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Preparation, Characterization and Catalytic Test of MoVSB and MoVNB Mixed Oxide Catalysts for Propane Ammonoxidation to Acrylonitrile

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Abstract: MoVSB and MoVNB mixed oxide catalysts were prepared using reflux method for the propane ammonoxidation reaction to acrylonitrile. These catalysts were characterized using N2 physisorption (BET), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and catalytic tests. The catalytic testing shows that the MoVSB0 catalyst has higher selectivity to ACN but lower conversion of propane as compared to MoVNB0 catalyst.

Key words: MoV mixed oxide catalyst, reflux method, propane ammonoxidation, 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 ammonoxidation 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, ammonoxidation and oxidative dehydrogenation reactions (Chary et al., 2003). A rational catalyst design which can improve paraffin ammonoxidation 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. Sb2O3 (Acros Organics, 99.8%) was dispersed in oxalic acid aqueous solution and stirred for 30 min. Then, hot aqueous solution of NH4VO3 (Fluka, 99%) and (NH4)2MoO4·4H2O (Fluka, 99%) was added to the mixture containing Sb2O3 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 Nb2O5 (Acros Organics, 99.8%) was used in this preparation.

Catalyst characterization: Specific surface area measurement of the catalysts was determined by N2 adsorption-desorption on a Thermo Finnigan Sorptomatic instrument. The X-ray diffraction (XRD) was carried out on Bruker D8 Advance diffractometer using Cu Kα radiation with a scanning range (2θ) from 20 to 60°. The morphology of the catalysts was studied by Scanning Electron Microscope (SEM) at a magnification of 5000X. The samples were coated with platinum using a sputter coater.

Catalytic performance test: Propane ammonoxidation 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 μm size. 0.5 g catalyst was loaded to the quartz reactor with feed composition (vol. %) of 5.8 C3H8, 7.0 NH3, 17.4 O2 and 69.8 He to give a total flow rate of 120 cm3 min⁻¹.

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 V$_2$O$_5$ phase is present at 2$\theta$ = 22.0°, 25.3°, 28.4°, 29.5°, 30.0° and 33.3° as the principal phase in the catalyst. The formation of V$_2$O$_5$ 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$_2$Mo$_{6}$$\delta$O$_{31}$ phase at 2$\theta$ = 22.0°, 26.8°, 28.5° and 30.6°. The crystal structure of Sb$_2$Mo$_{6}$$\delta$O$_{31}$ phase is related to hexagonal tungsten bronzes, where the

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoVSb</td>
<td>0.93</td>
<td>2.02</td>
</tr>
<tr>
<td>MoVNb</td>
<td>4.99</td>
<td>3.31</td>
</tr>
</tbody>
</table>

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

![X-ray diffraction for (a) MoVSb (b) MoVNb mixed metal oxide catalysts](image_url)

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

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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 MoSbO\textsubscript{5}V\textsubscript{1-x}O\textsubscript{2} (2θ = 15.0°, 21.2°, 25.5°, 26.1°, 30.1° and 33.5°) and orthorhombic Nb\textsubscript{2}O\textsubscript{5} (2θ = 22.8°, 28.2°, 29.0°, 36.5°, 37.0° and 46.0°) phases are observed in MoVNb catalyst as shown in Fig. 1b. According to Nowak and Ziolek (1999), Nb\textsubscript{2}O\textsubscript{5} begins to crystallize into TT or T phases at calcinations temperatures of 500°C. At 800°C, the M or B phase forms and at 1000°C and above, the H phase of Nb\textsubscript{2}O\textsubscript{5} is observed. In the present study, the samples were calcined at 600°C, therefore TT or T phase of Nb\textsubscript{2}O\textsubscript{5} were observed. These XRD results are in agreement with the study of Smits et al. (1993) as they have also observed TT- Nb\textsubscript{2}O\textsubscript{5} phase for V\textsubscript{1-x}O\textsubscript{2} catalyst calcined at 600°C. The TT or T phases of Nb\textsubscript{2}O\textsubscript{5} have long been thought to be the same due to their similar X-ray diffraction patterns (Nowak and Ziolek, 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 catalysts in the ammoxidation reaction of propane at 420°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 VSiO\textsubscript{2} 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 Nb\textsubscript{2}O\textsubscript{5} is selective for the dehydrogenation reaction of propane to propene where the addition of Nb\textsubscript{2}O\textsubscript{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 takes place on the VSB0 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 VSB0, 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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