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UNIVERSIDAD DE MÁLAGA

New highly active and selective nanostructured oxide catalysts

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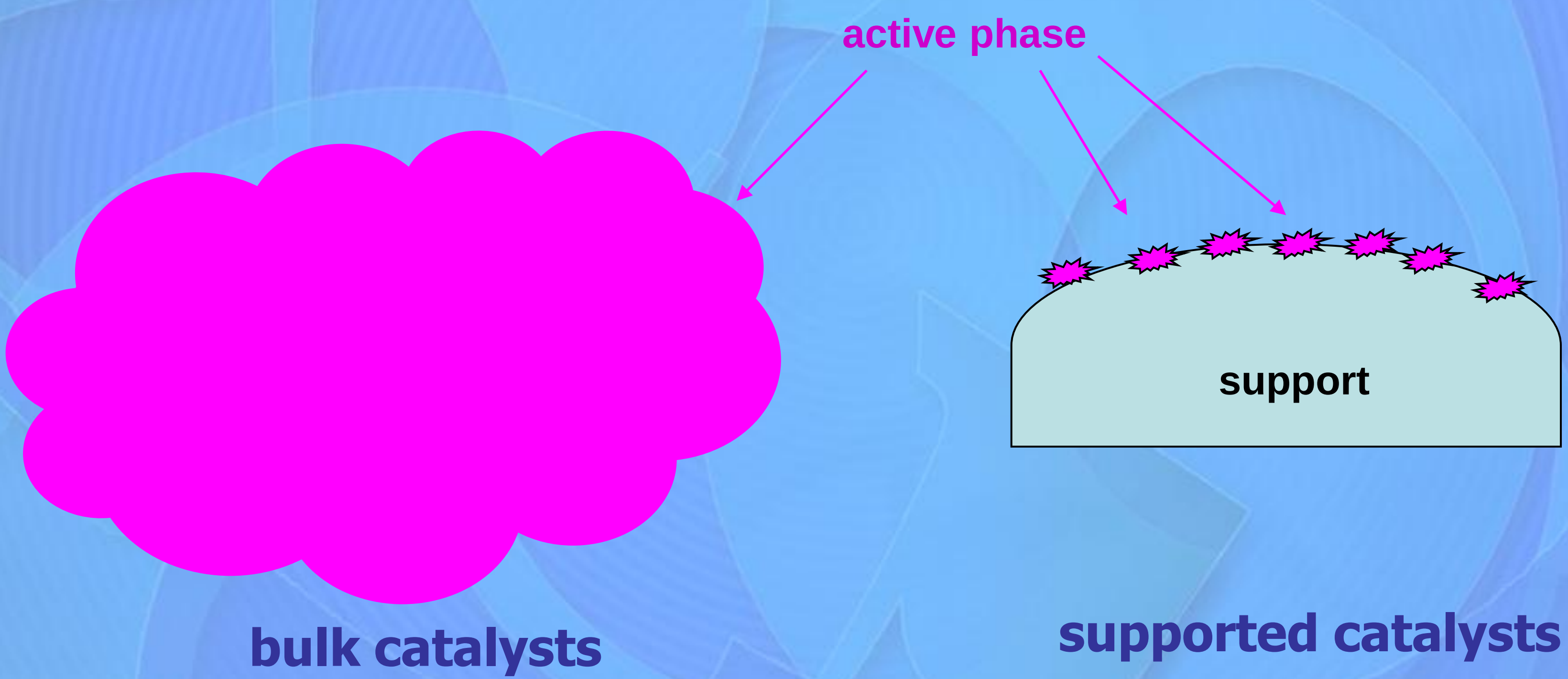
What is a nanostructured catalysts?

The catalytic active phase is nanoscaled on the surface of a support

Nanostructured catalysts



Main advantages:

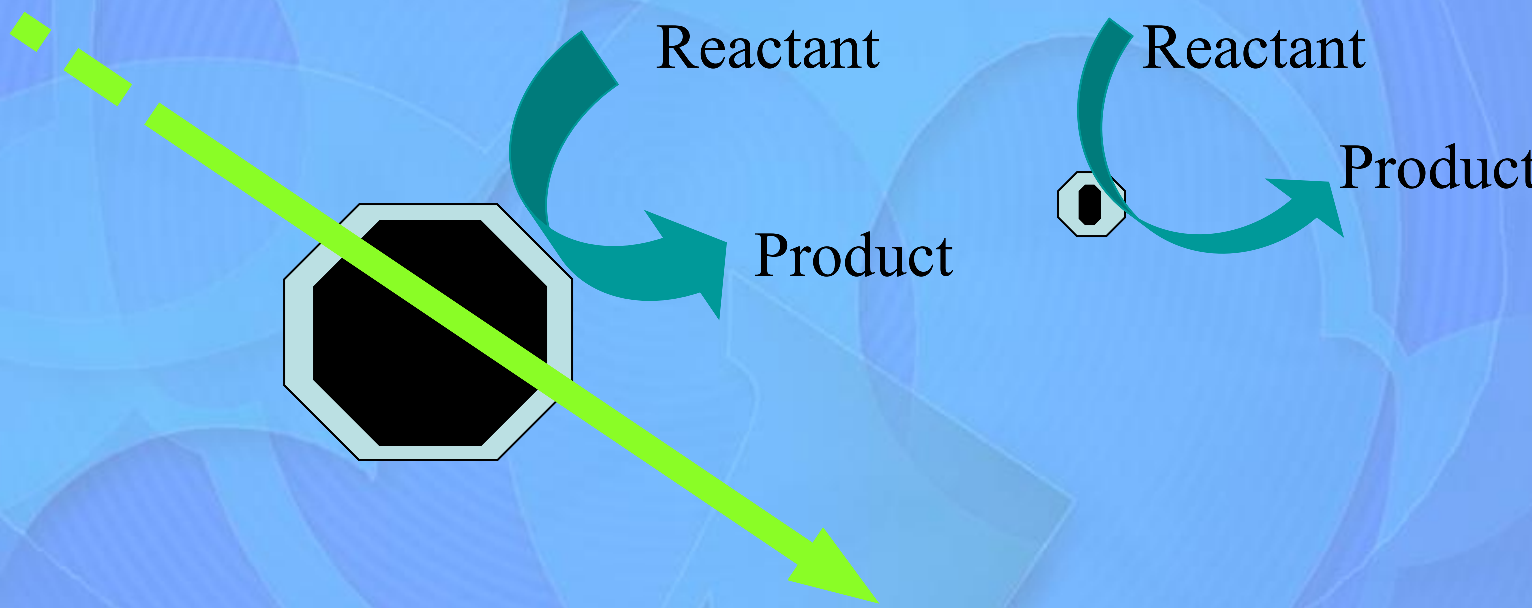
Industrial point of view:

Less expensive catalysts

Academic point of view:

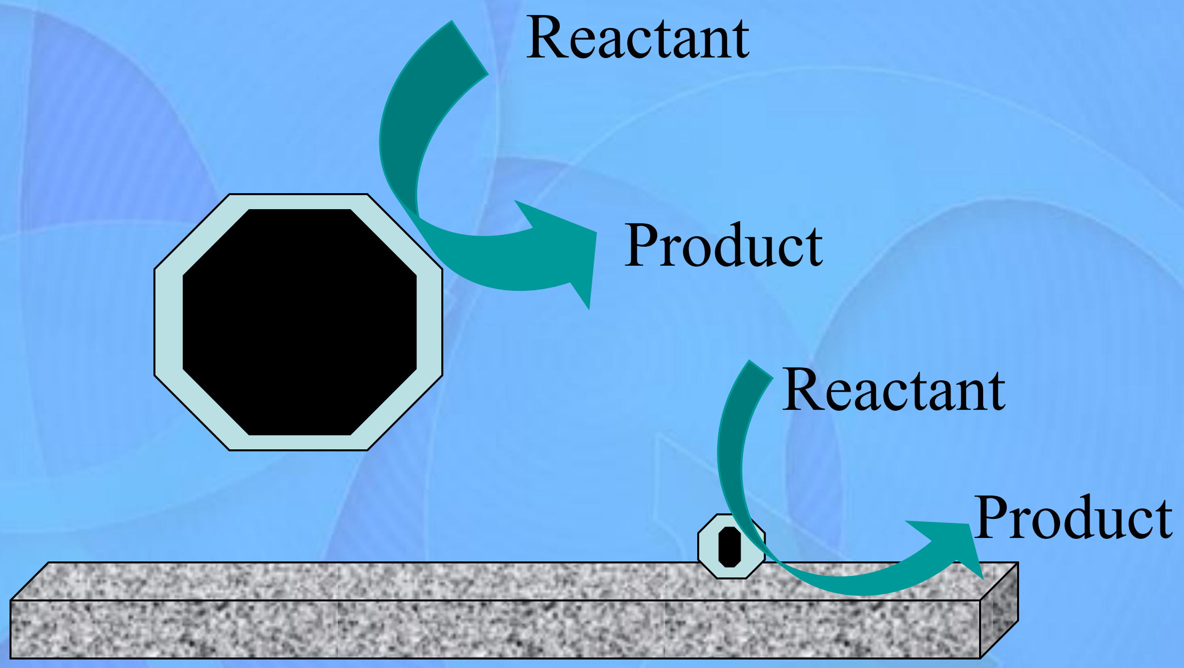
- **Support can modulate the activity**
- **Better insight on the nature of the active phase**

Characterization of the surface



Usually we obtain information about the bulk

Catalytic reactions take place at the surface of catalysts



Support

Coverage

Additives

Structure

Activity-selectivity

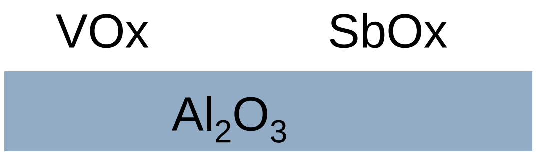
Activation / deactivation

Case 1: Sb-V-O catalytic materials for propane ammoxidation

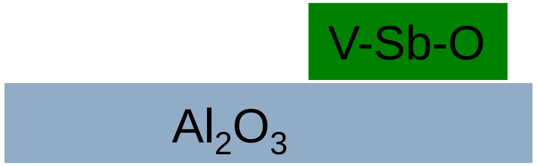
$$NH_3 + O_2 + C_3H_8 \longrightarrow CH_2{=}CH\text{-}CN$$

Case 1: $VSbO_4$ on alumina

Sb-V-O/Al_2O_3
Sb+V < low coverage
not active (surface vanadia)
Guerrero-Pérez et al. (2002)



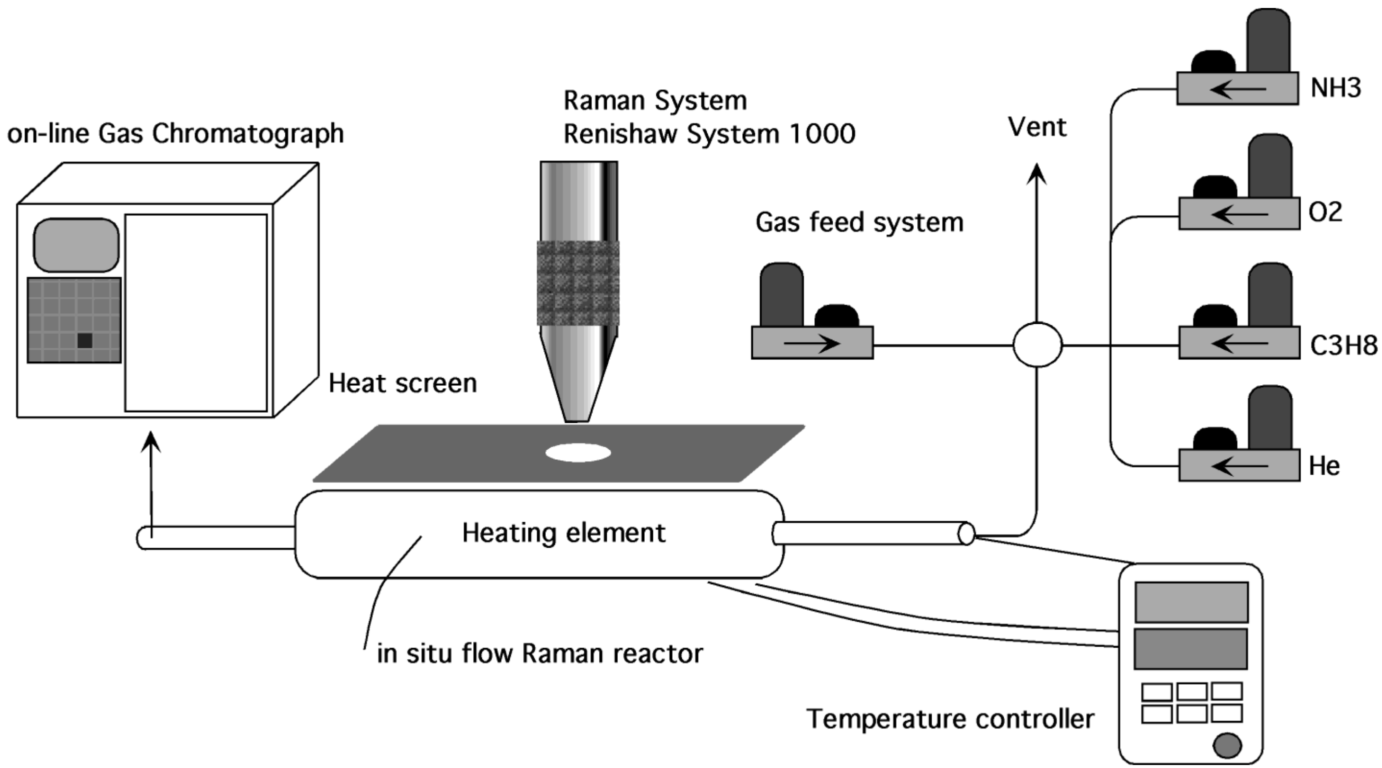
Sb+V ≥ high coverage
active ($VSbO_4$ phase)
Grasselli et col. (1992)
Guerrero-Pérez et al. (2002)



$VSbO_4$ phase on alumina is not stable at low coverages

Like the bulk system, $VSbO_4$ phase further forms during time-on-stream

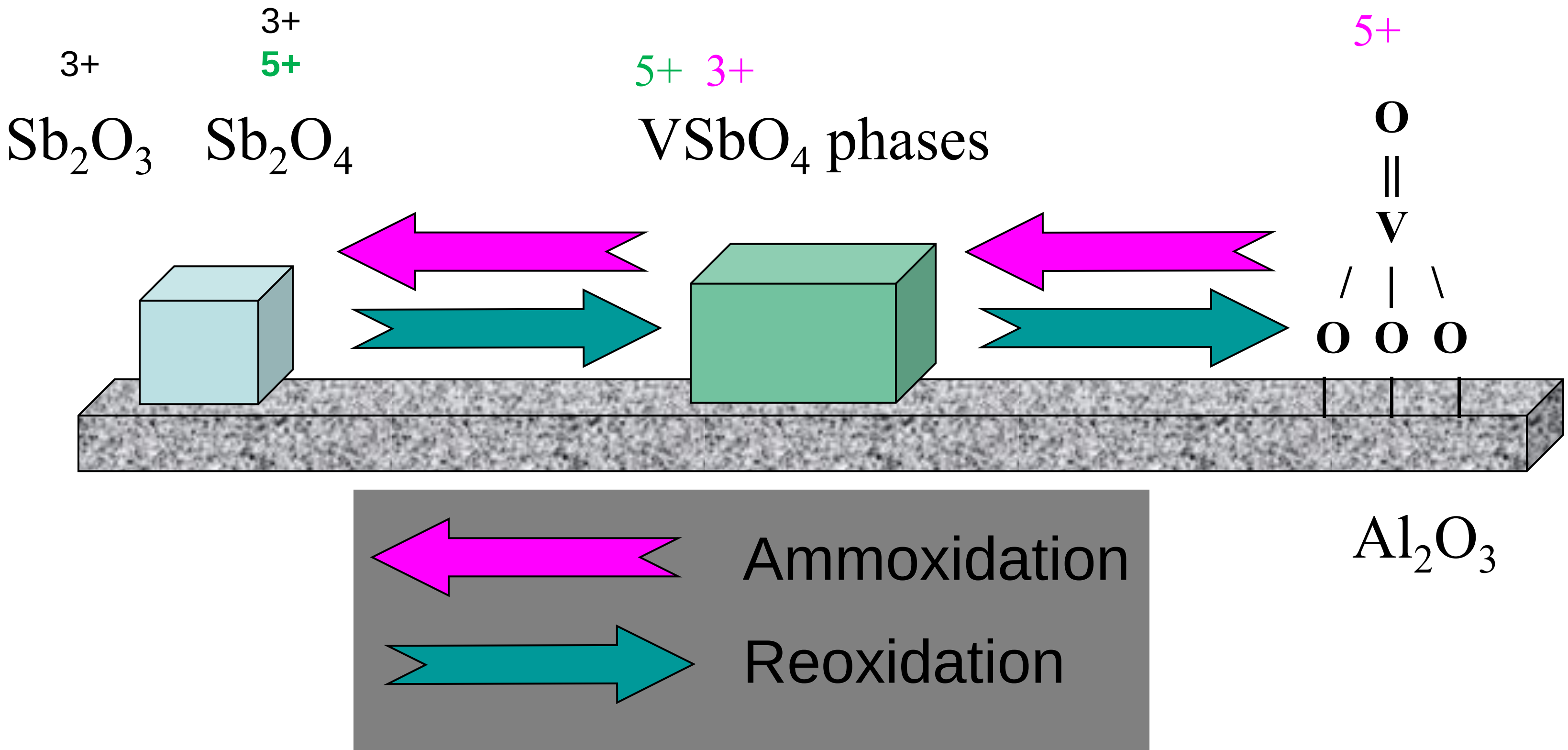
Case 1: Uncovering reaction mechanism by operando spectroscopy



Case 1: Uncovering reaction mechanism by operando spectroscopy

Dominant phase, during ammoxidation: $VSbO_4 + Sb_2O_4$

during reoxidation: $VOx + VSbO_4 + Sb_2O_3$

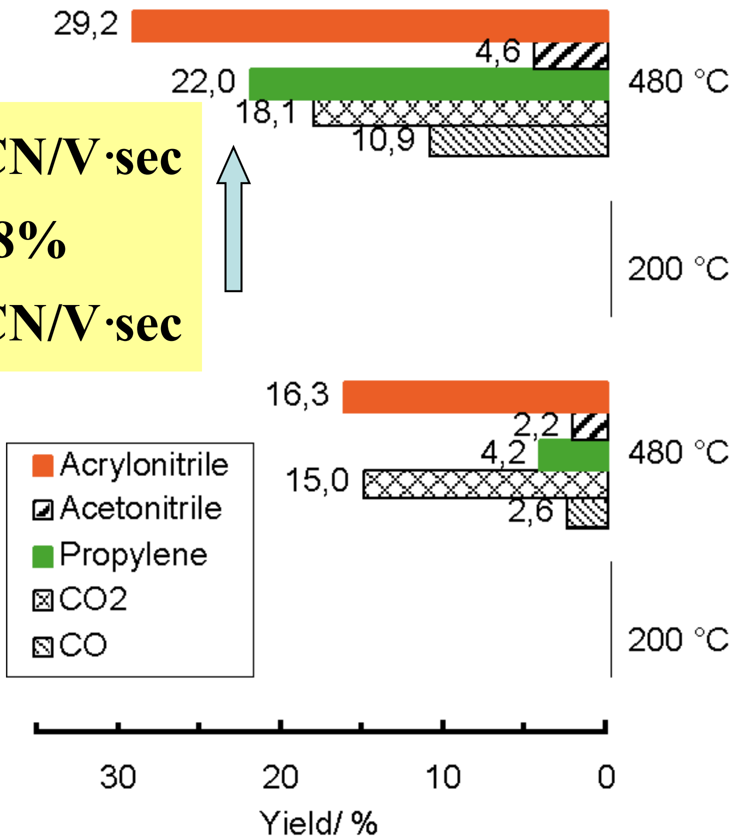


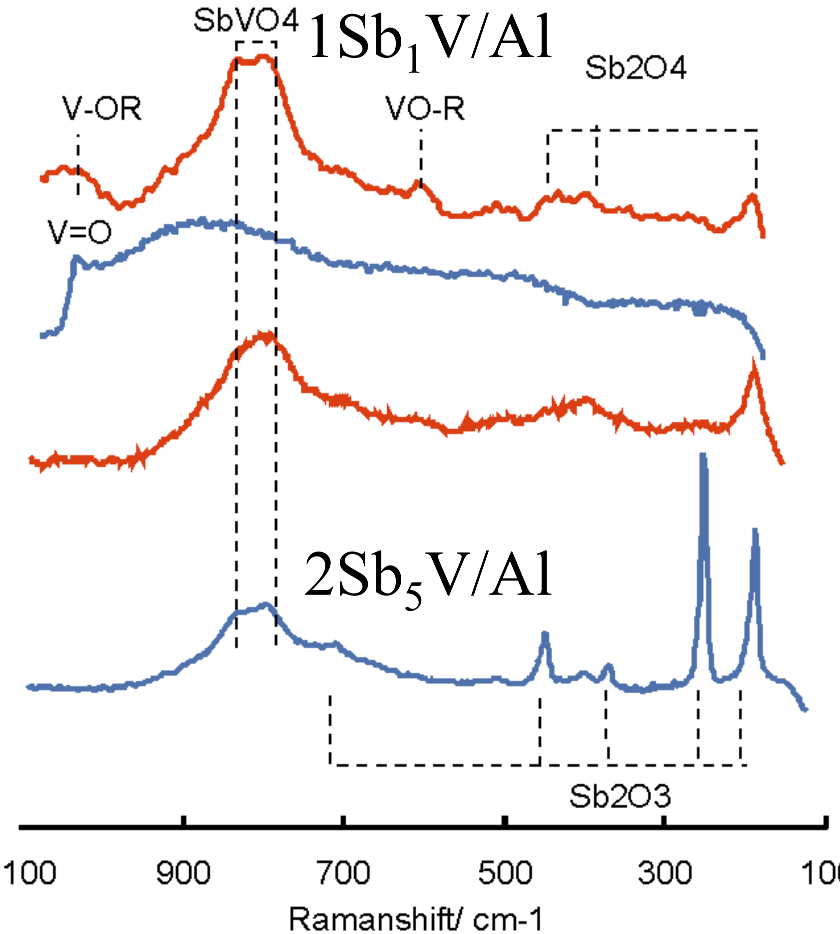
Case 1: Uncovering reaction mechanism by operando spectroscopy

8.8 ACN/V·sec

+48%

4.8 ACN/V·sec

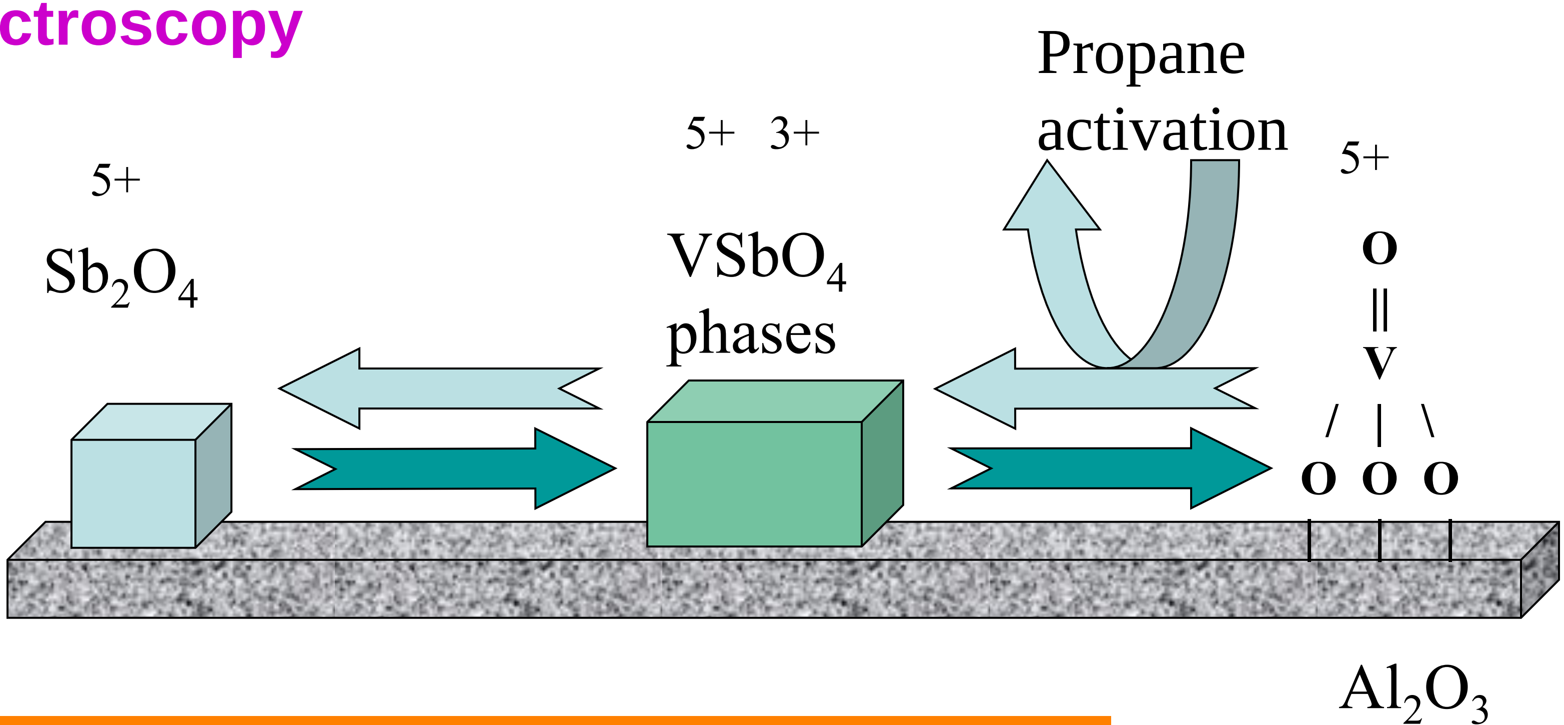




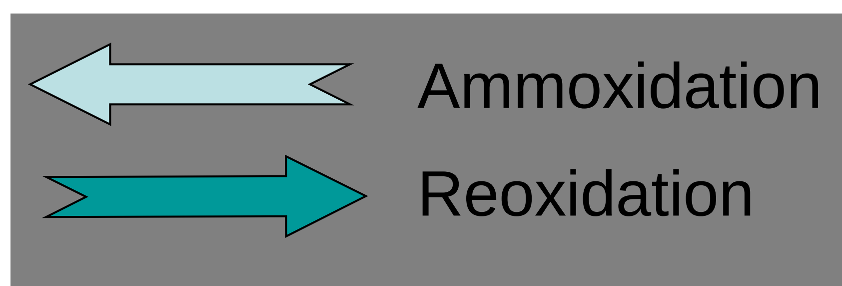
Surface vanadia on $SbVO_4$ species trigger conversion/selectivity specific rate

Bañares et al., J.Mater.Chem.(2002)

Case 1: Uncovering reaction mechanism by operando spectroscopy



Redox cycle between surface V^{5+} and bulk V^{3+} sites



Case 1: Sb-V-O catalytic materials for propane ammoxidation

- ✓ $VSbO_4$ active phase succesfully nanoscaled on the surface of alumina support.
- ✓ Identified active species during propane ammoxidation by Raman spectroscopy.
- ✓ Reaction Mechanism proposed.

Case 2: Mo-V-Te-Nb-O catalytic materials for propane oxidation

Acrylic acid ⇒ **useful chemical intermediate**

(fibers, polymers, resins…. and much more)

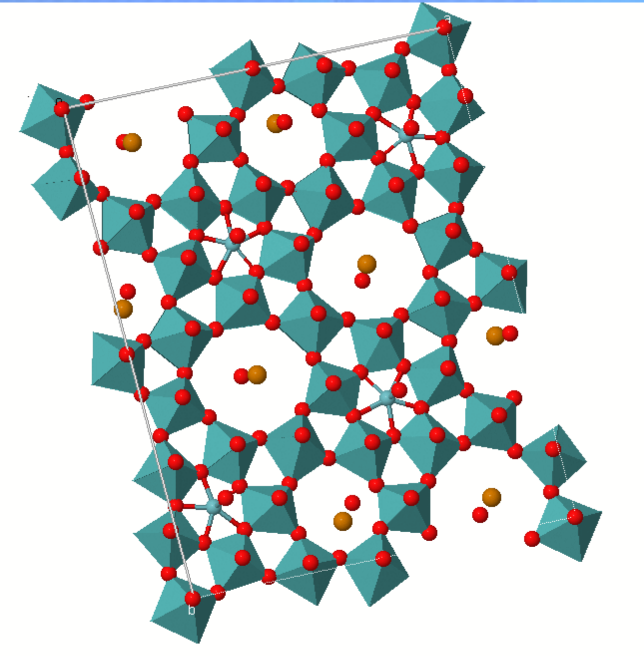
~~PROPYLENE~~ → ACROLEIN → ACRYLIC ACID

PROPANE

TWO STEPS

ONE STEP

Case 2: Mo-V-Te-Nb-O catalytic materials for propane oxidation



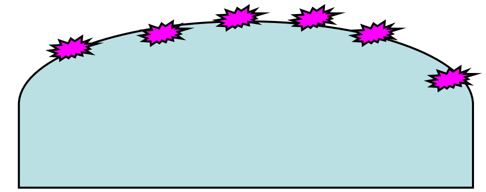
Previous studies: bulk catalysts

M1 and rutile: active phases

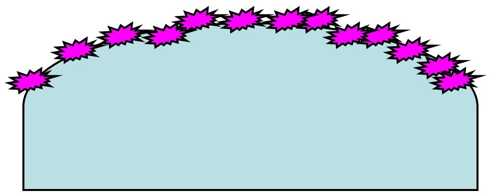
Grasselli et al.
Guliants et al.
Ueda et al.
López Nieto et al.

Case 2: Synthesis of nanostructured catalysts

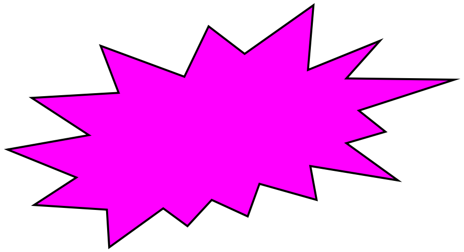
$4MoVNbTe/Al_2O_3$



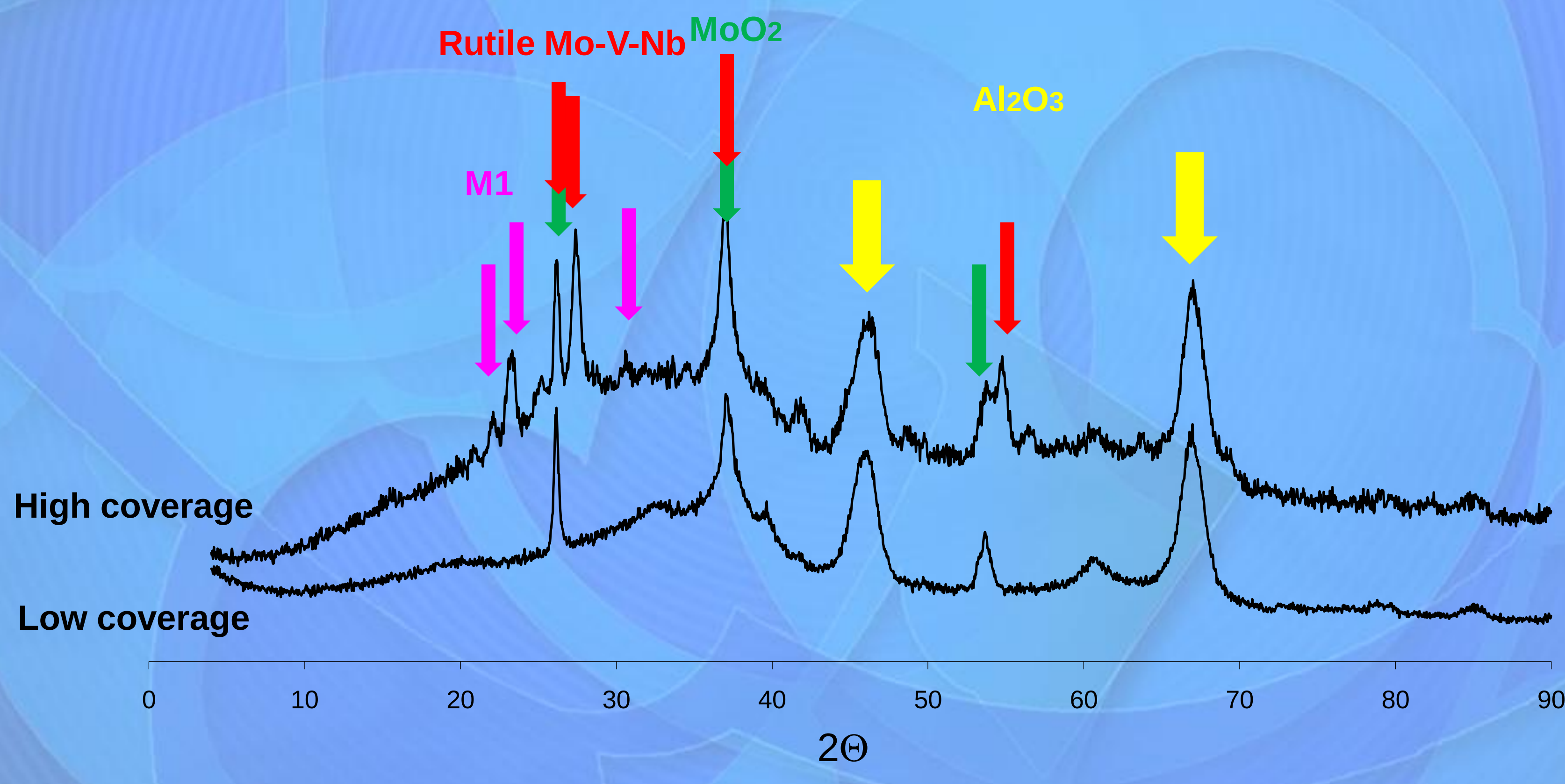
$12MoVNbTe/Al_2O_3$



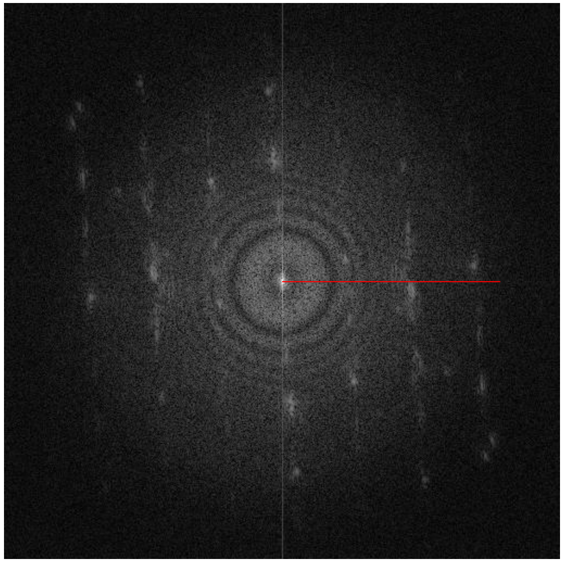
Bulk MoVNbTeO

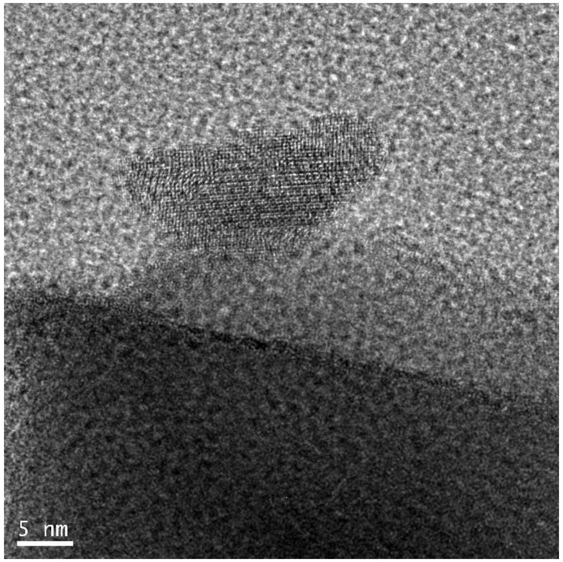


Case 2: XRD patterns of Mo-V-Te-Nb catalysts



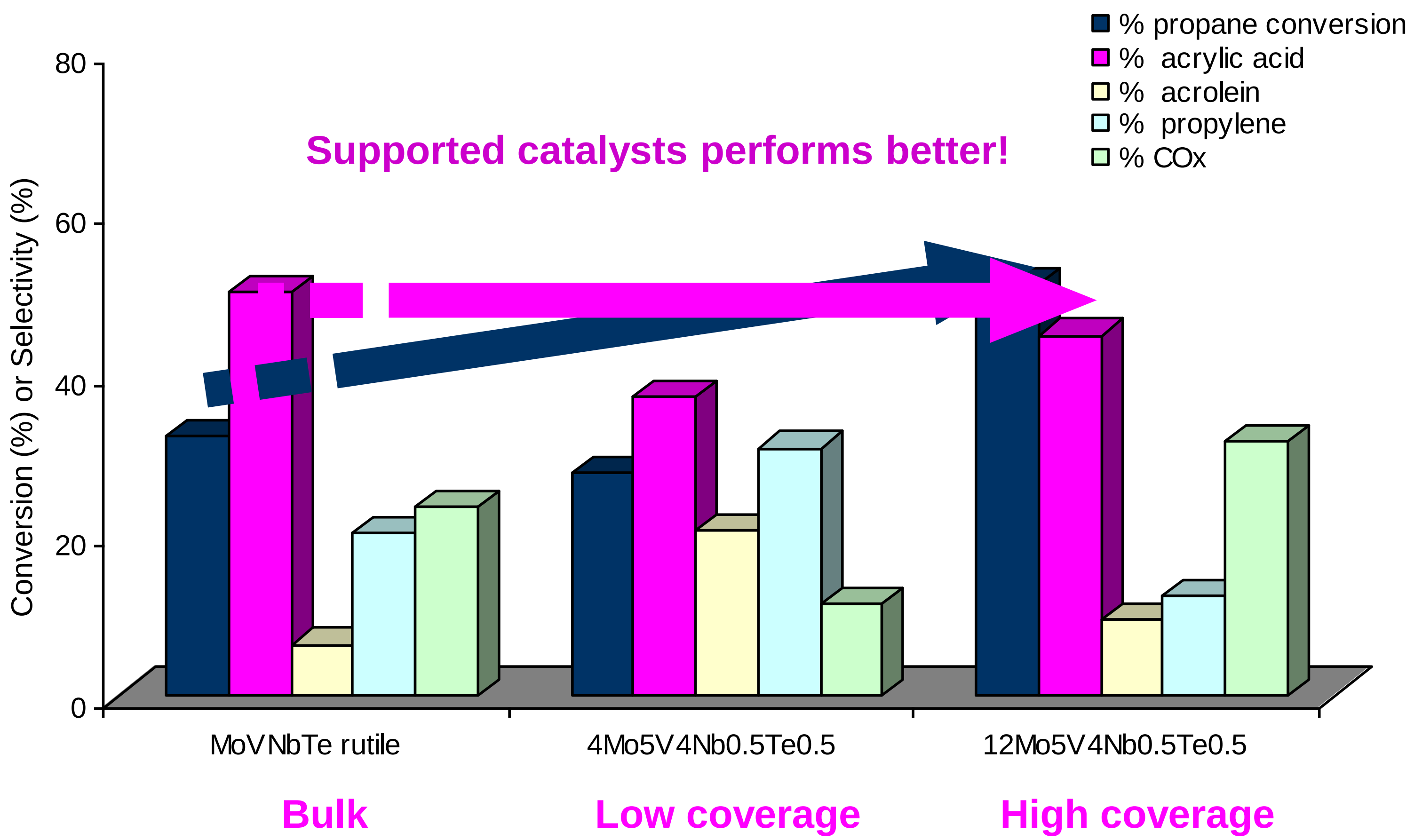
Case 2: Characterization of Mo-V-Te-Nb catalysts





HRTEM confirms the presence of M1 phase

Case 2: Mo-V-Te-Nb-O catalytic materials for propane oxidation



Case 2: Mo-V-Te-Nb-O catalytic materials for propane oxidation

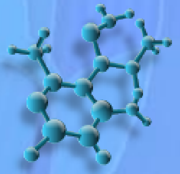
- Nanoscaled Rutile and M1 active phases have been succesfully supported on the surface of alumina.

- It is possible to obtain active and selective nanoscaled catalysts, that performs, even better, that the corresponding bulk catalysts.

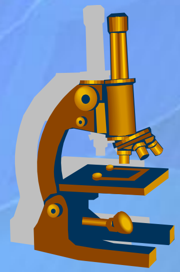
- **Mo-V-Nb-Te-O for propane oxidation**
- **Sb-V-O for propane ammoxidation**

Rutile and M1 active phases

✓ ***It have been possible to obtain active and selective nanoscaled catalysts.***



✓ ***Identification of active phase under reaction conditions.***



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http://www.uma.es/D36

Thank you very much for your attention!!!

Case 2: Raman spectra of Mo-V-Te-Nb catalysts