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 significantly lower price. The discovery of the Mo-V-Te-Nb family of mixed metal oxide catalysts has brought this goal within sight. Ushikubo et al. have patented a catalyst composition of MoVxTe3+y/2NbOy (M = Mo, V, Nb) which is capable of acrylic acid yields as high as 50% from propane.

EXPERIMENTAL

The catalyst synthesis was done in two steps using the slurry method.12

Ammonium heptamolybdate
Ammonium metavanadate
Hexametaphosphate

• No decrease was observed in the M2 peak intensity during M1 formation. Also, holding the precursor at lower temperatures for prolonged periods.

• The orthorhombic M1 phase starts to develop much later at 550 °C.

• Phase formation starts with stacking of the octahedral MoO6 layers, which are similar for both the orthorhombic M1 as well as the pseudo – hexagonal M2 phase.

• 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 MoO2 (M = Mo,V,Nb) and Mo2O5.

• 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.

RESULTS

Isothermal 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
10 444-490
11 490-537
12 537-583
13 583-600
14 600

In situ XRD scans during heat treatment in He – 25°C to 475°C at 2 K/min

• 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 crystallisation 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.

REFERENCES


EXPERIMENTAL (CONTD.)

A. 270°C at 10 K/min
B. 300°C at 2 K/min
C. 583-600°C
D. 600°C

• Active catalyst consists mainly of two crystalline phases: the orthorhombic – M1 phase, and the pseudo – hexagonal – M2 phase.

• These results are corroborated by TEM observations, which do not show any crystallites until 450°C.

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 MoO6 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 MoO2 phases.

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