From surface-inspired oxovanadium silsesquioxane models to active catalysts for the oxidation of alcohols with O_2 - the cinnamic acid/metavanadate system

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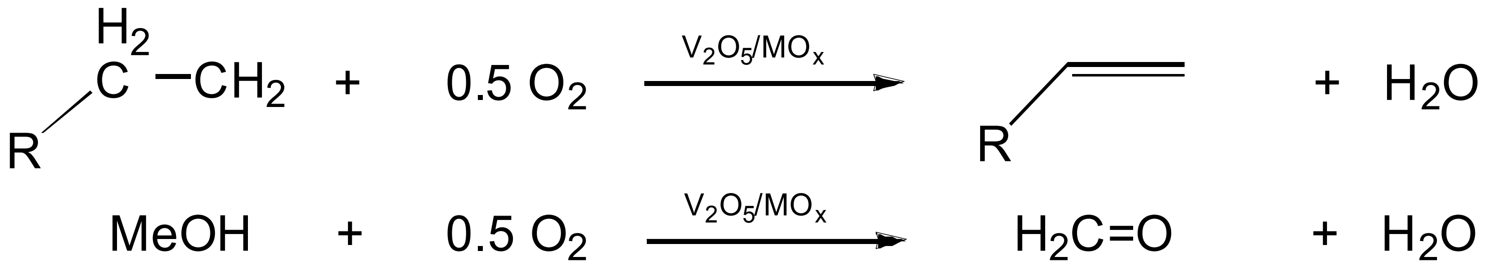
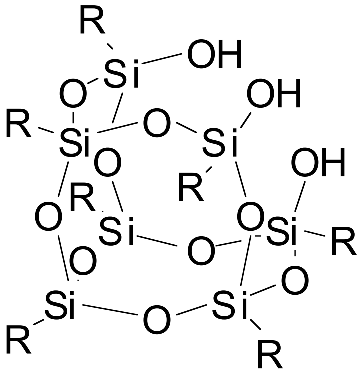
The oxidative dehydrogenation (ODH) with supported V_2O_5-catalysts

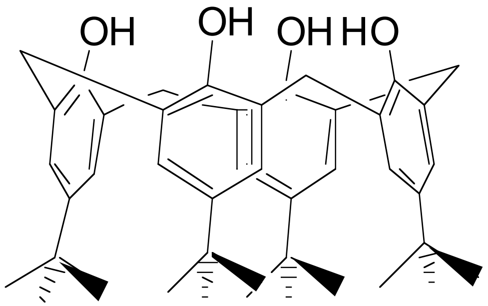


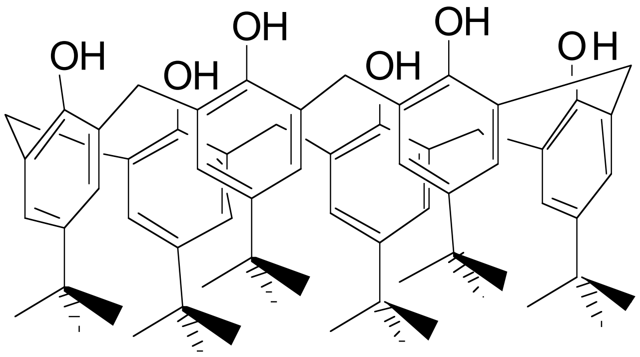
„The results of surface studies are the source of ideas for the molecular chemist in the construction of new molecules, the development of new reactions and, hopefully, the discovery of new catalysts.“

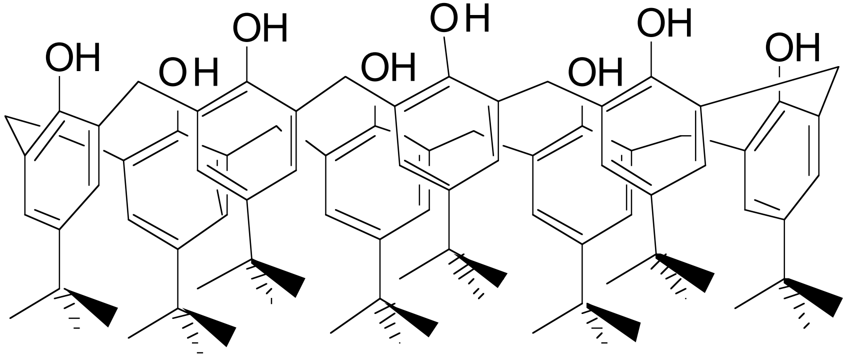
John A. Osborn, *J. Mol. Catal.* **1994**, *86*, 267

Ligands for the simulation of an oxidic environment

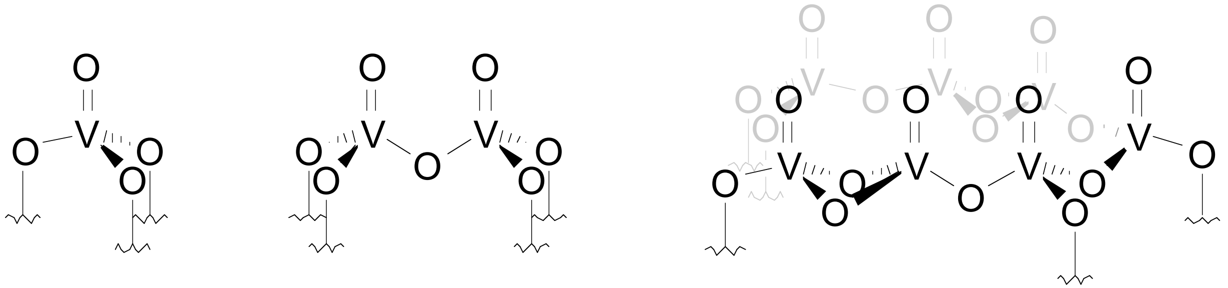




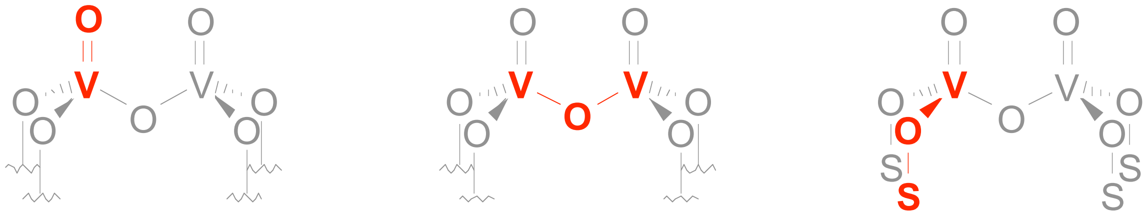




Active species?

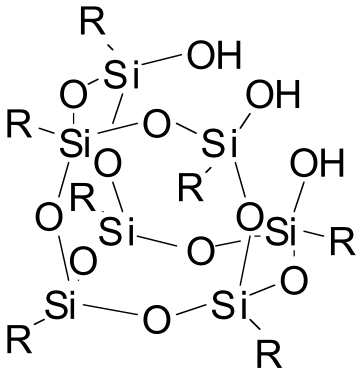


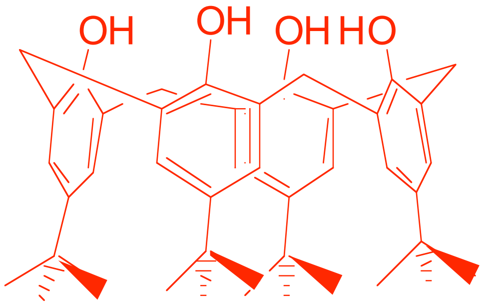
Active units?

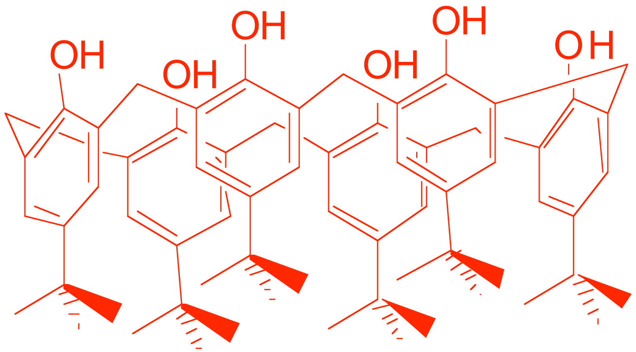


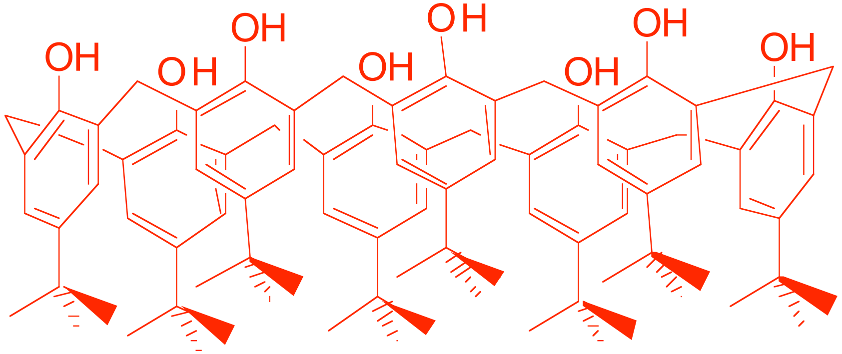
S = Support

1. Calixarene chemistry

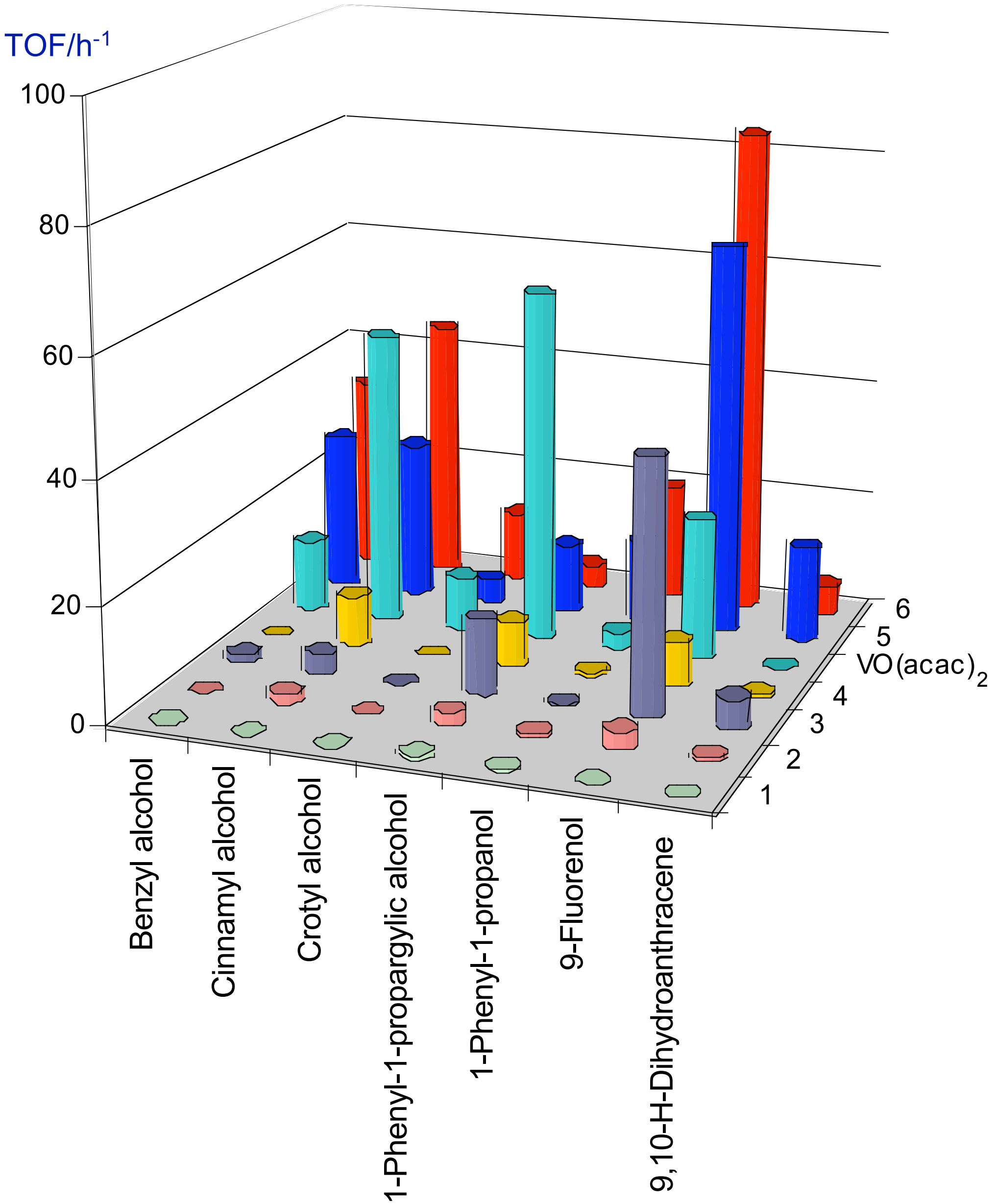






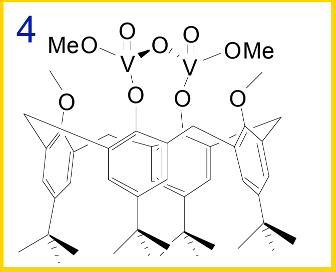


Test of model function: Catalytic activity in the ODH



$$\mathrm{RR'CHOH} + 0.5\ O_2 \xrightarrow{\text{Cat./80°C}} \mathrm{RR'C{=}O} + H_2O$$

4



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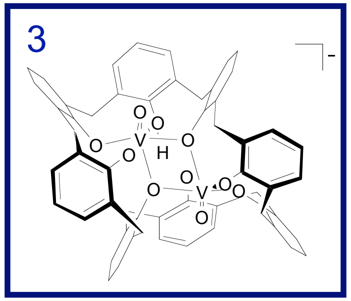

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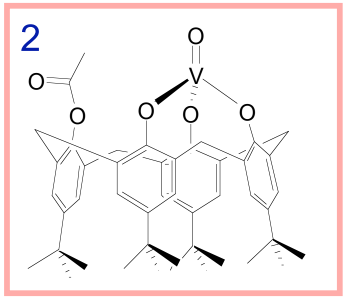
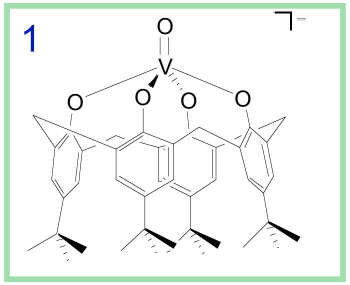


1



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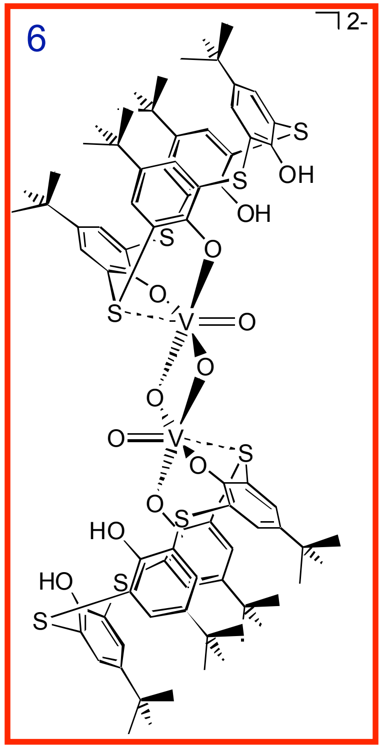

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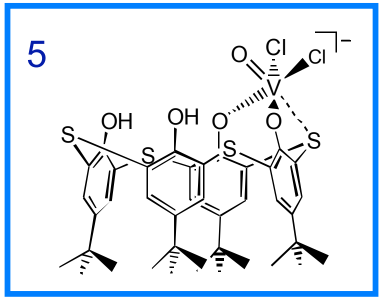
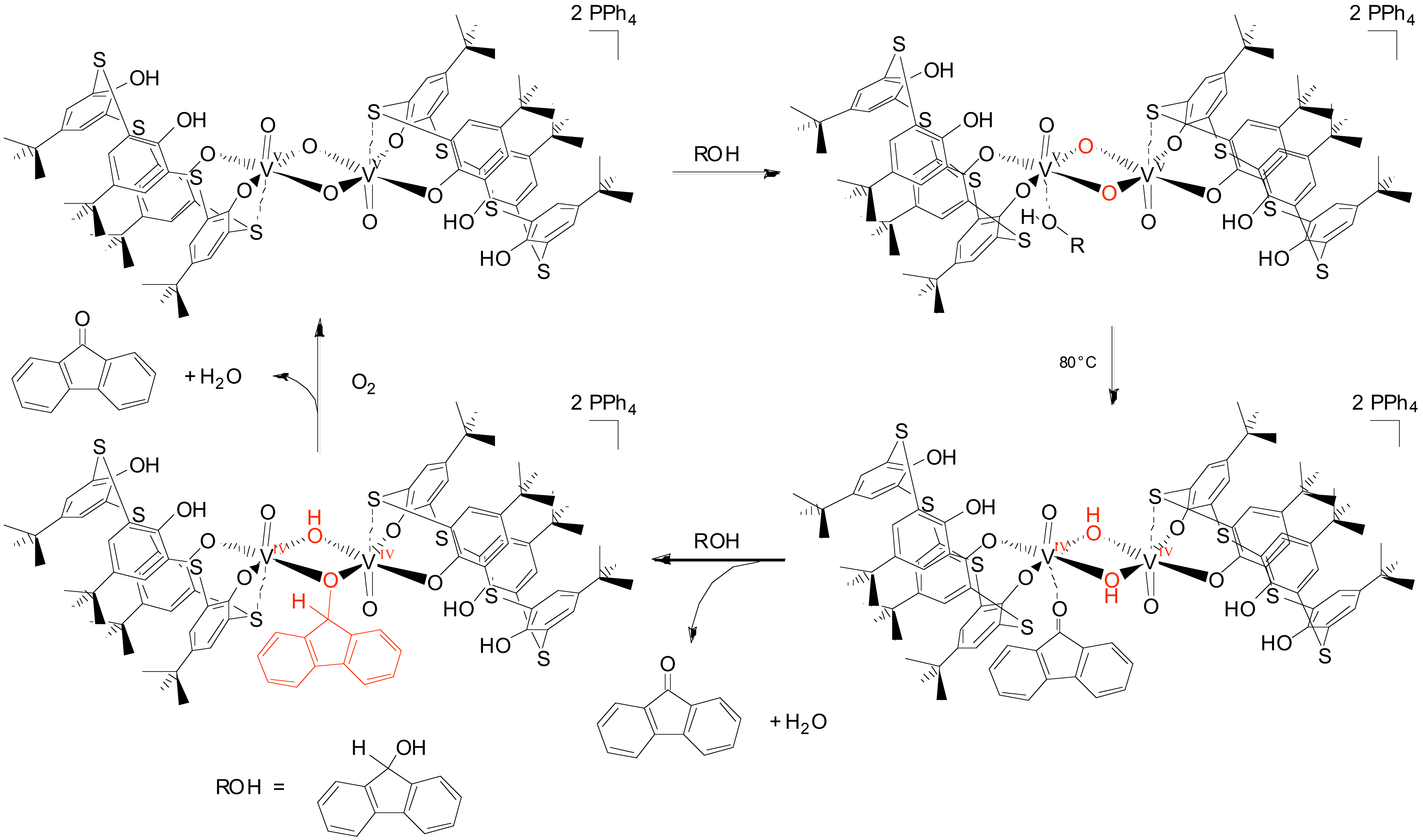
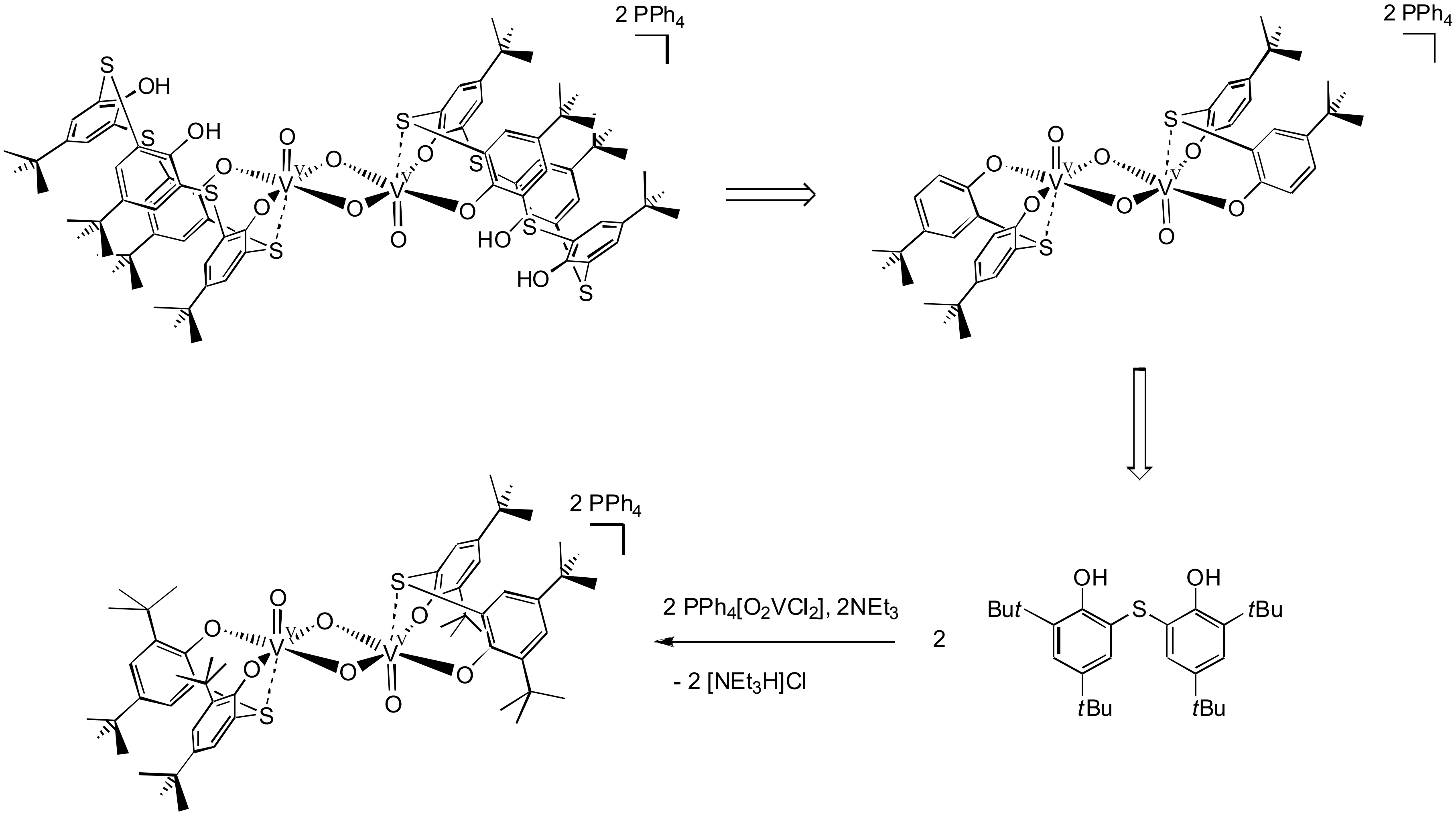


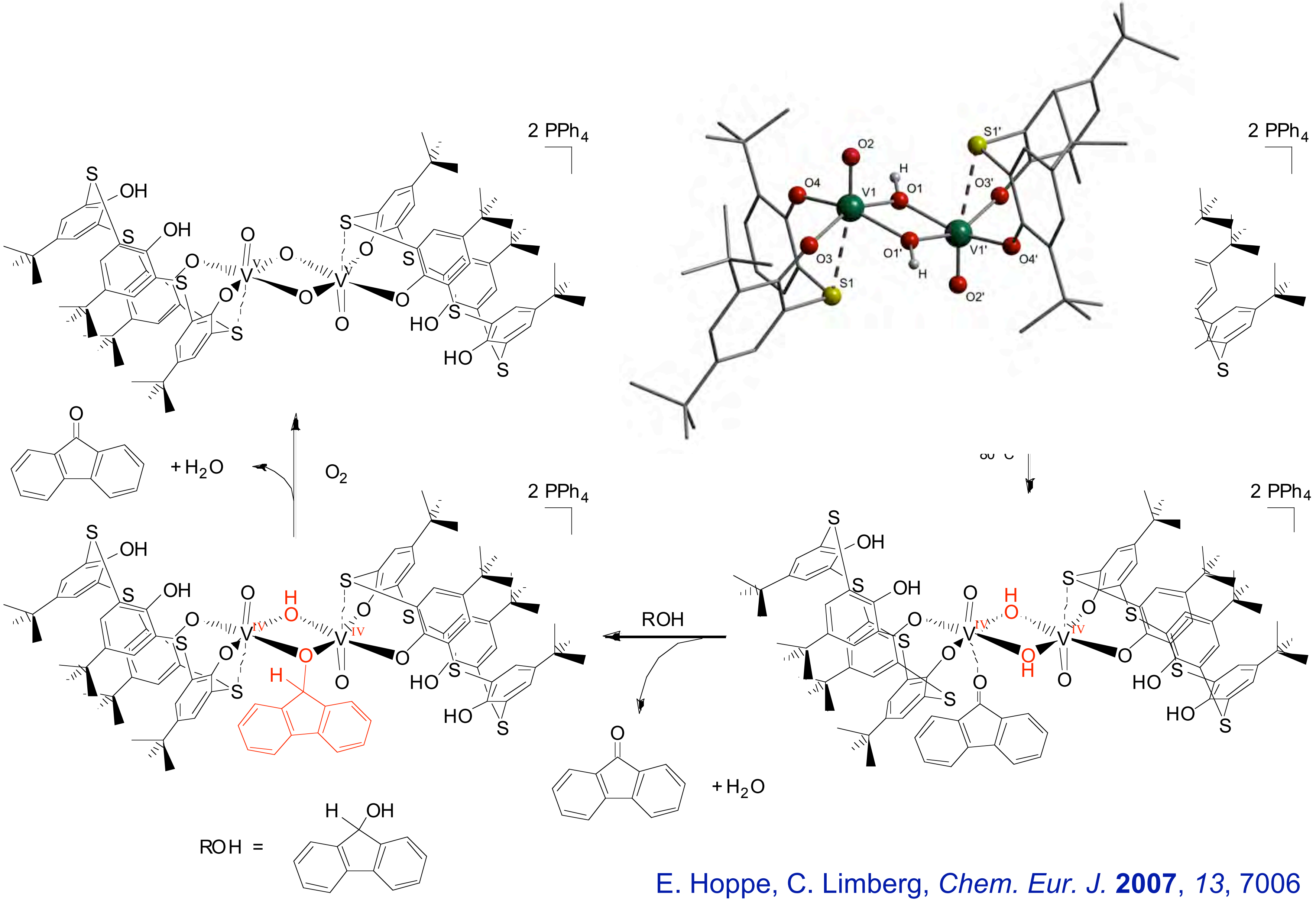
Proposal of a catalytic cycle



E. Hoppe, C. Limberg, *Chem. Eur. J.* **2007**, *13*, 7006

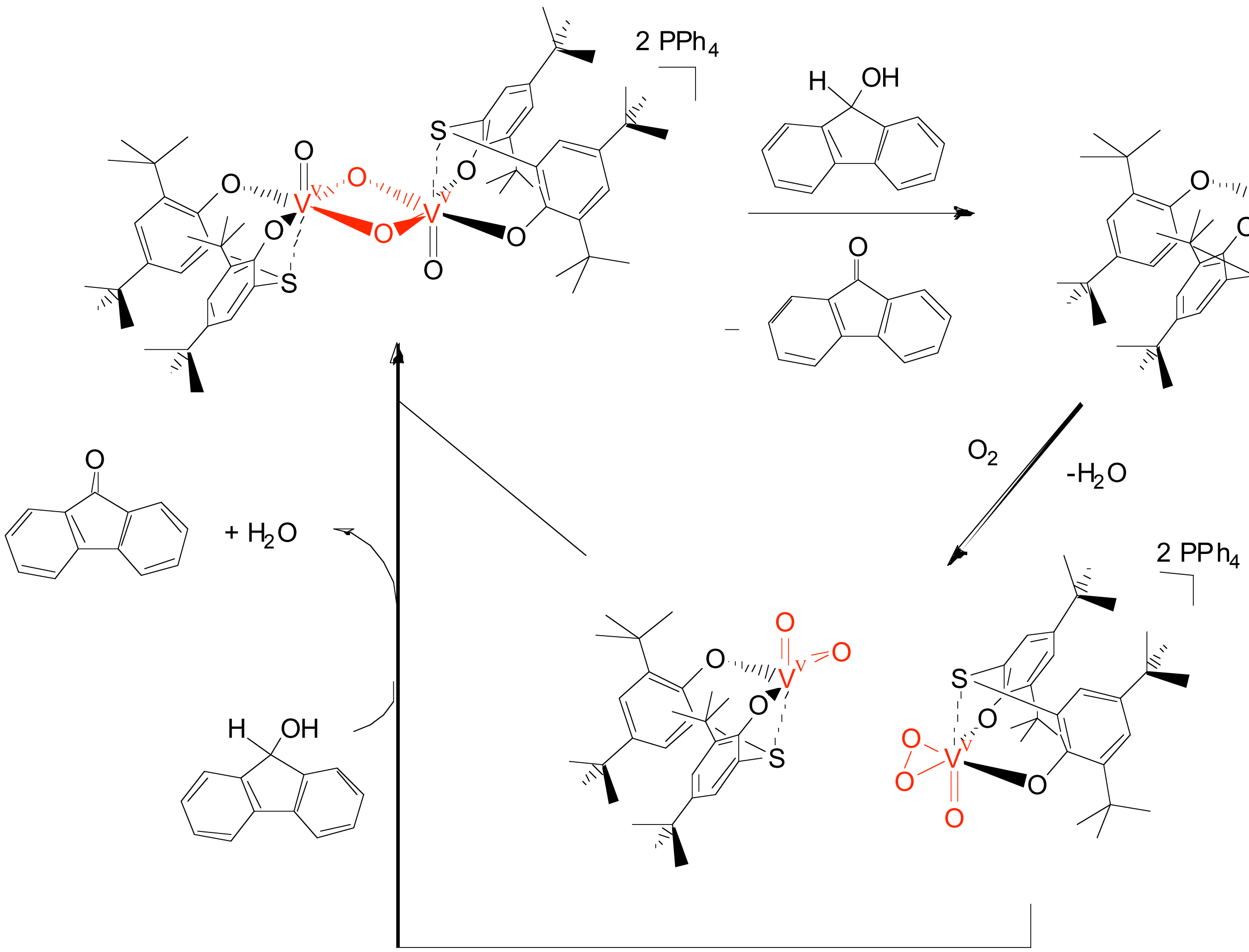
Addressing mechanistic questions

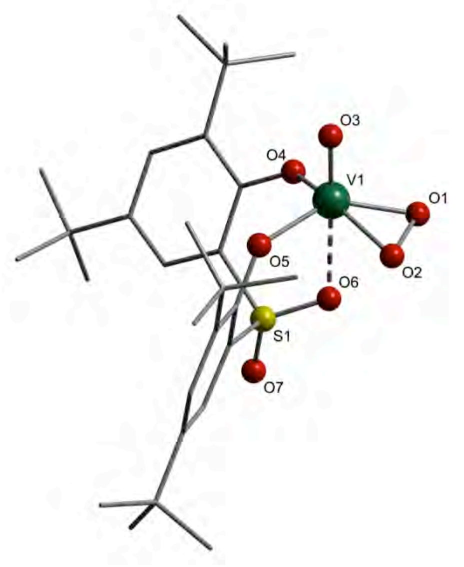




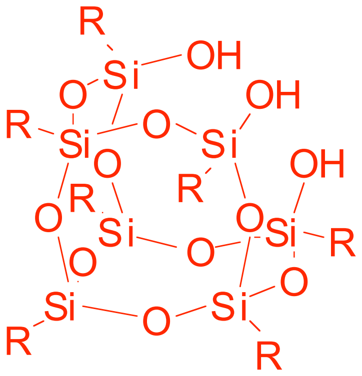
E. Hoppe, C. Limberg, *Chem. Eur. J.* **2007**, *13*, 7006

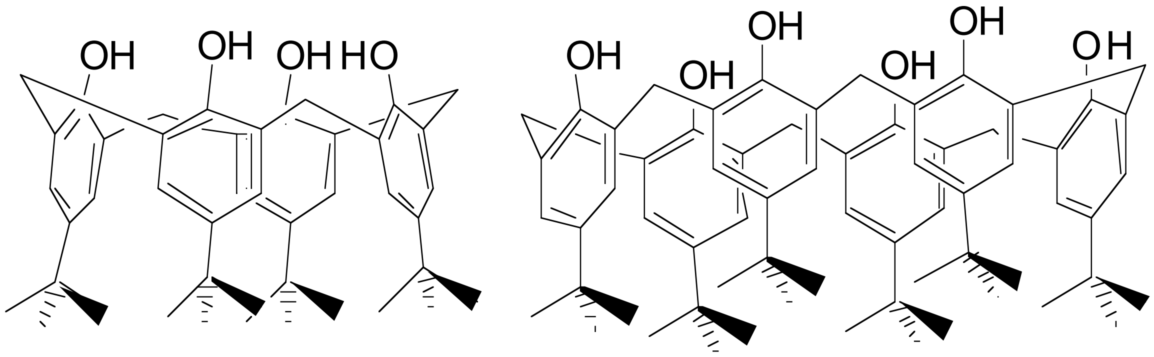
Reoxidation via Peroxides

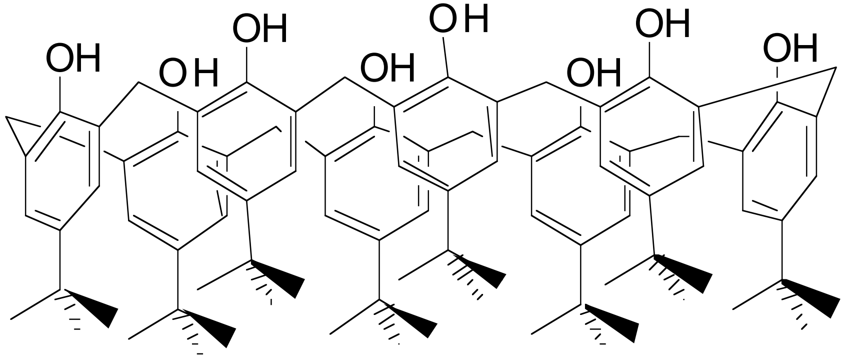




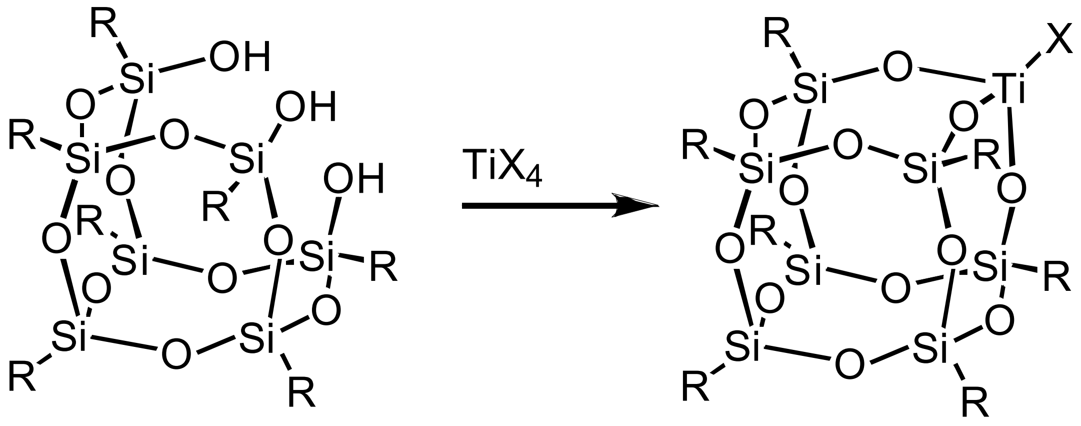
2. Silsesquioxane chemistry





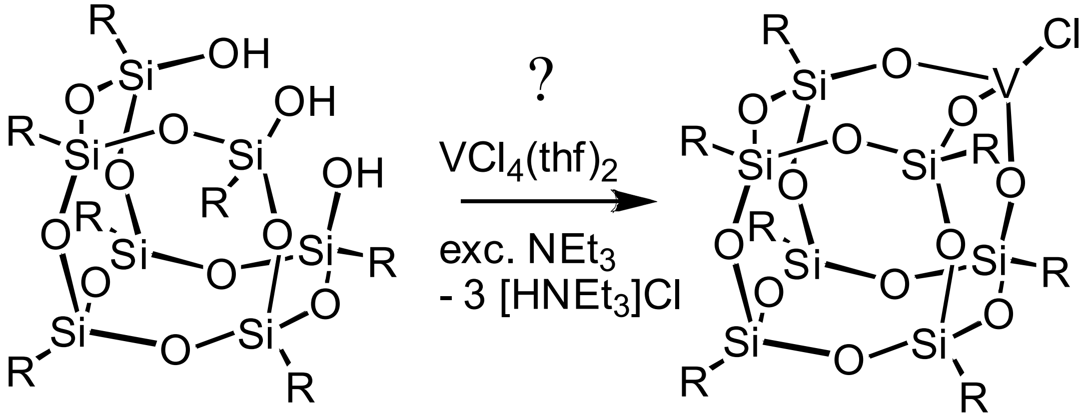


A mononuclear vanadium(IV) model



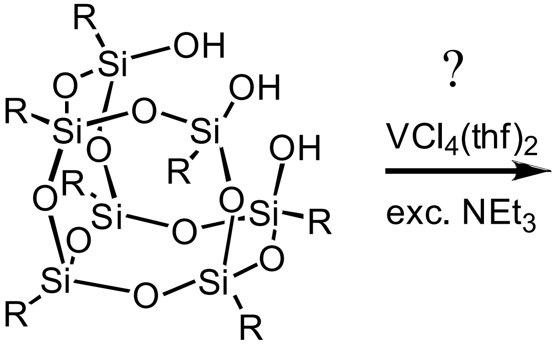
X = OEt, OiPr, OiBu, CH_2Ph, NMe_2

(a) Edelmann, F.T.; Gießmann, S.; Fischer, A. *J. Organomet. Chem.* **2001**, 80-89. (b) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Meetsma, A.; Thiele, S. K.-H.; van Tol, M. F. H. *Organometallics* **1998**, *17*, 5663-5673. (c) Crocker, M.; Herold, R. H. M.; Orpen, A. G. *Chem. Commun.* **1997**, 2411-2412. (d) Viotti, O.; Seisenbaeva, G. A.; Kessler, V. G. *Inorg. Chem.* **2009**, *48*, 9063-9065.

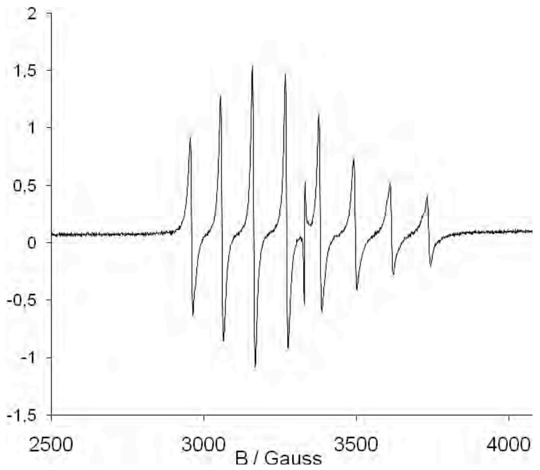


R = c-pentyl

The contents of the red-brown solution

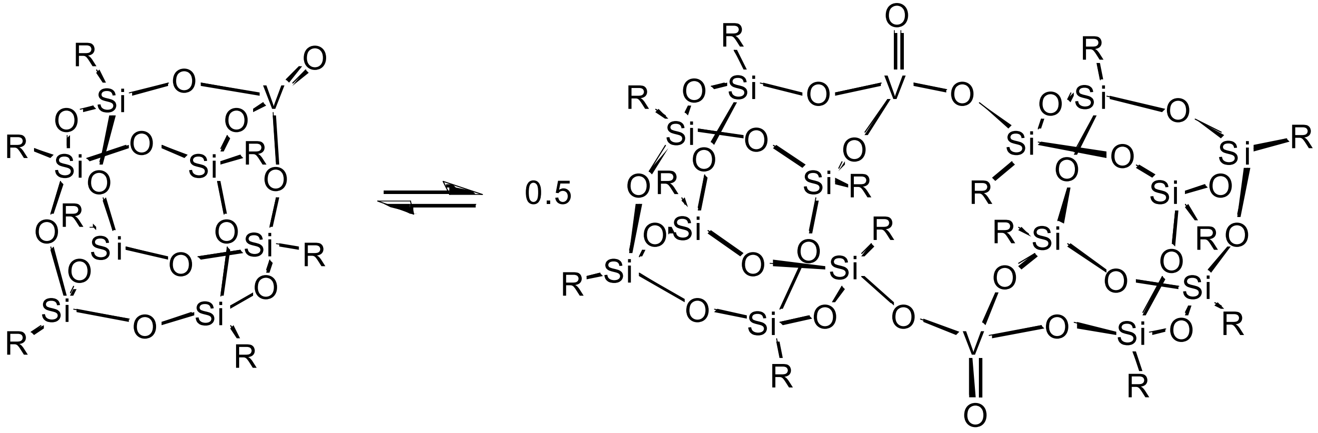


R = c-pentyl



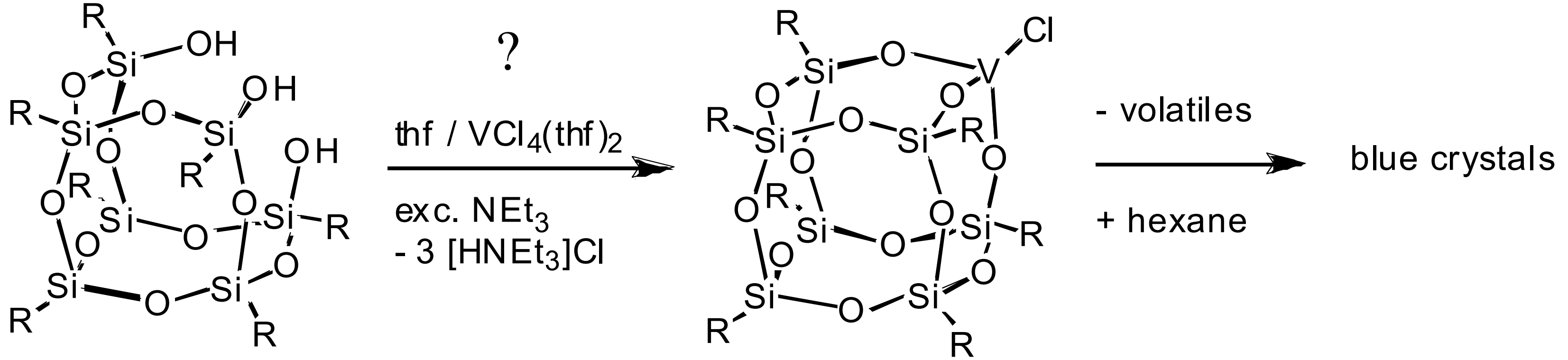
EPR spectrum of product in THF at 293 K

^{51}V NMR: presence of Feher-Komplex



Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689-1694.

Precipitation of a trinuclear complex from a hexane solution



?

thf / $VCl_4(thf)_2$

exc. NEt_3

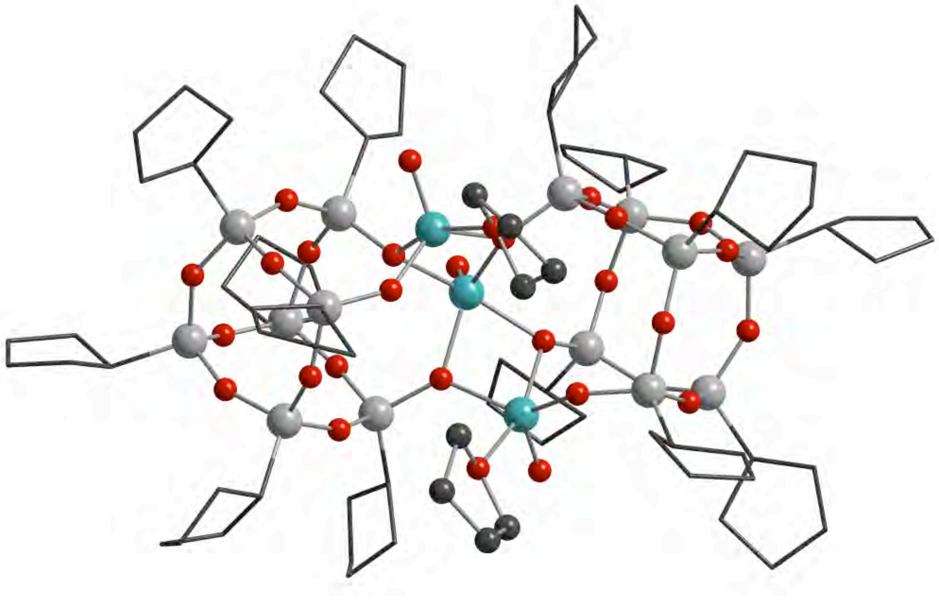
- 3 $[HNEt_3]Cl$

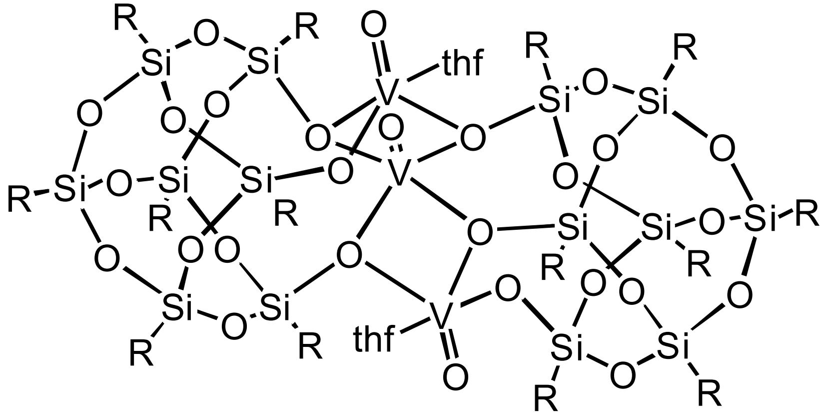
- volatiles

+ hexane

blue crystals

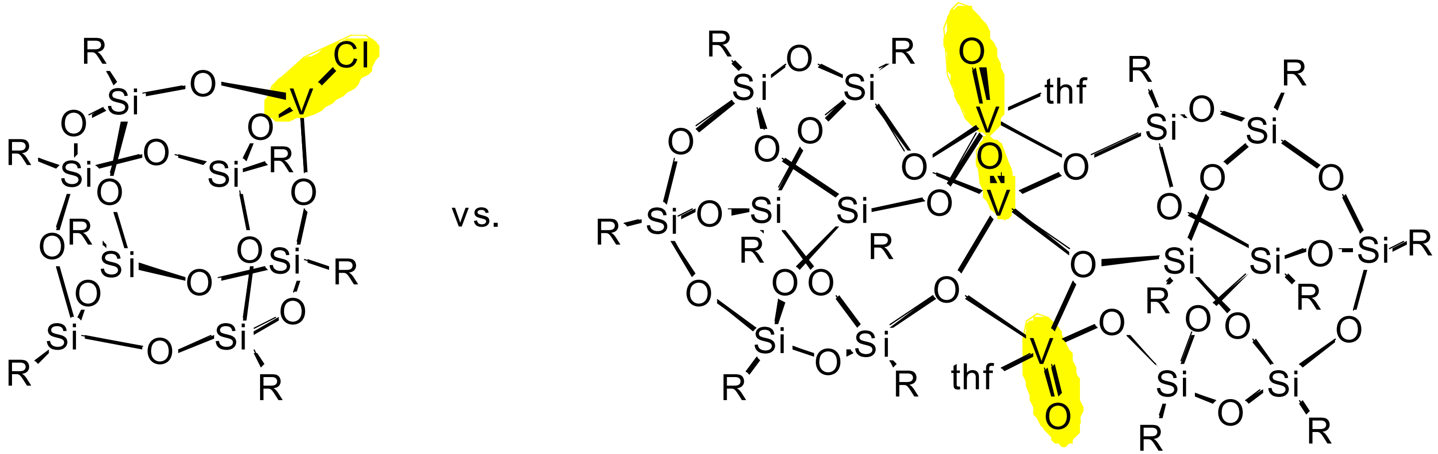
R = c-pentyl



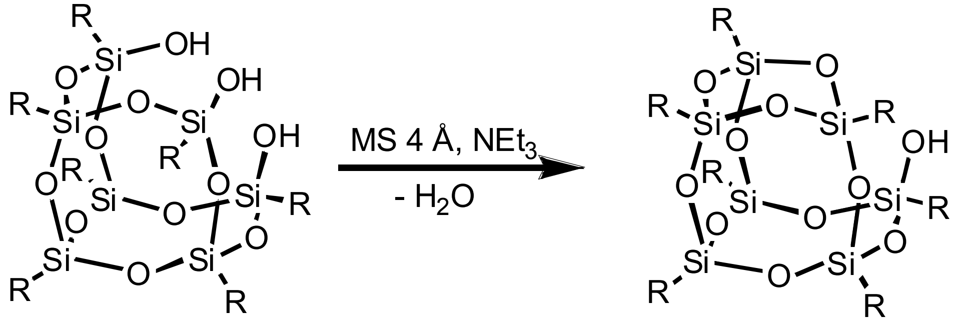


C. Ohde, C. Limberg, R. Stößer, S. Demeshko, *Inorg. Chem.* **2010**, DOI: 10.1021/ic902392y

The origin of the oxo ligands



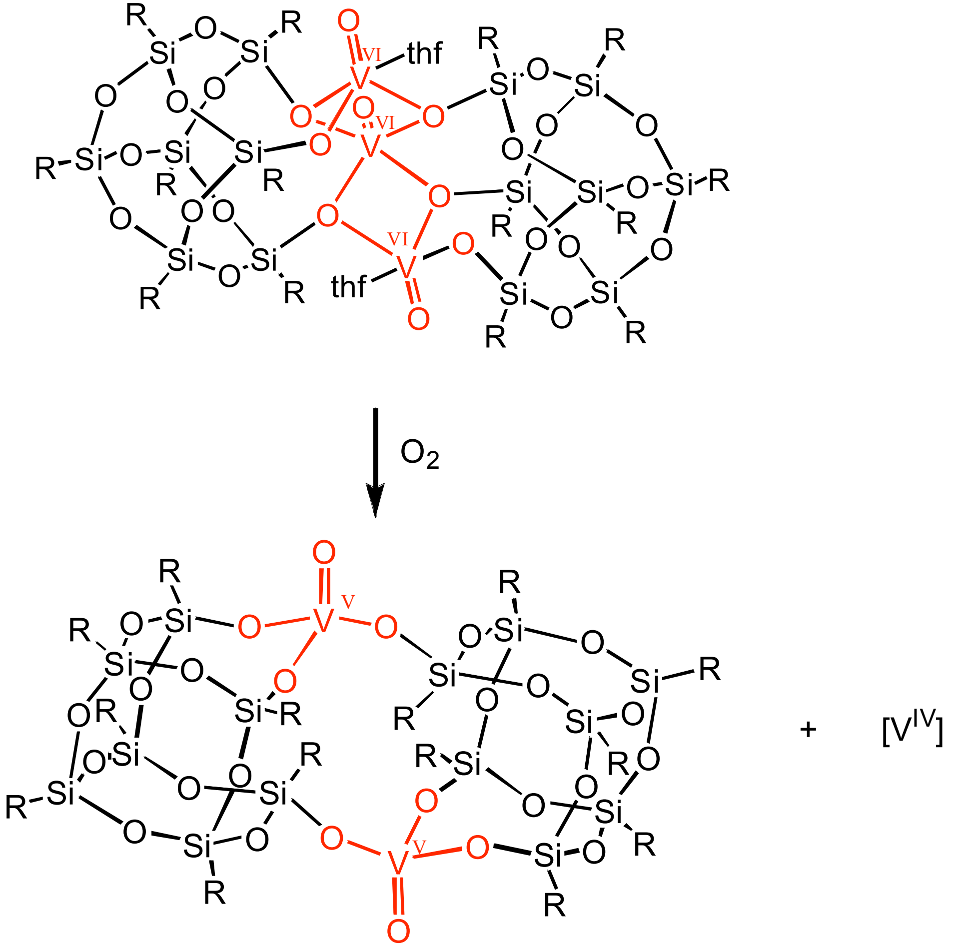
ligand decomposition + external traces of water

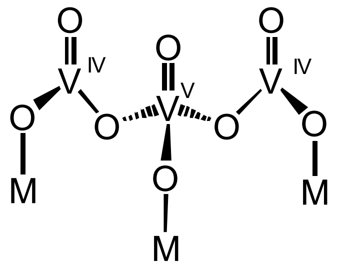


C. Ohde, C. Limberg, R. Stößer, S. Demeshko, *Inorg. Chem.* **2010**, DOI: 10.1021/ic902392y

Feher, F. J.; Rahimian, K.; Budzichowski, T. A.; Ziller, J. W.; Organometallics 1995, 14, 3920-3926.

A model for reduced trimers

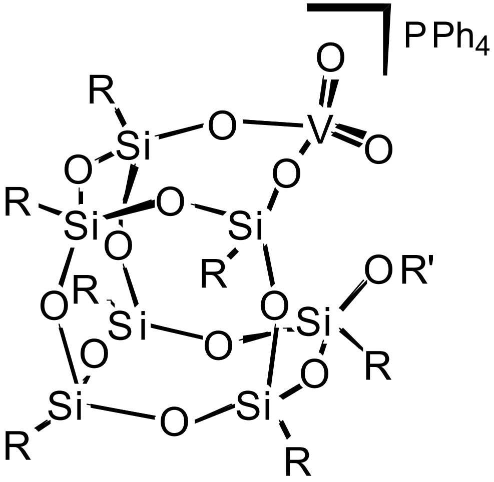




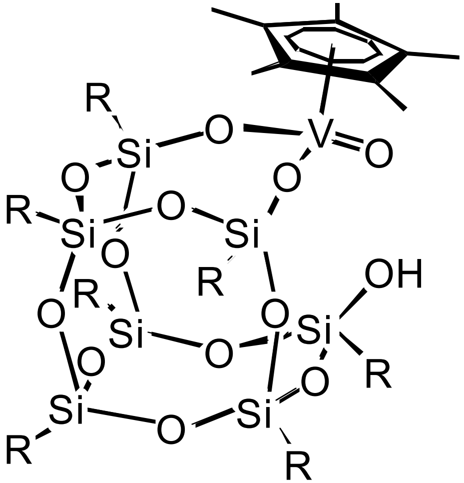
Klose, F.; Wolff, T.; Lorenz, H.; Seidel-Morgenstern, A.; Suchorski, Y.; Piórkowska, M.; Weiss, H. *J. Catal.* **2007**, *247*, 176-193.

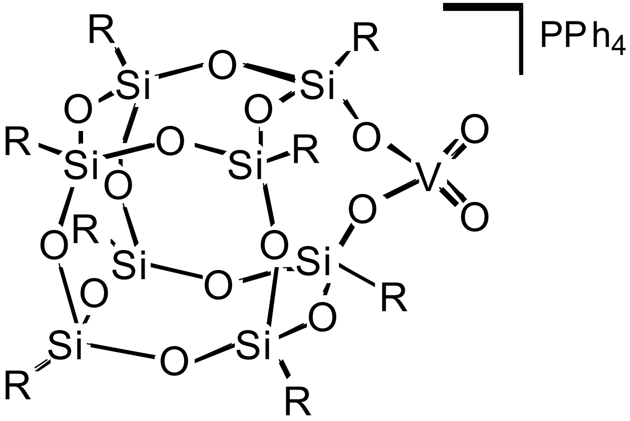
C. Ohde, C. Limberg, R. Stößer, S. Demeshko, *Inorg. Chem.* **2010**, DOI: 10.1021/ic902392y

Functional models?!



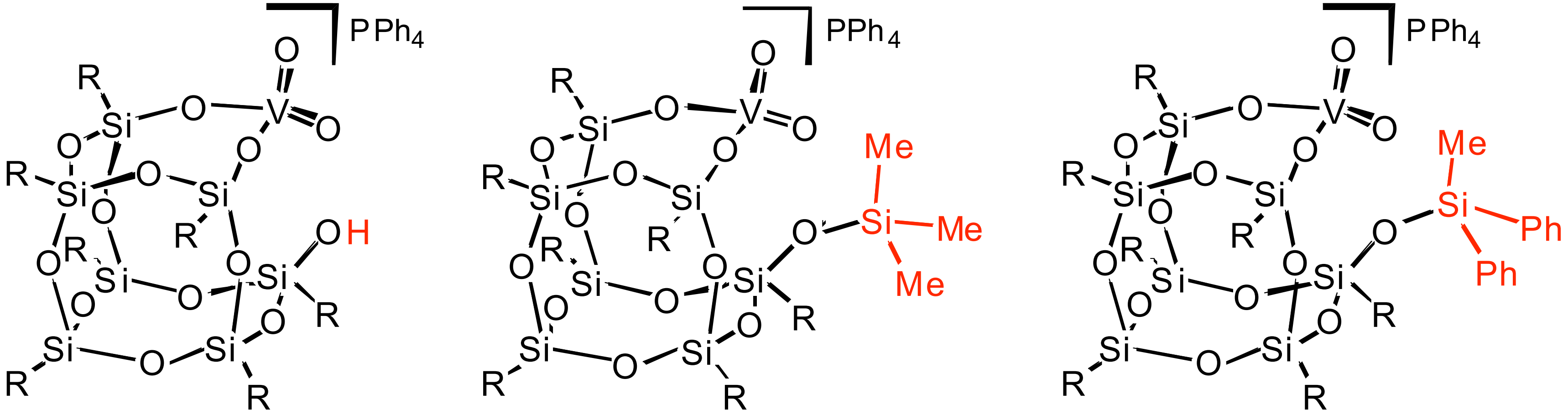
R' = H, $SiMe_3$, $SiMePh_2$
R = c-pentyl





$$R''R'''CHOH + 0.5\ O_2 \xrightarrow{Cat./80°C} R''R'''C{=}O + H_2O$$

Functional models?!

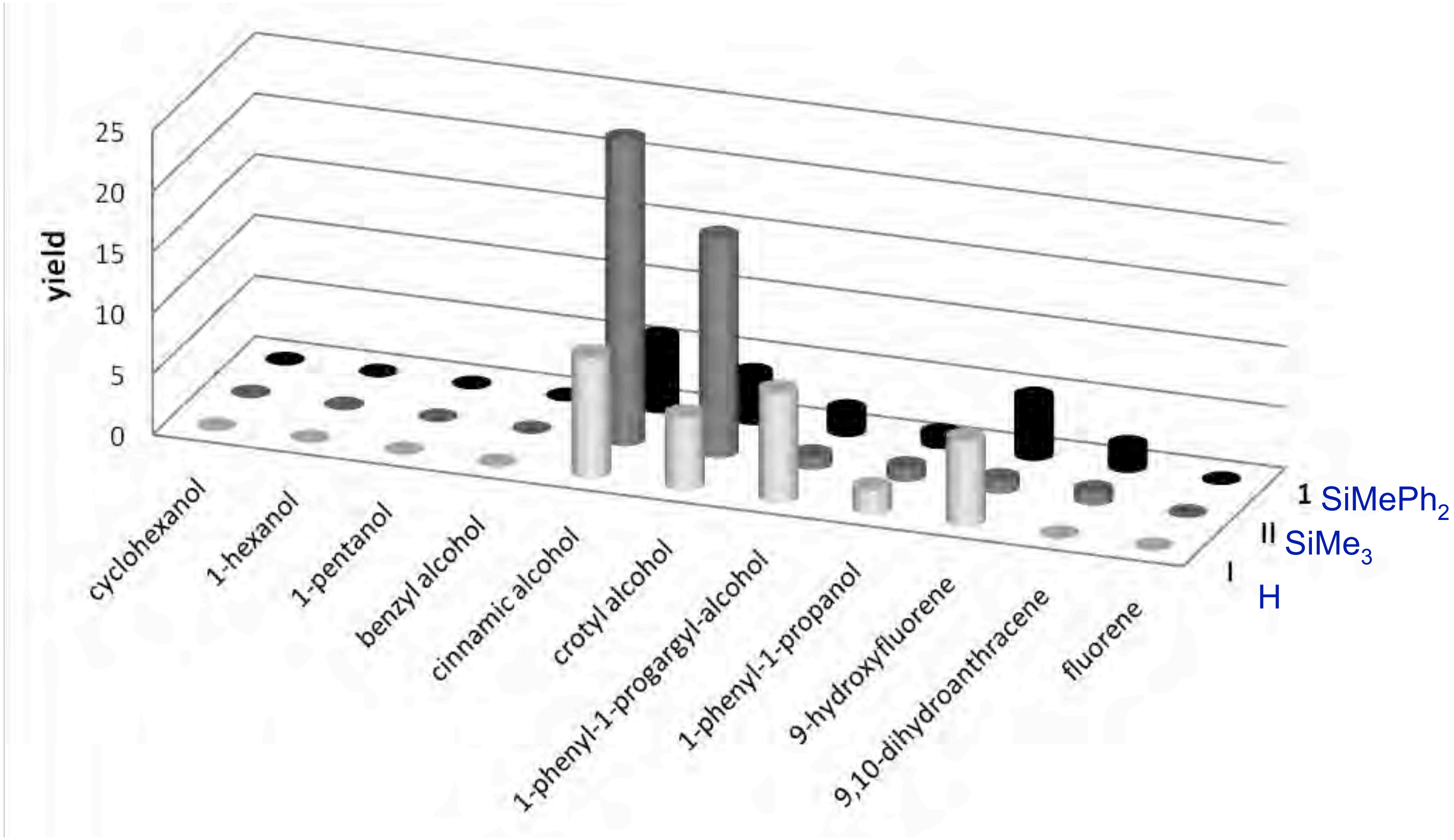


R = c-pentyl

$$\mathrm{R''R'''CHOH} + 0.5\ \mathrm{O_2} \xrightarrow{\mathrm{Cat/80°C}} \mathrm{R''R'''C{=}O} + \mathrm{H_2O}$$

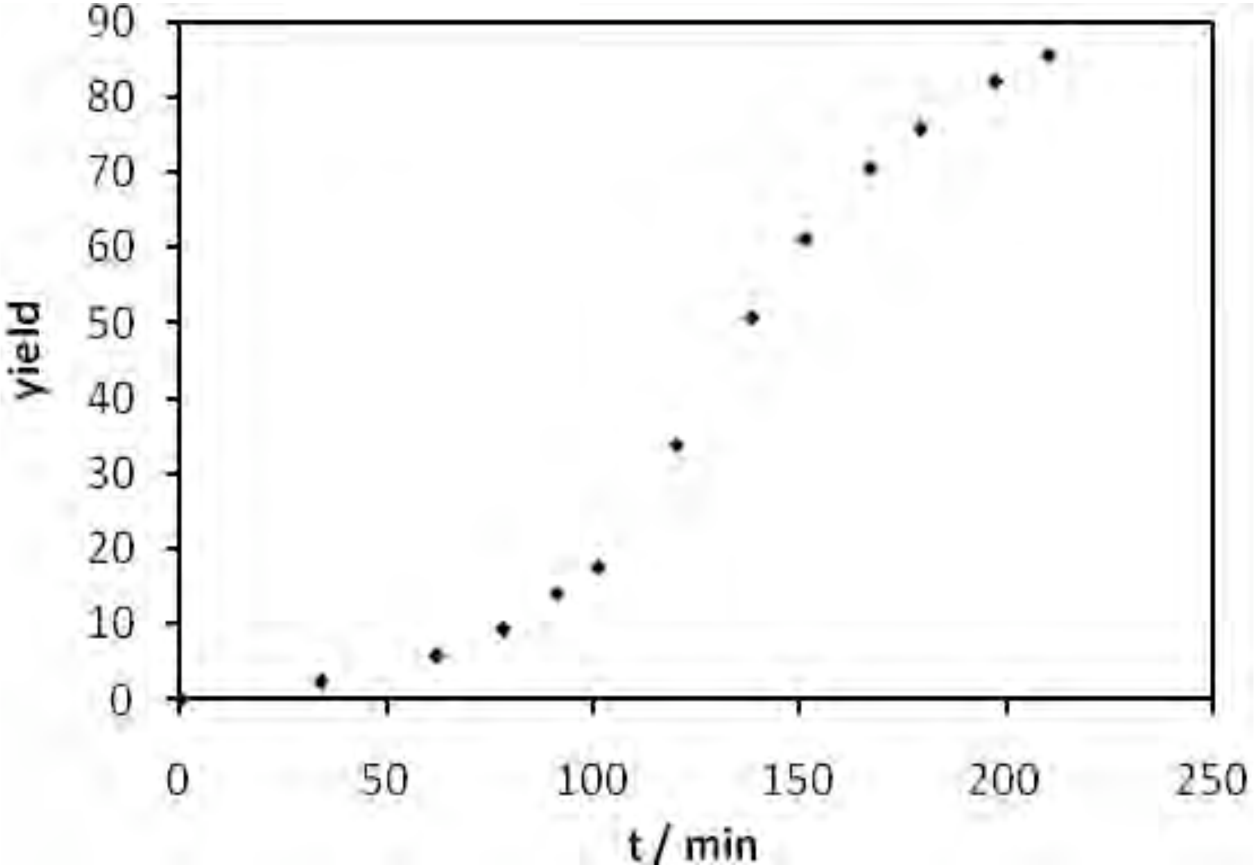
C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

Test of model function: Catalytic activity in the ODH



C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

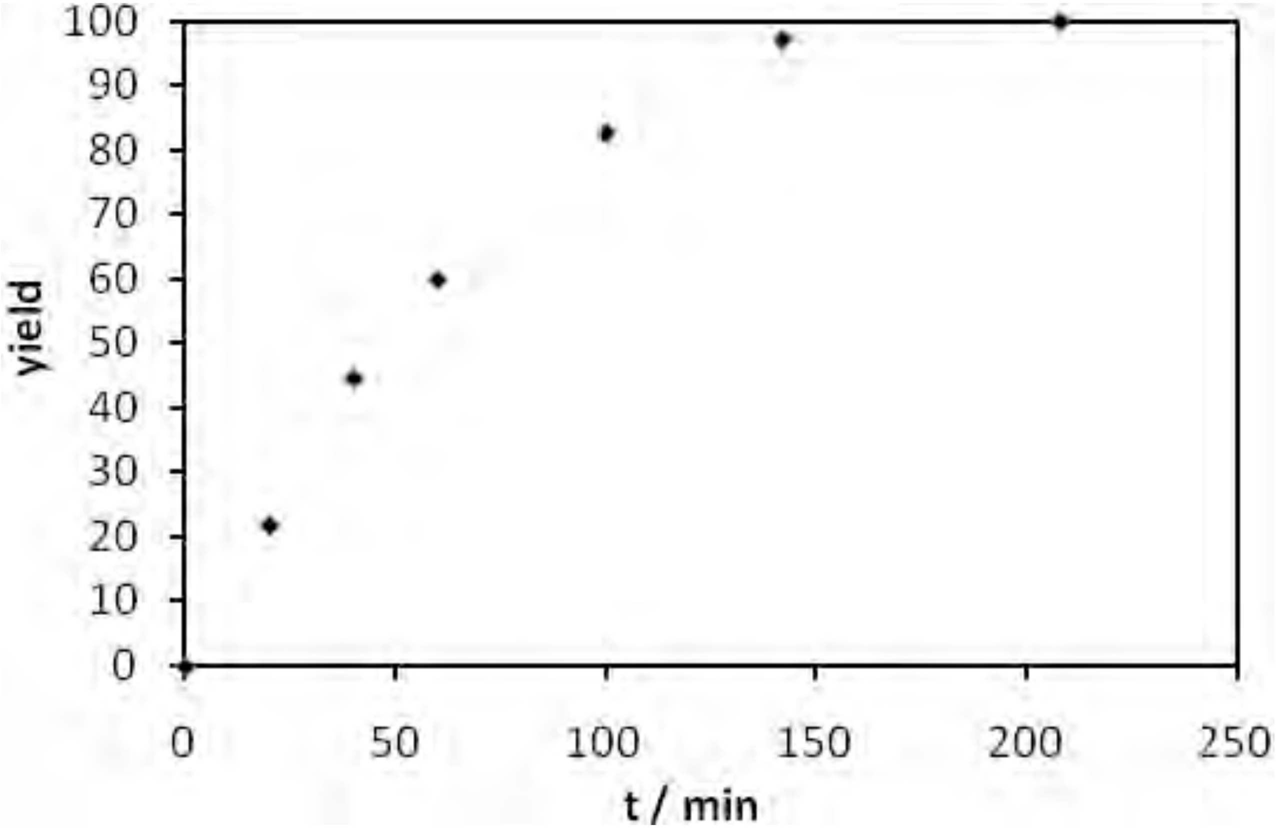
The course of catalysis



2 mmol cinnamic alcohol, 0.02 mmol Cat. and 1 g molecular sieves (3 Å) in 4 mL MeCN were heated to 80°C in an O_2/Ar atmosphere.

C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

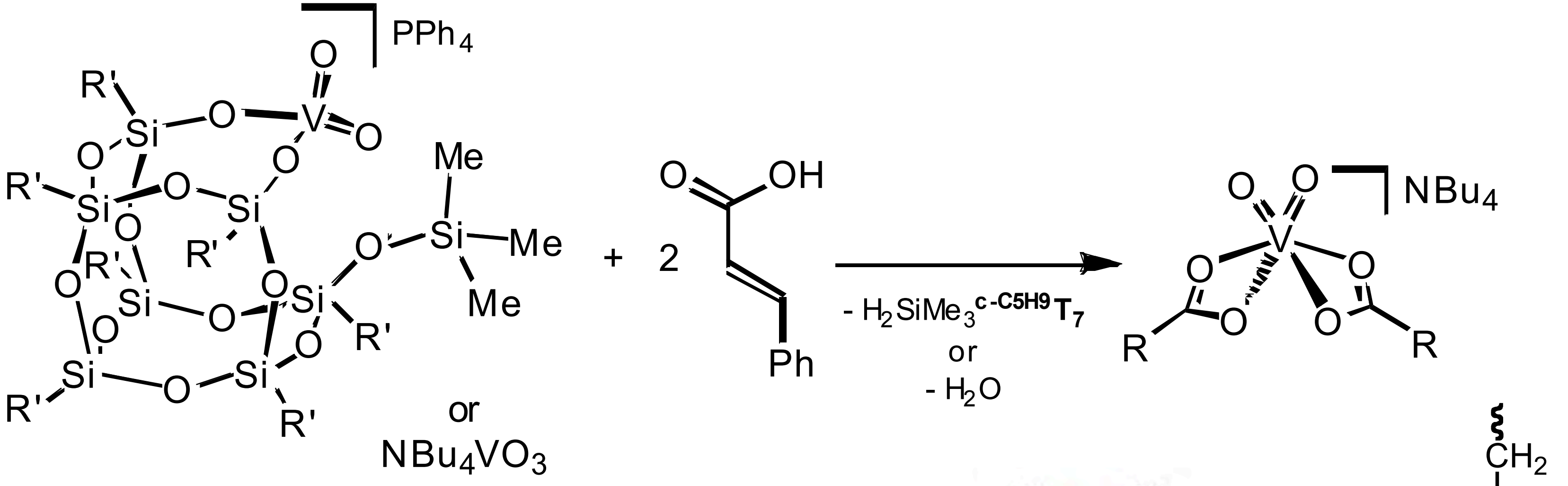
Cinammic acid generates the acive catalyst



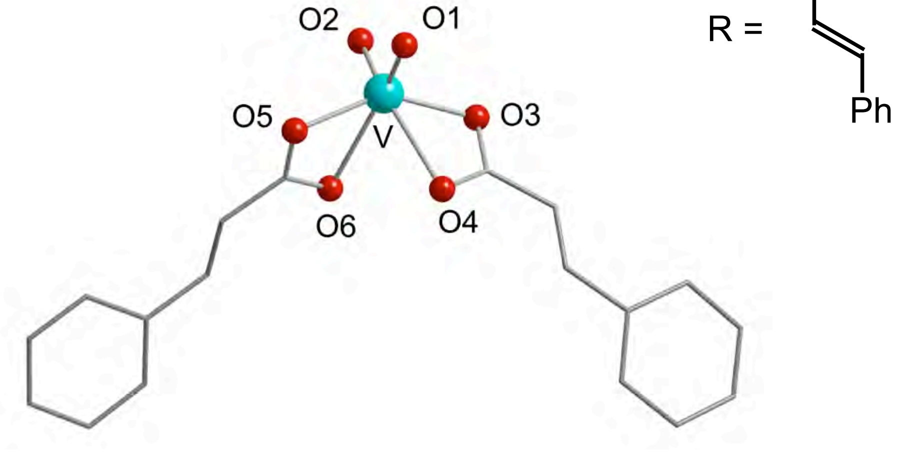
Oxidation of cinnamic alcohol in the presence of 5 mol% of cinnamic acid and 0.25 mol% of Cat.

C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

The role of the cynnamic acid

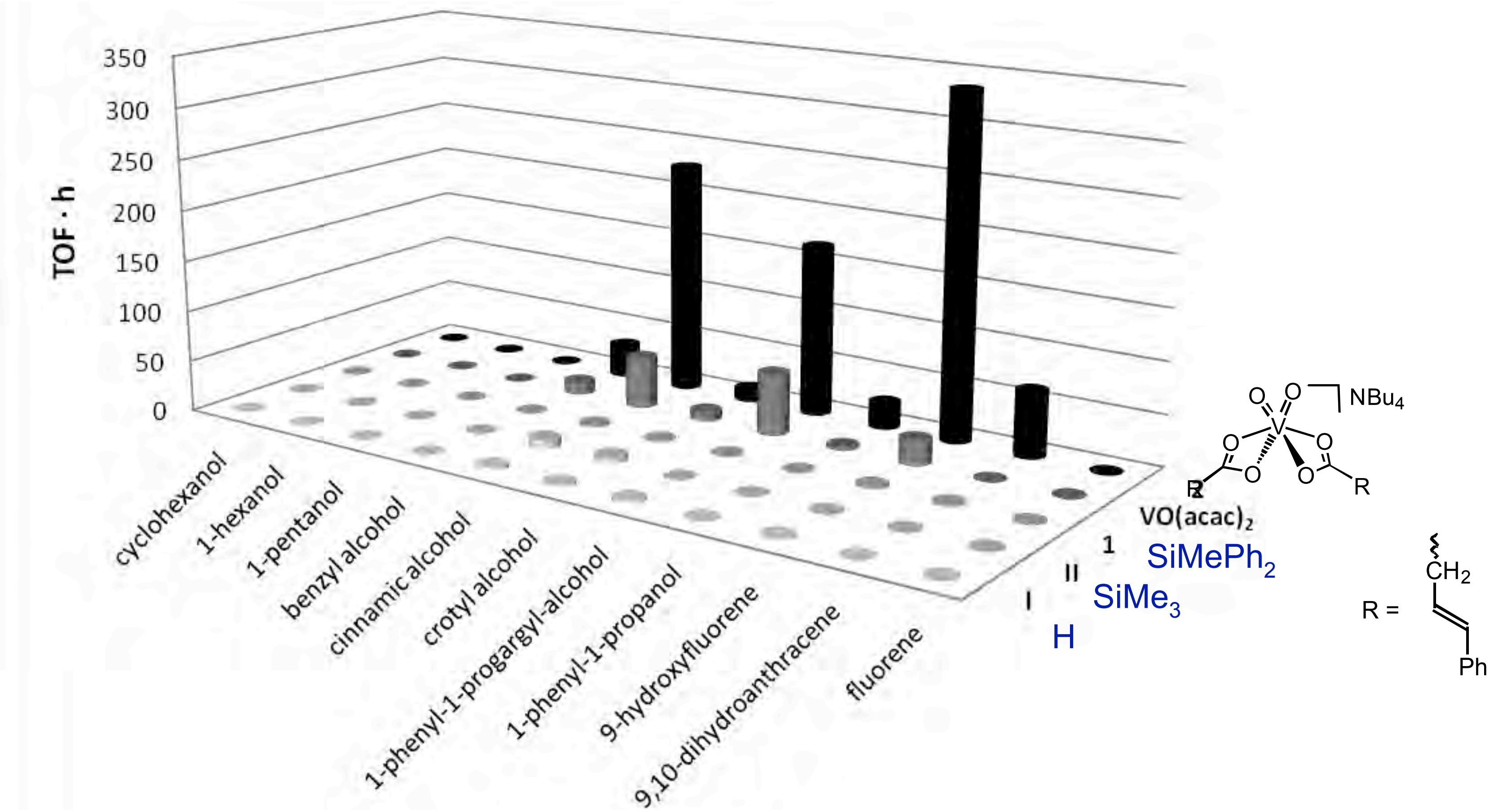


R‘ = c-pentyl



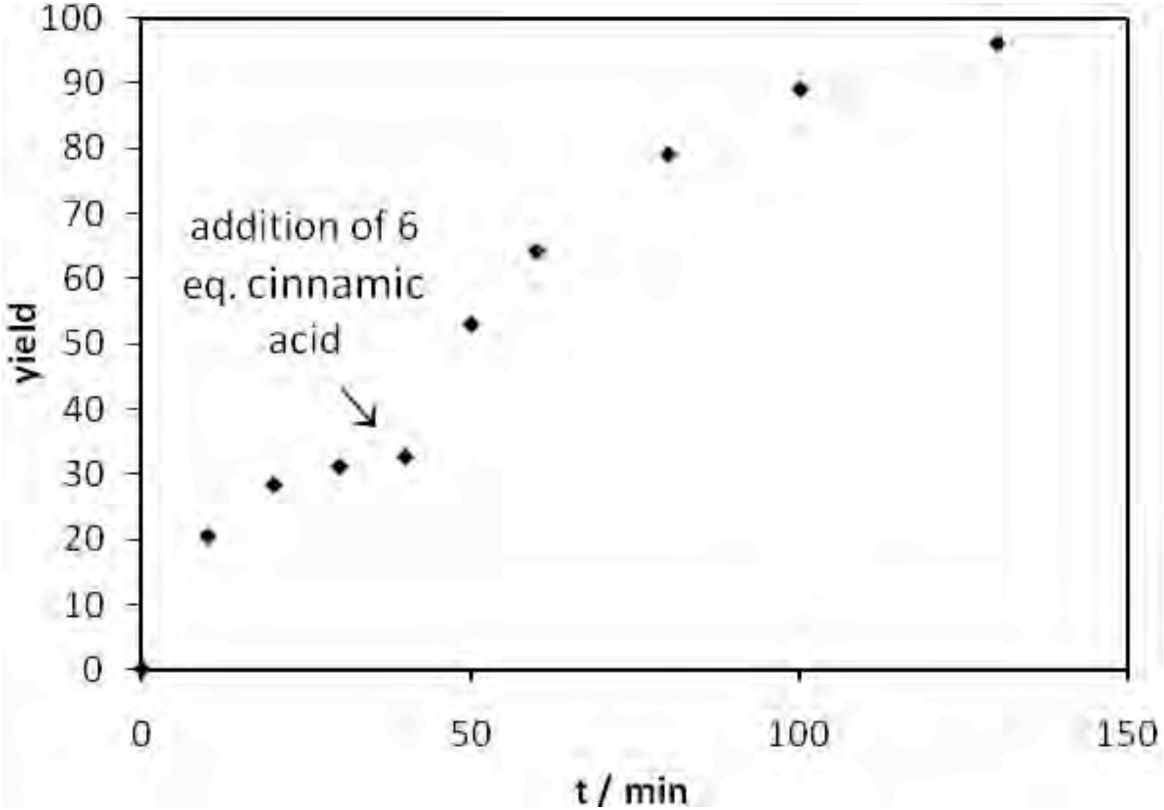
C. Ohde, C. Limberg, *Chem.- Eur. J.*
2010, accepted

Catalytic activity of the vanadyl cinnamate



C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

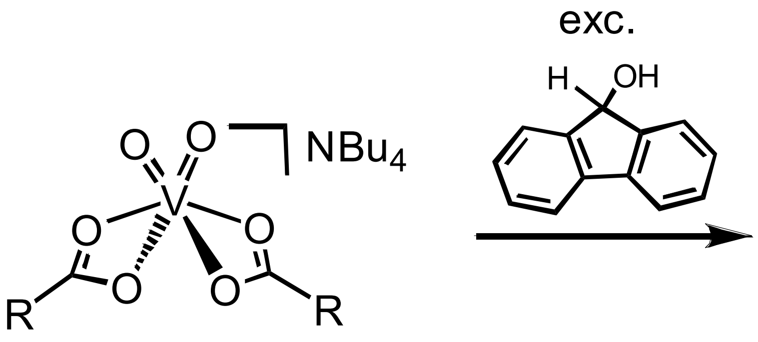
Loss of activity and regeneration

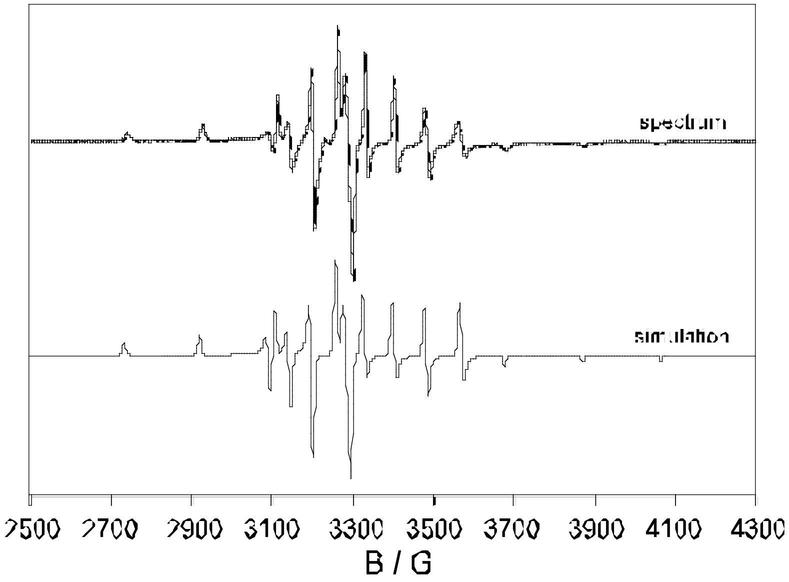


Oxidation of 9-hydroxyfluorene catalysed by the vanadylcinnamate; after 40 min 6 equivalents of cinnamic acid were added

C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

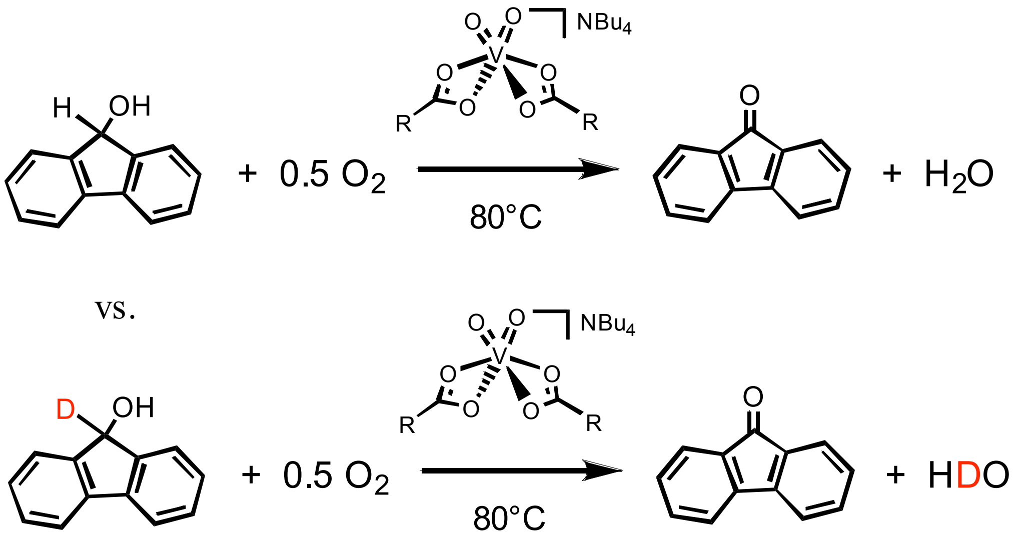
The reduced species within the catalytic cycle

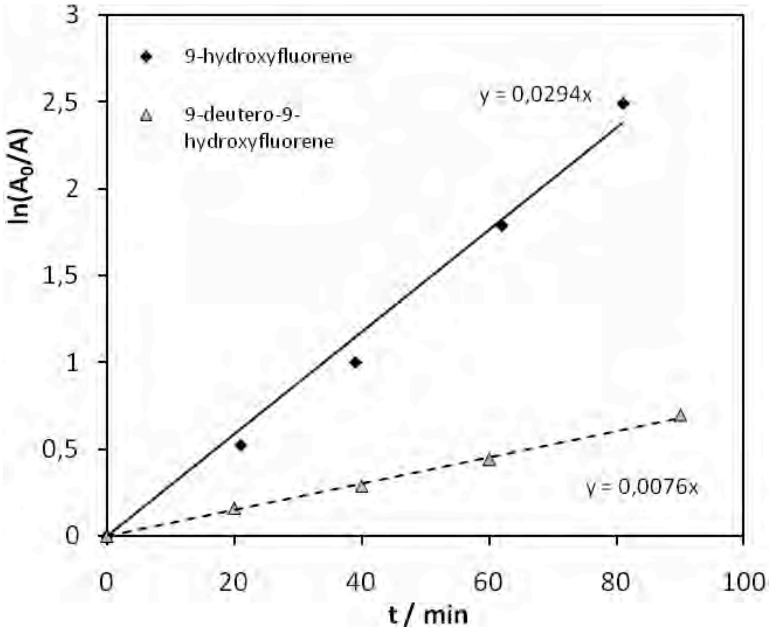




The reduced catalyst contains vanadium(IV)

The rate-determining step within the catalytic cycle



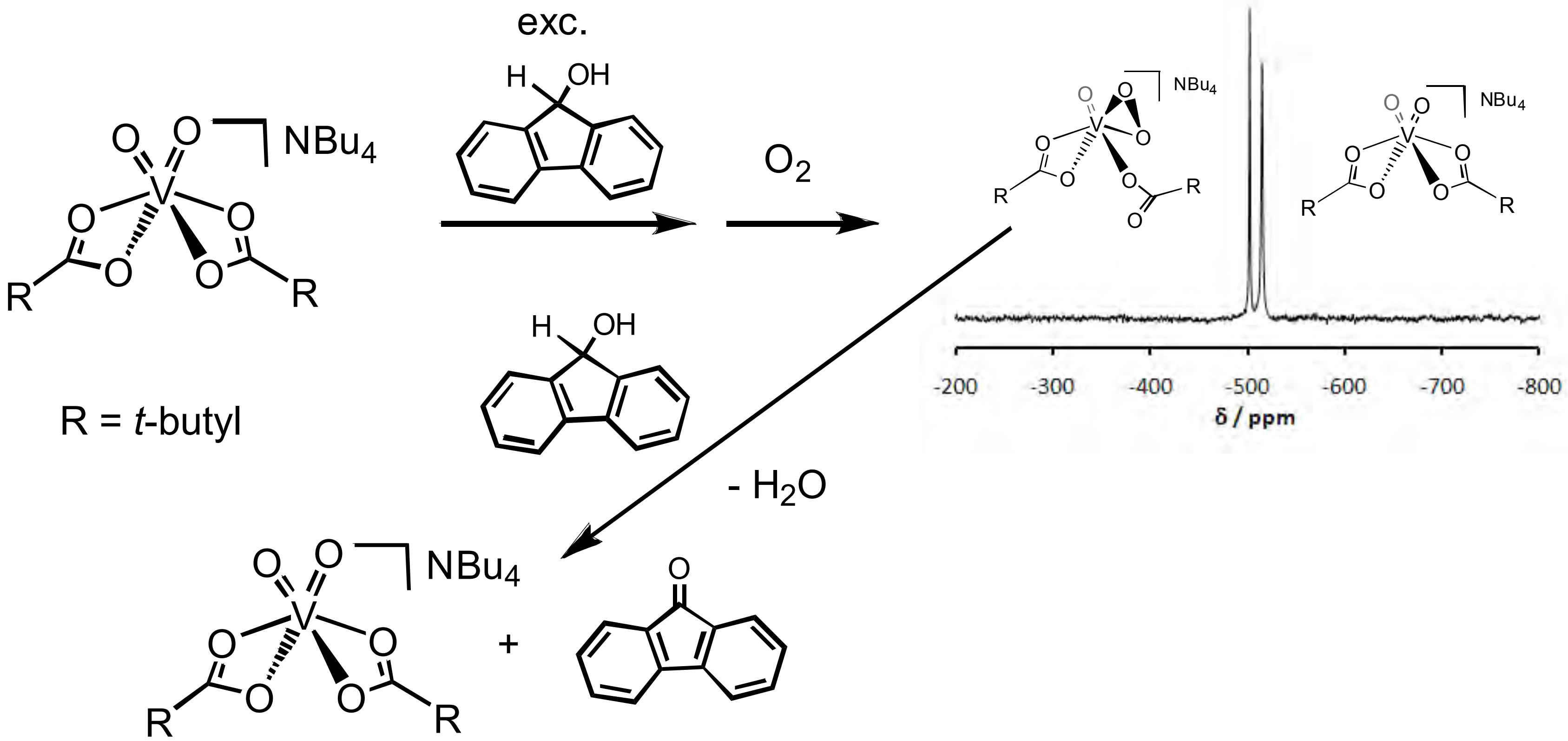


KIE: 3.9

➡ H atom transfer and quite symmetric transition state along the H-transfer coordinate, O···H···C

C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

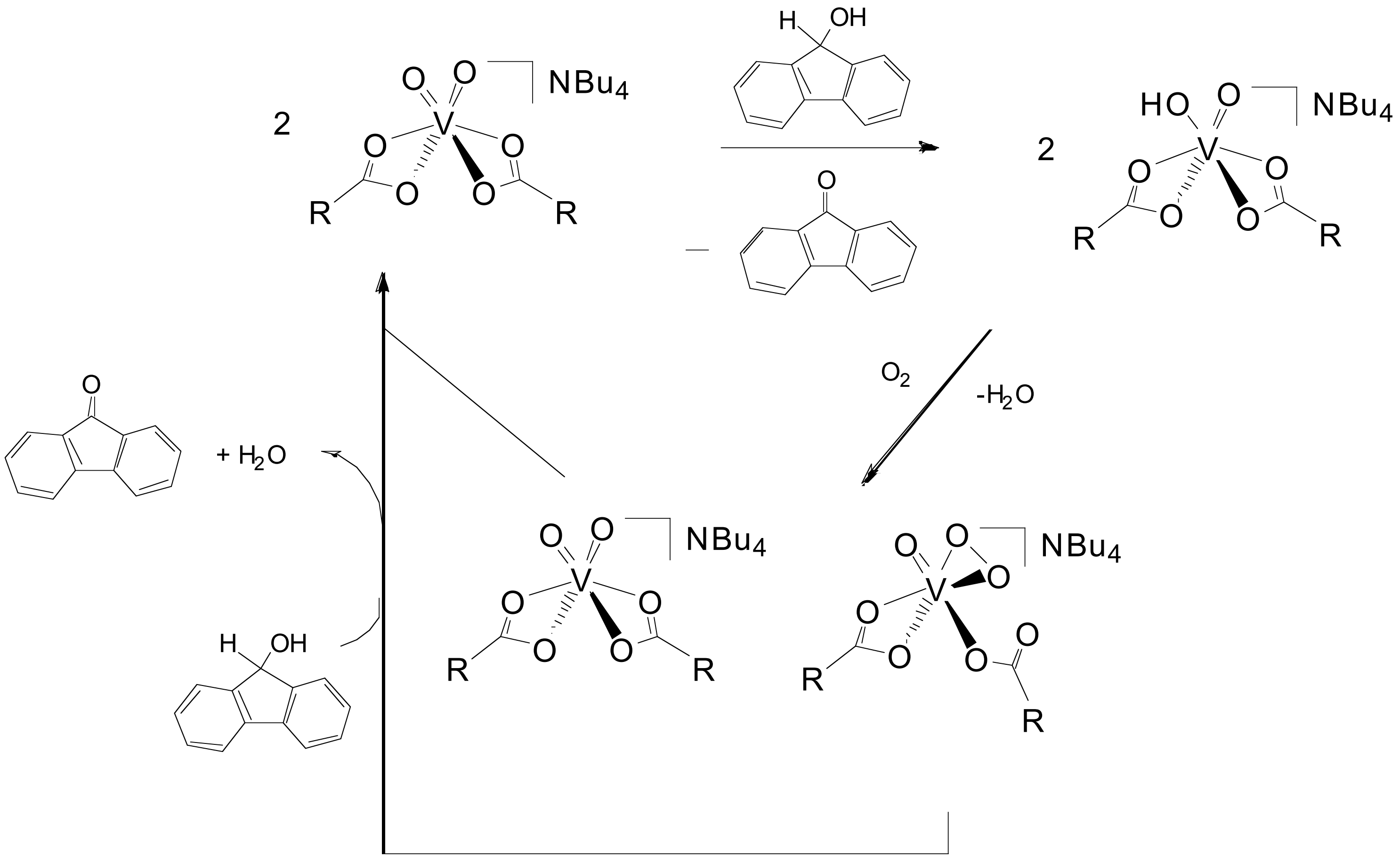
The reoxidation step within the catalytic cycle



R = *t*-butyl

Reoxidation takes place via peroxides

The complete catalytic cycle



C. Ohde, C. Limberg, *Chem.- Eur. J.* **2010**, accepted

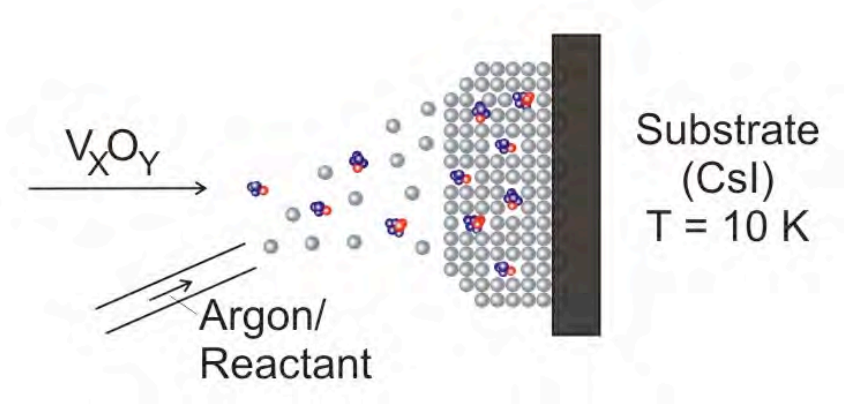
Cooperations

Detlef Schröder: ESI-MS with oxovanda calixarenes

Thorsten Siebert: fs-UV/Vis with oxovanada silsequioxanes

Christian Hess: Characterisation of supported molybdenumoxide catalysts by UV-Raman

3. Neutral V_xO_y clusters in cryogenic matrices



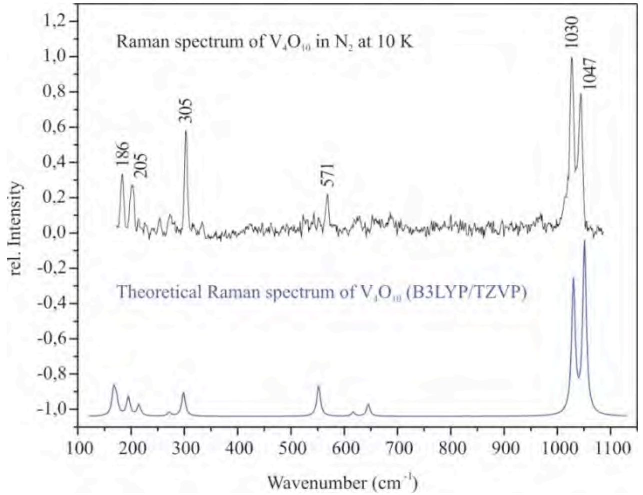
Small V_xO_y aggregates:

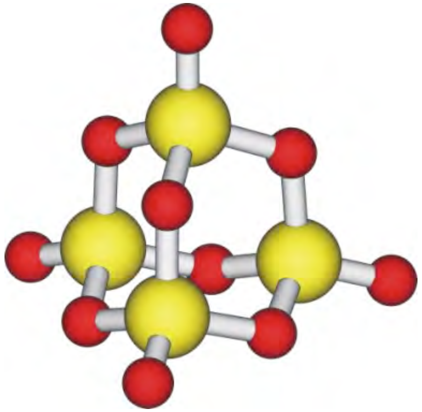
- simplest models
- quantum chemical investigation
- neutral V_xO_y clusters $\longleftrightarrow$ cationic/anionic s

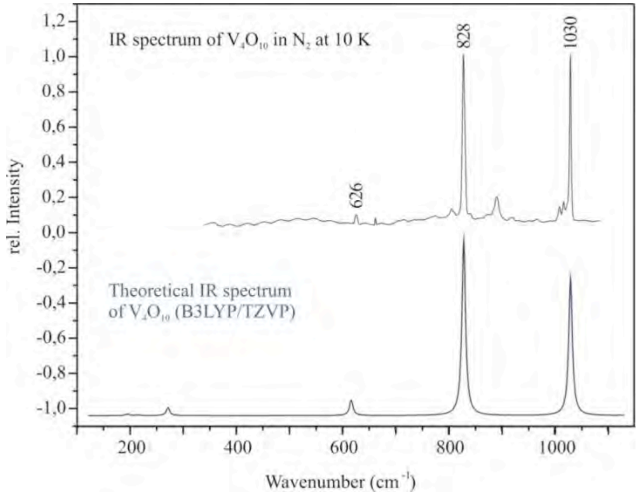
  (structure, spectroscopic properties, reactivity)

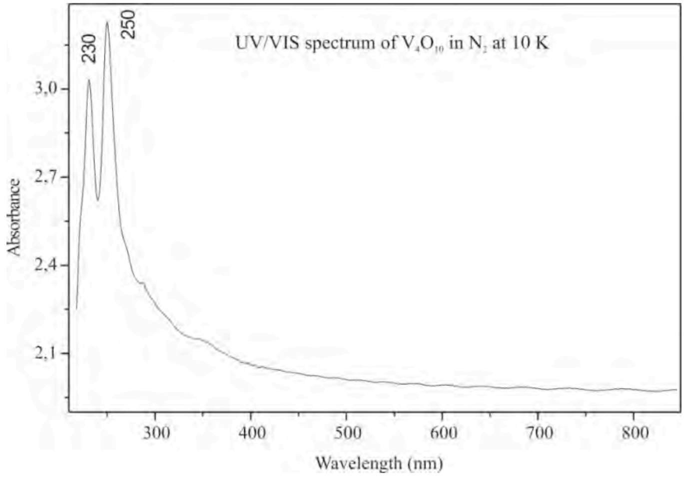
Matrix isolation
of V_xO_y clusters

V_4O_{10}


Raman spectrum of V_4O_{10} in N_2 at 10 K
Theoretical Raman spectrum of V_4O_{10} (B3LYP/TZVP)
186
205
305
571
1030
1047
rel. Intensity
1,2
1,0
0,8
0,6
0,4
0,2
0,0
-0,2
-0,4
-0,6
-0,8
-1,0
100
200
300
400
500
600
700
800
900
1000
1100
Wavenumber (cm^{-1})

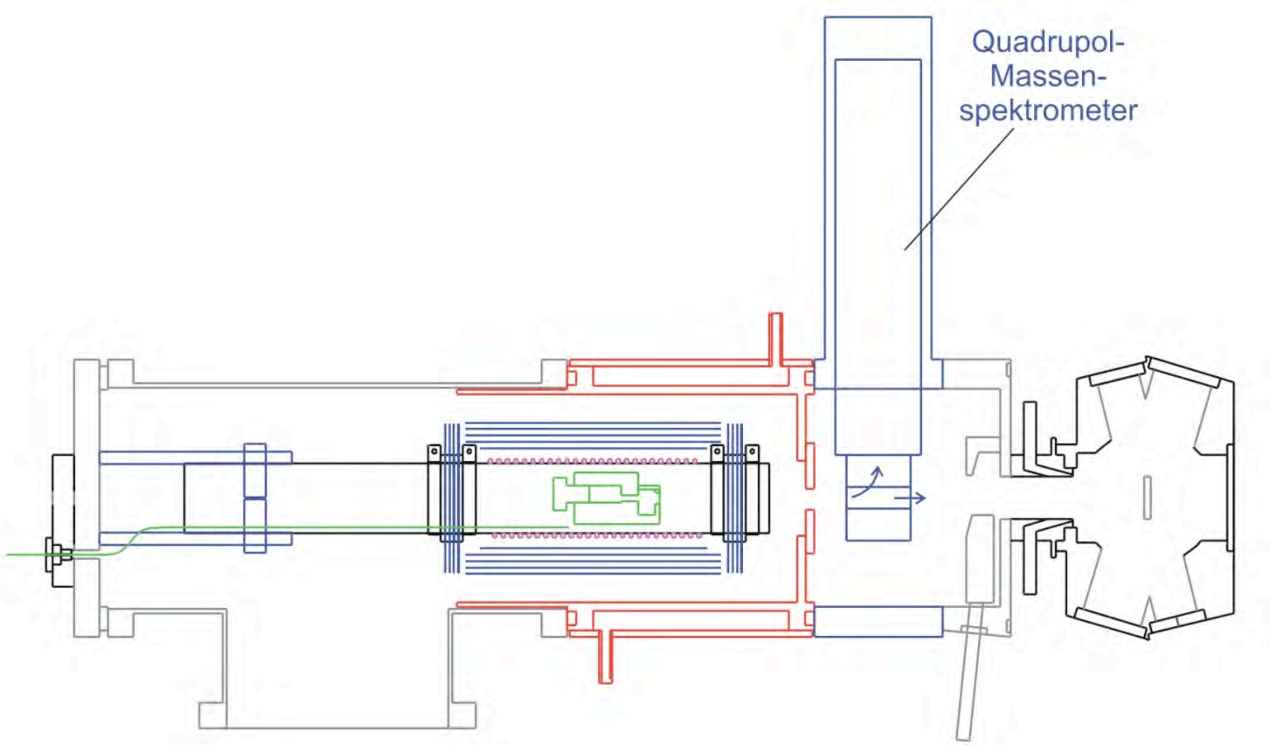



IR spectrum of V_4O_{10} in N_2 at 10 K
Theoretical IR spectrum of V_4O_{10} (B3LYP/TZVP)
626
828
1030
rel. Intensity
1,2
1,0
0,8
0,6
0,4
0,2
0,0
-0,2
-0,4
-0,6
-0,8
-1,0
200
400
600
800
1000
Wavenumber (cm^{-1})


UV/VIS spectrum of V_4O_{10} in N_2 at 10 K
230
250
Absorbance
3,0
2,7
2,4
2,1
300
400
500
600
700
800
Wavelength (nm)

Monitoring evaporation by mass spectrometry

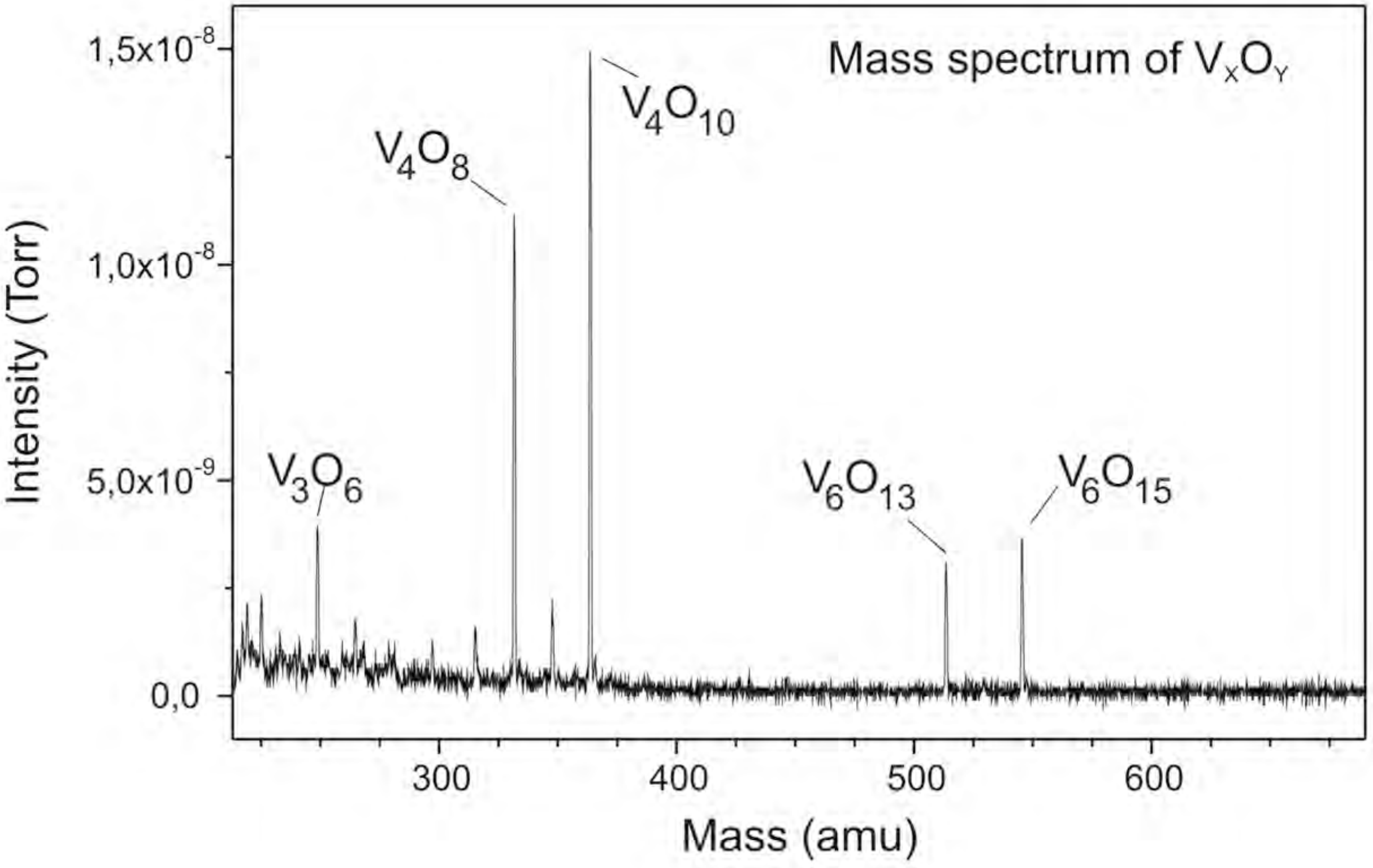
Synthesis of other V_XO_Y-Aggregates : V_4O_8, V_6O_{12}, V_6O_{14}, V_2O_4, ...



Mass spectrometer:

- Generation of V_4O_8, V_6O_{14}, … (from V_2O_5 or alkoxides)
- Increase of V_4O_{10} evaporation (→ more Raman intensity for reactivity studies)
- Minimization of O_2, CO_2, CO formation

Monitoring evaporation by mass spectrometry



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