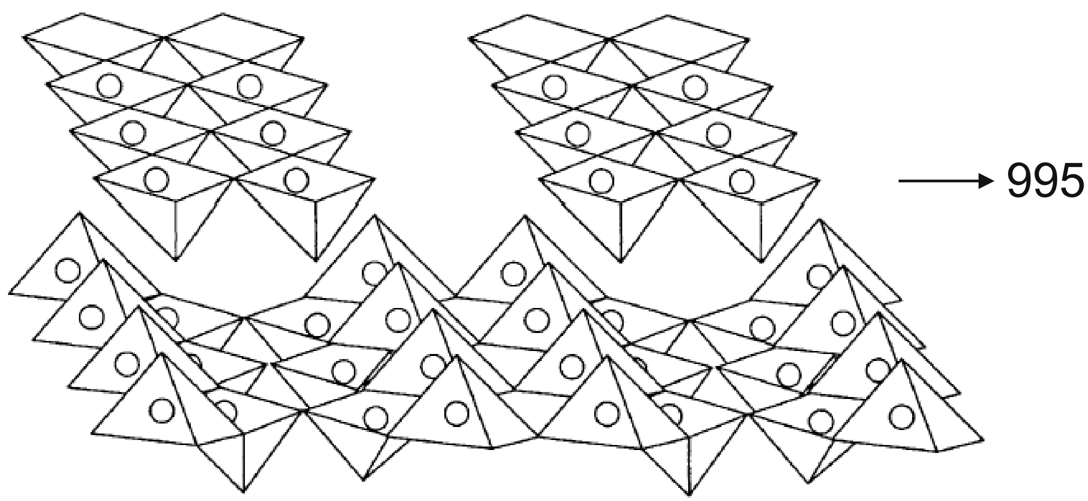
V-O-S coordination #
depends on the support



monomeric | dimeric | polymeric

0.01 – 0.16 V/nm²

1.2 – 14.2 V/nm²



crystalline V_2O_5

4.4 – 14.2 V/nm²

Wu et al., J. Phys. Chem. B 109(2005)2793

Influence of Alumina Structure

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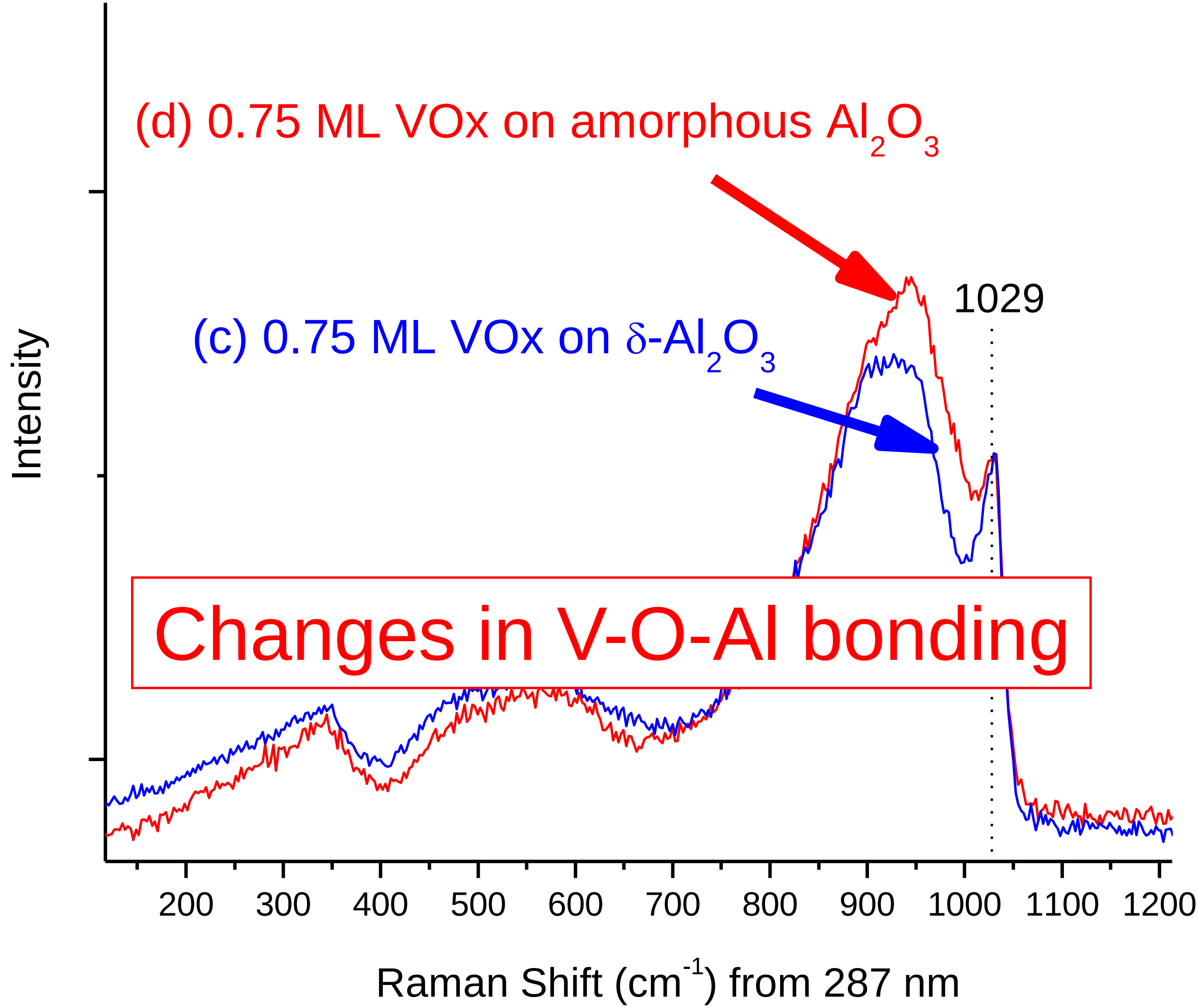

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VOx on α-alumina: No Vanadyl

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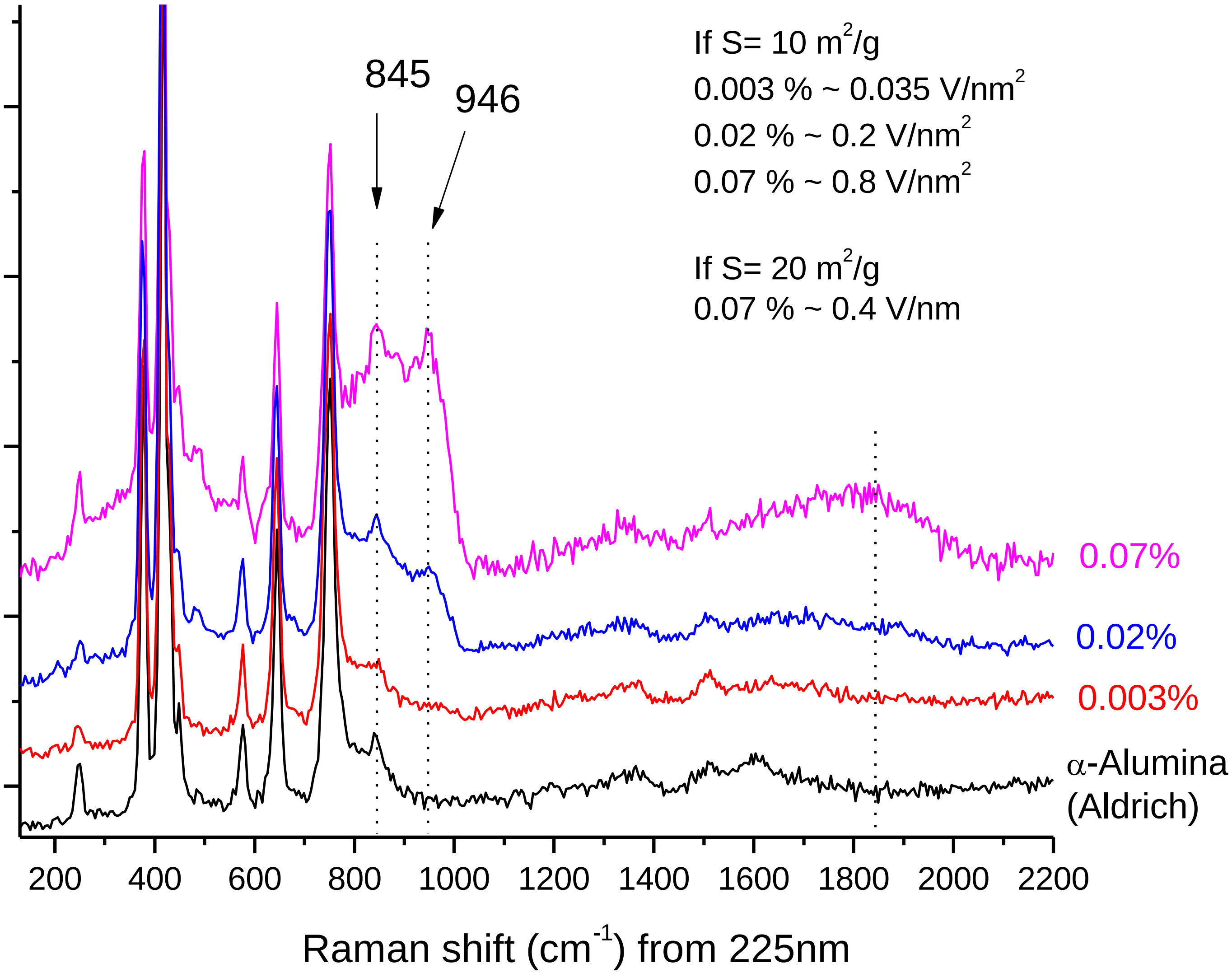

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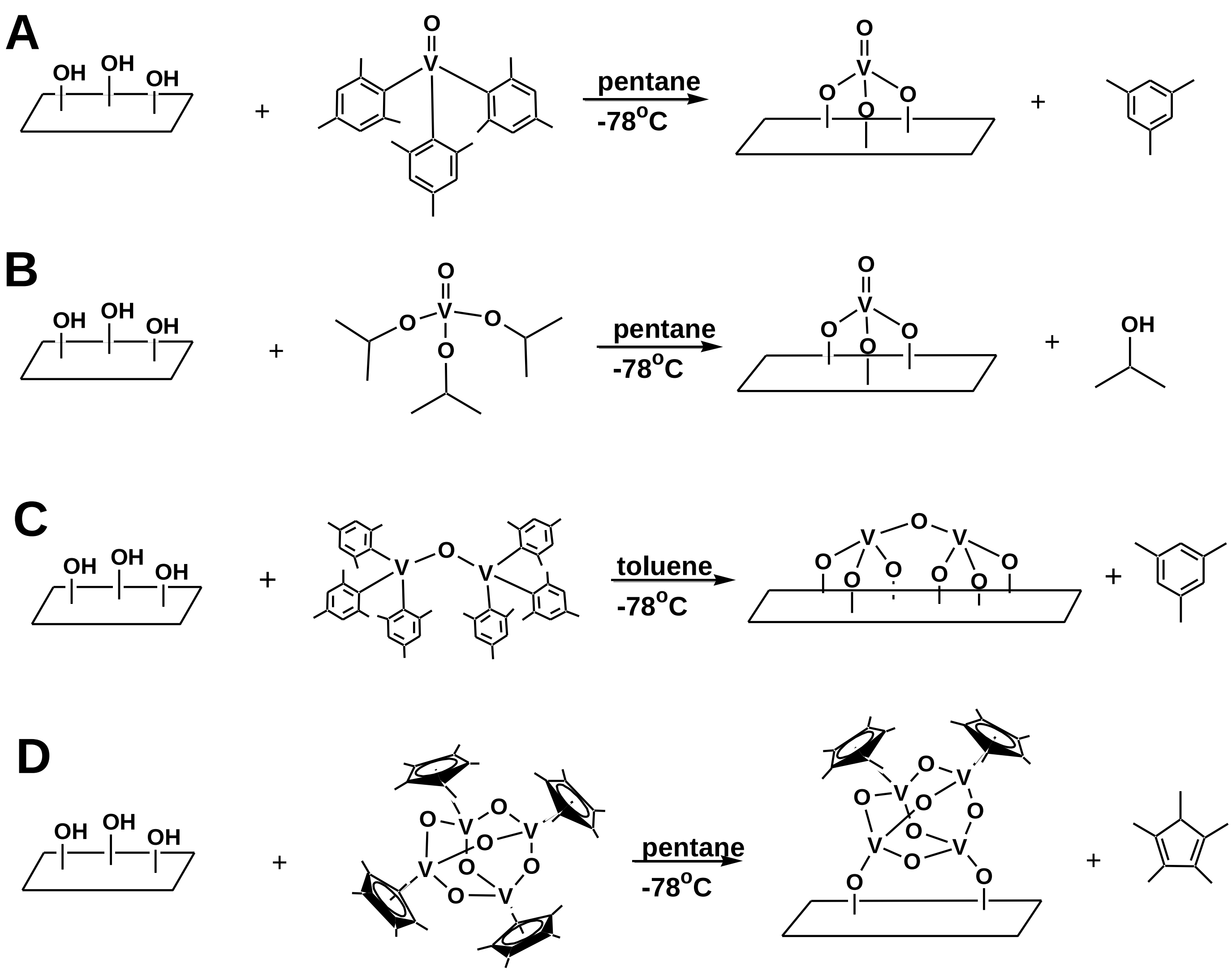
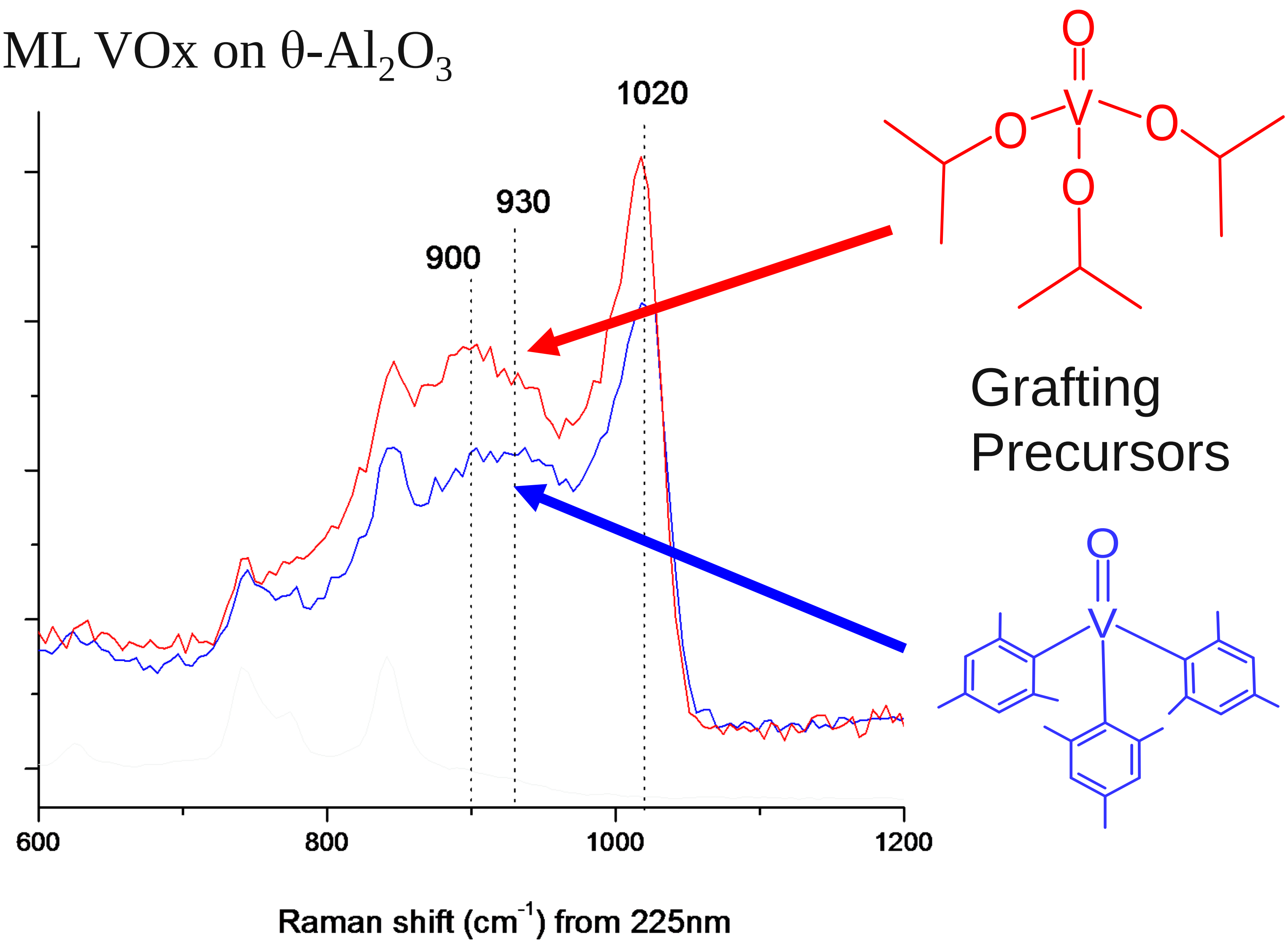
Organometallic Grafting

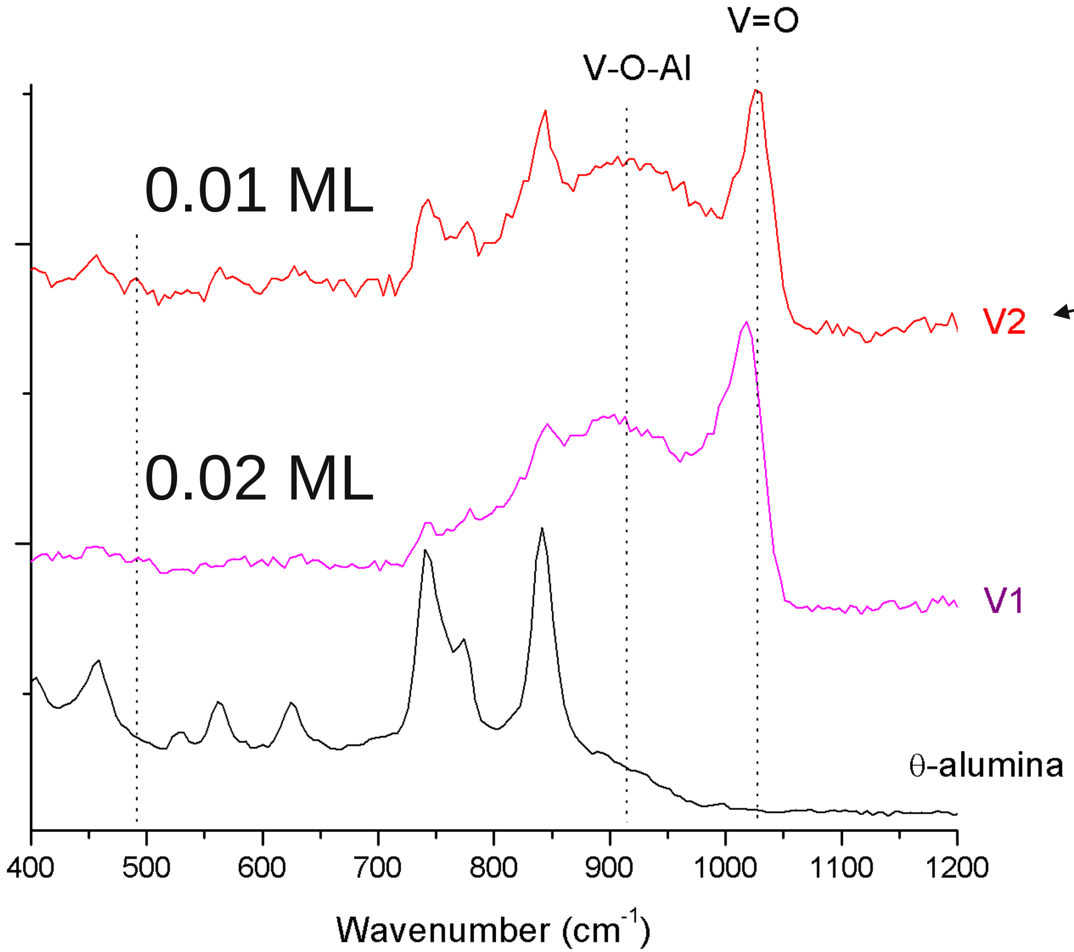


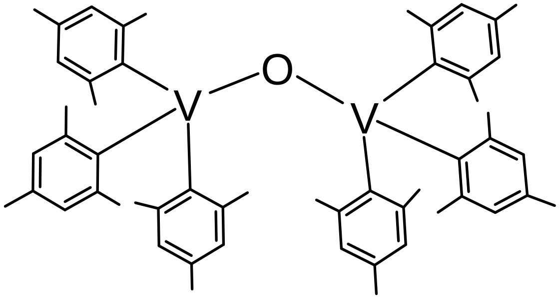
Al-O-V Bonding Depends on the Precursor

0.02 ML VOx on θ-Al_2O_3

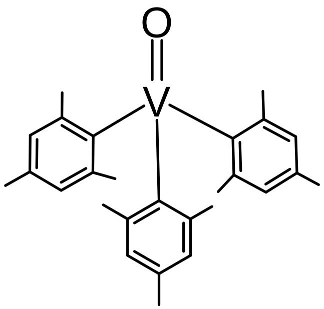


Shift in V=O from Monomer to Dimer = 10 cm^{-1}





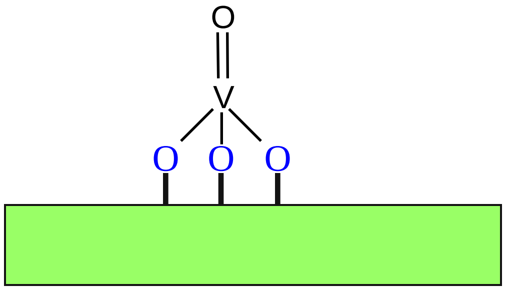
$[V(Mes)_3]_2(\mu\text{-}O)$

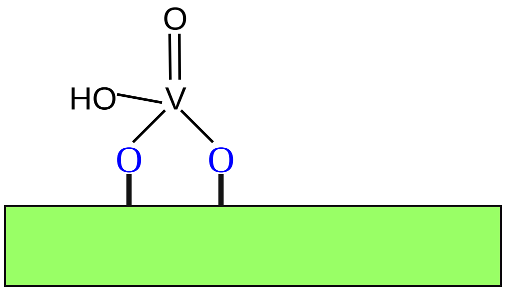


$O{=}V(Mes)_3$

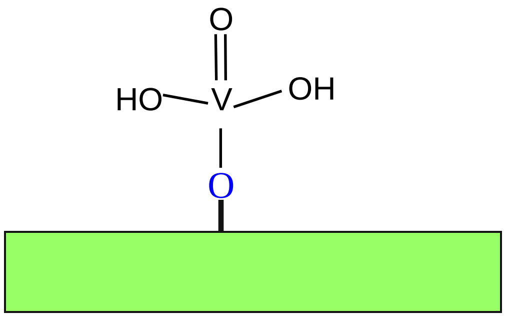
Precursors

Vanadia Grafting Hydroxyl Content





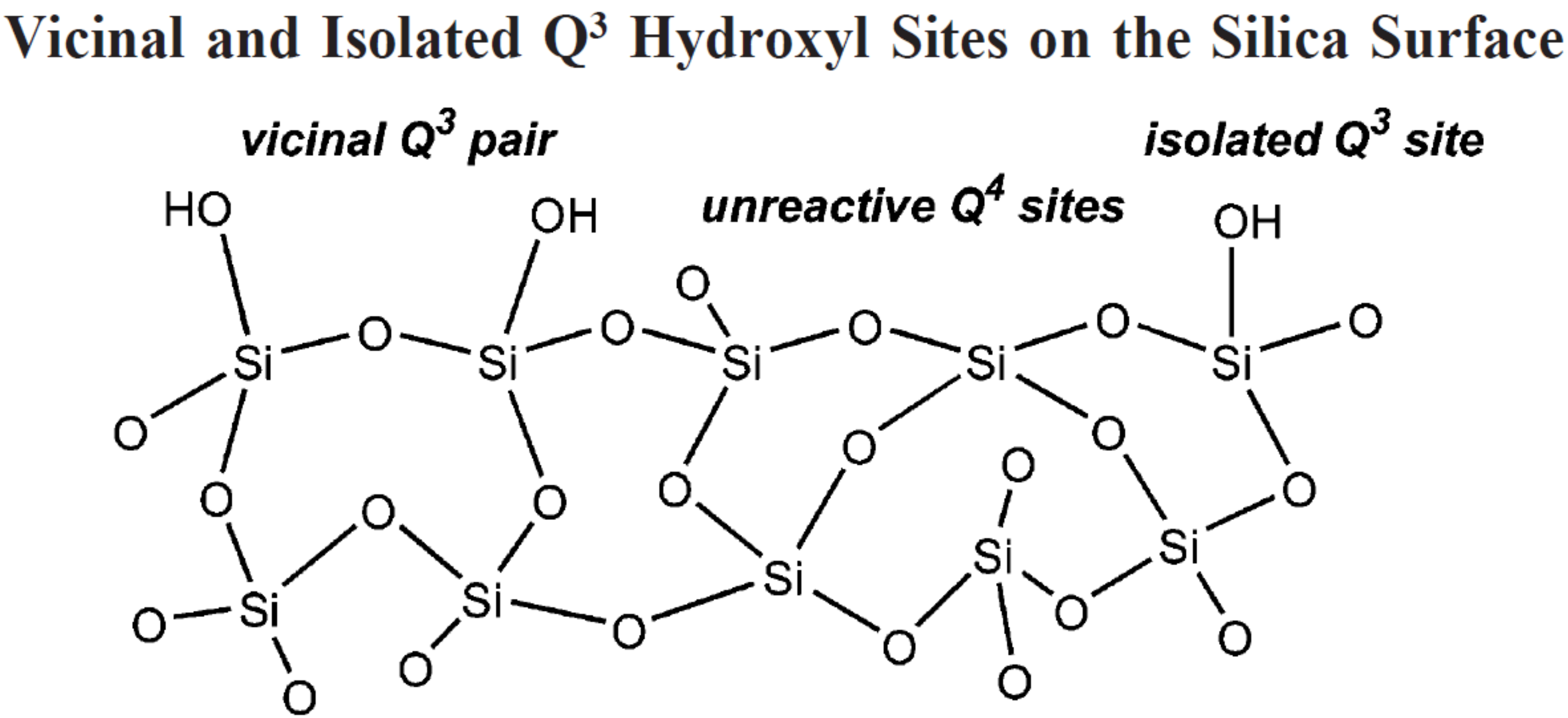
ALD Alumina



Silica *(Rice & Scott* Langmuir 1997*)*

$SrTiO_3$ (001)

Hydroxyl Structures on Silica



Scott et. al. *Organometallics* **2005**, *25*, 1891-1899

Conclusions

- Catalytic activity and selectivity depend on the molecular nature of supported vanadia species
- Raman spectroscopy identifies multiple, spectroscopically distinct alumina-supported VOx monomer species with varying reducibility.
- VOx molecular structure (number of hydroxyl groups) depends on the method of deposition and support.
- Combined experimental and computational evidence for partially hydrated VOx/alumina even under “dehydrated conditions”

- Knowledge of surface OH group structures and distributions is indirect
- Knowledge of surface OH group stability is poor

Acknowledgements

- **Raman spectroscopy: Zili Wu and Hack-Sung Kim**
- **Theory: Larry A. Curtiss and Stan Zygmunt**
- **Catalysis and TPR: Zili Wu and Hao Feng**

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