The effect of the supporting oxide on the activity of vanadia/ceria catalysts

TP C5: Cristina Popa, M. Veronica Ganduglia-Pirovano‡,

Joachim Sauer

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Publications 2009–2010

- **Ceria based systems**

  collaboration TP B1

  - M. V. Ganduglia-Pirovano, J. L. F. Da Silva, J. Sauer, **Phys. Rev. Lett.** 102, 026101 (2009).
  - M. Baron, H. Abbott, O. Bondarchuk, D. Stacchiola, A. Uhl, S. Shaikhutdinov, H.-J. Freund, C. Popa, M. V. Ganduglia-Pirovano, J. Sauer, **Angew. Chem. Int. Ed.** 48, 8006 (2009).
  - M. V. Ganduglia-Pirovano, C. Popa, J. Sauer, H. Abbott, A. Uhl, M.Baron, D. Stacchiola, O. Bondarchuk, S. Shaikhutdinov and H.-J. Freund, **J. Am. Chem. Soc.** xx, xxxxx (2010).

- **VO_x/alumina and VO_x/zirconia systems**

  - V. Brázdová, M.V. Ganduglia-Pirovano, and J. Sauer, **J. Phys. Chem. C** xx, xxxxx (2010).
  - A. Hofmann, M. V. Ganduglia-Pirovano, and J. Sauer, **J. Phys. Chem. C** 113, 18191 (2009).

- **Formaldehyde formation on V_2O_3(0001) and V_2O_5(001) surfaces**

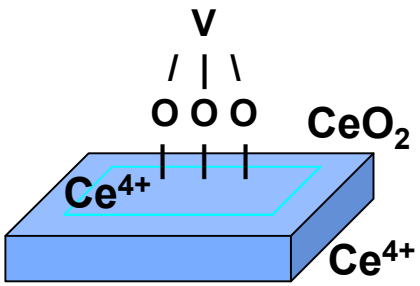
  collaboration TP C1

  - J. M. Sturm, D. Göbke, H. Kuhlenbeck, J. Döbler, U. Reinhardt,M. V. Ganduglia-Pirovano, J. Sauer, H.-J. Freund, **Phys. Chem. Chem. Phys.** 11, 3290 (2009).
  - D. Göbke, Y. Romanyshyn, S. Guimond, J. M. Sturm, H. Kuhlenbeck, J. Döbler, U. Reinhardt, M. V. Ganduglia-Pirovano, J. Sauer, H.-J. Freund, **Angew. Chem., Int. Ed.** 48, 3695 (2009).

VO_x/ceria: The experimental facts

2×10^{-10} mbar

combined in-situ
EPR, XANES,
Raman, IR



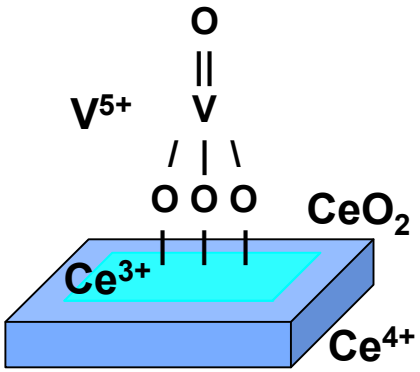
Real systems:
M. V. Marti´nez-Huerta, G. Deo,J. L. G. Fierro, M. A. Ban˜ares, J. Phys. Chem. C 112, 11441 (2008)

Model systems (B1)
M. Baron, H. Abbott, O. Bondarchuk, D. Stacchiola, A. Uhl, S. Shaikhutdinov, H.-J. Freund, C. Popa, M. V. Ganduglia-Pirovano, J. Sauer, Angew. Chem. Int. Ed. 48, 8006 (2009).

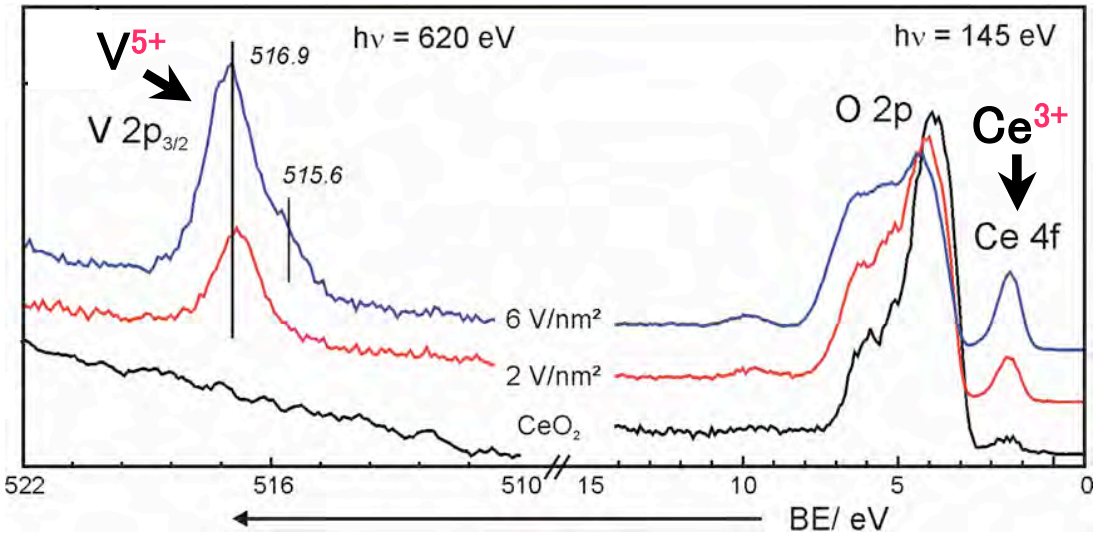
VO_x/ceria: The experimental facts

2×10^{-10} mbar

combined in-situ
EPR, XANES,
Raman, IR



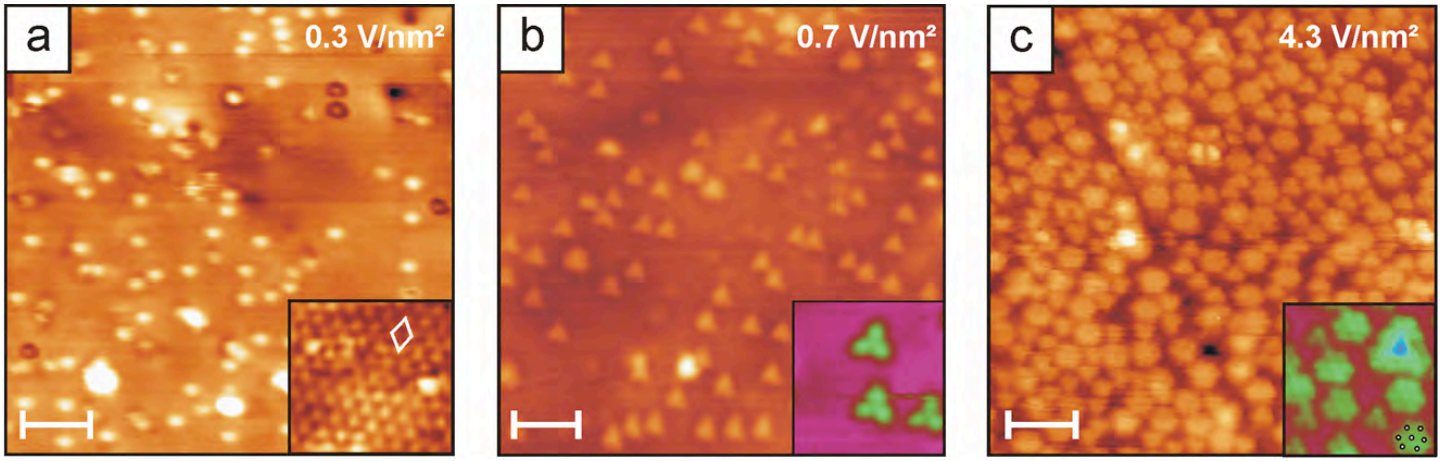
- XPS: Ce^{3+} and V^{5+}



VO_x/ceria: The experimental facts

- STM: Monomers, Dimers, Trimers
- XPS: Ce^{3+} and V^{5+}

U = +3.0 V

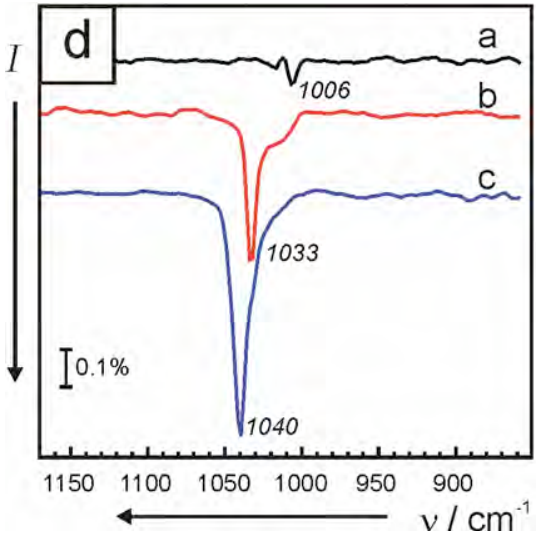


Monomer & Trimer: similar apparent height → „flat“ structures

Trimer: spot-spot distance ~ CeO_2 lattice (3.9 Å)

- IR: V=O stretching

blue shift ~25cm^{-1}



VO_x/support: The strategy

Structure → DFT(+U) + thermodynamics

- **Themodynamic stability → surface free energy** $\gamma(\mu_O(T,p); \mu_V(T,a))$
- **Electronic structure**
- **Vibrations (IR)**

Reactivity → Reactivity descriptors

e.g., $C_3H_8 + [V^{5+}O] \longrightarrow C_3H_7 + [V^{4+}OH] \xrightarrow[-C_3H_6]{} [V^{3+}]\cdots H_2O \xrightarrow[-H_2O]{} [V^{3+}]$

I. Reduction by hydrogen (Bronsted-Evans-Polyani)

$$[V^{5+}O] \xrightarrow{+\frac{1}{2}H_2} [V^{4+}OH] \xrightarrow{+\frac{1}{2}H_2} [V^{3+}]\cdots H_2O \xrightarrow[-H_2O]{} [V^{3+}]$$

Rozanska, Fortrie, Sauer, JPCC 111,6041 (2007)

II. O defect formation (Mars-van Krevelen)

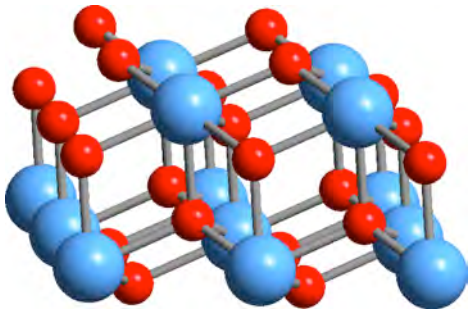
$$[V^{5+}O] \xrightarrow{-\frac{1}{2}O_2} [V^{3+}]$$

Sauer, Döbler, Dalton Trans.3116 (2004)

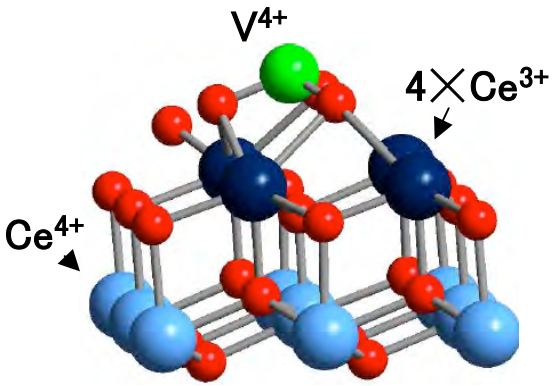
Theoretical models

Monomeric Species $CeO_2(111) + V + n \cdot ½O_2 \rightarrow VO_n/CeO_2(111)$

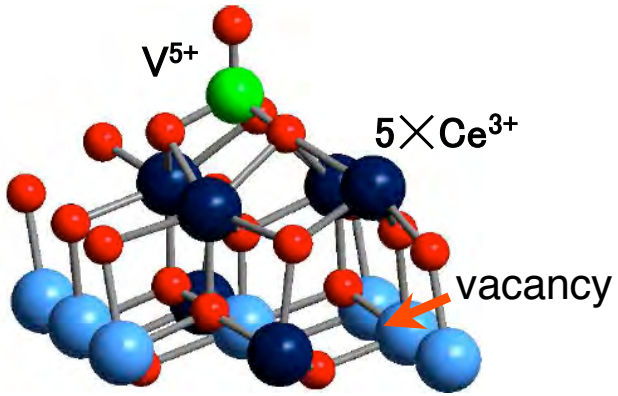
$CeO_2(111)$



$V/CeO_2(111)$



+1.48 eV



0

V^{5+}—O—Ce^{3+}

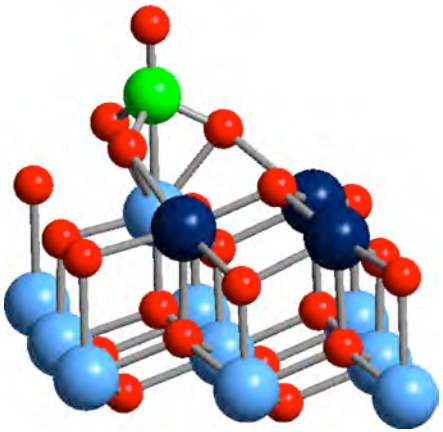
Baron. Abbott, Bondarchuk, Stacchiola, Uhl, Shaikhutdinov, Freund, Popa, Ganduglia-Pirovano, Sauer, Angew. Chem. Int. Ed. 48, 8006

PBE+U (2×2) u.cell

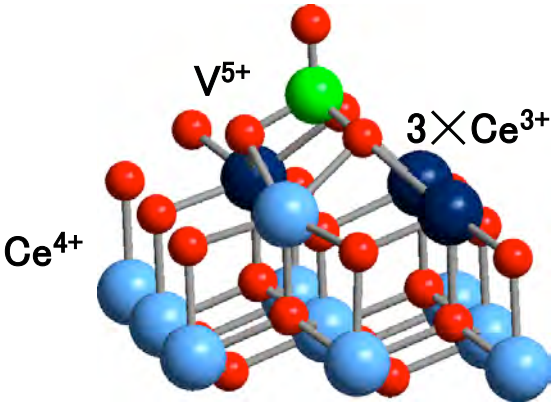
Theoretical models

Monomeric Species $CeO_2(111) + V + n \cdot ½O_2 \rightarrow VO_n/CeO_2(111)$

$VO/CeO_2(111)$



+1.23 eV



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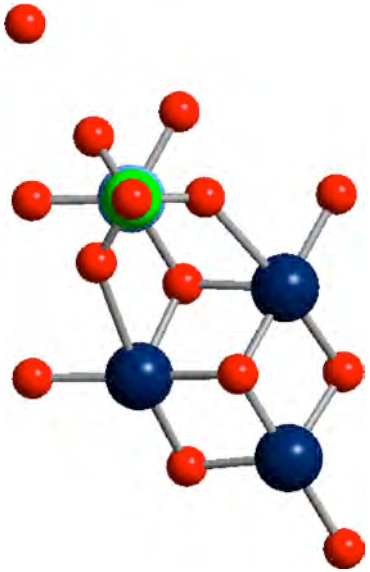
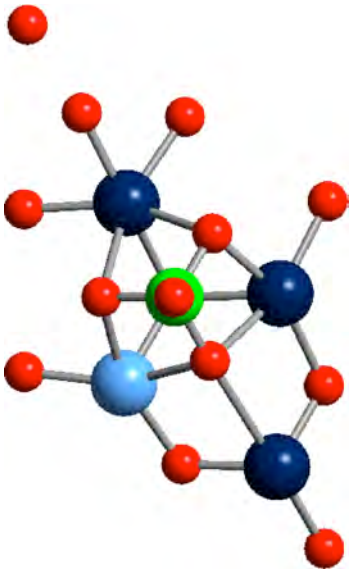
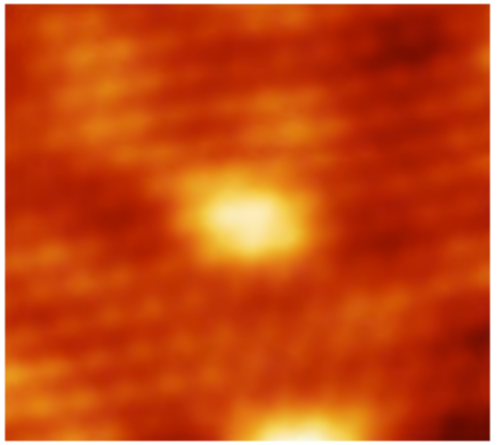
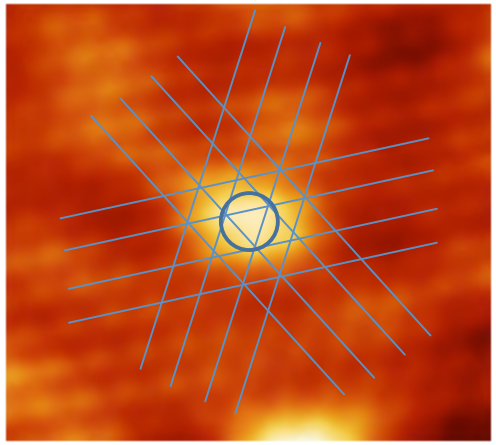






unoccupied states → imaged Ce lattice

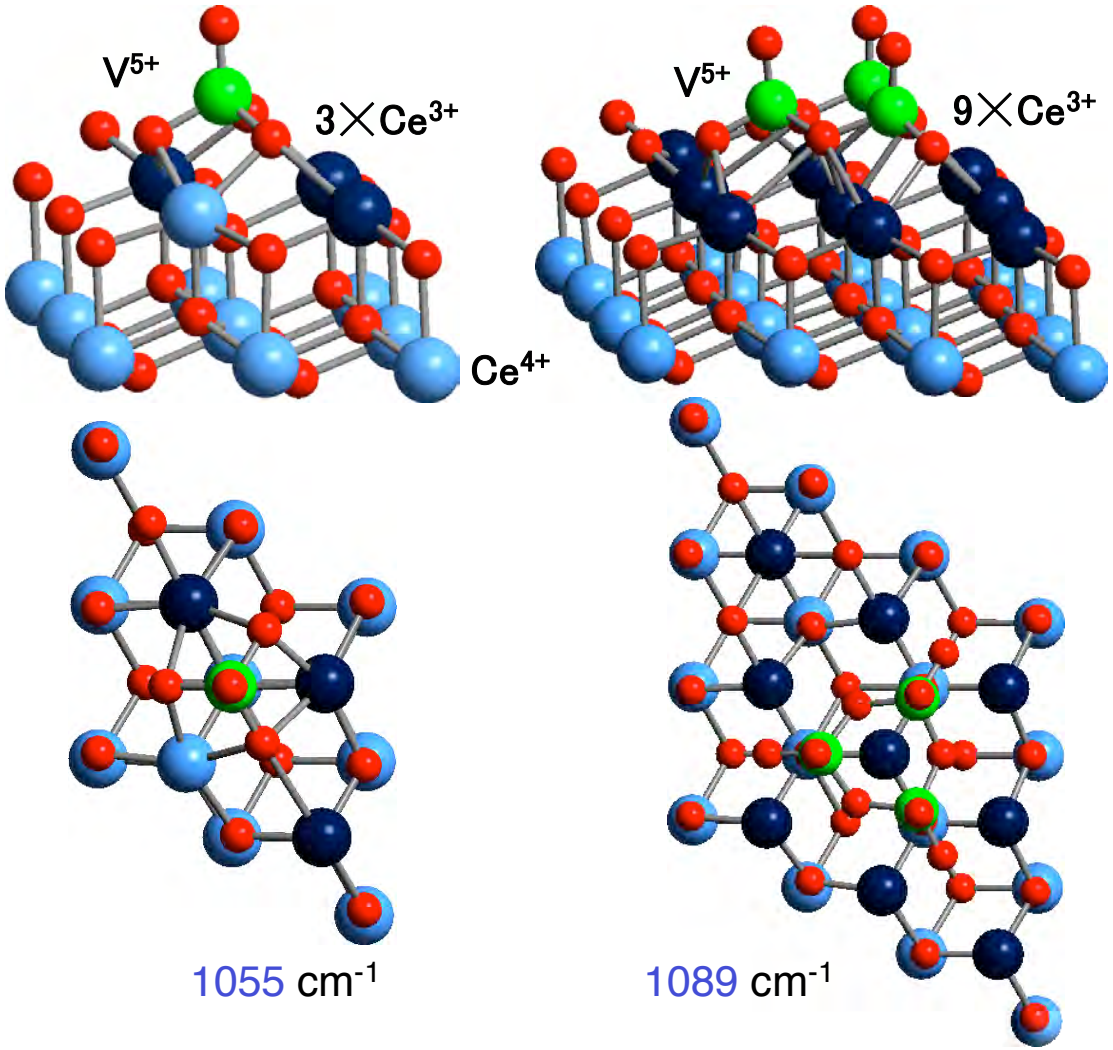


- lines marked the Ce lattice
- V sits clearly on a hollow site

Jerratsch, Nilius, Freund, unpublished

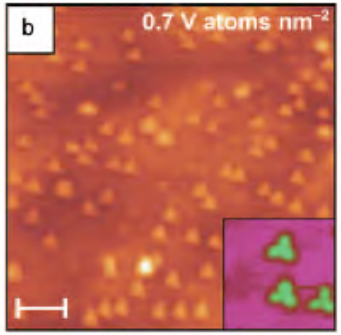
Vanadium oxide „monolayer" model catalysts

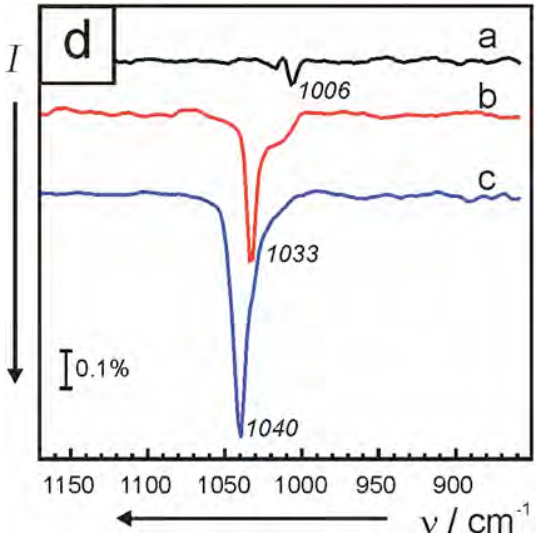
$VO/CeO_2(111)$ **$3VO/CeO_2(111)$**



1055 cm^{-1} 1089 cm^{-1}

blue shift ~34 cm^{-1} (exp: ~25cm^{-1})





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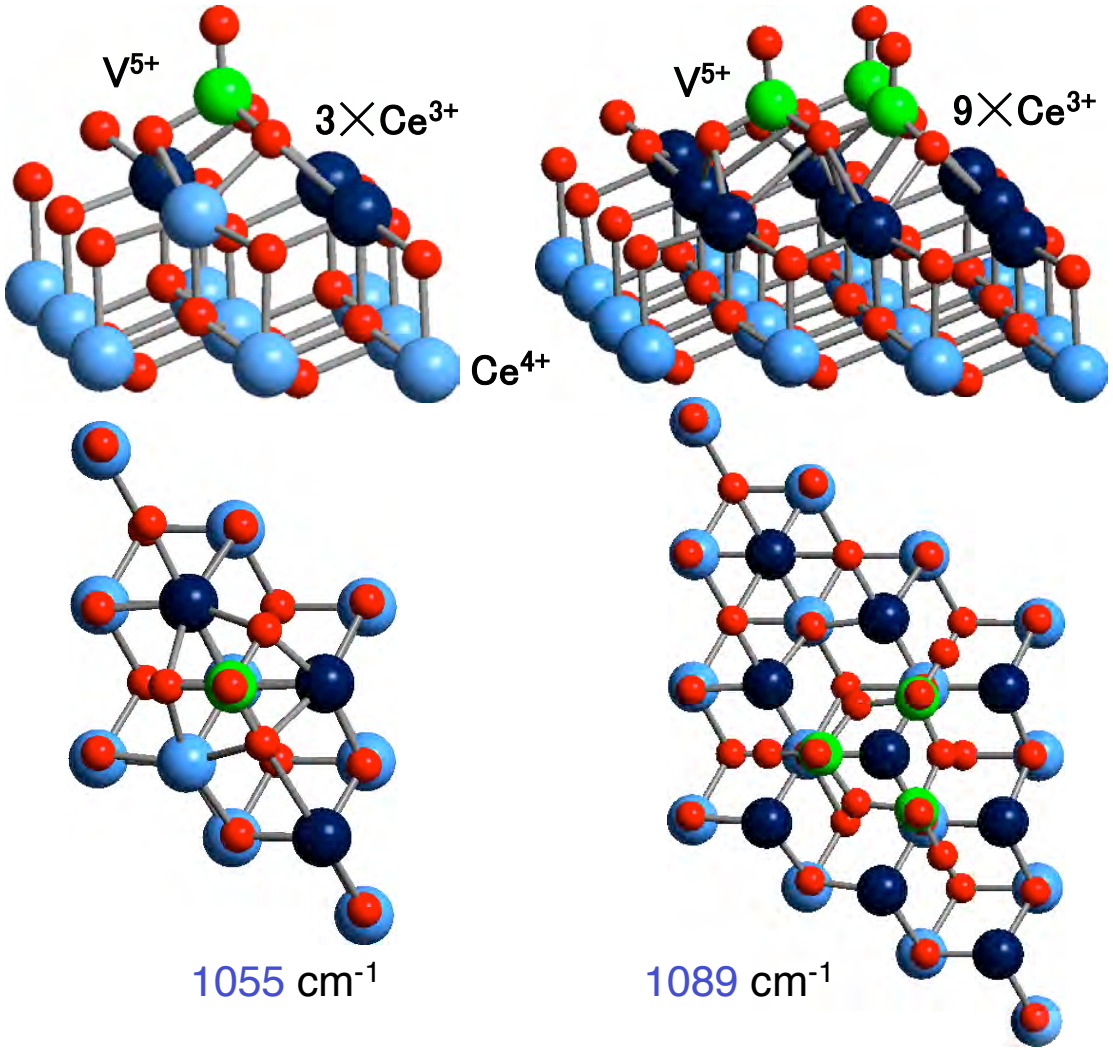
Vanadium oxide „monolayer" model catalysts

$VO/CeO_2(111)$ **$3VO/CeO_2(111)$**



blue shift ~34 cm^{-1} (exp: ~25cm^{-1})

Relative stability

Monomer vs Dimer

$2\times(VO/CeO_2) \rightarrow 2VO/CeO_2 + CeO_2$

+ 0.93 eV

Monomer vs Trimer

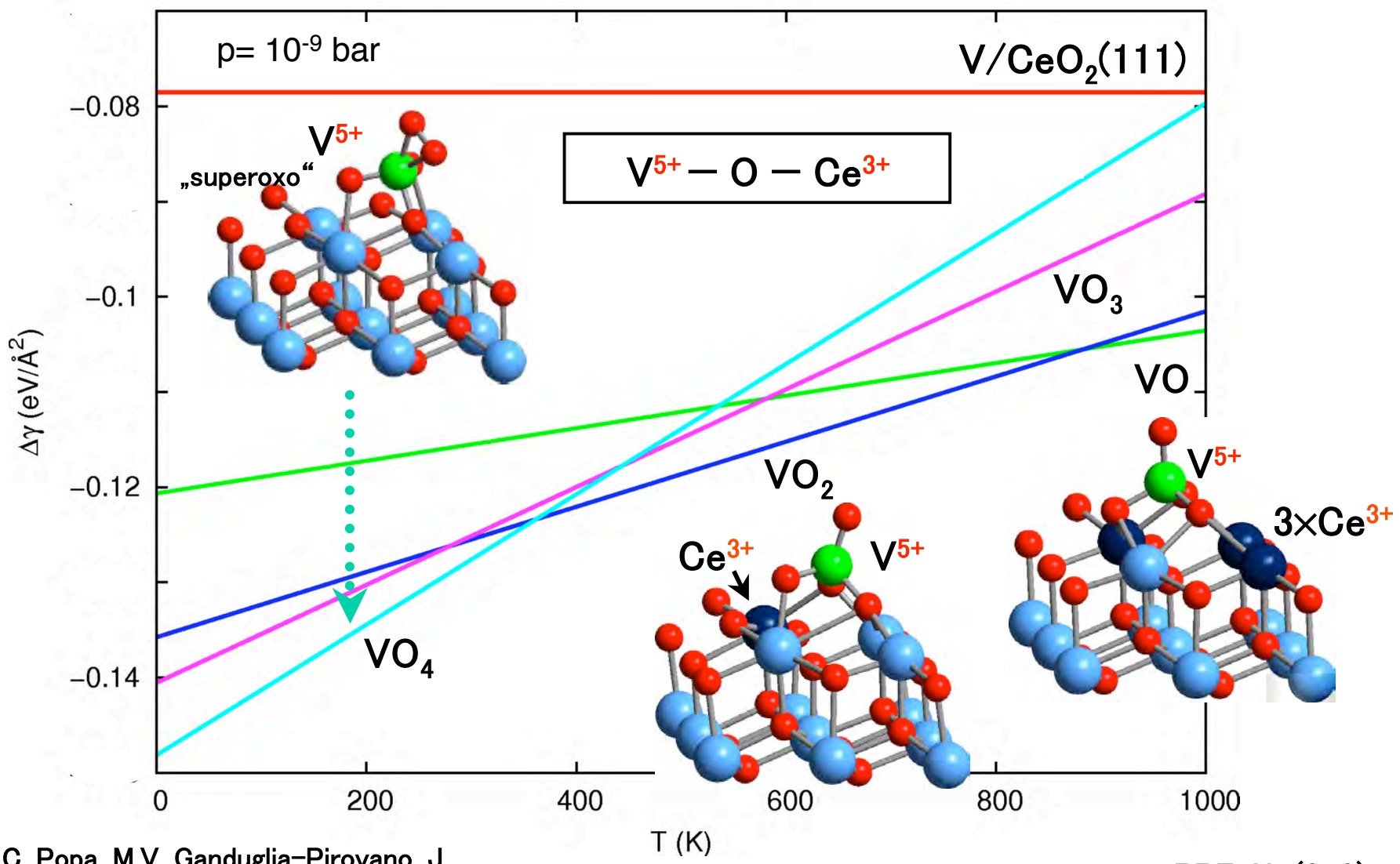
$3\times(VO/CeO_2) \rightarrow 3VO/CeO_2 + 2\ CeO_2$

+ 3.43 eV

Dimers and trimers kinetically stabilized

VO_x/ceria: Phase diagram

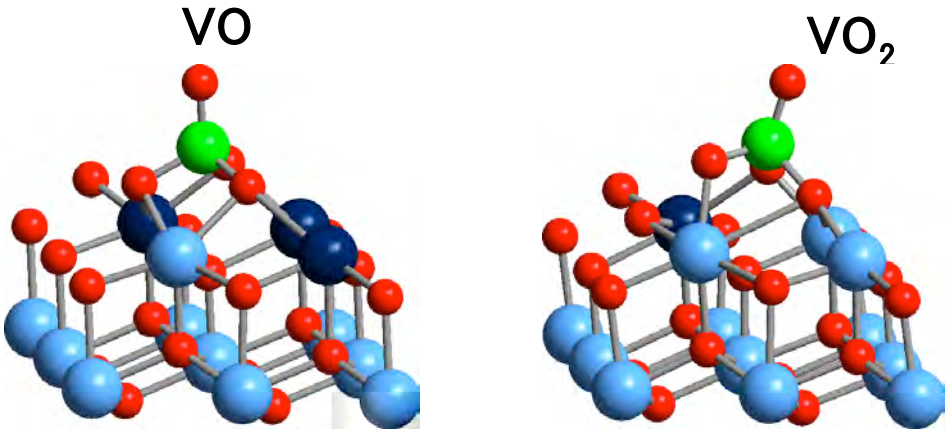
Monomeric Species $CeO_2(111) + V + n \cdot ½O_2 \rightarrow VO_n/CeO_2(111)$



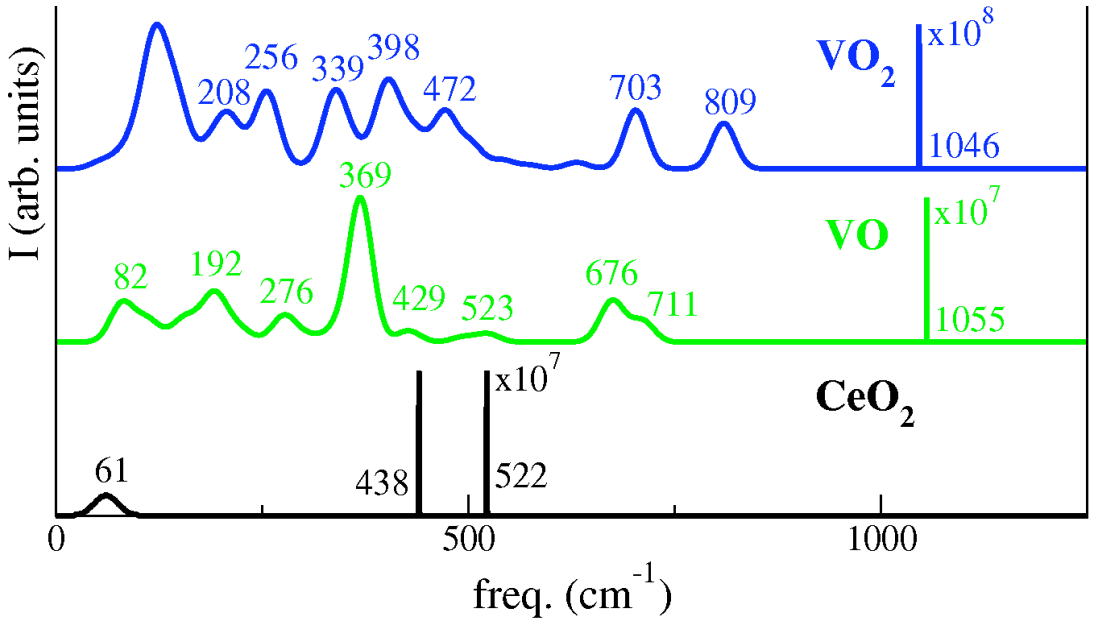
C. Popa, M.V. Ganduglia-Pirovano, J. Sauer, unpublished

PBE+U (2×2) u.cell

Monomeric species: Open questions



Can these two species be distinguished?



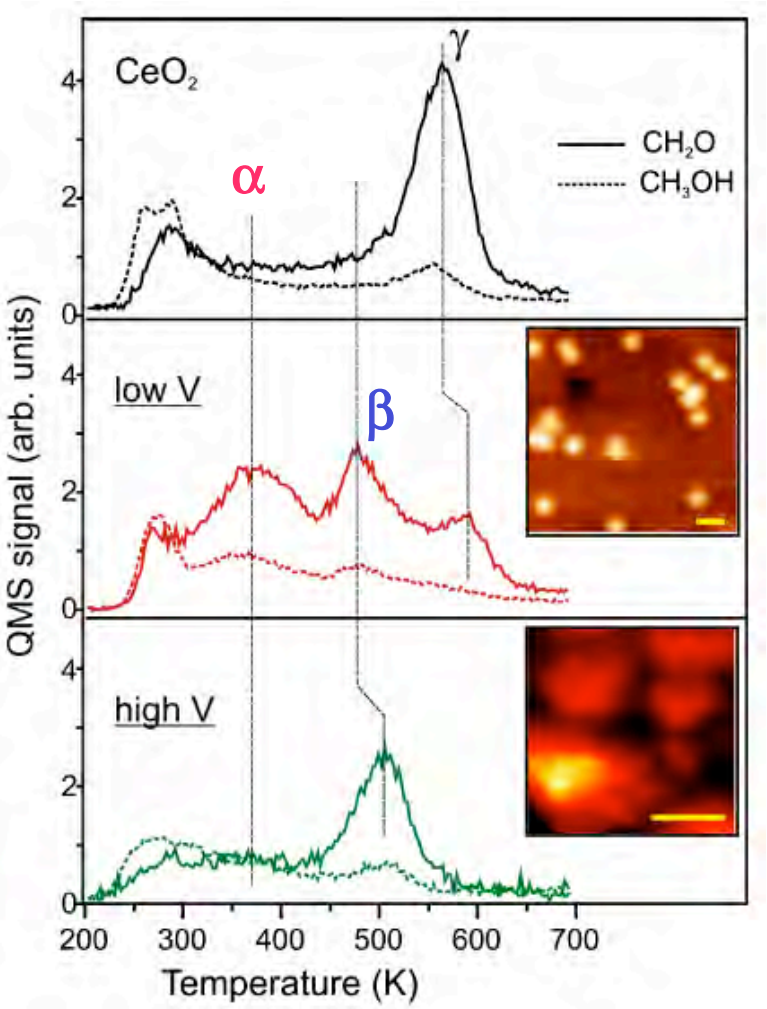
Vanadyl frequency (blue) shift ?

VO vs. 3VO : ~34 cm^{-1}

VO_2 vs. $3VO_2$: ??

VO_x/ceria: Methanol oxidation

$$CH_3OH + [V^{5+}O] \rightarrow CH_2O + H_2O + [V^{3+}]$$



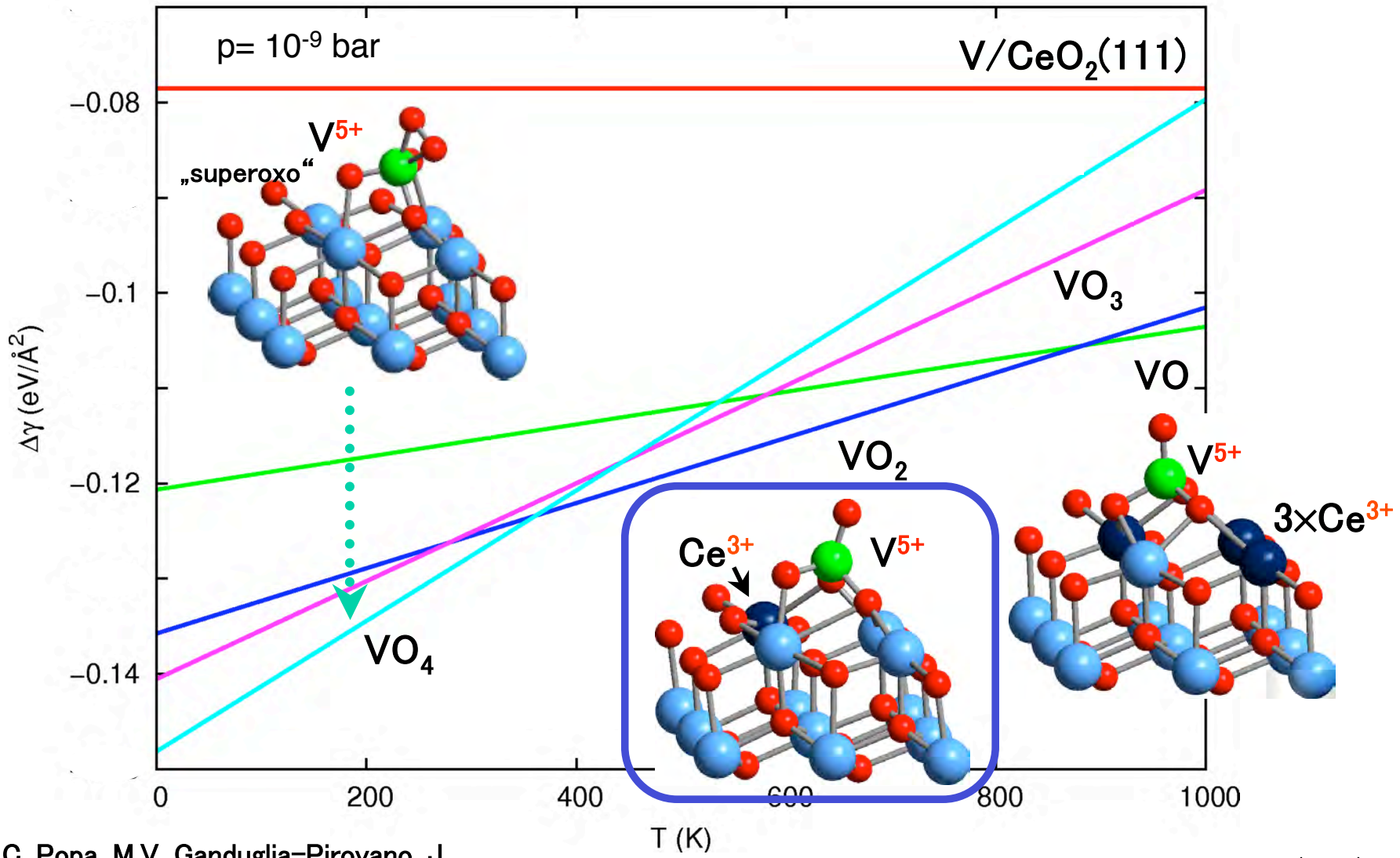
	T_{des}[K]	
γ	565–590	CeO_2
β	475–505	V_2O_5/CeO_2
α	370	?

Origin of low temperature reactivity?

Ganduglia-Pirovano, Popa, Sauer, Abbott,Uhl, Baron, Stacchiola, Bondarchuk, Shaikhutdinov, Freund, JACS in press.

VO_x/ceria: Phase diagram

Monomeric Species $CeO_2(111) + V + n \cdot ½O_2 \rightarrow VO_n/CeO_2(111)$

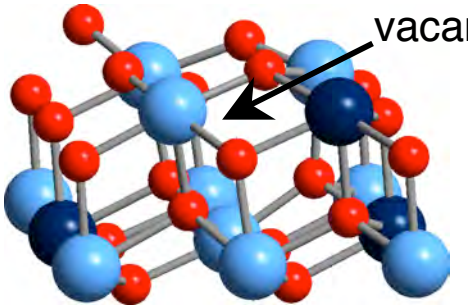


C. Popa, M.V. Ganduglia-Pirovano, J. Sauer, unpublished

PBE+U (2×2) u.cell

Reactivity: The origin of the support effect

$CeO_{2-x}(111)$

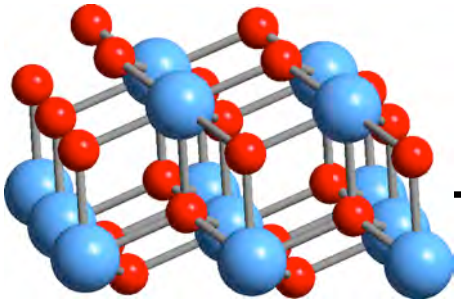


$2\times Ce^{3+}$

$-\frac{1}{2}\ O_2$

$+\ 1.87$

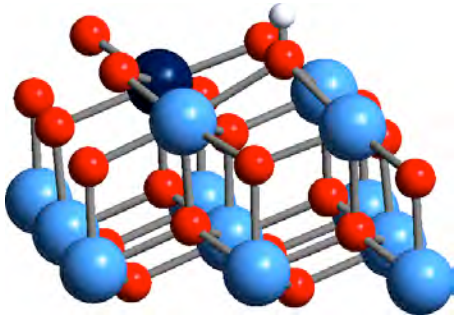
$CeO_2(111)$



$+\frac{1}{2}\ H_2$

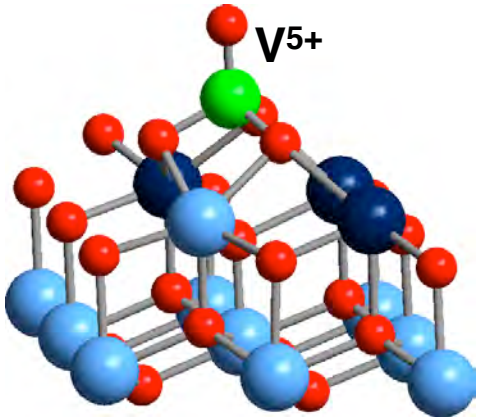
$-\ 1.21$

$H/CeO_2(111)$



$1\times Ce^{3+}$

$VO/CeO_2(111)$



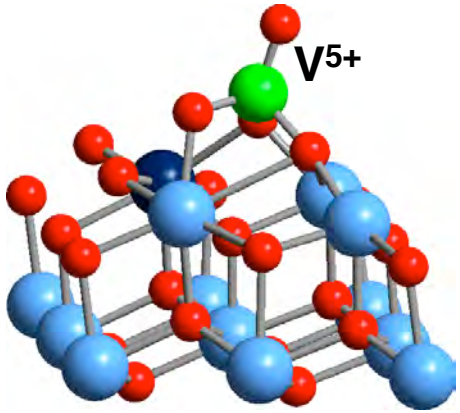
$3\times Ce^{3+}$

$-\frac{1}{2}\ O_2$

$+\ 0.79$

DFT (PBE+U)
[eV]

$VO_2/CeO_2(111)$

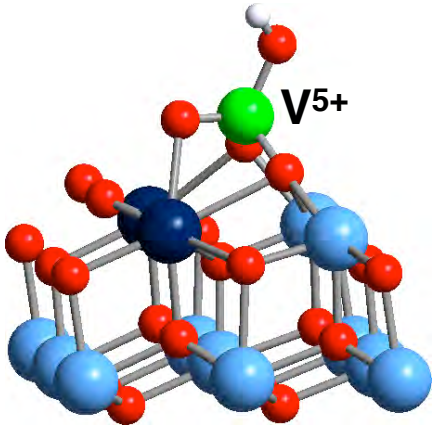


$1\times Ce^{3+}$

$+\frac{1}{2}\ H_2$

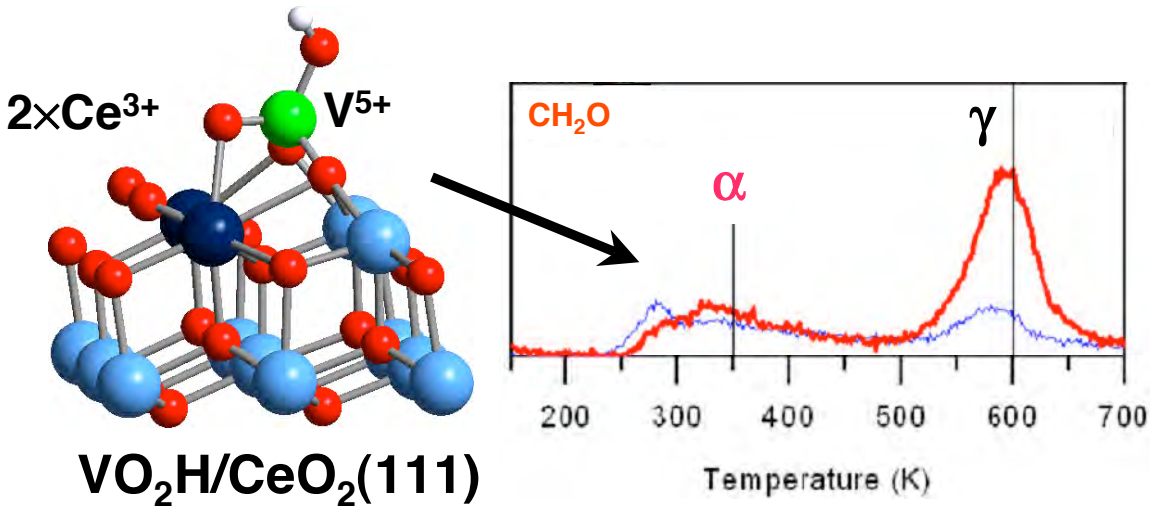
-1.47

$VO_2H/CeO_2(111)$



$2\times Ce^{3+}$

Reactivity: The origin of the support effect

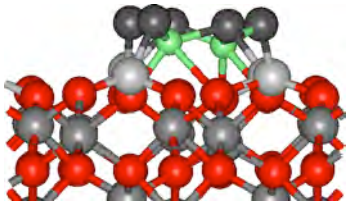
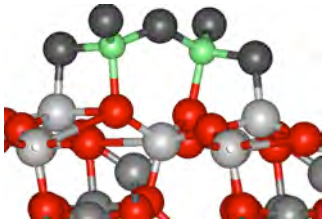
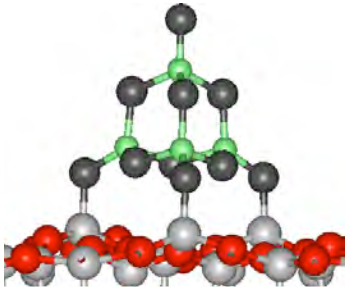
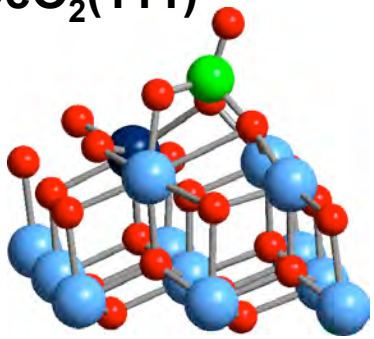


Vanadia promotes ceria reduction

Ganduglia-Pirovano, Popa, Sauer, Abbott,Uhl, Baron, Stacchiola, Bondarchuk, Shaikhutdinov, Freund, JACS in press.

VO_x/support: The support effect

$E_f(½O_2)$ [eV]

α-Al_2O_3(0001)	γ-Al_2O_3(100)	Thin Film	CeO_2(111)
			
2.79	4.00	3.72	0.79
$V^{5+} \rightarrow V^{4+}$	$V^{5+} \rightarrow V^{3+}$	$V^{5+} \rightarrow V^{3+}$	$V^{5+} \rightarrow V^{5+}$ $Ce^{4+} \rightarrow Ce^{3+}$

The high catalytic activity of VOx/ceria has its origin in the ability of ceria to stabilize reduced states by accommodating electrons in localized f-states, which is promoted by the supported vanadia species

The VO_x/CeO_2 system is more reactive than each component alone

Final remarks

Theoretical results concur with experimental findings

Structure

- ✓ The nature of the V^{5+}–O–Ce^{3+} interface is elucidated
- ✓ The structure of the „monolayer catalyst“ is linked to its vibrational signature

Reactivity

- ✓ THE support effect for VO_x/ceria is elucidated
- ✓ The low temperature reactivity for CH_3OH oxidation is explained
- ✓ Lower reactivity of VO_x/alumina than VO_x/ceria is found

Future

- Structure and properties of vanadia clusters on ceria
- Methanol oxidation reaction on ceria supported monomeric species
- How about VO_x/titania?