

**New highly active and selective nanostructured oxide catalysts**

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Nanostructured catalysts present valuable advantages from both industrial and academic points of view. Active nanostructured catalytic oxides can be supported on a non-expensive material that acts as support, such as alumina, to prevent sinterization. Thus, the amount of active phase required for a satisfactory catalytic performance can be minimized. In addition, the use of nano-scaled oxide phases maximizes the surface-to-volume ratio allowing a better insight on the nature of the active phase [1]. For instance, we have shown that nanoscaled Sb-V-O supported catalysts can perform even better than the corresponding bulk oxide catalysts [2] and the nature of the actual working phase uncovered [3]. Thus, presenting this work, we prepare nanoscaled molybdenum oxide based catalysts, well known as selective for propane partial oxidation reactions.

Two Mo-V-Nb-Te nanoscaled oxide catalysts have been prepared supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, one with a low surface coverage (4 atoms/nm<sup>2</sup> of support, submonolayer) and the other with high coverage (12 atoms/nm<sup>2</sup>, above monolayer). For comparative purposes, a conventional bulk MoVNbTeO oxide has also been prepared. Figure 1 shows the XRD patterns of these samples and Figure 2, the Raman spectra under dehydrated conditions. The rutile-like active phase can be identified by its XRD shoulder near 36.8° and the features near 80.3°. For the remaining peaks overlap with those of MoO<sub>3</sub> phase and also Raman spectra further confirm the presence of the rutile structure (broad Raman band near 820-840 cm<sup>-1</sup>) [2,3]; this band overlaps with those near 821 and 459 cm<sup>-1</sup> at high coverage, these bands are observed in catalysts containing the so-called M1 phase, which is active and selective; these bands could also be assigned to the stretching mode of bridging Mo-O-M (M= Mo, V) bonds of Te<sub>2</sub>M<sub>20</sub>O<sub>57</sub> in highly distorted surface on alumina [4]. The band near 990 cm<sup>-1</sup> is characteristic of the stretching modes of Mo=O and/or V=O bonds whereas the band near 370 cm<sup>-1</sup> corresponds to a molybdenum containing phase.

High-Resolution Transmission Electron Microscopy (HRTEM) can be used to directly image nanoparticles at scales approaching a single atom. The HRTEM analysis (Figure 3) of nanoscaled catalyst thermally treated in inert gas at 600°C reveal the presence of M1 (Te<sub>2</sub>M<sub>20</sub>O<sub>57</sub>; M= Mo, V, Nb) phase, as indicated by the regular particle morphologies. Inside the pentagonal rings are assumed to have Nb centers that edge-share oxygen with adjacent Mo sites; these Mo sites connect to one another by corner-sharing oxygen of the octahedral suggesting that Te and Nb are highly important for the structural order in M1 phase [5].

The results show that the rutile and M1 active phases for propane partial oxidation reaction have been prepared on the alumina support. Activity results (Table 1) confirm that higher loading sample (12Mo<sub>5</sub>V<sub>4</sub>Nb<sub>0.5</sub>Te<sub>0.5</sub>) presents higher conversion and higher acrylic acid selectivity than the bulk counterpart. Thus, a cheaper catalyst that performs better than the corresponding bulk material can be obtained by the use of nanoscaled catalysts.

Table 1. Catalytic results obtained in the propane partial oxidation reaction, AA sel. to Acrylic acid, and ACR to acrolein.

Reaction conditions: total flow 40 ml/min feed gas (% vol) C<sub>3</sub>/O<sub>2</sub>/H<sub>2</sub>O/He = 12.5/20.4/15.9/51.2, 200 mg, GHSV = 4800 h<sup>-1</sup>, T = 400°C.

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	% Conversion	% S <sub>AA</sub>	% S <sub>ACR</sub>	% S <sub>C<sub>3</sub>H<sub>6</sub></sub>	% S <sub>COx</sub>	% Y <sub>AA</sub>
γ-Al <sub>2</sub> O <sub>3</sub>	193	6.0	0	0	30.0	70.0	0
MoVNbTe rutile	26	32.1	50.2	6.3	20.2	23.3	16.1
4Mo <sub>5</sub> V <sub>4</sub> Nb <sub>0.5</sub> Te <sub>0.5</sub>	159	27.5	37.0	20.5	30.7	11.3	10.2
12Mo <sub>5</sub> V <sub>4</sub> Nb <sub>0.5</sub> Te <sub>0.5</sub>	74	51.0	44.7	9.5	12.4	31.5	22.8

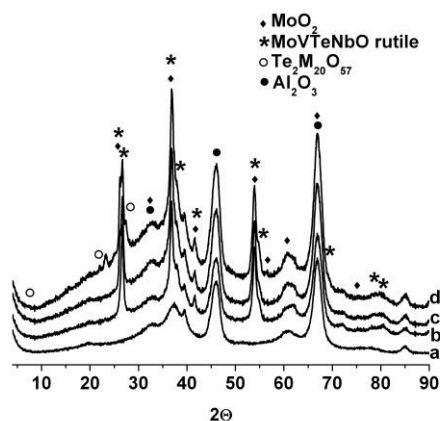


Figure 1. XRD of a) γ-Al<sub>2</sub>O<sub>3</sub> support, b) nanoscaled MVNbTeO rutile-type phase, and c) 4Mo<sub>5</sub>V<sub>4</sub>Nb<sub>0.5</sub>Te<sub>0.5</sub>, d) 12Mo<sub>5</sub>V<sub>4</sub>Nb<sub>0.5</sub>Te<sub>0.5</sub> supported catalysts.

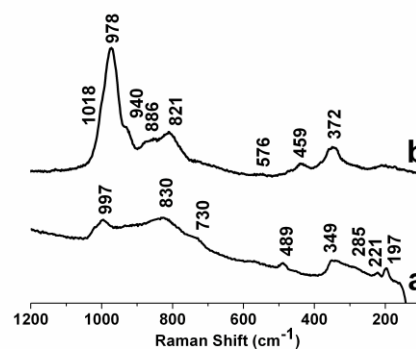


Figure 2. In situ Raman spectra under dehydrated conditions of a) 4Mo<sub>5</sub>V<sub>4</sub>Nb<sub>0.5</sub>Te<sub>0.5</sub>, and b) 12Mo<sub>5</sub>V<sub>4</sub>Nb<sub>0.5</sub>Te<sub>0.5</sub> supported catalysts.

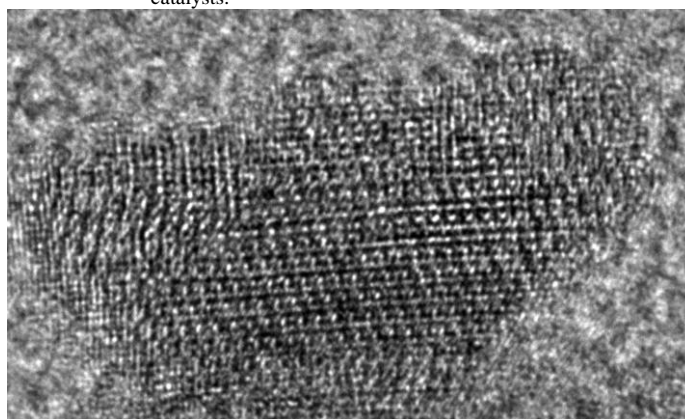
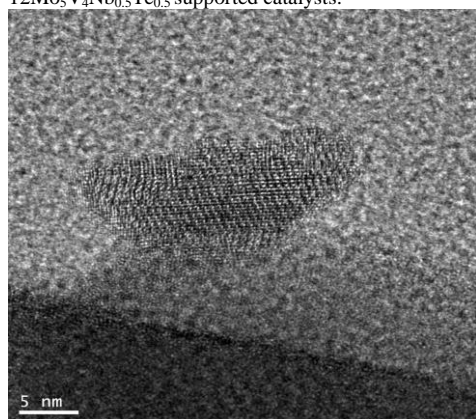


Figure 1. High Resolution TEM images showing the projection of the distorted M1 phase supported with occupied heptagonal channels for Nb cations in 12Mo<sub>5</sub>V<sub>4</sub>Nb<sub>0.5</sub>Te<sub>0.5</sub> catalyst.

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