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## Preparation, Characterization and Catalytic Test of MoVSb and MoVNb Mixed Oxide Catalysts for Propane Ammoxidation to Acrylonitrile

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**Abstract:** MoVSb and MoVNb mixed oxide catalysts were prepared using reflux method for the propane ammoxidation reaction to acrylonitrile. These catalysts were characterized using N<sub>2</sub> physisorption (BET), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and catalytic tests. The catalytic testing shows that the MoVSbO catalyst has higher selectivity to ACN but lower conversion of propane as compared to MoVNbO catalyst.

**Key words:** MoV mixed oxide catalyst, reflux method, propane ammoxidation, acrylonitrile

### INTRODUCTION

Interests in the production of acrylonitrile using propane as an alternative feed gas have motivated the development of new catalytic processes. The search for new propane ammoxidation catalysts has, so far, been rather empirical. The catalysts described in the literature contain elements having paraffin activating properties (e.g., V), olefin activating (e.g., Bi, Te) and O and/or NH inserting properties (e.g., Sb, Mo) Hamid *et al.* (2001), Grasselli (1999). The addition of niobium oxide to a mixture of molybdenum and vanadium oxides was found to improve the activity and selectivity for oxidation, ammoxidation and oxidative dehydrogenation reactions (Chary *et al.*, 2003). A rational catalyst design which can improve paraffin ammoxidation system should be able to keep the concentration of the propylene intermediate low during the process as to prevent its destruction by the paraffin activating catalyst. Therefore, in this study, the characterization and catalytic performance of the MoVSb and MoVNb mixed metal oxide catalysts were studied.

### MATERIALS AND METHODS

**Catalyst preparation:** MoVSb mixed metal oxide catalyst were prepared by reflux method. Sb<sub>2</sub>O<sub>3</sub> (Acros Organics, 99.8%) was dispersed in oxalic acid aqueous solution and stirred for 30 min. Then, hot aqueous solution of NH<sub>4</sub>VO<sub>3</sub> (Fluka, 99%) and (NH<sub>4</sub>)<sub>3</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Fluka, 99%) was added to the mixture containing Sb<sub>2</sub>O<sub>3</sub> and oxalic acid. The

mixture was reflux for 24 h. The resulting mixture was dried for 15 h at 120°C, ground into fine powder and later calcined in air at 350-600°C for a total of 10 h.

The same method was applied to prepare MoVNb mixed metal oxide catalyst, where Nb<sub>2</sub>O<sub>5</sub> (Acros Organics, 99.8%) was used in this preparation.

**Catalyst characterization:** Specific surface area measurement of the catalysts was determined by N<sub>2</sub> adsorption-desorption on a Thermo Finnigan Sorptomatic instrument. The X-ray diffraction (XRD) was carried out on Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation with a scanning range (2 $\theta$ ) from 20 to 60°. The morphology of the catalysts was studied by Scanning Electron Microscope (SEM) at magnification of 5000x. The samples were coated with platinum using a sputter coater.

**Catalytic performance test:** Propane ammoxidation reaction was carried out at 420°C and atmospheric pressure in a fixed bed reactor with an on-line Gas Chromatography (GC). The powdered catalysts were pelletized and crushed into 212-425  $\mu$ m size. 0.5 g catalyst was loaded to the quartz reactor with feed composition (vol. %) of 5.8 C<sub>3</sub>H<sub>8</sub>, 7.0 NH<sub>3</sub>, 17.4 O<sub>2</sub> and 69.8 He to give a total flow rate of 120 cm<sup>3</sup> min<sup>-1</sup>.

### RESULTS AND DISCUSSION

**Catalyst characterization:** The MoVSb and MoVNb mixed oxide catalysts prepared were characterized for their physicochemical properties using BET, XRD and SEM.

The nitrogen adsorption-desorption isotherms for both calcined catalysts showed type IV isotherm with a hysteresis loop of type B. The type IV isotherm is a characteristic of mesoporous solids with pore diameters between 2-50 nm. Type B hysteresis loop is a characteristic given by materials with open slit shaped capillary pores (Bond, 1987; Thomas and Thomas, 1967).

The MoVSb catalyst showed a lower BET surface area and smaller pore size as compared to MoVNB catalyst (Table 1). In this case, the atomic radius of the promoter plays an important role. The atomic radius of Sb and Nb were 0.159 and 0.146 nm. It is believed that Sb was deposited onto the opening of the pores but such deposition also leads to closing of some pores opening resulting in the reduction of the surface area.

XRD diffractogram of MoVSb mixed metal oxide catalyst is shown in Fig. 1a and b. The XRD pattern

shows that the solids are in crystalline phase with the presence of two different phases as intense and sharp diffraction patterns. The monoclinic VSbO<sub>4</sub> phase is present at 2θ = 22.0°, 25.3°, 28.4°, 29.5°, 30.0° and 33.3° as the principal phase in the catalyst. The formation of VSbO<sub>4</sub> phase is believed to occur during calcinations temperature range in between 400-500°C (Irmawati *et al.*, 2004).

The catalyst also exhibits the diffraction pattern of orthorhombic Sb<sub>2</sub>Mo<sub>10</sub>O<sub>31</sub> phase at 2θ = 22.0°, 26.8°, 28.5° and 30.6°. The crystal structure of Sb<sub>2</sub>Mo<sub>10</sub>O<sub>31</sub> phase is related to hexagonal tungsten bronzes, where the

Table 1: Textural properties of MoVSb and MoVNB mixed metal oxide catalysts

Catalysts	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Average pore size (nm)
MoVSb	0.93	2.02
MoVNB	4.90	3.31

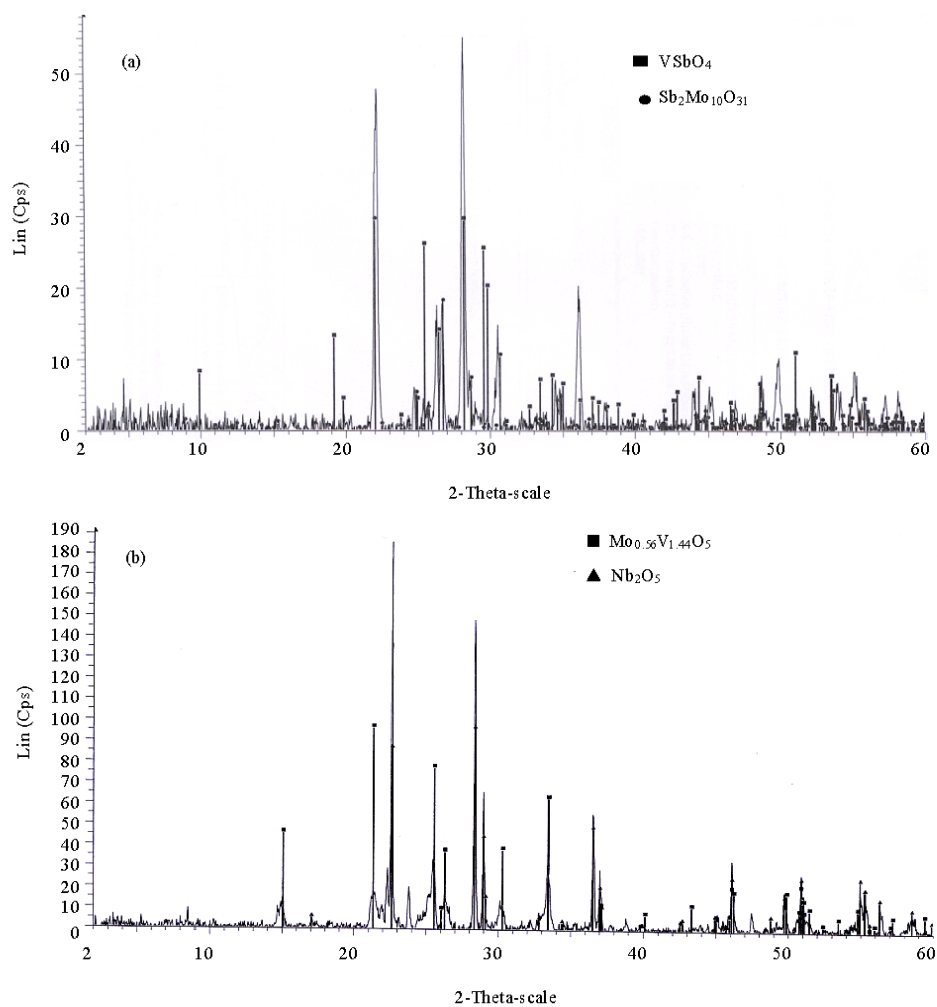


Fig. 1: X-ray diffraction for (a) MoVSb (b) MoVNB mixed metal oxide catalysts

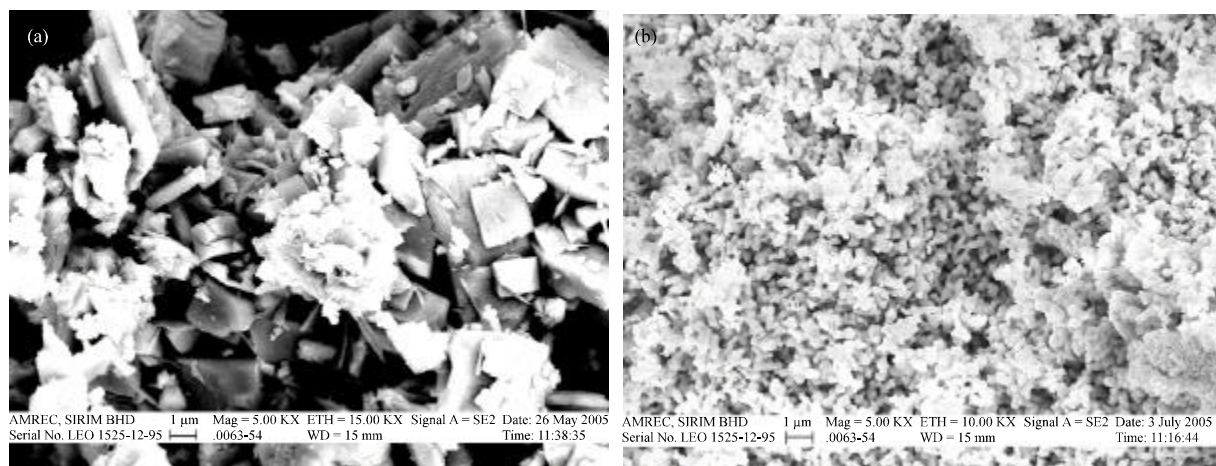


Fig. 2: SEM images of (a) MoVSb and (b) MoVNb mixed metal oxides catalysts

antimony atoms are being accommodated in hexagonal tunnels (Parmentier *et al.*, 1980). This must have resulted from the high temperature treatment during calcination process.

On the other hand, the sharp diffraction patterns of monoclinic  $\text{Mo}_{0.56}\text{V}_{1.44}\text{O}_5$  ( $2\theta = 15.0^\circ, 21.2^\circ, 25.5^\circ, 26.1^\circ, 30.1^\circ$  and  $33.5^\circ$ ) and orthorhombic  $\text{Nb}_2\text{O}_5$  ( $2\theta = 22.8^\circ, 28.2^\circ, 29.0^\circ, 36.5^\circ, 37.0^\circ$  and  $46.0^\circ$ ) phases are observed in MoVNb catalyst as shown in Fig. 1b. According to Nowak and Ziolk (1999),  $\text{Nb}_2\text{O}_5$  begins to crystallize into TT or T phases at calcinations temperatures of  $500^\circ\text{C}$ . At  $800^\circ\text{C}$ , the M or B phase forms and at  $1000^\circ\text{C}$  and above, the H phase of  $\text{Nb}_2\text{O}_5$  are observed. In the present study, the samples were calcined at  $600^\circ\text{C}$ , therefore TT or T phase of  $\text{Nb}_2\text{O}_5$  were observed. These XRD results are in agreement with the study of Smits *et al.* (1993) as they have also observed TT-  $\text{Nb}_2\text{O}_5$  phase for  $\text{V}_2\text{O}_5/\text{Nb}_2\text{O}_5$  catalyst calcined at  $600^\circ\text{C}$ . The TT or T phases of  $\text{Nb}_2\text{O}_5$  have long been thought to be the same due to their similar X-ray diffraction patterns (Nowak and Ziolk, 1999).

Figure 2a and b show the SEM micrographs of the MoVSb and MoVNb catalysts at 5 kx magnification. The SEM micrograph image of MoVSb catalyst displays a slab-like structure with sharp edges. On the other hand, the SEM image of MoVNb catalyst shows the presence of agglomerates. Both solids are in crystalline phase as observed from XRD diffractograms. It can be noticed that the MoVSb catalyst consists of big, non-uniform size and shape as compared to MoVNb catalyst. This is due to the calcined catalyst containing niobium become very fine crystals with homogeneous distribution of particle size and shape (Vitry *et al.*, 2003).

**Catalytic performance test:** Figure 3 shows a significant difference in the conversion of propane and its selectivity to ACN shown by the MoVSb and MoVNb

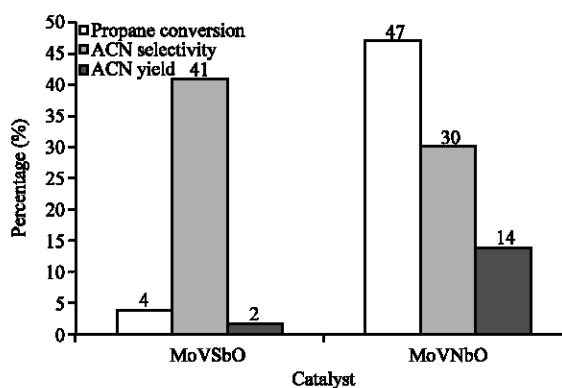


Fig. 3: MoVSb and MoVNb catalysts performance in the propane ammoxidation reaction to ACN

catalysts in the ammoxidation reaction of propane at  $420^\circ\text{C}$ . The MoVSb catalyst showed a higher selectivity to ACN but lower conversion of propane compare to MoVNb catalyst. Despite the small surface area of MoVSb catalyst, the  $\text{VSbO}_4$  phase that exists in the MoVSb catalyst has shown to be the active phase for NH insertion which favours the selectivity to ACN. Isolation and dispersion of the vanadium site at the surface of this phase has been recognized as the key factor required for achieving high activity and most important high ACN selectivity (Roussel *et al.*, 2002). Moreover, Asakura *et al.* (2000) reported that  $\text{Nb}_2\text{O}_5$  is selective for the dehydrogenation reaction of propane to propene where the addition of  $\text{Nb}_2\text{O}_5$  to MoV oxide catalyst increased the selectivity to ethene in the oxidative dehydrogenation of ethane.

From the results, it is clear that the yield to ACN is controlled by the existence of certain crystalline structures for simultaneous propane activation and NH

insertion leading to formation of ACN. In order to achieve high yield to ACN, sufficiently high propane conversion is necessary to benefit from high selectivity to ACN. It is suggested that higher propane conversion may be achieved using catalyst with high surface area as shown by MoVNb catalyst. Once the propane is converted, then the NH insertion mechanism will take place on the VSbO<sub>4</sub> phase leading to formation of ACN.

### CONCLUSION

The reflux preparation method leads to a crystalline structure in the MoVSb and MoVNb catalysts as determined by XRD and SEM. The existence of VSbO<sub>4</sub> phase in the MoVSb catalyst has shown to be the active phase for NH insertion, thus the MoVSb catalyst showed a higher selectivity to ACN.

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