UNIVERSITEIT GENT

FACULTY OF ENGINEERING

First principles kinetics of heterogeneously catalyzed reactions: oxidation of hydrocarbons over V_2O_5 catalysts

Konstantinos Alexopoulos, Marie-Françoise Reyniers, Guy B. Marin

*Laboratory for Chemical Technology, Krijgslaan 281 (S5), B-9000 Ghent, Belgium*

IDECAT
Integrated Design of
Catalytic Nanomaterials
for a Sustainable Production

http://www.lct.ugent.be

Overview

➢ Introduction

➢ V_2O_5: catalyst models

➢ Propylene adsorption on V_2O_5: cluster versus periodic

➢ Propylene activation on V_2O_5

- allylic C-H activation

- C=C activation

➢ V_2O_5 supported on TiO_2: catalyst models

➢ Propylene adsorption on V_2O_5 supported on TiO_2

➢ Conclusions

Selective hydrocarbon oxidation

- transform hydrocarbon (HC) to value-added and synthetically useful chemicals

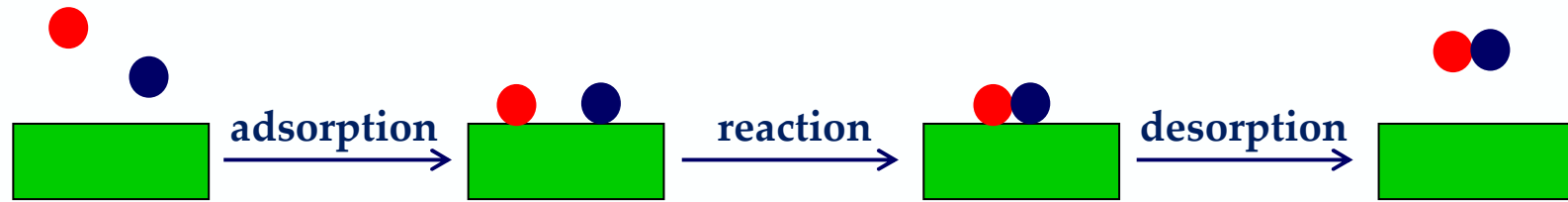- first step in total oxidation of organic pollutants (VOC)

$$HC \Rightarrow HCO$$
$$\searrow \quad \swarrow$$
$$CO_x$$
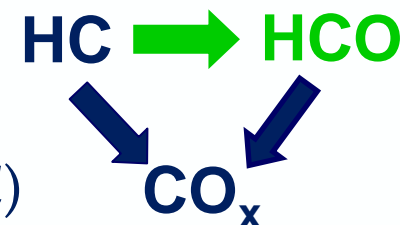
- • Goals: combined use of QM methods and experiment (steady state, transient, in-situ XANES/EXAFS) to obtain

    1. insight in reaction mechanism (qualitative)
    2. kinetic & thermodynamic data (quantitative)
    3. insight in the influence of the support (quantitative)
    4. insight in the catalyst structure under working conditions
    5. insight in catalyst properties on reactivity/selectivity

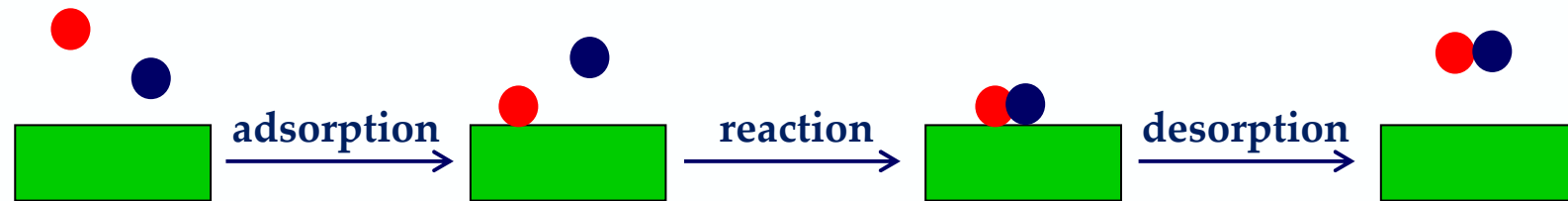 $\Rightarrow$ structure-activity relation

→ development of ab initio based fundamental kinetic model for catalyst optimization/design & process optimization
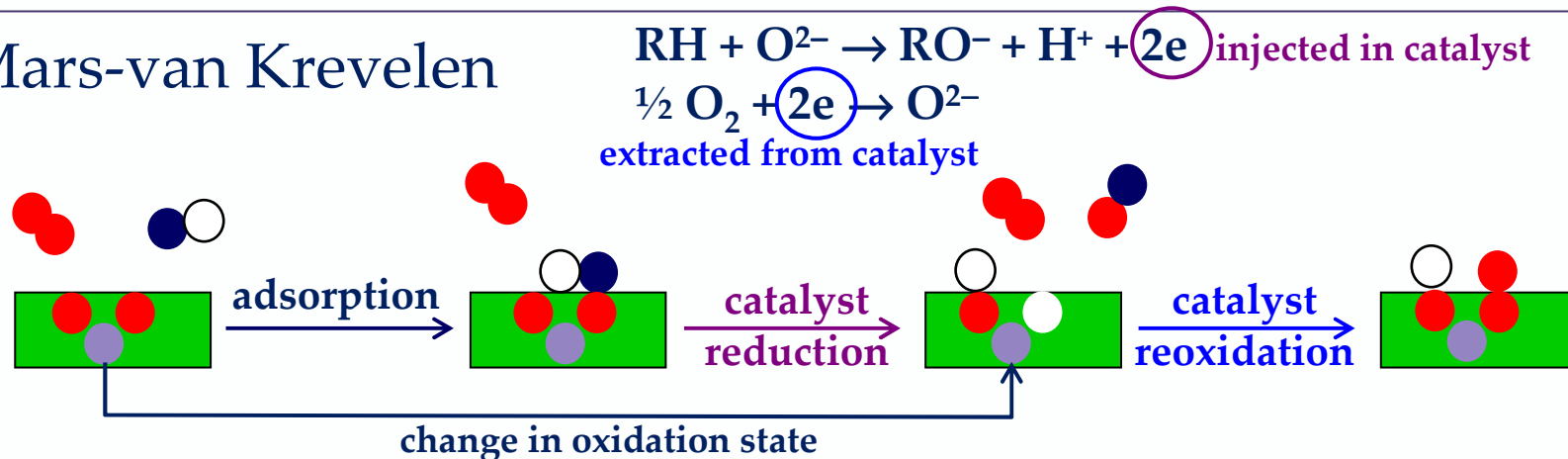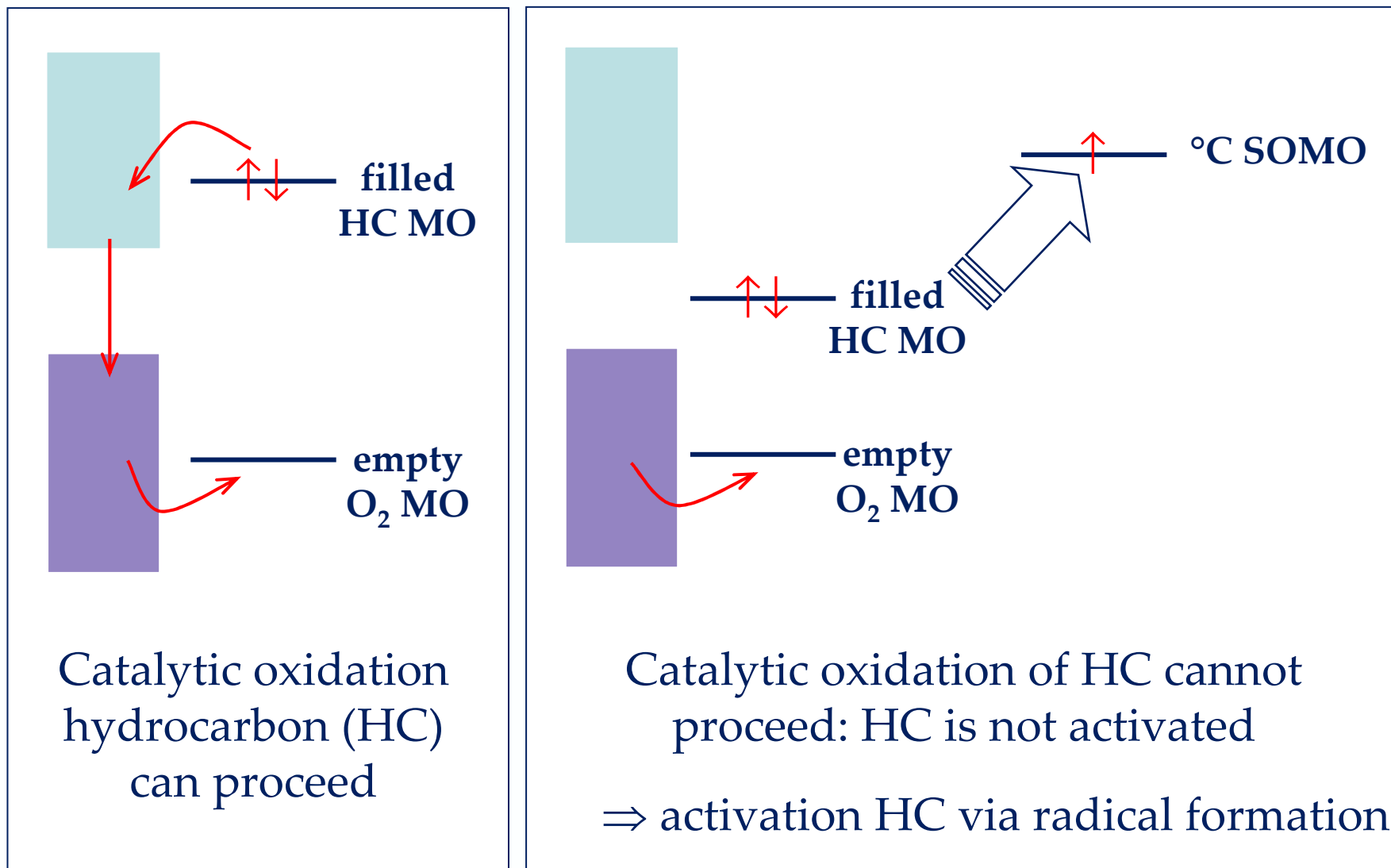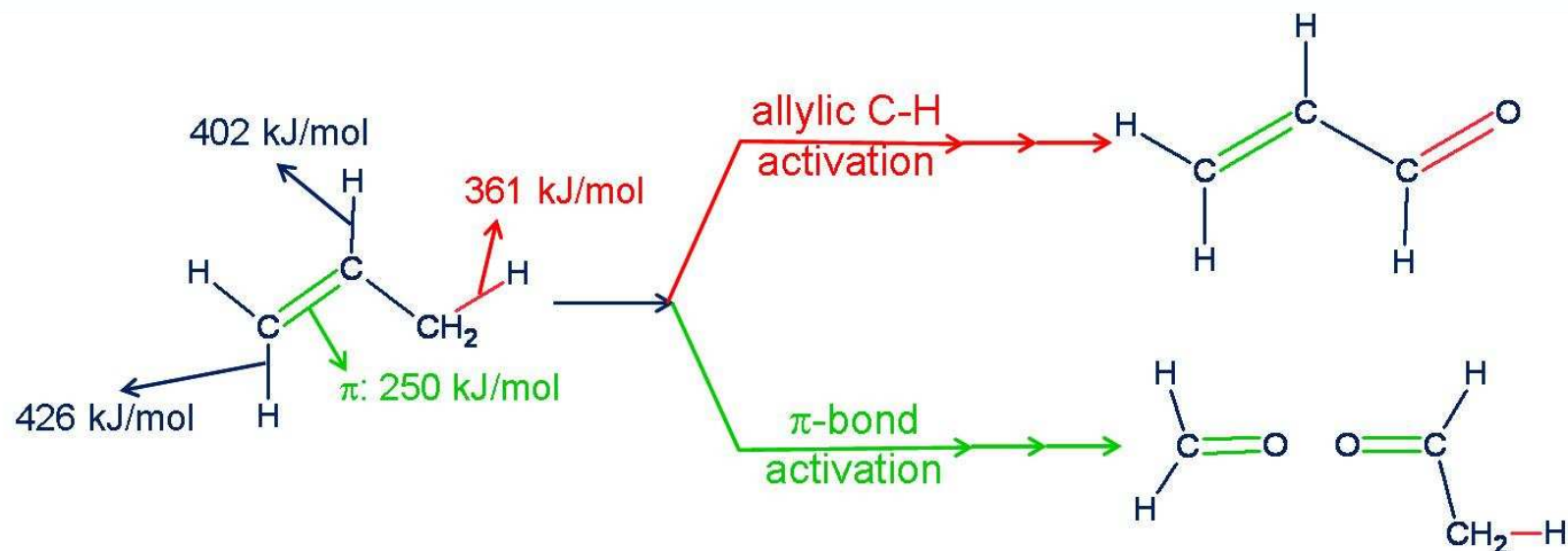
Mars-van Krevelen mechanism

Langmuir-Hinshelwood

adsorption → reaction → desorption

Eley-Rideal

adsorption → reaction → desorption

Mars-van Krevelen

$$RH + O^{2-} \rightarrow RO^- + H^+ + 2e \text{ injected in catalyst}$$
$$\tfrac{1}{2} O_2 + 2e \rightarrow O^{2-}$$
extracted from catalyst

adsorption → catalyst reduction → catalyst reoxidation

change in oxidation state

Electron transfer between catalyst and HC

filled HC MO

empty O$_2$ MO

Catalytic oxidation hydrocarbon (HC) can proceed

°C SOMO

filled HC MO

empty O$_2$ MO

Catalytic oxidation of HC cannot proceed: HC is not activated

$\Rightarrow$ activation HC via radical formation

Propylene activation on vanadium oxide

➤ Evaluation of different catalyst models

➤ Evaluation of various possible routes for C-H and C=C activation on different surface sites

➤ Evaluation of the influence of TiO_2 support
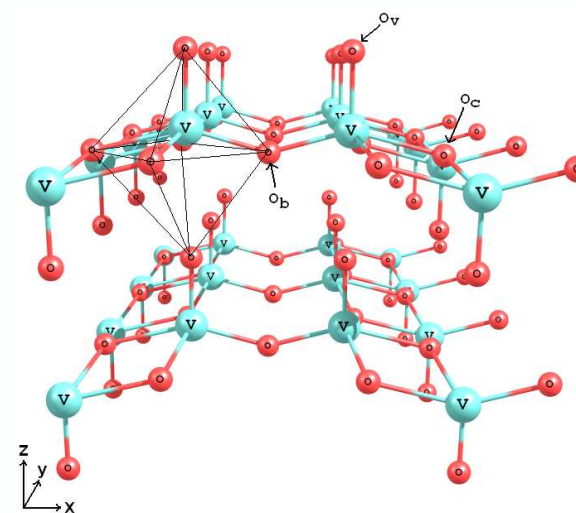
Vanadium oxide – crystal structure

- distorted VO_6 octahedra with V–O bond distances varying between small (1.58 Å) and large values (2.79 Å)

- layered structure: weak interlayer van der Waals type interaction

- surface oxygen atoms with different coordination number: vanadyl oxygen (Ov), bridge oxygen (Ob), chain oxygen (Oc) $\Rightarrow$ can have different catalytic reactivities

(001) surface
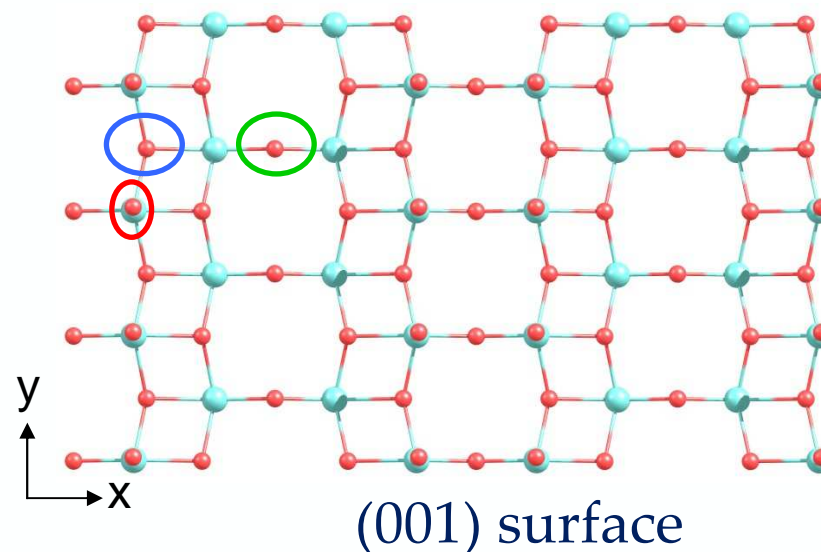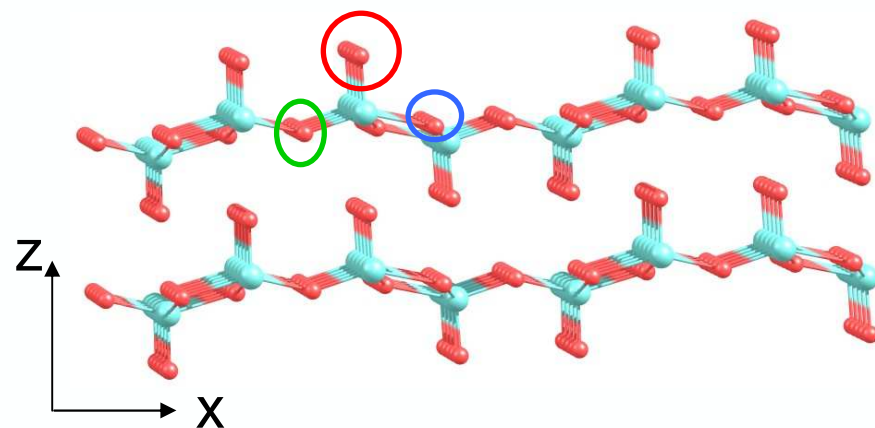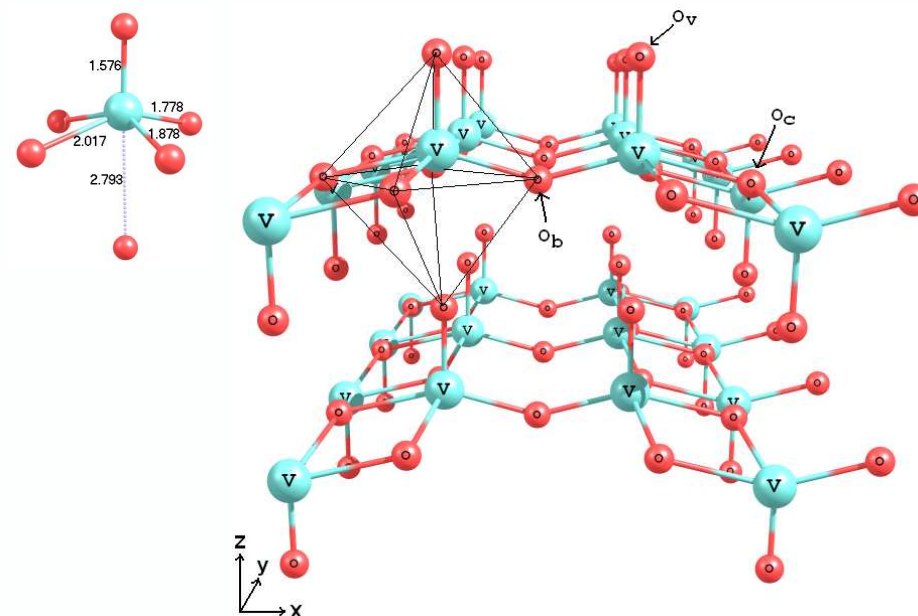
Computational methods

Density Functional Theory (DFT)

Cluster calculations

– TURBOMOLE and GAUSSIAN03

– Functional/Basis set: PBE0/TZVP

– Cluster models of different sizes = hydroxylated cutouts of the catalytic surface:

→ Electronic properties = f(size)
- energy
- atomic charges
- bond orders

Periodic calculations

– VASP

– GGA-PW91: geometry

– GGA-RPBE: energy

– PAW method of Blöchl for the description of the electron-ion interaction

– Spin polarization

– Surface slabs:

→ Electronic+structural properties
- number of atom layers
- thickness vacuum layer
- number of k-points
- DOS + band gap

Cluster models for V2O5 (001)

$V_2O_9H_8$

$V_6O_{20}H_{10}$

$V_{10}O_{31}H_{12}$
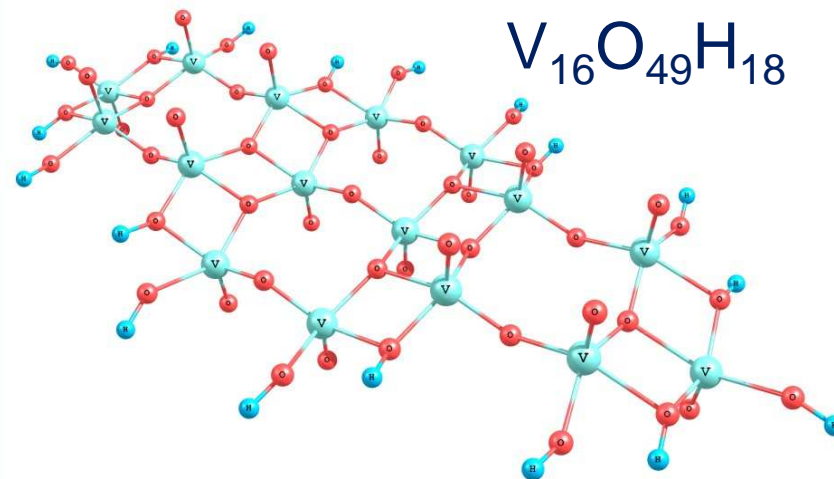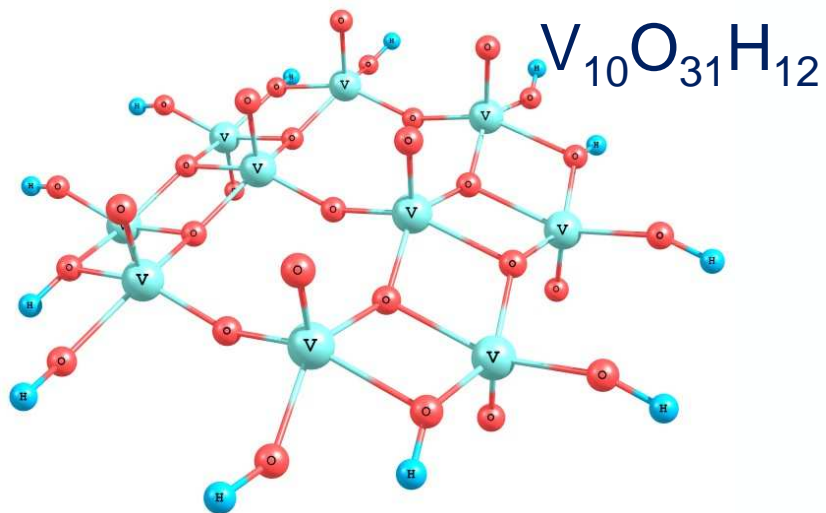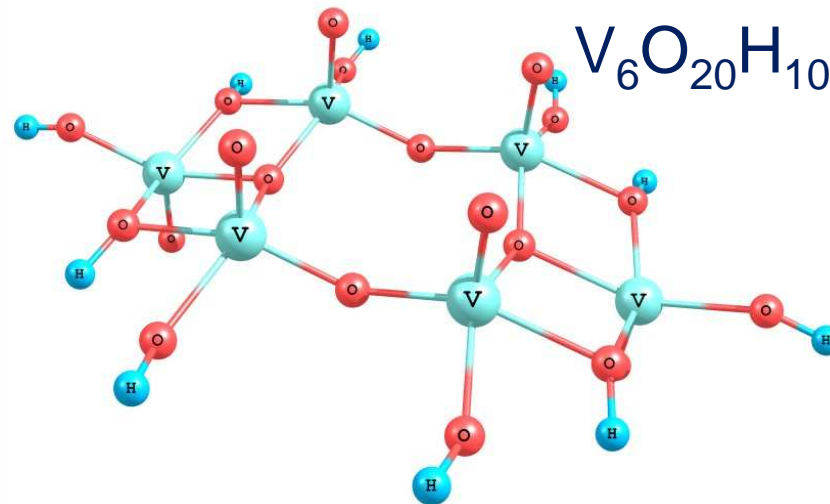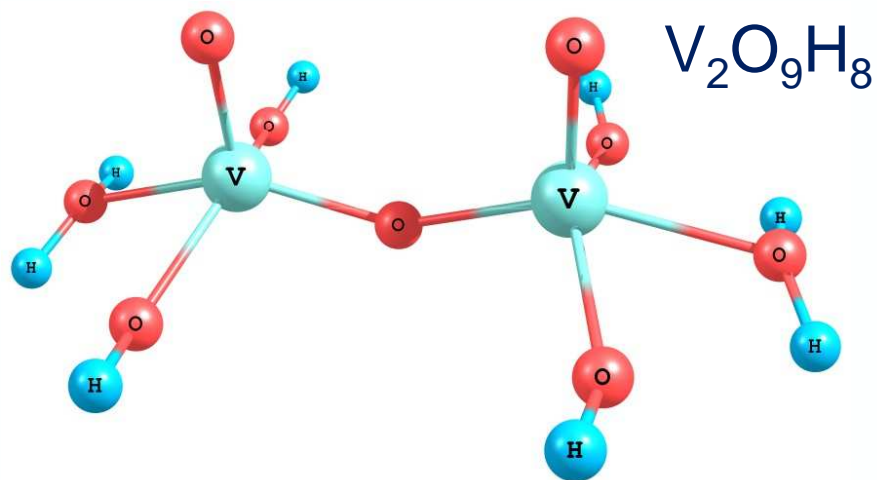
$V_{16}O_{49}H_{18}$

Cluster size convergence

atom	V2O9H8	V6O20H10	V10O31H12	V16O49H18
	Mulliken charge			
V	0,91	0.99	1.01	1.01
Ov	-0,31	-0.27	-0.26	-0.26
Ob	-0,50	-0.52	-0.55	-0.55
Oc	-0,60	-0.58	-0.59	-0.59

Mulliken atomic charges (with S-VWN/SV(P) using TURBOMOLE)

| bond	V2O9H8	V6O20H10	V10O31H12	V16O49H18
	bond orders			
V-Ov	2.05	2.09	2.09	2.10
V-Ob	2 x 0.80	2 x 0.83	2 x 0.83	2 x 0.83
V-Oc	0.40/-	0.38 / 2 x 0.51	0.35 / 2 x 0.55	0.35 / 2 x 0.55

Meyer Bond order indices (with B3LYP/6-31G* using GAUSSIAN03)

$\Rightarrow$ convergence of properties: $V_{10}O_{31}H_{12}$ or larger clusters

$\Rightarrow$ nucleophilicity order based on charges: Oc > Ob > Ov

10

Periodic (slab) model for V2O5 (001)
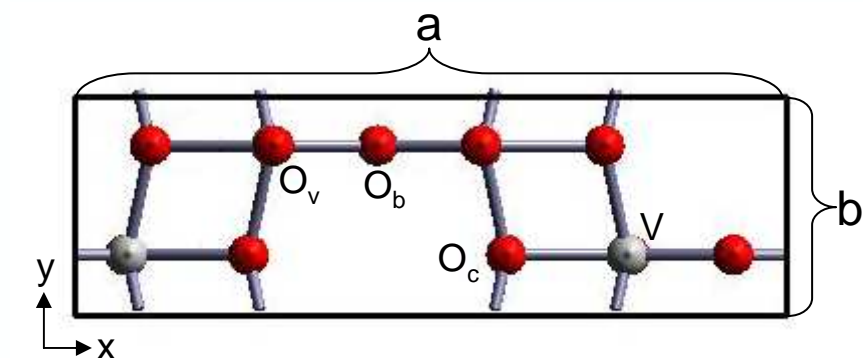
Primitive {1x1} unit cell is too small to place propane on top

~11 Å
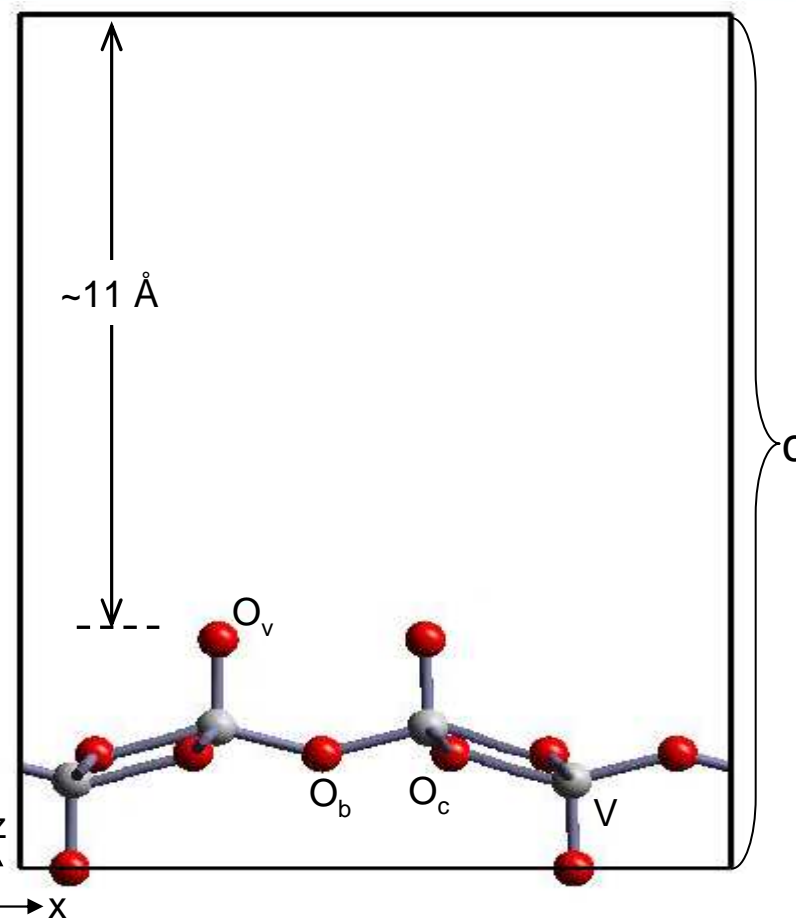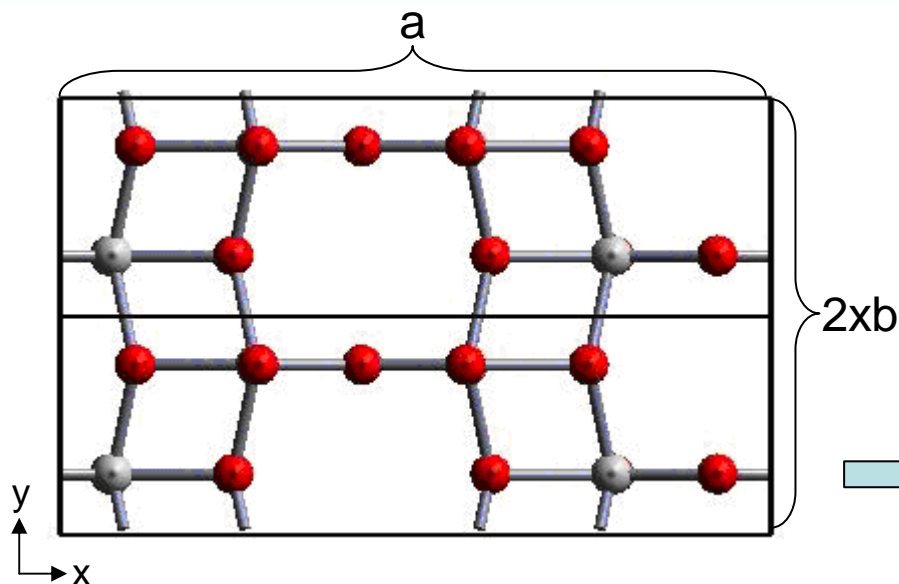
Surface supercells of at least {1x2} unit cell are used for modeling the oxidation reaction on vanadia

Periodic: bulk V2O5 versus slab

➢ Comparison atom positions in bulk V_2O_5 with 1-layer and 2-layer slab

	Bond length (Å)				
	V=Ov	V-Ob	V-Oc	V-Oc'	V⋯Ov
Exp.	1.58	1.78	1.88	2.02	2.79
Bulk	1.61	1.79	1.89	2.04	2.87
Slab-1layer	1.60	1.81	1.90	2.05	-
Slab-2layers	1.60/1.61	1.79/1.80	1.90/1.89	2.08/2.02	2.87

~11 Å

~8 Å
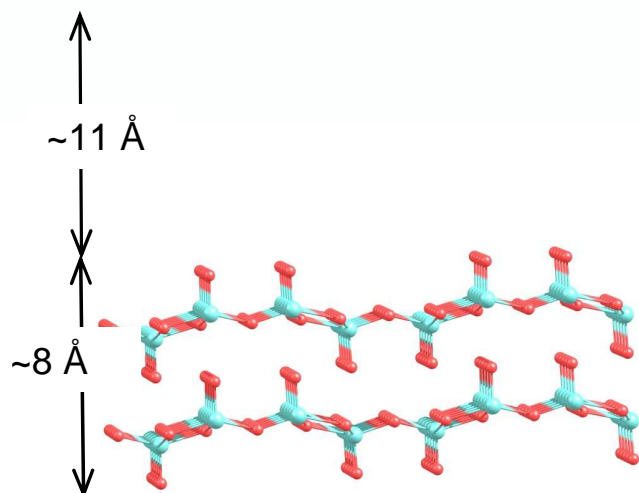
Good agreement between experimental and calculated structures

GGA/PAW using (8×8) mesh; E_{cutoff} = 400 eV ; optimized lattice parameters

Periodic: bulk V2O5 versus slab
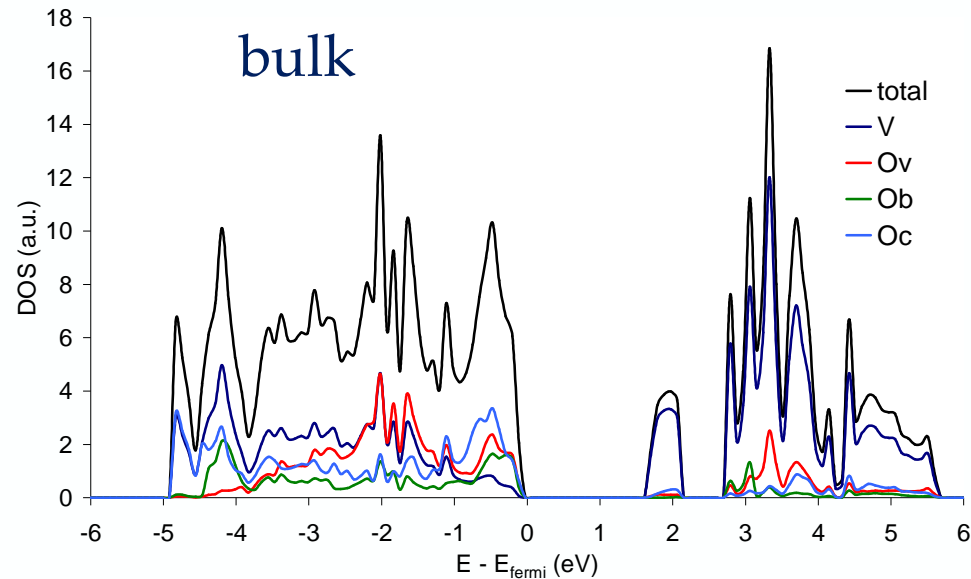
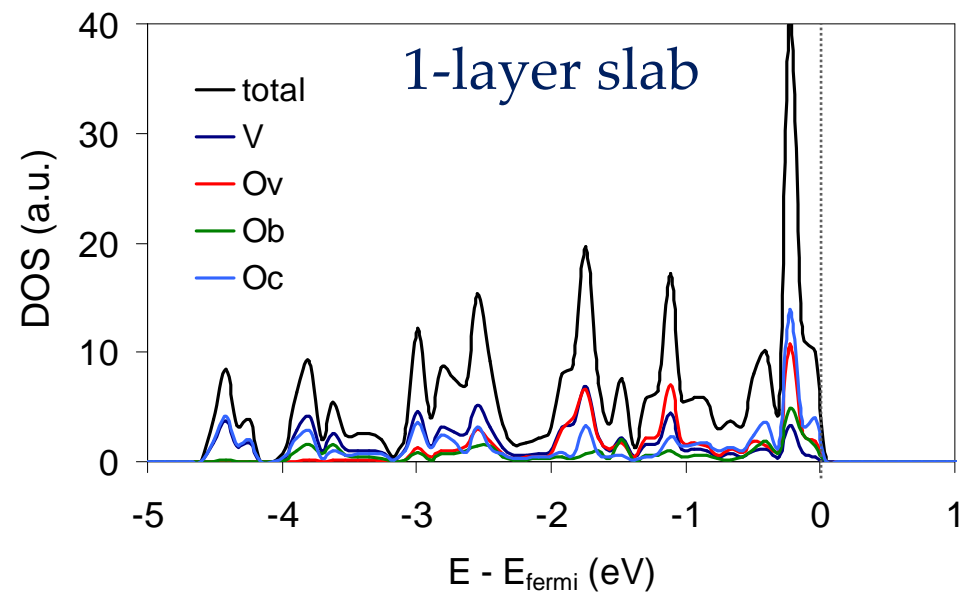| (eV)	experimental	bulk	1-layer	2-layer
E_{fermi}	6.7 ± 0.1	9.0	8.9	8.9
gap	2.3 ± 0.1	1.7	2.0	1.8
width	5.5 ± 0.5	4.9	4.5	4.7

$\Rightarrow$ weak interlayer binding: 1-layer slab provides reasonable model for V_2O_5 surface at reasonable computational cost

GGA/PAW using (8×8) mesh; E_{cutoff} = 400 eV ; optimized lattice parameters

V2O5: electronic properties cluster versus slab
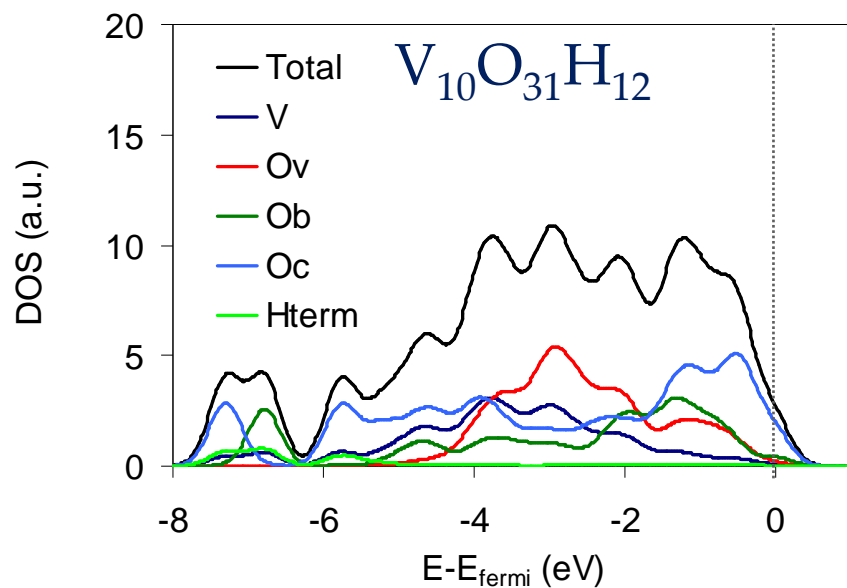
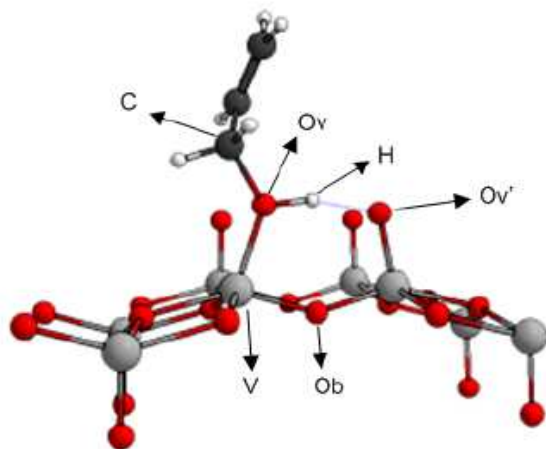|	E_{fermi}	gap	width	nucleophilicity order
$V_{10}O_{31}H_{12}$	8.3	4.1	8.5	Oc > Ob ≥ Ov
slab	8.9	2.0	4.7	Oc > Ov ≥ Ob
bulk exp.	6.7 ± 0.1**	2.3 ± 0.1*	5.5 ± 0.5***	

Cogan et al., J. Appl. Phys., 66, 1333 (1989)

**Witko et al., Surf.Sci., 375, 385 (1997)*

***Witko et al., Phys.Rev.B, 59, 10 583 (1999)*

Propylene adsorption on V2O5: clusters

$$CH_2=CH-CH_{3(g)} + Ov^* \longrightarrow CH_2=CH-CH_2Ov^*H$$

$$\Delta E_r = E_{adsorbed} - E_{cluster} - E_{propylene(g)}$$

Distances (Å)	V6O20H10		V10O31H12	
	closed shell	spin optimized	closed shell	spin optimized
		triplet		triplet
V-Ov	1.97	2.00	1.96	1.98
Ov-C	1.43	1.44	1.45	1.45
Ov-H	1.00	1.00	0.99	0.99
O'v-H	1.69	1.69	1.74	1.83
Angles (°)				
V-Ov-C	128.3	128.6	128.6	131.7
V-Ov-H	116.3	110.3	115.4	114.1
C-Ov-H	113.4	111.4	113.0	112.5
Ov-H-Ov'	160.8	164.0	157.8	157.7
Ob-V-Ov	85.6	87.5	87.8	89.2
ΔE_{chem} (kJ/mol)	+117	+12	+83	−43

Propylene adsorption on V2O5: cluster/periodic

$$CH_2=CH-CH_{3(g)} + Ov^* \longrightarrow CH_2=CH-CH_2Ov^*H$$

	V10O31H12		Periodic	
	closed shell	**spin optimized**	**single layer**	**double layer**
Distances (Å)		triplet	triplet	triplet
V-Ov	1.96	1.98	1.93	2.01
Ov-C	1.45	1.45	1.48	1.50
Ov-H	0.99	0.99	1.03	1.01
O'v-H	1.74	1.83	1.62	1.73
Angles (°)				
V-Ov-C	128.6	131.7	128.6	134.3
V-Ov-H	115.4	114.1	114.4	107.8
C-Ov-H	113.0	112.5	115.0	108.4
Ov-H-Ov'	157.8	157.7	163.1	166.9
Ob-V-Ov	87.8	89.2	88.4	88.0
ΔE_{chem} (kJ/mol)	+83	−43	+46	+42

$\Rightarrow$ cluster versus periodic: same local geometry, different energetics

16

Propylene adsorption on V2O5: cluster/periodic

triplet $V_{10}O_{31}H_{12}$

slab

SOMO-1   SOMO-2
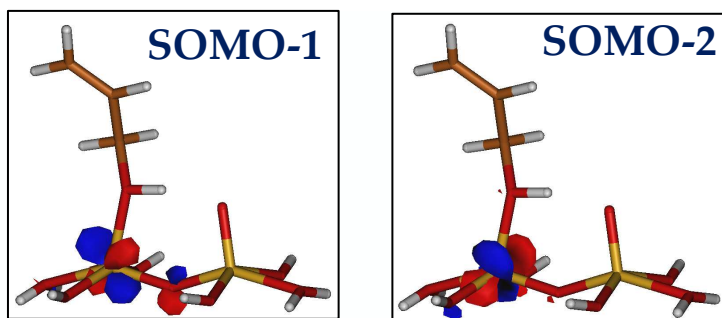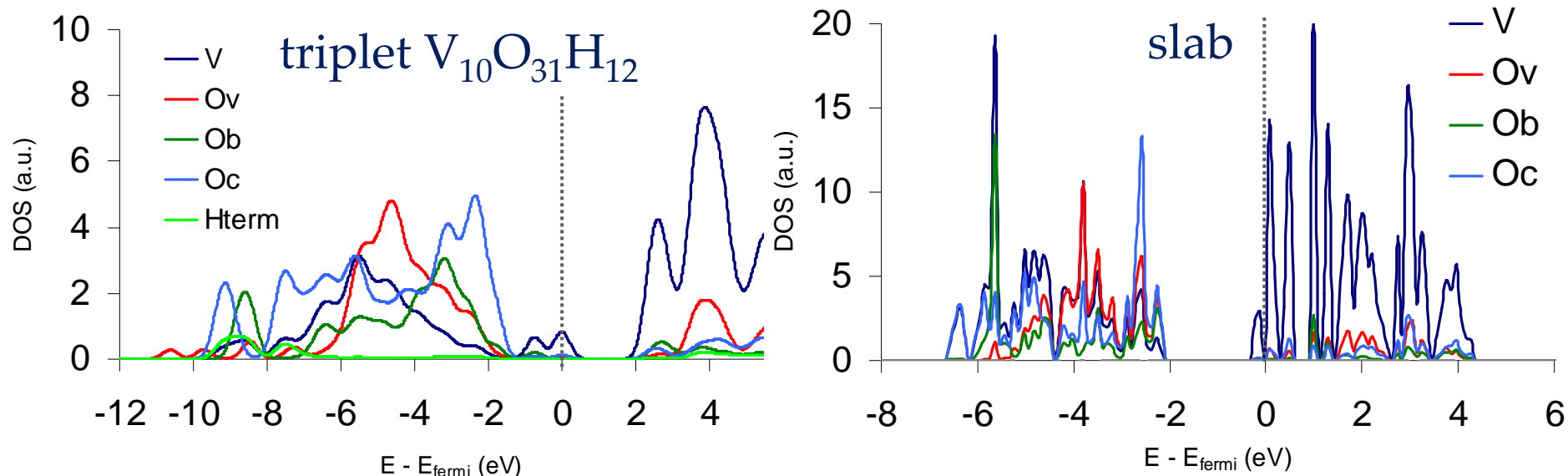
singly occupied MO's in cluster

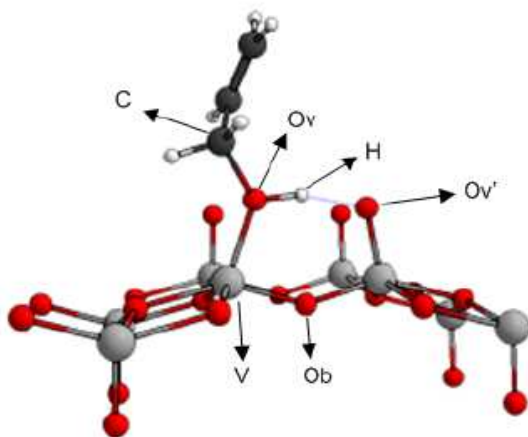| (eV)	E_{fermi}	gap	width
clean			
$V_{10}O_{31}H_{12}$	8.3	4.1	8.5
slab	8.9	2.0	4.5
propylene adsorption			
$V_{10}O_{31}H_{12}$	6.3	2.3	11.5
slab	4.7	0	4.5

$\Rightarrow$ periodic model is used for further study

17

Propylene C-H activation

- Formation of adsorbed alcoholic intermediate:

$$CH_2=CH-CH_2-H_{(g)} + O^* \rightarrow CH_2=CH-CH_2-O^*H$$

- Formation of allylic radical:

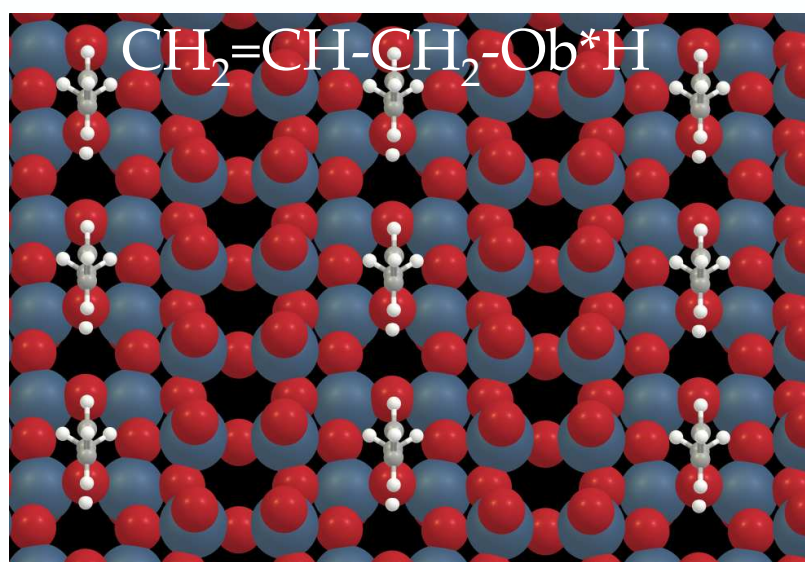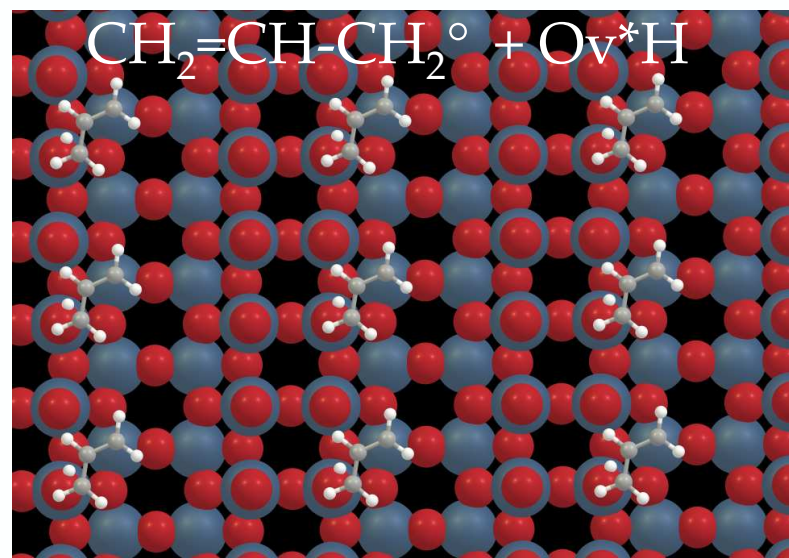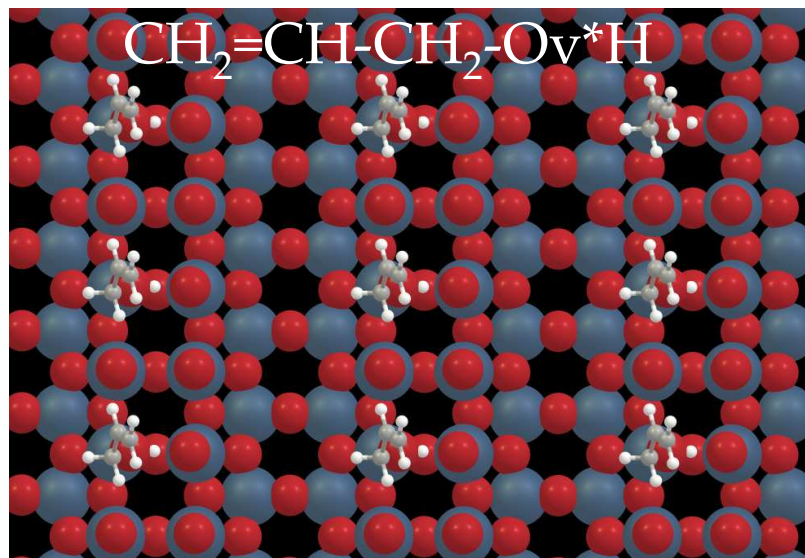$$CH_2=CH-CH_2-H_{(g)} + O^* \rightarrow CH_2=CH-CH_2^\circ + O^*H$$
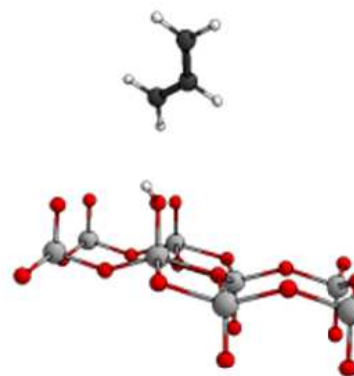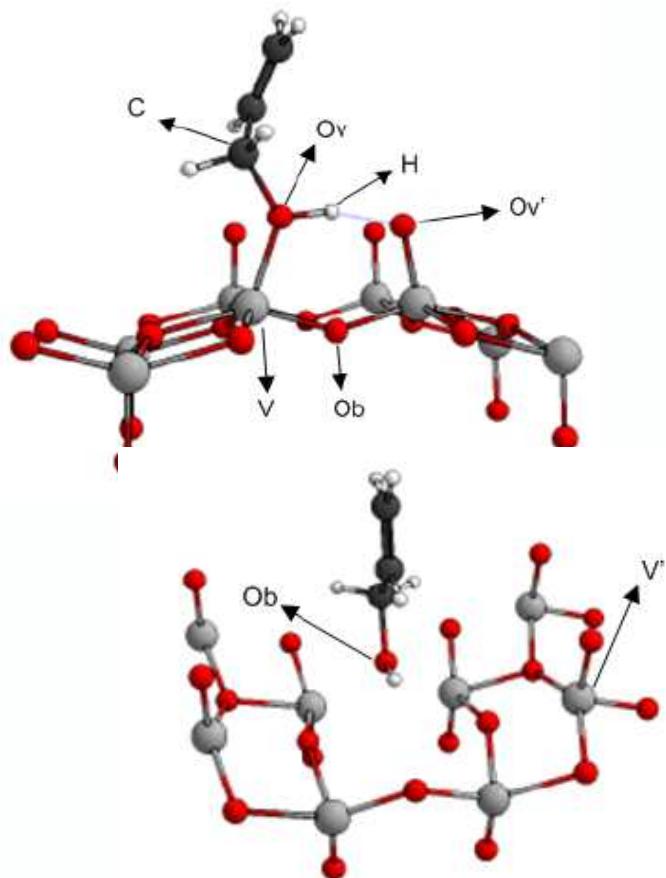

alcoholic intermediate on Ov   allylic radical and H adsorbed on Ov

Note: no stable intermediate could be located for interaction of allylic C-H with V-O groups of V_2O_5 (001) surface leading to heterolytic C-H bond cleavage

Allylic C-H bond activation on Ov and Ob

$CH_2=CH-CH_2-Ov*H$

$CH_2=CH-CH_2° + Ov*H$

$CH_2=CH-CH_2-Ob*H$

$CH_2=CH-CH_2° + Ob*H$
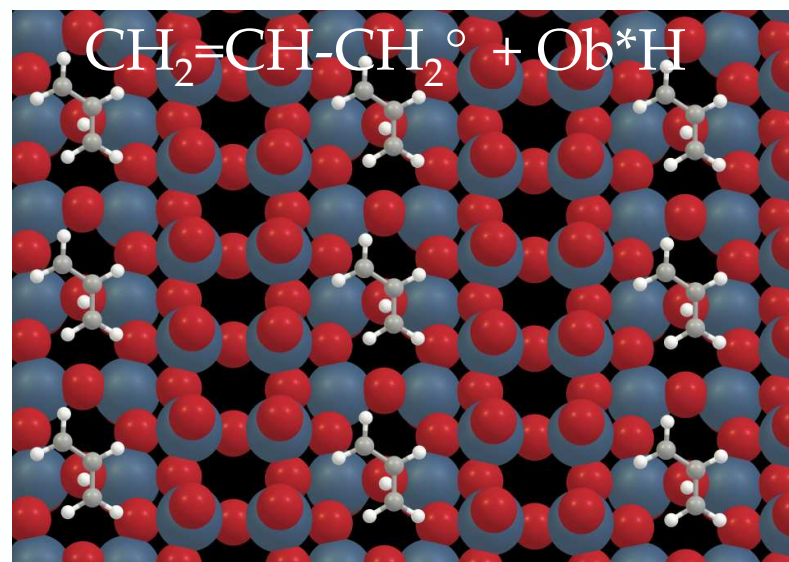
Allylic C-H activation on Ov and Ob

$$CH_2=CH-CH_{3(g)} + O^* \longrightarrow CH_2=CH-CH_2O^*H$$

1-layer slab V_2O_5			
Distances (Å)	Ov	Distances (Å)	Ob
V-Ov	1.93	V-Ob	2.16
Ov-C	1.48	Ob-C	1.52
Ov-H	1.03	Ob-H	0.99
Ov'-H	1.62	Oc-H	2.34
Angles (°)		Angles (°)	
V-Ov-C	128.6	V-Ob-C	117.2
V-Ov-H	114.4	V-Ob-H	102.1
C-Ov-H	115.0	C-Ob-H	110.0
Ov-H-Ov'	163.1	V-Ob-V	106.2
Ob-V-Ov	88.4	Ob-V-Ov	115.1
ΔE_{chem} (kJ/mol)	+46	ΔE_{chem} (kJ/mol)	+169

$\Rightarrow$ formation alcoholic intermediate on Ob: elongated V-O_b bonds

$\Rightarrow$ alcoholic intermediate on Ov more stable than on Ob

Propylene C-H activation: thermodynamics

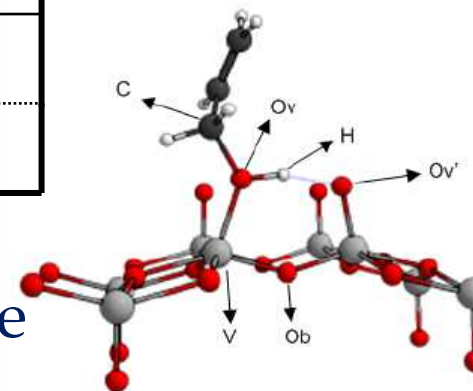$$\Delta E_r = E_{adsorbed} - E_{slab} - E_{propylene(g)}$$

Periodic slab	V_2O_5	
ΔE_r (kJ/mol)	Ov	Ob
$CH_2=CH-CH_2° + {}^*OH$	88	104
$CH_2=CH-CH_2O{}^*H$	46	169

$\Rightarrow$ alcoholic intermediate on Ov most stable

$\Rightarrow$ alcoholic intermediate on Ob least stable

$\Rightarrow$ Ob*H less stable than Ov*H

H adsorption

$$CH_2=CH-CH_2°_{(g)} + H°_{(g)}$$

kJ/mol

O* = Ob

$\Delta E_{chem} H_{O*v}$ $\Delta E_{chem} H_{O*b}$ O* = Ov

BDE C-H$_{allylic}$

361

104 $\Delta E_{r,O*b}$

88 $\Delta E_{r,O*v}$

$$CH_2=CH-CH_{3(g)} + O*$$ $$CH_2=CH-CH_2° + *OH$$
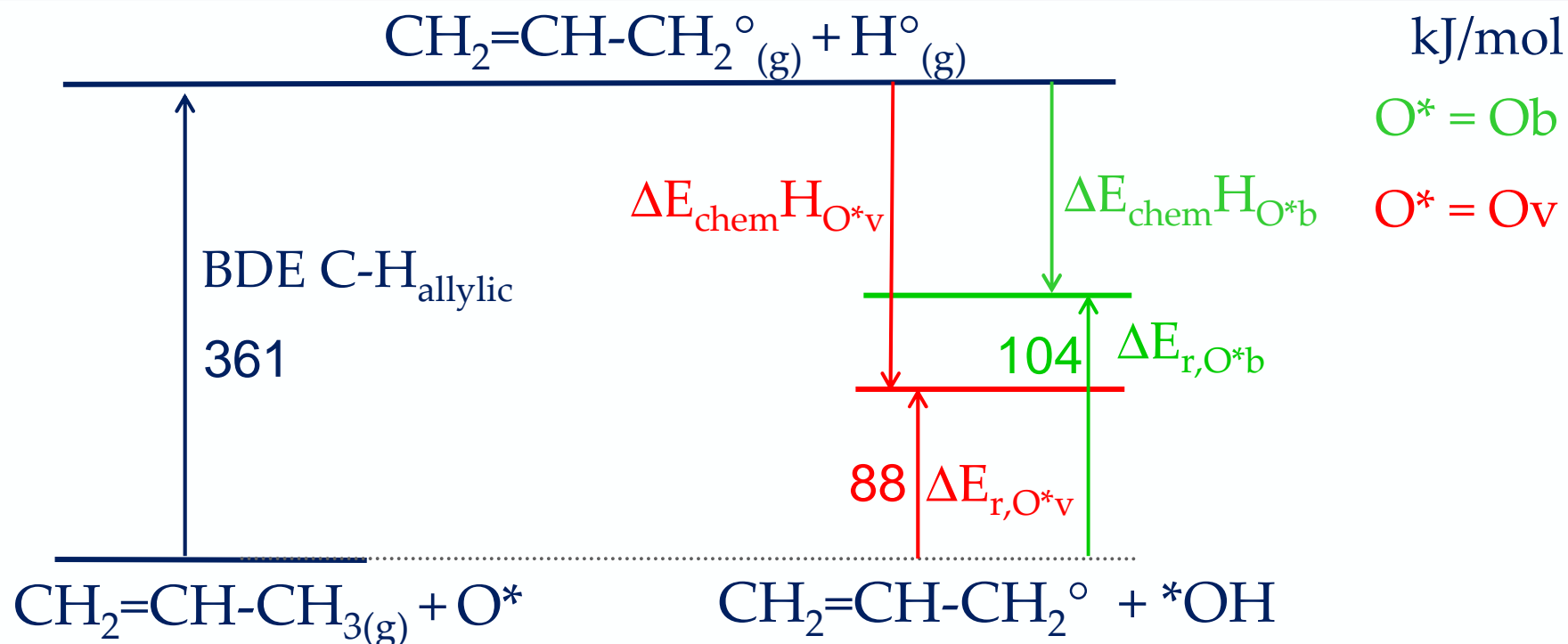
$$\Delta E_{chem} H_{O*} = \Delta E_{r,O*} - BDE\,CH_{allylic}$$

1-layer slab	V$_2$O$_5$	
(kJ/mol)	Ov	Ob
ΔE_{chem} HO*	−273	−257
Hermann et al	−294	−266

Hermann et al., Far. Disc., 114, 53 (1999)

Propylene C-H activation: energy diagram

formation alcoholic int. $\longleftarrow$ Propylene$_{(g)}$ formation allylic radical $\longrightarrow$

O* = Ob
O* = Ov
kJ/mol

176

169

156

139

116

E_a

104

88

46

CH$_2$=CH-CH$_2$O*H   CH$_2$=CH-CH$_{3(g)}$ + O*   CH$_2$=CH-CH$_2$° + *OH
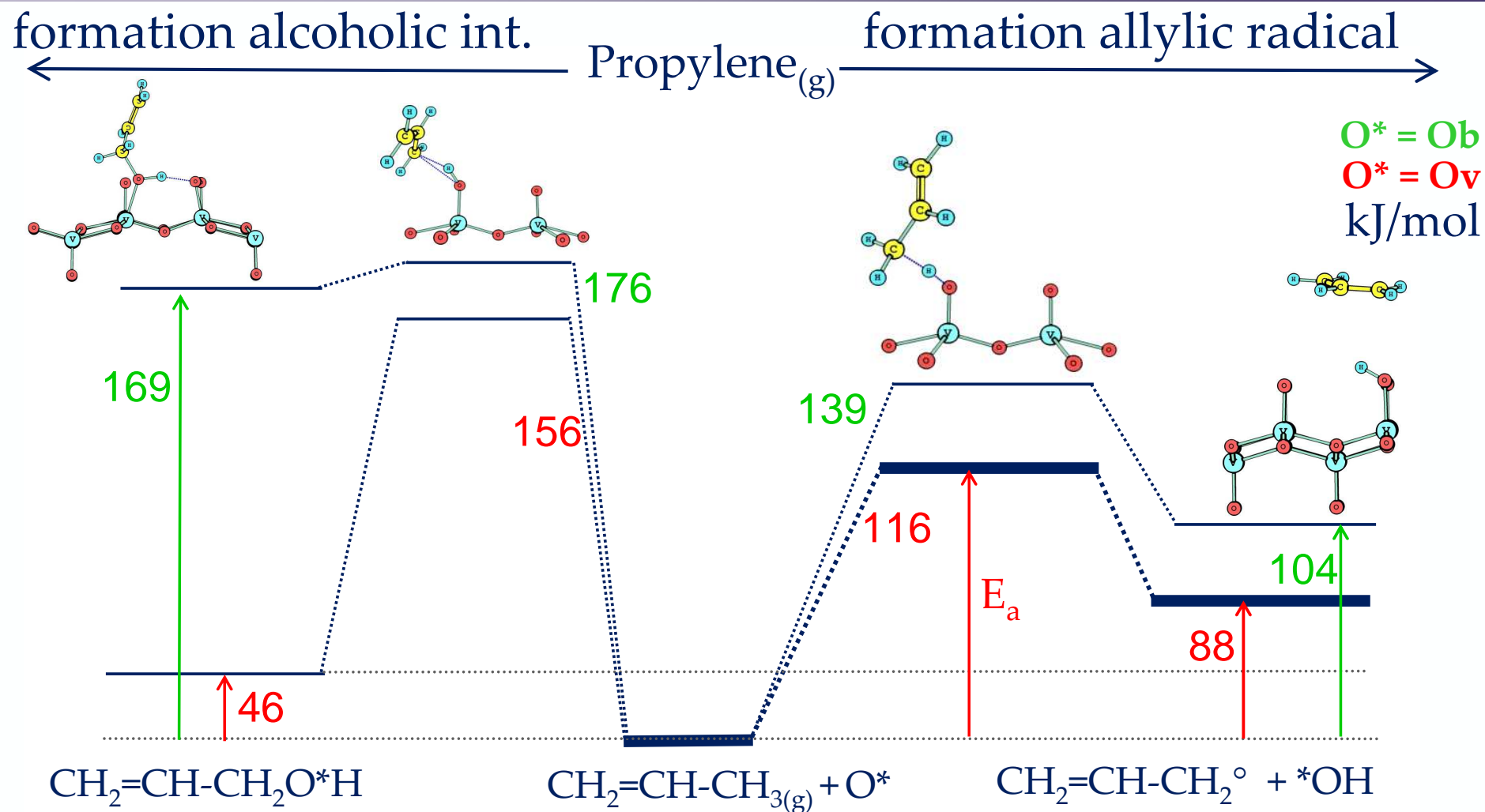
$\Rightarrow$ C-H activation on V$_2$O$_5$ preferentially via allylic radical

$\Rightarrow$ Ov is more reactive than Ob on V$_2$O$_5$

Propylene C=C activation

- Formation of adsorbed peroxy intermediate:

$$CH_2=CH-CH_2-H_{(g)} + 2O^* \rightarrow \underset{\underset{O_i^*}{|}}{CH_2}-\underset{\underset{O_{ii}^*}{|}}{CH}-CH_3$$
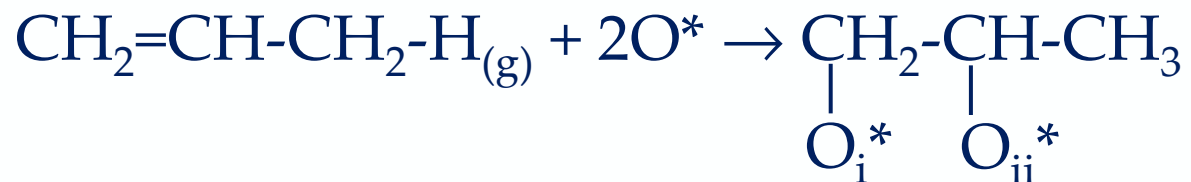
- Formation of epoxy intermediate:

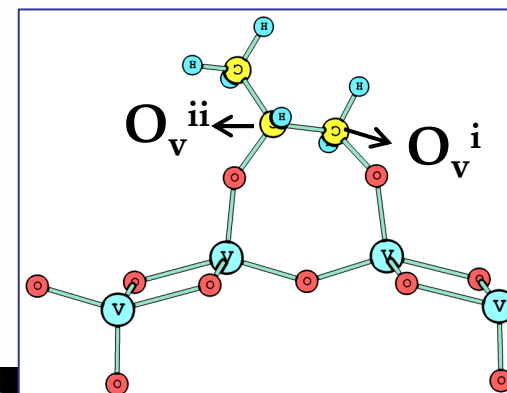$$CH_2=CH-CH_2-H_{(g)} + O^* \rightarrow CH_2-CH-CH_3$$
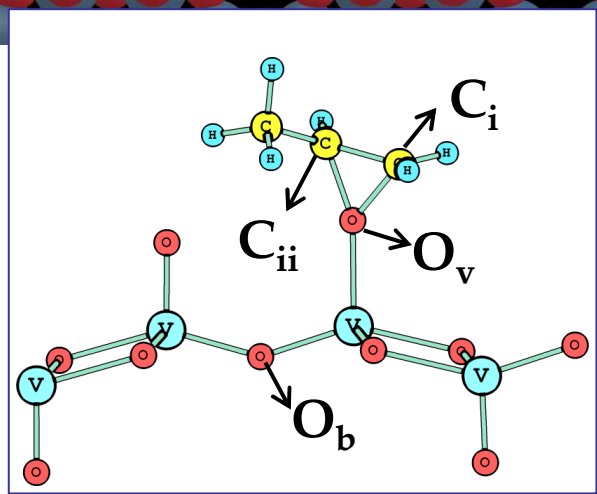$$\diagdown \underset{O^*}{\diagup}$$
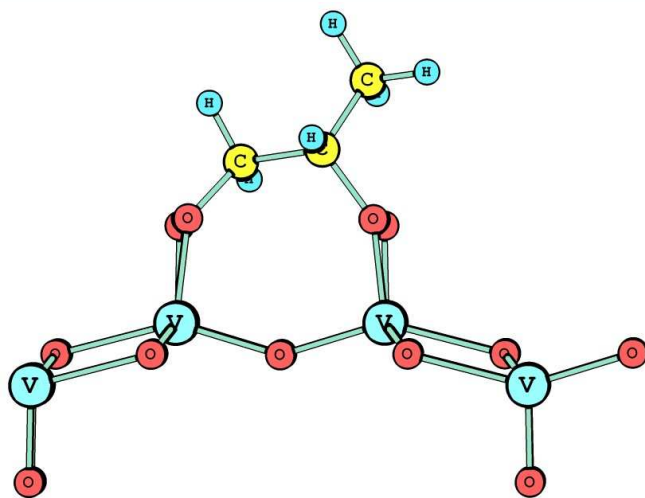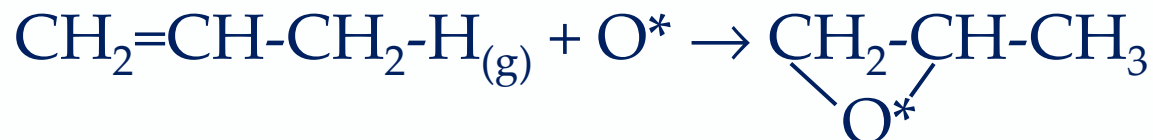
peroxy intermediate   epoxy intermediate
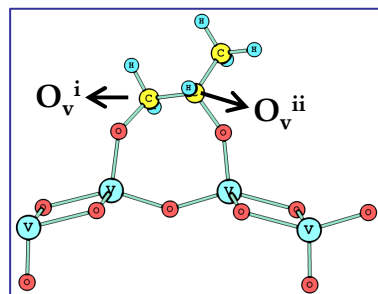
Propylene C=C bond activation over vanadyl Ov*

Epoxy Ov

$O_v^{ii} \leftarrow$ ... $\rightarrow O_v^i$

C_i

C_{ii} ... O_v

O_b
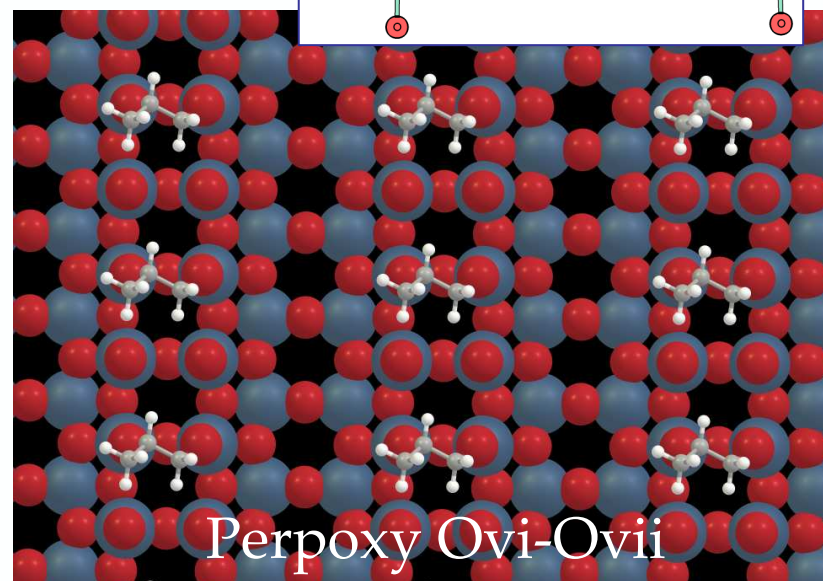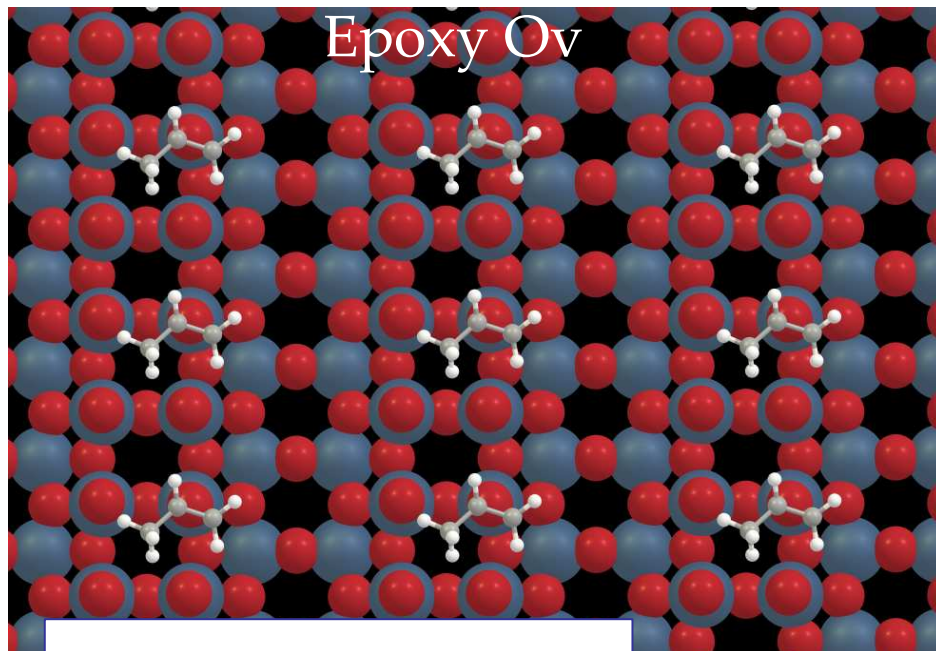
Perpoxy Ovi-Ovii

Propylene C=C bond activation over vanadyl Ov*
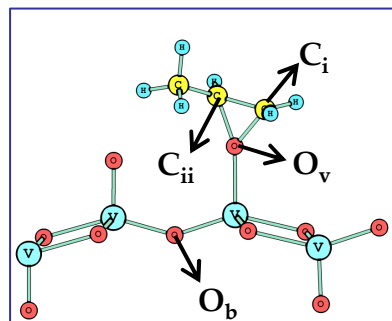
epoxy intermediate

peroxy intermediate

$\Rightarrow$ On Ov sites: peroxy intermediate is more stable than epoxy intermediate

Epoxy		Peroxy	
O_v		O_v^i, O_v^{ii}	
Distances (Å)		Distances (Å)	
C_i-C_{ii}	1.48	C_i-C_{ii}	1.53
C_i-O_v	1.46	C_i-O_v^i	1.43
C_{ii}-O_v	1.50	C_{ii}-O_v^{ii}	1.43
V-O_v	1.95	V-O_v^i	1.75
		V-O_v^{ii}	1.73
Angles (°)		Angles (°)	
V-O_v-C_i	135.9	V-O_v^i-C_i	136.5
V-O_v-C_{ii}	161.2	V-O_v^{ii}-C_{ii}	150.0
O_v-V-O_b	107.7	O_v^i-V-O_b	100.1
		O_v^{ii}-V-O_b	100.8
kJ/mol			
ΔE_r	+108		-20

Propylene C=C bond activation over valley O*

Peroxy Oci-Ovii

Peroxy Obi-Ocii

Peroxy Obi-Obii

Peroxy Oci-Ocii
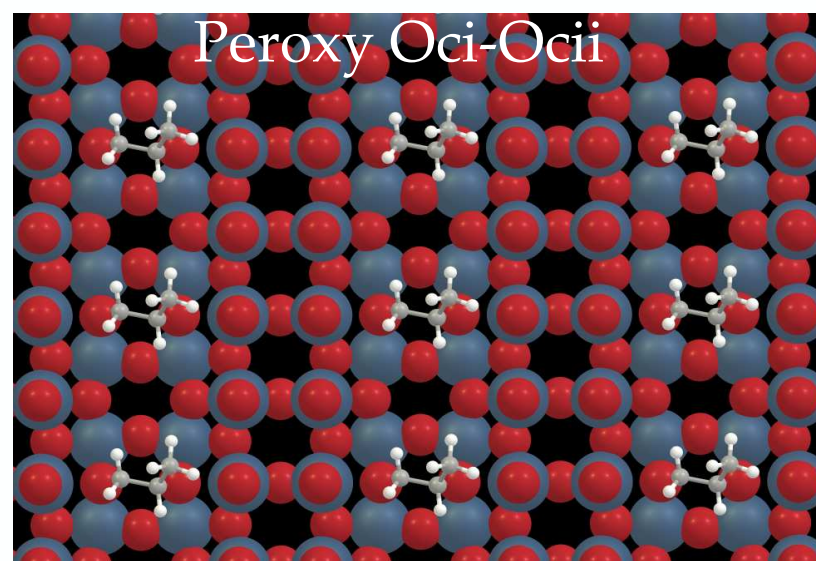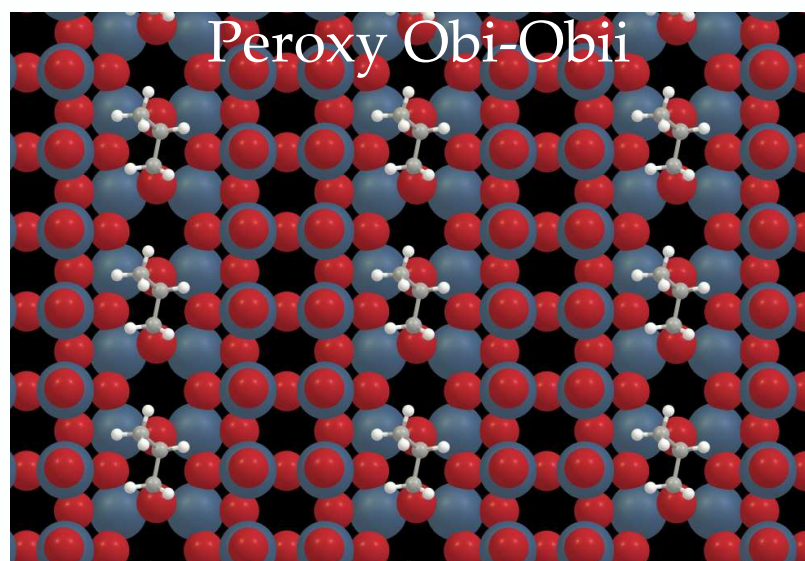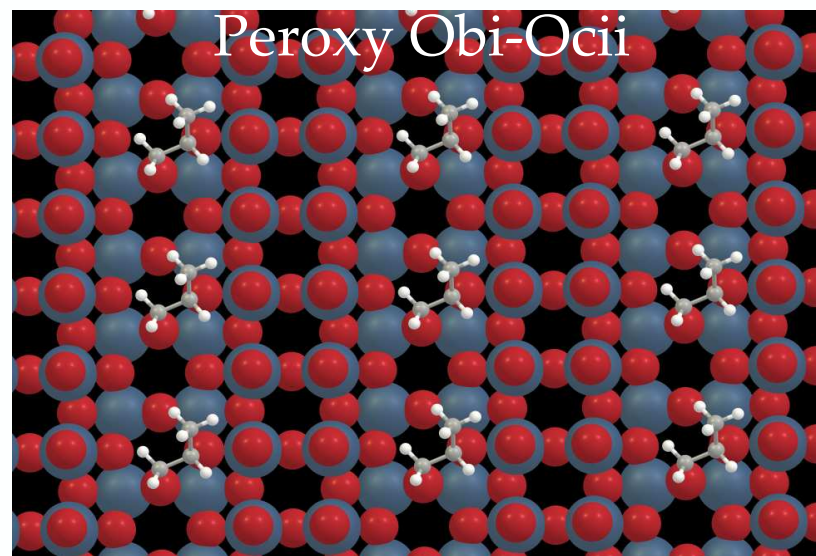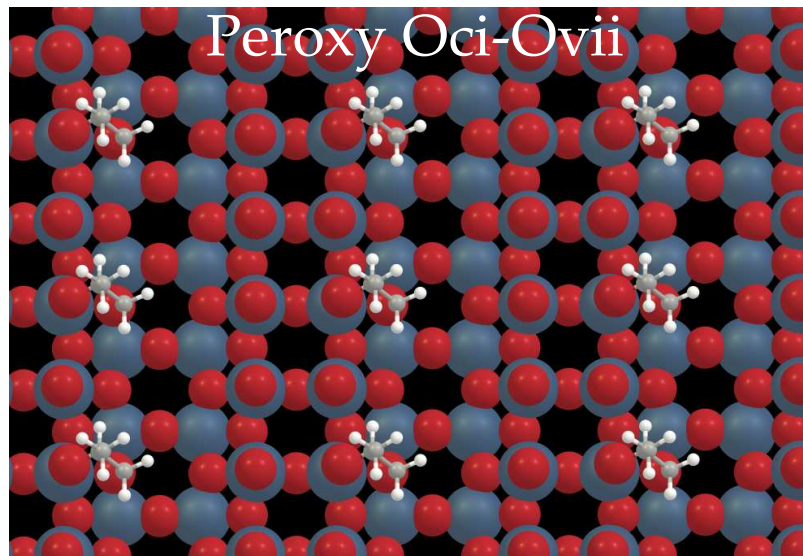
Propylene C=C bond activation over valley O*
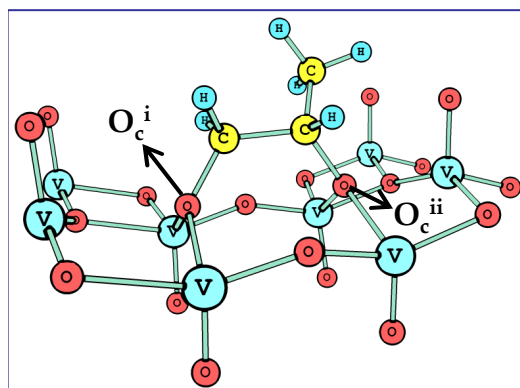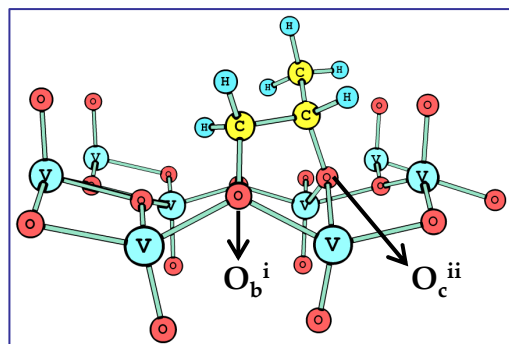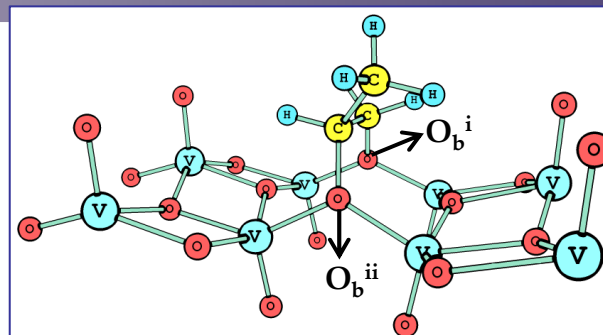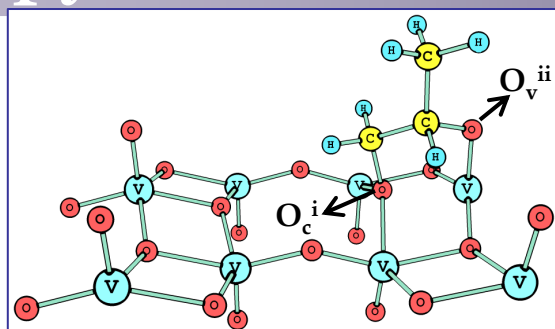
O_c^i, O_v^{ii}		O_b^i, O_c^{ii}		O_b^i, O_b^{ii}		O_c^i, O_c^{ii}	
Dist. (Å)		Dist. (Å)		Dist. (Å)		Dist. (Å)	
C_i-C_{ii}	1.52	C_i-C_{ii}	1.52	C_i-C_{ii}	1.58	C_i-C_{ii}	1.58
C_i-O_c^i	1.48	C_i-O_b^i	1.45	C_i-O_b^i	1.46	C_i-O_c^i	1.47
C_{ii}-O_v^{ii}	1.45	C_{ii}-O_c^{ii}	1.50	C_{ii}-O_b^{ii}	1.47	C_{ii}-O_c^{ii}	1.50
V-O_v^{ii}	1.78	V-O_b^i	1.97	V-O_b^i	1.98	V-O_c^i	2.47
V-O_c^i	2.17	V-O_c^{ii}	2.17	V-O_b^{ii}	1.96	V-O_c^{ii}	2.48
Ang. (°)		Ang. (°)		Ang. (°)		Ang. (°)	
O_c^i-C_i-C_{ii}	106.7	O_b^i-C_i-C_{ii}	108.9	O_b^i-C_i-C_{ii}	120.0	O_c^i-C_i-C_{ii}	124.0
O_v^{ii}-C_{ii}-C_i	106.1	O_c^{ii}-C_{ii}-C_i	106.2	O_b^{ii}-C_{ii}-C_i	115.7	O_c^{ii}-C_{ii}-C_i	120.6
V-O_c^i-V	121.3	V-O_b^i-V	124.9	V-O_b^i-V	122.4	V-O_c^i-V	124.2
O_v^{ii}-V-O_c^i	82.0	O_c^{ii}-V-O_b^i	78.2	V-O_b^{ii}-V	123.9	V-O_c^{ii}-V	121.8
kJ/mol							
ΔE_r	+54		+73		+103		+187

Propylene C=C activation: thermodynamics

$$\Delta E_r = E_{adsorbed} - E_{slab} - E_{propylene(g)}$$

epoxy on Ov

peroxy on Ov-Ov
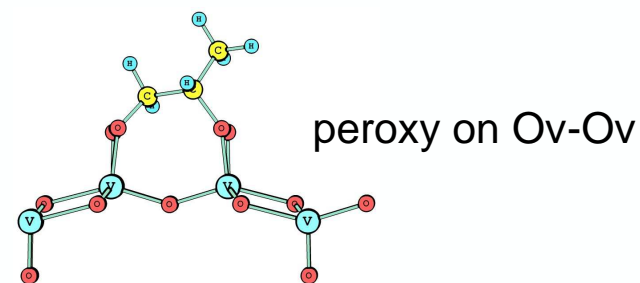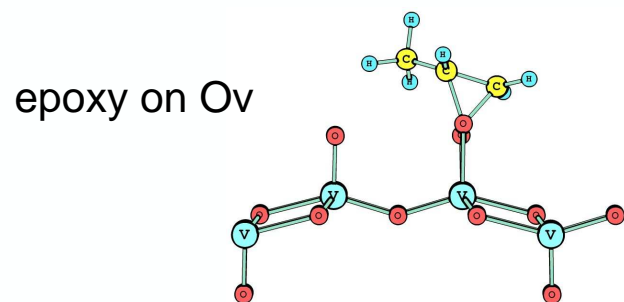
ΔE_r (kJ/mol)	1-layer slab V_2O_5							
active site(s)	O_v	O_v^i, O_v^{ii}	O_v^i, O_c^{ii}	O_c^i, O_v^{ii}	O_b^i, O_b^{ii}	O_b^i, O_c^{ii}	O_c^i, O_b^{ii}	O_c^i, O_c^{ii}
peroxy		-20	77	54	103	73	80	187
epoxy	108							

$\Rightarrow$ peroxy intermediate on Ov-Ov most stable

$\Rightarrow$ peroxy intermediate on Oc-Oc least stable

Propylene activation: energy diagram

formation peroxy int. $\longleftarrow$ Propylene$_{(g)}$ formation allylic radical $\longrightarrow$

kJ/mol

141

116

E_a

88

-20

CH$_2$=CH-CH$_{3(g)}$
+ Ov*

CH$_2$=CH-CH$_2$° + *OvH

CH$_2$-CH-CH$_3$
| |
O$_v$*   O$_v$*
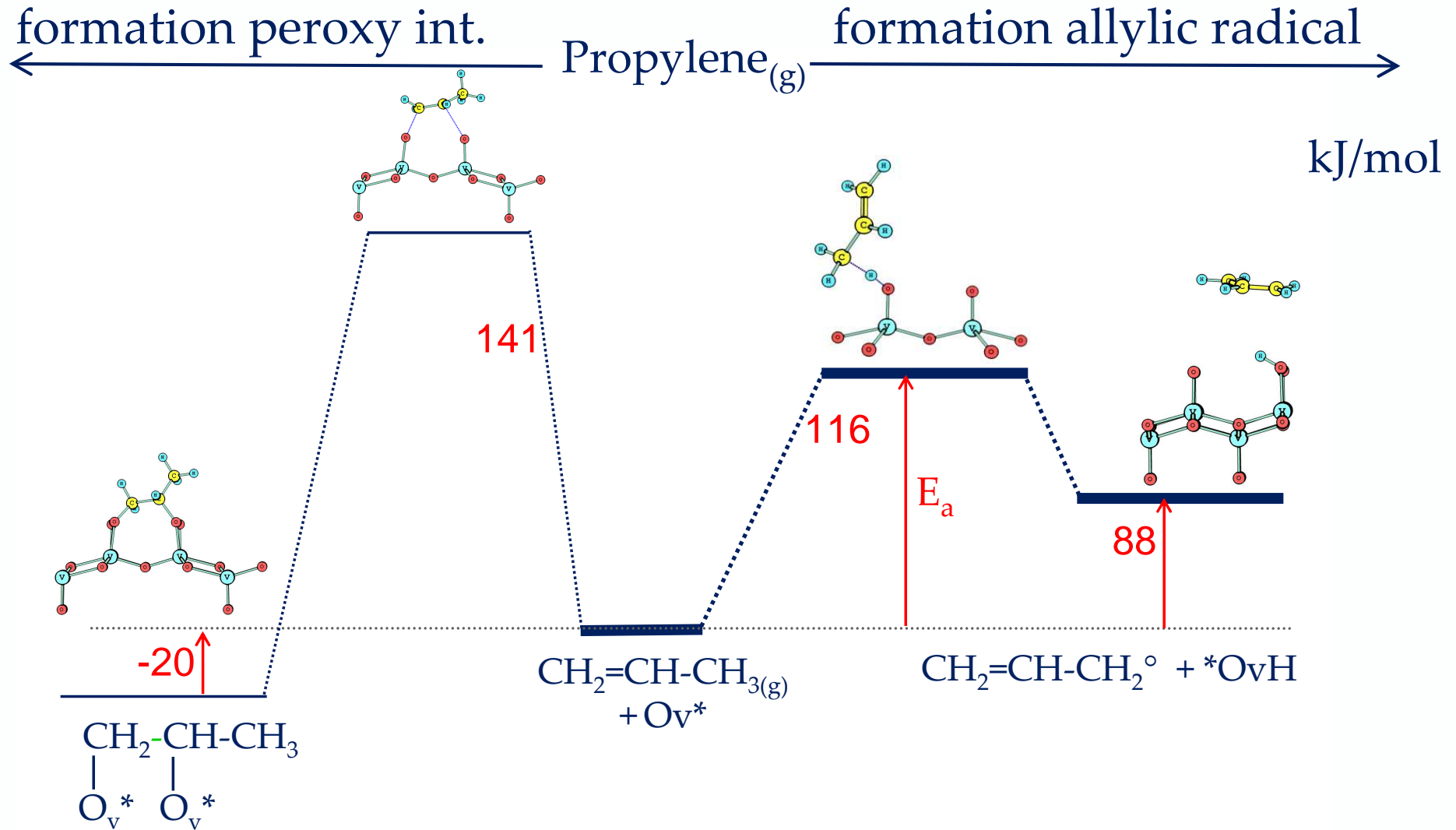
C-H activation on Ov via allylic radical is preferred over C=C
activation via peroxy intermediate

30

V2O5: O2 adsorption on oxygen vacancy

➢ dissociative adsorption of O_2 on an oxygen vacancy

$$O_2 + 2e \rightarrow O_2^{2-}$$

$+ O_{2(g)}$

$\Delta E_r = -90 \text{ kJ/mol}$
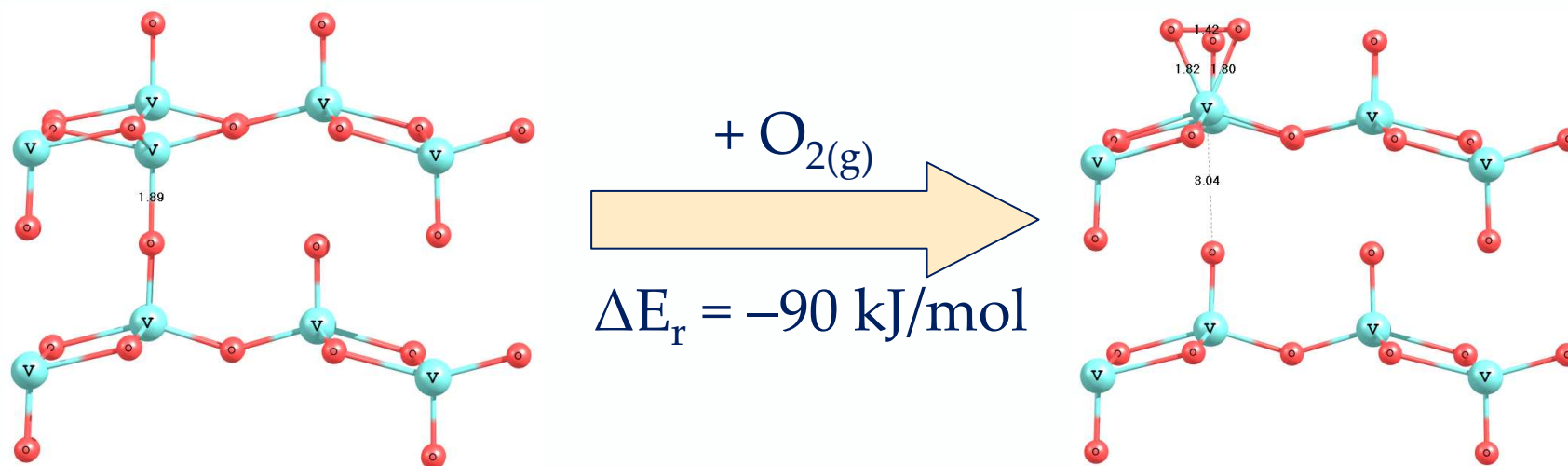
	atomic charges			
	$O_2^{2-}v$	Ov	Ob	Oc
slab/O_2^{2-}	-0.4	-0.8	-1.0	-1.2

Propylene adsorption on defect oxygen site

Peroxy O_2^{2-}v

Peroxy Ovi-Ovii
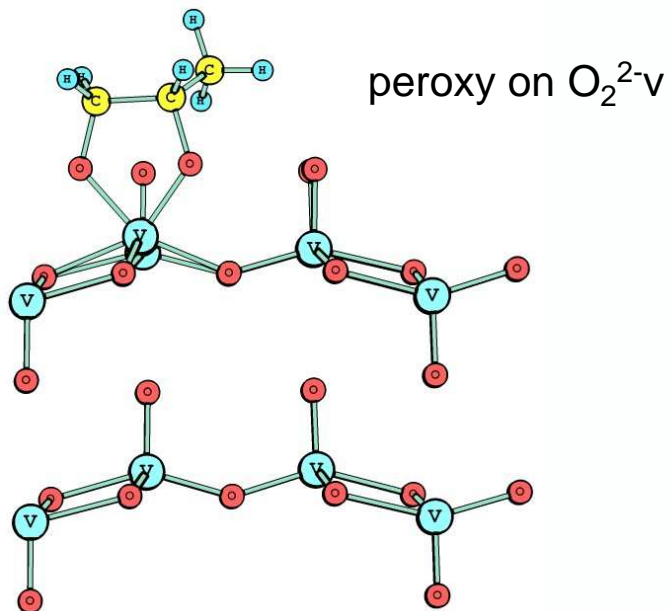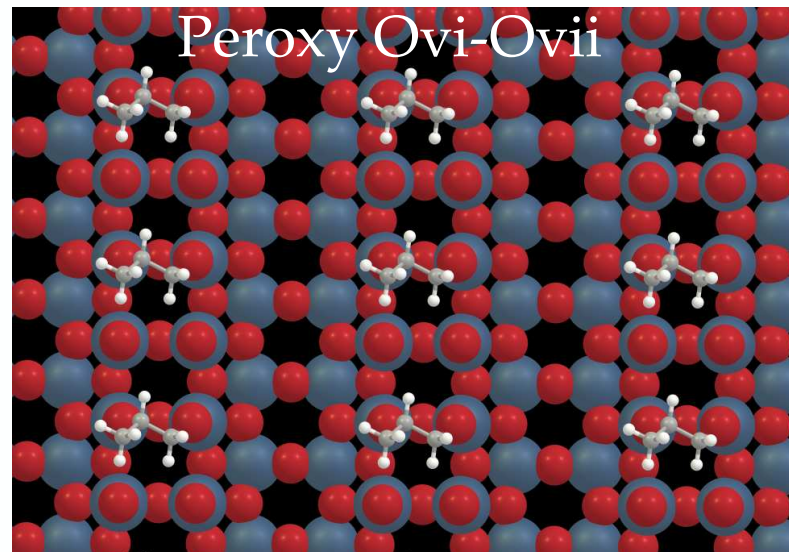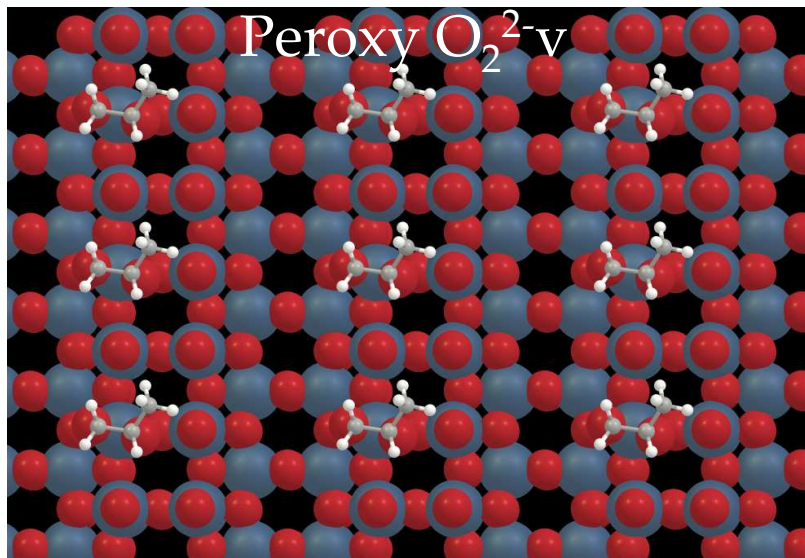
peroxy on O_2^{2-}v

peroxy on Ov-Ov

Propylene adsorption on defect oxygen site

peroxy on Ov-Ov

peroxy on O_2^{2-}v
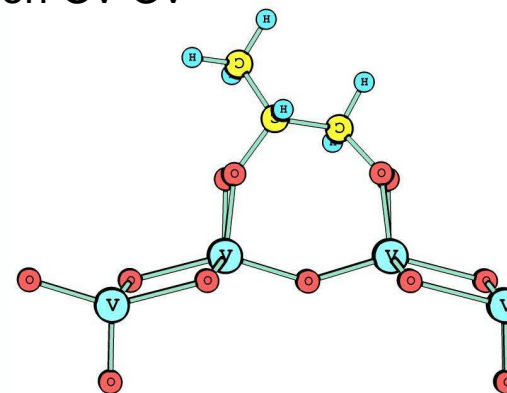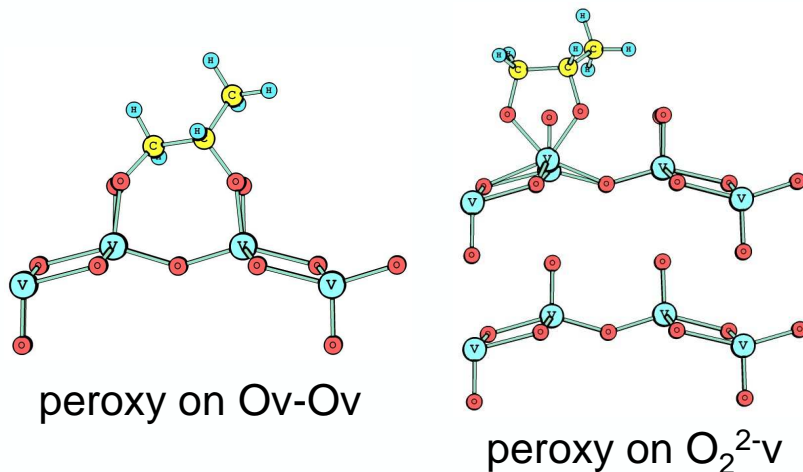
$\Rightarrow$ C=C bond activation: more likely on sites formed by dissociative adsorption of O_2 on vacancy?

$\Rightarrow$ further calculations of Eact required

	O_v^i, O_v^{ii}		O_2^{2-}v (instead of O_v)	
Distances (Å)			Distances (Å)	
C_i-C_{ii}	1.53		C_i-C_{ii}	1.54
C_i-O_v^i	1.43		C_i-O^i	1.40
C_{ii}-O_v^{ii}	1.43		C_{ii}-O^{ii}	1.42
V-O_v^i	1.75		V-O^i	1.85
V-O_v^{ii}	1.73		V-O^{ii}	1.80
Angles (°)			Angles (°)	
V-O_v^i-C_i	136.5		V-O^i-C_i	124.3
V-O_v^{ii}-C_{ii}	150.0		V-O^{ii}-C_{ii}	126.7
O_v^i-V-O_b	100.1		O^i-V-O^{ii}	77.7
O_v^{ii}-V-O_b	100.8		O^{ii}-V-O_b	78.2
kJ/mol				
ΔE_r	-20			-184

Propylene activation on V2O5: summary

➢1 or 2-layer periodic slab more suited than cluster

➢allylic C-H activation

- occurs preferentially on Ov via formation of allylic radical

$$E_{act}: Ov = 116 \text{ kJ/mol}; Ob = 139 \text{ kJ/mol}$$

➢C=C bond activation

- peroxy on O_2^{2-}v most stable intermediate
- more likely on electrophilic oxygen sites formed by dissociative adsorption of O_2 on vacancy than on Ov?
- further calculation of E_{act} required

Supported vanadia: V2O5/TiO2 (anatase)

- Used widely in industry and experiments as an effective catalyst for oxidation of hydrocarbons

- Catalyst structure: depends on vanadium loading
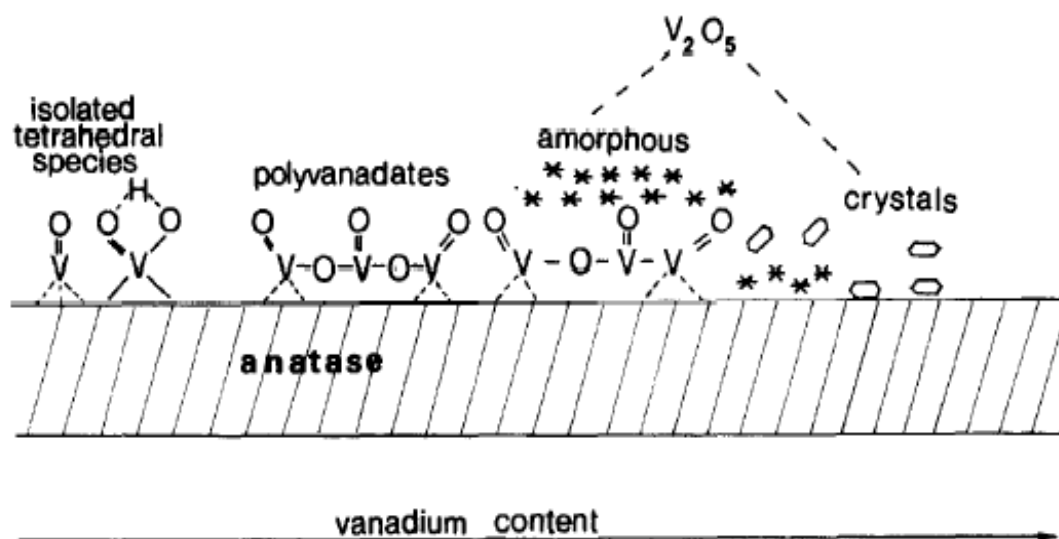
from B. Grzybowska-Świerkosz, Appl. Catal. A, 157, 263 (1997)

- High performance for "monolayer" of V_2O_5 on TiO_2 (anatase)

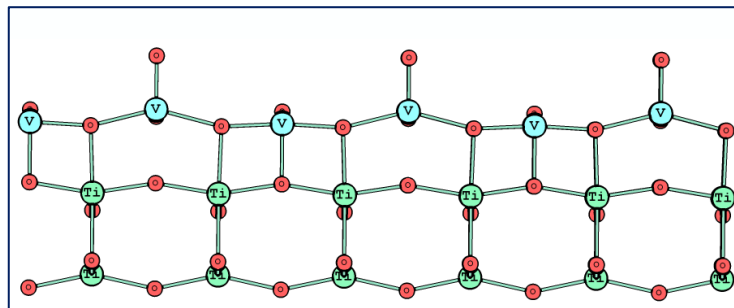# Influence of support: V2O5/TiO2 (anatase)

➤Weak interaction: support is high surface carrier for catalyst
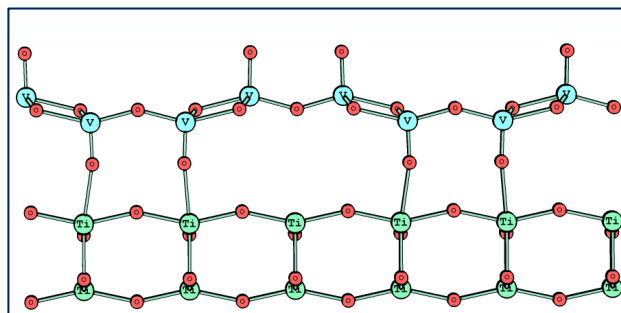
Model: crystallographic V_2O_5 (001) layer on top of TiO_2 (001) anatase

➤Strong interaction: synergy between catalyst and support

Model: epitaxial layer of V_2O_5 on TiO_2 (001) anatase

Supported V2O5: electronic structure

supported V_2O_5 (weak)   ### supported V_2O_5 (strong)
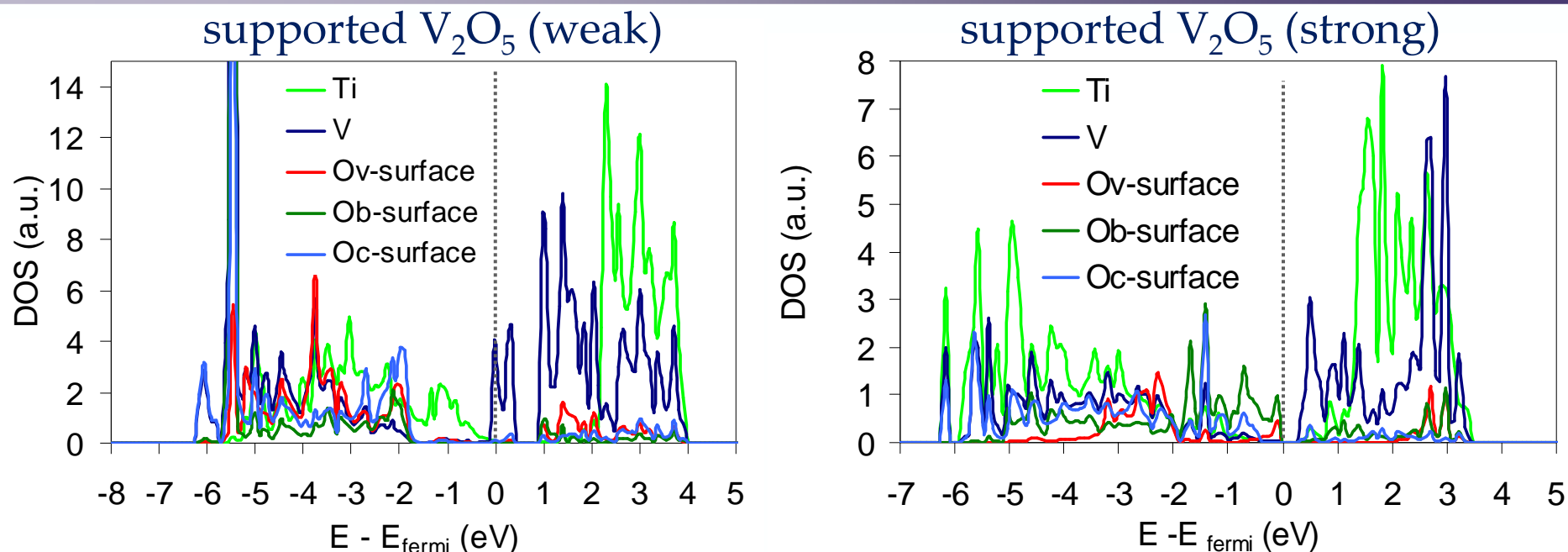
eV	E_{fermi}	gap	width	nucleophilicity order
V_2O_5	8.9	2.0	4.5	$Oc > Ov \geq Ob$
V_2O_5/TiO_2 strong	7.4	0.2	6.3	$Ob > Ov > Oc$
V_2O_5/TiO_2 weak	6.9	0.5	6.5	$Oc > Ov > Ob$

$\Rightarrow$ band gap is considerably smaller for the supported catalysts

$\Rightarrow$ weak: considerable contribution of Ti_d near E_{fermi}

$\Rightarrow$ strong: considerable contribution of Ob and Ov near E_{fermi}

37

Propylene adsorption: influence of support

$$CH_2=CH-CH_2-H_{(g)} + O^* \rightarrow CH_2=CH-CH_2-O^*H$$

ΔE_r (kJ/mol)	Ov	Ob
V$_2$O$_5$	+46	+169
V$_2$O$_5$/TiO$_2$ – weak	-	+154
V$_2$O$_5$/TiO$_2$ – strong	-87	-
Experimental*	-72 $\pm$ 8 kJ/mol	

$\Rightarrow$ weak interaction with support: small influence on propylene adsorption via allylic C-H

$\Rightarrow$ strong interaction with support: strong increase in stability of alcoholic intermediate

* Grabowski et al., Top. Catal., 3 (1996) 277

Propane adsorption: influence of support

$$CH_3CH_2\text{-}CH_{3(g)} + O_v{}^* \rightarrow (CH_3)_2CH\text{-}O^*H$$

ΔE_r (kJ/mol)	Ov
V_2O_5	+42
V_2O_5/TiO_2 – weak	+35
V_2O_5/TiO_2 – strong	-129

$\Rightarrow$ weak interaction with support: small influence on adsorption of propane via secondary C-H

$\Rightarrow$ strong interaction with support: strong increase in stability of secondary alcoholic intermediate

Conclusions

➢ periodic slab models best suited to model unsupported and supported V_2O_5 catalysts

➢ allylic C-H activation on V_2O_5 (001): preferentially on Ov via formation of allylic radical

$$E_{act}: Ov = 116 \text{ kJ/mol}; Ob = 139 \text{ kJ/mol}$$

➢ C=C bond activation on V_2O_5 (001): more likely to occur on sites formed by dissociative adsorption of O_2 on vacancy?
 - further calculation of E_{act} required

➢ strong interaction TiO_2 and monolayer vanadia:
 - strongly influences propylene adsorption via allylic C-H
 - ΔE_r corresponds well with experimentally observed value