

EFFECTS OF UREA IN THE PREPARATION OF SUPPORTED-
MOLYBDENUM TRIOXIDE VIA MICROWAVE INDUCED TECHNIQUE

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Special dedication to *Mak* and *Abah*
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ABSTRACT

The effect of urea in the preparation of MoO₃ supported on activated carbon (AC) was studied. The experiment was performed by using microwave-induced technique. The bamboo-based activated carbon was used as the supportive material of MoO₃. It was prepared via chemical activation using phosphoric acid as an activating agent and carbonized at 400 °C. Meanwhile, urea was selected as an additive to enhance the formation of MoO₃ because of its ability to extract Mo ion from the starting material ammonium heptamolybdate (AHM). The concentrations of urea to AHM were varied to see their effect to the formation of supported-MoO₃. Urea was first added to the precursor solution and mixed homogeneously before AC was introduced to the reaction media. After that, the mixture was treated under microwave radiation at 800 W for 2 minutes. The AC samples were characterized using BET surface area, Fourier transformed infrared spectroscopy and scanning electron microscope (SEM). Meanwhile, the supported-MoO₃ samples were characterized by X-ray diffraction and BET surface area analysis. The BET surface area obtained for AC and C supported-MoO₃ was 954.38 m²/g and 79.59 m²/g, respectively. The diffractogram obtained demonstrated the existence of orthorhombic α -MoO₃ and C material. After comparison, sample with 1:1 molar ratio of Mo/urea was selected as the optimum ratio to produce the supported-MoO₃. Higher concentration of urea led to the formation of amorphous MoO₃ and C. As conclusion, with the equal ratio to the Mo precursor solution, urea can be used as an additive in order to enhance the formation of supported-MoO₃. The surface area of supported-MoO₃ can be enhanced by using activated carbon as supportive material. Finally, the reaction can be well performed using microwave radiation as a greener and faster source of energy.

ABSTRAK

Kesan urea dalam penyediaan MoO_3 berpenyokong karbon teraktif (AC) telah di kaji. Experiment ini dijalankan dengan menggunakan bantuan teknik gelombang mikro-teraruh. Karbon teraktif daripada buluh digunakan sebagai bahan penyokong MoO_3 telah disediakan melalui pengaktifan kimia menggunakan asid fosforik sebagai agen pengaktifan pada suhu $400\text{ }^\circ\text{C}$. Manakala, urea telah dipilih sebagai bahan tambahan untuk meningkatkan pembentukan MoO_3 kerana ia berupaya untuk mengekstrak Mo ion daripada bahan mula yang kompleks, ammonium heptamolibdat (AHM). Kepekatan urea diubah untuk melihat kesannya terhadap pembentukan MoO_3 berpenyokong. Urea ditambah dengan bahan mula dan disebatikan sebelum AC dicampur ke dalam tindak balas. Selepas itu, bahan campuran dirawat di bawah gelombang mikro pada 800 W untuk 2 minit. Sampel AC telah diciri menggunakan luas permukaan BET, spektroskopi inframerah transformasi Fourier (FTIR), mikroskop elektron imbasan (SEM). Sementara itu, sampel MoO_3 berpenyokong telah dicirikan menggunakan pembelauan sinar X (XRD) dan luas permukaan BET. Luas permukaan BET tertinggi diperoleh bagi masing-masing karbon teraktif dan MoO_3 berpenyokong adalah $954.38\text{ m}^2/\text{g}$ dan $79.59\text{ m}^2/\text{g}$. Difraktogram yang diperoleh menunjukkan kewujudan $\alpha\text{-MoO}_3$ ortohombik dan C yang ketara. Selepas perbandingan, sampel dengan nisbah 1:1 molar Mo/urea telah dipilih sebagai nisbah optimum untuk menghasilkan MoO_3 berpenyokong C. Kepekatan urea yang tinggi akan cenderung kepada pembentukan MoO_3 amorfos. Kesimpulannya, dengan nisbah yang sama kepada larutan bahan mula Mo, urea boleh digunakan sebagai bahan tambahan dalam meningkatkan pembentukan MoO_3 . Luas permukaan MoO_3 berpenyokong boleh ditingkatkan dengan menggunakan karbon teraktif sebagai bahan penyokong. Akhirnya, tindak balas boleh juga dilakukan dengan menggunakan radiasi gelombang mikro sebagai sumber tenaga yang lebih hijau dan cepat.

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LIST OF ABBREVIATIONS

Mo	-	molybdenum
W	-	tungsten
AC	-	activated carbon
MoO ₃	-	molybdenum trioxide
AHM	-	ammonium heptamolybdate
FTIR	-	fourier-transformer infra-red spectroscopy
XRD	-	x-ray diffraction
NAA	-	nitrogen absorption analysis
TGA	-	thermo-gravimetric analysis
SEM	-	scanning electron microscope

CHAPTER 1

INTRODUCTION

1.1 Background of study

The effects of urea in the preparation of supported molybdenum trioxide (MoO_3) on activated carbon (AC) were examined in this study. The attempt was carried out using microwave-induced technique as a new alternative approach. MoO_3 is a common material that had been studied by scientist all over the world because of its high thermal stability and unique catalytic performance properties as novel catalyst in many catalytic reactions. Hence, this situation has put a pressure on the researchers for the preparation method of the material. The methodology design must be constructed, developed and exploited in such a way to achieve the simplest yet efficient approach that aligned with green chemistry concept. On account of that, this study reported another successful method of producing MoO_3 in the presence of an organic additive like urea. The molar ratio with respect to the concentration of urea to the precursor material was manipulated and the results were observed. Furthermore, this experiment also had proven the ability and competency of microwave radiation as the heating mechanism in the production of the supported MoO_3 . Conclusively; this attempt was aimed to produce MoO_3 in the easiest, harmless and less time-consuming experimental. Where, urea play role as the additive in order to enhance the accumulation of MoO_3 , AC play role as the surface area booster and microwave-induced technique play role as the heating technique

that provide sufficient energy for the reaction to occur in reasonable short experimental time.

An approach of using organic additive (e.g. urea) to extract out Mo ion from the bulkiness of starting precursor like ammonium heptamolybdate (AHM) has been investigated (Parvis *et al.*, 2010). The bulkiness structure of AHM can be illustrated in the Figures 1.1. Urea is claimed to form a nanostructure MoO₃ with a rod-like shape when AHM was mixed with it. The reaction took place at approximately 80 °C to form white precipitates and further calcinate at 500 °C to be claimed as crystal MoO₃ (Parvis *et al.*, 2010). The nitrogen atom with non-bonding electron pair is suggested as the functional group of urea that form bond with Mo ion. The smaller size of urea allows it to make bond easier with the metal centre as the steric hindered is weaker in the case of urea. The structure of urea can be illustrated as in Figure 1.2. However, another study proclaimed that, at 20 °C, urea react as the connector that bridged two Mo centre of the two adjacent edge-shared octahedral MoO₃ with its carbonyl oxygen as 2μ-ligand and formed a MoO₃(NH₂CONH₂) rod-liked crystal (Veen *et al.*, 2008). The role of urea in the formation of the extended structure of MoO₃ is claimed to be a dual one. It not only links the molybdenum oxide units into a helix, but it also connects the helices to form an extended structure. Therefore, the formation of MoO₃ material is suggested pretty much depending on their method of preparation.

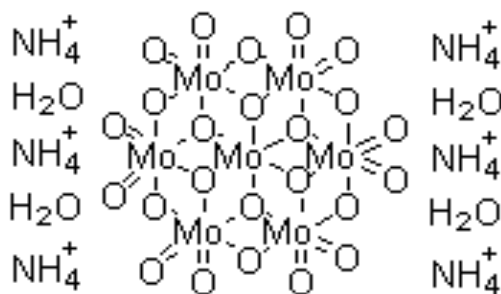


Figure 1.1: The structure of Ammonium Heptamolybdate (AHM)

Anyhow, this study had observed the effects of the additive concentration presence in the reaction atmosphere by manipulating its ratio with the precursor solution. Apparently, all of the final products for each parameter showed the formation of MoO₃, but their XRD diffractograms were slightly different to one and another. These interesting results will be further discussed in Chapter 4.

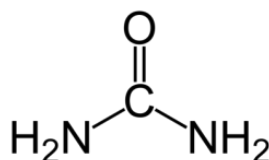


Figure 1.2: Structure of urea; use as an additive to enhance the MoO₃ formation.

Activated carbon (AC) is known as the carbon that has high surface area on its surfaces. The high surface area is contributed by the pores that can be constructed via chemical or physical activation process. The smaller pores size lead to the larger surface area which is great for adsorption process. The pores on AC were claimed to have a zero electron density which merits an intense van der Waals forces (from the near proximity of carbon atom) that responsible for the absorption process. By this advantage, AC is commonly used as the supported material for metal to increase their surface area and hence the active site for reaction (Ferrari *et al.*, 2002; Kaluza and Zdrzil., 2001; Liang *et al.*, 2003). In this study, AC carbon was prepared from bamboo via chemical activation process using phosphoric acid. The idea of using bamboo as the carbon sources to make activated carbon instead of using commercial one is to use fast-growing, cheap and potential recyclable carbon sources material. As for the activation process, the phosphoric acid has been chosen as the activating agent due to its reliability of producing high surface area carbon. The process of activation process in this study is classified as chemical activation process which preferable as supported for metal material. Furthermore, the process is less tedious compare to physical activation process. The AC prepared possesses the surface area within standard AC that is 500-2000 m²/g. The molar ratio of AC carbon presence in the reaction also was manipulated in this study to investigate the influence of MoO₃

formation. However, need to recap that the role of AC in this study was merely a supported material to increase the MoO₃ surface area and thus enhance its active site.

Microwave technique is a new method applied in synthesizing a material as the heating mechanism of it could provide a uniform and constant heating profile to the reaction (Qi and Yang., 2004; Larhed *et al.*, 2002). Microwave induced technique was also chosen as it complies to the green term because further reductions in activation energy consumption could be achieved as the heating process is origin at molecular level due to ionic conduction and dipole rotation. Nonetheless, it is internal and volumetric, which provide the advantages of uniform temperature, rapid temperature rise and saving of energy (Liu *et al.*, 2010). The electromagnetic energy of microwave heating ranges at the frequency of 30 MHz to 300 GHz. The process by which matter absorbs microwave energy is claimed as dielectric heating. A vital characteristic in this heating mechanism is the mobility of the dipoles and the ability to orient them according to the direction of the electric field. The orientation of the dipoles differs with the magnitude and the direction of the electric field. Molecules that have a permanent dipole moment are able to align themselves in complete rotation or at least partially with the direction of the field. Phase shifts and dielectric losses are the outcomes and cause of the electrical energy which is then been converted into kinetic or thermal energy (Phansi *et al.*, 2014). Therefore, this study took the uniqueness of microwave heating and applied it in the preparation of supported MoO₃ material.

1.2 Problem statement

MoO₃ material has received a considerable attention as an advanced material in recent years for their attractive physical and chemical properties including its stability at multiple oxidation states, mechanical hardness, thermal stability, superconductivity, and great performance in many catalytic reactions (Al-kandari *et*

al., 2004; Enneti and Wolfe, 2012). Most of the methods designed before this requires tedious work and involved high experimental cost, time and temperature. Therefore, this study has discovered several flaws of the preparation method and introduced a few approaches in order to overcome the weakness mentioned.

In this study, the common precursor salt with formula of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AHM) was chosen instead of metal powder or chloride, as the starting material to form the desired product, MoO_3 . This is due to the high number of Mo ion contained in it which is great for the formation of the final product. Furthermore, the reaction is tidy and requires fewer steps to form the oxide compared to the other starting materials. However, problem arises because the structure of AHM is bulky and requires high activation energy which means high temperature for the rearrangement of the Mo and oxygen molecules as in crystal structure orientation. The introduction of urea as an additive is to lower the reaction energy and enhance the accumulation of MoO_3 molecules. This attempt was investigated the effects of the MoO_3 formation when the concentration of the additive was increased.

One of the properties that essential to the catalytic performance of MoO_3 is its surface area. In fact, for any material, surface area is important when it comes to the catalytic reaction. This is because the higher surface area provides a greater number of active sites of the catalyst where the reaction usually took place. In this experiment, AC carbon was added to the MoO_3 with the purpose of as the metal supporter and also to increase the surface area of the final product. AC with the highest surface area should be used to prepare the supported- MoO_3 material. The concern of AC will react with MoO_3 and convert into other product like carbide, can be put aside as the conversion of MoO_3 to carbide requires specific atmosphere and different approaches (Covington *et al.*, 2012).

Although conventional heating method for the preparation of Mo-based materials has been developed before, there is still a room to improvise the drawbacks

learnt. Thus this experimental took advantage of this situation to study the competency of microwave induced technique as an alternative technique to prepare Mo materials in the presence of organic additive, urea. The idea was to lower the energy consumed. With the unique heating mechanism of microwave that origin from the molecular level, provide heat from internal to external, a reaction should experiences a constant, steady and rapid heat supplied. These advantages were surplus to the formation of high thermal stability of one material like MoO_3 .

1.3 Objective of study

The objectives of this research are:

1. To prepare and characterize AC from raw bamboo via chemical activation using phosphoric acid as the activating agent.
2. To investigate the effects of urea in the preparation of the supported- MoO_3 via microwave-induced technique

1.4 Scope of study

The scope of study in this trial can be divided into three parts. The first part was to prepare activated carbon from an inexpensive, fast-growing and abundant plant like bamboo. The intension of producing the AC instead of using commercial one was because of adapting one of the green chemistry principles which utilize a recyclable material that can reduce cost of experiment and also to seek potential on bamboo as a new carbon sources for preparing AC. The prepared activated carbon from bamboo is far cheaper and its surface area obtained is within the range of commercial AC ($500\text{-}2000\text{ m}^2/\text{g}$). Thus, by utilizing a higher surface carbon sources

as metal supporter will lead to the formation of high surface area Mo oxides. A high surface area property will grant a great catalytic performance for the Mo oxides when they are used as a catalyst. Therefore, this study took this approach and investigated the effects of the addition of supported material like AC onto the Mo oxides.

Secondarily, the prime focus of this study was laid on the effects of urea in the formation of supported-MoO₃. The conventional method of preparation MoO₃ by heating and calcinating AHM precursor solution was modified by using microwave induced technique and introducing urea as an extracting agent in the reaction atmosphere to ease the formation of MoO₃. The molar concentration of urea to the starting solution of AHM was manipulated to observe the results.

Lastly, the final purpose of this study was to explore the ability of microwave in the preparation of supported metal oxide. Nowadays, microwave heating technique is regularly use on the daily basic of domestic activity like cooking food or baking cakes. The microwave working principle is becoming preferable to the domestic users because of the ability of it to cook food very fine in a short time. This is because microwave heating provide a constant heat that origin from the molecular level which give a steady and speedy temperature rise. In the preparation of MoO₃ crystal, requires a stable heat supply that provides sufficient energy for the crystallization to occur. Therefore, this study took the concept of it and applied it in the preparation of supported-MoO₃ material.

1.5 Significant of study

Transition metal oxides attract considerable interest due to their suitability for use in electronic and magnetic devices, in heterogeneous catalysis and in a number

of other applications including gas sensors. These compounds are characterized by the incomplete d-shell of the metal cations, which makes them exhibit wide variety of properties. Therefore, studies in their method of preparation could be very interesting and demanding for the future work. The method designed must adapt few characters like less tedious steps, low cost, high efficiency and involved low energy in the process. Therefore, this study took a few approaches in order to equip the experimental conditions mentioned.

This study highlighted the 1) use of bamboo as an alternative source of preparing AC and also its role as a supportive material to enhance the metal oxide surface area; 2) use of urea as an additive and their concentration effects on the formation of supported MoO_3 ; 3) efficiency and competency of new source of energy which was microwave radiation. The process of synthesizing supported MoO_3 in the bulk and economically applicable could bring a big impact to the catalytic, electrical and sensor industry. The modifications of the method preparation by the highlights mentioned above make this investigation more interesting. Above all, this study expects to accomplish a new method that has better efficiency, safer and greener compared with the conventional method.

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