

Photocatalytic of Thiophene Desulfurization

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Abstract: Thiophene, found in the fuels is a heterocyclic five membered ring consist of sulfur as the heteroatom, with two pairs of electrons at the S atom along with a pair in the six-electron π -system and the others in the ring. Thiophene give negative impacts to living things and also atmosphere. The presence of sulfur in fuels will lead to the emission of sulfur dioxide to the atmosphere and lead to atmospheric pollution such as acid rain. Thiophene is difficult to remove by using conventional desulfurization process such as hydrosulfurization (HDS). Thus, photocatalytic process is the best alternative method available to degrade the thiophene. Photocatalytic process only requires minimal quantity of catalyst and the by product is almost zero or less harmful to environment and living things. The process efficiency depends strongly on the chosen photocatalyst. ZnO/KCC provide great potential as the photocatalyst. Hence, this review paper focus on the photocatalytic thiophene desulfurization using ZnO/KCC as the photocatalyst.

Keywords: Thiophene, desulfurization, photocatalyst, ZnO/KCC, dendrimetric structure

1. Introduction to Thiophene

Thiophene, also known as sulfur pollutant, is one of sulfur-containing compounds (SCCs) presence in petroleum. Thiophene (C_4H_4S) is a heterocyclic five membered ring consist of sulfur as the heteroatom, with two pairs of electrons at the S atom along with a pair in the six-electron π -system and the others in the ring [1]. Thiophene can be either an n-type donor or π -type donor. The n-type donor is when the lone pair of electrons of the sulfur atom is donated to a surface cation (S-M bond). While, the π -type donor is when the delocalized electrons of the thiophene is utilized to form a π -complex with the cation [2]. Aromatic species as thiophene are the common impurities found in fuels due to its reactivity [1]. In addition, thiophene has benzene-like structure and the chemical properties also similar to benzene where, it has colorless liquid with mild pleasant odor at room temperature. The high reactivity of thiophene toward sulfonation of the thiophene separation from the benzene make them difficult to separate by using conventional distillation. In addition, thiophene is flammable and toxic aromatic compound, and insoluble in water. Thiophene is more stable than the analogous furan because the sulfur in the thiophene contains larger bonding radius to tolerate positive charges better. Thus, an inductive energy pull toward sulfur [3], [4].

However, thiophene give negative impacts to living things and atmosphere. The presence of sulfur in fuels will lead to the emission of sulfur dioxide to the atmosphere and lead to atmospheric pollution such as acid rain. The sulfur

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dioxide will further destruct the leaf tissue of the plant to become dry and papery and also, will affect the respiration system for instance irritation of the nose and throat [5]. Table 1 shows the Canada National Energy Board, (2006) that represent the toxicological data of thiophene and derivatives.

Table 1 - The toxicological data for thiophene and derivatives (Canada National Energy Board, 2006)

	Thiophene	2-Methylthiophene	3-Methylthiophene	2-Acetylthiophene	2-Bromothiophene
Acute Toxicity					
Oral LD ₅₀	1400 mg/kg (rat)	3200 mg/kg (mouse)	2300 mg/kg (rat)	50 mg/kg (mouse)	200–250 mg/kg (rat)
Dermal LD ₅₀	830 mg/kg (rabbit)	no data	2000 mg/kg (guinea pig)	370 mg/kg (rat)	134 mg/kg (rat)
Inhalation LC ₅₀	9500 mg/kg (mouse)	no data	10 g/m ³ , 2 h (rat)	1460 mg/m ³ , 1 h (rat)	1.04 mg/L, 4 h (rat)
Irritation					
Skin	yes	expected	yes	not reported	yes
Eye	yes	expected	yes	predicted	yes
Skin sensitization	no data	no data	not found in tests	no data	no data
Occupational exposure limits	none specified	none specified	none specified	2 ppm (provisional)	1 ppm (provisional)
Ecotoxicity					
	possibly only slight harm to aquatic organisms	possibly only slight harm to aquatic organisms	possible only slight harm to aquatic organisms	harmful to aquatic organisms	expected only slight harm to aquatic organisms
Persistence					
	expect ultimate biodegradability	expect ultimate biodegradability	expect ultimate biodegradability	expect ultimate biodegradability	expect very slow biodegradability
Stability					
Materials to avoid	strong oxidizers	strong oxidizers	strong oxidizers	strong oxidizers	strong oxidizers
Conditions	stable under normal conditions	stable under normal conditions	stable under normal conditions	stable under normal conditions	slow decomposition unless cool/dark
Combustion products	toxic oxides of S+CO, CO ₂	toxic oxides of S+CO, CO ₂	toxic oxides of S+CO, CO ₂	toxic oxides of S+CO, CO ₂	HBr during storage (prolonged), CO, CO ₂

2. Thiophene Desulfurization

According to [6], thiophene is difficult to remove by using conventional desulfurization process such as hydro-sulfurization (HDS). This is because the presence of the aromatic and the low density of the sulfur atom make it difficult to oxidize the thiophene molecule. Thiophene is often uses as model of molecule for research under catalytic C-S bond scission and hydrodesulfurization (HDS) mechanism [2]. Oxidative desulphurization method (ODS) has become the top method for deep sulfurization of diesel fuel. Nonetheless, the process involved biphasic oxidation of organosulfur compound in liquid phase required H₂O₂ at 60°C to 80°C, atmospheric pressure in order to degrade sulfoxides and sulfones. Where, both by-products can be separated from the fuel by various separation method such as precipitation, extraction or adsorption [7]. Conversely, photocatalytic process has gained a lot of attention for thiophene desulfurization. Therefore, an efficient photocatalyst has been developed to oxidize thiophene using photocatalytic process. The performance of the photocatalytic process is relying on the photocatalyst stability, particle size, surface area, band gap and the recombination of the electron-hole lifetime [8].

2.1 Photocatalytic of Thiophene Desulfurization

Photocatalytic degradation process has been applied in many cases for a complete degradation of organic pollutants into very small and harmless species by not using any chemicals [9]. Photocatalytic process is the best method to degrade the pollutants present in water using various wavelength ranges of light or UV radiation. Moreover, this process only require minimal quantity of catalyst and the by product is almost zero or less harmful to environment and living things [10]. According to [11], there are several steps such as adsorption-desorption, electron-hole pair production, recombination of electron pair and chemical reaction involved in the photocatalytic degradation process. In this process, the photocatalyst will be exposed to the ultraviolet (UV) light and hydroxyl radicals ($\cdot\text{OH}$) will be produced. Then, the organic pollutant will be degraded and formed into carbon dioxide (CO₂), clean water (H₂O) and inorganic constituents [12], [13]. Hydroxyl radical is the primary oxidizing species in the photocatalytic oxidation process [14]. There are many factors that affect the effectiveness of the photocatalytic process. One of the factors is the selection of the photocatalyst. The important attribution of the photocatalytic system is the desired band gap, suitable morphology, high surface area, reusability and stability [15].

Based on the recent study, photocatalysis process undergo electronic excitation of molecule or solid which lead into light absorption and commonly, the UV light alters the ability to gain or lose electrons of the process, lead to promote decomposition of the pollutants to harmless by-product [16], [17]. Moreover, with an appropriate light

irradiation, the photocatalyst creates electron or hole pairs with free electrons produced in the empty conduction band leaving positive holes in the valence band. Then the electron or hole pairs will initiate to form chemical reaction and finally mineralize the pollutant around it. The process occurs when a semiconductor is illuminated by light with greater energy than its bandgap. Then the electron being promoted from valence band (VB) to the conduction band (CB). Besides, these photo-reduced pairs lead to combination with emission of thermal energy that involve with electron acceptor or donor species adsorbed on the surface of the catalyst particles [18], [19]. Photocatalytic degradation has high efficiency towards the application of nanoparticles as photocatalyst to treat the waste water [13].

Titanium dioxide (TiO_2), zinc oxide (ZnO), iron (III) oxide (Fe_2O_3), cerium oxide (CeO_2) cadmium sulphide (CdS) and zinc sulfide (ZnS) are the example of the metal semiconductor material that being used as the photocatalyst due to the cost-efficient, effective and environment-friendly material [20]. TiO_2 , ZnO and CeO_2 are the semiconductors that have large energy gap between the other semiconductors. The larger energy gap will contribute better result for photocatalyst application [10]. TiO_2 is the one that is being actively used and extensively used in most research. However, it is reported that ZnO show higher efficiency in the photocatalytic degradation process than TiO_2 [20]. Other than that, according to Saravanan et al., (2016) [10], ZnO is supercilious compared to the other semiconductors because it is affordable for commercial consideration.

In order to understand the photocatalytic degradation of thiophene in membrane photocatalytic reactor, Fig. 1 shows the illustration for mechanism of photocatalytic process to degrade thiophene. The photocatalytic process was initiated by the absorbed UV light by ZnO photocatalyst. Then, an electron-hole pair was generated, occurred only if the supplied energy is more than the bandgap energy of the material. Band gap is the energy difference between the valence band (VB) and the conduction band (CB). The exposure to the illuminated light energy was the reason the CB electron of the photocatalyst got excited. This phase was called the 'photoexcitation' state. The photo generated electron was negatively charged while the hole is positively charged ($h\nu$) or known as the high oxidative potential of the hole in ZnO due to the direct oxidation of thiophene [21].

Then, the reaction of the hole and hydroxide ion form very reactive hydroxyl radicals. The formation of the hydroxyl radical was in unstable state and reactive, which help the thiophene to be degraded. In the CB, the molecular oxygen was reduced to superoxide anion by electron. Due to the presence of organic scavengers or hydrogen peroxide (H_2O_2), the radical may form organic peroxide. Then the H_2O_2 will be reacted to form hydroxyl radical and holes to generate ($\cdot\text{HO}_2$). The production of hydroxyl radicals due to the electrons in the conduction band and being showed that the main reason of the thiophene mineralization [12].

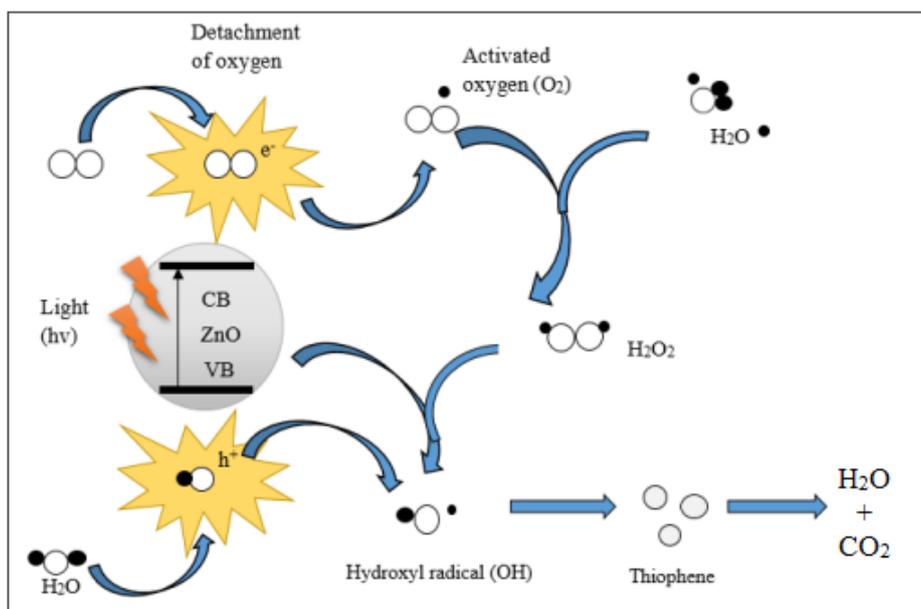


Fig. 1 - Photocatalytic degradation mechanism of thiophene [12]

There are several parameters that affect the performance of the photocatalytic degradation which are temperature, catalyst concentration, substrate concentration, initial pH, radiation intensity, and oxidants concentration. In the term of temperature effect, the photocatalytic degradation process does not require any heating due to the true activation energy is zero and in addition it has a small apparent activation energy [22]. Next, in term of catalyst concentration, the mass of catalyst is directly proportional to the initial rates of reaction despite the configuration of the catalyst. Theoretically, the higher the amount of the concentration of catalysts resulting into the increasing number of active site available for adsorption. However, previous study made by [22] stated that the increasing amount of catalyst concentration over

certain fixed limit for the process does not give any significant changes related to the efficiency of the degradation due to maximum limit of photon absorption within the reactor is reached.

Besides, when excess photocatalyst was inserted into the process, it will cause the penetration light blocking and scattering of light in the reactor. This will result in the formation of the electron hole due to decreasing availability of active sites [11]. The loading of photocatalysts is also important to the process depend on the volume of the wastewater. Table 2 provides the example of loading of certain photocatalyst and its degradation efficiency.

Table 2 - Dependence of photocatalytic activity on catalyst loading [11]

Source of catalyst	Light sources	Catalyst preparation method	Catalyst used	Organic pollutant	Catalyst concentration (mg/L)	Irradiation time (mins)	Degradation efficiency (%)
TiCl ₄ and cobalt (III)	UV radiation	Sol-gel method	Codoped TiO ₂	2-Chlorophenol	10	180	96.4
2,4-pentanedio nate	100W mercury lamp	Sol-gel method	Codoped TiO ₂	2-Chlorophenol	Control (zero catalyst)	180	10
					5		50
					10		90
					30		90

2.2 ZnO/KCC Nanoparticles as the Photocatalyst

Based on [23], photocatalyst was made from metal oxide semiconductor materials because it comply to the primary photocatalytic system which is light absorption and able to induce a charge separation process, forming positive holes that permit the oxidation of organic pollutant. Other than that, the effectiveness depends on the characteristic of the semiconductor particle, such as the position of the band gap potentials, the semiconductor surface properties and the mobility and recombination rate of the charge carrier produced by UV light absorption. According to the [24], ZnO is one of the nanoparticles (NPs) that is recommended for degradation of inorganic and organic contaminants by using photocatalysis process in various matrices. ZnO has been known as the photocatalyst that yield high photo-sensitivity, low cost and chemically stability [25].

Zinc oxide comes with the molar mass of 81.4084 g/mol and the appearance of the ZnO is amorphous white. ZnO is equal to or greater than the band gap which is 3.2 eV. Other than that, this metal oxide is odourless and the density is 5.606 g/cm³. The boiling point and melting point of ZnO are 2360 °C and 1975 °C respectively. In addition, to choose a suitable photocatalytic semiconductor, it is required to identify the band structure which are the band edge position and the band gaps. This is because the wide band gap of the semiconductor can be activated under ultraviolet (UV) irradiation [26]. The high excitation binding energy of ZnO will permit for excitonic transition at room temperature and it mean that the high radiative recombination efficiency for spontaneous emission where lower threshold voltage for laser emission [27]. This also supported by [12], where the stable wurzite crystal structure of ZnO that have large exciton binding energy will give efficient degradation under UV light at room temperature. Based on [28], higher adsorption of organic molecule due to the higher efficiency of surface are significant in order to achieve high performance of photocatalysis degradation. The surface area of ZnO is relatively high which around 90 m² /g [29]. Fig.2 shown morphology of the ZnO nanoparticle by using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The structure grown in the hexagonal shape that indicate good feature of the ZnO nanoparticles. ZnO may also exists in the shape of sphere other than hexagonal [30].

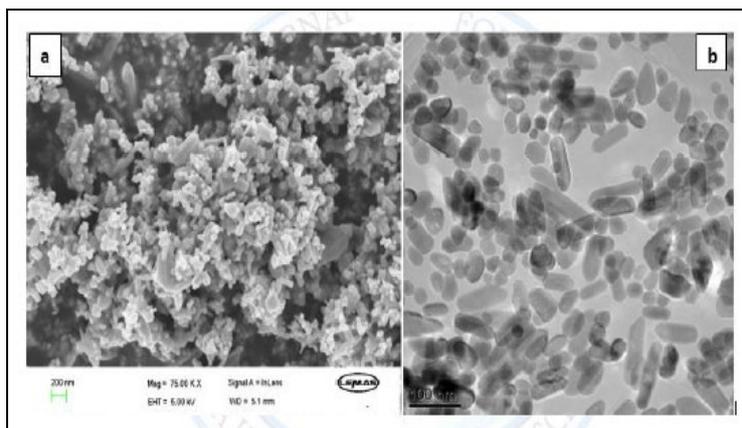


Fig. 2 - a) SEM image of ZnO nanoparticles; b) TEM image of ZnO nanoparticles [30]

ZnO nanoparticles gain a wide attention due to their higher surface area and reactivity. It is also good photosensitivity, non-toxic nature, chemical stability and low cost [31]. It is classified as the best biofriendly absorbers of UV radiation that purposely come to the earth from the sun through the atmospheric ozone layer [32]. ZnO can also be synthesized under mild condition to form the crystal structure through anisotropic growth to provide large surface to volume ratio [33].

Modified fibrous silica, KCC is known as a new type of mesoporous silica material which has also gain attention in many applications such as catalysis, hydrogen storage, and capture conversion of CO₂ due to high surface areas, fibrous surface morphology, wide pore diameter, high mechanical, and thermal stability. However, the study on the application of KCC is still limited. KCC is mainly used for its high effectiveness due to its microstructures and mesostructured. Moreover, the fibrous morphology of KCC-1 is expected to be enhancing the accessibility of active sites and continuously improving its performance on adsorption process [34]. In addition, it allows the active molecules to disperse on the bigger internal surface area thus improving the performance of the catalysts. Fig.3 shows image of high surface area of silica nanosphere under Scanning Electron Microscopy (SEM).

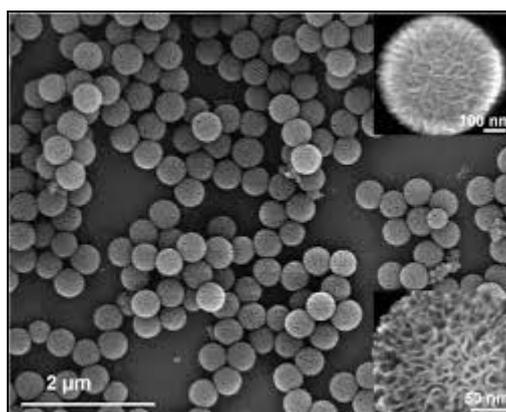


Fig. 3 - High surface area silica nanosphere under SEM [33]

Recently, the performance of the KCC as supported catalyst has been published. According to the [35], the usage of the metal such as cerium (Ce), nickel (Ni) and ruthenium (Ru) loaded on KCC-1 support resulted in the conversion of cellulose into short chain polyols in high pressure autoclave apparatus and show a better result. The Ce/KCC gave the highest performance due to its metal and also owing to the large surface area and the average pore diameter compared to the bare KCC. An investigation on the Titanium Oxide (TiO₂) coating on the KCC-1 has been done by [36]. It was reported that photocatalytic activity increased significantly. Fig.4 shows TiO₂ loaded on the KCC-1. The high area surface is due to the fibers of the fibrous instead of the size of the pores [36]. In addition, KCC is used as the silica catalyst and effectively used also in adsorption, and drug delivery, due to the unique dendrimer morphology, high surface area and good thermal stability. In addition, KCC have high accessibility allow reactants to pass through the active site as it work as supported catalyst [37].

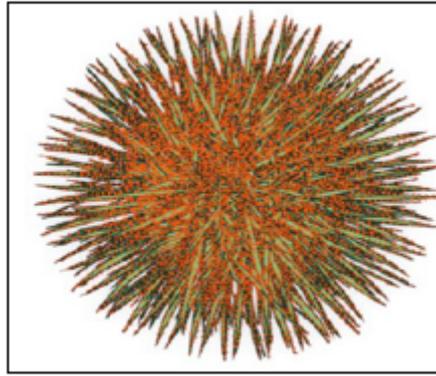


Fig. 4 - Metal Oxide loaded on KCC [37]

The uniqueness of KCC is that it has high surface area thus makes it easy access to improve the performance efficiency. In addition, it carries great physical properties, fibrous morphology, hydrothermal properties, and high mechanical ability. The porous nanoparticle types are functioned to adsorb the unwanted molecules from the end product. Therefore, the choosing of the size of the porous is important. The larger porous types of KCC, the higher efficiency of adsorption of the reaction, thus the shorter time taken to complete the reaction. Normally KCC has high surface area up until $800 \text{ nm}^2/\text{g}$ along with diameter of pores of 8 nm^2 and by using the scanning electron microscopy (SEM), it analysed that silica nanosphere are able to withstand up to temperature of 950°C [38]. Additionally, KCC can remain unchanged even though up to 216 MPa pressure of mechanical compressing act upon it. The structure of KCC was confirmed by high-resolution transmission electron microscopy as illustrated in Fig. 5.

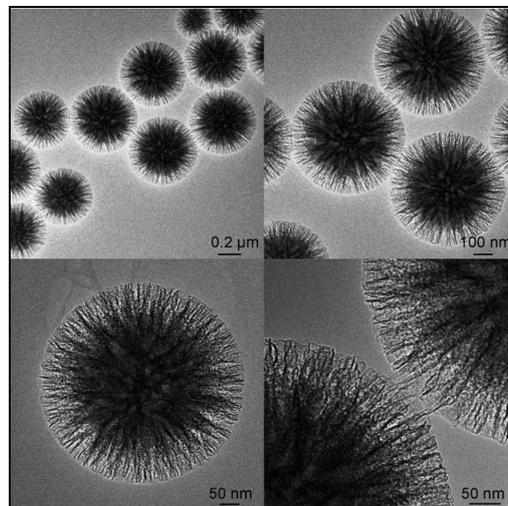


Fig. 5 - HRTEM image of silica nanosphere KCC [38]

3. Conclusion

Thiophene normally found in fuel, contained sulfur give negative impacts to living things and also atmosphere when burned by emitting sulfur dioxide to the atmosphere and lead to atmospheric pollution such as acid rain. Conventional thiophene desulfurization was not able to degrade significantly. Hence, photocatalytic process is one of the best methods to degrade the thiophene. The photocatalytic process only requires a minimal quantity of catalyst and the by product is almost zero or less harmful to environment and living things. The process efficiency depends strongly on the chosen photocatalyst. ZnO/KCC provide great potential as photocatalysts. Zinc oxide comes with the molar mass of 81.4084 g/mol and the appearance of the ZnO is amorphous white. ZnO is equal to or greater than the band gap which is 3.2 eV . While, KCC is gaining attention due to its properties such as high surface areas, fibrous surface morphology, wide pore diameter, high mechanical, and thermal stability. Combining both nanoparticles resulted in higher photocatalytic activity.

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