ROLE OF NICKEL PROMOTER ON ACTIVE SITE OF MoVTeNb OXIDE CATALYST FOR SELECTIVE OXIDATION OF PROPANE

(Peranan Nikel-Pengalak Pada Bahagian Aktif Mangkin Oksida Movtenb Bagi Proses Pengoksidaan Pemilih Propana)

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Abstract

Role of Ni-promoters on the modification of active sites of MoVTeNb oxide catalysts for selective oxidation of propane was investigated. This Ni-metal promoter of MoVTeNb oxide catalyst was prepared by co-precipitation method. The catalysts were characterized by BET, XRD, SEM-EDX and TGA-DSC. The characterisation results show an important difference depending on the weight loading of Ni-metal promoter. From the XRD analysis, structure of orthorhombic *M1, M2,* $TeMo_5O_{16}$, $V_{0.95}Mo_{0.97}O_5$ and Mo_5O_{14} phases was investigated. From literature it is known that the successful catalyst for selective oxidation of propane to acrylic acid should be a mixture of two phases of orthorhombic and hexagonal variant of the MoVTeNb catalyst system which is referred to *M1* and *M2* phases [11]. At low-magnification of SEM analysis it has revealed the multi-phase nature of the Ni-metal promoter. The segregation of nickel metal in the MoVTeNb oxide catalysts was proven elemental presence by the EDX method. BET result showed that the surface areas of Ni-promoter catalysts were increase when the weight loading of Ni-promoter increases from 0.005at% to 0.05at%. TGA and DSC results also agree that the addition of small amounts of Ni-promoter affects the thermal behavior of the oxide mixture. This indicates that the catalytic operation of the nickel promoter acts as a structural promoter by changing the redox behavior of the whole metal-ligand system.

Keywords: Ni-Promoter MoVTeNb oxide catalyst, BET, SEM-EDX, XRD, TGA and DSC.

Abstrak

Peranan Ni-pengalak pada pengubahsuaian pusat aktif mangkin oksida MoVTeNb bagi proses pengoksidaan pemilih propane telah dikenalpasti. Ni-pengalak mangkin oksida MoVTeNb telah disediakan dengan kaedah *co-precipitation*. Mangkin telah dicirikan dengan kaedah penciri BET, XRD, SEM-EDX dan TGA-DSC. Hasil penciri menunjukkan perbezaan penting yang bergantung kepada jisim Ni-pengalak. Daripada analisis XRD, struktur fasa ortorombik *M1, M2,* $TeMo_5O_{16}$, $V_{0.95}Mo_{0.97}O_5$ dan Mo_5O_{14} telah dikenalpasti. Daripada kajian lepas telah diketahui bahawa mangkin yang berjaya bagi proses pengoksidaan pemilih propane kepada asid akrilik seharusnya mempunyai campuran dua fasa varian ortorombik dan heksagonal yang merujuk kepada fasa *M1* dan *M2* [11]. Pada magnifikasi-rendah analisis SEM telah mengenalpasti pelbagai fasa sifat asal Ni-pengalak mangkin oksida MoVTeNb. Segregasi logam nikel pada mangkin oksida MoVTeNb telah disahkan kehadiran elemennya dengan kaedah penciri EDX. Hasil penciri BET menunjukkan luas permukaan mangkin Ni-pengalak bertambah apabila jisim Ni-pengalak bertambah daripada 0.005at% kepada 0.05at%. Hasil penciri TGA dan DSC juga bersetuju bahawa penambahan sedikit amoun Ni-pengalak memberi kesan kepada sifat termal campuran oksida. Ini menunjukkan operasi pemangkinan bagi Ni-pengalak bertindak sebagai struktur pengalak bagi mengubah sifat redoks bagi keseluruhan system ligan logam.

Keywords: Mangkin oksida Ni-Pengalak MoVTeNb, BET, SEM-EDX, XRD, TGA dan DSC.

Introduction

Generally, multimetal oxide catalysts are Mo-based and most of them contain V as a major component. Most patents claim that Mo is an essential element of commercial catalyst for propylene oxidation to acrylic acid while V is another essential element used as commercial catalyst for acrolein oxidation to acrylic acid [1]. Mixed oxide catalyst lacking V is very active for propylene oxidation [2-4] and is not very active for propane oxidation [5, 6].

The potential of Mo and V based mixed oxide catalyst in propane oxidation was reported by Bartek *et al.* [7]. However, the most effective catalysts to date for propane oxidation to acrylic acid are those Mo-V-Te-Nb-O catalysts reported by Ushikubo *et al.* [8] and Lin and Linsen [1]. In fact, a catalyst with the same four components was first found to be effective for propane ammoxidation to acrylonitrile process [9]. It has been

quite unexpected that the same catalyst can function so well for two different reactions without needs future for compositional modification. Although the two reactions, propane oxidation and propane ammoxidation may share some fundamental reaction steps, such as propane activation and propane oxidative dehydrogenation, there are significant different between the two [1]. For instance, ammonia activation and addition steps for nitrile formation are unique to propane ammoxidation acrylonitrile and do not exist in propane oxidation. Furthermore, acrylonitrile and acrylic acid differ significantly with respect to the acidity and thermal stability. Nevertheless, this Mo-V-Te-Nb mixed metal oxide catalyst was shown to be remarkably robust and efficient for both reactions [10].

The performance of Mo-V-Te-Nb-O catalysts for propane oxidation to acrylic acid has been shown to be significantly better than that of any other multi-component metal oxides *(MMO)* type of catalysts, or any *VPO* or *HPC* type of catalysts. However, it is difficult to prepare active Mo-V-Te-Nb-O catalysts that exhibit the claimed performance in either propane ammoxidation to acrylonitrile or propane oxidation to acrylic acid [11]. In this case, not only the composition of the catalyst is of importance, but also the preparation method also greatly gives varying effectiveness of the catalyst of essentially the same composition. For example, the performance of $Mo_1 V_{0.3} Te_{0.23} Nb_{0.1} O_n$ catalysts can vary from very poor (no yield) [1, 13], mediocre (14% acrylic acid yield) [14], to excellent (more then 40% acrylic acid yield) [1, 13]. These performance differences reflect different structure of the catalysts prepared under different preparation conditions [1, 13, 15].

Manhua *et al.* reported the reaction-pathways in selective oxidation of propane over a mixed metal oxide catalyst. He showed some the catalytic properties of a Mo-V-Te-Nb-O metal oxide catalyst in the selective oxidation of propane and its corresponding partial oxidation intermediate. He proposed that different catalysts gives different oxidation pathway. Mo-V-Te-Nb-O catalysts showed direct oxidation pathway of propylene to CO_x as well [16].

Ueada *et al.* studied nickel molybdate modified with telluromolybdate for selective oxidation of propane to acrylic acid and acrolein. He observed synergistic effect between nickel molybdates and telluromolybdate, and the selectivity of acrylic acid and acrolein are 87%. It was achieved at 9% weight loading of telluromolybdate. Sb-modified nickel molybdate was also found to be effective for this reaction, although the yield was low compare with Te-modified catalysts [17].

Experimental

The Ni-promoter MoVTeNb oxide catalysts were prepared according to standard method of Manhua *et al.* with the addition of nickel metal at two different weight loading, 0.05 and 0.005 atomic percent [1]. The Ni metal was introduced to the first slurry, where the slurry solutions consisted of five metals: ammonium heptamolybdate, ammonium metavanadate, telluric acid, nickel nitrate and ammonium niobium oxalate. 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 nickel 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 $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Ni_{0.05}O_x$ and $Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Ni_{0.005}O_x$ 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 catalysts.

Results and Discussion

Surface Area Study

Table 1 show the information obtained from the nitrogen physisorption of Ni-promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ oxide catalysts system which prepared at two different weight loading (0.05 and 0.005 at%), where S_{BET} represents for specific surface areas ($m^2 gram^{-1}$) and P_V represents for pore volume ($cm^3 gram^{-1}$). This catalyst systems show the adsorption isotherms of type II with the present of hysteresis loop, indicating the presence of mesopores and the hysteresis loop is of type E, indicating the presence of pores having varying width (Figure 1).

The total surface area of these catalysts in the range of 10 to 7 m^2g^{-1} whilst the pore volume shows negligible changes when the standard system were promoter with Ni promoter. The surface areas of Ni-promoter catalysts increase when the weight loading of Ni-promoter increases from 0.005 to 0.05. One would expect the low dosage of promoter added to MoVTe would not significantly perturb the initial surface area of the standard recipe catalysts whilst relatively higher dosage of 0.05 probably could modify the texture of the catalysts. It is taken that the variation of 3 m^2g^{-1} in surface area is within the experimental repeatability rather than inherent of the treatment that systems have been subjected to.

From the BET surface area results, it is can anticipate that the higher surface area catalysts would exhibit higher activity. Hence, the surface area result is one of the major contributive factors governing catalyst activity [11]. From overall result also, found that the p/p_o range is maintained around 0.01 to 0.03. This is show that the BET equation is linear and the BET plot can be expected to give a yield the true value.

Table 1: BET result for Ni-promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ oxide catalyst system at two different weight loading, 0.05 and 0.005 atomic percent compare with standard method catalyst.

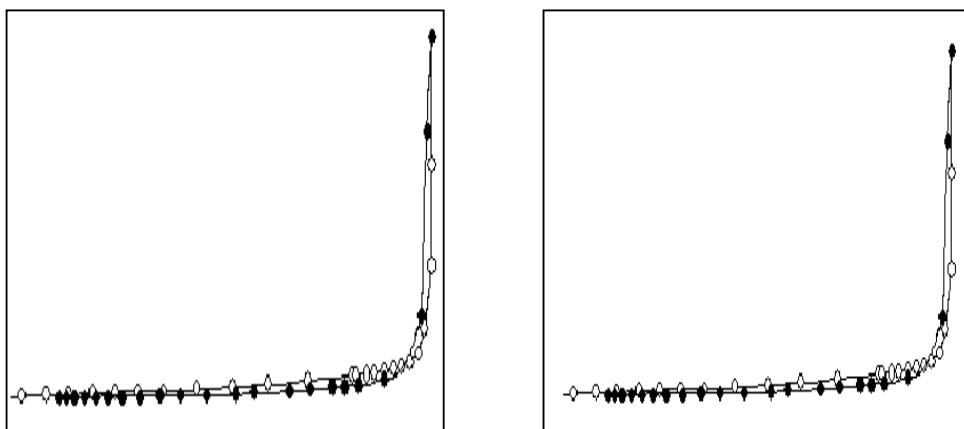| Catalysts	Promoter	S_{BET} (m^2 g^{-1})	P_V (cm^3 g^{-1})
$Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}O_X$	SM	10.5	0.01
$Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Ni_{0.05}O_x$ (I)	(0.05 at%)	10.6	0.02
$Mo_{1.0}V_{0.3}Te_{0.23}Nb_{0.12}Ni_{0.005}O_x$ (II)	(0.005 at%)	7.3	0.03

SM : Standard method catalyst

Figure 1: BET type II isotherm of Ni-metal promoter Mo-V-Te-Nb-O$_x$ catalysts system.

Surface Morphology & Elements Composition
The extensive investigation of morphology and local chemical composition is complied in the Figures 2 and 3 for EDX which is Figure 4 is for SEM. The low-magnification SEM images reveal a coarsely granular structure typical of a mixture of well-shaped crystals. The Ni promoter catalyst, 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 *M1* and *M2* phase.

The Ni promotion catalyst clearly shows where a separate of structured NiO phase is discernible on the platelets of the molybdo-tellurate phase. This is the consequence of the chemical similarity of V that are as early transition metals electronically more compatible with the molybdate matrix than the later transition metals Ni whose cohesion energy in binary oxides is a driver for separate phase formation in an electron-rich matrix of molybdo-tellurates.

In summary, the SEM-EDX analysis has revealed the multi-phase nature of the MoVTe samples. It has further confirmed that the phase formation occurs kinetically after the gas evolution of the ligand removal. In some cases the ligand removal did not happen. The pre-calcination led to a carbon-inorganic composite material with maybe interesting but non-catalytic properties. The promotion had little morphological effect besides separate phase formation of the later transition metal oxides.
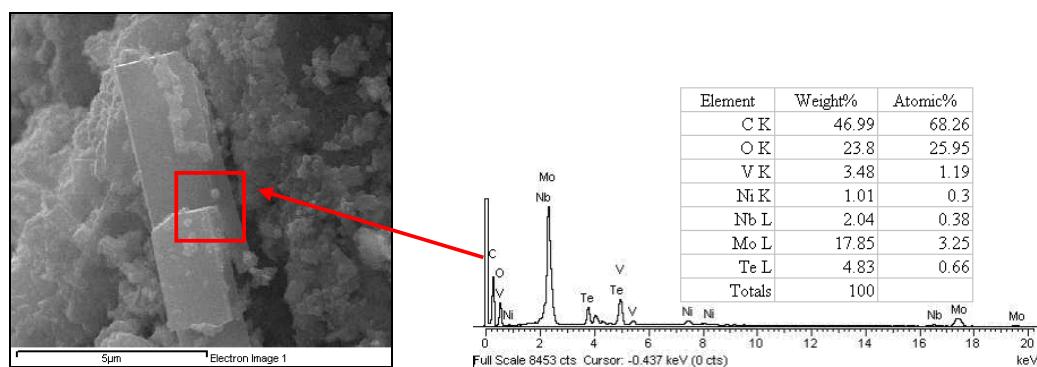

Element	Weight%	Atomic%
C K	46.99	68.26
O K	23.8	25.95
V K	3.48	1.19
Ni K	1.01	0.3
Nb L	2.04	0.38
Mo L	17.85	3.25
Te L	4.83	0.66
Totals	100	

Figure 2: SEM-image (left) and EDX (right) of the final $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst system adding nickel as a promoter with weight loading 0.05 atomic percent.
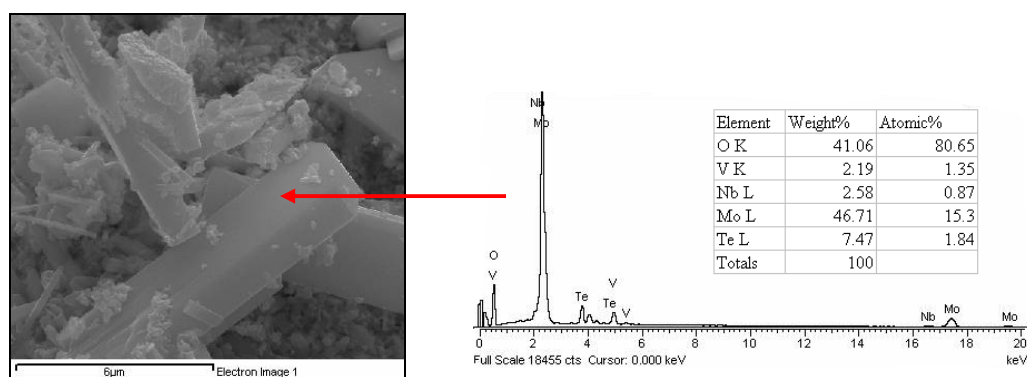

Element	Weight%	Atomic%
O K	41.06	80.65
V K	2.19	1.35
Nb L	2.58	0.87
Mo L	46.71	15.3
Te L	7.47	1.84
Totals	100	

Figure 3: SEM-image (left) and EDX (right) of the final $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst system adding nickel as a promoter with weight loading 0.005 atomic percent.
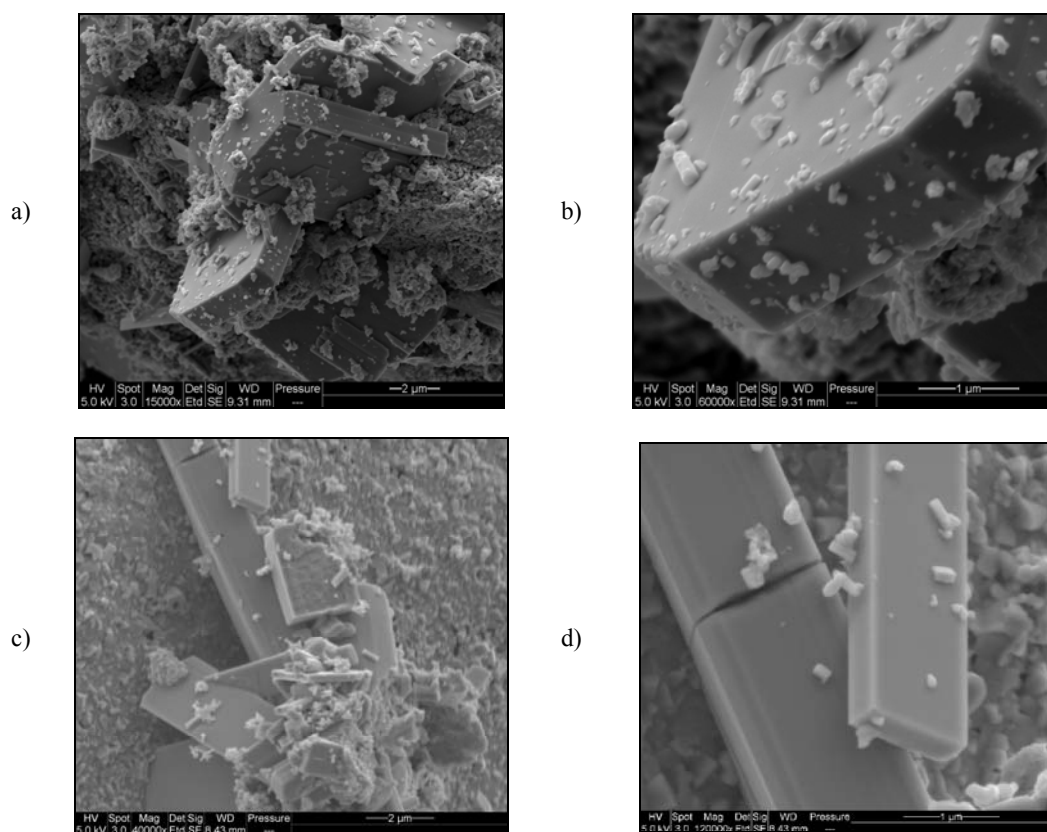
Figure 4: SEM-image of the Ni- promoter catalyst with weight loading 0.05 at% (Figure a, b) and 0.005 at% (Figure c, d) as a promoter.

Crystallography Study

Figure 5 shows the XRD patterns of Ni-promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ oxide catalyst. From literature it is claims that the successful $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ 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 [12]. 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.

From the XRD patterns, it is clearly shows that adding nickel, as a promoter affects the crystallinity of the catalyst sample. This is unexpected as so little additional material that would barely give rise to any discernible diffraction intensity have an effect on the overall structure. This shows that at least one of the prompting functions is that of a structural promoter affecting the phase formation. The observation implies further that within the limits of reproducible diffraction data acquisition the poor quality of the diffraction patterns is not the effect of self-absorption but of on an average poor diffraction power pointing to coherence length problems when taking into account the overall good crystalline morphology seen in the SEM/EDX part. It occurs further that the abundance of the ortho phase in the mixture indicated by the famous five reflections and by the now discernible low-angle reflections has markedly increased in the 0.05% sample. In accordance with the thermal analysis data this observation fits the idea that during calcinations there should be no reducing components in the system: the addition of the transition metal catalyzes the gasification of ligands and thus reduces the abundance of residual species consuming oxygen during the crucial phase formation process in the main calcination reaction. The SEM-micrographs of this catalyst (*Figure 4 a, b*) shows that at high weight loading segregation of a Ni phase on the crystals of the Anderson phase occurs whereas at low loading (*Figure 4 c, d*)

no effect on the sample morphology was detected. Table 2 summarised of the crystalline phase of promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}NiO_x$ catalyst system compared with the standard method catalyst.
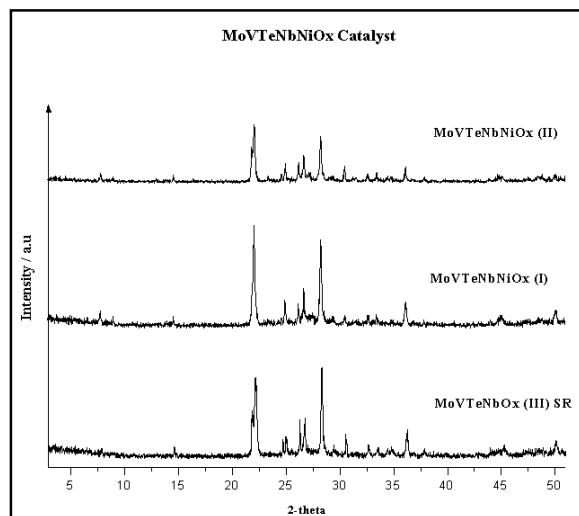

Figure 5: X-ray Powder diffraction pattern of Ni-promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst with weight loading 0.05 at% (MoVTeNbNiOx I) and 0.005 at% (MoVTeNbNiOx II), compared with standard method catalyst (MoVTeNbOx III).

Table 2: Summary of Ni-promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ crystalline phase.

Sample	Metal (Atomic weight)	XRD crystalline phases
MoVTeNbOx (III)	SM	$M2$; $TeMo_5O_{16}$; $V_{0.95}Mo_{0.97}O_5$
MoVTeNbNiOx (I)	Ni (0.05)	$M2 + TeMo_5O_{16} + V_{0.95}Mo_{0.97}O_5$
MoVTeNbNiOx (II)	Ni (0.005)	$M2 + TeMo_5O_{16} + V_{0.95}Mo_{0.97}O_5$

SM : Standard method catalyst
MoVTeNbOx Ni (I) : Catalyst adding Ni-promoter with weight loading 0.05at%.
MoVTeNbOx Ni (II) : Catalyst adding Ni-promoter with weight loading 0.005at%.

Thermal Behavior Study
Figure 6 and 7 shows the compilation of data for the Ni-promoter MoVTeNb oxide catalyst system. The top line compares the TG-DTG data and the lower lines compare the TG-DSC traces. It is significant that the total weight loss in the promoted systems is much larger than the addition of cation should give rise to. There is also no proportionality in this additional weight loss. The most likely explanation is the catalytic effect of removing redox-active ligands under auto reducing conditions.

In the Ni system the addition of the large amount of promoter seriously affects the kinetics of ligand decomposition. The steep changeover in rates at 435 K indicates a kinetically hindered (explosive) decomposition that will affect the microstructure and the crystallization behavior due to creation of local overheating and strong multiple crackling during liberation of volatile ligands. This effect leads also to the pronounced splitting of the main signals in DSC and DTG. It is apparent that for Ni the choice of the final pre-

calcination temperature is inadequate if the system should be still reactive. The phase formation processes of supramolecular oxides are occurring at lower temperatures due to the catalytic ligand removal and hence the pre-calcination temperatures should be re-adjusted.
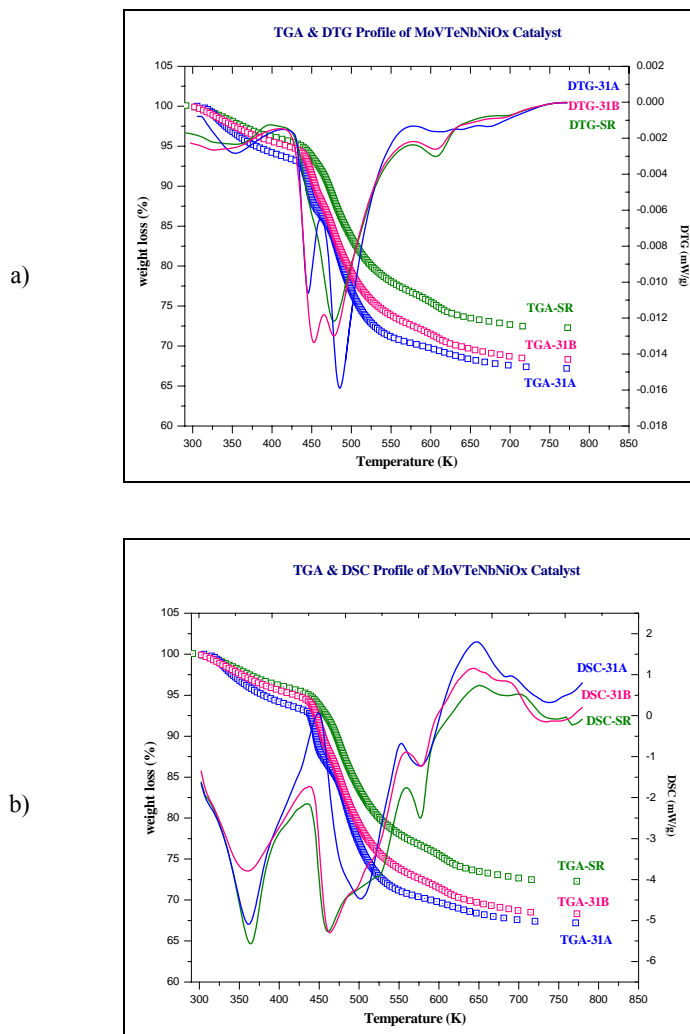

Figure 6: TGA, DTG and DSC curves for Ni-promoter $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst system whereas sample number 31A due to MoVTeNbNiOx (I), 31B due to MoVTeNbNiOx (II) and SR represent for standard method catalyst patterns.

Conclusions

In summary, the successful of modified active site of Ni-promoter on $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst is depends on several parameters involved in preparing the catalyst, which includes the method of preparation and activation procedure and amount of the metal promoter. Various solids prepared, composing of Mo, V, Te, Nb and oxides 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 modification of MoVTeNb oxide catalyst, which in turn is crucial to a systematic and rational approach in catalyst design.

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