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

- Bulk catalysts
- Active phase
- Supported catalysts

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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

Catalytic reactions take place on the surface of catalysts.
Case 1: Sb-V-O catalytic materials for propane ammoxidation

\[ \text{NH}_3 + \text{O}_2 + \text{C}_3\text{H}_8 \rightarrow \text{CH}_2=\text{CH-CN} \]
Case 1: V$\text{SbO}_4$ on alumina

Sb-V-O/$\text{Al}_2\text{O}_3$
Sb+V < low coverage
  not active (surface vanadia)
Guerrero-Pérez et al. (2002)

Sb+V ≥ high coverage
  active (V$\text{SbO}_4$ phase)
Grasselli et col. (1992)
Guerrero-Pérez et al. (2002)

V$\text{SbO}_4$ phase on alumina is not stable at low coverages

Like the bulk system, V$\text{SbO}_4$ phase further forms during time-on-stream
Case 1: Uncovering reaction mechanism by operando spectroscopy
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Dominant phase, during ammoxidation: $\text{VSbO}_4 + \text{Sb}_2\text{O}_4$

during reoxidation: $\text{VO}_x + \text{VSbO}_4 + \text{Sb}_2\text{O}_3$

Ammoxidation

Reoxidation

Al$_2$O$_3$
**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

- V$\text{SbO}_4$ active phase successfully 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

ONE STEP

TWO STEPS

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

Previous studies: bulk catalysts

M1 and rutile: active phases

Grasselli et al.
Guljants et al.
Ueda et al.
López Nieto et al.
Case 2: Synthesis of nanostructured catalysts

4MoVNbTe/Al₂O₃

12MoVNbTe/Al₂O₃

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

High coverage

Low coverage

2\(\Theta\)
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

Supported catalysts performs better!
Case 2: Mo-V-Te-Nb-O catalytic materials for propane oxidation

- Nanoscaled Rutile and M1 active phases have been successfully 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

- 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

- VOx
- MoOx
dispersed on alumina

MoOx visible at low coverages

High coverage

Low coverage

1100 900 700 500 300 100