

## PREPARATION OF MOLYBDENUM CARBIDE VIA MICROWAVE INDUCED ALLOYING

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**Abstract.** The concept of “Green Chemistry” was first introduced in 1990. One of the criteria accepted was to perform an energy efficient processes and reactions. Microwave technique was found to be promising method to promote and support “Green Chemistry” since it offers low energy usage and faster reaction time. Based on this idea, this study focused on the preparation of molybdenum carbide using microwave specially modified for this purpose. Commonly, process requires high temperature and pressure conditions thus might lead to inefficient and required high amount of energy. In this study, commercially obtained activated carbon was impregnated with molybdenum solution followed by Microwave Induced Alloying (MIA) method with 2 minutes irradiation time in inert condition of nitrogen atmosphere. Ratios of carbon to molybdenum loading were varied respectively according to their stoichiometric molar ratio. The products obtained were characterized using XRD analysis. As a result, molybdenum carbide was successfully prepared using this method.

*Keywords:* Microwave induce alloying; carbon; molybdenum

**Abstrak.** Konsep “Green Chemistry” telah diperkenalkan pada tahun 1990 dan salah satu dari aspek yang telah dipersetujui adalah proses dan tindakbalas yang dirancang perlulah efisien dari segi penggunaan tenaga. Teknik gelombang mikro telah diperkenalkan sebagai kaedah yang berpotensi untuk mempromosi dan menyokong “Green Chemistry” kerana penggunaan tenaga yang rendah dan tempoh tindakbalas yang singkat. Berdasarkan idea tersebut, kajian ini difokuskan kepada penyediaan molibdenum karbida menggunakan ketuhar gelombang mikro yang telah diubahsuai. Secara kebiasaannya, proses pengalioian memerlukan suhu dan tekanan yang tinggi dan keadaan ini mendorong kepada ketidakefisienan dan penggunaan tenaga yang tinggi. Dalam kajian ini, sumber karbon yang didapati secara komersil telah direndam di dalam larutan molibdenum, kemudian diikuti dengan proses Pengalioian Dorongan Gelombang Mikro dengan kitaran 2 minit dalam lengai atmosfera nitrogen. Nisbah karbon dan molibdenum telah dioptimumkan dan berkisar padaimbangan nisbah stiokiometrinya. Kesemua produk dicirikan secara kima dengan menggunakan analisis XRD. Hasil kajian ini menunjukkan molibdenum karbida telah berjaya disediakan menggunakan teknik ini.

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*Kata kunci:* Pengaloiian dorongan gelombang mikro; karbon; molybdenum

## 1.0 INTRODUCTION

Transitional Metal Carbides (TMC) is a type of metal-derived compound with the incorporation of carbon in the metal lattice. The incorporation of carbon into lattices of early transition metals (IVB-VIB) produces compounds with unique physical, chemical and catalytic properties, which combine the characteristic properties of three different types of materials; covalent solids, ionic crystals and transition metals. They all have the physico-chemical properties of high melting point and hardness, high thermal and mechanical stability as well as excellent catalytic performance reaction for example in hydrogenation reaction, which is similar to the precious noble metal such as Pt, Rh and In [1-3]. Generally, transition metals have high binding energies, which will prevent facile desorption and repeated reactions. With the introduction of carbon at molecular level, their catalytic behaviors can be increased by tempering the binding energy of the adsorbates through the addition of carbon and subsequent carbide formation [4]. A good performance of TMC in the traditional reaction catalyzed by precious noble metal is expected and is attributed by the increase in electronic density of the metal after carburization [5].

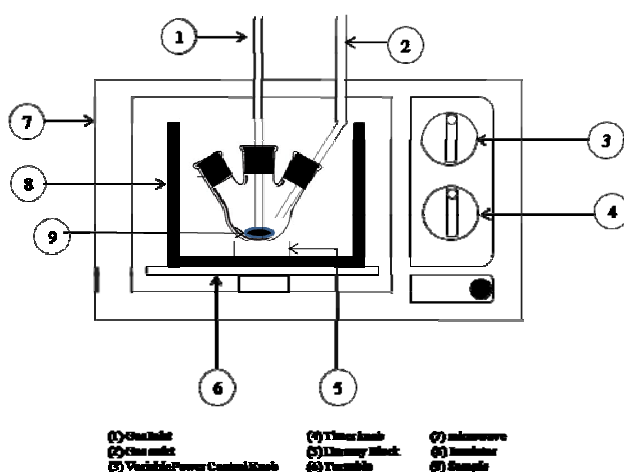
Generally, interaction between molybdenum and carbon may produce three known compositions, namely MoC, Mo<sub>3</sub>C<sub>2</sub> and Mo<sub>2</sub>C. Mo<sub>2</sub>C on the other hand have two identified phase which are orthorhombic  $\alpha$ -Mo<sub>2</sub>C and hexagonal  $\beta$ -Mo<sub>2</sub>C [6]. Several process was reported on preparation of Molybdenum Carbide, such as powder metallurgical process via reaction between metal with carbon black and carburized at high temperatures (1500 - 2000°C), direct temperature programmed reduction of Molybdenum Oxide, mixture of hydrocarbon and hydrogen such as methane, ethane, buthane and toluene, sonochemical synthesis via molybdenum hexacarbonyl with black power and microwave-assisted method [7 -11]. Today, many researchers have turn to create easier, faster and energy saving ideas for TMC synthesis and microwave looks promising. Yacob *et al.*, [12] on the other hand introduced Microwave Induced Alloying (MIA) using simple modified microwave household oven and successfully synthesized WC alloys. This method of preparation thus looks promising Mo<sub>2</sub>C simple, easy to upscale, cheap and can

produce large amount of samples ready many catalytic reactions. Thus, goal of this research is to prepare molybdenum carbide via Microwave Induced Alloying (MIA), focused on heterogeneous solid-liquid alloying technique and determine the liability and effectiveness of this method.

## 2.0 EXPERIMENTAL METHODS

### 2.1 Preparation of Molybdenum Carbide

1 M molybdenum solution was prepared using 17.65g ammonium heptamolybdate (AHM) was transferred into 100 ml volumetric flask and marked up with distilled water. In order to AHM dissolve completely, this solution was further sonicated using laboratory ultrasonic bath for 15 minutes. Then, 0.5 g of carbon (7 mol) was dispersed in 11.91 ml of 1M molybdenum solution (2.0 mol) in three-neck flat bottom flask. The nitrogen gas was bubbled in the flask to make free oxygen-atmosphere for the reaction. The microwave induced-alloying was performed in modified domestic microwave oven (Figure 1) using 800 W power and 2 minutes of radiation time. After that, the product was washed using hot water to eliminate excess of molybdenum and dried in oven at  $105 \pm 5^\circ\text{C}$  overnight. The entire ratio for preparation of molybdenum carbide was listed in Table 1.



**Figure 1** The schematic diagram of modified microwave oven

**Table 1** List of the ratio for preparation of molybdenum carbide

Ratio (mol:mol)	Molybdenum	Carbon
0.5:7	0.5	7
1.0:7	1.0	7
1.5:7	1.5	7
2.0:7	2.0	7
2.0:3	2.0	3
2.0:4	2.0	4
2.0:5	2.0	5
2.0:6	2.0	6

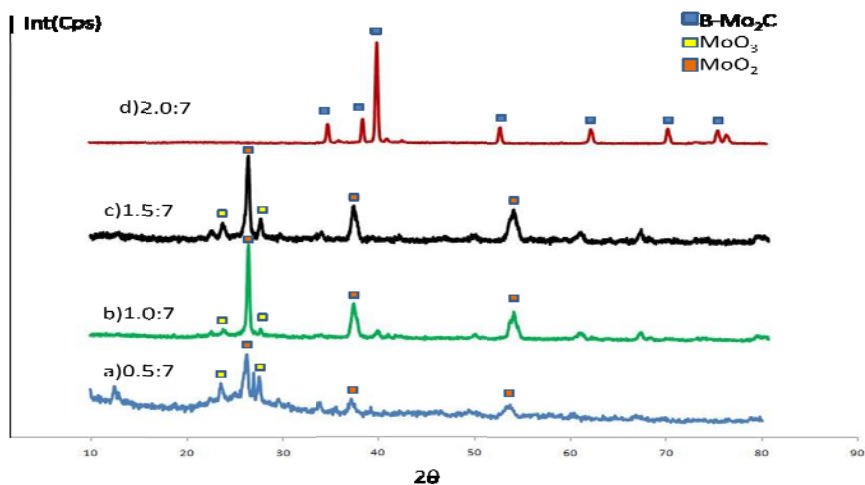
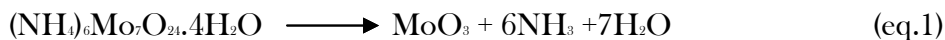
## 2.2 Characterization Technique

The identification of the prepared  $\text{Mo}_2\text{C}$  were carried out using Bruker X-ray powder diffractometer. The XRD diffractograms were recorded with  $\text{CuK}\alpha$  radiation source with  $\lambda = 0.15418$  nm at 40 kV and 40 mA. The  $2\theta$  range used was from  $10^\circ$  to  $90^\circ$  at a scanning speed of 0.05 per second. The identification of peaks is based on JCPDS-ICDD ( $\text{MoO}_3$ : 35 - 609,  $\text{MoO}_2$ : 32 - 671, hcp  $\beta$ - $\text{Mo}_2\text{C}$ : 35 - 787) database incorporated in the software.

## 3.0 Result and Discussion

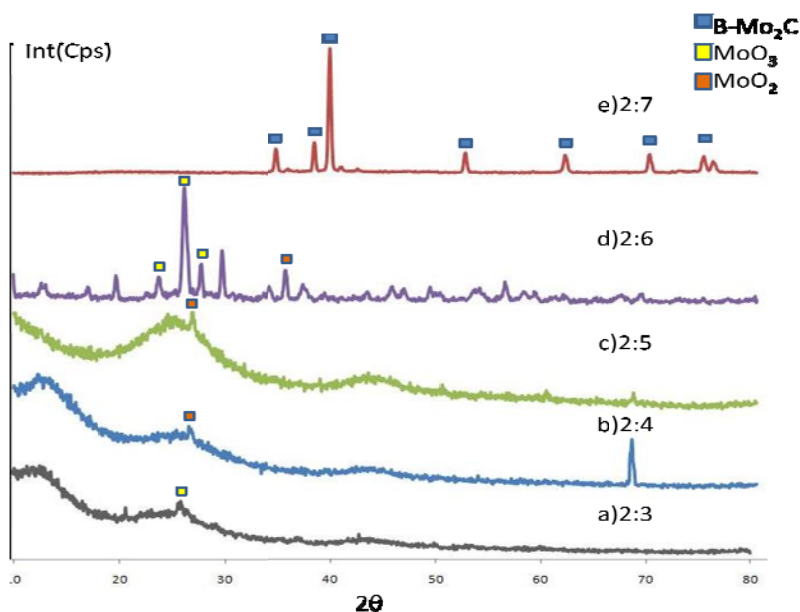
Previous study conducted by Wallace *et al.*, [6] successfully produced hexagonal  $\beta$ - $\text{Mo}_2\text{C}$  using high power microwave (3kW) in just only 20s. Their research however used solid-solid precursor system for both starting materials. In this study on the other hand, the center of attention is an application of heterogeneous solid-liquid precursor system which molybdenum's source was in liquid form while carbon remained as solid. Main inspiration of this system is the penetration of the molybdenum towards carbon. As Mo in liquid form, higher possibility for molybdenum ions to penetrate into the pore at activated carbon compared to solid Mo. Moreover, this idea enhances production of molybdenum carbide with the purpose of catalyst application.

In this study, molybdenum carbide was prepared by Microwave Induced Alloying by varied the molybdenum ratio while keeping carbon constant. The time of exposure was kept at 2 minutes. As in **Figure 2**, addition ratio of molybdenum at 0.5, 1.0 and 1.5 produced molybdenum oxide and molybdenum trioxide only. No significant peaks for molybdenum carbide ( $34.4^\circ$ ,  $38.0^\circ$ ,  $39.4^\circ$ ,  $61.5^\circ$ ,  $69.6^\circ$  and  $74.6^\circ$ ) were found at these three XRD diffractograms. Conversely, intensity of the identified peaks for  $\text{MoO}_2$  ( $26.2^\circ$ ,  $37.0^\circ$  and  $53.5^\circ$ ) and  $\text{MoO}_3$  ( $23.5^\circ$ ,  $26.9^\circ$ ) were increased with increases of molybdenum content. This event confirmed that AHM was firstly decomposed to  $\text{MoO}_3$  (refer to eq.1). Subsequently, the produced  $\text{MoO}_3$  was reacted with carbon and only produced  $\text{MoO}_2$ . Limitation of molybdenum amount causes this reaction stop at the production of molybdenum oxide. By increasing ratio of molybdenum at 2.0, generation of molybdenum carbide was occurred as their identified peaks illustrated at the XRD diffractogram. Additionally, this diffractogram also showed the considerable peaks for molybdenum oxide and trioxide were not appeared. This can be concluded that the  $\text{MoO}_2$  and  $\text{MoO}_3$  were transformed to the hexagonal  $\beta\text{-Mo}_2\text{C}$  when using the ratio 2.0:7. The reaction mechanisms are stated below in equation 1 and 2 [6, 13].



**Figure 2** XRD patterns for a) 0.5:7, b) 1.0:7, c) 1.5:7 and d) 2.0:7 prepared molybdenum carbides respectively

This experiment was repeated with changing the amount of carbon source in the total ratio while weight of molybdenum was keeping invariable at 2 and the result showed at Figure 3. The diffractograms for 2:3, 2:4 and 2:5 were unclear and showed any identified peaks for target and intermediate compounds. However, at 2:3 ratio, small significant peak for  $\text{MoO}_3$  appeared indicates that decomposition of AHM (refer to eq.1) has take place. Further addition of carbon at 4 and 5 ratios gave minimal impact for this reaction as only small intensity of characteristic peak for  $\text{MoO}_2$  emerged. Nevertheless, this phenomenon is incomprehensible to conclude that next steps of the mechanism take place. Great transformation was demonstrated when addition of carbon increased to 6 and 7 ratio. At 2:6 ratio, sharp and intense peak which significant for  $\text{MoO}_3$  become more visible at the XRD diffractogram compared to other samples. However, only low intensity of characteristic peaks for  $\text{MoO}_2$  recorded proved that the incomplete transformation from  $\text{MoO}_3$  in the sample cause by limitation of carbon content. Preparation of molybdenum carbide was achieved at 2.0:7 ratio, similar to previous experiment with all oxides species in the samples were transformed to molybdenum carbides.



**Figure 3** XRD patterns for a) 2:3, b) 2:4, c) 2:5, d) 2:6 and d) 2.0:7 prepared molybdenum carbides respectively

From these experiments, the domination of molybdenum oxide compound was found in both experiments, beyond of our expectation. Our theory suggested that decomposition of AHM will produce  $\text{MoO}_3$  only and further alloy with carbon to produce  $\text{Mo}_2\text{C}$ . Conversely, present of carbon was reacted with  $\text{MoO}_3$  to produce intermediate species,  $\text{MoO}_2$  before produced our target compound. This theory was supported by previous research regarding decomposition of AHM and production of molybdenum carbide [6, 13]. Moreover, this study proved that liquid-solid system works perfectly in microwave alloying technique and produced molybdenum carbide. Generally, water's molecule is economical and proven microwave absorber. The polar molecule of water ( $\epsilon$ : 80) transformed microwave into dielectric heating energy and initiated this experiment [14-15].

#### **4.0 Conclusion**

Goal of this research was successfully achieved. The molybdenum carbide was flourishing prepared using mixture of ammonium heptamolybdate and carbon. Furthermore, the optimum ratio for this preparation was found at 2.0:7 ratios in both experiments, proved that this technique is applicable to prepare molybdenum carbide. On the other hand, generation of molybdenum carbide started with decomposition of ammonium heptamolybdate to molybdenum trioxide, followed by reduction process to produce molybdenum dioxide, initiated by carbon. The prepared molybdenum dioxide was further reacted with remaining carbon to produce molybdenum carbide.

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