

ADSORPTION AND PHOTOCATALYTIC REMOVAL OF  
DIMETHYLARSENIC ACID USING TITANIA AND ZINC OXIDE  
THIOL FUNCTIONALIZED ZSM-5 ZEOLITE

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A thesis submitted in fulfillment of the  
requirements for the award of the degree of  
Master of Science (Chemistry)

Faculty of Science  
Universiti Teknologi Malaysia

FEBRUARY 2015

## ABSTRACT

This research is to correlate physicochemical properties of metal oxides-ZSM-5 functionalized thiol with their catalytic properties towards adsorption and photocatalytic removal of dimethylarsenic acid (DMA).  $\text{TiO}_2$  and ZnO were attached on the surface of the ZSM-5 zeolite by impregnation. The impregnation of these metal oxides were carried out on the surface of the ZSM-5 followed by modification of functional group on ZSM-5 surfaces with thiol to form  $\text{TiO}_2$  impregnated ZSM-5 functionalized with thiol ( $\text{TiO}_2$ -ZSM5-SH) and ZnO impregnated ZSM-5 functionalized with thiol (ZnO-ZSM5-SH). Characterizations by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), diffuse reflectance ultraviolet-visible spectroscopy (DR UV-Vis) and energy dispersive X-ray (EDX) proved that the metal oxides were successfully attached on the surface of the ZSM-5. It was demonstrated that the modification of functional group on ZSM-5 surface with thiol was also successful. Images from high-resolution transmission electron microscope (HRTEM) and scanning electron microscope (SEM) showed  $\text{TiO}_2$ -ZSM5-SH and ZnO-ZSM5-SH appeared as crystalline agglomerated particles.  $\text{TiO}_2$ -ZSM5-SH had shown better performance in the photocatalytic removal of DMA by 49% compared to 41% removal by ZnO-ZSM5-SH. On the contrary,  $\text{TiO}_2$ -ZSM5-SH gave lower percentage in the adsorption of DMA which was 23% as compared to 36% with ZnO-ZSM5-SH. Results showed that  $\text{TiO}_2$ -ZSM5-SH and ZnO-ZSM5-SH possess photocatalytic properties. The percentage removal of DMA had increased to 49% for  $\text{TiO}_2$ -ZSM5-SH and 41% for ZnO-ZSM5-SH compared to the use of bare  $\text{TiO}_2$  (20%) and ZnO (23%). These proved that thiol functionalization on ZSM-5 enhanced the ability of both materials to remove DMA.

## ABSTRAK

Penyelidikan ini bertujuan mencari korelasi antara sifat fisikokimia logam oksida-ZSM-5 berfungsi tiol dengan sifat pemangkin terhadap penjerapan dan penyingkiran pemfotomangkin asid dimetilarsenik (DMA).  $\text{TiO}_2$  dan ZnO berikat dengan permukaan zeolit ZSM-5 menerusi pengisitepuan. Pengisitepuan logam oksida telah dilakukan ke atas permukaan ZSM-5 diikuti dengan pengubahsuaian kumpulan berfungsi pada permukaan ZSM-5 dengan tiol untuk membentuk  $\text{TiO}_2$  terisitepu ZSM-5 berfungsi tiol ( $\text{TiO}_2$ -ZSM5-SH) dan ZnO terisitepu ZSM-5 berfungsi tiol (ZnO-ZSM5-SH). Pencirian oleh pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi ultralembayung-cahaya nampak pantulan terbaur (DR UV-Vis) dan penyebaran tenaga sinar-X (EDX) membuktikan bahawa logam oksida berjaya diisitepu ke atas permukaan ZSM-5. Pengubahsuaian kumpulan berfungsi pada permukaan ZSM-5 oleh tiol juga telah berjaya. Imej hasil daripada mikroskop kehantaran elektron resolusi tinggi (HRTEM) dan mikroskop imbasan elektron (SEM) menunjukkan  $\text{TiO}_2$ -ZSM5-SH dan ZnO-ZSM5-SH muncul sebagai zarah bergumpal berhablur.  $\text{TiO}_2$ -ZSM5-SH menunjukkan prestasi lebih baik dalam penyingkiran pemfotomangkin DMA sebanyak 49% berbanding dengan 41% penyingkiran oleh ZnO-ZSM5-SH. Sebaliknya,  $\text{TiO}_2$ -ZSM5-SH memberi peratus penjerapan DMA yang lebih rendah iaitu 23% berbanding 36% oleh ZnO-ZSM5-SH. Keputusan menunjukkan bahawa  $\text{TiO}_2$ -ZSM5-SH dan ZnO-ZSM5-SH mempunyai sifat pemfotomangkin. Peratus penyingkiran DMA telah meningkat kepada 49% untuk  $\text{TiO}_2$ -ZSM5-SH dan 41% untuk ZnO-ZSM5-SH berbanding penggunaan  $\text{TiO}_2$  (20%) and ZnO (23%). Ini membuktikan bahawa ZSM-5 berfungsi tiol meningkatkan keupayaan kedua-dua bahan untuk menyingkirkan DMA.

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

The field of catalysis has been widely investigated with various type of catalysts synthesized and applied for the main target as an essential approach in environmental remediation. The effort of modifying the catalyst in order to enhance its uses and efficiency has contributed to the significant findings and results that are beneficial. Generally, it is accepted that catalysis holds an important role in the industries especially two remarkable industry segments, chemicals, reagents, oil and petroleum processing are highly depending on catalysis. A lot of modern, cost and energy efficient environmental technologies involve catalytic and biocatalysis which offers exciting opportunities for the invention and production of a broad range of pharmaceuticals and specialty chemicals and for remediation of the environment (Nur, 2006).

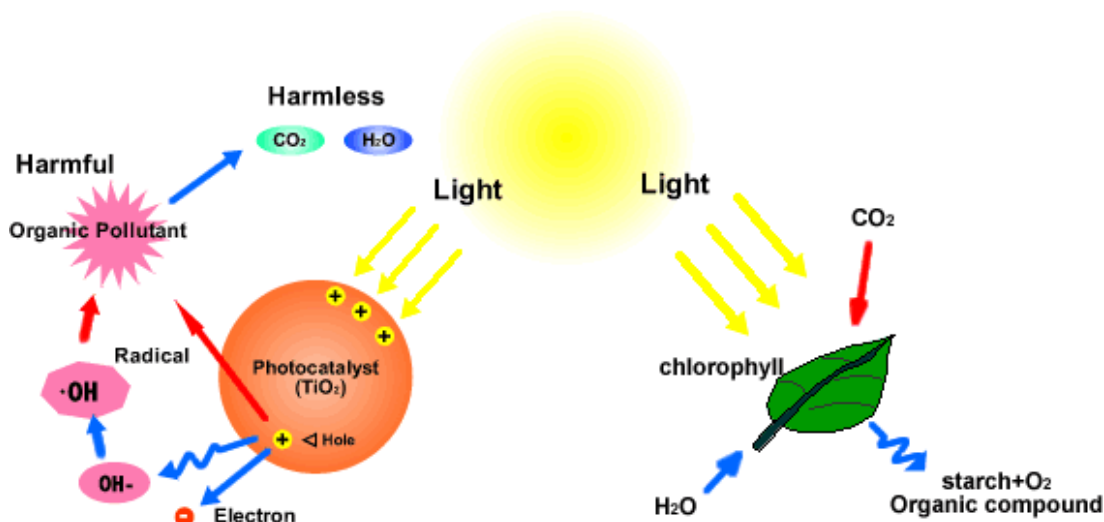
The term catalysis is defined as a substance that evokes chemical actions which would not be taken place in its absence. A catalyst is a substance that transforms reactants into products through an uninterrupted (speed up chemical reactions) without being consumed during the process. Many materials have the potential to serve as catalyst includes metals, metal compounds (oxides, sulphides, and nitrides), organometallic complexes and enzymes (Nur, 2006). Historically, catalysis has always been a great interest especially in the petroleum and chemical industries. It has been applied to invent and produce new or improved products and processes (Satterfield, 1991). The immense growth and the remarkable increase of size of industries has affected the environment not necessarily by the emissions of

the manufacturing plants but also by some of the useful products which has proven as the major success of catalysis in these industries. An increasing public awareness which has demanded for better prevention and the search for new solutions in catalysis already began earlier in 1970s and recently, it has been of a great concern (Ertl *et al.*, 2008). The aim and emphases in the field of catalysis are:

- 1) Catalytic removal of hazardous effluents, harmful organic compounds such as chlorinated compounds, sulfur compounds, carbon monoxide and nitrogen oxides from environment and elimination of used catalyst from static or mobile sources in soil, water and air.
- 2) Basic theory and understanding, modelling and characterization of catalysts and its related processes to be applied in environment.
- 3) Natural catalytic processes that occurred in the environment.
- 4) Catalytic reactions where conversion of wastes into useful products.
- 5) Clean and safe manufacturing where toxic chemicals is being replaced with non-toxic catalysts, solvents and experimental conditions.
- 6) Fuel cells and fuel processing of hydrocarbon to hydrogen for production of clean energy.
- 7) Application of photocatalysis for environmental remediation.
- 8) New combustion technologies and catalysts on catalytic.

Photocatalysis in the other word is defined by in the presence of a catalyst, an accelerated photoreaction occurred where adsorbed substrate absorbed light in a catalysed photolysis reaction. Photocatalysis is well explained by the theory of 'Honda-Fujishima effect' describing the process of photocatalysis which was initially based from the photosynthesis process (Fujishima and Honda, 1971). The similarity of both processes is that it involves the aid of 'photo' in other word, light as an aid to proceed the process of converting initial harmful or toxic compounds into nontoxic and safe products such as carbon dioxide and water. This process is also known as mineralization. Figure 2.1 shows the illustration of photosynthesis and photocatalysis processes.





**Figure 1.1:** The process of photocatalysis and photosynthesis which final reactions resulted in the emission of carbon dioxide and production of water (Fujijsjima and Honda, 1971).

Photocatalytic activity (PCA) is basically depends on the creation of electron-hole pairs by catalyst, which generates free radicals such as hydroxyl radicals:  $\text{OH}\cdot$  in photogenerated catalysis. These radicals are able to undergo secondary reactions. As it was discovered that water electrolysis by titanium dioxide is achievable, its comprehension has been made possible. Advanced oxidation process (AOP) is the commercial application for this process. There are various techniques in achieving AOP's, either involving the use of  $\text{TiO}_2$  and UV light or not. Basically, the main factor of this process is the production and the use of hydroxyl radicals in the reaction (Wu and Chang, 2006 and Akihiko, 2007).

Photocatalyst is a term to describe a catalyst that is active in response of light exposure. The definition of photocatalyst is also includes as photosensitization where a photochemical conversion process is achievable as a result of initial absorption of radiation by photosensitized. Several materials were reported can act as good photocatalysts include metal, metal compounds and organometallic compounds. In this work, it is focused to utilize the application of the most promising photocatalysts which are titanium dioxide and zinc oxide. Both of these photocatalysts are well known for their excellent performance in photocatalysis (Qamar and Muneer, 2005).

Titanium dioxide ( $\text{TiO}_2$ ) is well known as titania is a white colour solid existed generally in the form of fine powders with molecular weight of 79.87 g/mol. Natural titania is usually not in its pure form and it is mainly found contaminated with metals such as iron. Titanium's oxidation state is IV and its  $d$ -electron configuration is  $d^0$ . The white colour of titania is described by the lack of metal centred or  $d-d$  transitions. It exists in several polymorphs and two common forms of titania are anatase and rutile. Titanium dioxide is a semiconductor where its highest occupied molecular orbital (HOMO) is termed as valence band and lowest unoccupied molecular orbital (LUMO) is termed as conduction band. When electrons from oxygen are transferred to the vacant titanium  $d$ -orbitals, it was resulting in the ligand to metal charge transfer due to the effective light absorption by titania. Since anatase band gap is 3.2 eV and rutile is 3.0 eV, it will result in the appearance of a sharp absorption band at around 390 – 400 nm as this transition is in the UVA region. It has been reported that when it is spiked with nitrogen ions, it can enhance the properties of  $\text{TiO}_2$  as a photocatalyst under visible light (Asahi *et al.*, 2001).

Focusing at the electronic processes, irradiation of UV light will highly promote the electron to the conduction band and results a hole in the valence band. It is essentially a vanishing of the electron density that was localized on that orbital, and it was marked as a positive charge to symbolize the loss of negative electron. The hole owns powerful oxidizing properties where the orbital and it is highly preferable to retrieve the electron density that just lost after light irradiation. It can easily be retrieved by recombining the electron in the conduction band with the valence band recombination which is a total of radiative and non-radiative processes. Based on the energy gap law, as the rutile energy levels are closer mean that the non-radiative process is more efficient, hence it is more efficient for recombination.

Since alternative pathways to recombination are possible, so the application of these materials as photocatalysts is highly suggested. The hole can easily oxidize water on the surface of the material resulting in the formation of hydroxyl radicals. Hydroxyl radicals are known to be a powerful oxidizing agent and can simply oxidize any organic species that existed near its surrounding and ultimately mineralized them by forming carbon dioxide and water as the end products.

Meanwhile, in the upper conduction band, the recombination of electron-hole is not possible since there are no holes, since it has already oxidized surface bound water. It will rapidly reduce oxygen to form superoxide anion as an alternative process which subsequently will react with water to form the hydroxyl radical again (Bahnemann, 2004).

The type of semiconductor where metal oxide particularly  $\text{TiO}_2$  was reported showing the best photo stability and hence highest sustained photocatalytic activity (Fox and Dulay, 1993). Previous studies have revealed that the structure of  $\text{TiO}_2$  will affect its photocatalytic activity. It was reported that the distortion of crystal structure was affecting the charge separation of photogenerated electron and hole (Kudo *et al.*, 2000). Photocatalytic activity of  $\text{TiO}_2$  was also affected by the presence of the lattice structure of anatase and rutile. Mainly, the preferred type of  $\text{TiO}_2$  is in anatase form since the photocatalytic activity of anatase is better than rutile (Tada *et al.*, 2002). The distortion of each octahedron and the assembly pattern of the octahedra chains in rutile and anatase are the reasons of the difference in their crystal structure. The octahedron structure in anatase is significantly distorted which caused its symmetry lower than orthorhombic. The Ti-Ti distances in anatase (3.79 and 3.04 Å) are longer than in rutile (3.57 and 2.96 Å) whereas the Ti-O distances in anatase (1.934 and 1.980 Å) are shorter than in rutile (1.949 and 1.980 Å) (Burdett *et al.*, 1987). For anatase structure, each octahedron is in contact with eight neighbors which four sharing an edge oxygen pairs and four sharing a corner oxygen atom. Meanwhile, for the structure of rutile, each octahedron is in contact with 10 neighbor octahedrons where two sharing edge oxygen pairs and eight sharing corner oxygen atoms. In rutile, octahedron is irregular and it shows a slight orthorhombic distortion. The differences in lattice structures caused by the different weight densities and electronic band structures between these two forms of  $\text{TiO}_2$  which has significantly affecting its photocatalytic activity (Yates *et al.*, 1995). Other than that, the adsorbability on  $\text{TiO}_2$  particles significantly increased as the size of particles decreased. The best adsorption on  $\text{TiO}_2$  was reported when the particle size of  $\text{TiO}_2$  was less than 30 nm (Xu *et al.*, 1999). Other uses of *titania* also include as a white pigment. It is called titanium white, Pigment White 6 or known as CI 77891. The applications of this pigment are such as in paint, food colouring, sunscreen and cosmetics (Park *et al.*, 2004).

Zinc oxide with the formula ZnO is an inorganic compound. Naturally occurring ZnO appears as white powders, nearly insoluble in water. The mineral form of ZnO which is known as *zincite* abundantly exists in the earth's crust. The ZnO powder is massively used as an additive into numerous products and materials such as paint and lubricants (Hernández et al., 2008). It has also been widely investigated on the properties as a photocatalyst. Since ZnO has almost similar band gap energy as TiO<sub>2</sub>, it is expected that the photocatalytic activity of ZnO is as efficient as TiO<sub>2</sub>.

Similar to TiO<sub>2</sub>, the size and shape of ZnO was also affecting its photocatalytic activity. It was reported that a hexagonal plate-like particle were reported to hold five times higher activity in the photocatalytic degradation of methylene blue as compared to the use of rod-shaped ZnO particles. This has clearly proved that the (00 $\bar{1}$ ) faces and the terminal polar (001) exhibit more active surfaces than the nonpolar surfaces perpendicular to them (i.e., 100, 101) for photocatalysis (Tsang *et al.*, 2009). The larger exposure of polar faces contributes to higher photocatalytic activity. The high activity of ZnO could be assigned to the (001) face, the face with the intrinsically highest energy among all the faces. Due to its positive charge, the OH<sup>-</sup> ions could preferably adsorb onto this face (Dodd *et al.*, 2009). It has contribute to a higher rate for production of OH• radicals and as well as degradation of the pollutant during photocatalysis. Other than that, it was reported that particle morphology of ZnO significantly affects its photocatalysis where spherical agglomerate of ZnO gives the best photocatalytic activity as compared to rod-like, single sphere and star-like ZnO particles (Haneda and Li, 2003).

However, it has been revealed that the photocorrosion phenomenon has been frequently occurring with the illumination of UV lights and has become the main reason for the decreasing efficiency of photocatalytic activity of ZnO in aqueous solutions (Tian *et al.*, 2012). For application of ZnO as photocatalyst in gas phase, the photocorrosion will not be a problem. Apart from that, some studies have confirmed that ZnO holds a better efficiency for photodegradation in aqueous solutions as compared to *titania*. ZnO was proven with excellent photocatalytic performance for the photodegradation of dyes (Tian *et al.*, 2012)

The ability of a these material to create an electron-hole pair in the presence of UV is defined as photocatalytic activity. The resulting free-radicals are high efficient oxidizers for an enormous range of organic materials. The photocatalytic activity of  $\text{TiO}_2$  and  $\text{ZnO}$  has been extensively investigated because of its significant potential in remediation, sanitation, sterilization, and others useful applications (Fujishima *et al.*, 1999). The photocatalytic activity efficiency of metal oxides can be controlled and enhanced by coating it with other materials such as silica and carbon (Leary and Westwood, 2011).

The discovery of photocatalysis was found and explained by the Honda-Fujishima effect (Fujishima and Honda, 1971). The basic theory of photocatalysis was demonstrated by an experiment where titanium oxide electrode was exposed in an aqueous media under strong light. During the reaction, gas bubbles were evolved from the surface of the electrode. However, no bubbles are visible from the surface of the electrode when the light was switched off. It was confirmed that hydrogen was generated at the counter of platinum electrode as it was found that the bubbles consisted of oxygen. This phenomenon was known as photocatalysis where the basic phenomenon is light being absorbed by the titanium dioxide in the water and the water molecule are broken into hydrogen and oxygen. However, the decomposition reaction of water is slow, thus any organic materials can be decomposed preferentially.

Fundamental fields in application of photocatalyst has been widely known such as in air purification; decomposition of aldehyde and removal of  $\text{NO}_x$ , water purification, decomposition of organic materials and degradation of environmental hormones, self-cleaning (anti-fogging and anti-contamination), decomposition of oil and superhydrophilic effects, anti-bacteria and sterilization, degradation of bacteria and sterilization of *Escherichia coli* and Methicillin Resistant *Staphylococcus aureus* (MRSA) (Shiraishi *et al.*, 2009).

Titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) have been reported as among the best photocatalysts that can enhance the removal of organic pollutants (Liao *et al.*, 2004). Being well-known semiconductor materials,  $\text{TiO}_2$  and  $\text{ZnO}$  have been extensively investigated due to their distinctive electronic, acoustical and optical

properties (Zhang et al., 2002, Gui et al., 2005 and Park et al., 2004). Great efforts have been and still developing on arsenic remediation by adsorption using potential materials especially the use of modified metal oxide with other materials such as carbon nanotubes (Mitra and Ntim, 2011), silica (Chen and Cao, 2006), carbide (Zhang et al., 2006) and zeolite (Langford and Xu, 1997). The potential ability of metal oxide-zeolite structures photocatalyst has been recognized in the photocatalytic removal of organics (Jung et al., 1997 and Sun et al., 2011).

Throughout the years, there are many on-going researches on traditional techniques for arsenic removal such as oxidation precipitation (Borho and Wilderer, 1996), coagulation (Hansen *et al.*, 2006), adsorption (Panda *et al.*, 1997), ion-exchange and membrane separation (Clifford, 1999). Other techniques which include foam flotation (Peng and Di, 1994), solvent extraction (Iberhan and Wisniewski, 2003) and bioremediation (Katsoyiannis *et al.*, 2002) are also widely employed. Among the techniques, adsorption technique is fast evolving where selective adsorption using mineral oxides, polymer resin, biological materials and activated carbon show an increase in interest.

More recent researches have been focused on the application of activated carbon to replace normal carbon material (Dias *et al.*, 2007). Adsorption of metal ions on carbon is more complex than uptake of organic compounds because ionic charges from metal ions affect the removal kinetics of solution. Activated carbon especially that commercially available is very selective for heavy metals adsorption and it is pricey (Kanawade and Gaikwad, 2011). Despite its spectacular use to remediate wastewater, it is high-priced and requires a vast quantity. In addition, adsorption capacity of activated carbon depends on various factors including temperature, pH, ionic strength, activated carbon's properties, adsorbate's chemical properties, and etc (Mohan and Pittman, 2007).

Many approaches have been carried out in order to remove organic arsenic (Lafferty and Loeppert, 2005, Jing et al., 2005 and Lim et al., 2009). In other work, it was reported that phenylarsonic acid can be degraded by hydroxyl radical mediation. However, this method involves extensive procedures which include the use of  $\gamma$ -radiolysis (O'Shea *et al.*, 2007). Other method includes anion exchange where

hexafluoroarsenate was successfully removed from water (Daus *et al.*, 2007). The disadvantage of this method is that there was possible competitive effect between anions present in the sample. Other than that, photo-oxidation of *p*-arsanilic acid was also investigated, where ozone and hydrogen peroxide were used as the oxidants (Czaplicka *et al.*, 2014). However, this method produced a solid phase of arsenic derivatives, which was not favourable.

Meanwhile, the use of silica as catalyst support has been extensive due to the stability of this material to act as host and template in various synthesis procedures (Tryk *et al.*, 1998 and Yi *et al.*, 2006). It was reported that silica increased the surface area of materials that led to higher adsorption (Aznar *et al.*, 1996). Various types of highly dispersed metal oxide species on supports such as silica (Takenaka *et al.*, 1997, Tanaka *et al.*, 1992, Tanaka *et al.*, 2002, Yoshida *et al.*, 2003, alumina (Teramura *et al.*, 2001) as well as zeolites (Yeom and Frei, 2001) have been reported to be active photocatalytically. Silica-based photocatalysts have been developed for several selective reactions and in most cases, the photocatalytic active sites are highly dispersed metal oxide species of quantum size at atomic level located on the surface of silica (Yoshida, 2003). The fact that the covalently bonded functional group on the silica is present, it will give specific functions and attributes such as binding sites, charge density, redox properties or even stereochemical configuration (Cano-Serano *et al.*, 2003). Various types of functional groups, including nitrile, alkyl, thiol, epoxide, amine and phenyl have been incorporated into silica materials (Gui, 2008). Studies revealed that the effect of silica modified TiO<sub>2</sub> has successfully improved the photocatalytic degradation of methyl orange (Li *et al.*, 2004) and aqueous pollutant such as pesticide-paraquat. It was also found that the use of ZnO modified with montmorillonite, a phyllosilicate, has shown better photocatalytic activity in the degradation of methylene blue (Fatimah *et al.*, 2011). Many findings have found that the modification of metal oxides with silica has significantly increased the surface area for more effective adsorption on substrates (Yoshida, 2003, Tanaka and Vohra, 2003 and Aznar *et al.*, 1996).

The advancement on the ability to degrade organic pollutants by photocatalysis is believed to be supported by the introduction of zeolites as they are also made of silica and alumina (Amereh and Afshar, 2010 and Kumar *et al.*, 2006).

This has been proven by several studies which focused on the preparation of metal oxides especially  $\text{TiO}_2$  and  $\text{ZnO}$ , as catalysts and the introduction of zeolite as supporting materials. These materials were then successfully applied in the reduction of metal ions such as chromium (Shao *et al.*, 2009), photocatalytic for decomposition of acetophenone (Paramasiram *et al.*, 2009), photodegradation and photocatalytic removal of pesticides and herbicides (Anandan *et al.*, 2006 and Shankar *et al.*, 2004). It was also reported that the incorporation of  $\text{TiO}_2$  into ZSM-5 zeolite by impregnation method had shown excellent photodegradation removal efficiency for ethylene diamine tetraacetic acid (EDTA) by 99.9% removal at  $3 \times 10^{-3}$  M of EDTA concentration (Mohamed *et al.*, 2005). In addition, functionalized zeolite surface or silica modifications are of great interest since they owe several potential applications in environmental and industrial processes. However, it is still not clear if metal oxide/zeolite-based photocatalyst can aid in the adsorption or removal of organic arsenic such as dimethylarsenic acid (DMA).

Zeolite has been utilized in wide areas of applications including separation and adsorption agent, shape selective solid catalyst, moisture control agent, building materials, chromatographic column filler, ion exchange agent and more applications that lead to extensive studies on the advancement of its application (Jacobs, 1977). Zeolites are well-defined structures of microporous crystalline solids. Generally the frameworks of zeolites are made up of silicon, aluminium and oxygen where water, cations or other molecules incorporated within the pores. Naturally occurrences of zeolites are minerals, and they are extensively mined in places all around the world. For research work, usually the synthetically produced zeolites will be used. The unique properties of zeolites which are shape-selective are also the main factor for their application in molecular adsorption (Miller *et al.*, 2002).

The morphology, framework and topology of a zeolite give the astounding physical and chemical properties of these alumino-silicates micro crystals. Among the most remarkable properties of zeolites are the thermal stability, selective adsorption, molecular sieve effect, high specific surface area, ion exchange capability and hydrophilicity (Gui, 2008). The good ability of zeolites is that it can preferentially adsorb only certain and specific molecules while able to exclude others which has offered a wide range of applications on molecular sieving. This is applied



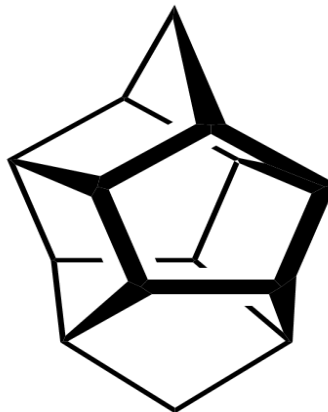
when only certain sizes and shapes of molecules can access the pores of zeolites. In other cases, it was demonstrated where *para*-xylene was successfully purified by silicallite proving that different types and sizes of molecules may enter the zeolites pores but some will diffuse through the channels and pores rapidly, trapping others sieved that was left behind (Miller, 2002).

Other than that, cation-containing zeolites are widely applied in gas separation, based on their electrostatic interactions with the metal ions (cation) where molecules can be differentiated. In addition, due to its properties which hold high affinity towards water, it is also extensively used as desiccants. In contrary, hydrophobic silica zeolites hold high affinity in absorbing organic solvents. Based on their versatile properties, zeolites have the ability to sieve molecules based on differences of shape, size and polarity of the molecules. It is also diversely applied in industries as molecular sieves due to its abilities of “filtering” some molecules of different sizes (Meng-Dong *et al.*, 2002).

As reactions can take place within the pores or internal cavities of zeolites, the function of zeolites to act as catalysts were achieved. Most important reactions is catalysed by hydrogen-exchanged zeolites which have the framework-bound protons that give rise to very high acidity. This particular characteristic of zeolites is widely exploited and applied in many organic reactions, including fuel synthesis, isomerisation and crude oil cracking. Zeolites can also act as oxidation or reduction catalysts which often prepared by the introduction of metal into its framework (Iwamoto *et al.*, 1998). Its applications are as such the use of titanium incorporated with ZSM-5 in the production of copper zeolites and caprolactam in the destruction of NO<sub>x</sub> (Marcus and Cornier, 1999). Thus, it is possible for further investigation on the applications of zeolites as support materials for photocatalysis. The study of zeolite potential as supporting materials for metal oxides has been extensively investigated (Robert, 1972, Kuwahara and Yamashita, 2010).

ZSM-5 is synthetic aluminosilicate zeolite made up of high silica and low aluminium content. ZSM-5 structure is composed of channels with intersecting tunnels. The aluminium sites in ZSM-5 are highly acidic. The substitution of Al<sup>3+</sup> in place of the tetrahedral Si<sup>4+</sup> silica requires the presence of an added positive charge

(H<sup>+</sup>) which contributed to the high acidity of the zeolite. The reaction and catalysis chemistry of the ZSM-5 is highly based to its acidity. Figure 2.3 shows the basic unit of ZSM-5.

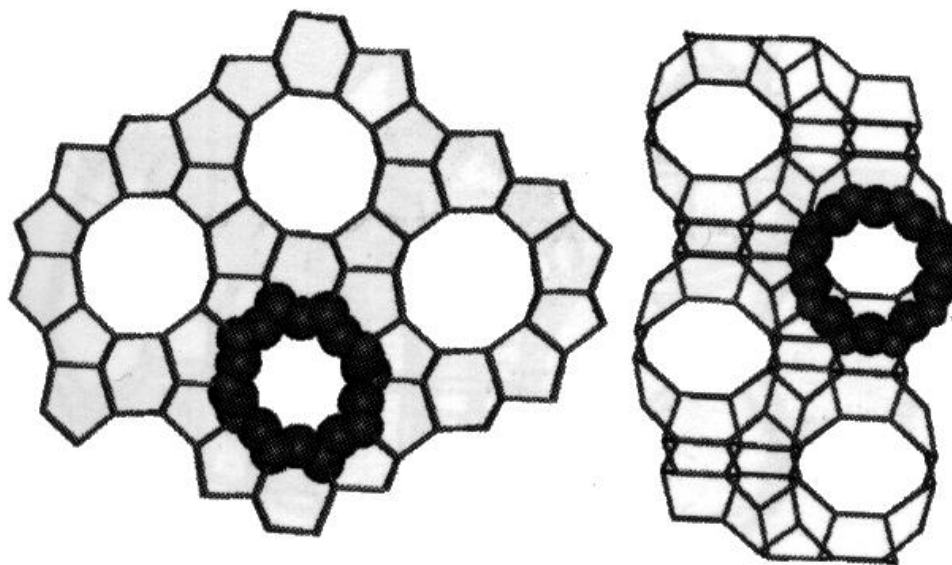


**Figure 1.2:** Pentasil unit of ZSM-5.

Historically, ZSM-5 catalyst was first successfully synthesized by Argauer and Landolt in the year of 1972 (Kokotailo *et al.*, 1978). ZSM-5 zeolite is made up of channels defined by ten-membered rings with a medium pore. The synthesis procedure of ZSM-5 involved three different types of solutions. The first solution was made up of alumina, sodium and hydroxide ions in the presence of excess base where the alumina will eventually form soluble  $\text{Al}(\text{OH})_4^-$  ions. The second solution has a templating agent which is the tetrapropylammonium cation. The third solution contained the elemental building blocks for the framework structure of a zeolite which is the source of silica in ZSM-5. By mixing the three solutions, supersaturated tetrapropylammonium ZSM-5 will be formed which then being calcined for recrystallization to produce a solid ZSM-5 zeolite (Robert, 1971).

Generally, ZSM-5 is a medium pore-sized zeolite that has contributed to the active research on its applications. Since ZSM-5 is a highly siliceous zeolite, it is widely employed as a catalyst in organic synthesis, petroleum refining and petrochemical industries due to its high solid acidity, hydrophilicity, and its resilience in strong acidic medium (Gui, 2008). ZSM-5 has a framework formed by 5-1 secondary building units categorized in MFI structure type. It is categorized as a medium pore class zeolite ( $\sim 6 \text{ \AA}$ ), having a channel system with pore size

between 4.5 Å to 6.5 Å, formed by two types of 10-membered oxygen rings. One pore type has straight but slightly elliptical openings ( $5.5 \times 5.1$  Å). The second type, perpendicular to the first channel is a sinusoidal and zig-zags channel with a cross-section of  $5.6 \times 5.4$  Å. Its catalytic properties are due to its acidity while the unique pore systems give the catalyst its shape selective character (Rehman *et al.*, 2009) Figure 2.4 shows the MFI topology of ZSM-5 (Kokotailo *et al.*, 1978).



**Figure 1.3:** MFI topology and pore system of ZSM-5 with dark atoms show the space-filling view.

On the other hand, the introduction of DMA in environment as herbicide is to eliminate unwanted vegetation especially in various types of woody plant, grasses and weeds. It was also use as soil sterilant and in timber thinning (MacDonald *et al.*, 2013). The uses of DMA in agricultural has become one of the causes of arsenic pollutants to the environment because DMA is directly recessed back to the environment (Mahimairaja *et al.*, 2005). Even some mechanisms may have occurred to transform DMA into monomethylarsenic acid (MMA), As (III) or As (V), the inorganic arsenic compounds in water and soil can undergo biochemical transformations, which will result in the formation of DMA. DMA is expected to be tightly bound to soil with low mobility. The pKa value of DMA is 1.57, indicating that the compound exists as anion and it is not expected to volatilize (Gailer and Irgolic, 1994).

In ambient atmosphere, the oxidation of methylated arsines gaseous that are released to air as biological conversion products from fungi and bacteria will contribute to the formation of DMA (Cracelius, 1977). When it is released to air, DMA will exist solely as vapor with an estimated vapor pressure of  $4.6 \times 10^{-3}$  mm Hg at 25°C. This vapor phase DMA will be degraded by photochemical reaction in the atmosphere producing hydroxyl radicals with half-life estimated to be around 31 days. As the use of DMA is mainly in agricultural activities, the contamination of arsenic in soil will definitely take place and will further affect the safeness of groundwater source, which is mainly use for human consumption. Arsenic pollutant in natural water is a worldwide problem as it was reported in several countries like USA (Burkel and Stoll, 1999), China (Mandal and Suzuki, 2002), Chile (Buchet and Lison, 2000), Bangladesh (Karim, 2000), Taiwan (Xia and Liu, 2004), Mexico (Cebrian *et al.*, 1983), Argentina (Smedley *et al.*, 2002), Cambodia (Agusa *et al.*, 2002), Vietnam (Berg *et al.*, 2001), New Zealand (McLaren and Kim, 1995), Japan (Kondo *et al.*, 1999), India (Dhar *et al.*, 1997) and Nepal (Shrestha *et al.*, 2003).

The arsenic is harmful to human health especially by long term drinking exposure of contaminated water. It can cause skin, bladder, lung, kidney cancer as well as hyperkerotosis (skin thickening neurological disorder), pigmentation changes, nausea, loss of appetite and muscular weakness (Jain and Ali, 2000, Kipping *et al.*, 1997 and Albert *et al.*, 1981). Acute poisoning will result by several symptoms such as abdominal pain, oesophageal vomiting, and bloody diarrhea (Jain and Ali, 2000 and Ng *et al.*, 2003). So it is crucial to prepare a material that can remediate this harmful pollutant using simple synthesis procedures, low cost materials and is practical.

On the other hand, organoarsenics are compounds where chemical bond between carbon and arsenic is existed. Generally, organoarsenic compounds which are known as organoarsenicals are produced industrially to be used in agricultural as fungicides, herbicides and insecticides. However, the applications of organoarsenic in land activities are diminishing in step as the use of organoarsenic is lessening due to the growing concerns about the negative impact of arsenic on the environment and living organisms especially human. The parent compound of organoarsenicals

compounds is arsine which is known to be highly toxic, hazardous and carcinogen. Arsenic occurrence is commonly in two oxidation states which are As (III) and As (V). Despite their toxicity, organoarsenics are also well known in the field of biomolecules.

Nevertheless, organoarsenics are known to be less toxic as compared to inorganic arsenic. Some of the known most toxic organoarsenics being used in the environment are such as monomethylarsenic acid (MMA), monosodium methylarsenate (MSMA), disodium methylarsenate (DSMA) and dimethylarsenic acid (DMA). Focusing on dimethylarsenic acid (DMA), it is known as dimethylarsinic acid, cacodylic acid, hydroxydimethylarsine oxide, arsecodile etc. The chemical compound formula is  $(\text{CH}_3)_2\text{AsO}_2\text{H}$ . The common functions of DMA are as a weed control and defoliation before cotton harvesting (Xu *et al.*, 2007). DMA was recognized as troublesome pollutants in groundwater especially at area with the history of agricultural activities and pesticide manufacturing without proper discarding had significantly contributed to the release of DMA into the environment (Bednar *et al.*, 2002). However, it is considered as less toxic as compared to inorganic arsenic species (Pongratz, 1998) and widely used as herbicides on agricultural lands, golf courses, orchards etc. According to a research project conducted by Dr. John F. Stolz in his collaborative research entitled: Biogeochemical Controls on the Dynamics of Organoarsenic Transformation, organoarsenic compounds are widespread in nature, occurring in freshwater and marine as well as terrestrial environments. Organisms, including bacteria, fungi, algae, invertebrates, vertebrates and even humans, can biotransform arsenic (As), converting inorganic to organic As, and in some cases vice-versa, producing a range of structurally simple to complex organoarsenic compounds in the environment (Huang and Matzner, 2007).

In addition to natural sources, organoarsenicals have been synthesized for agricultural, medicinal, and military uses. Biomethylation of inorganic arsenic compounds mainly produce organoarsenic compounds via processes mediated by enzymes related to vitamin B12 (Dopp *et al.*, 2010). For saprophyte like mold *Scopulariopsis brevicaulis*, it will produce a large amount of trimethylarsine in the presence of inorganic arsenic (Kaise *et al.*, 1998, Bentley and Chasteen, 2002). In

some marine foods specifically fish, algae and mushrooms, the organic compound of arsenic known as arsenobetaine, is found in larger concentrations. Arsenobetaine was initially encountered and identified in the Western rock lobster (Edmonds *et al.*, 1977). For a safe consumption, the average intake of this compound for a person is only about 10 – 50 µg/day. However, values about 1000 µg are not very unusual following the high demand for consumption of fish or mushrooms by human (Cullen and Reimer, 1989). Luckily, there is minimum harm reported in consuming fish because this arsenic compound is nearly non-toxic (Francesconi and Edmonds, 1998).

Arsenosugars, which is a collectively of carbohydrates that bound to arsenic are also can be found in marine algae especially seaweeds. Arsenic containing lipids are also identified and known (Rumpler *et al.*, 2008). Even though arsenic compounds and its derivatives are known to be harmful and toxic for humans, one of the first synthetic antibiotics to treat syphilis and trypanosomiasis was Salvaran which contain arsenic but the use of this antibiotic has been banded due to the awareness of toxicity and carcinogenic of arsenic. Arsenicin A is the only polyarsenic compound isolated from a natural source (Mancini *et al.*, 2006).

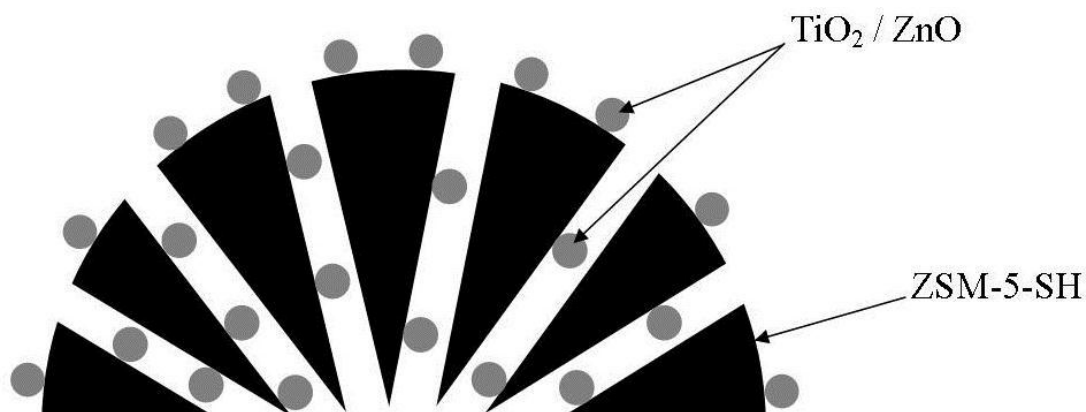
The use of organoarsenicals in the poultry industry has significantly increased as the industry has grown. Roxarsone (3-nitro 4-hydroxybenzenearsonic acid) was introduced to poultry feed up to 45.5 g per ton for the purpose of improving feed efficiency, weight gain and pigmentation. Roxarsone is removed from feed for five days period before slaughter, resulting in the low arsenic concentrations in the tissue which below the USFDA limit of 0.5 mg/kg. The majority (95%) of the As is excreted from the animal, resulting in elevated As (15 to 77 mg/kg) in poultry litter. Because of the rich of nutrients in poultry litter, more than 90% of it is applied as fertilizer for agriculture. The disposal of poultry waste through land application such as fertilizer has resulted in release of an estimated 106 kg/year of arsenic to the environment (Oyewumi and Schreiber, 2012).

In their recent work, they have demonstrated that arsenic in poultry litter is highly water soluble and thus potentially mobile. Biotransformation of roxarsone and other organoarsenicals has been documented in the laboratory, but to date, there is

little known about the ultimate fate of roxarsone, and other organoarsenicals, in watersheds (Oyewumi and Schreiber, 2012). Contamination of these hazardous organic compounds especially the resulting from industries will remain as a major pollution problem. This is because they are often detected to be responsible for ecosystem disruption and harmful to body.

Generally, there are mainly two synthesis procedures reported that can be applied to obtain surface functionalized materials. The first method is via grafting or post-synthesis functionalization with organosilane onto extracted pure or previously calcined silica. The second method is a direct co-condensation reaction of different organosiloxanes that occurs in the presence of surfactant solutions (Diaz *et al.*, 2004). Direct assembly pathways are preferred because it displays a more uniform distribution of organo groups on the framework walls (Gui, 2008). Furthermore, direct assembly allows better cross-linking of the silane moiety to the silica framework. In this work, the desired catalysts are made of three essential components, which are TiO<sub>2</sub> and ZnO particles produced from their precursor (titanium tetrachloride (TiCl<sub>4</sub>) and zinc nitrate [Zn(NO<sub>3</sub>)<sub>2</sub>] respectively), thiol functionalization using 3-Mercaptopropyltrimethoxysilane (MPTS) and ZSM-5 zeolite.

In this work, the similar impregnation method to incorporate TiO<sub>2</sub> and ZnO with ZSM-5 has been applied with some modifications via grafting method to produce the catalysts namely TiO<sub>2</sub> impregnated ZSM-5 functionalized with thiol (TiO<sub>2</sub>-ZSM5-SH) and ZnO impregnated ZSM-5 functionalized with thiol (ZnO-ZSM5-SH). The presence of ZSM-5 acts as a support to increase the surface area adsorption and the active site for functionalization of thiol. The presence of thiol group on ZSM-5 is believed to aid the adsorption of DMA since thiol groups have high affinity towards DMA (Cullen *et al.*, 1984), while TiO<sub>2</sub> and ZnO act as the photocatalysts to remove DMA. These catalysts were further applied to evaluate their potential in aiding the removal and adsorption of dimethylarsenic acid (DMA). The conceptual model of the catalyst composites is illustrated in Figure 1.1.



**Figure 1.4:** Illustration of proposed structure of TiO<sub>2</sub>-ZSM5-SH and ZnO-ZSM5-SH.

## 1.2 Problem Statement

Despite all efforts that have been done to enhance the photocatalytic activity of metal oxides; TiO<sub>2</sub> and ZnO, studies on the effect of functionalization of ZSM-5 with thiol in the photocatalytic removal of organoarsenic has yet to be clarified. This work focuses on the effect of functionalization of ZSM-5 with thiol in the photocatalytic removal of DMA. Hence the introduction of zeolite in this study was not only to act as the catalyst support to increase surface area for DMA adsorption but also to provide functionalized sites which can react with the pollutant for better removal. As far as the toxicity and environmental problems caused by arsenic compounds are concerned, it is strongly necessary to remove organoarsenics in order to clean up the environment from these contaminants where the attempt to remove DMA in aqueous solution was implemented in this work.



### 1.3 Objectives

- To synthesize TiO<sub>2</sub> impregnated on ZSM-5 functionalized with thiol (TiO<sub>2</sub>-ZSM5-SH) and ZnO impregnated on ZSM-5 functionalized with thiol (ZnO-ZSM5-SH) via impregnation method and grafting procedure.
- To study the physicochemical properties of the synthesized TiO<sub>2</sub>-ZSM5-SH and ZnO-ZSM5-SH.
- To study the effect of functionalization of ZSM-5 with thiol in the photocatalytic removal and adsorption of dimethylarsenic acid (DMA).

### 1.4 Scope of Study

This study utilized the used of titanium dioxide and zinc oxide to produce metal oxide thiol functionalized ZSM-5 zeolite since both of the metal oxides are known to be active in the UV region. Impregnation method was applied in this work to prepare the metal oxides-zeolite composites where both TiO<sub>2</sub> and ZnO are expected to adhere to ZSM-5's surfaces. The metal oxides act as the photoactylts while the ZSM-5's surfaces were modified by thiol to replace the hydroxyl group. The thiol groups are believed to act as the active sites for the interaction with DMA or its derivatives, such as MMA, As (III) and As (V) (Froba *et al.*, 2006, Hao *et al.*, 2009, and Hao *et al.*, 2009). In other words, this study is carried out to study the effect of functionalization of ZSM-5 with thiol in the photocatalytic removal and adsorption of DMA.

## 1.5 Significance of Study

TiO<sub>2</sub> and ZnO were applied with functionalization of ZSM-5 zeolites with thiol as the support. The purpose for modification of ZSM-5 zeolite is to enhance the potential of these materials and to evaluate the capability of thiol as an efficient aid to support the removal of organoarsenic from aqueous solutions since thiol groups are proven to be active with DMA (Froba *et al.*, 2006 and Hao *et al.*, 2009). The choice of applying TiO<sub>2</sub> and ZnO as the photocatalysts is due to their stability and nontoxic properties. The abilities of TiO<sub>2</sub> and ZnO as effective photocatalysts have also been proven by extensive studies (Jung *et al.*, 1997, Amereh and Afshar, 2010, and Hao *et al.*, 2009). Due to the severe health hazards contributed by the continuous exposure of arsenic in environment, it is listed by the Environmental Protection Agency as one of 129 priority pollutants (Irwin *et al.*, 1997). It is also listed among the 25 most hazardous substances which hold the most significant potential threat to human health at priority superfund sites. Due to the different hazards attributed to arsenic compounds such as DMA and its derivatives, there is a necessity for determining, degrading and removing this material from the environment.

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**LIST OF SYMBOLS**

$e^-$	-	Electron
eV	-	Electron volt
$h^+$	-	Hole
$\lambda$	-	Lambda
$\Theta$	-	Theta
$^{\circ}\text{C}$	-	Celcius
%	-	Percent
h	-	Hours
Min	-	Minutes
$R^2$	-	Linear Least Square
m	-	Meter
cm	-	Centimeter
$\mu\text{m}$	-	Micrometer
nm	-	Nanometer
mL	-	Mililitre
L	-	Liter
g	-	Gram
ppb	-	Part Per Billion
kV	-	Kilo Volt
AOP	-	Advanced oxidation process
DMA	-	Dimethylarsenic acid
DR UV-Vis	-	Diffuse Reflectance UV-Visible Spectroscopy
EDX	-	Energy Dispersive X-Ray
FTIR	-	Fourier Transform-Infrared
HOMO	-	Highest Occupied Molecular Orbital

HR-TEM	-	High Resolution Transmission Electron Spectroscopy
KBr	-	Potassium bromide
LUMO	-	Lowest Occupied Molecular Orbital
MFI	-	Modernite Framework Inverted
MMA	-	Monomethylarsenic acid
MPTS	-	3-mercaptopropyltrimethoxysilane
PDF	-	Powder Diffraction File
SEM	-	Scanning Electron Microscopy
TiO <sub>2</sub> -ZSM5-SH	-	Titanium dioxide thiol functionalized ZSM-5
UV	-	Ultra Violet
UV-Vis	-	Ultra Violet Visible
XRD	-	X-Ray Diffraction
ZnO-ZSM5-SH	-	Zinc oxide thiol functionalized ZSM-5
ZSM-5	-	Zeolite Soconile Mobile – 5



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