

Novel Mo-V Based Mixed Oxide Catalysts for Propane Ammoxidation

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Introduction

The most important method for the current production of acrylonitrile is the ammoxidation of propylene. Since propane is a cheaper and more abundant raw material, it is of great commercial interest to replace propylene by propane. MoVTeNbO mixed oxide is reported to be a promising catalyst for this reaction [1-3]. This catalyst system may contain several phases, while, the most important phases in terms of catalytic activity are orthorhombic, known as M1 and pseudo-hexagonal, known as M2. However, the performance of this catalyst in propane ammoxidation is still insufficient to compete with commercial propylene ammoxidation process. These catalysts further suffer from limited thermal stability due to the volatility of tellurium. Therefore, it is of interest to investigate the effect of introducing other metals in the M1 and M2 structures that are expected to improve the thermal stability of these mixed metal oxides without compromising the catalytic performance of this system in propane ammoxidation. In this study, we investigated the effects of Fe and Te substitution into the Mo-V-O lattice on its stability and catalytic behavior.

Materials and Methods

The hydrothermal synthesis of mixed oxides was conducted in a static autoclave at 448 K according to a reported procedure [4]. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, hydrated VOSO_4 , TeO_2 were used as precursors for Mo, V and Te. Ammonium Iron(II) sulfate and Iron (III) sulfate were used as Fe source. Hydrothermal synthesis was conducted at 448 K. After hydrothermal treatment, the product was filtered, washed with H_2O and dried overnight in air at 363 K. This catalyst precursor was calcined in a tubular furnace under ultra pure N_2 at 773 K for 2h and characterized by powder X-ray diffraction.

Results and Discussion

The XRD patterns of the three component Mo-V-Fe- O_x system synthesized using Ammonium Iron (II) sulfate as Fe source and calcined at 773 K corresponded to that of M1 phase (Figure 1). However, the crystallinity was lower than that of the three component Mo-V-Te- O_x system. The XRD patterns of four component $\text{Mo}_1\text{V}_{0.45}\text{Te}_{0.11}\text{Fe}_{0.04}\text{O}_x$ and $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.11}\text{Fe}_{0.09}\text{O}_x$ catalysts synthesized using Ammonium Iron (II) sulfate as the Fe source and calcined at 773 K showed peaks corresponding to the pure and well-crystallized M1 phase (Figure 2). These results indicated that the M1 phase can be still obtained by introducing Fe in the synthesis. However, the solid products synthesized using Iron (III) sulfate as an Fe source and calcined under the same conditions were not phase pure (M1 or M2) indicating the significant influence of Fe source (results not shown here). The results of propane ammoxidation reaction indicate that the catalysts are active for this reaction and the optimum activity is observed at 673 K. The selectivity to acrylonitrile increases and that to propylene decreases with temperature. At 693K, the acrylonitrile selectivity of 41% is observed at 15% conversion indicating that the Fe-containing catalysts were more active and selective to acrylonitrile than the Mo-V-O M1 catalyst.

Significance

Acrylonitrile is one of the most important bulk chemicals and more than 5 billion kg/year of acrylonitrile are produced world wide using the SOHIO/BP process [1]. Replacing the olefin feed (propylene) with the more abundant and less expensive propane would provide a significant economic advantage for the production of acrylonitrile. Our work addresses the urgent need to develop suitable catalysts that possess high activity, selectivity and stability for this transformation.

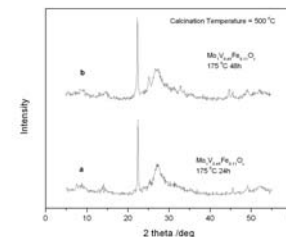


Figure 1. XRD patterns of $\text{Mo}_1\text{V}_{0.49}\text{Fe}_{0.11}\text{O}_x$ catalyst calcined at 773 K under ultra pure N_2 (a) Hydrothermal synthesis at 175 °C for 24 h and (b) Hydrothermal synthesis at 175 °C for 48 h.

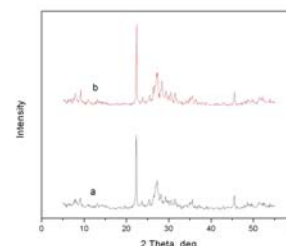


Figure 2. XRD patterns of (a) $\text{Mo}_1\text{V}_{0.45}\text{Te}_{0.11}\text{Fe}_{0.04}\text{O}_x$ and (b) $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.11}\text{Fe}_{0.09}\text{O}_x$ catalysts calcined under ultra pure N_2 at 773 K.

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