

METAL-PROMOTER MoVTeNb OXIDE CATALYSTS FOR SELECTIVE OXIDATION: SYNTHESIS AND CHARACTERIZATION OF ACTIVE PHASE

Rubia Idris¹ & Sharifah Bee Abd Hamid²

¹School of Science and Technology

Universiti Malaysia Sabah, 88999 Kota Kinabalu, Sabah, Malaysia

²Combinatorial Technologies & Catalysis Research Centre (COMBICAT)

Institute For Postgraduate Study, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

ABSTRACT. *Several parameters involved in preparing the modified $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalysts system for the selective oxidation of propane to acrylic acid were investigated. These included the role of three types of transition metal promoter (Co, Cu and Ni) to the MoVTeNb oxide based catalyst was prepared by co-precipitation method. The role of the metal-promoter is to catalyse the active phase formation and it was found that each metal element plays a critical role to the performance of effective metal-promoter MoVTeNb oxide catalyst. Characterization results from XRD, SEM-EDX and TPR show an important difference depending on the weight loading and the types of metal-promoter. The XRD analysis identifies the phase inventory of metal-promoter MoVTeNb oxide catalysts. The structure of orthorhombic M1, M2, $TeMo_5O_{16}$, $V_{0.95}Mo_{0.97}O_5$ and Mo_5O_{14} phase was investigated. From literature it is known that the successful catalyst should be a mixture of two phases of orthorhombic and hexagonal variant of the MoVTeNb system which is referred to M1 and M2 phases. At low-magnification of SEM analysis has revealed the multi-phase nature of the metal-promoter MoVTeNb oxide catalysts. The absence of segregation metal-promoter in the MoVTeNb oxide catalysts is proven elemental presence by the EDX method. The TPR analysis identifies the addition of small amount of transition metal-promoter to the MoVTeNb oxide catalyst system will increased the reducibility amount of oxygen removed. As a lattice oxygen hypothesis, highest yield of labile oxygen would be available for selective oxidation process.*

KEYWORDS. Metal-promoter MoVTeNb oxide catalysts, XRD, SEM-EDX and TPR

INTRODUCTION

Today the major industrial process for acrylic acid production is by gas-phase catalytic oxidation. This commercial process used worldwide for making acrylic acid via two-step process, which is from propane to propylene then goes to acrylic acid (Lin *et al.*, 1999). Alternatively, acrylic acid can be produced from one-step oxidation of propane in gas phase with molecular oxygen and then goes to acrylic acid which is this extensive effort to replace the propylene (Bartek *et al.*, 1993). Recently the use of multi-component oxides catalysts based on molybdenum, vanadium, niobium and tellurium is seems to be a major breakthrough leading for promising developments of selective oxidation process of propane to acrylic acid (Grasselli, 1999). The potential of Mo and V based mixed oxide catalyst in propane oxidation was reported by Bartek *et al.* (1993). However, the most effective catalysts for selective oxidation of propane to acrylic acid a Mo-V-Te-Nb oxide based (Ushikubo *et al.*, 1994)

$\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ oxides catalyst has been reported which are able to give yields of acrylic acid above 40% (Hatano *et al.*, 1991; Lin, 2001). The preparation method and thermal pretreatment conditions in the production of these catalysts have proven to be crucial for the activity of the final catalyst (Beato *et al.*, 2006). Due to the complexity of these catalysts, preparation and characterization are formidable tasks. Small variations in preparation parameters and elemental stoichiometry, can result in grossly different products. Thus a high degree of control is needed in the preparation phase. To ensure homogeneity of the final product, several characterization techniques are employed throughout the preparation route.

MATERIALS AND METHODS

Catalyst Synthesis

Metal-promoter MoVTenb oxide catalyst was prepared by co-precipitation method according to patent which consisted of five metals: ammonium heptamolybdate, ammonium metavanadate, telluric acid, cobalt nitrate / chromium nitrate / nickel nitrate and ammonium niobium oxalate (Ushikubo *et al.*, 1994). Initially the ammonium heptamolybdate (6.43g from Sigma) was dissolved in 105g-deionizer water by heating and stirring, followed by the addition of ammonium metavanadate (1.27g from Aldrich) and telluric acids (1.93g from Aldrich) then followed by metal promoter (Co/Cu/Ni) salt at two different weights loadings of 0.005M and 0.05M. This was indicated by a change of color from yellow to dark orange. The suspension was stirred and heated at 353 K and then leave to cool to room temperature. An aqueous solution of niobium oxalate (4.33 mmol, which is 0.403 g of niobium ammonium oxalate in 28.65 g of aqueous solution) was added to this solution. The obtained slurry was stirred vigorously for 10 minute, then dried using rotavapor vacuum at 323 K, with speed of rotation 150 rpm and pressure of 36mbar for 2 hours. The catalyst precursor of chemical composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{P}_{<0.1}\text{O}_x$ was precalcine at temperature 548K under air by using air oven at heating rate 10 K min^{-1} and hold for 1 hour. The catalyst precursor was calcined at temperatures 873 K under flow of argon (10 ml min^{-1}) using Carbolite CWF 1200 furnace at heating rate of 2 K min^{-1} and hold for 2 hours to generate the active catalyst.

X-Ray Powder Diffraction (XRD)

The powder XRD analysis was carried out using a Bruker X-ray Diffraction model D-8 to obtain a crystalline phase of the precursors and catalysts, at ambient temperature. About 200 to 500 mg of sample powder was mounted on an alumina sample holder. Diffraction pattern were obtained by employing CuK_α radiation ($\lambda = 1.54019\text{ \AA}$) generated by Bruker glass diffraction X-ray tube broad focus 2.7 kW type. The sample was continuously scanned at the range of $2\Theta = 2$ to 80° with a scanning rate of $0.02^\circ\text{ sec}^{-1}$. The values of the d-spacing, intensity and full width at half maximum (FWHM) were calculated using basic process version 2.6 software. The diffractograms obtained were matched against the Joint Committee on Powder Diffraction Standards (JCPDS) PDF 1 database version 2.6 to confirm the catalytic phase.

Scanning Electron Microscope (SEM-EDX)

The sample was adhered on the aluminium stub using carbon conductive tape. The stub was then mounted on the stub holder and loaded into the chamber and evacuated for analysis. Images were recorded at COMBICAT with a Quanta 200 FEI microscope instrument and INCA-Suite version 4.02 for ECK analysis. The following settings were used: accelerating voltage, 5 kV; Detector type, ETD-SE; working distance: 8-10 mm.

Temperature Program Reduction (TPR)

A Thermofinnigan TPDRO 1100 instrument is used to carry out the temperature-programmed reduction. About 100 -200 mg of the catalyst was pre-treated by heating it at 393 K under N₂ flow (1bar, 20cm³ min⁻¹) and hold for 45 minutes to eliminate possible contaminants and completely oxidised the metal portion of the catalyst. It was then cooled to room temperature. After that, the flow was switch add to 5% hydrogen in argon (1bar, 20 cm³ min⁻¹). The temperature was raised from ambient to 923 K at a heating rate of 3K min⁻¹ and hold under flow of gas for 30 minute. The reduction was measured by monitoring the hydrogen consumption with the TCD detector.

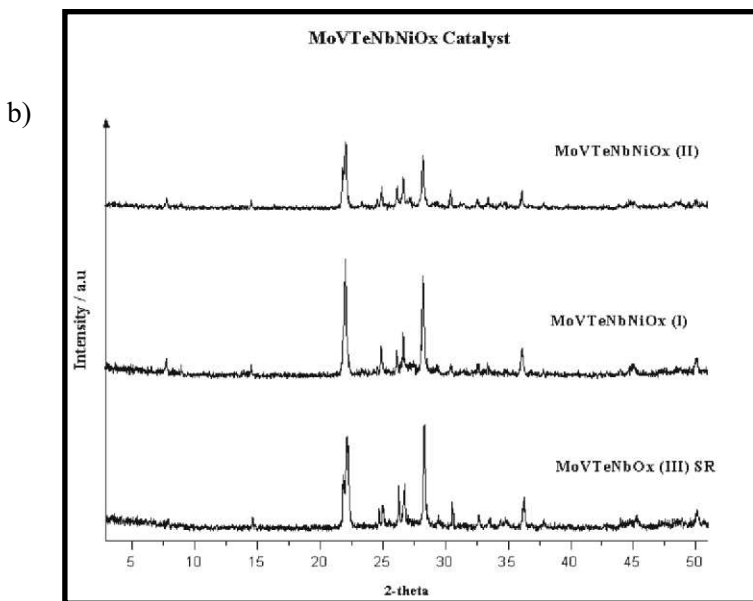
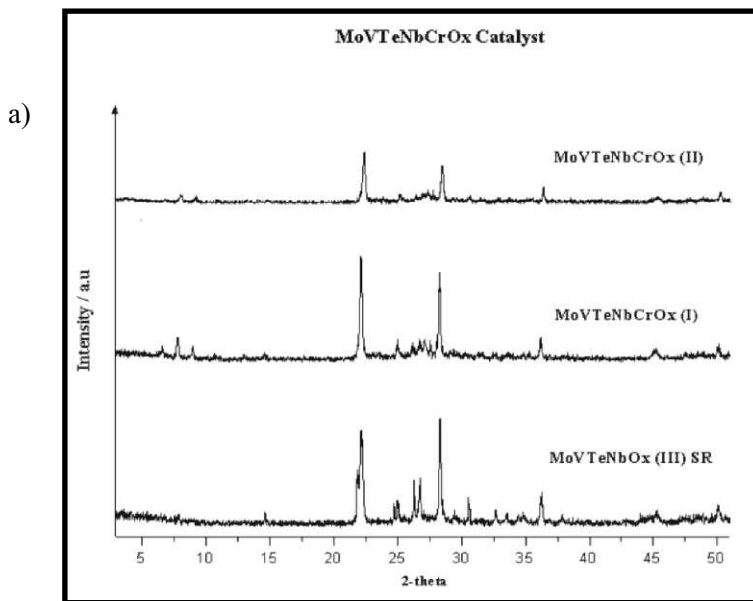
RESULTS AND DISCUSSION

Crystallography Study

Figure 1a, b and c shows the XRD patterns of metal-promoter MoVTeNb oxide catalyst. From literature it is claims that the successful Mo₁V_{0.3}Te_{0.23}Nb_{0.12}O_x catalyst should present strong Bragg reflection at 2θ = 22.1, 28.2, 36.2, 45.2, and 50.0 (“famous five”). These famous five lines suggest as fingerprint the formation of a recently reported as Te-V-Mo-O or Te-V-Nb-Mo-O (TeMO) crystalline phase designated as “M1” in the Grasselli work (Grasselli *et al.*, 2003 and De santo *et al.*, 2003). This selection peaks is characterizes as mixture of orthorhombic and hexagonal phase which is referred to M1 and M2 phases. The ortho phase is the key relevance for the function of MoVTeNb oxide catalysis. Without its presence there is little catalytic activity in propane to acrylic acid conversion.

The XRD patterns of metal-promoter MoVTeNb oxide catalyst (Figure 1 a, b and c) it is clearly shows that the famous five strong Bragg reflection at 2θ = 22.1, 28.2, 36.2, 45.2, and 50.0 is present. Benefiting from the identical calcinations conditions from previous studies, the effect of the different transition metal additives on the structure-formation processes can be directly compared and related to the structure of the non-promoter system. In agreement with the observation in the Ni system it is evident that Cr addition strongly enhances the abundance of the ortho phase and even when only 0.005% was added (Figure 1 and Table 1). The fact that a different metal ion is more efficient in modifying the phase formation may be indicative that it is of relevance at which point in thermal pre-history of the sample the detrimental reducing species are removed. Both the temperature level and the local thermal overheating during the catalysed oxidation are different for Ni and Cr. In particular, the effect of a thermal shock during pre-calcination that was clearly evidenced in the EDX and TPR data (Table 1 and Table 2) may be of beneficial function in bringing about the ortho phase. This phase is the least stable phase in the phase cocktail of the MoVTe system and either forms with the most demanding kinetics or is most easily destroyed at the high calcinations temperatures used for the phase formation process during the main calcination. The fact that a very crystalline variant of the ortho phase is obtained if no calcination but hydrothermal synthesis is applied (Ueda *et al.*, 2001) underlines this kinetic liability of the target phase. In Co addition, it seems not to interfere with the redox

chemistry of the ligand removal and hence also not to affect the phase formation process. This observation allows the exclusion on the notion that the function of the transition metal addition could be something different than changing the calcination chemistry; all transition metals would stabilize defects in a densely packed arrangement of octahedral by either providing tetrahedral linkers (Cr, Ni) or by inducing strain due to different distortion for Mo, V and dopant-containing octahedral. This effect is well-documented in close-packed oxides but plays only a negligible role in the present non-densely packed structures that are tolerant to cation substitution already in the reference system.



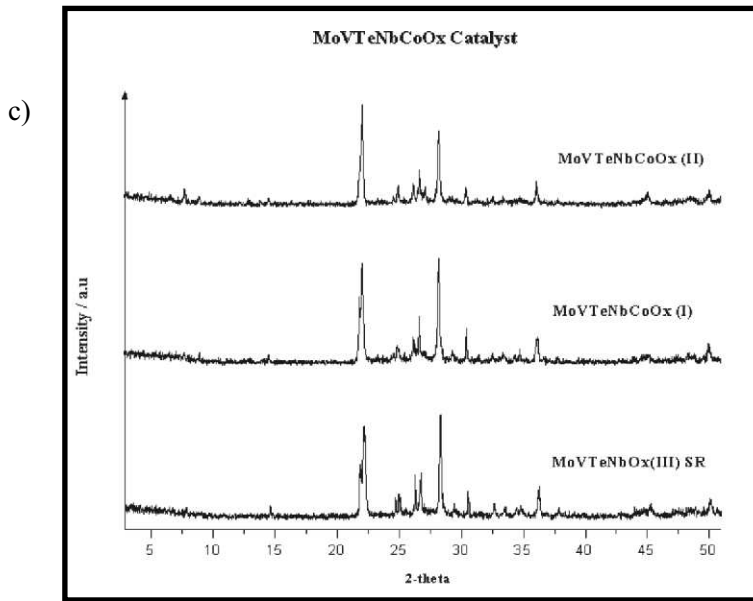


Figure 1. XRD patterns of metal-promoter (a) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{CrO}_x$ catalyst, (b) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{NiO}_x$ catalyst and (c) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{CoO}_x$ catalyst which is (I) refer to 0.05 at% and (II) refer to 0.005 at% of promoter metal weight loading.

Surface Morphology and Element Composition

The extensive investigation of morphology and local chemical composition of metal-promoter MoVTeNb oxide catalyst is comply in the Figures 2. The low-magnification of SEM images reveals a coarsely granular structure typical of a mixture of well-shaped crystals for the majority of samples. Two exceptions to this morphology assignment are noted; i) The Cr promoter is fully homogeneously distributed over all particles and exhibits no enrichment in any discernible segregation. ii) The Ni promoter, on the contrary is ex-soluted from the platelets and forms surface aggregates of probably NiO on their surfaces. Ni is definitely not co-substituted with V for Mo in the Anderson phase.

The micro morphology of the promoter samples (Figure 2) shows little general deviation from the morphology mix of the unpromoter samples. The only clear exception is the case of Ni promotion where a separate nanostructured NiO phase is discernible on the platelets of the molybdo-tellurate phase. The absence of any such segregation of the Cr promoter despite its proven elemental presence by EDX is a confirmation of the expected high dispersion of Cr in the molybdate matrix. This is the consequence of the chemical similarity of Cr and V that are as early transition metals electronically more compatible with the molybdate matrix than the later transition metals Ni and Co whose cohesion energy in binary oxides is a driver for separate phase formation in an electron-rich matrix of molybdo-tellurates.

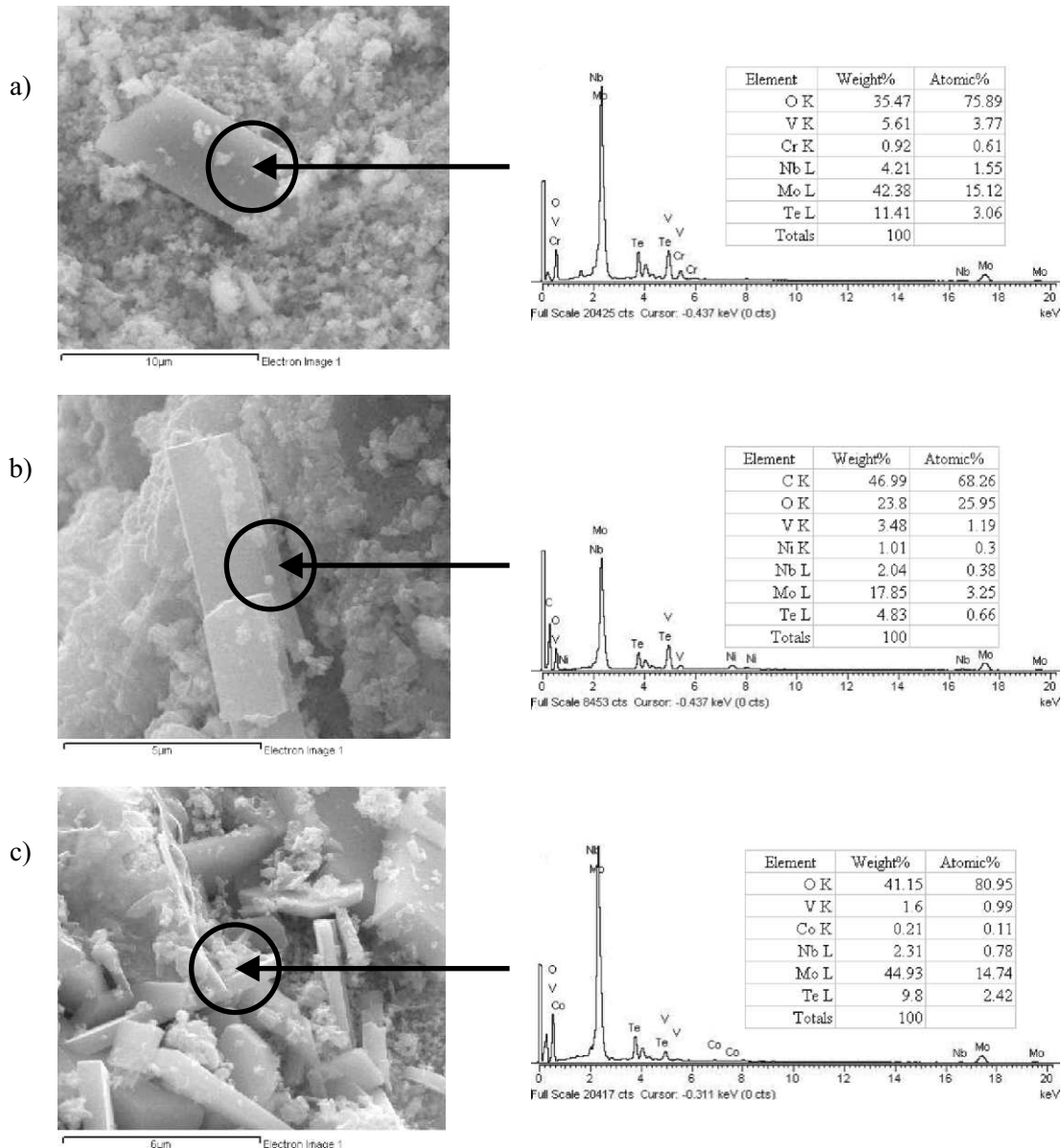


Figure 2. SEM-EDX results of the metal-promoter, (a) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{CrO}_x$ catalyst, (b) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{NiO}_x$ catalyst and (c) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{CoO}_x$ catalyst.

Table 1. EDX result of metal-promoter MoVTenb catalyst at two different weights loading.

Catalysts	Phase (from XRD)	Atomic Ratio				
		V / Mo	Nb / Mo	Te / Mo	Te / Mo + V + Nb	Te + Nb / Mo + V
MoVTenbO _x Ni (I)	M2 + $\text{TeMo}_5\text{O}_{16}$ + $\text{V}_{0.95}\text{Mo}_{0.97}\text{O}_5$	0.24	0.009	0.18	0.14	0.22
MoVTenbO _x Ni (II)	M2 + $\text{TeMo}_5\text{O}_{16}$ + $\text{V}_{0.95}\text{Mo}_{0.97}\text{O}_5$	0.18	0.07	0.18	0.15	0.21

MoVTeNbO _x Cr (I)	M2 + TeMo ₅ O ₁₆ + V _{0.95} Mo _{0.97} O ₅	0.29	0.13	0.2	0.14	0.26
MoVTeNbO _x Cr (II)	M2 + TeMo ₅ O ₁₆ + V _{0.95} Mo _{0.97} O ₅	0.18	0.006	0.21	0.17	0.24
MoVTeNbO _x Co (I)	M2 + TeMo ₅ O ₁₆ + V _{0.95} Mo _{0.97} O ₅	0.13	0.05	0.21	0.18	0.23
MoVTeNbO _x Co (II)	M2 + TeMo ₅ O ₁₆ + V _{0.95} Mo _{0.97} O ₅	0.26	0.06	0.24	0.18	0.24

MoVTeNbO_x Ni(I) : Ni-promoter (0.05at %) ; MoVTeNbO_x Ni(II) : Ni-promoter (0.005at%).
 MoVTeNbO_x Cr(I) : Cr- promoter (0.05at %) ; MoVTeNbO_x Cr(II) : Cr-promoter (0.05at %).
 MoVTeNbO_x Co(I) : Co-promoter (0.05at %) ; MoVTeNbO_x Co(II) : Co-promoter (0.05at %).

Reduction Behavior

Figure 3 show the oxygen consumption of metal-promoter MoVTeNb oxide catalysts with two different compositions, 0.05 at% and 0.005 at%. From TPR profile of nickel-promoter gives a single reduction peak. This profile show when the weight loading of nickel ~0.005 gives a single peak reduction with a small lump at temperature 685K and the maximum reduction temperature at 737 K. The total oxygen removed from the catalyst surface is 4.5×10^{21} atom gram⁻¹, which is around 49.3% of oxygen was removed from the catalyst surface, respectively. But when the weight loading of nickel promoter increased to ~0.05 the reduction peak shifted to low temperature and only one maximum reduction temperature can see at 724 K with the total oxygen removed is 4.1×10^{21} atom gram⁻¹ where around 45.3% of oxygen was removed. The TPR profile of chromium-promoter catalyst also presents a single sharp peak with a small lump. When the catalysts with low promoter weight loading (0.005 atomic %) the TPR profile gives a single reduction peak at maximum temperature 763 K with a small lump, but when the weight loading increase to 0.05 atomic percent maximum reduction temperature shifted to lower temperature at 759 K and the small lump at 720 K.

Total oxygen removed for Mo₁V_{0.3}Te_{0.23}Nb_{0.12}CrO_x catalyst with low promoter weight loading (0.005 atomic %) are almost 4.2×10^{21} atom gram⁻¹ which is 46.7% of oxygen removed from the surface and for the Mo₁V_{0.3}Te_{0.23}Nb_{0.12}CrO_x catalyst with high promoter weight loading (0.05 atomic %) the total oxygen removed is almost 4.5×10^{21} atom gram⁻¹ which is around 49.3% of oxygen was removed from the catalyst surface, respectively. The TPR profile of cobalt-promoter catalysts shows only one single sharp peak. The Mo₁V_{0.3}Te_{0.23}Nb_{0.12}CoO_x catalysts with low promoter weight loading (0.005 atomic %) gives a value of total oxygen removed is almost 3.1×10^{21} atom gram⁻¹ at the maximum reduction temperature 793K. But for Mo₁V_{0.3}Te_{0.23}Nb_{0.12}CoO_x catalyst with high promoter weight loading the maximum reduction temperature was shifted to low temperature at 776 K and gives total oxygen removed is 3.2×10^{21} atom gram⁻¹, respectively. Overall, from the TPR result of metal-promoter MoVTeNb oxide catalyst system, low nickel weight loading (0.005 atomic %) and high chromium weight loading (0.05 atomic %) gives a better catalytic activity performance where this catalysts gives a higher oxygen removed from the catalyst surface which is, this lattice oxygen can assumed as selectivity for the selective oxidation process.

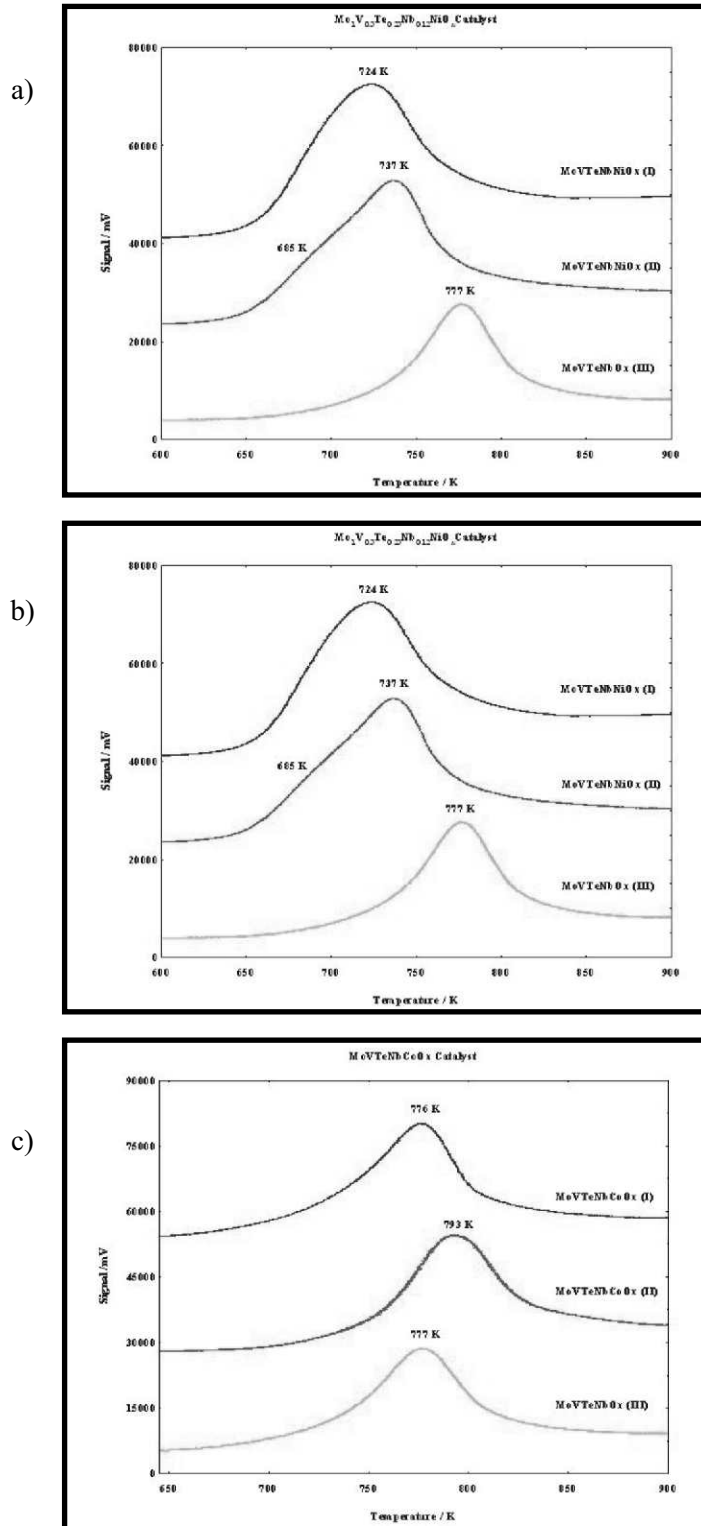


Figure 1. TPR profile of metal-promoter, (a) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{CrO}_x$ catalyst, (b) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{NiO}_x$ catalyst and (c) $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{CoO}_x$ catalyst, which is (I) refer to 0.05 at% and (II) refer to 0.005 at% of promoter metal weight loading.

The reduction activation energy of metal-promoter and un-promoter $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ system can be calculated with the Redhead equation (Taufiq Yap Yun Hin, 1997) as follows:

$$\frac{E_r}{RT_m^2} = \left(\frac{A_r}{\beta} \right) [\text{H}_2]_m \exp\left(\frac{-E_r}{RT_m} \right) \quad (1)$$

Where E_r is the reduction activation energy (kJ mol^{-1}), T_m is the peak maximum temperature (K) in the rate of the consumption of H_2 , A_r as a reduction pre-exponential term ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) which is given the value of a standard collision number of $10^{13} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ and $[\text{H}_2]_m$ is the gas phase concentration of hydrogen (mol cm^{-3}) at the peak maximum. Table 3 shows the value of reduction activation energy of metal-promoter $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ catalyst.

Table 2. Data summarized from TPR profiles of metal-promoter $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{P}_{<0.01}\text{O}_x$ system.

Type of Catalysts	Reduction activation energy, E_r (KJ mol-1)	T_{\max} / K	Amount O_2 removed (mol gram ₁)	Amount O_2 removed (Atom gram ⁻¹)	Percentage Oxygen removed (%)
MoVTeNbNiOx(I)	135.0	724	6.8×10^{-3}	4.1×10^{21}	45.3
MoVTeNbNiOx(II)	128.5 137.3	685 737	1.7×10^{-3} 5.7×10^{-3}	1.0×10^{21} 3.4×10^{21}	49.3
MoVTeNbCrOx(I)	135.2 141.4	720 759	1.2×10^{-3} 6.2×10^{-3}	7.2×10^{21} 3.7×10^{21}	49.3
MoVTeNbCrOx(II)	142.2 147	763 786	3.6×10^{-3} 3.4×10^{-3}	2.2×10^{21} 2.1×10^{21}	46.7
MoVTeNbCOOx(I)	144.6	776	5.3×10^{-3}	3.2×10^{21}	35.3
MoVTeNbCoOx(II)	147.8	793	5.1×10^{-3}	3.1×10^{21}	34

Surface area: MoVTeNbNiOx(I) : $10.61 \text{ m}^2 \text{g}^{-1}$
 MoVTeNbNiOx(II) : $7.33 \text{ m}^2 \text{g}^{-1}$
 MoVTeNbCrOx(I) : $11.48 \text{ m}^2 \text{g}^{-1}$
 MoVTeNbCrOx(II) : $9.42 \text{ m}^2 \text{g}^{-1}$
 MoVTeNbCoOx(I) : $5.29 \text{ m}^2 \text{g}^{-1}$
 MoVTeNbCoOx(II) : $10.56 \text{ m}^2 \text{g}^{-1}$

$$\text{Percentage of oxygen removed (\%)} = \frac{\text{Total amount of oxygen removed (mol g}^{-1}\text{)}}{\text{Total amount of oxygen Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x \text{ (mol g}^{-1}\text{)}} \times 100\% \quad (2)$$

CONCLUSION

The successful modified $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ catalyst is depends on several parameters involved in preparing the catalyst, which includes the method of preparation and activation procedure, types of promoter metal and amount of the metal promoter. Various solids prepared, composing of Mo, V, Te, Nb and oxides of the support and promoter are further characterised to define their structural, thermal and chemical properties. This information would directly contribute to the understanding of catalyst synthesis and the defects properties of the catalyst, which in turn is crucial to a systematic and rational approach in catalyst design.

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