REACTIVITY INDICES AND BONDING IN V_2O_5 BASED MATERIALS

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Why is Vanadium interesting?

Applications

- catalysis : selective oxidation reactions

  DeNOx, alkane ODH, H_2SO_4 synthesis,…
- alloys: with steel

  Ford Model T 1908
- energy: V, Li…

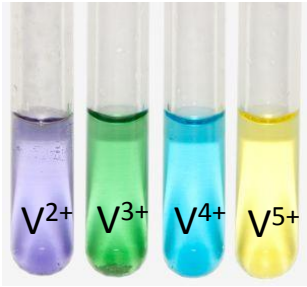
  storage batteries, solar panels, defibrillators,…

Rich chemistry: redox, acid/base

^{23}V: [Ar] $4s^2$ $3d^3$

Questions

- structure/reactivity?
- role of V oxidation state?
- role of agregation?
- reactivity indices?



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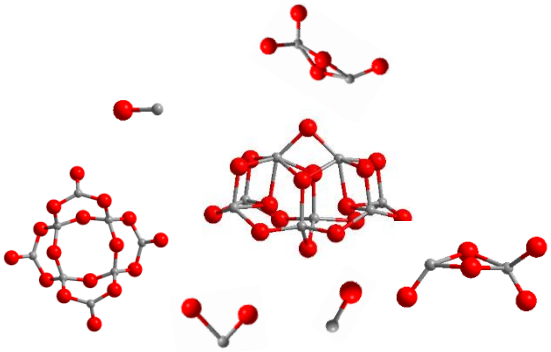
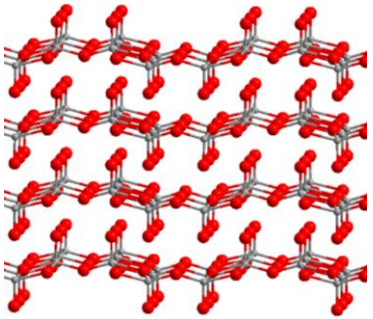
The structure of V_2O_5

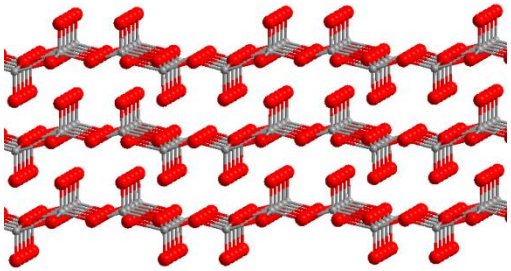


Gas-phase clusters

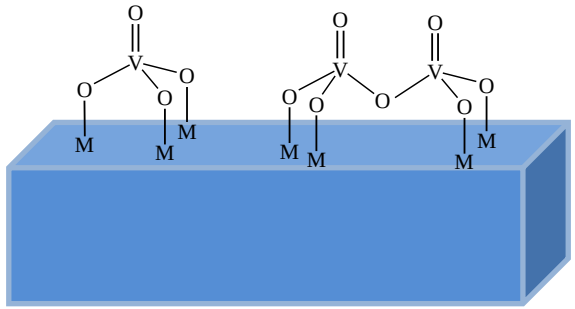


Bulk

V_2O_5



Surfaces



Supported catalysts

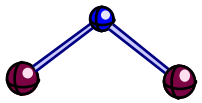
- common features: structural patterns, redox reactivity
- differences: characterization techniques, structural knowledge, applications

➡ Use theoretical tools to understand structure/reactivity relationships

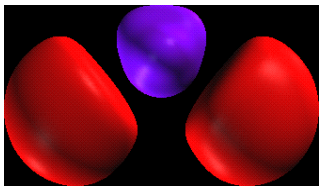
The gas-phase clusters $V_xO_y^{0/+}$

Experiments

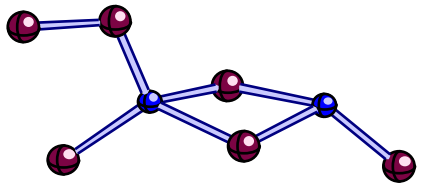
- Collision Induced Dissociation
- Dissociation channels:
  - stable units $VO_{1/2}$, $V_2O_{4/5,}$ $V_3O_{6/7}$
  - easily lose O_2 VO_4, $V_2O_{6/7}$
- Neutral and charged systems
- Reactivity: O_2, methanol,...



$VO_2^+ {}^1A_1$



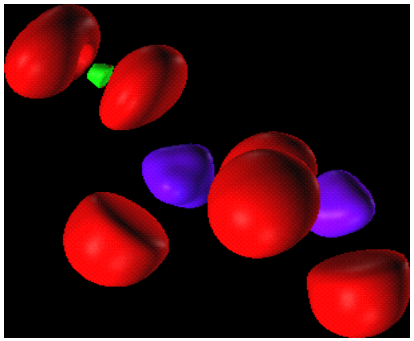
$VO_2 {}^2A_1$



$V_2O_6^+ {}^2A$

Calculations

- optimized geometries for different stoichiometry V_xO_y
- stability, reactivity towards O_2, methanol, H_2
- Bonding: topological analysis of $\rho(r)$ and ELF
  V-O bonds: unshared electron interaction, covalent
  O-O bonds: shared electron interaction, CT
- Standard molecular codes



$V_2O_6^+ {}^2A$

- V=O and V-O-V bonds
- reactivity of undercoordinated sites: V

J. Phys. Chem. A 105 (2001) 9760
Theor. Chem. Acc. 105 (2001) 299; 108 (2002) 12
Chem. Phys. Lett. 333 (2001) 493

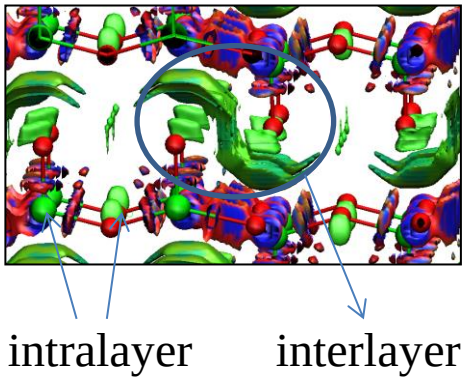
The bulk V_2O_5 and its surfaces

Experiments

- DRX indicate a layered structure
- Surface science techniques: probe molecules, spectroscopy

reactivity V=O V-O-V sites

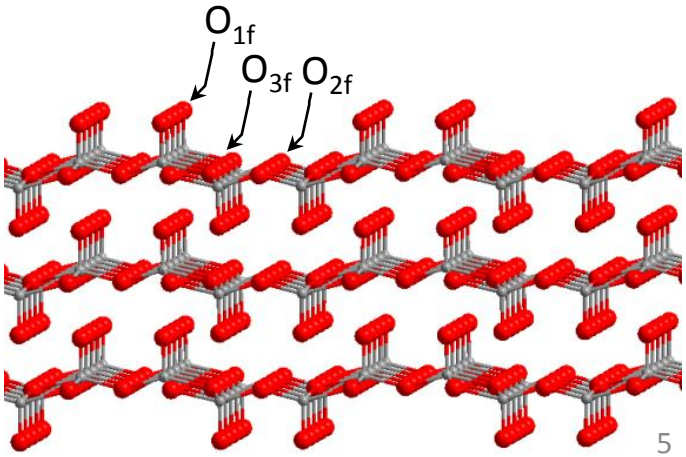
Bulk V_2O_5 seen by NCI



Calculations

- Bulk structure: description of the interlayer interactions
- Surfaces: description of the surface geometry and electronic structure, reactivity towards probe molecules

  model for vanadia-containing catalysts
- Standard molecular codes, **periodic codes**

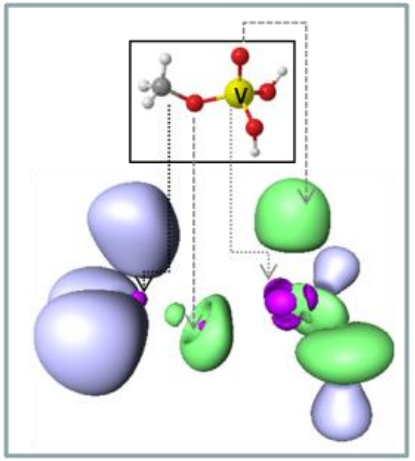


- different oxygen sites: V=O, V-O-V
- reactivity of undercoordinated V sites
- reactivity of O sites: dependent on the partner

The supported catalysts

Experiments

- Catalytic measurements
  activity, selectivity, redox acid/base
- Raman spectroscopy
  V=O V-O-V V-O-M sites, polymerization, coverage



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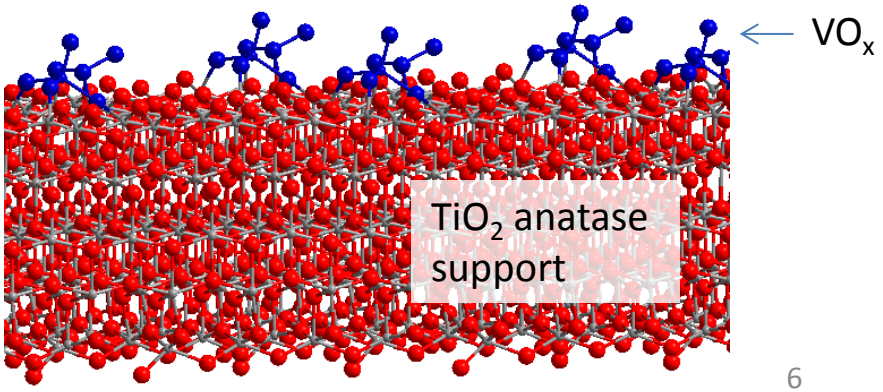
Calculations

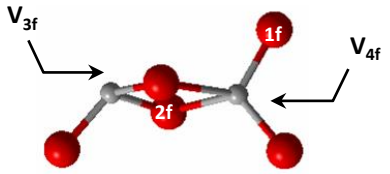
- Building realistic models
- stability, reactivity towards probe molecules: water, methanol, H_2
- Bonding: topological analysis of $\rho(r)$ and ELF on molecular models
- Standard molecular codes, periodic codes

- different oxygen sites: V=O, V-O-V, V-O-Ti
- reactivity of undercoordinated V and Ti sites
- reactivity of O sites?
- role of coverage

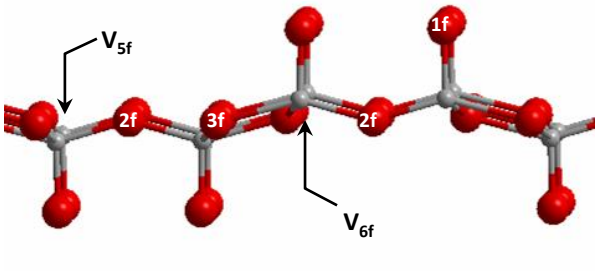


Comparing V_2O_5-based materials

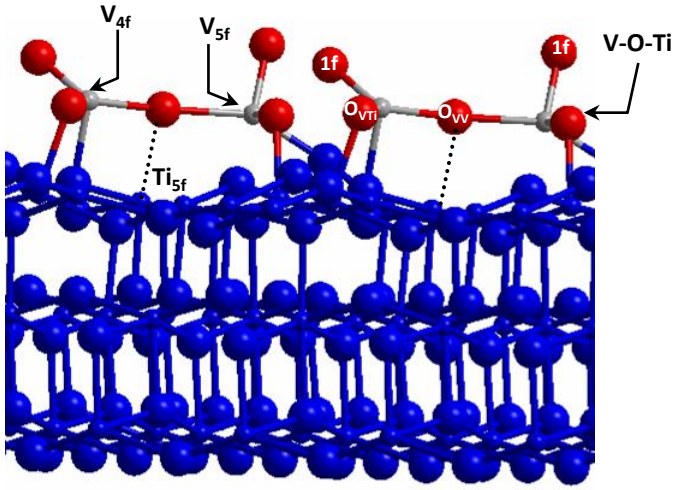
gas-phase cluster



(001) V_2O_5



supported V_2O_5/TiO_2



Common features

- presence of V=O, V-O-V groups, undercoordinated V
- Similar reactivity like redox, acid/base

Differences

- Coordination increases with agregation, structure changes
- New sites in the supported material
- Properties calculated at different computational levels, models

How to compare the three materials on the same foot?

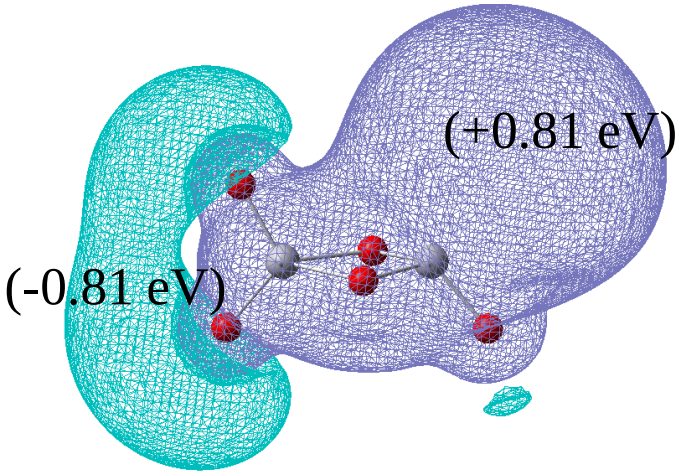
- use periodic boundary conditions for all
- choose the appropriate properties to compare

Predicting reactivity: reactivity indices

Molecular Electrostatic Potential

hardness ~ acid/base

$$V(\underline{R}) = \sum_A \frac{Z_A}{|\underline{R}_A - \underline{R}|} - \int \frac{\rho(\underline{r})}{|\underline{r} - \underline{R}|} d\underline{r}$$

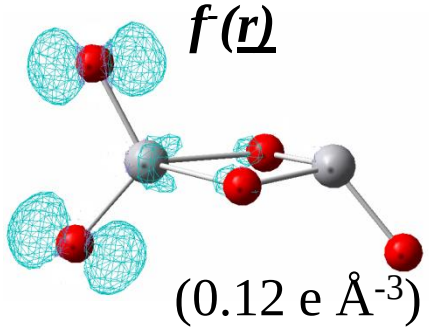


Fukui function

softness ~ electron transfer

$$f^+(\underline{r}) = \rho_{N_0+1}(\underline{r}) - \rho_{N_0}(\underline{r})$$ Nucleophilic

$$f^-(\underline{r}) = \rho_{N_0}(\underline{r}) - \rho_{N_0-1}(\underline{r})$$ Electrophilic

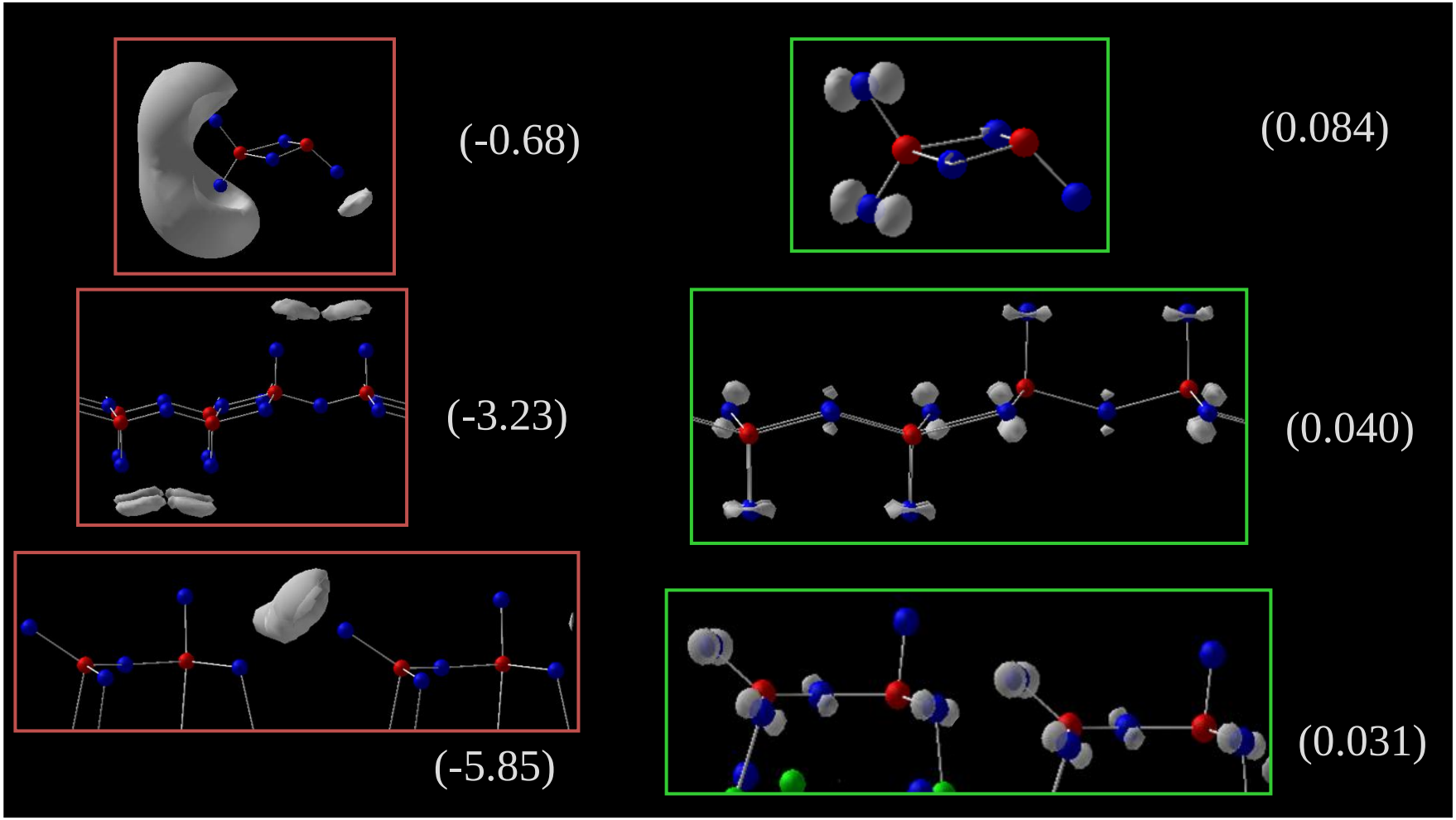


- The undercoordinated V is acidic, the terminal oxygen sites are basic
- Ionisation will take place from terminal oxygens
- Validation from standard molecular calculations to periodic calculations (Gaussian vs VASP): qualitative agreement

Predicting reactivity: reactivity index

EP in eV

$f^{-}(\underline{r})$ in eÅ^{-3}



- Terminal oxygens are preferred in hard-hard electrophilic reactions
- Soft-soft electrophilic reactions would take place on different sites for each material
- Comparison between the different materials towards the same partner

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Conclusion

- V_2O_5 occurs in different forms

  -Structure and reactivity have differences and similarities

- Bonding can be successfully explored by using ELF, QTAIM, NCI methods, adapted to the model
- periodic conditions allows a comparison of the materials on the same level
- conceptual DFT gives qualitative and quantitative description of the reactive regions
- **understand and predict activity and selectivity in chemical reactions**

Perspectives

- extend the application in periodic systems: DOS, band structure
- correlate with energetics
- apply to solid state, surface science, heterogeneous catalysis

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V_2O_5, ELF

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NCI & more

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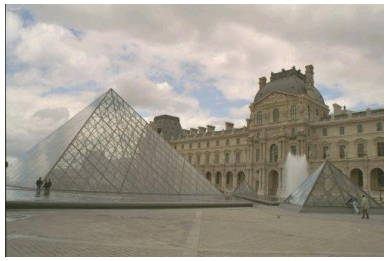

ÉGIDE

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GENCI