

CHAPTER IV
PREPARATION OF MOLYBDENUM OXIDE VIA SOL-GEL PROCESS
USING MOLYBDENUM GLCOLATE AS PRECURSOR

4.1 Abstract

Preparation of molybdenum oxide from molybdenum glycolate synthesized directly from the reaction of two commercially available molybdenum oxide and ethylene glycol, via the Oxide One Pot Synthesis (OOPS) process is achieved through sol-gel process. Due to the moisture stability of molybdenum glycolate precursor molybdenum oxide gel was formed using hydrochloric acid, nitric acid or non-acid catalysts. The prepared molybdenum oxides (MoO_3) were characterized using TGA, BET, SEM and XRD techniques, giving the orthorhombic structure at the calcinations temperature of 350°C . The crystallinity and morphology of the products are affected by the calcinations temperature and acid type. The effects of reaction temperature, calcinations time and heating rate and adding methanol with nitric acid catalyst do not significantly influence the crystallinity and morphology. The specific surface areas of prepared molybdenum oxide are less than $60 \text{ m}^2/\text{g}$.

KEYWORDS: Molybdenum glycolate, Molybdenum oxide and Sol-gel process

4.2 Introduction

Crystalline molybdenum trioxide has a two-dimensional layered structure showing interesting lithium intercalation properties. Molybdenum oxide, especially MoO_3 , is of interest for battery cathodes, catalysis and electrochromic materials. The most common form of crystalline MoO_3 is the orthorhombic phase (α - MoO_3) where vertex-sharing chains of distorted MoO_6 octahedra share edges with other similar chains to form the layers. These two-dimensional layers are stacked in a staggered arrangement and weakly held together by van der Waals bonds. Molybdenum trioxide thus forms a very stable 2D layered oxide compound. These layers can be propped open by intercalated species, such as, protons, solvated lithium and sodium ions, as well as larger molecules. Its open structure and the ease of creating oxygen vacancies in the structure make it an ideal candidate for lithium secondary batteries and electrochromic windows. Lithium capacity of up to 1.5 Li/Mo and discharge capacity of over 300 mA h/g have been reported.

Sol-gel synthesis of MoO_3 is desirable because low synthesis temperature can lead to the formation of amorphous or metastable phases not available through traditional synthesis methods. The low temperature phase can exhibit properties that are substantially different from the crystalline phase. Although it is often assumed that lithium intercalation occurs between the two-dimensional layers of the crystalline MoO_3 , previous experiments have not been able to show a direct correlation between the degree of crystallinity and the Li capacity of MoO_3 . Even more interest is that certain amorphous molybdenum oxides have exhibited better intercalation behavior compared to that of crystalline MoO_3 .

Molybdenum oxides produced by the sol-gel method were reported by Dong and Dunn that MoO_2 and MoO_3 aerogel exhibited surface area of 170 m^2/g and 150-180 m^2/g , respectively, while the MoO_3 xerogel gave surface area of 4 m^2/g [3]. It was proposed that the presence of terminal oxygen atom when molybdenum alkoxide was hydrolyzed was the main obstacle for sol-gel methods to form a three-dimensional gel network, making the pore collapsed during the gel drying process. Thus, in this

work, the more moisture stable molybdenum glycolate was used to produce a higher surface area molybdenum oxide via the sol-gel process. Various sol-gel conditions were also studied.

4.3 Experimental

Materials

Molybdenum (VI) oxide (MoO_3) was purchased from Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) and acetonitrile were purchased from Farmitalia Carlo Erba (Barcelona) and Lab-Scan Company Co.Ltd., respectively. Both were distilled using standard methods before use.

Equipment

FTIR measurement was used to analyze functional groups in sol, gel and powdery samples in a 400 to 4000 cm^{-1} range. The spectra are obtained on a Nicolet instrument, Nexus 670 model. The powdery samples are pressed into pellet form with dried KBr while the sol and gel were spread onto ZnSe substrate. TGA thermograms were carried out on a Perkin Elmer thermal analyzer with a heating rate of 10°C/min over 30°-800°C temperature range. Crystal morphology was characterized using a JEOL 5200-2AE scanning electron microscope. X-ray diffractometer (XRD) patterns were obtained on a Rigaku X-ray diffractometer at a scanning speed of 2°/sec and $\text{CuK}\alpha$ as source. Peak positions are compared with standard JCPDS files to identify crystalline phases. Surface area of all samples was measured using the five-point BET method on a Quantachrome Corporation Autosorb I with flowing a gaseous mixture of nitrogen and helium through the analyzer at constant rate of 30 cm^3/min . Nitrogen gas was used to calibrate the analyzer and also as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 12 h at 200°C prior to exposure to the adsorbent gas.

Methodology

Synthesis of Molybdenum Glycolate

Following the method of Wongkasemjit [13], molybdenum glycolate was synthesized directly from inexpensive and widely available starting materials, MoO₃ and ethylene glycol, via the oxide One Pot Synthesis (OOPS) process. The white product was characterized using FTIR and TGA.

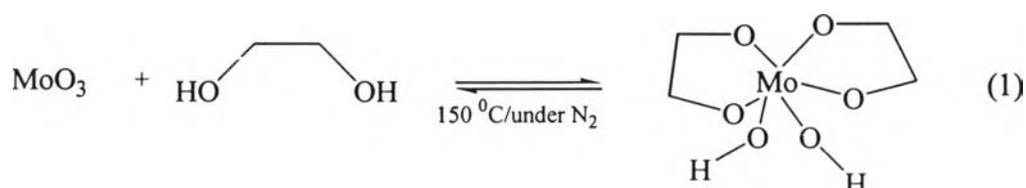
Sol-gel Process of Molybdenum Glycolate

Molybdenum glycolate was mixed with either 2 M hydrochloric acid solution, 2 M nitric acid or non-acid solution. Various volume ratios of H₂O/HNO₃, H₂O/HNO₃/MeOH, hydrolysis ratios, calcinations temperatures, times and heating rates were investigated. The mixture was vigorously stirred to form sol, followed by heating the sol at 40°, 50° and 60°C for 1, 2 and 3 h to form gel. The gels were dried at 110°C for 12 h before calcinations at temperature varied from 300° to 600°C for calcinations time ranging from 1 to 7 h and heating rate ranging from 0.25 to 1.0°C/min. The calcined product, molybdenum oxide, was characterized using XRD, SEM and BET.

4.4 Results and Discussion

Synthesis of Molybdenum Glycolate Precursor

Molybdenum glycolate precursor was synthesized via the ‘Oxide One pot Synthesis’ (OOPS) process, as shown in eq.1. Since water is a by-product of the reaction, it must be removed from the system to drive the reaction forward.



TGA analysis of molybdenum glycolate, shown in fig.1, shows five mass loss transitions at 150°, 210°, 350°, 430° and 720°C with 55.7 % ceramic yield,

corresponding to $\text{Mo}(\text{OH})_2(\text{O}(\text{CH}_2)_2\text{O})_2$ having 56.7% theoretical yield. For FT-IR result (Fig. 2) the bands observed were $3500\text{-}3000\text{ cm}^{-1}$ (s, νOH), $2968\text{-}2860\text{ cm}^{-1}$ ($\nu\text{C-H}$), $1344\text{-}1258\text{ cm}^{-1}$ ($\nu\text{CH-OH}$), 946 cm^{-1} ($\nu\text{Mo-O-C}$) and 533 cm^{-1} ($\nu\text{M-O}$).

Effect of Reaction Temperature

To study the effect of the gelation temperature, XRD, SEM and BET were employed. The gelation temperature studied was started from 40° to 60°C for different acid catalysts. For HCl acid, the calcinations temperature was ranged from 350° to 600°C for 3 h. It was found that using HCl catalyst the results from both SEM (Fig.3, 4, 5 and 6) and XRD (Fig.7, 8 and 9) did not show significant differences on neither crystallinity nor morphology of the molybdenum oxide products, except for the peak intensities. Table 1, showing the BET results obtained at the calcinations temperature of 350°C for 3h, indicates that the specific surface areas of molybdenum oxide differs slightly for different gelation temperatures. For HNO_3 , the calcinations temperature was 350°C for 3h the SEM and XRD results (Fig.12 and 13) also gave similarly crystallinity, but the crystal shape or size was totally different from those using HCl. The specific surface area showing in table 2 was larger than MoO_3 synthesized using HCl catalyst. Again, the specific surface area of the product using either HCl or HNO_3 acid did not give much difference in the reaction temperature range. Thus, the appropriate reaction temperature was 50°C .

Effects of Calcinations Temperature

The effect of calcinations temperature was studied to find the suitable condition for giving complete crystallinity. The calcinations temperature was varied from 300 to $600\text{ }^\circ\text{C}$ by fixing the other variables as follows: 2 M HNO_3 or 2 M HCl, reaction temperature of $50\text{ }^\circ\text{C}$, heating rate of $1^\circ\text{C}/\text{min}$ and calcinations time of 3 h. It was found that the crystallinity of MoO_3 was improved with increasing calcinations temperature. As increasing the temperature, the crystallinity indeed increases. Surprisingly, complete crystals were obtained after increasing the calcinations temperature up to 350°C , as shown in Fig. 14-16. The XRD results show broad and low intensity peak at 300°C , indicating that the product contains not only

the crystalline phase, but also amorphous phase. The TGA result of the product calcined at 300°C (Fig.14) also shows small amount of water and organic residue. The specific surface area of MoO₃ showing in table 3 decreases when the calcinations temperature increases due to well packing rearrangement to dense structure of the product at high temperature. Therefore, it can be concluded that calcinations temperature of 350°C gave complete crystallinity.

Effect of calcinations time

Calcinations time studied was ranged from 1 to 7 h. Other variables were fixed as follows: 2 M HNO₃ or 2 M HCl, reaction temperature of 50°C, heating rate of 1°C/min and calcinations temperature of 350°C. SEM and XRD results (Fig.17, 18, 19 and 20) show slightly different morphology of the products and give complete crystallinity for 1 h calcinations time at 350°C. The calcined product was also analyzed using TGA to confirm the presence of carbon residue for calcinations temperature and time of 350°C and 1 h respectively, see Fig.21. The result clearly shows pure molybdenum oxide. Specific surface areas of molybdenum oxide prepared using HNO₃ in table 4 give the same result for this range of calcinations time, 10 m²/g. Thus, the appropriate calcinations time used for other studies is 1 h.

Effect of Acid Type

The effect of acid type was observed, using the same concentration of both HCl and HNO₃ acids to distinguish crystallinity, morphology and specific surface area of the products. It was found that the average crystal size of products synthesized using HCl catalyst is 5 μm while those using HNO₃ are in the average of 1 μm. Although the XRD results (Fig.12 and 13) of those products obtained from using both 2 M HCl and 2 M HNO₃ seemed to be the same, the SEM results, see Fig. 15 and 16, illustrate different morphologies. The crystal shape of molybdenum oxide synthesized using HCl is more regular, larger crystal size and, pellet-like, identified as orthorhombic pattern [3, 14], while that of the product obtained using HNO₃ is smaller and more irregular. The BET results in table 4 show that the prepared MoO₃ using HCl or HNO₃ at the reaction temperature of 50°C and the calcinations temperature of 350°C for 3 h gives low surface area and low pore volume.

Effect of Nitric Acid Concentration

The amount of nitric acid was studied by varying water to nitric acid volume ratio at 5, 5.7, 6.6, 8, 10, 13.3 and 20, and 1 h aging time, 2 h heating temperature, 350°C calcinations temperature and 1 h calcinations time. The SEM results (Fig 23 showing only 5 and 20 volume ratios) are small and irregular for all volume ratios. The morphology of the products does not significantly different, indicating that the amount of nitric acid in this range does not affect to morphology of the products. Similarly, XRD in fig. 22 show the same result. The specific surface area of MoO₃ showing in table 5 was improved. The volume ratio H₂O/HNO₃ of 8 gave the highest surface area.

When we reduced the calcinations temperature and time of the H₂O/HNO₃ ratios of 6.6, 8 and 13.3 to 300°C and 1h, respectively, as shown in Fig 24 and 25, the SEM results indeed show amorphous along with crystalline phases. Although, the calcinations time was increased to 3h at the calcinations temperature of 300°C, the morphology resulted in no difference.

Effect of Heating Rate

Study of heating rate was carried out using the condition of calcinations temperature and time of 350°C and 1 h, respectively, reaction temperature of 50°C and HNO₃/H₂O volume ratio of 8. The heating rate was varied from 1°C/min to 0.25°C/min, the SEM and XRD results shown in Fig. 26 and 27, respectively, demonstrate that they gave completely crystallinity and slightly difference in shape or size for all heating rates. However, the specific surface area of molybdenum oxide decreased when the heating rate decreased showing in table 7 due to lower heating rate providing longer time for molecules to arrange themselves while removing organic residue from molybdenum oxide gel. Since there was not much different surface area at the heating rate of 0.1-1.0 °C/min, thus the heating rate of 1.0°C/min was used to study for the next effect.

Effect of Methanol Solvent

Addition of methanol into the sol-gel mixture was studied by varying the methanol amount (50 to 200 μl) in the volume ratios of $\text{H}_2\text{O}:\text{HNO}_3:\text{MeOH}$ at 8:1:1, 8:1:2, 8:1:3, 8:1:4. Again the morphology of the calcined products does not show a significant change in shape or size. It can clearly be seen in Fig. 15 that they are irregularly shaped and small plate-like. XRD results (Fig. 16) show complete crystallinity at 350°C calcinations temperature for 1 h, having high intensity and sharp peaks. The more methanol added to the system, the lower intensity, but the phase transition was not affected. The specific surface areas of prepared MoO_3 (table 8) using various amounts of methanol and nitric acid catalyst were similar, but smaller.

Effect of Non-acid Catalyst

Molybdenum oxide gels can be formed without an acid catalyst at a reaction temperature of 50°C. However, it takes much longer time to form the gel. At the same condition as acid catalysis system, the XRD and SEM results, see Fig.32,33 and 34, show amorphous along with crystalline phases unless the calcinations temperature and/or time were increased. The specific surface area was not improved showing in table 9.

4.5 Conclusions

The surface area of prepared MoO_3 is lower than 60 m^2/g . Moisture stable molybdenum glycolate precursor could be used to synthesize the orthorhombic phase of molybdenum oxide after calcinations at 350°C. Both HCl and HNO_3 give different morphology and slightly different surface area. The calcinations temperature, time and heating rate do influence the surface area, crystallinity and morphology of the molybdenum oxide products, as well. The reaction temperature and the amounts of methanol and nitric acid do not affect the crystallinity and morphology of molybdenum oxide.

4.6 Acknowledgements

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4.7 References

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Table 1 Surface area measurements for prepared MoO₃ using HCl at different reaction temperature and calcied at 350 °C for 3h.

Reaction temperature (°C)	Surface area (m ² /g)
40	5
50	4
60	5
Commercial MoO ₃	4

Table 2 Surface area measurements for prepared MoO₃ using HNO₃ at different reaction temperature and calcined at 350 °C for 3h.

Reaction temperature (°C)	Surface area (m ² /g)
40	11
50	10
60	12

Table 3 Surface area measurements for prepared MoO₃ using 2M HCl or 2M HNO₃, at reaction temperature of 50 °C and calcined at 350 °C for 3h.

Type of acids	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
HCl	3	0.006	215
HNO ₃	10	0.05	0.8

Table 4 Surface area measurements for prepared MoO₃ using HNO₃, reaction temperature of 50 °C and at different calcinations temperature for 3h.

Calcination temperature °C	Surface area (m ² /g)
300	45
350	10
400	8
500	5
600	5

Table 5 Surface area measurements for prepared MoO_3 using HNO_3 , reaction temperature of $50\text{ }^\circ\text{C}$, calcinations temperature of $350\text{ }^\circ\text{C}$ for various calcinations time.

Calcination time (h)	Surface area (m^2/g)
1	10
3	10
5	10
7	10

Table 6 Surface area measurements of prepared MoO₃ at different heating rate, H₂O/HNO₃ volume ratio of 8 and calcined at 350 °C for 1h.

The heating rate (°C/min)	Surface area (m ² /g)
1	16
0.50	17
0.25	11

Table 7 Surface area measurements of prepared MoO₃ at various volume ratio of H₂O/HNO₃ and calcined at 350 °C for 1h.

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Volume ratios of H ₂ O/HNO ₃	Surface area (m ² /g)
20	13
13.3	13
10	16
8	16
6.6	15
5.7	14
5	13

Table 8 Surface area measurements of MoO₃ at various volume ratio of H₂O:HNO₃:MeOH and calcined at 350 °C for 1h.

Volume ratio of H ₂ O:HNO ₃ :MeOH	The specific surface areas (m ² /g)
8:1:1	13
8:1:2	13
8:1:3	14
8:1:4	13

Table 9 Surface area measurements of MoO₃ without acid catalyst and calcined at 350 °C for different calcinaion time.

Calcination time (h)	The surface areas (m ² /g)
1	9
3	5

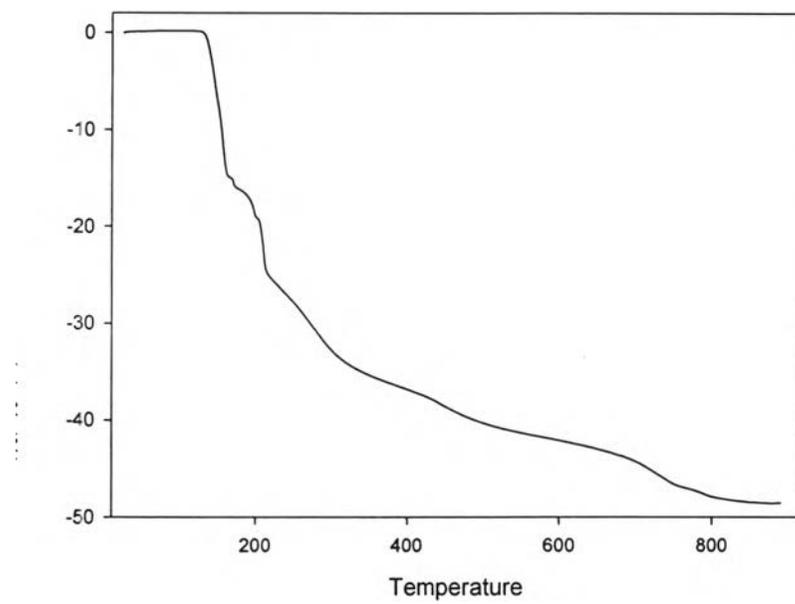


Figure 1 TGA profile of molybdenum glycolate.

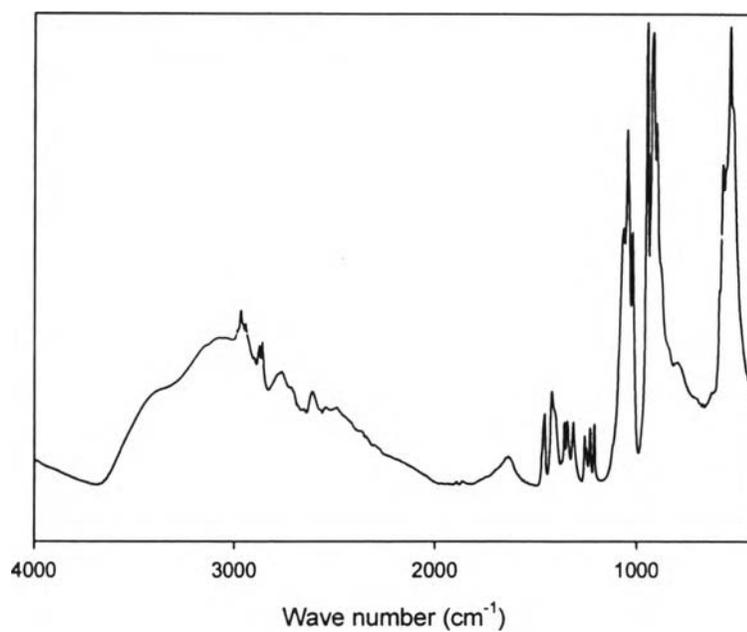


Figure 2 IR spectrum of molybdenum glycolate.

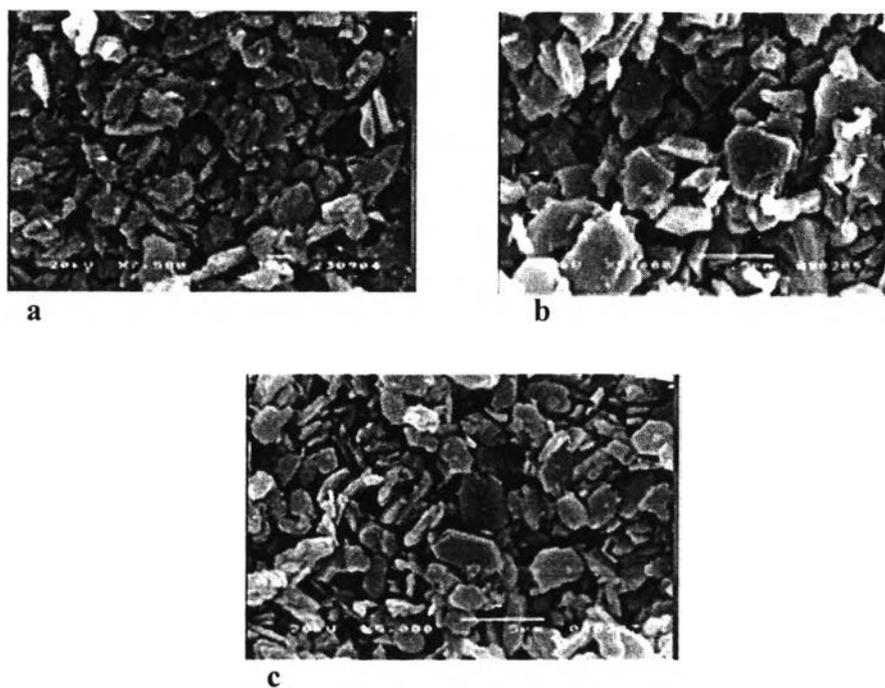


Figure 3 The SEM images of prepared MoO_3 using HCl calcined at 350°C for 3h and reaction temperature of; (a) 40° , (b) 50° and (c) 60°C .

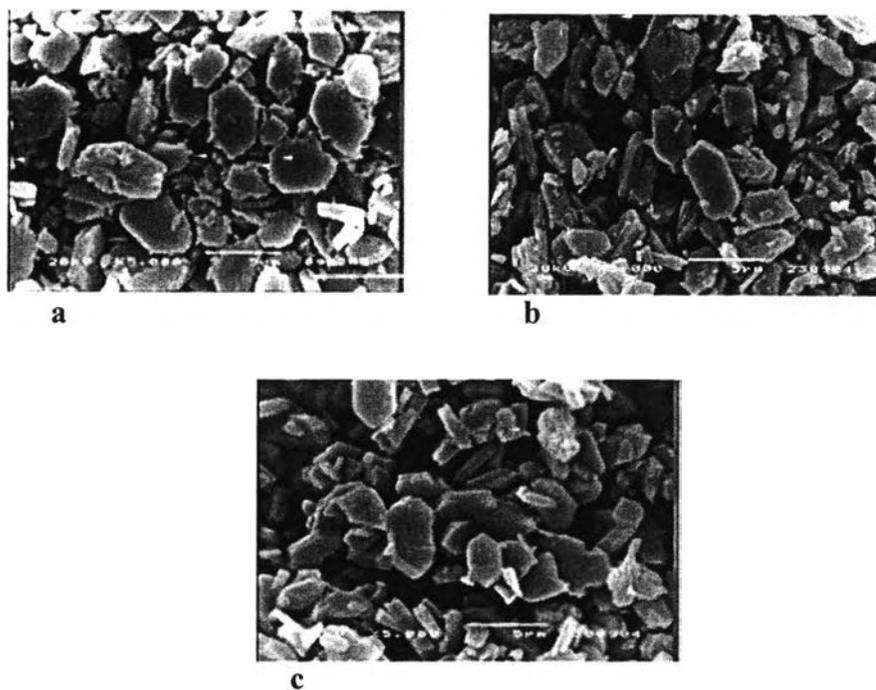


Figure 4 The SEM images of prepared MoO_3 using HCl calcined at 400°C for 3h and reaction temperature of; (a) 40° , (b) 50° and (c) 60°C .

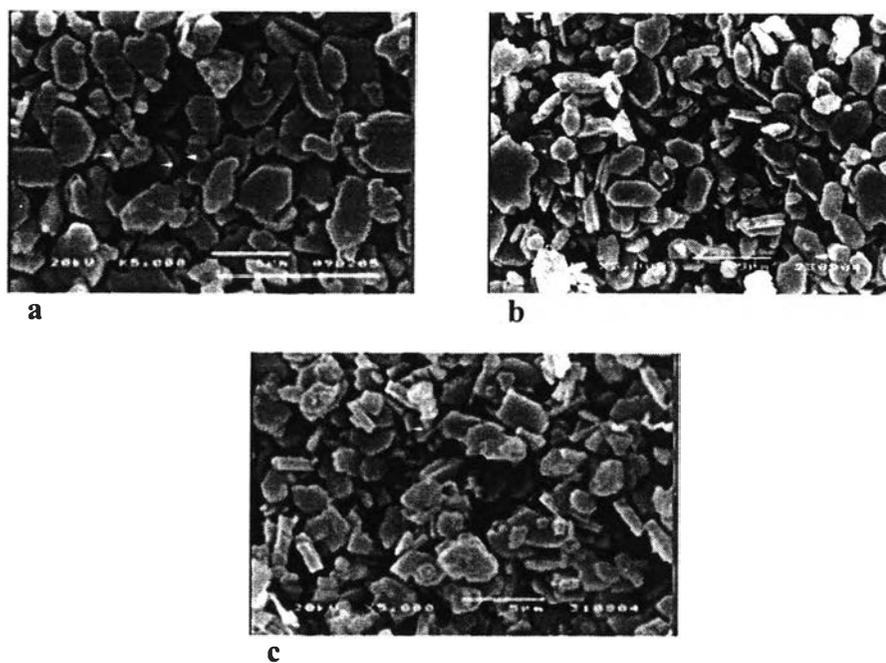


Figure 5 The SEM images of prepared MoO_3 using HCl calcined at $500\text{ }^\circ\text{C}$ for 3h and reaction temperature of; (a) 40° , (b) 50° and (c) 60°C .

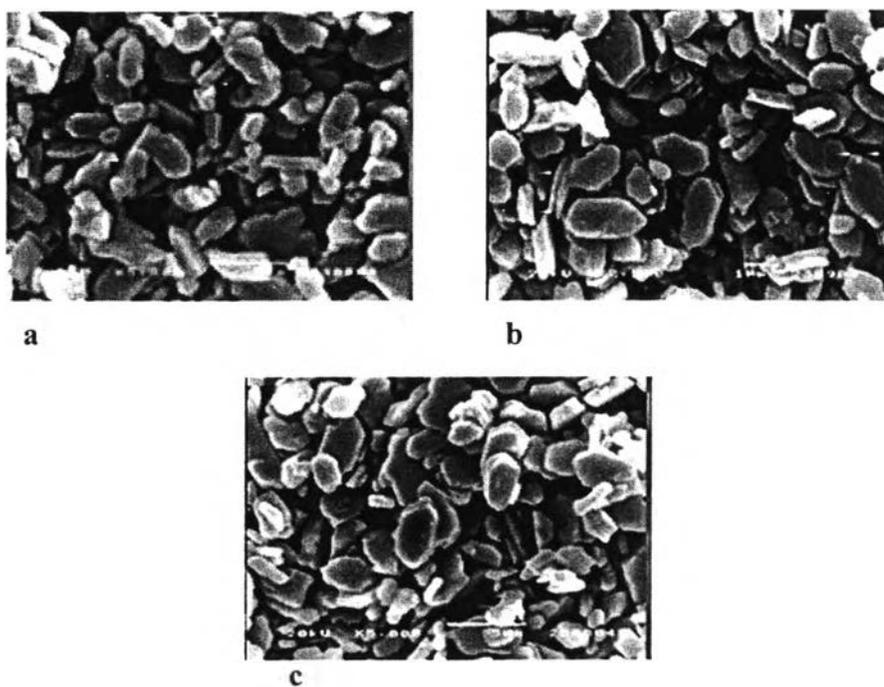


Figure 6 The SEM images of prepared MoO_3 using HCl calcined at 600 °C for 3h and reaction temperatures of; (a) 40°, (b) 50° and (c) 60°C.

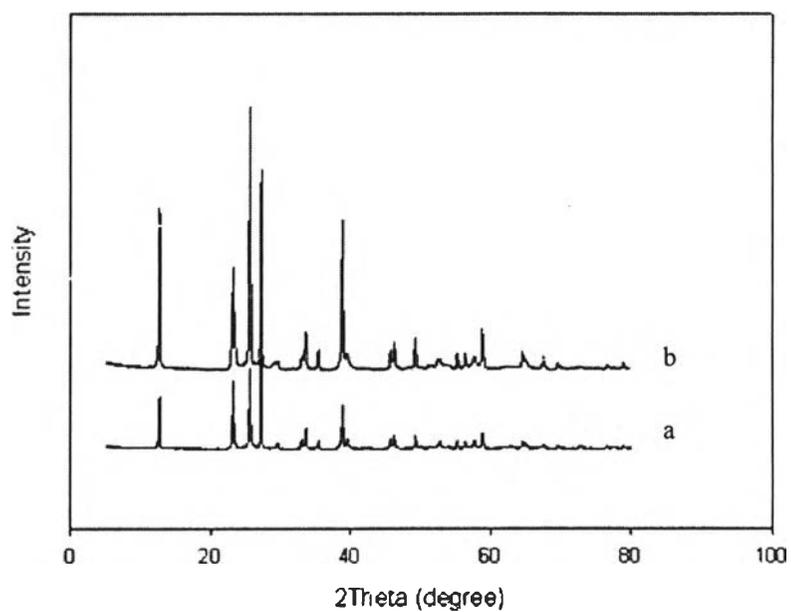


Figure 7 The XRD patterns of prepared MoO_3 using HCl, reaction temperature of 40°C and calcined at; (a) 350° and (b) 600°C for 3 h.

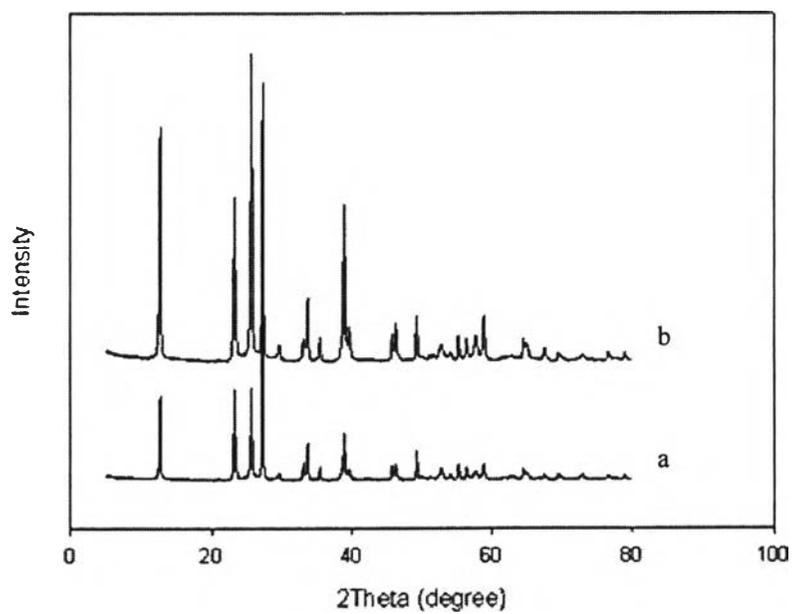


Figure 8 The XRD patterns of prepared MoO₃ using HCl, reaction temperature of 50 °C and calcined at; (a) 350° and (b) 600 °C for 3 h.

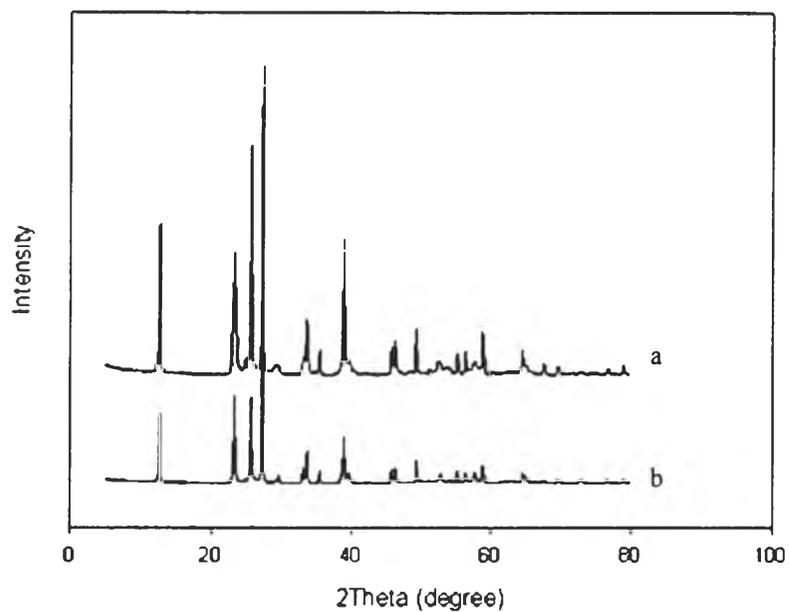


Figure 9 The XRD patterns of prepared MoO_3 using HCl, reaction temperature of 60°C and calcined at ; (a) 350° and (b) 600°C for 3h.

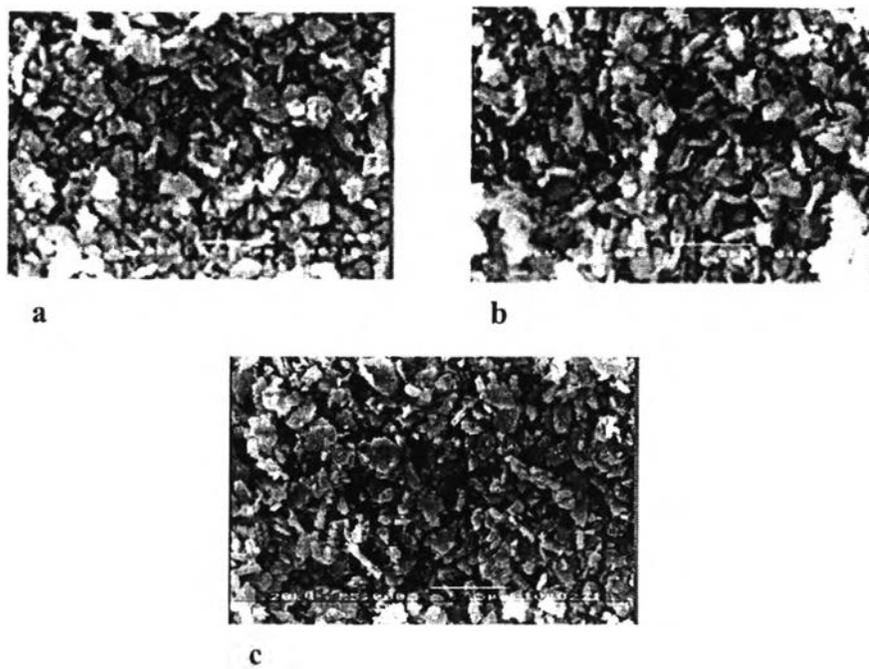


Figure 10 The SEM images of prepared MoO_3 using HNO_3 calcined at 350°C for 3 h and reaction temperature of; (a) 40° , (b) 50° and (c) 60°C .

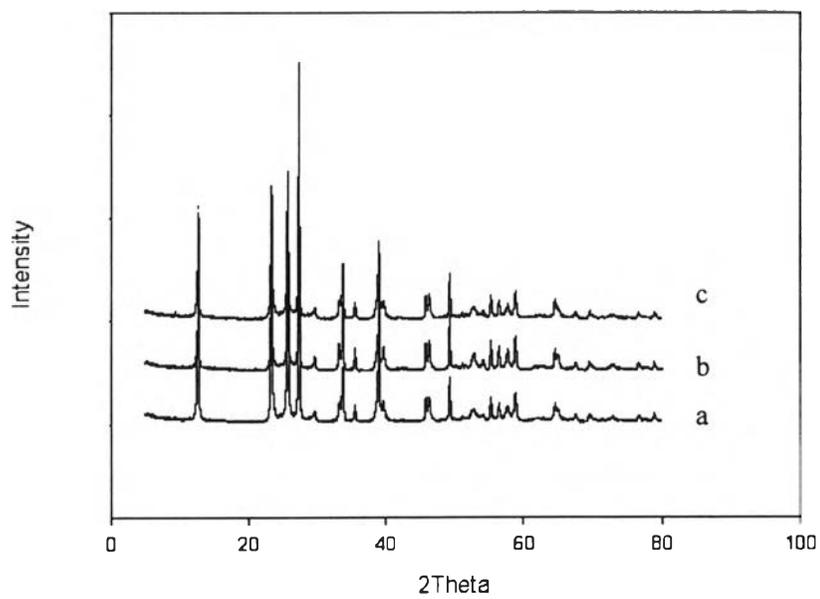


Figure 11 The XRD patterns of prepared MoO₃ using HCl calcined at 350°C for 3h and reaction temperature of; (a) 40° , (b) 50° and (c) 60°C.

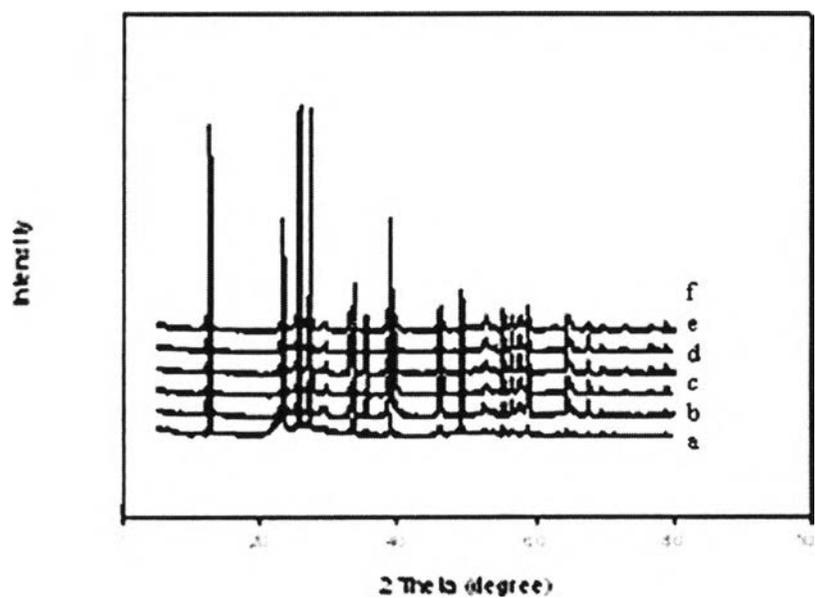


Figure 12 XRD patterns of molybdenum oxides prepared using 2M HCl and calcined for 3 h at; (a) 300°, (b) 325°, (c) 350°, (d) 400°, (e) 500° and (f) 600°C.

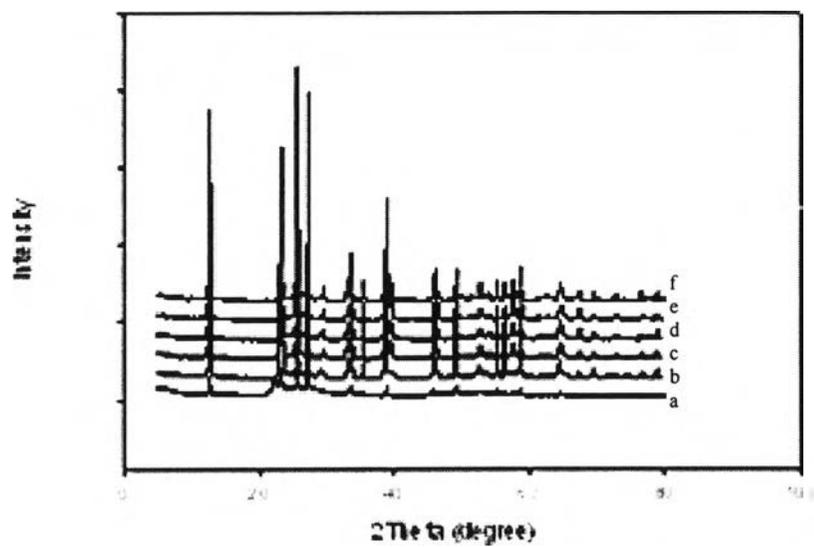


Figure 13 XRD patterns of molybdenum oxides prepared using 2M HNO₃ and calcined for 3 h at; (a) 300°, (b) 325°, (c) 350°, (d) 400°, (e) 500° and (f) 600°C.

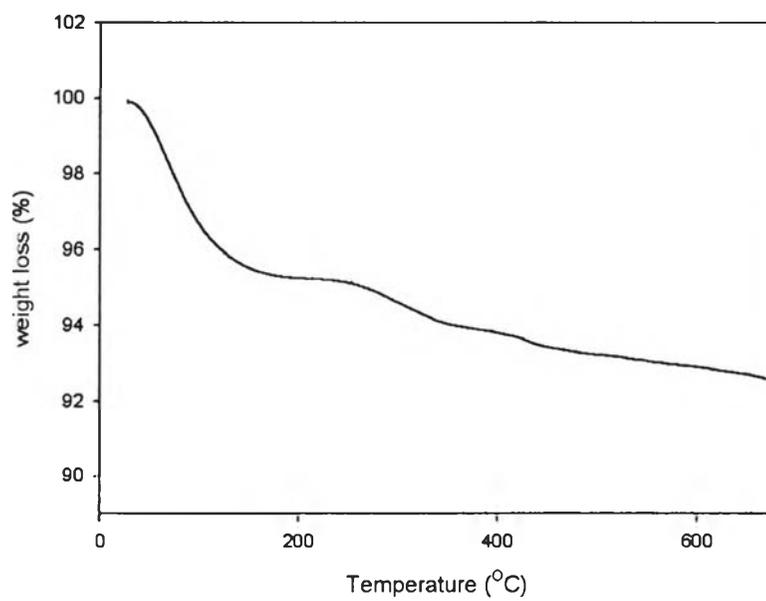


Figure 14 The TGA thermogram of molybdenum oxide gel using HNO_3 calcined at 300°C for 3h.

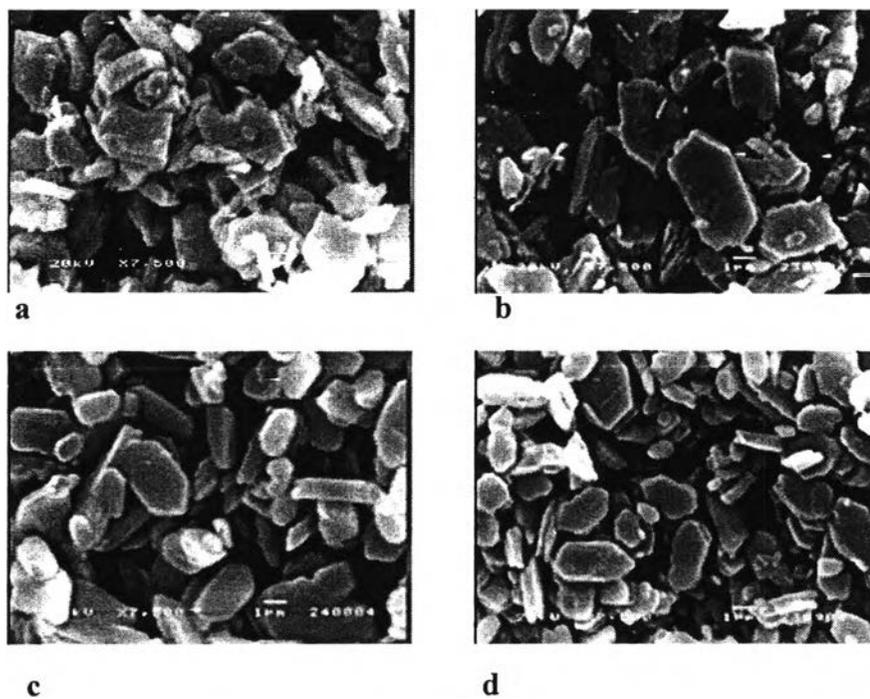


Figure 15 The SEM images molybdenum oxides prepared using 2M HCl and calcined for 3 h at; (a) 300°, (b) 350° , (c) 400°, (d) 500° and (e) 600°C.

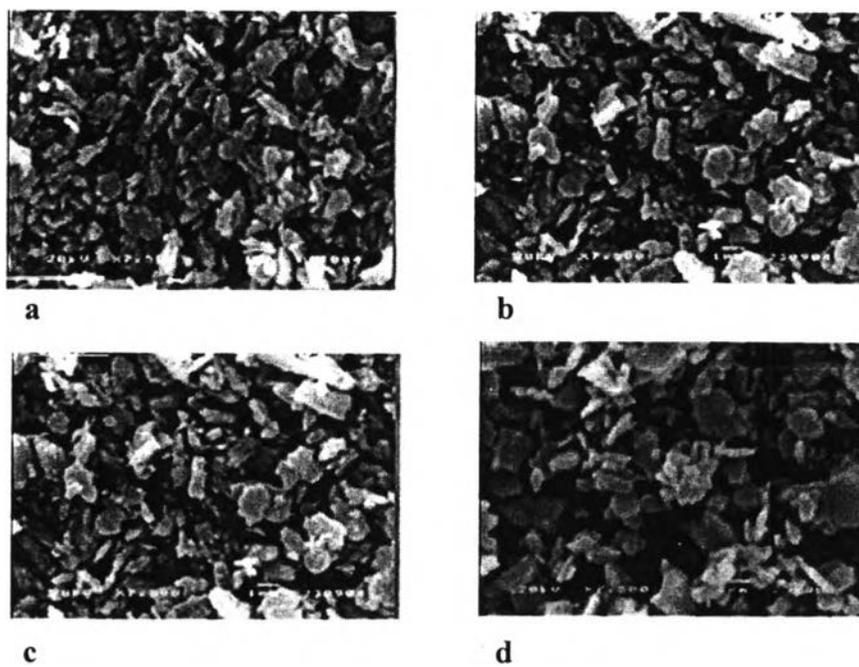


Figure 16 The SEM images molybdenum oxides prepared using 2M HCl and calcined for 3 h at; (a) 300°, (b) 350° , (c) 400°, (d) 500° and (e) 600°C.

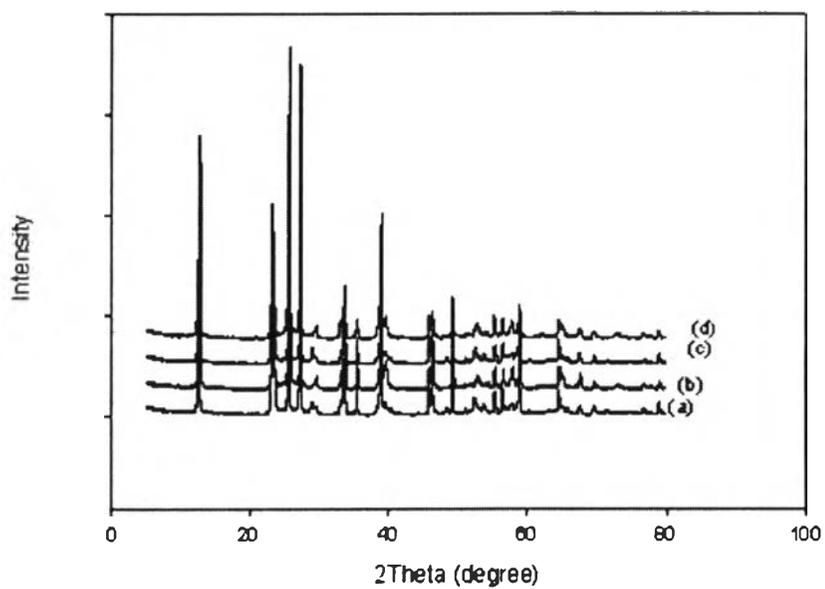


Figure 17 XRD patterns of MoO₃ prepared using 2M HCl and calcined at 350°C for; (a) 1, (b) 3, (c) 5 and (d) 7h.

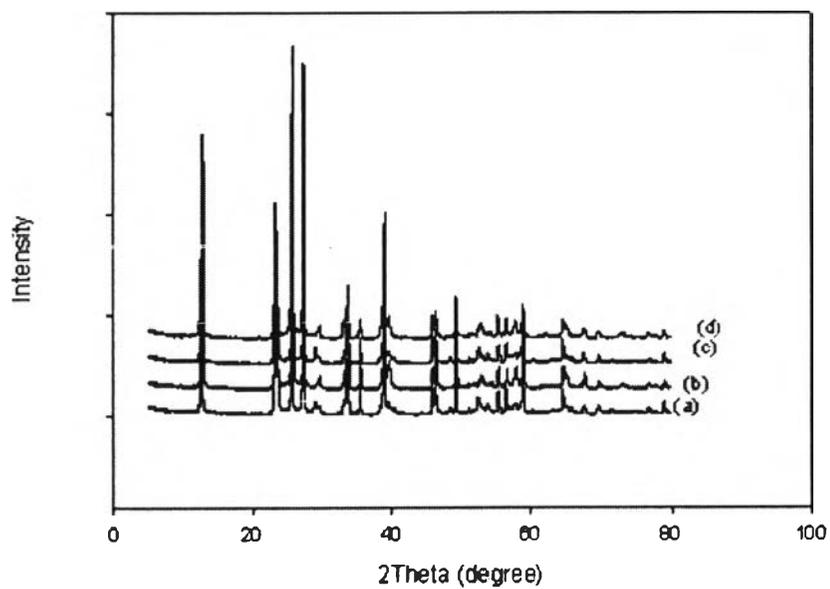


Figure 18 XRD patterns of MoO₃ prepared using 2M HNO₃ and calcined at 350°C for; (a) 1, (b) 3, (c) 5 and (d) 7h.

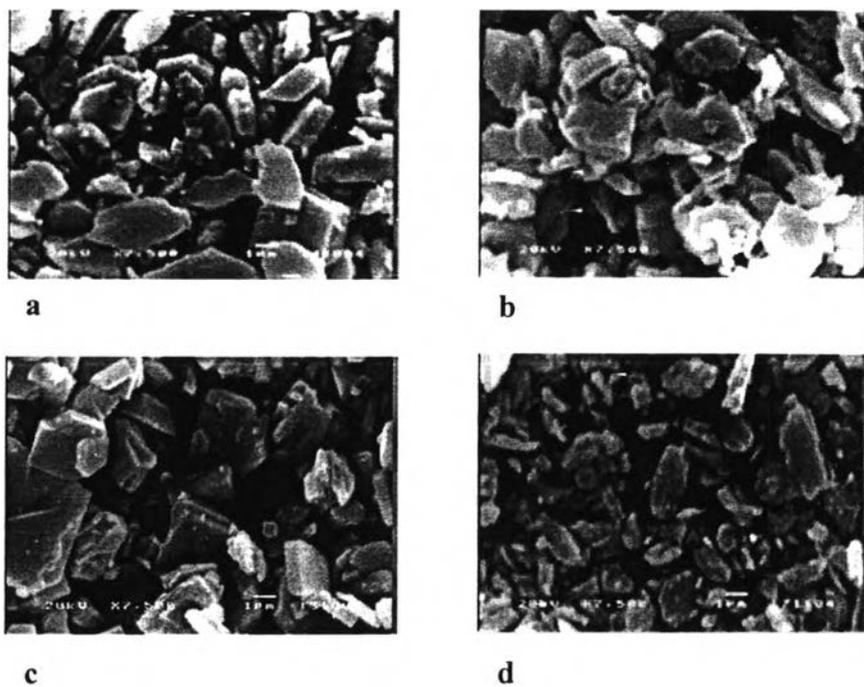


Figure 19 SEM images of molybdenum oxide prepared using 2 M HCl calcined at 350°C for; (a) 1, (b) 3, (c) 5 and (d) 7h.

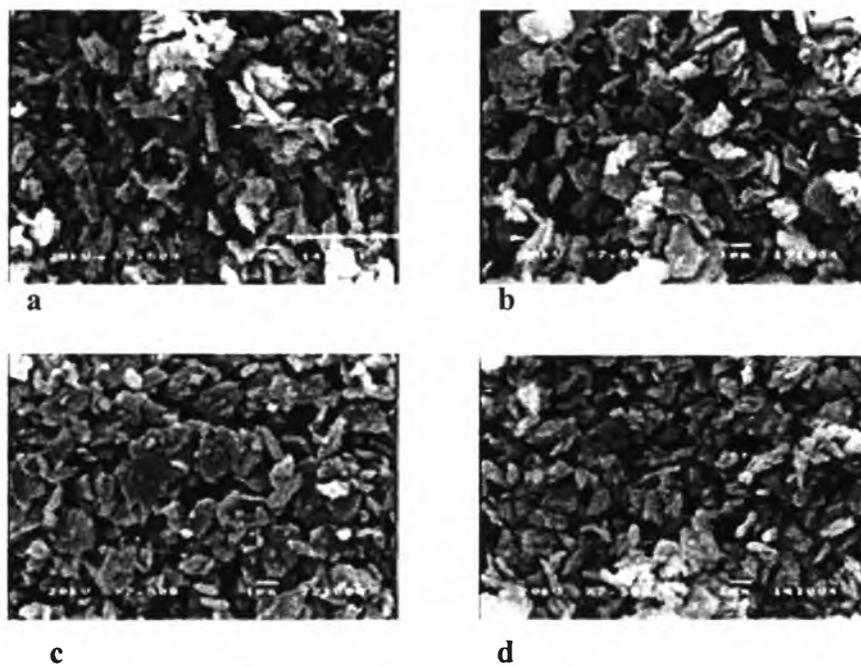


Figure 20 SEM images of molybdenum oxide prepared using 2 M HNO₃ calcined at 350°C for;(a) 1, (b) 3, (c) 5 and (d) 7h.

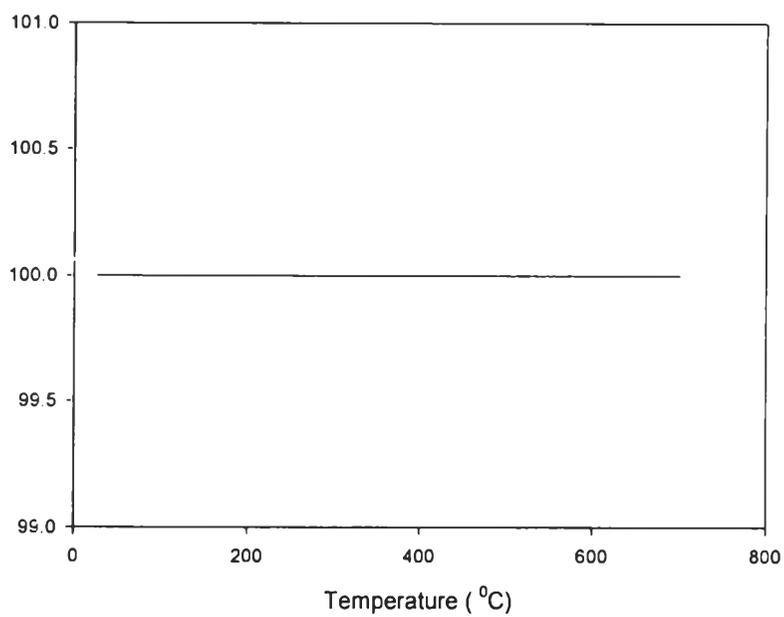


Figure 21 The TGA thermogram of molybdenum gel calcined at 350°C for 1h.

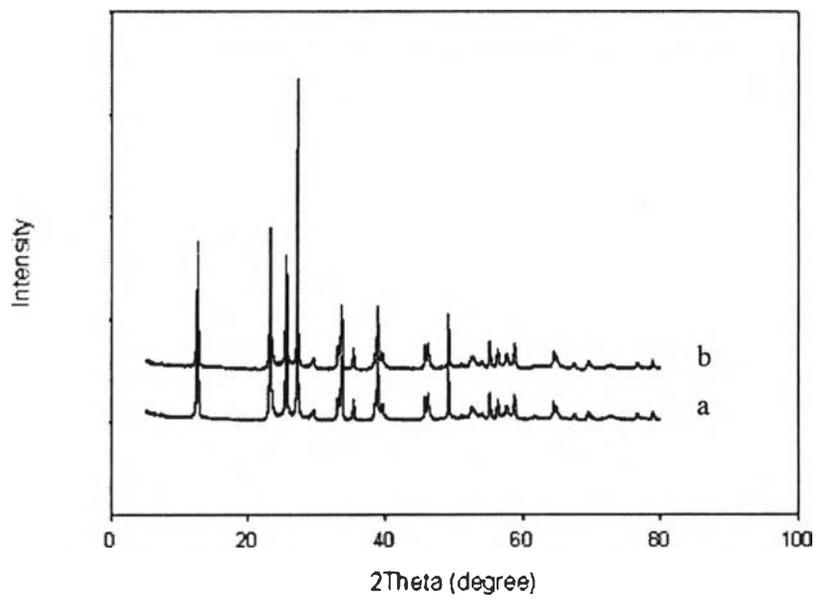


Figure 22 The XRD patterns of prepared molybdenum oxide using H₂O/HNO₃ volume ratio of; (a) 20 and (b) 5.

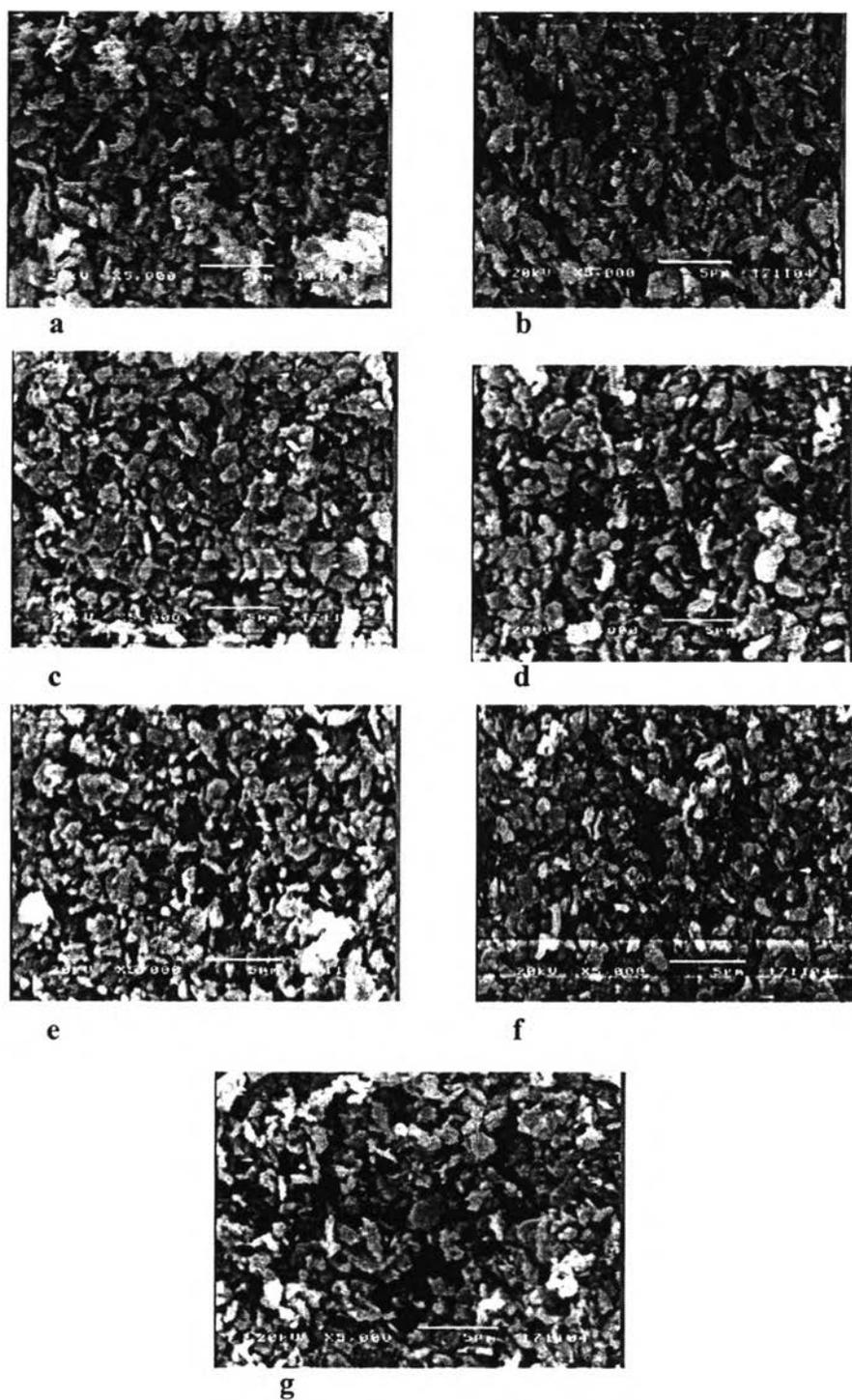


Figure 23 The SEM images of prepared MoO_3 using the various amount of HNO_3 , calcined at 350°C for 1h and $\text{H}_2\text{O}/\text{HNO}_3$ volume ratio of; (a) 20, (b) 13.3, (c) 10, (d) 8, (e) 6.6, (g) 5.7 and (h) 5.

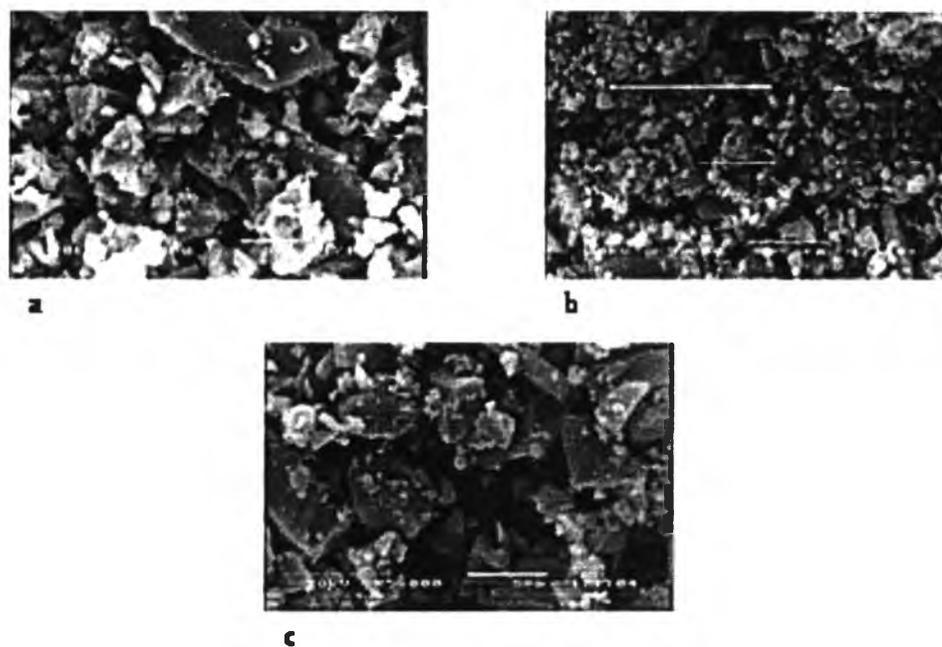


Figure 24 The SEM micrographs of prepared molybdenum oxide at calcinations temperature of 300°C for 1 h and H₂O/HNO₃ volume ratio of: (a) 13.3, (b) 8 and (c) 6.6

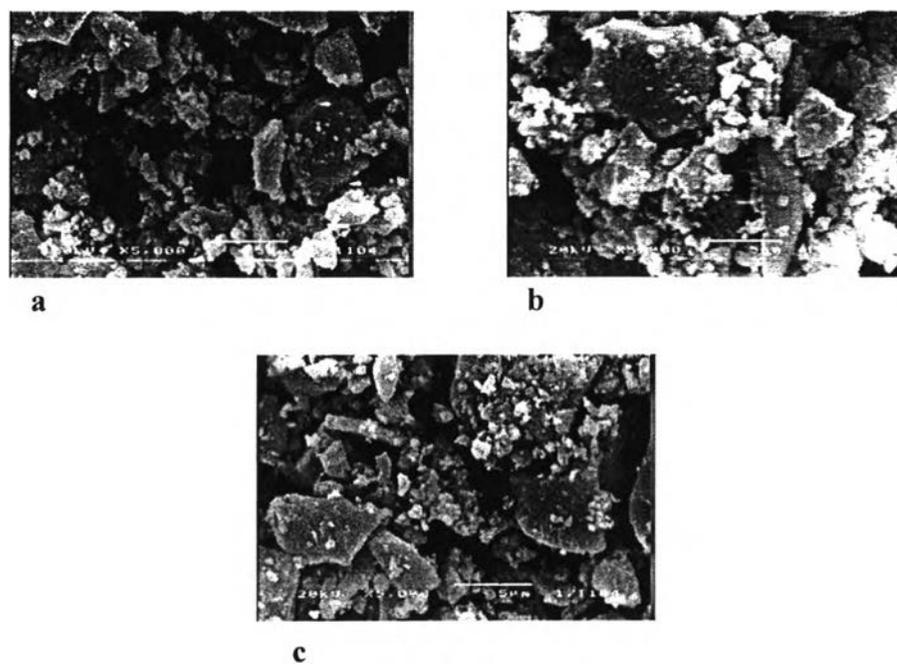


Figure 25 The SEM images of prepared molybdenum oxide calcined at 300°C for 3h and H₂O/HNO₃ volume ratio of; (a) 13.3, (b) 8 and (c) 6.6.

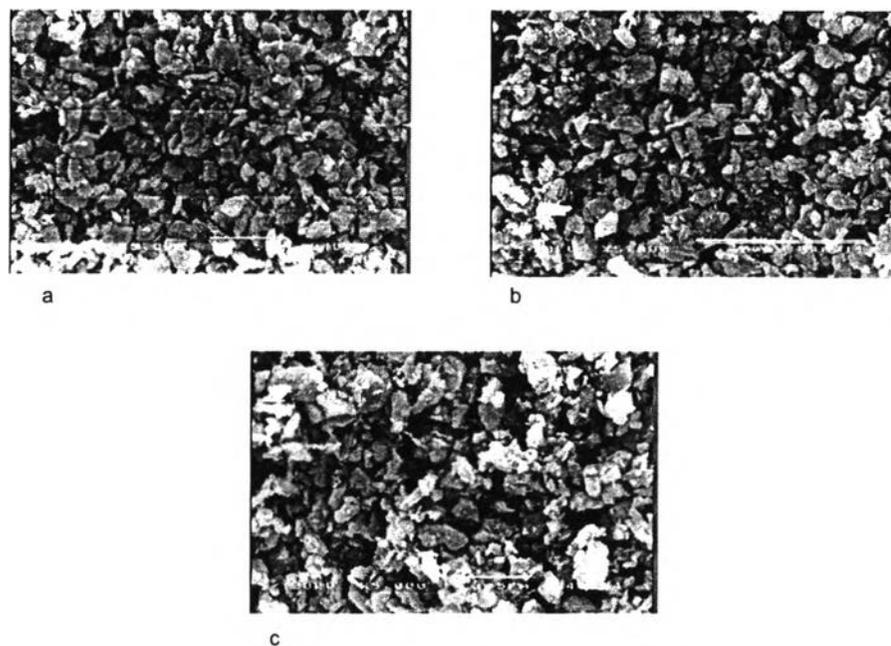


Figure 26 The SEM images of prepared MoO₃ using H₂O/HNO₃ volume ratio of 8, reaction temperature of 50 °C, calcined at 350 °C for 1h and heating rate of; (a) 1, (b) 0.5, and (c) 0.25 °C/min.

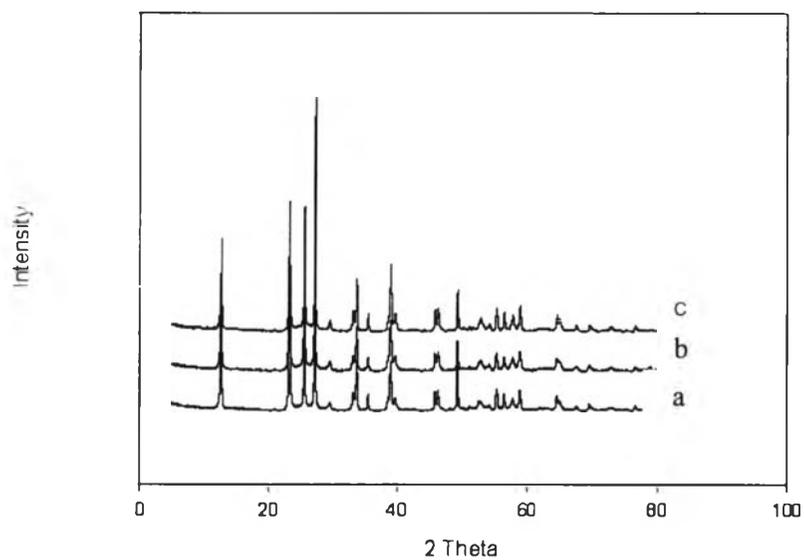


Figure 27 The XRD patterns of prepared MoO₃ using H₂O/HNO₃ volume ratio of 8, reaction temperature of 50 °C, calcined at 350 for 1h and heating rate of; 1, (b) 0.5, and (c) 0.25 °C/min.

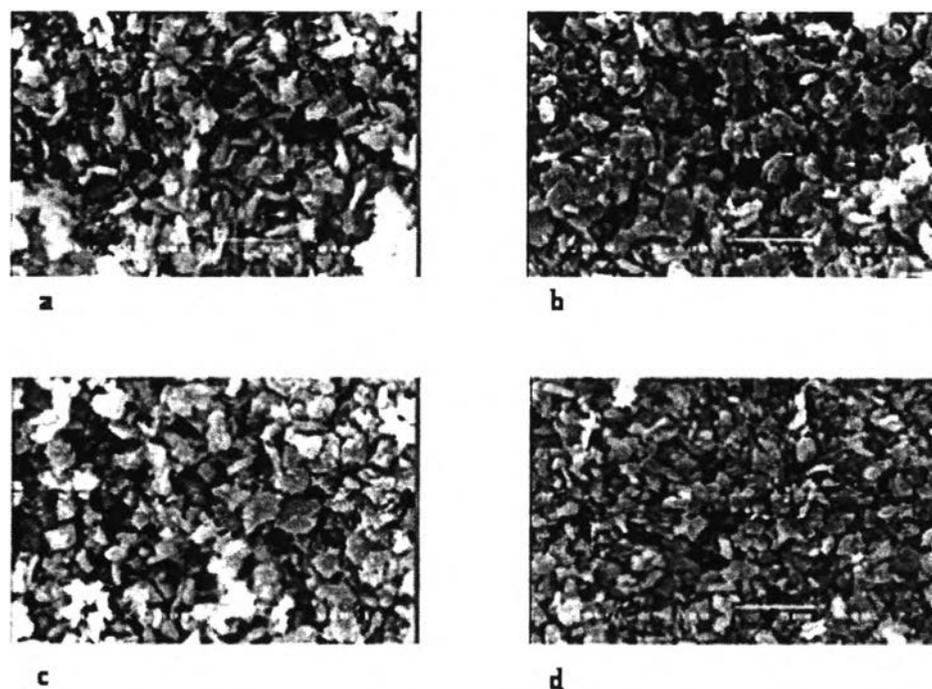


Figure 28 The SEM images of adding methanol on prepared MoO₃ calcined at 350 °C for 1h and H₂O: HNO₃ : MeOH volume ratio of; (a) 8:1:4, (b) 8:1:3, (c) 8:1:2 and (d) 8:1:1.

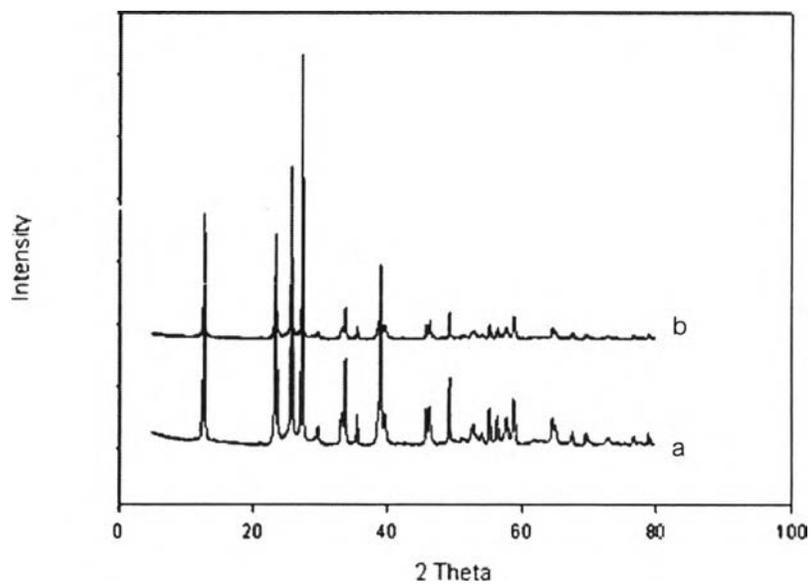


Figure 29 The XRD patterns of MoO₃ calcined at 350⁰C for 1h and H₂O: HNO₃ : MeOH volume ratio of; (a) 8:1:1 and (b) 8:1:4.

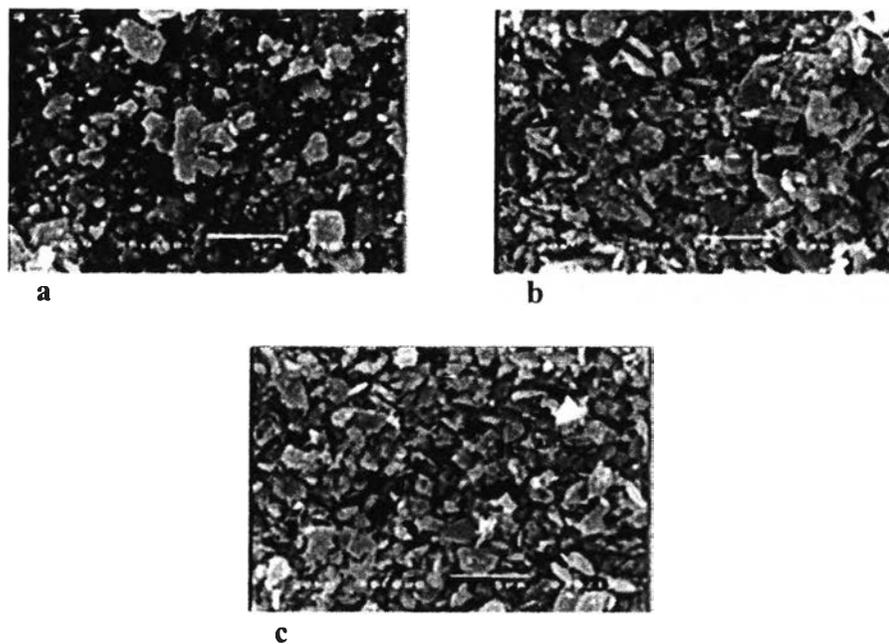


Figure 30 SEM images of prepared MoO_3 using non-acid, reaction temperature of 50°C and calcined at 300°C for; (a) 3h, (b) 5h and (c) 7h.

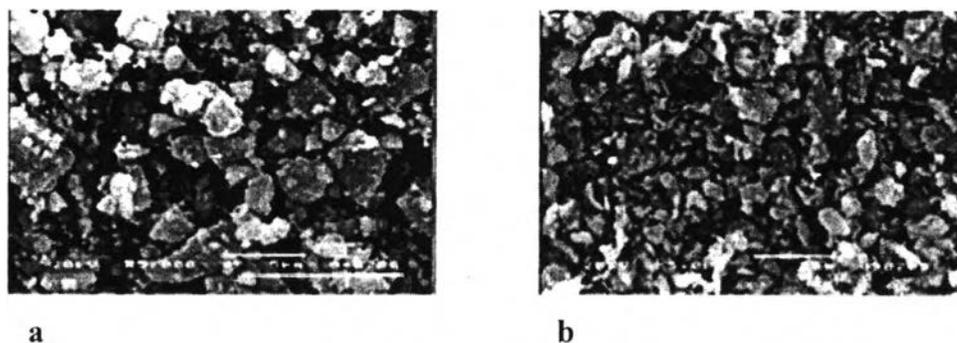


Figure 31 The SEM images of prepared MoO_3 using non-acid, reaction temperature of 50°C and calcined at 350°C for; (a) 1 and (b) 3h.

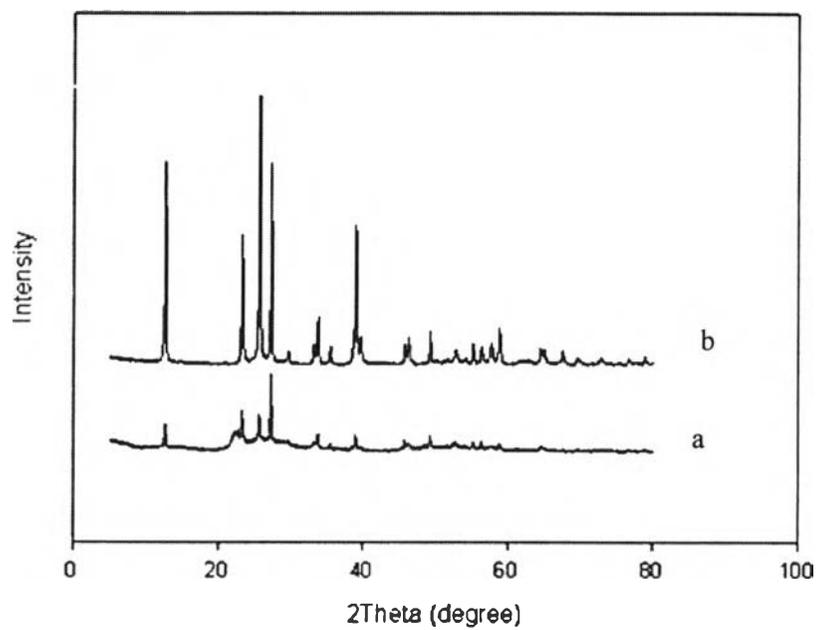


Figure 32 XRD patterns of prepared MoO_3 using non-acid, reaction temperature of 50°C and calcinations at 350°C for; (a) 1 and (b) 3h.