THE EFFECT OF SUPPORT ON THE ACTIVITY AND SELECTIVITY OF MoVNbTe CATALYST FOR PROPANE AMMoxidATION REACTION

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Abstract
MoVNbTe catalyst has been prepared using slurry method for the ammoxidation of propane to acrylonitrile (ACN). To study the effect of support on the catalytic activity of this catalyst, 10% (wt/wt) of MoVNbTe was loaded to silica (SiO2), alumina (Al2O3) and magnesia (MgO) via incipient wetness impregnation method. All MoVNbTe catalysts were calcined in air at 350-600 °C for a total of 10 h. The textural, morphological and microstructural characteristics of these catalysts were determined using scanning electron microscopy, X-ray Diffraction (XRD) and physical adsorption of Nitrogen gas. The catalytic activity of all catalysts was tested using a fixed-bed reactor with online GC at 420 °C. Results show that the physicochemical properties of these catalysts are greatly influenced by the support used.

Introduction
Acrylonitrile (ACN) is an important intermediate for the preparation of fibers, synthetic resins, synthetic rubbers, etc. Presently, ACN is produced by ammoxidation of propene in a fluidized-bed reactors using mixed metal oxide catalysts. The lower price of propane relative to propene has since long provided an incentive for the development of a process for the direct conversion of propane to ACN [1]. High yields of ACN from propane have been reported on a Mo-V-Te-Nb catalyst since the early 1990s. However, neither catalyst has been commercialised. Apparently, the new propane ammoxidation processes have yet to be successful in challenging the existing commercial process, which utilizes propylene as the starting material and is very efficient [2].

Mo-V-Nb-Te-O mixed metal oxide catalysts have been proposed in the last years as the most active and selective in the ammoxidation of propane to ACN, the selective oxidation of propane to acrylic acid and in the oxidative dehydrogenation of ethane to ethylene. The presence of Te-containing crystalline phases has been suggested to facilitates the selective reactions from propylene, favouring the formation of acrylic acid or ACN during the oxidation of propane [3]. This catalyst have high activities for the production of ACN and achieved 50-60% ACN yields at relatively low reaction temperature. It was emphasized that a specific crystal structure is effective for the propane ammoxidation. Oshihara et al. [4] suggested that structural arrangement of active sites is quite important to achieve selective oxidation. Selective oxidation pathway from alkenes to desired oxygenates may consist of many reaction step, for example dehydrogenation, oxygen insertion, hydration and so on. These reactions should occur quickly and sequentially to avoid undesired oxidation to COx because intermediate products are generally more reactive than alkenes. In order to achieve the quick sequential reaction, catalytically active elements for the reaction should be place geometrically near to each others. If a
surface near matrix having ordered active sites on catalysts could be constructed, high activity and selectivity can be expected. In this sense, well crystallined mixed oxides are the candidates for active and selective catalysts for alkane oxidation.

The MoVNbTeO$_x$ catalytic system comprises of three crystalline phases, normally orthorhombic Mo$_{7.5}$V$_{1.5}$NbTeO$_{29}$ (M1), pseudo-hexagonal Mo$_{4.67}$V$_{1.33}$Te$_{1.82}$O$_{19.82}$ (M2) and a trace of monoclinic TeMo$_5$O$_{16}$ which are formed during calcinations under N$_2$. The orthorhombic structure is reported to have 3 dimensionally complex structures with 5, 6 and 7 membered rings units composed of an arrangement of MO$_6$ octahedra and MO$_7$ pentagonal bipyramids (M=Mo,V,Nb) that is isotopic with Cu-Nb-O-X (X=Cl, Br, I) and Cs-Nb-W-O system [5].

Grasselli et al. [6] has reported that the yield of ACN in the ammoxidation of propane to ACN goes over an optimum as the Nb/Te ratio is varied. Since an essentially linear relationship exists between the amount of M1 phase and the Nb/Te ratio, the ACN yield therefore also passes over an optimum at moderate concentrations of M1 in the system. The maximum ACN yield from propane of 61.8% when 86% propane conversion and 72% ACN selectivity at 420 $^\circ$C was achieved with a nominal catalyst composition of Mo$_{0.6}$V$_{0.187}$Te$_{0.14}$Nb$_{0.085}$O$_x$, identified by combinatorial methodology, comprised of 60% Mo$_{7.5}$V$_{1.5}$NbTeO$_{29}$ (M1), 40% Mo$_{4.67}$V$_{1.33}$Te$_{1.82}$O$_{19.82}$ (M2) and a trace of TeMo$_5$O$_{16}$.

The M1 phase is the paraffin activating phase owing to the presence of V$^{5+}$ centres. However it is also capable of transforming propane directly to ACN, since it contains the remaining key ammoxidation elements at the active center and within bonding distance. The M2 phase (lacking of V$^{5+}$ centers) is incapable of converting paraffins, but is an excellent olefin ammoxidation catalyst. Thus when the two phases are in close (nano-scale) contact under reaction conditions, they can cooperate with each other where the M1 phase converting primarily the propane directly to ACN while the M2 phase converts any unconverted propylene generated on the M1 phase to ACN. In this manner the M2 phase is the co-catalyst or mop-up phase, catalytically assisting the M1 phase [6].

In this paper, the effect of SiO$_2$, MgO and Al$_2$O$_3$ as support for the MoVNbTe catalyst was studied. Loading of MoVNbTe to support is thought to improve the physical properties and its catalytic performance in ammoxidation reaction.

### Experimental

#### Catalyst Preparation

The unsupported catalyst was prepared by dissolving ammonium metavanadate (R&M, AR) in sulfuric acid (R&M, AR) and added to a solution containing ammonium molybdate (R&M, AR), ammonium niobium oxalate (R&M, AR) and telluric acid (Fischer, AR). Then resulting mixture was drying for 17 h at 120 $^\circ$C before it was calcined in air at 350 $^\circ$C for 4 h and 600 $^\circ$C for 6 h.

10% (w/w) MoVNbTe catalyst was supported on SiO$_2$ (Scintran, AR), Al$_2$O$_3$ (Aldrich, AR) and MgO (Fluka, 97%) using incipient wetness impregnation method. Ammonium metavanadate (R&M, AR), ammonium molybdate (R&M, AR) and oxalic acid (Fisher, AR) was dissolved in a required amount of deionised water and added to a solution containing ammonium niobium oxalate (R&M, AR) and telluric acid (Fischer, AR). The support was then added to the solution and left to stand for 2 h. The impregnated samples were dried at 120 $^\circ$C for 17 h and later calcined in air at 350-600 $^\circ$C for total of 10 h.

#### Catalyst Characterization

The surface area determination was carried out following a BET procedure using nitrogen gas in a Micrometics ASAP-2010. The X-ray powder diffraction data were recorded on a Bruker DS Advance diffractometer using a Cu Ka radiation with the scanning angles (2$\theta$) from 2$^\circ$ to 80$^\circ$ at room temperature. The morphology of the catalysts was studied by Scanning Electron Microscope (SEM) using LEO 1530 EFSEM at magnification of 10 kx where the samples were coated with platinum using a Sputter Coater.

#### Catalytic Activity Test

Activity measurements were performed using a conventional plug flow fixed-bed reactor with on-line gas chromatography at atmospheric pressure. The correctness of the analytical determinations was checked by carbon balance (based on propane converted). The tests were made using 0.5 g sample with particle size of 212-
The feed gas molar ratio are 5.8% propane, 7.0% ammonia, 17.4% oxygen and 69.8% helium with temperature reaction at 420 °C. The total flow rate was 120 ml min⁻¹ corresponding to a gas-space velocity (GHSV) of about 1200 h⁻¹.

Results and Discussion

Scanning Electron Microscopy (SEM)

The SEM images of the catalysts were observed at 10 000 magnification and they shows the presence of agglomerate morphology. The unsupported catalyst (Figure 1a) give aggregates of small cylinder-shaped crystallites system with about 300-500 nm length. However, the supported catalysts (Figure 1b-d) give a variable shape and size morphologies where they represents the morphologies of the support itself.

BET Surface Area

The specific surface area of all catalysts as determined by N₂ physisorption is presented in Table 1 where unsupported MoVNbTe catalyst has a very low surface area (1.55 m²g⁻¹). From SEM micrograph (Figure 1a) it can be seen that only limited number of pores exists within the catalyst system, therefore the total surface area is low. The surface area of the supported catalysts are higher than that of unsupported catalyst. The higher surface area in the supported catalysts are predominantly given by the characteristic of the supports which have surface areas in the range of 39.21-200 m²g⁻¹. However, the surface areas of the support reduced significantly when MoVNbTe was loaded into them. The surface area of the MgO are 39.21 m²g⁻¹. When 10% (w/w) of MoVNbTe was loaded onto the MgO, the surface area decreased to 25.42 m²g⁻¹. These show that the metal oxides loaded have been deposited onto the surface. The surface area of the SiO₂ support are 200.00 m²g⁻¹. When 10% (w/w) MoVNbTe was loaded onto the SiO₂, the surface area of the catalyst reduced significantly to 13.13 m²g⁻¹. SEM micrograph of the MoVNbTe/SiO₂ catalyst (Figure 1c) shows the existence of many small crystallites which looks like honeycomb structure.

The surface area and average pore size of Al₂O₃ support are 176.70 m²g⁻¹ and 4.15 nm, respectively. However, loading of 10% (w/w) MoVNbTe onto the pores significantly reduced the surface area of the catalyst to 76.61 m²g⁻¹ while the average pore size increased to 5.20 nm. SEM micrograph of the catalyst (Figure 1d) shows that the catalyst is in the form of big aggregate suggesting that some of the pores have collapsed forming that surfaces with bigger average pore size.
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Table 1 BET Surface area (m² g⁻¹) of the samples with different supported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoVNbTeO₅</td>
<td>1.55</td>
<td>-</td>
</tr>
<tr>
<td>MoVNbTe/MgO</td>
<td>25.42</td>
<td>-</td>
</tr>
<tr>
<td>MoVNbTe/SiO₂</td>
<td>13.13</td>
<td>-</td>
</tr>
<tr>
<td>MoVNbTe/Al₂O₃</td>
<td>76.61</td>
<td>5.19</td>
</tr>
<tr>
<td>MgO</td>
<td>39.21</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>213.70</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>176.60</td>
<td>4.15</td>
</tr>
</tbody>
</table>

The adsorption-desorption of these catalysts are shown in Figure 2(A–G). From the isotherm, it shows that MoVNbTe (Figure 2A), MoVNbTe/MgO (Figure 2C) and MoVNbTe/SiO₂ (Figure 2E) catalysts have a Type III adsorption-desorption curves according to IUPAC classification [8]. It shows a non-porous material which has a weak adsorbate-adsorbent interaction [9]. It also show that the support isotherm is still same after the metal was loading to the support as can be shown in Figure 2B, 2C and 2D, 2E. For MoVNbTe/Al₂O₃ catalyst has Type IV adsorption-desorption curve which is show a mesopores materials. This catalyst has hysteresis loop of Type E which has a sloping adsorption branch and a steep desorption branch [8]. It has a tubular or ink bottle pores of varying radius.
Figure 2. Adsorption-desorption isotherm of (A) MoVNbTe catalyst, (B) MgO support, (C) MoVNbTe/MgO catalyst, (D) SiO\textsubscript{2} support, (E) MoVNbTe/SiO\textsubscript{2} catalyst, (F) Al\textsubscript{2}O\textsubscript{3} and (G) MoVNbTe/Al\textsubscript{2}O\textsubscript{3} catalyst.

XRD

Figure 3a shows the diffractogram of the unsupported MoVNbTe catalysts having 3 types of crystal phases, namely tetragonal, monoclinic and hexagonal. The strong peaks appear at 2\theta value of 22.3°, 23.5°, 25.0° and 26.1° representing the tetragonal structures of (Nb\textsubscript{0.09}Mo\textsubscript{0.91})O\textsubscript{0.28} phase. The monoclinic structures of TeMo\textsubscript{5}O\textsubscript{16} was observed at 2\theta value of about 30.5°. The peaks at 2\theta of 27.0°, 28.4°, 38.5° and 48.5° are referred to the tetragonal structures of (VO)MoO\textsubscript{4} while the monoclinic structures of V\textsubscript{2}O\textsubscript{3} was observed at 2\theta of about 37° and 53.9°.

Figure 3b shows the diffractogram of MgO with very intense peak at 2\theta 36.9°, 42.5°, 62.0°, 74.3° and 78.1° owing to the crystalline phases of MgO. There are very small peaks appear at 2\theta between 26° to the 28° when MgO was loaded with 10% MoVNbTe. These peaks could be attributed to the crystalline phases of crystalline (Nb\textsubscript{0.09}Mo\textsubscript{0.91})O\textsubscript{0.28}, TeMo\textsubscript{5}O\textsubscript{16} and (VO)MoO\textsubscript{4} not properly formed (Figure 3c). Figure 3a also show that the intensities of the MgO phases were reduced significantly as a result of interferences by the metals loaded.

Figure 3d shows the diffractogram supported of the SiO\textsubscript{2} support. No crystalline phase was observed as SiO\textsubscript{2} is an amorphous material. However, there are appearance of very weak peaks in the 2\theta range of 22-24° which could be due to the formation of (Nb\textsubscript{0.09}Mo\textsubscript{0.91})O\textsubscript{0.28} nano crystallites (Figure 3e). Figure 3f and 3g show the diffractograms of Al\textsubscript{2}O\textsubscript{3} support and MoVNbTe/Al\textsubscript{2}O\textsubscript{3} respectively. There was no crystalline phase observed in both figures showing that both materials are amorphous materials.
Catalytic Performance

Figure 4 shows the propane conversion and selectivity to ACN given by each catalyst. The unsupported MoVNbTe has a very low propane conversion (1%) which could be due to the low surface area of the catalyst (1.55 m²/g), limiting the conversion of propane from taking place. However, the selectivity to ACN is quite high, owing to the existence of some crystalline phases ((Nb₀.⁰⁹Mo₀.⁹¹)O₀.⁲₈, TeMo₅O₁₆, (VO)MoO₄ and V₂O₅) required for the formation of ACN.

Introduction of a support improves the conversion of propane by two-fold to seventy-fold due to improvements in the surface area of the MoVNbTe supported catalysts enabling the reaction to occur. The magnitude of the improvements corresponds to the improvement in the surface areas of the supported catalyst (MoVNbTe/SiO₂ < MoVNbTe/MgO < MoVNbTe/Al₂O₃). However, the selectivity to ACN reduces as insufficient formation of crystalline phases within the supported catalysts. Among the supported catalysts, MoVNbTe/MgO shows a better selectivities to ACN (40%) due to the existence of the ((Nb₀.⁰⁹Mo₀.⁹¹)O₀.⁲₈), TeMo₅O₁₆ and (VO)MoO₄ phases. The selectivity reduced further in MoVNbTe/SiO₂ catalyst as only (Nb₀.⁰⁹Mo₀.⁹¹)O₀.⁲₈ nanocrystallites were present within the catalyst. The MoVNbTe/Al₂O₃ catalyst has the lowest selectivity of only 10% as there was no existence of any crystalline phase detected within the catalyst.
The MoVNbTeO\textsubscript{x} develop by Mitsubishi has been reported as the most active and selective catalyst in the ammoxidation of propane. The maximum selectivity to ACN for MoVNbTeO\textsubscript{x} is 72\% with 86\% propane conversion at 420 °C [10-12]. This result was achieved with a composition of approximately 60\% M1, 40\% M2 and a trace of TeMo\textsubscript{5}O\textsubscript{16}. From the XRD analysis, the M1 and M2 phases do not exist in this catalyst. This is why this catalyst is not give a higher conversion and selectivity. Grasselli [11] reported that the M1 phase is responsible for the paraffin activation while the M2 phase is rather ineffective for this reaction.

Watanabe and Koyasu [13] studied several methods for preparing MoVNbTeO\textsubscript{x}, mixed oxide, and found that MoVNbTeO\textsubscript{x} prepare by hydrothermal reaction method showed a good selectivity with 52\% at 91\% conversion of propane. Other products observed mainly are CO and CO\textsubscript{2}, but small amounts of acetonitrile and hydrogen cyanide were also produced.

**Conclusion**

Supporting the MoVNbTe catalyst with Al\textsubscript{2}O\textsubscript{3}, MgO and SiO\textsubscript{2} improves the surface area of the catalyst, thus increases the propane conversion. However, the introduction of these supports hindered the formation of crystalline phases required for the ammoxidation to ACN. Insufficient existence of these crystalline phases reduces the selectivity to ACN.

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