In situ XRD studies of the effect of catalyst pre-treatment strategies on the bulk structure and performance of Mo-V-Te-Nb catalysts for selective oxidation of propane.

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INTRODUCTION

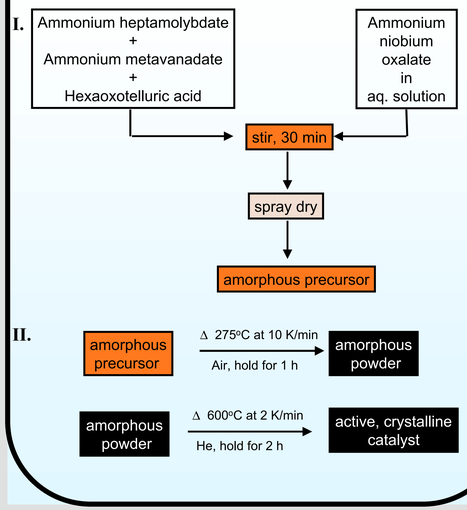
The dominant industrial process for producing acrylic acid is the selective oxidation of propylene, in two steps via acrolein, using molecular oxygen over molybdenum based multi-component oxide catalysts. Current research efforts are concentrated towards utilizing propane, rather than propylene, as the feedstock in this process because of its abundant availability and significant lower price. The discovery of the Mo-V-Te-Nb family of mixed metal oxide catalysts has brought this goal within sight.[1] Ushikubo et al have patented a catalyst composition of $MoV_{0.3}Te_{0.23}Nb_{0.125}O_x$ which is capable of acrylic acid yields as high as 50% from propane. [2]

OBJECTIVE

- The active catalyst consists mainly of two crystalline phases: the orthorhombic – M1 phase, and the pseudo – hexagonal – M2 phase.
- The catalyst synthesis is done via a slurry method using water - soluble salt precursors of the constituent elements, followed by heat treatment of the precipitate that is formed.
- The structure formation mechanism in the slurry phase has been extensively investigated using *in situ* Raman techniques. However the product precipitate is amorphous and the actual crystallization occurs only during the heat treatment step.
- This poster attempts to study this active catalyst structure formation mechanism using *in situ* XRD, in order to control the phase formation.

EXPERIMENTAL

The catalyst synthesis was done in two steps using the slurry method. [3]

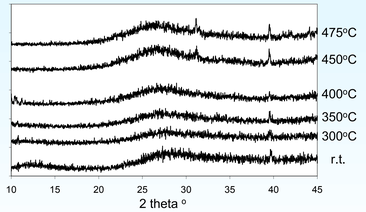


EXPERIMENTAL (CONTD.)

- *In situ* XRD analysis was performed during this heat treatment steps using an Anton-Paar HTK 16 High Temperature Camera mounted on a Bruker D8 ADVANCE diffractometer.
- Using CuKα radiation, with a wavelength of 1.542 Å, XRD scans were performed continuously in a range of 5° - 40° 2θ (step width 0.02°, counting time 0.75 s/step)

RESULTS

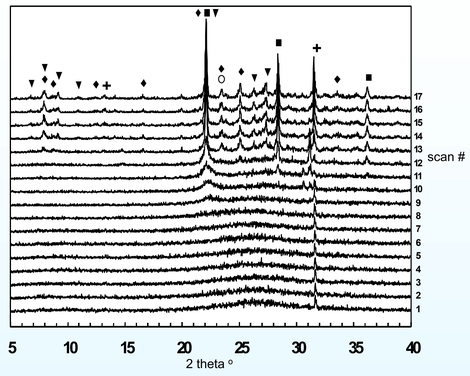
Isothermal XRD scans during heat treatment in **vacuum** – 25°C to 475°C at 2 K/min



- Crystalline peaks are not observed until 450°C. There is some rearrangement of the broad, amorphous bumps.
- These results are corroborated by TEM observations, which do not show any crystallites until 450°C.

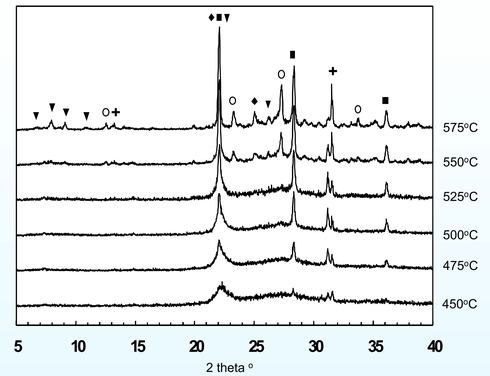
RESULTS

In situ XRD scans during heat treatment in He – 25°C to 600°C at 2 K/min



Scan #	Temperature range [°C]
1-7	25-351
8	351-397
9	397-444
11	490-537
12	537-583
13	583-600
14	600

Isothermal XRD scans during heat treatment in He – 25°C to 600°C at 2 K/min



Legend	Phase
▼	M1 - orthorhombic
■	M2 – pseudo-hexagonal
♦	M_5O_{14} (M = Mo,V,Nb)
○	MoO_3
+	Pt_xTe_y – formed by alloying with the Pt sample holder

CONCLUSIONS

- Phase crystallization is initiated at 425°C, which is much lower than the final heat treatment temperature of 600°C.
- Phase formation starts with stacking of the octahedral MO_6 building blocks in the 001 direction. The *c* parameter is similar for both the orthorhombic M1 as well as the pseudo – hexagonal M2 phase, and other minor MoO_x phases.
- This is followed by the formation of the pseudo – hexagonal M2 phase at 475°C, as seen by XRD peaks at 28.4° and 36.2° 2θ. The crystallinity increased with increasing temperature, as seen from the rise in peak intensities.
- The orthorhombic M1 phase starts to develop much later at 550°C. This phase is accompanied by other minor phases like M_5O_{14} (M = Mo,V,Nb) and MoO_3.
- No decrease was observed in the M2 peak intensity during M1 formation. Also, holding the precursor at lower temperatures for prolonged periods followed by increasing the temperature to 600°C still results in formation of M1. This indicates the presence of different seed materials for the two active phases.

REFERENCES

1. M. M. Lin, Appl. Catal. A: General, 207 (2001) 1.
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3. T. Ushikubu, I. Sawaki, K. Oshima, K. Inumaru, S. Kobayakawa, K. Kiyono, US Patent 005422328A (1995).

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