6.0 Surface modification on MoVTeNb oxide catalyst

6.1 Effect of leaching in different solvent

Leaching is one of the many techniques to modify the materials inside or outside of the catalyst. This study is working on the hypothesis that leaching induced one or more of the following three effects which are considered to be beneficial to the performance of the catalysts.

- (i) Phase purification by the removal of '*useless ions*' in the catalysts (non-M1 phase) and keep the 'useful active component in M1 phase'.
- (ii) Surface modification by nanostructuring of active M1 phase.
- (iii) Bulk modification.

In this study, 10 samples have been selected for further modification using leaching or purification technique. Details of the samples are tabulated in Table 6.1 for references.

Sample Code	Description
422	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ catalyst without leaching
551	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in water for 1 h
562	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in ammonia for 1 h
566	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in nitric acid for 1 h
675	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ catalyst without leaching
679	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in water for 1 h

Table 6.1: List of samples MoVTeNb samples selected for surface modification

Sample Code	Description
680	Undiluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in water for 24 h
675	Diluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ catalyst without leaching
676	Diluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in water for 1 h
678	Diluted $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}$ leached in water for 24 h

Figure 6.1 depicted the TEM images of MoVTeNb catalyst. As we can see from the images, there are two phases present in the samples which are amorphous and crystalline phase. The leaching procedure was done on the amorphous part which are believed can improved the performance on the bulk of the catalyst.



Figure 6.1: TEM images of crystalline phase MoVTeNb oxide.

Nanostructuring is verified by microscopic inspection allowing to study locally the relevance of the M1 structure for catalysis and to unravel the relative spatial arrangements of phases on several length scales using SEM and TEM techniques (see Figure 6.1). The leaching procedure was introduced in order to eliminate excess molybdenum oxide being active to for detrimental total oxidation of propene (Mestl G. 2002). The change in

conductivity of the leaching solution was used as in situ monitor to select the best sample of leaching.



Figure 6.2: Conductivity curves undiluted MoVTeNbIOx samples leached in different solvents

Leaching of calcined materials in different solvents show changed of conductivity pattern in different proportion. The calcined sample has been chosen as good sample for leaching process because it is crystalline which is resistance to leaching and thus provides a good and stable matrix from which weakly bonded "*useless ions*" can be leached out.

Figure 6.2 depicts the conductivity curves for calcined sample leaching with different types of solvent i.e., water, ammonia and nitric acid. Ammonia is not a good leaching agent as shown by the unchanged conductivity. It seem that no changes in concentration or nor charge transfer happened. Whilst leaching in nitric acid, which is a more aggressive solvent, shows increasing of conductivity in comparison to leaching in H_2O . The increasing

of conductivity means that there are changes in concentration and mobility of ionic transfer. The catalytic reaction shown that catalyst leached in water gave the best yield of acrylic acid compared to catalyst leached in NH_3 and HNO_3 . This shows that H_2O is the optimal treating agent while HNO_3 is being too aggressive and ammonia solution being too mild to exert any effect. Additionally the enrichment of elements in the treating agent released from the sample was determined by X

6.1.1 Catalytic Reactivity by Temperature Programmed Reaction Spectroscopy (TPRS)

Leached of calcined MoVTeNb oxide catalyst with different solvents were synthesized and studied with respect to their catalytic reactivity using temperature-programmed reaction spectroscopy (TPRS) of acrylic acid from propane.





Figure 6.3: Catalytic data on the non-leached sample (422), leached in water (551), leached in ammonia (562) and leached in nitric acid (566)

Figure 6.3 showed the catalytic reactivity studies of MoVTeNb oxide catalyst leached in different solvent i.e. in water, 0.1 M of nitric acid and 0.1 M ammonia solution. Based from the result, the leached sample showed some improvement on activities. Therefore, the conversion of propane has been increased in sample leached with water compared to non-leached sample and other solvents. Catalyst-551 has shown some increment on production of carbon monoxide, acryloic acid and acrolein signals. The others leached catalysts such

as catalyst_562 and catalyst_566 show very poor activity compared to non-leached catalyst. It is might be due to the properties of strong acid and base will destroy the surface structure of the catalyst. The leaching had been given some influences on improvement in catalytic reactivity towards acrolein and acrylic acid. It can be seen from the SEM result, the morphology of both catalyst seem to be destroyed and there is no needle-like shape can detected. The XRD results show there is no influence on the bulk structure.

6.1.1.2 Structural Analysis by Powder X-Ray Diffraction (XRD)

Powder X-ray diffraction is used to identify phases of crystalline material from aqueous MoVTeNbOx solution. From literature (Graselli, Millet, Nieto & Ueda *et al.*), it is known that a successful catalyst should be a mixture of two phases namely of an orthorhombic and a hexagonal variant of the MoVTeNb system, often referred to as M1 and M2 phases respectively, in certain optimal composition. The structural analysis was measured by XRD, XRF and SEM. XRD measurement is used to identify the phase inventory of the bulk catalysts. The M1 phase was identified by the major XRD reflections at 6.6° , 7.8° , 9.0° , 13.0° , 22.1° , 26.2° , 26.8° , 27.6° and 45.2° , while the M2 phase was characterized by the major reflections at 22.1° , 28.3° , 36.2° and 44.6° [Ushikubo 1997, Al-Saeedi 2003, Millet 2001, Aouine 2001, Vitry 2003, DeSanto 2003, Grasselli 2003, Oshihara 2001]. Although a significant overlap of the XRD reflections at $20 < 10^{\circ}$, while the presence of reflections at $20 < 10^{\circ}$, while the presence of the M2 phase is manifested in the characteristic reflection at $20 = 28.3^{\circ}$ [Guliants, 2004].



Figure 6.4: XRD patterns of calcined MoVTeNb catalyst leached at different solvent with reference peaks: () M1 () M2

Table 6.2: Rieveld quatification analysis for non-leached and leached in different solvent

Sample code	Concentration of M1	Concentration of M2
	(%)	(%)
422	52.21	47.79
551	45.36	54.64
562	58.74	41.26
566	47.88	52.12

Figure 6.4 present the X-ray diffraction patterns and Table 6.2 is Rietveld analysis of undiluted system leached with different solvent i.e., water, ammonia and nitric acid. All catalysts seem to give a similar XRD pattern. The XRD reflections showed the presence of mixture M1 and M2 phases. Rietveld quantification analysis has been done to confirm of any changes in composition of non-leached and leached samples. Based from the analysis,

the ratio between M1 and M2 for non-leached sample is 50%: 50%. Composition of M1 and M2 still remain as standard sample after leaching in water and nitric acid. The ratio of M1 phase increased when sample was leached in ammonia around 60 %. Unfortunately, there is no improvement in catalytic activity can be observed.

The diffraction patterns show that the bulk structure was not affected by purification process. The appearance of peaks at $2\theta = 6.6^{\circ}$, 7.8° , 9.0° , 22.1° , 27.6° , 28.3° and 36.2° can mainly be related to an orthorhombic Te₂M₂₀O₅₇ (M=Mo, V and Nb) phase [Botella 2002] as same as in reflection of M1 phase. In addition to these, peaks at $2\theta = 22.1^{\circ}$, 28.2° , 36.2° and 45.2° and 50.0° can be related also to Te_{0.33}MO_{3.33} (M = Mo, V, Nb), a crystalline phase with a XRD pattern similar to that of a hexagonal tungsten bronze (K _{0.13-0.33}WO₃, HTB) [Botella 2002, Garcia 2002 and Millet 2002]. The reflection of $2\theta = 22.1^{\circ}$ is due to psuedo hexagonal M2 phase. Furthermore, the sample also detected mixture phase from weak reflection of TeMo₅O₁₆ (JCPDS-31-874) and MoO₃ (JCDPS-47-1320).

6.1.1.3 Morphology and elemental composition Analysis by Scanning Electron Microscope SEM- EDX and XRF.

SEM analysis present the morphology of the samples prepared, which reveal the multiphase nature of non-leached and leached Mo-V-Te-Nb oxide catalyst. All images show characteristics of the MoVTeNb oxide catalyst by leaching method to identify morphology and elemental composition of the materials. The differences of morphology each sample before and after post-treatment with different leaching agent are shown in Figure 6.4. Figure 6.5 (i) – (iv) shows the morphology of SEM images of before leaching and after leaching in different types of solvents. i) Before leaching (catalyst_422)



Elements	Normalized to Mo			
	theory	spot a	spot b	spot c
Мо	1.000	1.000	1.000	1.000
V	0.300	0.263	0.310	0.433
Te	0.230	0.118	0.343	0.210
Nb	0.125	0.183	0.071	0.216

ii) After leaching in water (catalyst_551)



Elements	Normalized to Mo			
	theory spot a		spot b	
Мо	1.000	1.000	1.000	
V	0.300	0.257	0.327	
Те	0.230	0.119	0.316	
Nb	0.125	0.219	0.164	



iii) After leaching in ammonia solution (catalyst_562)

	Elements	Normalized to Mo			
-		theory	spot a	spot b	spot c
	Mo	1.000	1.000	1.000	1.000
	V	0.300	0.283	0.301	0.337
	Te	0.230	0.140	0.238	0.284
	Nb	0.125	0.180	0.130	0.160

iv) After leaching in nitric acid (catalyst_566)



Elements	Normalized to Mo			
	theory	spot a	spot b	
Мо	1.000	1.000	1.000	
V	0.300	0.328	0.147	
Te	0.230	0.246	0.220	
Nb	0.125	0.128	0.071	

Figure 6.5: SEM images for MoVTeNbOx before and after leaching. (i); before leaching, (ii) after leaching bi-distilled water,(iii); after leaching in ammonia and (iv); after leaching in nitric acid.

The morphology of non-leached sample has changed after treatment with different solvent for 1 hour. As known that morphology of spray drying is spherically ball shaped with uneven surface, which contains several types of dents caused by solidification process. However, all balls have different morphology after activation process (see Figure 6.5 (i)). The balls contain two types of surfaces i.e. needle-like surface and smooth surface. After leaching with water, the balls remain with the same surface. As we can see from the EDX, the needle-like surface consist more vanadium and less tellurium. The smooth surface consist more tellurium metal (Figure 6.5(ii)). Furthermore, leaching with nitric acid and ammonia surprisingly gave different morphology from the non-leached sample. As known in the previous standard SEM images from the standard catalyst, all particles are spherically ball shaped with an uneven surface, which contains several types of dents and needle-like surface. However, most of the morphology features from the leached samples with nitric acid seem to have been destroyed probably due to the strong base. In Figure 6.5 (iii), the smooth surface mostly consistent with the element composition. While the needlelike balls show increasing of niobium and decreasing of vanadium and tellurium. Furthermore, nitric acid is a strong acid and obviously gave some different morphology to the catalyst after leached. The balls consist of two type morphology; uneven surface (destroyed surface) and needle-like surface. Based from the EDX result, the needle-like had less amounts of vanadium and tellurium. Therefore, the effect of leaching had some influence on the catalytic activity and reactivity. The catalytic reactivity for catalyst_562 and catalyst_566 had showed very poor on acrylic acid and acrolein production compared to catalyst_551 and catalyst_422.

X-Ray Fluorescence Analysis (XRF)

As described from the methodology section, XRF has been used to confirm the elemental composition before and after leaching process. Table 6.3 tabulates the XRF result analysis for each sample leached in different solvents. From the result, the catalyst_551 had very little amount of metal leached-out from the samples. Catalyst_562 showed very extremely metal has been leached-out for the sample compared to the catalyst_566. Vanadium and tellurium are the metals which have been leached during the process. Furthermore, the EDX also indicates small amount of vanadium and tellurium at some spots.

Table 6.3: Elemental composition for leaching samples

a) Filtrated solution

Sample	Normalized to Mo			
	Mo	V	Te	Nb
Theory	1.000	0.300	0.230	0.125
551 (H ₂ O)	1.000	0.023	0.034	0.023
562 (NH ₃)	1.000	0.216	0.176	0.026
566 (HNO ₃)	1.000	0.033	0.136	0.031

b) Remaining solid

Sample	Normalized to Mo			
	Mo	V	Te	Nb
Theory	1.000	0.300	0.230	0.125
551 (H ₂ O)	1.000	0.241	0.251	0.120
562 (NH ₃)	1.000	0.262	0.219	0.132
566 (HNO ₃)	1.000	0.221	0.041	0.009

In conclusion, the SEM/EDX analysis has revealed the multi-phase nature of the MoVTeNbOx catalyst. Leaching in the leaching agent i.e., water, ammonia and nitric acid does not give any influence in improving the M1 concentration. The morphology almost destroyed for catalyst after leached with strong ammonia and acid solution while the morphology of sample leached with water remain in spherically ball shaped although the surface becomes roughen with some small long needles crystal. The XRF analysis also showed only leaching with strong base can removed some metals from the sample especially vanadium and tellurium. These two elements are mostly give strong influence on catalytic activity of propane oxidation.

In addition, the XRD profile of the leached samples indicates that the leaching solvent only leached out the elements from the surface. The structure of the bulk still remains as the non-leached sample. The catalytic reactivity by TPRS showed that the catalyst leached with water gave very good signal on acrylic acid and acrolein. The production of carbon dioxide also can be detected high in catalyst-551. The catalyst_562 and catalyst_566 showed very poor activities towards propane oxidation to acrylic acid.

6.2 Effect of leaching in different time for undiluted and diluted MoVTeNb oxide catalyst

Nanostructuring can be achieved, offering the chance to optimise not only the surface morphology (roughness) but also the geometric surface area of the unsorted oxide.



Figure 6.6: Development of conductivity in undiluted & diluted MoVTeNbIOx samples during leaching in water for 1 and 24 hrs

Conductivity measurement has been used to study the electron charge movement during leaching process. The conductivity graph for undiluted and diluted MoVTeNb oxide catalyst leached in water are shown in Figure 6.6. The measurement has been done using synthesis reactor(LabMax) with in-situ conductivity probe. The experiment was done in room temperature by dissolving 1 g of sample into 100 ml of water and measured the conductivity. All conductivity – time curves shown in Figure 6.6 begin with slow increment to highest solution conductivity. In diluted system, the peak was drastically increased in conductivity compared to the undiluted system. This case is same for the prolong leaching time applied. The conductivity curves become stable when leaching time nearly 24 hours.

The conductivity of diluted system increased drastically due to the high concentration of the solution. In addition, the diluted system has alumina support compared to the undiluted system. Alumina support is a porous and acidic material which carrying an electrical charge very fast. As known from the literature, ion pairing is one of the important problems in ionic conductivity, which is can affect the charge carrier mobility. Coordination will increase the cation-anion distance. Therefore, the conductivity will increase by adding neutral ligand to coordinate with cation-anion and decrease ion pair formation (Lee H S., X.Q. *et al.* 1995). The conductivity also gave some information on electron charge transfer or metals ion has been leached out during the process.

6.2.1 Catalytic Reactivity for undiluted and diluted by TPRS

The catalytic reactivity studies have been carried out by TPRS for propane oxidation reaction. Selected samples of undiluted and diluted catalyst have measured from room temperature to 500 o C.







Figure 6.7: Catalytic reactivity studies of undiluted and diluted MoVTeNb oxide leached in water for 1 and 24 hours.

The catalytic reactivity data is plotted in Figure 6.7 for both undiluted and dilute MoVTeNb oxide system. Leaching of the diluted samples leads to higher propane conversion at less selective to acrolein and acrylic acid. From the data, the signal of acrolein and acrylic acid increase for pure diluted samples. Leaching effect has been influence on catalytic reactivity for undiluted system. It is could be due to the removal the 'useful metal ion' from the surface of the catalyst. Therefore, diluted catalysts which have been leached for 1 or 24 hours is not active for production of acrolein or acrylic acid.

6.2.2 Catalyst Screening and effect of dilution of water leached catalyst by HT

Nanoflow

The effect of dilution of the catalyst using aerosil300 toward the catalytic performance of selective oxidation of propane to acrylic acid has been carried out under feed gas composition of propane/oxygen/nitrogen/steam = 1/2/18/9, gas hourly space velocity of $1200h^{-1}$, volume catalytic bed of 0.5 ml and temperature of 673 K using Nanoflow catalytic reactor. The result is shown in Figure 5.2. In this figure 5.2 presents the catalytic performance for selective oxidation of propane to acrylic acid over undiluted (671) MoVTeNb mixed-metal oxide catalyst.

This figure shows that both catalysts are active for selective oxidation of propane towards acrylic acid. However, the undiluted catalyst presents a higher propane conversion (55%) than that (27%) of diluted catalyst. This loss of conversion would be roughly consistent with the geometric dilution factor as per volume unit of catalyst the diluted system contains only about half of the active mass when neglecting the difference in bulk densities and assuming that no dispersion of the active mass was achieved (all BET surface areas are at about 1-5 m²/g). Both catalysts are also selective to acrylic acid, but for diluted catalyst presents a much higher selectivity to acrylic acid (66%) than that only (14%) of undiluted catalyst. As a consequence, the diluted catalyst presents a higher acrylic acid yield (18%) than that (7%) of undiluted catalyst.



Figure 6.8: Catalytic performance of undiluted and diluted MoVTeNb oxide catalyst

It has been known that most of heterogeneous catalysts sinter to some extent when used. Sintering of the active component decreases the surface area, and thus reduces the activity of the catalyst. Diluted metal catalyst shows much higher resistance to sintering. It is plays an important role to preserve the catalytic performance of the MoVTeNb mixed metal oxide. Besides maintaining the active surface area for the active component, to avoid sintering, and to maximize the access to the geometric surface of the active component, the diluent has also an important role as a *'heat sink'*. With the *'heat sink'* features from the diluent, the active component does not build up excessive heat.

It can be seen from Figure 6.8 that the undiluted catalyst exhibits a higher propane conversion than that of diluted catalyst and also features a much lower selectivity to acrylic acid than that of diluted catalyst. At the reaction temperature (673 K), propane is activated, so that it easily converts to products. However, the desired product (oxygenated

hydrocarbon, i.e., acrylic acid) is less stable at high temperature; so that it tends to be further oxidized. Therefore, undiluted catalyst (catalyst_675) presents a high propane conversion and a low selectivity to acrylic acid as it can be suspected that the local temperature is exceeding the useful limit to minimize total combustion. Consequently, the diluted catalyst (catalyst_671) exhibits a lower propane conversion than that of undiluted catalyst, but it overcompensates this in productivity by a higher selectivity to acrylic acid than that of undiluted catalyst.

The nature of the active and selective sites in the MoVTeNb mixed-metal oxide catalysts is still under discussion. Although, at first, the catalytic results for the ammoxidation of propane were thought to be related to the presence of a single-crystalline phase (Ushikubo *et al.*, 1995 and 1997), they were later associated with the formation of two major phases, denoted M1 and M2 phases (Ushikubo *et al.*, 1997; Ushikubo, 2000). The catalytic behavior of MoVTeNb catalysts in the oxidation of propane to acrylic acid could also be explained by the presence of three moieties: (i) a V-Nb-O phase as paraffin activator; (ii) a Te-Mo-O phase to oxidize olefins to aldehyde; and (iii) a V-Mo-O phase to convert the aldehyde to corresponding acid (Botella *et al.*, 2002). Lin (2003) reported that Ushikubo and co-workers (1997) further suggested that phase M1 is effective for propane activation and that phase M2 is less active for propane conversion but very selective for the subsequent step of propylene ammoxidation. From the explanation above, it can be suggested that the active component, which plays a very important role in the selective oxidation of propane to acrylic acid is the M1 phase.



Figure 6.9: Catalytic performance of leached sample for 1 hr (679) and 24 hrs (680) and non-leached (675) of undiluted MoVTeNb oxide.



Figure 6.10: Catalytic performance of leached sample for 1 hr (676) and 24 hrs (678) and non-leached (675) of diluted MoVTeNb oxide.

In Figure 6.9 and 6.10 showed the catalytic activity of undiluted and diluted leached sample of MoVTeNb oxide catalyst. The leaching times were 1 hour and 24 hours respectively. The purpose of leaching of the catalysts using water is to remove the *'useless ions'* in the catalysts (non-M1 phase) and to keep the *'useful active component in M1 phase'*. This should be beneficial as the *'useless ion'* may well catalyze themselves unwanted other reactions leading to foreign products or eventually to CO₂. The fact that during variation of the GHSV the material balance deteriorated is a clear indications that other products than those investigated by the GC analytics can form. Figure 7.3 shows that the leaching process of the undiluted catalyst does not affect too much to the propane conversion, but it affects to selectivity to acrylic acid. It also shows that the best catalytic performance is reached by leaching the catalyst for 1 hour. It is probably because 24 hours leaching is too long time to leach catalyst.

Figure 6.10 reveals that the propane conversion for the diluted catalyst increases significantly with leaching time (from 28% for unleached catalyst to 39% for leached catalyst 24 hours), while the selectivity to acrylic acid is constant. Leaching effects in diluted systems is different than in undiluted systems although we know that the amount and type of ions removed is identical in both cases. Even though without leaching process, the presence of diluent have affected the formation of the active surface, and the effect of better heat transport further add to the higher selectivity. The long leaching time is advantageous to the catalyst performance, implying that a change in accessibility to active sites has occurred. However, these active sites could not be measured by BET surface area analysis because they showed roughly the same value. As the standard error of these BET

measurements is high for low exposed surfaces, it may be well that an increase surface area could not be identified.

6.2.3 Structural Analysis by Powder XRD

In this study, the XRD reflections observed were compared to the simulation data of M1 and M2 phases. The simulation is based on data published by DeSanto *et. al.* [DeSanto, 2003]. The lattice parameters were adjusted slightly to yield a better match of the peak positions. A quantitative analysis was further attempted by using Bruker TOPAS software. Rietveld refinement on the catalysts was performed using crystal model proposed by Grasselli et al. There is work that show leaching could modify the structure of the catalyst and causes a change in distribution of M1 and M2 phase in the bulk. This effect is followed by a concomitant improvement of catalytic performance as claimed by Borgmeier *et al.* [30]. However, in this present work such relationship could not be established as reflected by the relatively constant intensity distribution of reflection peaks. A quantitative analysis was further attempted by using Bruker TOPAS software. *Rietveld* refinement on the catalysts was performed using crystal model proposed by the relatively constant intensity distribution of reflection peaks. A quantitative analysis was further attempted by using Bruker TOPAS software. *Rietveld* refinement on the catalysts was performed using crystal model proposed by Grasselli *et al.*



Figure 6.11: XRD patterns of undiluted & diluted MoVTeNb catalyst leached in water(●) M1phase and (■) M2 phase.

All XRD patterns for undiluted and diluted of non-leached and leached catalysts are plotted in Figure 6.11. The M1 phase can be identified by the major reflection peaks at $2\theta = 6.6^{\circ}$, 7.8°, 9.0°, 22.1°, 27.6°, 28.3° and 36.2° can mainly be related to an orthorhombic Te₂M₂₀O₅₇ (M=Mo, V and Nb) phase (Millet, Roussel et al. 2002). Furthermore, the M2 phase has strong reflection peaks at 2= 22.1°, 28.2°, 36.2° and 45.2° and 50.0° can be related to Te_{0.33}MO_{3.33} (M = Mo, V, Nb), a crystalline phase with a XRD pattern similar to that of a hexagonal tungsten bronze (K _{0.13-0.33}WO₃, HTB) (Botella, López Nieto et al. 2002; Garcia-Gonzalez, Lopez Nieto et al. 2002; Millet, Roussel et al. 2002) or pseudo hexagonal phase. In this study, the diffraction pattern was fitted with structure models of M1 and M2 phases published by Desanto *et.al* ((Desanto, R.K. et al. 2004). The famous five fingers print for M1 and M2 phases are 2 are 2 θ = 22.1 ° and 45.1 ° for orthorhombic M1phase and 2 θ = 28.3 °, 36.4 ° and 50.3 ° for pseudo hexagonal M2 phase.

In order to investigate the relative percentage and composition, *Rietveld* quantification analysis has been done. The quantification data are tabulated in Tables 6.4. The ratios of M1 phase remain 60-70% and M2 phase about 30-40%. This also indicates that when the leaching process occurs in stable / oxide phase, the structure or chemical bonds were strong enough to resist breakage and thus could not be leached out easily. This agreement can be supported by the TEM and EDX results, where only amorphous surface has been leached-out during the process.

Table 6.4: Quantitative analysis for undiluted and diluted leached in H ₂ O for 1 h and 24 h
by TOPAS.

Sample code	Concentration of M1	Concentration of M2
	(%)	(%)
675	58.4	41.6
679	59.4	40.6
680	59.6	40.4
671	60.2	39.8
676	57.3	42.7
678	60.6	39.4

6.2.4 Morphology and elemental composition Analysis by Scanning Electron Microscope (SEM)- EDX and X-Ray Fluorescence (XRF)

The morphology of all samples before and after leaching have been compiled in Figures 6.12 and 6.13 which exhibits the characteristic SEM images and EDX for elemental composition of MoVTeNb oxide catalyst.

i) Before leaching (675)



Elements	Normalized to Mo			
		spot	spot	spot
	theory	а	b	с
Mo	1.000	1.000	1.000	1.000
V	0.300	0.323	0.280	0.263
Te	0.230	0.346	0.221	0.118
Nb	0.125	0.082	0.027	0.183

ii) Leaching for 1 hr (679)



Elements	Normalized to Mo				
	theory	spot a	spot b		
Мо	1.000	spot a 1.000	1.000		
V	0.300	0.289	0.265		
Te	0.230	0.290	0.102		
Nb	0.125	0.124	0.146		

iii) Leaching for 24 hrs (680)



Elements	Normalized to Mo				
	theory	spot a	spot b		
Mo	1.000	1.000	1.000		
V	0.300	0.261	0.266		
Te	0.230	0.245	0.090		
Nb	0.125	0.065	0.140		

Figure 6.12: Morphology of undiluted MoVTeNb oxide before and after leached in water for 1 and 24 hours

Diluted MoVTeNb oxide catalyst

i) Before leaching (671)



Elements	Normalized to Mo				
	theory	spot a			
Mo	1.000	1.000			
V	0.300	0.476			
Te	0.230	0.355			
Nb	0.125	0.117			
Si	-	3.907			

ii) Leaching for 1 hr (676)



iii) Leaching for 24 hrs (678)

Elements	Normalized to Mo				
	theory	spot a	spot b		
Mo	1.000	1.000	1.000		
V	0.300	0.345	0.246		
Te	0.230	0.296	0.158		
Nb	0.125	0.113	0.097		
Si	-	4.666	4.081		

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	1 1 1 1 1	A PARA	S. S. M. S. Star Star	Te	0.230	0.247	0.274
2ª	和一位的子	R A MARTIN	AL PARAMENT ALL AND A	Nb	0.125	0.217	0.158
	公会 图130	4 335	and the second second	Si	-	3.369	3.027
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Figure 6.13: Morphology of diluted MoVTeNb oxide before and after leached in water for 1 and 24 hours

The effect of leaching time for undiluted and diluted samples gave some influences on morphology and catalytic activity. For undiluted system, the morphology features of the samples remain as the standard sample (non-leached). When the sample leached for 1 hour, the morphology still remains spherically ball shaped with smooth and needle-like surface. The EDX reveals that smooth surface containing high amount of tellurium and less of niobium. In contrast, leaching for 24 hours has different morphology where the ball with needle-like structure becomes agglomerated due to the longer time leaching process. Therefore, no changes in elemental composition detected from EDX analysis. In addition, leaching in 1 hour seems to be a good duration time in order to remove any impurities from the surface and the needle-like structure still remains as non-leached sample. The catalytic result also presents that leaching in 1 hour more selective to acrylic acid.

In diluted system, most of the morphology features are spherically balls with roughness surface. After 1 hour leaching, the morphology of the sample present that the ball becomes more roughen than non-leached sample. Leaching in 24 hours reveals more interesting image where the ball contains small balls surrounding the big ball. The EDX analysis configures that in excess of vanadium and tellurium. It is probably of long time leaching process could remove some of the support or unnecessary material. If refer to XRD data, no structural composition changed before and after leaching. There are no significant changes on catalytic activity for non-leached and leached sample.

Overall, the leaching process has given some effect on the catalytic activity of the catalyst. As known before, the performance of undiluted and diluted system have give big influences in catalytic performance. Even though without leaching process, the diluent or support still presents very high conversion of propane and more selective to acrylic acid. Leaching in longer time seems not give promising in improvement of catalytic activity. It might be because of some of ions or useful elements have been removed from the surface and change the surface structure of the catalyst. The optimum time of leaching has been identified in this study.

6.2.5Fluorescence Analysis (XRF)

The filtrated solution and remaining samples from the leaching process has been measured using XRF analysis. The distribution graph is plotted in Figure 6.14 and Table 6.5.

Table 6.5: XRF analysis of undiluted and diluted MoVTeNb oxide catalyst before and after surface purification.

Sample Code	Normalized to Mo					
	Mo	V	Те	Nh	Si	
Theory	1.000	0.300	0.230	0.125	-	
		Undi	luted			
675	1.000	0.226	0.220	0.124	-	
679	1.000	0.222	0.211	0.123	-	
680	1.000	0.242	0.207	0.126	-	
		Dilı	ıted			
671	1.000	0.356	0.379	0.123	0.371	
676	1.000	0.245	0.324	0.127	0.356	
678	1.000	0.256	0.317	0.127	0.410	

a) Remaining solid

b) Filtrated solution

Sample Code		Normalized to Mo				
	Мо	V	Те	Nb	Si	
Theory	1.000	0.300	0.230	0.125	-	
		Undi	luted			
679	0.001	0.035	0.162	0.015	-	
680	0.003	0.103	0.378	0.035	-	
Diluted						
676	0.005	0.138	0.415	0.015	0.598	
678	0.007	0.118	0.188	0.022	0.101	





Figure 6.14: XRF analysis of undiluted and diluted MoVTeNb oxide catalyst for nonleached and leached at 1 and 24 hours.

Figure 6.14 represents distribution of remaining solid and filtrated samples for undiluted and diluted system after leached for 1 and 24 hours. In totality, the percentage of metal removed from the solid is only around 0.15 to 0.4 % for tellurium and 0.05 to 0.15 % for vanadium. Based from the previous study, tellurium and vanadium can easily removed from the surface. Therefore, the catalytic activity diluted sample and long time leaching have given poor catalytic activity. EDX also support that this two elements have been removed during purification process. Inhomogeneous element distribution is one of the factors that affected on catalytic performance.

6.3 Structure-function relationship in selective oxidation reactions over MoVTeNb oxide catalyst.

The effect of the preparation method and surface purification on the formation of crystal phases and catalytic performance of the MoVTeNb oxide catalyst in selective oxidatiob of propane to acrylic acid were investigated.

Multiple functions the selective oxidation catalysts need to perform may include activation of the organic molecule, hydrogen abstraction, oxygen insertion, oxygen activation, and regeneration of the active site (s).



Figure 6.15: Schematic representation on the effect of phase formation and stability in the MoVTeNb mixed oxide catalyst.

Correlation between the synthesis parameter, phase formation and catalytic performance of the MoVTeNb mixed oxide catalyst had been study to gain understanding fundamental knowledge in catalyst system prepared by FHI and COMBICAT. Therefore, in Figure 6.15 explained in details the interplay kinetic of formation and stability of the active phase in the MoVTeNb oxide system.

High sensitivity of M1 and M2 phase formation to some parameters of synthesis such as pH, presence of oxoacids in the starting solution, method of slurry drying, redox conditions during heat treatment and ligand removal points to the importance of the nature of precursors in the catalyst preparation (Popova G.Y., Andrushkevich T.V. *et al.* 2009).

Sample	M1 (%)	M2 (%)	M1/(M1+M2)	Conversion	Selectivity	Yield
ID				(%)	(%)	(%)
675	58.4	41.6	0.584	52	14	7
679	59.4	40.6	0.594	46	41	19
680	59.6	40.4	0.596	53	15	8
671	60.2	39.8	0.602	28	66	18
676	57.3	42.7	0.573	32	71	23
678	60.6	39.4	0.606	39	70	27

Table 6.6: Phase composition and catalytic performance of MoVTeNb oxide catalyst



Figure 6.16: Phase composition and catalytic performance of MoVTeNb oxide catalyst

Structure function relationship has plays important role in determine the developing in good catalytic activity. Therefore, the data in Table 6.4 and Figure 6.16 illustrate the structure activity relationship of combining all non-leached and leached in undiluted and diluted MoVTeNb system.

From the plot, linear correlation between conversion to ratio M1 / (M1+M2) and selectivity to M1/(M1+M2) were made. The leaching has given some effect on increased in M1 phase. In undiluted system, the optimum leaching time has increased the selectivity towards acrylic acid. This can be expected as the leaching process served to purify the catalysts by removing of unwanted species. In contrast, the diluted system not gives any linear correlation between ratio of M1 phase to selectivity towards acrylic acid. In addition, leaching in longer time seems can give increase the conversion of propane but not selective to acrylic acid. It is probably due to the COx production.

Transition metals oxides may exhibit very different behavior when supported compared to unsupported form. When supported, transition metal oxides often exist as an isolated species. However, as metal loading increases, poly-aggregates or clusters form and crystalline domains can appear above monolayer coverage (Ozkan U.S. and Watson R.B. 2005). In this study, the support materials act as diluents to the active material where the ratio between supports to active material is 50:50.