

# Photocatalytic Degradation and Reaction Pathway Studies of Chlorinated Hydrocarbons in Gaseous Phase

W.A.W. Abu Bakar<sup>1,\*</sup>, R. Ali<sup>1</sup> and M.Y. Othman<sup>1</sup>

**Abstract.** *TiO<sub>2</sub> was doped with various types of first row transition metals towards the degradation of dichloromethane, chloroform, carbon tetrachloride and a mixture of carbon tetrachloride and chloroform. Zn<sup>2+</sup>/Fe<sup>3+</sup>/TiO<sub>2</sub> photocatalyst with the ratio of 0.0005: 0.0005: 1 was revealed as the best catalyst in this study. 41.05% of dichloromethane, 49.45% of chloroform and 37.84% of carbon tetrachloride were degraded by this catalyst in the presence of UV light (6 W, 354 nm), irradiated for 90 minutes, and oxidized VOCs gases were analyzed using GC-FID. In this study, the new species of  $\text{CHCl}_2^+$ ,  $\text{CH}_2\text{Cl}^+$ ,  $\text{CCl}_2^+$  and  $\text{OCl}^+$ .  $\text{CHCl}_2^+$  was detected to form from the photocatalytic degradation of chloroform while some new fragments, such as  $\text{OCl}^+$ ,  $\text{CHCl}_2^+$  and  $\text{CH}_2\text{Cl}^+$ , are observed during the photocatalytic degradation of carbon tetrachloride.*

**Keywords:** *Photocatalyst; Dichloromethane; Chloroform; Carbon tetrachloride titanium dioxide; Chlorinated hydrocarbon; mineral components.*

## INTRODUCTION

Photocatalytic oxidation (PCO) harnesses radiant energy from natural or artificial light sources with a heterogeneous catalyst to degrade the organic pollutants into their mineral components. In recent years, photocatalytic oxidation of organic compounds in the gaseous-phase using TiO<sub>2</sub> as a catalyst appears to be a promising process for the remediation of ground water and air polluted by Volatile Organic Hydrocarbons (VOC). The high degree of recombination between photogenerated electrons and holes is a major limiting factor controlling the photocatalytic efficiency [1]. In this case, the deposited metal on the surface of TiO<sub>2</sub> can act as a sink for a photoinduced charge carrier promoting an interfacial charge transfer process.

Brezova et al. [2] found that the best results for the photodegradation of phenols were obtained

on dopant free TiO<sub>2</sub>, Li<sup>+</sup>/TiO<sub>2</sub>, Zn<sup>2+</sup>/TiO<sub>2</sub> and Pt<sup>0</sup>/TiO<sub>2</sub> catalysts. Recently, some research has co-doped transition metals such as Fe<sup>3+</sup> with Zn<sup>2+</sup> into TiO<sub>2</sub> [3]. It was found that co-doped TiO<sub>2</sub> shows better degradation of phenol than metal doped TiO<sub>2</sub>. Navio et al. [4] reported that Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O containing low amounts of Fe<sup>3+</sup> ions are more efficient for nitrite oxidation than pure TiO<sub>2</sub>. The photocatalytic degradation of carboxylic acid by Fe<sup>3+</sup>-doped TiO<sub>2</sub> had been studied by Arana et al. [5]. It was revealed that all catalysts calcined at 773 K are able to totally degrade formic acid after 1.5 hours in reaction. Arroyo et al. [6] found out that the transformation of anatase to rutile depends significantly on Mn<sup>2+</sup> concentration and it seemed that the dopant segregation occurs for Mn<sup>2+</sup> concentration up to 1.5 mol%, which is responsible for the acceleration of the anatase-rutile transformation. An increase in the degradation activity of phenol by 1-2 times is observed in the case of co-doping Zn<sup>2+</sup> and Fe<sup>3+</sup> with TiO<sub>2</sub>. The maximum photocatalytic activity occurred at the concentration of approximately 0.5 mole% Zn<sup>2+</sup> and 1 mole% Fe<sup>3+</sup> above which the co-doping had a reduced and eventually detrimental effect on the activity. The maximum photodegradation

1. Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

\*. Corresponding author. E-mail: wanazelee@yahoo.com

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of chloroform in solution using  $\text{TiO}_2$  co-doped with  $\text{Fe}^{3+}$  and  $\text{Eu}^{3+}$  is more than 5 times compared with the one produced by pure nanocrystalline  $\text{TiO}_2$ . In nanocrystalline  $\text{TiO}_2$ , there are cooperative actions of the 2 dopants where  $\text{Fe}^{3+}$  is served as hole trap while  $\text{Eu}^{3+}$  is served as an electron trap [7]. Feiyen et al. [8] investigated that the VOCs degrade in air following first-order kinetics in the range of 80-500 ppm. However, when the initial concentration of chloroform is higher than 600 ppm, the reaction seems to follow second-order kinetics, with respect to chloroform concentration.

So far, research in photocatalysts mostly focused on the degradation of organic compounds in the aqueous system, such as organic compounds ( $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}/\text{TiO}_2$ ), methyl dyes ( $\text{Fe}^{3+}/\text{TiO}_2$ ), Rhodamine B ( $\text{Fe}^{3+}/\text{TiO}_2$ ) and carboxylic acid or fatty acid ( $\text{Fe}^{3+}/\text{TiO}_2$ ). Only a few studies have been published which consider the photocatalytic degradation of gaseous VOCs using doped  $\text{TiO}_2$ . As such, the present investigation is directed to degradation of some volatile organic compounds, eg. dichloromethane, chloroform and carbon tetrachloride, in the gaseous phase.

## EXPERIMENTAL

### Catalyst Preparation

$\text{TiO}_2$  sol-gel was prepared by modification of the sol-gel method reported by Kato et al. [9]. 6 g of polyethylene glycol (PEG) (2000) were dissolved in 600 mL ethanol. 85.2 g titanium tetraisopropoxide, 31.8 g diethanolamine and 5.4 mL deionized water were added to the solution. For preparation of a catalyst with dopants, the metal salt was weighed based on the required amount, and dissolved with 135 mL sol-gel. The mixture was stirred till homogeneous. The sol-gel was then used to prepare  $\text{TiO}_2$  thin films. A hollow pyrex glass cylinder was used as the support substrate. The  $\text{TiO}_2$  thin film was prepared by the dip-draw method for 5 times to get a homogeneous thin film on the support. After that, the thin film was dried in the oven at  $80^\circ\text{C}$  for 1 hour. Finally, it was calcined with an elevated temperature of  $2^\circ\text{C}/\text{min}$ , up to  $500^\circ\text{C}$  for 1 hour.

### Photocatalytic Activity Testing

All photocatalytic degradation experiments of dichloromethane, chloroform and carbon tetrachloride were conducted in a home built fixed bed annulus glass reactor with exactly 100 mL. The reactor was equipped with an electromagnetic pump to circulate the sample, a glass compartment to place the catalyst, and a UV light with wavelength of  $\sim 354$  nm.

Reactor effluent was analyzed every 10 minutes for 90 minutes using GC-FID. All experiments were carried out under atmospheric pressure and at room temperature ( $28-30^\circ\text{C}$ ). For the mechanistic study, a Hewlett-Packard System 5890 Series II GC and 5989 MS were used to analyze fragments that may form during the photocatalytic degradation of the VOCs. A mixture of  $\text{CHCl}_3$  and  $\text{CCl}_4$  with a ratio of 1.09: 1 was used as the low concentration mixture and 1.24: 1 as the high concentration mixture for the testing.

### Catalyst Characterization

The absorption spectrum for metal ions doped  $\text{TiO}_2$  and undoped  $\text{TiO}_2$  was recorded by a UV-Vis-NIR Shimadzu UV-3101 PC Spectrophotometer in the wavelength range of 300-540 nm. The surface morphology of the potential catalyst was characterized using a Philip XL 40 Microscope with magnification of 5000 and 30 kV scanning voltage. XRD analysis was done by using a diffractometer D5000 Siemens Crystalloflex with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ). Scans were performed in a step mode of 0.20 seconds/step. The data obtained was analyzed by a PC interfaced to the diffractometer using software called Diffrac Plus. The results were then compared with the accumulated Powder Diffraction File (PDF) data which comes with the software used in this technique.

## RESULTS AND DISCUSSION

### Photocatalytic Degradation of Dichloromethane, Chloroform and Carbon Tetrachloride

Table 1 depicts the percentage degradation of dichloromethane, chloroform and carbon tetrachloride catalyzed by doped and undoped  $\text{TiO}_2$  catalyst.  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst with the ratio of 0.0005; 0.0005: 1 shows the best degradation activities compared to other metals-doped  $\text{TiO}_2$  and pure  $\text{TiO}_2$  catalysts. In the photocatalytic degradation process, a good dopant must be able to act as both the electron and hole trap, so that the recombination process between photogenerated electrons and holes can be suppressed. It is believed that there is a synergistic effect in photocatalytic activity when both  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  metal ions were co-doped into  $\text{TiO}_2$ . The effect may be explained by the cooperative operation of the  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  in trapping charge carriers and mediating the interfacial charge transfer process.  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  dopants in  $\text{TiO}_2$  can be randomly dispersed on the  $\text{TiO}_2$  surface in the form of their oxides [3]. Due to the difference in the energy band position, the dispersed oxides on the  $\text{TiO}_2$  surface will involve

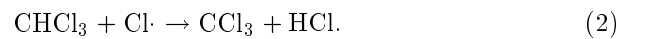
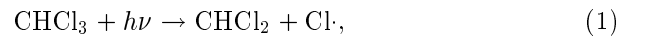
**Table 1.** Percentage degradation of dichloromethane, chloroform and carbon tetrachloride using doped and pure TiO<sub>2</sub> catalysts for 90 minutes.

| Catalysts  | Dopant Ratios     | % Degradation                   |                   |                  |
|--|-------------------|---------------------------------|-------------------|------------------|
|  |                   | CH <sub>2</sub> Cl <sub>2</sub> | CHCl <sub>3</sub> | CCl <sub>4</sub> |
| Mn <sup>2+</sup> /TiO <sub>2</sub>                   | 0.0003: 1         | 11.95                           | 13.06             | 10.94            |
|  | 0.0005: 1         | <b>16.47</b>                    | <b>19.57</b>      | <b>15.87</b>     |
|  | 0.001: 1          | 11.49                           | 13.12             | 12.12            |
| Fe <sup>2+</sup> /TiO <sub>2</sub>                   | 0.0003: 1         | 22.08                           | 29.08             | 13.42            |
|  | 0.0005: 1         | <b>33.79</b>                    | <b>34.21</b>      | <b>20.80</b>     |
|  | 0.001: 1          | 22.76                           | 30.84             | 12.36            |
| Fe <sup>3+</sup> /TiO <sub>2</sub>                   | 0.0003: 1         | 34.53                           | 35.74             | 22.07            |
|  | 0.0005: 1         | <b>36.02</b>                    | <b>43.10</b>      | <b>35.42</b>     |
|  | 0.001: 1          | 33.91                           | 35.11             | 24.44            |
| Zn <sup>2+</sup> /TiO <sub>2</sub>                   | 0.0003: 1         | 34.01                           | 34.43             | 22.77            |
|  | 0.0005: 1         | <b>34.89</b>                    | <b>36.98</b>      | <b>27.44</b>     |
|  | 0.001: 1          | 33.98                           | 34.77             | 23.32            |
| Cu <sup>2+</sup> /TiO <sub>2</sub>                   | 0.0003: 1         | 31.84                           | 34.27             | 22.46            |
|  | 0.0005: 1         | <b>34.30</b>                    | <b>36.14</b>      | <b>25.67</b>     |
|  | 0.001: 1          | 32.81                           | 34.45             | 23.07            |
| Zn <sup>2+</sup> /Fe <sup>3+</sup> /TiO <sub>2</sub> | 0.0003: 0.0005: 1 | 34.27                           | 36.55             | 32.89            |
|  | 0.0005: 0.0005: 1 | <b>41.05</b>                    | <b>49.45</b>      | <b>37.84</b>     |
|  | 0.0005: 0.001: 1  | 34.06                           | 39.02             | 32.73            |
| Cu <sup>2+</sup> /Fe <sup>3+</sup> /TiO <sub>2</sub> | 0.0003: 0.0005: 1 | 31.87                           | 36.11             | 24.10            |
|  | 0.0005: 0.0005: 1 | <b>36.76</b>                    | <b>42.55</b>      | <b>33.88</b>     |
|  | 0.0005: 0.001: 1  | 33.56                           | 38.63             | 31.03            |
| Pure TiO <sub>2</sub>                                | –                 | 20.93                           | 23.87             | 17.40            |

some charge transfer between them and TiO<sub>2</sub> during illumination. The valence band of TiO<sub>2</sub> is lower than Fe<sub>2</sub>O<sub>3</sub>, so, the photogenerated holes can move into ZnO, while the photogenerated electrons can move into Fe<sub>2</sub>O<sub>3</sub>.

From Table 1, the rate of degradation of the studied chlorinated hydrocarbons follows the order: CHCl<sub>3</sub> > CH<sub>2</sub>Cl<sub>2</sub> > CCl<sub>4</sub>. It is reported that chloroform will show Cl-sensitized degradation when its concentration is above 500 ppm [8]. The concentration of chloroform that was used in the photocatalytic degradation process is more than 500 ppm. Hence, the degradation of chloroform is expected to undergo

Cl-sensitized degradation (Equations 1 and 2)

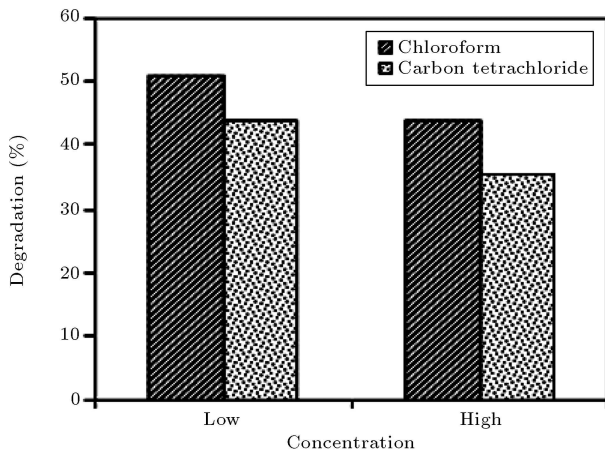


Since dichloromethane has two chlorine atoms in its structure, Cl-sensitized degradation is lower than in the degradation of chloroform, which has three chlorine atoms in its structure. Therefore, dichloromethane shows lower levels of degradation than chloroform. Carbon tetrachloride shows the lowest levels of degradation in this study. Carbon tetrachloride is a stable

compound, thus, chlorine radicals do not attack the C-Cl bond and, hence a Cl-sensitized degradation does not happen in  $\text{CCl}_4$ .

In a real industrial application, chlorinated VOCs are found in nature. Therefore, photocatalytic degradation of chloroform and carbon tetrachloride mixtures has been carried out using a  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst. The initial concentration of chloroform used in the photocatalytic degradation is 222 ppm for low and 528 ppm for high concentrations of chloroform. Meanwhile, the initial concentration of carbon tetrachloride used is 203 ppm for low concentration and 427 ppm for high concentrations of the mixture. It is noted that 50.89% and 43.87% of chloroform and carbon tetrachloride were degraded, respectively, at 90 minutes for low concentrations of mixture (chloroform: carbon tetrachloride = 1.09: 1). However, for high concentrations of mixture (chloroform: carbon tetrachloride = 1.24: 1), only 43.85% and 35.32% of chloroform and carbon tetrachloride were degraded, respectively, at 90 minutes. This indicates that the amount of chloroform and carbon tetrachloride being degraded depends on the amount of hydroxyl radicals on the catalyst, which, in turn, depends on the number of holes generated on the catalyst. With a higher concentration of chloroform and carbon tetrachloride mixture, the generated hydroxyl radicals are insufficient to degrade the chloroform and carbon tetrachloride.

According to Figure 1, the degradation of chloroform is higher than carbon tetrachloride. During illumination using the UV lamp (6 W,  $\lambda = 354 \text{ nm}$ ), Cl-radicals are formed, since the mixture contained chloroform and carbon tetrachloride. The Cl-radicals do not attack C-Cl bonds in carbon tetrachloride. Therefore, Cl-radicals formed during the illumination of the UV lamp may contribute to the degradation

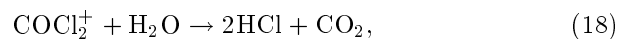
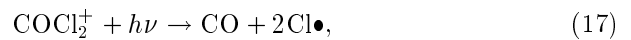
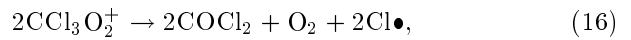
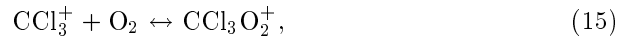
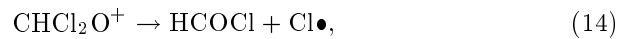
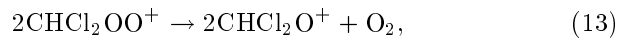
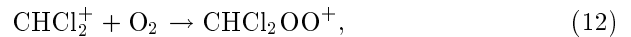
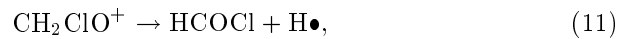
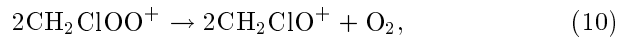
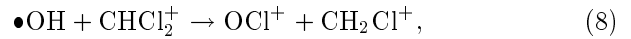
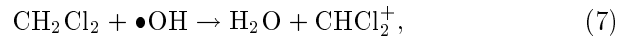
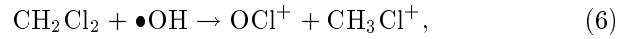
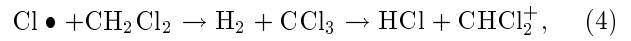
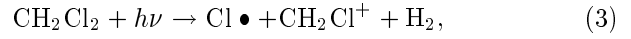


**Figure 1.** Percentage degradation of chloroform/carbon tetrachloride mixture at 90 minutes using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst.

of chloroform. Consequently, more chloroform was degraded.

#### Reaction Pathway for the Photocatalytic Degradation of Chlorinated Hydrocarbons Using $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$ Photocatalyst; UV $\lambda = 354 \text{ nm}$ for 90 Minutes

When photocatalytic degradation of VOCs was conducted, the information obtained from the use of GC-MS was used to predict the possible reaction pathway of the photocatalytic degradation process. Fragments obtained before and after illumination of the UV light for dichloromethane, using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst and analyzed using GC-MS, are depicted in Appendices A and B. A model for the photocatalytic degradation of dichloromethane is proposed as follows:

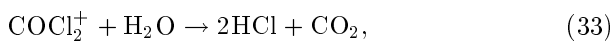
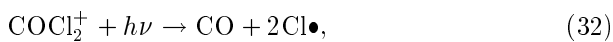
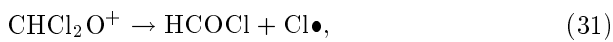
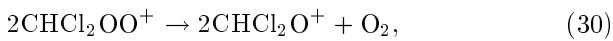
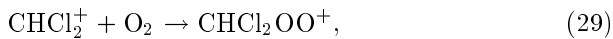
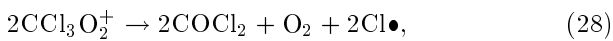
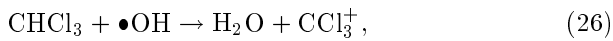
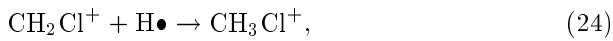
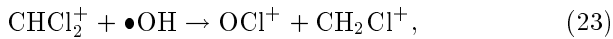


Chlorine radicals were formed during the illumination



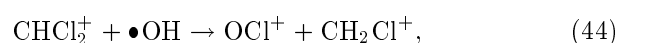
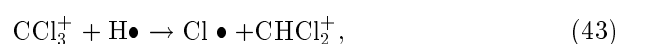
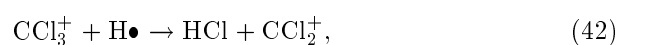
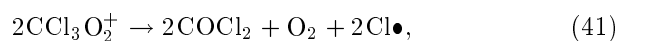
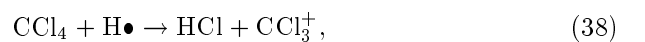
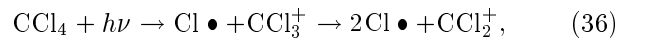
of  $\text{CH}_2\text{Cl}_2$  using UV light. Chlorine radicals are expected to attack dichloromethane to initialize the degradation process (Equation 3). Besides that,  $\bullet\text{OH}$  will attack dichloromethane to form  $\text{OCl}^+$  and  $\text{CH}_3\text{Cl}^+$  through Equation 6 or  $\text{H}_2\text{O}$  and dichloromethane through Equation 7. In the photocatalytic degradation of dichloromethane, it is expected that  $\text{CCl}_3^+$  will react with  $\text{O}_2$  to form  $\text{CCl}_3\text{O}_2^+$  (Equation 15). However,  $\text{CCl}_3\text{O}_2^+$  is not detected in this study. This may be due to the formation of fragments and their fast reaction time, which renders them unable to be detected.  $\text{COCl}_2^+$  formed from  $\text{CCl}_3\text{O}_2^+$  is expected to undergo photolysis (Equation 18) in the presence of moist air. In the termination process,  $\text{Cl}\bullet$  will recombine to form  $\text{Cl}_2$  (Equation 19), while  $\text{H}\bullet$  will combine with  $\bullet\text{OH}$  to form  $\text{H}_2\text{O}$  (Equation 20). In this study, only a small amount of phosgene was detected. This may be due to the  $\text{COCl}_2^+$  formed during the photocatalytic degradation process, which is expected to undergo photolysis (Equation 18).

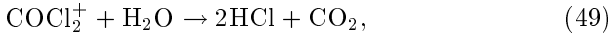
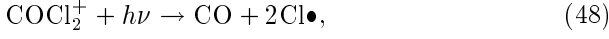
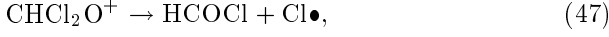
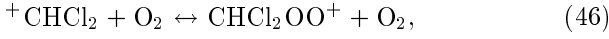
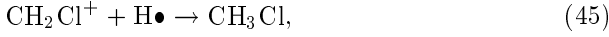
In a case of chloroform, the fragments obtained before illumination of UV light for dichloromethane, using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst and analyzed by using GC-MS are shown in Appendices C and D. A possible reaction pathway for the photocatalytic degradation of chloroform is as follows:



A previous research conducted by Feiyen et al. [8] about photodegradation of chloroform and carbon tetrachloride with no catalyst using a low mercury lamp obtained 92% degradation at 254 nm and 6% at 185 nm and observed fragments such as  $\text{CHCl}_2^+$ ,  $\text{CCl}_3^+$ ,  $\text{CCl}_3\text{O}_2^+$ ,  $\text{CHCl}_2\text{OO}^+$  and  $\text{CHCl}_2\text{O}^+$ . In the presence of UV light with  $\sim 354$  nm, the photocatalytic degradation of chloroform results in the formation of  $\text{Cl}\bullet$  and  $\text{CHCl}_2^+$ . Then,  $\text{Cl}\bullet$  and  $\text{CHCl}_2^+$  will decompose into  $\text{CCl}_2^+$  and  $\text{HCl}$  (Equation 21). The fragments which are not observed in the research done by Feiyen, but which are observed in this study, are  $\text{CHCl}_2^+$ ,  $\text{CH}_2\text{Cl}^+$ ,  $\text{CCl}_2^+$  and  $\text{OCl}^+$ .  $\text{CHCl}_2^+$  formed from the photocatalytic degradation of chloroform can react with  $\bullet\text{OH}$  to form  $\text{CH}_2\text{Cl}^+$  (Equation 23).  $\text{CH}_2\text{Cl}^+$  reacts with  $\text{H}\bullet$  to form  $\text{CH}_3\text{Cl}^+$  through Equation 24. When chloroform is degraded, it will not only be attacked by  $\text{Cl}\bullet$  but also  $\bullet\text{OH}$  to form  $\text{H}_2\text{O}$  and  $\text{CCl}_3^+$  (Equation 26). Similar to the photodegradation of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_3\text{O}_2^+$  that is expected to form from the reaction between  $\text{O}_2$  and  $\text{CCl}_3^+$  through Equation 27 is also not observed in this study. Phosgene formed from  $\text{CCl}_3\text{O}_2^+$  is expected to undergo hydrolysis, since the photocatalytic degradation of chloroform was carried out under ambient conditions, which contain moist air, as has similarly been reported [8] as a prerequisite for the process of phosgene photolysis.

Fragments such as  $\text{CCl}_3^+$ ,  $\text{CCl}_2^+$  and  $\text{CCl}_3\text{O}_2^+$  were observed by Feiyen et al. [8] during the photodegradation of carbon tetrachloride. In this study, some new fragments such as  $\text{OCl}^+$ ,  $\text{CHCl}_2^+$  and  $\text{CH}_2\text{Cl}^+$  were also observed. The fragments obtained before and after illumination of UV light for carbon tetrachloride, using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst and analyzed by using GC-MS, are given in Appendices E and F. As such, the new reaction pathway proposed is as follows:



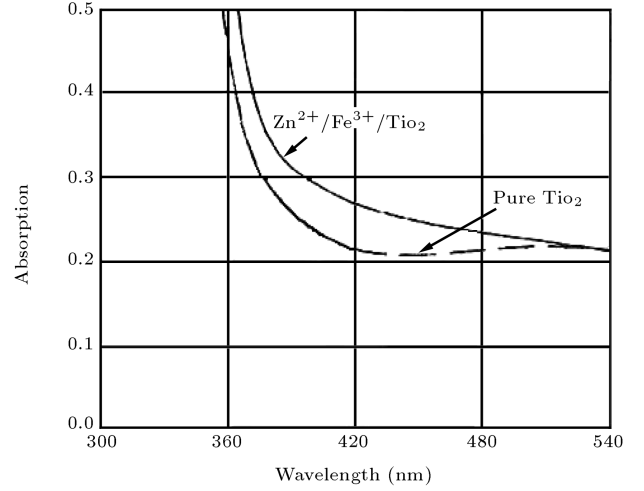


Chlorine radicals formed in the presence of UV light will not attack the C-Cl bond in carbon tetrachloride, hence, chlorine radicals sensitized degradation does not happen in the case of carbon tetrachloride [8]. During the illumination of UV, the produced  $\text{Cl}\bullet$  will react with  $\text{CCl}_3^+$  to form  $\text{Cl}\bullet$  and  $\text{CCl}_2^+$  (Equation 36). Carbon tetrachloride can be attacked by  $\bullet\text{OH}$  to form  $\text{HCl}$  and  $\text{CCl}_3^+$  (Equation 38).  $\text{CCl}_3^+$  produced in the photocatalytic degradation of carbon tetrachloride can react with  $\text{O}_2$  to form  $\text{CCl}_3\text{O}_2^+$  (Equation 40) or react with  $\text{H}\bullet$  to produce  $\text{CCl}_2^+$  and  $\text{CHCl}_2^+$  (Equations 42 and 43). However, in this study,  $\text{CCl}_3\text{O}_2^+$  is unable to be detected. Similar to previous cases,  $\text{CHCl}_2\text{OO}^+$  is unable to be detected. Since the presence of  $\text{CHCl}_2\text{O}^+$  is able to be identified by GC-MS,  $\text{CHCl}_2\text{OO}^+$  is presumed to be present in the photocatalytic degradation of carbon tetrachloride. A small amount of phosgene is also detected because it is rapidly hydrolyzed to  $\text{CO}_2$  and  $\text{HCl}$  in the presence of moisture.

## Characterization of Catalyst

### UV-Vis Spectroscopy

A higher wavelength or red shift is noted for  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst compared to the pure  $\text{TiO}_2$  (Figure 2). This indicates a decrease in the band gap value of the respective catalyst. This catalyst also has higher absorbance than the pure  $\text{TiO}_2$  catalyst in the visible region. The red shift in the optical energy gap is considered to be due to the energy level for dopants, which lies below the conduction band edge ( $E_{cb}$ ) and above the valence band edge ( $E_{vb}$ ) of  $\text{TiO}_2$ . The introduction of such energy levels in the band gap induces the red shift in the band gap transition and the visible light absorption through a charge transfer between a dopant and  $cb$  (or  $vb$ ) or a  $d-d$  transition in the crystal field, according to the energy level. Jiang and Gao [10] had also found out that an addition of  $\text{Fe}^{3+}$  into  $\text{TiO}_2$  had shifted the absorption edge to a higher wavelength.



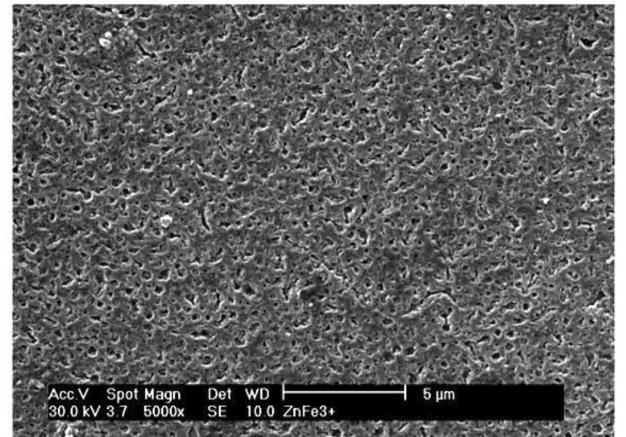
**Figure 2.** UV-Vis absorption spectra for  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst and pure  $\text{TiO}_2$  thin film.

### Scanning Electron Microscope (SEM)

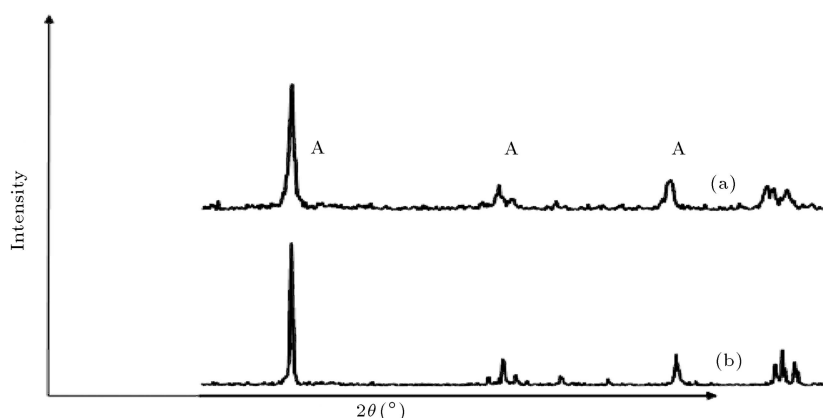
Figure 3 shows the SEM micrograph of  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  thin film. It was found that pores are produced on the thin film. Pores are produced because PEG contained in the sol-gel decomposes at  $450^\circ\text{C}$  [11]. In the preparation of  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  thin film, PEG was added into the sol-gel and the catalyst was calcined at  $500^\circ\text{C}$ . Therefore, it is expected that pores exist in the catalyst and this result is in a good agreement with the obtained micrograph.

### Powder X-Ray Diffraction (XRD)

Figure 4 illustrates the diffractogram of a commercial  $\text{TiO}_2$  anatase structure and the prepared catalyst of  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  (0.0005:0.0005:1) taken in the powdery form for comparison. It is obvious that the prepared  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst possesses an anatase structure. However, the peaks due to the dopants were not detected and this could be explained



**Figure 3.** SEM micrograph of  $\text{Zn}^{2+}$  co-doped  $\text{Fe}^{3+}/\text{TiO}_2$  with magnification of  $5000\times$ .



**Figure 4.** Powder XRD diffractogram of a)  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  (0.0005: 0.0005: 1) and b)  $\text{TiO}_2$  anatase (commercial) catalysts.

by the low quantity of dopants present in the prepared catalyst material.

## CONCLUSIONS

The photocatalytic degradation of the studied VOCs is found to depend on the concentration and type of dopant ions and to the type of VOCs. It is revealed that the catalyst with optimum dopant ratio gives the highest percentage degradation of studied VOCs; an example for  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst is 0.0005: 0.0005: 1. The rate of degradation of the studied chlorinated hydrocarbons follows the order:  $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{CCl}_4$ . Interestingly, the photocatalytic degradation pathway studies using GC-MS for VOCs are able to detect new reaction pathways for chloroform and carbon tetrachloride using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  catalyst.

## ACKNOWLEDGMENTS

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## APPENDICES

## Appendix A

Fragments obtained before illumination of UV light for dichloromethane using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst; analyzed by using GC-MS.

|  |        |        |        |        |        |        |        |
|--|--------|--------|--------|--------|--------|--------|--------|
| Scan 57 (1.007 min): MYB 4152.D<br>dichloromethane |        |        |        |        |        |        |        |
| m/z  | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
| 10.15  | 94     | 20.60  | 4543   | 34.50  | 3157   | 47.35  | 44424  |
| 10.45  | 108    | 21.80  | 81     | 35.40  | 18680  | 48.30  | 19344  |
| 10.75  | 102    | 22.60  | 130    | 36.40  | 4962   | 49.30  | 238144 |
| 11.05  | 110    | 23.60  | 108    | 37.40  | 6214   | 50.30  | 9240   |
| 12.75  | 3177   | 25.05  | 491    | 38.40  | 1513   | 51.30  | 67432  |
| 13.75  | 10011  | 26.05  | 532    | 40.35  | 44032  | 52.20  | 713    |
| 14.75  | 192128 | 28.55  | 919360 | 41.35  | 7945   | 53.20  | 76     |
| 16.60  | 53560  | 29.55  | 24440  | 42.35  | 5238   | 54.20  | 53     |
| 17.70  | 22792  | 30.55  | 832    | 43.35  | 964    | 54.50  | 43     |
| 18.60  | 94128  | 32.40  | 641024 | 44.35  | 6177   | 55.30  | 93     |
| 19.70  | 946    | 33.40  | 809    | 45.35  | 167    | 56.25  | 156    |
| Scan 57 (1.007 min): MYB 4152.D<br>dichloromethane |        |        |        |        |        |        |        |
| $\text{CH}_2\text{ClO}^+$                          | m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    |
|  | 56.85  | 56     | 67.00  | 64     | 76.65  | 58     | 85.90  |
|  | 57.95  | 48     | 67.80  | 63     | 77.25  | 40     | 86.90  |
|  | 58.75  | 56     | 69.20  | 88     | 78.35  | 40     | 87.90  |
|  | 59.55  | 41     | 70.10  | 763    | 78.95  | 31     | 88.85  |
|  | 60.15  | 64     | 70.70  | 49     | 79.45  | 55     | 89.95  |
|  | 61.15  | 74     | 71.30  | 80     | 80.50  | 62     | 90.95  |
|  | 62.65  | 59     | 72.00  | 561    | 81.00  | 44     | 91.15  |
|  | 63.25  | 57     | 73.95  | 53     | 81.90  | 1950   | 91.55  |
|  | 64.90  | 64     | 73.95  | 116    | 82.90  | 16368  | 92.85  |
|  | 65.40  | 59     | 74.95  | 33     | 83.90  | 143232 | 93.35  |
|  | 66.40  | 33     | 75.25  | 32     | 84.90  | 12404  | 93.95  |
| Scan 57 (1.007 min): MYB 4152.D<br>dichloromethane |        |        |        |        |        |        |        |
| $\text{CHCl}_2\text{O}^+$                          | m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    |
|  | 94.75  | 43     | 100.90 | 34     | 108.45 | 26     | 118.60 |
|  | 95.35  | 42     | 101.60 | 30     | 109.85 | 21     | 119.60 |
|  | 95.85  | 49     | 102.70 | 31     | 111.05 | 24     | 120.65 |
|  | 96.30  | 36     | 103.20 | 31     | 111.85 | 38     | 121.55 |
|  | 96.90  | 59     | 104.10 | 24     | 112.50 | 24     | 122.75 |
|  | 97.70  | 44     | 105.25 | 45     | 113.80 | 30     | 123.25 |
|  | 98.80  | 61     | 105.85 | 28     | 114.30 | 50     | 123.65 |
|  | 99.40  | 26     | 107.35 | 32     | 115.70 | 32     | 124.35 |
|  | 100.00 | 45     | 107.65 | 27     | 115.90 | 37     | 125.05 |
|  | 100.30 | 30     | 107.95 | 26     | 116.60 | 157    | 125.85 |
|  | 100.60 | 32     | 108.25 | 27     | 117.60 | 283    | 126.05 |
| Scan 57 (1.007 min): XYB 4152.D<br>dichloromethane |        |        |        |        |        |        |        |
| m/z  | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
| 126.35   | 30     | 135.50 | 20     | 146.00 | 43     | 156.05 | 30     |
| 126.62   | 30     | 135.70 | 27     | 147.40 | 33     | 160.15 | 20     |
| 126.85   | 28     | 117.15 | 26     | 149.80 | 23     | 160.75 | 26     |
| 127.66   | 29     | 128.25 | 11     | 180.70 | 29     | 161.80 | 27     |
| 128.25   | 28     | 139.05 | 25     | 151.20 | 21     | 163.00 | 33     |
| 129.00   | 30     | 139.35 | 20     | 153.55 | 25     | 163.60 | 22     |
| 129.40   | 49     | 140.35 | 27     | 154.15 | 23     | 163.80 | 22     |
| 131.00   | 25     | 141.15 | 28     | 154.95 | 24     | 164.20 | 24     |
| 131.60   | 21     | 141.45 | 23     | 155.35 | 28     | 165.80 | 36     |
| 133.00   | 33     | 142.45 | 37     | 156.45 | 21     | 167.10 | 25     |
| 134.00   | 34     | 143.75 | 29     | 156.65 | 21     | 167.40 | 21     |
| Scan 57 (1.007 min): MYB 4152.D<br>dichloromethane |        |        |        |        |        |        |        |
| m/z  | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
| 168.00   | 25     | 185.85 | 20     | 199.70 | 23     | 220.25 | 22     |
| 168.60   | 27     | 186.95 | 29     | 201.10 | 20     | 222.95 | 42     |
| 169.85   | 40     | 187.75 | 22     | 201.25 | 20     | 229.00 | 32     |
| 174.65   | 23     | 190.05 | 29     | 203.15 | 30     | 229.60 | 23     |
| 177.40   | 24     | 191.55 | 22     | 205.75 | 60     | 231.10 | 30     |

## Appendix B

Fragments obtained after illumination of UV light for dichloromethane using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst; analyzed by using GC-MS.

Scan 57 (1.008 min): MYB 4167.D

dichloromethane

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
|-------|--------|-------|--------|-------|--------|-------|--------|
| 10.35 | 104    | 21.30 | 77     | 30.55 | 923    | 44.35 | 6860   |
| 10.65 | 94     | 21.80 | 44     | 32.50 | 623872 | 45.35 | 156    |
| 11.25 | 122    | 22.10 | 38     | 34.50 | 3314   | 47.35 | 37944  |
| 12.75 | 3758   | 22.70 | 83     | 35.40 | 17160  | 48.30 | 18520  |
| 13.85 | 8731   | 23.20 | 54     | 36.40 | 4520   | 49.30 | 225472 |
| 14.75 | 211840 | 23.50 | 65     | 37.40 | 5801   | 50.30 | 8133   |
| 16.60 | 52992  | 23.70 | 65     | 38.40 | 1473   | 51.30 | 57600  |
| 17.70 | 20912  | 24.25 | 107    | 40.35 | 46984  | 52.20 | 702    |
| 18.70 | 93224  | 25.05 | 462    | 41.35 | 7037   | 52.90 | 47     |
| 19.70 | 966    | 28.55 | 880192 | 42.35 | 4703   | 53.40 | 44     |
| 20.60 | 4437   | 29.55 | 22456  | 43.35 | 777    | 54.00 | 54     |

$\text{CH}_2\text{Cl}^+$

$\text{CH}_3\text{Cl}^+$

$\text{OCl}^+$

Scan 57 (1.008 min): MYB 4167.D

dichloromethane

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
|-------|--------|-------|--------|-------|--------|-------|--------|
| 55.60 | 82     | 61.55 | 41     | 68.00 | 59     | 77.15 | 47     |
| 56.35 | 104    | 62.25 | 38     | 69.20 | 89     | 77.75 | 25     |
| 57.15 | 46     | 62.45 | 38     | 70.10 | 653    | 78.55 | 30     |
| 57.75 | 27     | 63.05 | 74     | 71.00 | 74     | 79.15 | 38     |
| 58.15 | 40     | 63.75 | 54     | 72.00 | 428    | 79.45 | 39     |
| 58.65 | 49     | 64.40 | 46     | 73.15 | 65     | 79.95 | 48     |
| 58.95 | 55     | 65.00 | 53     | 73.95 | 130    | 81.90 | 1810   |
| 59.15 | 46     | 65.50 | 26     | 74.85 | 41     | 82.90 | 15626  |
| 59.95 | 68     | 66.10 | 34     | 75.35 | 30     | 83.90 | 128688 |
| 60.45 | 51     | 66.70 | 43     | 75.85 | 45     | 84.90 | 11414  |
| 61.05 | 52     | 67.00 |        |       | 48     | 85.90 | 79536  |

$\text{CH}_2\text{ClO}^+$

$\text{CCl}_2^+$

$\text{CHCl}_2^+$

Scan 57 (1.008 min): MYB 4167.D

dichloromethane

| m/z   | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|-------|--------|--------|--------|--------|--------|--------|--------|
| 86.90 | 2604   | 94.75  | 66     | 102.60 | 38     | 111.25 | 31     |
| 87.90 | 11767  | 96.15  | 58     | 103.20 | 37     | 112.35 | 41     |
| 88.85 | 165    | 96.80  | 85     | 103.80 | 22     | 113.50 | 31     |
| 90.15 | 35     | 97.60  | 37     | 104.10 | 23     | 114.20 | 40     |
| 90.85 | 25     | 97.90  | 35     | 104.55 | 32     | 115.60 | 34     |
| 91.65 | 25     | 98.90  | 62     | 105.05 | 26     | 116.60 | 177    |
| 91.95 | 23     | 99.80  | 49     | 106.55 | 50     | 117.60 | 260    |
| 92.25 | 28     | 100.90 | 24     | 107.15 | 29     | 118.60 | 144    |
| 92.45 | 26     | 101.10 | 24     | 109.95 | 26     | 119.60 | 224    |
| 92.85 | 31     | 101.50 | 28     | 110.25 | 21     | 120.55 | 52     |
| 93.65 | 22     | 102.30 | 39     | 110.55 | 21     | 121.55 | 113    |

$\text{COCl}_2^+$

$\text{CHCl}_2\text{OO}^+$

$\text{CCl}_3^+$

Scan 57 (1.008 min): MYB 4167.D

dichloromethane

| m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 122.45 | 29     | 133.00 | 27     | 145.20 | 27     | 158.35 | 21     |
| 123.45 | 23     | 133.20 | 26     | 148.50 | 28     | 159.05 | 30     |
| 124.15 | 23     | 133.60 | 32     | 149.30 | 22     | 159.55 | 21     |
| 125.45 | 35     | 134.30 | 22     | 150.60 | 30     | 160.45 | 28     |
| 126.15 | 22     | 135.70 | 23     | 151.30 | 34     | 161.90 | 26     |
| 127.45 | 41     | 136.30 | 23     | 152.20 | 34     | 162.10 | 28     |
| 128.15 | 29     | 137.05 | 29     | 152.85 | 27     | 162.80 | 24     |
| 128.70 | 26     | 137.35 | 36     | 154.95 | 22     | 165.00 | 31     |
| 129.50 | 46     | 137.55 | 28     | 156.05 | 31     | 165.70 | 20     |
| 130.30 | 24     | 140.25 | 22     | 157.15 | 23     | 168.40 | 20     |
| 131.50 | 47     | 140.85 | 21     | 158.05 | 22     | 168.70 | 21     |

$\text{CHCl}_2\text{O}^+$

Scan 57 (1.008 min): MYB 4167.D

dichloromethane

| m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 169.85 | 22     | 182.80 | 23     | 198.80 | 21     | 242.50 | 24     |
| 170.15 | 26     | 183.70 | 27     | 205.75 | 51     | 245.80 | 20     |
| 171.15 | 28     | 184.50 | 23     | 206.85 | 23     |        |        |
| 172.05 | 36     | 184.70 | 24     | 209.90 | 28     |        |        |
| 173.05 | 25     | 187.15 | 34     | 212.00 | 20     |        |        |

## Appendix C

Fragments obtained before illumination of UV light for chloroform using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst; analyzed by using GC-MS.

Scan 57 (1.008 min): MYB 4167.D

| dichloromethane |        |       |        |       |        |       |        |
|-----------------|--------|-------|--------|-------|--------|-------|--------|
| m/z             | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
| 10.35           | 104    | 21.30 | 77     | 30.55 | 923    | 44.35 | 6860   |
| 10.65           | 94     | 21.80 | 44     | 32.50 | 623872 | 45.35 | 156    |
| 11.25           | 122    | 22.10 | 38     | 34.50 | 3314   | 47.35 | 37944  |
| 12.75           | 3758   | 22.70 | 83     | 35.40 | 17160  | 48.30 | 18520  |
| 13.85           | 8731   | 23.20 | 54     | 36.40 | 4520   | 49.30 | 225472 |
| 14.75           | 211604 | 23.50 | 65     | 37.40 | 5801   | 50.30 | 8133   |
| 16.60           | 52992  | 23.70 | 65     | 38.40 | 1473   | 51.30 | 57600  |
| 17.70           | 20912  | 24.25 | 107    | 40.35 | 46984  | 52.20 | 702    |
| 18.70           | 93224  | 25.05 | 462    | 41.35 | 7037   | 52.90 | 47     |
| 19.70           | 966    | 28.55 | 880192 | 42.35 | 4703   | 53.40 | 44     |
| 20.60           | 4437   | 29.55 | 22456  | 43.35 | 777    | 54.00 | 54     |

$\text{CH}_2\text{Cl}^+$

$\text{CH}_3\text{Cl}^+$

$\text{OCl}^+$

Scan 57 (1.008 min): MYB 4167.D

| dichloromethane |        |       |        |       |        |       |        |
|-----------------|--------|-------|--------|-------|--------|-------|--------|
| m/z             | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
| 55.60           | 82     | 61.55 | 41     | 68.00 | 59     | 77.15 | 47     |
| 56.35           | 104    | 62.25 | 38     | 69.20 | 89     | 77.75 | 25     |
| 57.15           | 46     | 62.45 | 38     | 70.10 | 653    | 78.55 | 30     |
| 57.75           | 27     | 63.05 | 74     | 71.00 | 74     | 79.15 | 38     |
| 58.15           | 40     | 63.75 | 54     | 72.00 | 428    | 79.45 | 39     |
| 58.65           | 49     | 64.40 | 46     | 73.15 | 65     | 79.95 | 48     |
| 58.95           | 55     | 65.00 | 53     | 73.95 | 130    | 81.90 | 1810   |
| 59.15           | 46     | 65.50 | 26     | 74.85 | 41     | 82.90 | 15626  |
| 59.95           | 68     | 66.10 | 34     | 75.35 | 30     | 83.90 | 128688 |
| 60.45           | 51     | 66.70 | 43     | 75.85 | 45     | 84.90 | 11414  |
| 61.05           | 52     | 67.00 |        |       | 48     | 85.90 | 79536  |

$\text{CH}_2\text{ClO}^+$

$\text{CCl}_2^+$

$\text{CHCl}_2^+$

Scan 57 (1.008 min): MYB 4167.D

| dichloromethane |        |        |        |        |        |        |        |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| m/z             | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
| 86.90           | 2604   | 94.75  | 66     | 102.60 | 38     | 111.25 | 31     |
| 87.90           | 11767  | 96.15  | 58     | 103.20 | 37     | 112.35 | 41     |
| 88.85           | 165    | 96.80  | 85     | 103.80 | 22     | 113.50 | 31     |
| 90.15           | 35     | 97.60  | 37     | 104.10 | 23     | 114.20 | 0      |
| 90.85           | 25     | 97.90  | 35     | 104.55 | 32     | 115.60 | 34     |
| 91.65           | 25     | 98.90  | 62     | 105.05 | 26     | 116.60 | 117    |
| 91.95           | 23     | 99.80  | 49     | 106.55 | 50     | 117.60 | 260    |
| 92.25           | 28     | 100.90 | 24     | 107.15 | 29     | 118.60 | 144    |
| 92.45           | 26     | 101.10 | 24     | 109.95 | 26     | 119.60 | 224    |
| 92.85           | 31     | 101.50 | 28     | 110.25 | 21     | 120.55 | 52     |
| 93.65           | 22     | 102.30 | 39     | 110.55 | 21     | 121.55 | 113    |

$\text{COCl}_2^+$

$\text{CHCl}_2\text{OO}^+$

$\text{CCl}_3^+$

Scan 57 (1.008 min): MYB 4167.D

| dichloromethane |        |        |        |        |        |        |        |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| m/z             | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
| 122.45          | 29     | 133.00 | 27     | 145.20 | 27     | 158.35 | 21     |
| 123.45          | 23     | 133.20 | 26     | 148.50 | 28     | 159.05 | 30     |
| 124.15          | 23     | 133.60 | 32     | 149.30 | 22     | 159.55 | 21     |
| 125.45          | 35     | 134.30 | 22     | 150.60 | 30     | 160.45 | 28     |
| 126.15          | 22     | 135.70 | 23     | 151.30 | 34     | 161.90 | 26     |
| 127.45          | 41     | 136.30 | 23     | 152.20 | 34     | 162.10 | 28     |
| 128.15          | 29     | 137.05 | 29     | 152.85 | 27     | 162.80 | 24     |
| 129.50          | 46     | 137.55 | 28     | 156.05 | 31     | 165.70 | 20     |
| 130.30          | 24     | 140.25 | 22     | 157.15 | 23     | 168.40 | 20     |
| 131.50          | 47     | 140.85 | 21     | 158.05 | 22     | 168.70 | 21     |

$\text{CHCl}_2\text{O}^+$

Scan 57 (1.008 min): MYB 4167.D

| dichloromethane |        |        |        |        |        |        |        |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| m/z             | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
| 169.85          | 22     | 182.80 | 23     | 198.80 | 21     | 242.50 | 24     |
| 170.15          | 26     | 183.70 | 27     | 205.75 | 51     | 245.80 | 20     |
| 171.15          | 28     | 184.50 | 23     | 206.85 | 23     |        |        |
| 172.05          | 36     | 184.70 | 24     | 209.90 | 28     |        |        |
| 173.05          | 25     | 187.15 | 34     | 212.00 | 20     |        |        |

## Appendix D

Fragments obtained after illumination of UV light for chloroform using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst, analyzed by using GC-MS.

Scan 57 (1.012 min): MYB 4087C.D  
chloroform

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund.                                     |
|-------|--------|-------|--------|-------|--------|-------|--|
| 10.85 | 99     | 22.60 | 117    | 36.40 | 4079   | 47.25 | 57888                                      |
| 11.75 | 217    | 23.50 | 71     | 37.40 | 6033   | 48.20 | 21840                                      |
| 12.75 | 3490   | 24.45 | 116    | 38.40 | 1245   | 49.20 | 18000 $\rightarrow \text{CH}_2\text{Cl}^+$ |
| 13.75 | 10952  | 25.15 | 133    | 40.35 | 43720  | 50.20 | 7896 $\rightarrow \text{CH}_3\text{Cl}^+$  |
| 14.75 | 179840 | 28.55 | 916416 | 41.35 | 657    | 51.20 | 189 $\rightarrow \text{OCl}^+$             |
| 16.60 | 62472  | 29.55 | 31480  | 41.85 | 697    | 52.40 | 63   |
| 17.60 | 127280 | 30.55 | 1184   | 42.35 | 588    | 53.20 | 23   |
| 18.60 | 557312 | 32.40 | 632768 | 42.75 | 591    | 54.50 | 46   |
| 19.60 | 4814   | 33.40 | 1486   | 43.35 | 345    | 54.80 | 49   |
| 20.60 | 5045   | 34.40 | 3315   | 44.35 | 7615   | 55.10 | 47   |
| 21.90 | 67     | 35.40 | 19656  | 45.35 | 409    | 55.40 | 51   |

Scan 57 (1.012 min): MYB 14087C.D  
chloroform

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
|-------|--------|-------|--------|-------|--------|-------|--------|
| 56.15 | 74     | 63.15 | 101    | 73.15 | 68     | 85.90 | 2306   |
| 57.05 | 52     | 64.20 | 29     | 73.95 | 251    | 86.90 | 20432  |
| 57.55 | 57     | 65.00 | 53     | 75.05 | 50     | 87.90 | 237    |
| 58.35 | 140    | 66.20 | 27     | 76.25 | 28     | 88.65 | 37     |
| 58.55 | 132    | 67.80 | 44     | 76.95 | 141    | 89.15 | 23     |
| 59.65 | 138    | 68.80 | 67     | 77.95 | 36     | 89.75 | 29     |
| 60.15 | 57     | 69.10 | 70     | 78.95 | 39     | 90.25 | 36     |
| 60.45 | 62     | 70.10 | 1303   | 81.90 | 8285   | 91.05 | 20     |
| 61.45 | 30     | 71.20 | 70     | 82.90 | 221568 | 91.25 | 21     |
| 62.25 | 57     | 72.00 | 1065   | 83.90 | 7833   | 91.55 | 21     |
| 62.55 | 64     | 72.95 | 66     | 84.90 | 135936 | 92.25 | 24     |

Scan 57 (1.012 min): MYB 14087C.D  
chloroform

| m/z   | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|-------|--------|--------|--------|--------|--------|--------|--------|
| 92.95 | 27     | 100.40 | 23     | 110.85 | 25     | 122.62 | 111    |
| 93.95 | 33     | 100.90 | 57     | 111.45 | 31     | 123.55 | 179    |
| 94.75 | 28     | 102.10 | 33     | 112.40 | 40     | 124.25 | 23     |
| 95.95 | 85     | 102.80 | 38     | 113.70 | 28     | 124.55 | 38     |
| 96.40 | 24     | 104.10 | 27     | 115.50 | 25     | 126.15 | 45     |
| 96.60 | 24     | 104.95 | 23     | 116.60 | 2250   | 126.75 | 28     |
| 97.10 | 25     | 107.05 | 24     | 117.60 | 4129   | 127.55 | 29     |
| 97.60 | 26     | 107.65 | 20     | 118.60 | 2280   | 128.25 | 30     |
| 98.10 | 29     | 108.85 | 39     | 119.60 | 3814   | 129.50 | 44     |
| 99.20 | 26     | 109.05 | 33     | 120.55 | 730    | 129.70 | 44     |
| 99.90 | 36     | 109.95 | 26     | 121.55 | 1206   | 130.10 | 22     |

Scan 57 (1.012 min): MYB 14087C.D  
chloroform

| m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 130.40 | 22     | 148.60 | 23     | 166.40 | 23     | 192.05 | 29     |
| 131.30 | 33     | 148.90 | 27     | 169.15 | 32     | 192.75 | 20     |
| 133.10 | 23     | 149.70 | 24     | 171.85 | 27     | 193.60 | 27     |
| 133.70 | 31     | 150.50 | 24     | 174.45 | 20     | 198.00 | 23     |
| 135.80 | 24     | 153.55 | 32     | 178.00 | 24     | 198.90 | 21     |
| 136.85 | 28     | 154.35 | 23     | 179.10 | 28     | 199.80 | 20     |
| 138.15 | 26     | 156.95 | 39     | 184.40 | 31     | 201.45 | 22     |
| 140.75 | 24     | 157.55 | 27     | 186.55 | 25     | 203.75 | 25     |
| 140.95 | 24     | 159.05 | 28     | 189.25 | 26     | 205.85 | 87     |
| 144.90 | 30     | 159.65 | 20     | 189.55 | 22     | 207.05 | 36     |
| 147.80 | 24     | 163.10 | 20     | 190.15 | 26     | 209.15 | 22     |

Scan 57 (1.012 min): MYB 14087C.D  
chloroform

| m/z    | abund. | m/z | abund. | m/z | abund. | m/z | abund. |
|--------|--------|-----|--------|-----|--------|-----|--------|
| 211.10 | 21     |     |        |     |        |     |        |
| 213.00 | 28     |     |        |     |        |     |        |
| 216.80 | 22     |     |        |     |        |     |        |
| 219.65 | 20     |     |        |     |        |     |        |
| 220.45 | 43     |     |        |     |        |     |        |

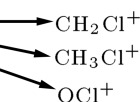
## Appendix E

Fragments obtained before illumination of UV light for carbon tetrachloride using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst, analyzed by using GC-MS.

Scan 57 (1.012 min): MYB 4087C.D

chloroform

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
|-------|--------|-------|--------|-------|--------|-------|--------|
| 10.85 | 99     | 22.60 | 117    | 36.40 | 4079   | 47.25 | 57888  |
| 11.75 | 217    | 23.50 | 71     | 37.40 | 6033   | 47.20 | 21840  |
| 12.75 | 3490   | 24.45 | 116    | 38.40 | 1245   | 49.20 | 18000  |
| 13.75 | 10952  | 25.15 | 133    | 40.35 | 43720  | 50.20 | 7896   |
| 14.75 | 179840 | 28.55 | 916416 | 41.35 | 657    | 51.20 | 189    |
| 16.60 | 62472  | 29.55 | 31480  | 41.85 | 697    | 52.40 | 63     |
| 17.60 | 127280 | 30.55 | 1184   | 42.35 | 588    | 53.20 | 23     |
| 18.60 | 557312 | 32.40 | 632768 | 42.75 | 591    | 54.50 | 46     |
| 19.60 | 4814   | 33.40 | 1486   | 43.35 | 345    | 54.80 | 49     |
| 20.60 | 5045   | 34.40 | 3315   | 44.35 | 7615   | 55.10 | 47     |
| 21.90 | 67     | 35.40 | 19656  | 45.35 | 409    | 55.40 | 51     |



Scan 57 (1.012 min): MYB 4087C.D

chloroform

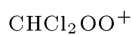
| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |
|-------|--------|-------|--------|-------|--------|-------|--------|
| 56.15 | 74     | 63.15 | 101    | 73.15 | 68     | 85.90 | 2306   |
| 57.05 | 52     | 64.20 | 29     | 73.95 | 251    | 86.90 | 20432  |
| 57.55 | 57     | 65.00 | 53     | 75.05 | 50     | 87.90 | 237    |
| 58.35 | 140    | 66.20 | 27     | 76.25 | 28     | 88.65 | 37     |
| 58.55 | 132    | 67.80 | 44     | 76.95 | 141    | 89.15 | 23     |
| 59.65 | 138    | 68.80 | 67     | 77.95 | 36     | 89.75 | 29     |
| 60.15 | 57     | 69.10 | 70     | 78.95 | 39     | 90.25 | 36     |
| 60.45 | 62     | 70.10 | 1303   | 81.90 | 8285   | 91.05 | 20     |
| 61.45 | 30     | 71.20 | 70     | 82.90 | 221568 | 91.25 | 21     |
| 62.25 | 57     | 72.00 | 1065   | 83.90 | 7833   | 91.55 | 21     |
| 62.55 | 64     | 72.95 | 66     | 84.90 | 135936 | 92.25 | 24     |



Scan 57 (1.012 min): MYB 4087C.D

chloroform

| m/z   | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|-------|--------|--------|--------|--------|--------|--------|--------|
| 92.95 | 27     | 100.40 | 23     | 110.85 | 25     | 122.65 | 111    |
| 93.95 | 33     | 100.90 | 57     | 111.45 | 31     | 123.55 | 179    |
| 94.75 | 28     | 102.10 | 33     | 112.40 | 40     | 124.25 | 23     |
| 95.95 | 85     | 102.80 | 38     | 113.70 | 28     | 124.55 | 38     |
| 96.40 | 24     | 104.10 | 27     | 115.50 | 25     | 126.15 | 45     |
| 96.60 | 24     | 104.95 | 23     | 116.60 | 2250   | 126.75 | 28     |
| 97.10 | 25     | 107.05 | 24     | 117.60 | 4129   | 127.55 | 29     |
| 97.60 | 26     | 107.65 | 20     | 118.60 | 2280   | 128.25 | 30     |
| 98.10 | 29     | 108.85 | 39     | 119.60 | 3814   | 129.50 | 44     |
| 99.20 | 26     | 109.05 | 33     | 120.55 | 730    | 129.70 | 44     |
| 99.90 | 36     | 109.95 | 26     | 121.55 | 1206   | 230.10 | 22     |



Scan 57 (1.012 min): MYB 4087C.D

chloroform

| m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 130.40 | 22     | 148.60 | 23     | 166.60 | 23     | 192.05 | 29     |
| 131.30 | 33     | 148.90 | 27     | 169.15 | 32     | 192.75 | 20     |
| 133.10 | 23     | 149.70 | 24     | 171.85 | 27     | 193.60 | 27     |
| 133.70 | 31     | 150.50 | 24     | 174.45 | 20     | 198.00 | 23     |
| 135.80 | 24     | 153.55 | 32     | 178.00 | 24     | 198.90 | 21     |
| 136.85 | 28     | 154.35 | 23     | 179.10 | 28     | 199.80 | 20     |
| 138.15 | 26     | 156.95 | 39     | 184.40 | 31     | 201.45 | 22     |
| 140.75 | 24     | 157.55 | 27     | 186.55 | 25     | 203.75 | 25     |
| 140.95 | 24     | 159.05 | 28     | 189.25 | 26     | 205.85 | 87     |
| 144.90 | 30     | 159.65 | 20     | 189.55 | 22     | 207.05 | 36     |
| 147.80 | 24     | 163.10 | 20     | 190.15 | 26     | 209.15 | 22     |



Scan 57 (1.012 min): MYB 4087C.D

chloroform

| m/z    | abund. | m/z | abund. | m/z | abund. | m/z | abund. |
|--------|--------|-----|--------|-----|--------|-----|--------|
| 211.10 | 21     |     |        |     |        |     |        |
| 213.00 | 28     |     |        |     |        |     |        |
| 216.80 | 22     |     |        |     |        |     |        |
| 219.65 | 20     |     |        |     |        |     |        |
| 220.45 | 43     |     |        |     |        |     |        |



## Appendix F

Fragments obtained after illumination of UV light for carbon tetrachloride using  $\text{Zn}^{2+}/\text{Fe}^{3+}/\text{TiO}_2$  as catalyst, analyzed by using GC-MS.

Scan 59 (1.036 min): MYB 4200.D  
carbon tetrachloride

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |  |
|-------|--------|-------|--------|-------|--------|-------|--------|--|
| 10.15 | 75     | 21.40 | 65     | 36.40 | 2816   | 49.30 | 25840  | $\longrightarrow \text{CH}_2\text{Cl}^+$ |
| 10.45 | 64     | 22.60 | 104    | 37.40 | 7848   | 50.30 | 802    |  |
| 10.75 | 81     | 23.30 | 87     | 38.40 | 890    | 51.20 | 4686   | $\longrightarrow \text{OCl}^+$           |
| 10.95 | 79     | 24.35 | 64     | 40.35 | 38440  | 52.30 | 91     |  |
| 12.75 | 4224   | 25.05 | 112    | 41.35 | 1258   | 52.90 | 48     |  |
| 14.75 | 142144 | 28.55 | 883776 | 42.35 | 1061   | 53.20 | 56     |  |
| 16.70 | 43416  | 29.55 | 20160  | 43.35 | 457    | 54.30 | 38     |  |
| 17.70 | 19440  | 30.55 | 618    | 44.35 | 6046   | 54.60 | 38     |  |
| 18.70 | 85000  | 32.50 | 556864 | 45.45 | 119    | 55.50 | 36     |  |
| 19.60 | 463    | 34.50 | 2656   | 47.35 | 42736  | 55.90 | 34     |  |
| 20.60 | 3888   | 35.40 | 24592  | 48.30 | 2066   | 56.05 | 34     |  |

Scan 59 (1.036 min): MYB 4200.D  
carbon tetrachloride

| m/z   | abund. | m/z   | abund. | m/z   | abund. | m/z   | abund. |  |
|-------|--------|-------|--------|-------|--------|-------|--------|--|
| 56.45 | 47     | 66.00 | 32     | 77.05 | 38     | 87.90 | 959    |  |
| 56.65 | 43     | 66.50 | 26     | 77.45 | 29     | 88.55 | 27     |  |
| 57.35 | 62     | 67.50 | 20     | 78.95 | 30     | 91.25 | 27     |  |
| 58.65 | 3135   | 68.60 | 39     | 79.75 | 30     | 92.55 | 22     |  |
| 59.65 | 3322   | 70.10 | 1657   | 79.95 | 26     | 93.95 | 23     |  |
| 60.65 | 904    | 71.00 | 34     | 81.90 | 37736  | 94.95 | 30     |  |
| 61.55 | 110    | 72.10 | 1088   | 82.90 | 2458   | 96.25 | 24     |  |
| 62.25 | 52     | 73.95 | 168    | 83.90 | 33840  | 96.70 | 21     |  |
| 63.15 | 362    | 74.75 | 28     | 84.90 | 1714   | 97.60 | 37     |  |
| 64.20 | 31     | 75.55 | 47     | 85.90 | 98.77  | 98.30 | 20     |  |
| 65.20 | 116    | 76.05 | 21     | 87.00 | 325    | 99.40 | 35     |  |

Scan 59 (1.036 min): MYB 4200.D  
carbon tetrachloride

| m/z    | abund. | m/z    | abund. | m/z    | abund. | m/z    | abund. |  |
|--------|--------|--------|--------|--------|--------|--------|--------|--|
| 100.00 | 25     | 112.15 | 22     | 123.55 | 88     | 141.85 | 25     |  |
| 102.00 | 31     | 112.40 | 25     | 124.35 | 36     | 143.45 | 22     |  |
| 102.60 | 31     | 112.60 | 23     | 125.95 | 21     | 144.45 | 21     |  |
| 103.60 | 32     | 113.40 | 30     | 127.25 | 24     | 145.30 | 29     |  |
| 104.10 | 25     | 114.20 | 49     | 129.60 | 26     | 145.90 | 22     |  |
| 104.85 | 22     | 116.60 | 173184 | 131.00 | 22     | 148.20 | 23     |  |
| 105.05 | 21     | 118.60 | 168000 | 134.20 | 34     | 150.10 | 27     |  |
| 105.75 | 27     | 119.60 | 1985   | 135.60 | 25     | 151.20 | 22     |  |
| 106.65 | 21     | 120.55 | 51200  | 135.90 | 20     | 151.40 | 23     |  |
| 107.75 | 28     | 121.55 | 628    | 136.10 | 22     | 154.15 | 22     |  |
| 108.45 | 26     | 122.55 | 4902   | 138.55 | 25     | 156.75 | 33     |  |

Scan 59 (1.036 min): MYB 4200.D  
carbon tetrachloride

| m/z    | abund. | m/z     | abund. | m/z | abund. | m/z | abund. |  |
|--------|--------|---------|--------|-----|--------|-----|--------|--|
| 158.15 | 23     | 230.960 | 21     |     |        |     |        |  |
| 163.10 | 24     | 232.70  | 22     |     |        |     |        |  |
| 185.25 | 20     | 233.45  | 28     |     |        |     |        |  |
| 195.50 | 23     | 234.35  | 21     |     |        |     |        |  |
| 196.10 | 23     | 247.20  | 22     |     |        |     |        |  |
| 201.45 | 29     |         |        |     |        |     |        |  |
| 202.15 | 28     |         |        |     |        |     |        |  |
| 205.75 | 47     |         |        |     |        |     |        |  |
| 217.35 | 29     |         |        |     |        |     |        |  |
| 224.15 | 24     |         |        |     |        |     |        |  |
| 227.00 | 21     |         |        |     |        |     |        |  |

## BIOGRAPHIES

**Wan Azelee Wan Abu Bakar** was born in 1959 in Kelantan, Malaysia. After graduation from the Department of Chemistry at the National University of Malaysia in 1983, he continued his studies into heterogeneous catalysis at Nottingham University, in England, and received his PhD in 1995. He then joined Universiti Teknologi Malaysia, where he is presently a Professor of Inorganic Chemistry. Professor Wan Azelee Wan Abu Bakar is the author of 100 papers published in national and international journals and 4 chemistry text books for university students.

**Rusmidah Ali** was born in 1957 in Klang, Selangor, in Malaysia. She obtained her BS degree in Chemistry in 1980 from Universiti Kebangsaan Malaysia, and then

received her MS and PhD degrees from Southampton University, in the UK, in 1983 and 1987, respectively. She then joined Universiti Teknologi Malaysia, where she is presently Associate Professor of Inorganic Chemistry. She is author of 30 papers published in national and international journals and 11 books.

**Mohd Yusuf Othman** was born in 1952 in Pahang, Malaysia. After graduation from Universiti Kebangsaan Malaysia in 1975, he continued his studies at University College, Swansea at the University of Wales, receiving his MS and PhD degrees in 1978 and 1985, respectively. He then joined Universiti Teknologi Malaysia and became an Associate Professor in the Department of Chemistry in 1991. He is author of 20 papers published in national and international journals.