



EFFECT OF pH ON THE PHYSICOCHEMICAL PROPERTIES AND REDUCIBILITY OF MoVTenbO_x CATALYSTS

(Kesan pH Terhadap Sifat Fizikokimia dan Kebolehturunan Mangkin MoVTenbO_x)

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Abstract

A range of MoVTenbO_x catalysts were synthesised by slurry method assisted with a microwave irradiation. The pH of the synthesis solution was varied at pH = 1, 3, 5, and 7 and the obtained solid were calcined in air at 553 K for 1 hour and followed in N₂ at 873 K for 2 hours. The calcined samples were characterised and their reduction properties were evaluated. The pH of the synthesis solution was shown to affect the physicochemical properties where the formation of orthorhombic M1 phase was obtained for catalysts prepared at pH 1 and 3. The reducibility of the catalyst is improved for catalyst prepared at pH 3 as compared to those prepared at pH 1. Although higher synthesised pH (5 and 7) gave much higher reducibility of the metal oxides, however the removable oxygen could be of the unselective ones.

Keywords: MoVTenbO_x catalysts, pH, reducibility, propane, acrylic acid

Abstrak

Satu siri mangkin MoVTenbO_x telah disintesis menggunakan kaedah buburan dibantu oleh radiasi gelombang mikro. Nilai pH bagi larutan sintesis telah dikaji pada pH = 1, 3, 5, dan 7 dan pepejal yang diperolehi telah dikalsin dalam udara pada 553 K selama 1 jam dan diikuti dalam nitrogen pada 873 K selama 2 jam. Sampel terkalsin telah dicirikan dan sifat kebolehturunan telah dikaji. Di dapati, pH bagi larutan sintesis memberi kesan kepada ciri fizikokimia di mana pembentukan fasa ortorombik M1 telah terjadi bagi mangkin yang disediakan pada pH 1 dan 3. Kebolehturunan mangkin ini dipertingkatkan bagi mangkin yang disediakan pada pH 3 berbanding yang disediakan pada pH 1. Walaupun mangkin yang disediakan pada pH yang lebih tinggi (5 dan 7) memberikan kebolehturunan logam oksida lebih tinggi, namun penyingkiran oksigen mungkin menjadi tidak selektif.

Kata kunci: mangkin MoVTenbO_x, pH, kebolehturunan, propana, asid akrilik

Introduction

MoVTenbO_x is a quaternary mixed metal oxide catalyst consists of four different elements which are molybdenum, vanadium, tellurium and niobium. The catalyst is reportedly the most effective catalyst system for the vapour phase catalytic oxidation of propane to form acrylic acid [1-6]. It is because the catalyst contains necessary active sites which is fundamental in propane oxidation [7]. The active MoVTenbO_x system possesses two crystalline phases which are orthorhombic M1 phase, Te₂M₂₀O₅₇ (M = Mo, V, Nb), and hexagonal M2 phase, Te_{0.33}MO_{3.33} (M = Mo, V, Nb) [8]. The significant difference exists among these two phases is that the M1 phase contains V⁵⁺ centres, as an agent for propane activation [4, 7]. Meanwhile, M2 is incapable of activating propane, but it does convert

propylene. Figure 1 suggested the reaction pathway in oxidation of propane to acrylic acid. For the reaction to occur successfully, the catalyst need at least three important active sites. The first site is a V-Mo-O phase for the activation of propane. After hydrogen is successfully abstracted from propane to form propene, a second site which is a Te-Mo-O phase is needed to oxidise propene into aldehyde. Finally, a third site, a V-Mo-O phase is needed for another oxygen insertion to convert aldehyde into acrylic acid. It is recognized that the V^{5+} ion activates alkane by first H abstraction and followed by second H abstraction to produce the allylic radical before the insertion of oxygen [9].

It has been reported that the synthesis parameters affect the properties of the final catalyst. In this context the pH of synthesis solution is of high importance because the chemical composition and phase formation depend closely on it [10-12]. The catalyst precursors suggest the presence of Anderson-type heteropolyanion, $(NH_4)_6TeMo_6O_{24} \cdot nH_2O$ in the samples prepared at $pH > 3$ and favouring the formation of amorphous materials at $pH < 3$ [12]. The acidity of the catalyst's surface was suggested to affect the binding and reactivity of propene molecules which possess a basic character [13]. Higher synthesis pH promotes the formation of MoO_3 after heat treatment, which is known to be inactive in propane oxidation [10]. The heat-treated (873K in a N_2 stream) samples from precursors prepared at lower pH suggests the presence of $Te_2M_{20}O_{57}$, $Te_{0.33}MO_{3.33}$ ($M = Mo, V, Nb$) and $Mo_{5-x}(V/Nb)_xO_{14}$ crystalline phases which possibly involved in the active and selective alkane activation to acrylic acid [12].

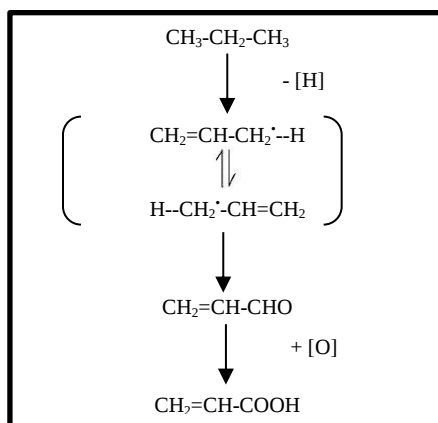


Figure 1. Reaction pathway in oxidation of propane to acrylic acid

In the present work, the MoVTenbOx catalysts were prepared by using a slurry method assisted with microwave irradiation. During the synthesis, the pH of the solution was varied and its effect on the physicochemical properties and reducibility were studied.

Materials and Methods

Catalyst preparation

$Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalysts were prepared by a slurry method followed by microwave irradiation according to the patented procedure [14].

Commercial chemicals which were ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck), ammonium metavanadate, NH_4VO_3 (Merck), telluric acid, $Te(OH)_6$ (Sigma-Aldrich) and ammonium niobium oxalate, $(NH_4)_2Nb_2(C_2O_4)_5$ (Sigma-Aldrich), were used as the sources for Mo, V, Te and Nb respectively. The microwave used in this study was the conventional Panasonic microwave model no. NN-S554WF (750 W).

The synthesis process begun by dissolving ammonium heptamolybdate tetrahydrate in a 15 ml of irradiated deionised H_2O . The solution was irradiated before ammonium metavanadate was added. The solution was then irradiated, followed by the addition of telluric acid. The irradiated ammonium niobium oxalate solution was added

to the MoVTe suspension that were separately prepared using ammonium niobium oxalate dissolved in 5 ml of deionised H₂O. Finally, the resulting orange slurry formed were irradiated for 3 min. The pH of resultant slurry precursor was recorded with the value of 4.5 (± 0.01) using Thermo-line PHS-3BW digital pH meter.

The pH of the final slurry was adjusted by using 1 M aqueous sulphuric acid for pH range 1 to 3 and 1 M of an aqueous ammonium hydroxide for pH 5 to 7. Then, the solution was left overnight and later dried using a rotary evaporator at 353 K. These samples were denoted as MVTN_{1p}, MVTN_{3p}, MVTN_{5p}, and MVTN_{7p} respectively.

The precursor samples were later calcined for 1 h in air at 553 K to remove the organic substances and followed by 2 h in the N₂ stream at 873 K to control the phase formation of the catalyst. These samples were denoted as MVTN_{1c}, MVTN_{3c}, MVTN_{5c}, and MVTN_{7c} respectively.

Catalyst characterization

All the catalysts were characterized by the following analytical techniques. Powder X-ray diffraction patterns were collected by using a Shimadzu Model XRD 6000 Diffractometer equipped with CuK α radiation with wavelength, $\lambda = 1.542$ Å which were continuously scanned in the range of $2\theta = 2^\circ - 60^\circ$ at a scanning rate of 2° min^{-1} . Induced coupled plasma-atomic electron spectroscopy (ICP-AES) measurements of bulk MoVTenbOx compositions were carried out using a model Perkin Elmer Emission Spectrometer Plasma 1000. Fourier Transform Infrared Spectroscopy (FTIR) were analysed using a Perkin Elmer 1725X spectrometer by employing the standard KBr method and the spectra were recorded in the 400 cm^{-1} to 4000 cm^{-1} regions. Field emission-scanning electron microscopy (FESEM) images were collected using Nova 200 NanoLab at an accelerating voltage of 5.0 kV. The aluminium stud was used with the carbon paint was tapped on the sample and coated with gold.

Reducibility study

Temperature programmed reduction in hydrogen (H₂-TPR) analysis was carried out by using ThermoFinnigan TPDRO 1110 Instrument. Before subjecting the catalyst to a reducing environment, it was pre-treated under a N₂ flow by heating sample to 423 K at a heating rate of 10 K min^{-1} . After which, the nitrogen gas was switched to hydrogen (5 % H₂ in Argon) and temperature programming up from 323 K to 1223 K at a heating rate of 10 K min^{-1} . The amounts of water, H₂O which was produced was flowed through the thermal conductivity detector.

Results and Discussion

Physicochemical properties of MoVTenbOx catalysts

The XRD patterns of four precursors prepared at different pH are shown in Figure 2. At pH 1, there are no visible peaks due to metal oxide crystal phase can be observed. The MVTN_{1p} displays two humps at $2\theta = 6^\circ - 15^\circ$ and $21^\circ - 35^\circ$ which reckons that the sample is amorphous due to randomly distributed of atoms in the solid particles [15]. As the pH of synthesis solution increases, the metal oxide peaks become apparent. All of the other three samples (MVTN_{3p}, MVTN_{5p}, and MVTN_{7p}) exhibited sharp peaks at $2\theta = 10.3^\circ, 12.5^\circ, 13.1^\circ, 16.0^\circ, 18.1^\circ, 23.2^\circ, 25.0^\circ$ and 27.8° suggesting the orderly arranged of the atoms. The peaks suggested the presence of Anderson-type heteropolyanion (NH₄)₆TeMo₆O₂₄·7H₂O and/or (NH₄)₇TeMo₅VO₂₄·8H₂O [15, 16]. A similar case has been reported, whereby an Anderson-type heteropolyanion, (NH₄)₆TeMo₆O₂₄·nH₂O was formed in samples prepared at pH 3.0–4.5 whereby at pH < 3 the heteropolyanion partially decomposed with the formation of mostly amorphous materials and at a very low pH 1.0–1.5 indicates the present of polyoxovanadates in the precursors [12]. Therefore, as observed in this work at low pH the crystallinity of heteropolyanion compounds decreases and amorphous materials are observed due to the partial incorporation of heteroatoms or the heteroatoms are highly dispersed on the compounds. The results show that pH influences the incorporation of heteroatoms (V and Nb) on heteropolyanion which determines the formation of active crystalline phases.

The XRD patterns of calcined samples are shown in Figure 3. The peaks evolved for samples synthesised at pH 1 and 3 i.e. MVTN_{1c} and MVTN_{3c}, respectively suggests the presence of orthorhombic M1 and hexagonal M2 phases. The presence of both phases can be clearly indicated by $2\theta = 6.6^\circ, 7.9^\circ, 9.0^\circ, 22.1^\circ$ and 45° which correspond to orthorhombic M1 (JCPDS: 58-790) meanwhile $2\theta = 22.1^\circ, 28.3^\circ, 36.2^\circ$ and 50° correlate to hexagonal M2 phase (JCPDS: 57-1099). On the other hand, the two other samples which are MVTN_{5c} and MVTN_{7c} synthesised at pH 5

and 7 respectively, show the occurrence of hexagonal M2 phase and the additional peaks at $2\theta = 7.7^\circ, 8.9^\circ, 22.1^\circ, 24.2^\circ$ and 31.3° which can be correlated to the existence of tetragonal phase, $(V_{0.07}Mo_{0.93})_5O_{14}$ (JCPDS: 31-1437).

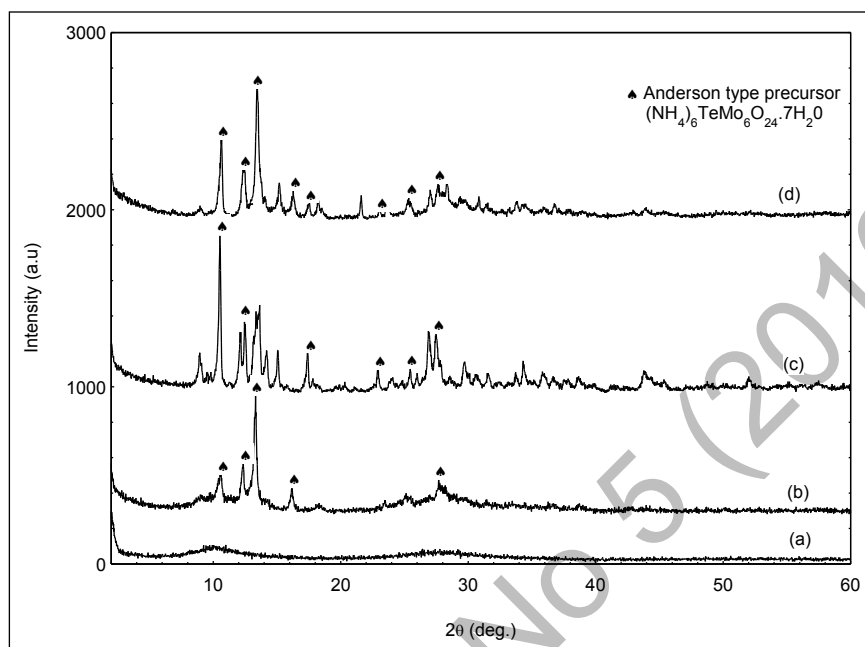


Figure 2. XRD patterns of precursor MoVTenbOx catalysts (a) MVTN_{1p} (b) MVTN_{3p} (c) MVTN_{5p} (d) MVTN_{7p}

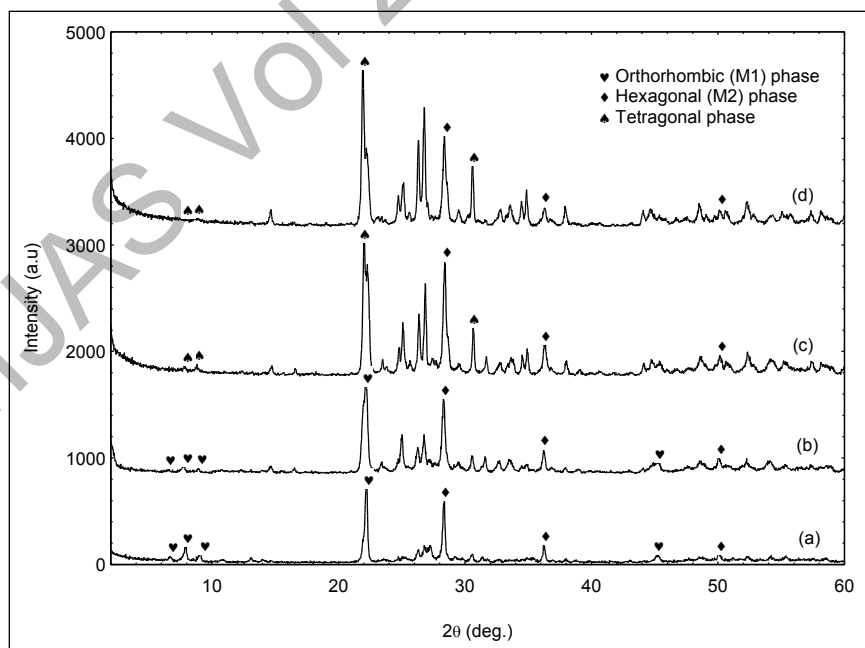


Figure 3. XRD patterns of calcined MoVTenbOx catalysts (a) MVTN_{1c} (b) MVTN_{3c} (c) MVTN_{5c} (d) MVTN_{7c}

It can be noted that orthorhombic M1, hexagonal M2 and tetragonal phases have the same diffraction peak of 22.1° which suggests that the mixture of phases in the samples [15]. The formation of these phases may be due to the formation of pseudo-amorphous or semi crystalline Anderson-type compound (ammonium containing phase) which has been observed during precursor stage [17].

The crystallite size of the calcined MoVTenbOx catalysts can be determined by using the full width half maximum (FWHM) for three characteristic peaks of orthorhombic M1 phase at $2\theta = 6.6^\circ$, 7.9° and 9.0° . The crystallite size was estimated by the using the Debye Scherrer equation as in (1).

$$t = \frac{0.9\lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad (1)$$

where, t = crystallite size, $\lambda = 1.5438 \text{ \AA}$, θ = Bragg angle, β_{hkl} = the full width at half maximum (FWHM) of the peak in radian.

The value of crystallite size in Table 1 suggested that the crystallite size of the MVTN_{1c} and MVTN_{3c} samples are 35.12 nm to 36.42 nm respectively. The values are in the nanometer range, which gives a good indication of the pH influence on the catalyst particle size. However, there is no orthorhombic phase were present in MVTN_{5c} and MVTN_{7c}, therefore particle size for these samples were not calculated.

Table 1. Crystallite size and bulk composition of MVTN_{1c}, MVTN_{3c}, MVTN_{5c} and MVTN_{7c}

Sample	2 θ (°)	FWHM (°)	t (nm)	Bulk composition ¹ (Mo: V: Te: Nb)
MVTN _{1c}	6.5	0.2005	39.8	1.0: 0.29: 0.17: 0.10
	7.7	0.2825	28.2	
	8.6	0.2137	37.4	
	Average: 35.12			
MVTN _{3c}	6.6	0.2445	32.6	1.0: 0.29: 0.17: 0.09
	7.7	0.2550	31.3	
	8.9	0.1760	45.4	
	Average: 36.42			
MVTN _{5c}	NA ²			1.0: 0.29: 0.17: 0.09
MVTN _{7c}	NA ²			1.0: 0.29: 0.17: 0.09

Preparative composition of Mo: V: Te: Nb = 1.0: 0.3: 0.23: 0.12, ¹Determined by ICP-AES, ²NA: Not applicable

The bulk compositions of Mo-V-Te-Nb mixed oxide catalysts determined by ICP-AES are summarised in Table 1. The bulk compositions of all the oxides were not so different from the preparative compositions. The Mo element is justified in all samples as Mo is the main component in the mixture. For all samples, the V element obtained which is 0.29 are closely resemble to the theoretical value of 0.3. The molar ratio of the Mo and V element are important in the catalyst system because these elements are responsible for the structural formation of the MoVTenbOx catalysts and M1 phase will be formed with Mo:V ratios higher than 0.14 [6,18].

The difference is found in the tellurium contents which were slightly lower in the bulk. A possible explanation for the loss of tellurium could be related to the presence of oxalate anions (reducing agent) from the starting material of

niobium oxalate, which could facilitate the reduction of tellurium cations to metallic Te [19] that were detached away from the structure during calcination. The Nb content is also found lower after calcination in all samples. It has been reported that Nb play the same structural role as vanadium in order to obtain the mono-phasic orthorhombic M1 structure [20]. In the case of the catalyst in this work, the condition of lower amount of Nb gave MoVTenbOx catalysts containing several phases as has been observed in the XRD analysis. Still, the presence of Nb despite of its amount is important for the stability of the element in the solid structure.

The FTIR spectra of the precursors are shown in Figure 4. The bands around 3178 cm^{-1} and 1441 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the tetrahedral ammonium cation [16]. The H–O–H bending mode is observed in the range 1668 cm^{-1} and bands at 1301 cm^{-1} could be attributed to stretching and vibration modes of C=O, a stretching combination of C–O and C–C associated with the oxalate anion [15]. Meanwhile, the absorption band at 1101 cm^{-1} is discovered to only exist in sample MVTN_{1p} that can be related to the S=O stretching [20]. This is caused by the presence of sulphate group while incorporating H₂SO₄ during pH adjustment of precursor solution. In this case, only two samples required H₂SO₄ during pH adjustment, which are MVTN_{1p} and MVTN_{3p}. However, this peak only intense for MVTN_{1p} and almost unnoticeable for MVTN_{3p}. This is due to the reason that the pH of the solution before adjustment was around pH 4.3, so only little amount of H₂SO₄ ions present in the MVTN_{3p} solution, compared to MVTN_{1p}. In addition, the sharp peak detected around 884 cm^{-1} corresponds to no vibrations and bands around 623 cm^{-1} can be due to the Mo–O, Te–O and Mo–O–Te vibrations, since the different bands of these vibrations overlapped in this range [16]. The stretching of V=O group and V–O–Me (Me= Mo, Te, Nb) gave the absorption band around 449 cm^{-1} .

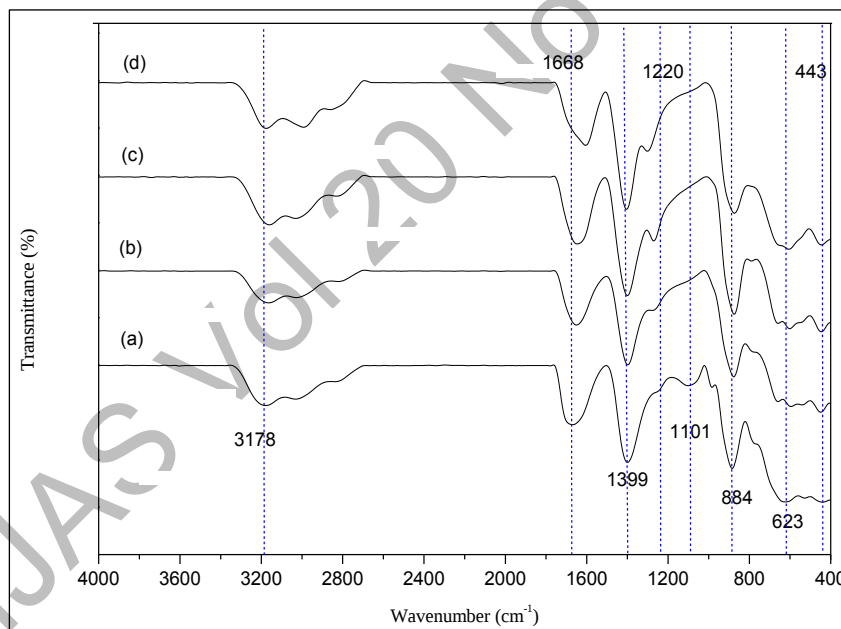


Figure 4. FTIR spectra of precursor MoVTenbOx catalysts (a) MVTN_{1p} (b) MVTN_{3p} (c) MVTN_{5p} (d) MVTN_{7p}

For the calcined samples, there are no bands observed in the region above 1000 cm^{-1} as can be seen in Figure 5, therefore it is sufficient to show spectra of low frequency region [15]. The disappearance of the high frequency region above 1000 cm^{-1} indicates that all of the organic species functional groups such as hydroxyl, sulphate, ammonium and water are completely removed from the samples during calcination. The band at 861 cm^{-1} and 699 cm^{-1} are assigned to asymmetric stretching vibrations of bridging Mo–O–M bonds ($M = \text{Mo, Nb, Te}$) [12] which lies in the range of $800 - 1000\text{ cm}^{-1}$. The bands around 530 cm^{-1} and 431 cm^{-1} can be assigned to V = O group and V–O–Me bonds ($M = \text{Mo, Te, Nb}$) in the range of $400 - 600\text{ cm}^{-1}$ [16].

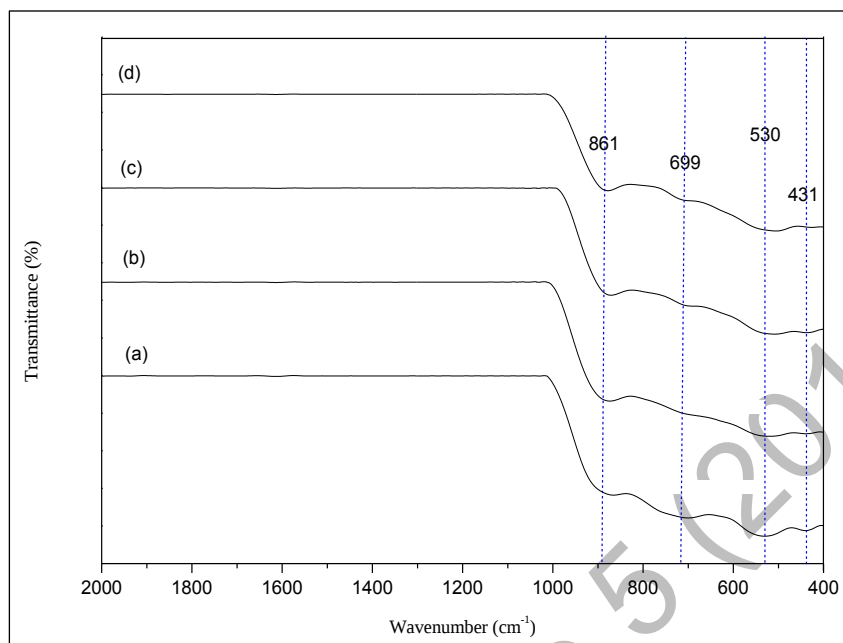


Figure 5. FTIR spectra of calcined MoVTenNbOx catalysts (a) MVTN_{1c} (b) MVTN_{3c} (c) MVTN_{5c} (d) MVTN_{7c}

The morphology of calcined catalysts was investigated by FE-SEM analysis. The images are shown in Figure 6. The micrographs display the formation of rod-shaped morphology in all of the samples. This kind of morphology is similar to the reported works [21, 22]. The formation of a rod-shaped morphology could be due to V⁵⁺ derived from ammonium metavanadate in the synthesis step which contribute to the formation of long and large needles during the slurry synthesis [22]. For catalyst synthesised at pH 1, it gives a more homogeneous and rather disperse particles as compared to catalysts prepared at higher pH. Not to be denied is the presence of other shaped particles, thus stating the mixture of phases in accordance with the XRD patterns which showed mixed phase of the calcined catalyst [12].

Reducibility properties

The study on the catalyst reducibility is important in a mixed metal oxide catalyst used for the oxidation reaction. It will give an indication of the availability of the oxygen for insertion into reactants. During the reduction process, hydrogen gas is in contact with the oxygen species from the surface of the catalyst. The hydrogen is consumed and formed water vapour in the gaseous state as a product, leaving an oxygen vacancy on the catalysts. The interaction of the gas phase hydrogen with catalyst can be represented as in equation (2).



where (g) = gaseous species, (s) = surface or lattice species and $\square$ = oxygen vacancy.

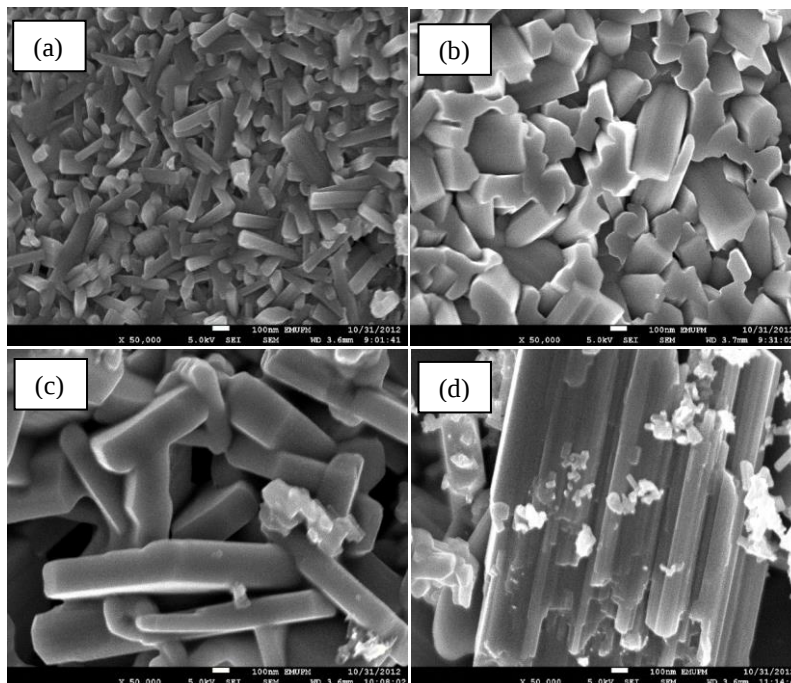


Figure 6. FESEM image of calcined MoVTenbOx catalysts (a) MVTN_{1c} (b) MVTN_{3c} (c) MVTN_{5c} (d) MVTN_{7c} [23]

The reduction profiles of MoVTenbOx catalysts are shown in Figure 7. There are at least two peak maximum which are overlapped with each other are observed in all of the samples. The occurrence of multiple reduction peaks indicates the presence of a number of reducible metal oxide species present in the catalyst.

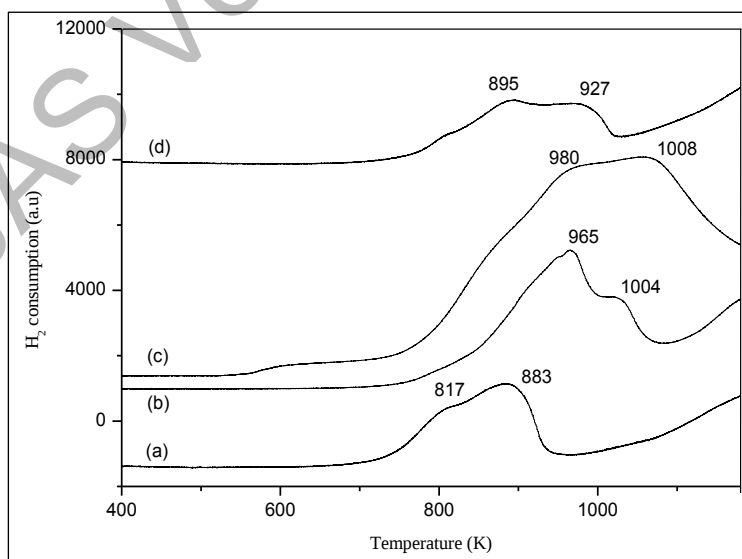


Figure 7. H₂-TPR profiles of calcined MoVTenbOx catalysts (a) MVTN_{1c} (b) MVTN_{3c} (c) MVTN_{5c} (d) MVTN_{7c}

The reduction peak suggests reductive decomposition of metal oxides where MoO_n reduced at 948 K and 995 K for a stepwise reduction of $\text{Mo}^{6+} \rightarrow \text{Mo}^{4+}$ and $\text{Mo}^{4+} \rightarrow \text{Mo}^0$ under H_2 -TPR, meanwhile VO_n reduced at temperature of 913 K and 943 K from $\text{V}_2\text{O}_5 \rightarrow \text{VO}_2$ [24,25]. Additionally, reduction of Nb^{5+} to Nb^{4+} occur at around 1243 K [26].

The reduction activation energy of the catalysts can be calculated using the modified version of the Redhead equation as stated in equation (3). The results are summarised in Table 2.

$$\frac{E_r}{RT_m^2} = \left(\frac{A_r}{\beta}\right) [\text{H}_2]_m \exp\left(\frac{-E_r}{RT_m}\right) \quad (3)$$

where, E_r = reduction activation energy (kcal mol^{-1}), T_m = peak maximum temperature (K) in the rate of production of H_2 , A_r = reduction pre-exponential term ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) which is given a standard collision number of $10^{13} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, β = heating rate (Ks^{-1}) and $[\text{H}_2]_m$ is the gas phase concentration of hydrogen (mole cm^{-3}) at the peak maximum.

Table 2. The reduction activation energy, E_r and total O_2 removed determined from H_2 -TPR for (a) MVTN_{1c} (b) MVTN_{3c} (c) MVTN_{5c} (d) MVTN_{7c}

Sample	T_{max} (K)	Reduction activation energy, E_r (kJ mol^{-1})	O_2 removed (atom g^{-1}) $\times 10^{21}$
MVTN_{1c}	817	136.5	0.72
	883	147.5	1.67
			Total = 2.39
MVTN_{3c}	965	161.2	4.67
	1004	167.7	0.94
			Total = 5.61
MVTN_{5c}	980	163.7	8.39
	1008	168.4	7.26
			Total = 15.65
MVTN_{7c}	895	149.5	1.60
	927	154.9	1.05
			Total = 2.65

The values of reduction activation energy, E_r for all samples is more than 100 kJ mol^{-1} indicates that the oxygen species are strongly bonded. Thus, these strongly bonded oxygen species that has been removed in these samples may be originated from the surface and/ or lattice of the catalyst [27].

Interaction of hydrogen with MoVTenbOx mixed oxides during H_2 -TPR involves the adsorption of hydrogen on all active sites of the molybdenum oxide surface, taken up the oxygen species and caused the reduction of the MoO_n component. The higher amount of oxygen removed indicate the high activity of the catalysts. The amount of oxygen removed of each sample can be estimated by integrating the area under the peak. For catalyst prepared at pH 1, the total amount of removable oxygen is $2.39 \times 10^{21} \text{ atom g}^{-1}$ whereas the amount is doubled to $5.61 \times 10^{21} \text{ atom g}^{-1}$ when synthesised at pH 3. This is an indication of the high removable oxygen of the catalyst when prepared at pH 3 which was contributed by the formation of the much desired orthorhombic M1 phase. Although the catalyst prepared at pH 5 gives a much higher of removable oxygen species ($15.65 \times 10^{21} \text{ atom g}^{-1}$), nevertheless it could be the unselective oxygen species due to the catalyst does not contains the orthorhombic M1 but hexagonal M2 phase instead. The same goes with catalyst prepared at pH 7.

Conclusion

The results revealed that the pH of the slurry strongly influences the formation of crystalline Anderson-type heteropolyanions for catalysts prepared at pH 3, 5 and 7. While the as-synthesised sample at pH 1 showed the presence of pseudo-amorphous materials which allow for the formation of orthorhombic M1 phase upon calcination. The formation of orthorhombic M1 phase is also observed in pH 3 samples (after calcination), but none was found in the other samples. Therefore, high acidity condition is required for the formation of desired catalyst phase. Although, all of the catalysts give similar reduction profiles in the anaerobic hydrogen-TPR, the lattice oxygen that were removed in catalysts which contains orthorhombic M1 could be the selective ones. This is because, the catalysts with M1 phase can undergo charge transfer on the Mo and V sites with the lattice oxygen could be involved in the abstraction of H at the vanadium sites and oxygen insertion at the molybdenum sites. There is a clear relationship between synthesis pH and catalyst properties, suggesting that the reducibility of crystalline phases is a key factor in the propane selective oxidation into acrylic acid.

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