

Study on Catalytic and Photocatalytic Decontamination of (2-Chloroethyl) Phenyl Sulfide with Nano-TiO₂

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Abstract:

Catalytic and photocatalytic reactions of (2-chloroethyl) phenyl sulfide (2-CEPS), a mimic of bis (2-chloroethyl) sulfide (i.e. Sulfur mustard) were studied on the surfaces of titanium oxide. TiO₂ nanoparticles (anatase, rutile and mixture of 80% anatase/20% rutile) along with bulk TiO₂ were tested as reactive sorbents for reaction of 2-CEPS at room temperature (25±0.5°C). Reactions were monitored by GC-FID technique and reaction products were characterized by GC-MS. Data explores the role of hydrolysis and elimination reactions in the reaction of 2-CEPS on titanium oxide. In these reactions, 2-CEPS undergo photocatalytic reactions to yield (2-hydroxyethyl) phenyl sulfide, (2-ethoxyethyl) phenyl sulfide and vinyl phenyl sulfide. Also data reveals that the maximum decontamination of 2-CEPS was related to nano-TiO₂ (80% anatase/ 20% rutile)/ UV.

Keywords: Catalytic, Photocatalytic, Decontamination, Nano-TiO₂, (2-Chloroethyl) phenyl sulfide.

1. INTRODUCTION

Decontamination of air polluted by chemical and biological warfare agents (CWAs and BWAs) in an indoor space is of great importance to the chemical and biological defense as well as the counterterrorism field. Military chemists have always been trying to develop some new methods to safely and conveniently eliminate these pollutants [1]. North Atlantic Treaty Organization (NATO) has classified agents of chemical terrorism as blister agents (e.g. Sulfur mustard or HD), nerve agents (e.g. Tabun), asphyxiates (e.g. Arsine), choking agents (e.g. Phosgene) and incapacitating/behavior altering agents [2]. (2-Chloroethyl) ethyl sulfide (2-CEES) and (2-chloroethyl) phenyl sulfide (2-CEPS) are examples of mustard simulate. These compounds contain a single chlorine atom on the β carbon relative to the sulfur atom. While halogenated organic compounds are known to undergo hydrolysis reactions at the carbon-chlorine bonds in solution

and on surfaces, the hydrolysis reaction occurs at temperature above ~400 K or is carried out under acid/base hydrolysis conditions. The presence of a sulfur atom in the organic molecule in α or β position to the chlorinated carbon is known to activate the carbon-chlorine bond, allowing hydrolysis to occur at temperatures near room temperature [3]. Various methods are known in the literature for neutralization of CWAs, which make use of either chemical neutralization (oxidative/ hydrolytic) or incineration [4,5]. Klabunde and co-workers have extensively developed nanoparticulate metal oxide materials such as Al₂O₃, CaO and MgO for decontamination of CWAs at ambient temperature, which were demonstrated to be much more reactive than common oxides [6-8]. Application of nanosized inorganic oxide materials as reactive sorbents has been a promising approach for the decontamination of CWAs. Strong adsorbability and enhanced reactivity towards the toxicants make

them the potential materials for the decontamination applications [9]. Recently, it was revealed that the photocatalysis technique had a favorable potential to mineralize a range of toxic substances, and was regarded as a most promising technology to purify the polluted air [10,11]. Photocatalytic oxidation of 2-CEES was widely studied. The experimental results indicated that photocatalytic degradation of 2-CEES mainly proceeds via oxidation of S atom, cleavage of S–C bond and oxidation of C atoms [12-15]. Nano-TiO₂ is one of the most common catalysts that used for purification fields. It is well known that titanium oxide has three crystalline forms of brookite, anatase and rutile. Only rutile and anatase have been used in most photocatalytic investigations. Both phases are semiconductors with a bandgap of 3.23 eV for anatase and 3.10 eV for rutile [16]. Under UV light illumination, absorption of photons creates an electron-hole pair if the energy is higher than the bandgap. The pairs migrate at the surface, are trapped by the titanium and OH surface groups, and finally form OH° and HO₂° radicals. These free radicals cause the oxidation of organic compounds [17].

The goal of the present work is to investigate the catalytic and photocatalytic potential of nano-TiO₂ for decontamination of 2-CEPS. TiO₂ nanoparticles (anatase, rutile and mixture of 80% anatase/ 20% rutile) along with bulk TiO₂ were tested for reaction of 2-CEPS at room temperature.

2. MATERIALS AND METHODS

2.1. Materials

Nanocrystalline TiO₂ (15-45 nm) were prepared by titanium tetraisopropoxide (Ti(OiPr)₄) via sol-gel method in acidic condition according to the Ref. [18]. The effect of calcination temperature on phase transformation of TiO₂ (brookite, anatase and rutile) was determined by X-ray diffraction (XRD) patterns. Also, the surface morphology of the calcinated powders was observed on a scanning electron microscopy (SEM). (2-chloroethyl) phenyl sulfide was synthesized in our laboratory (raw materials were supplied from Merck Co.) and bulk TiO₂ was purchased from Merck Co.

2.2. Photochemical reactor

The photochemical reactor applied in the present study is like an annular reactor and has two parts (Figure 1). The reactor consists of a jacketed quartz tube of the following dimensions: 3.4 cm i.d., 4 cm o.d., and 21 cm length. This holds a medium pressure mercury vapor lamp (MPML) of 125 W. This is placed in a pyrex glass-outer reactor with dimensions of 5.7 i.d. and 35 cm height. The solution was taken in the outer reactor and stirred uniformly using a magnetic stirrer during the course of reaction. The light source was centrally placed inside the quartz cell and predominated emitted the wavelength of 254 nm corresponding to the energy of 4.88 eV. The pre-weighted amounts of catalyst was added to the solution and maintained in suspension using magnetic stirring in the reactor. The samples were collected and analyzed by GC-FID. In addition, the catalytic reaction of 2-CEPS was also tried in a similar reactor, without MPML.

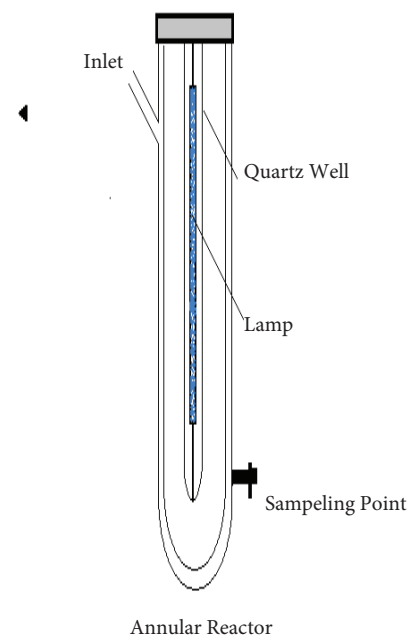


Figure 1: Photochemical reactor

2.3. Experimental procedure

Catalytic and photocatalytic reactions of 2-CEPS

were carried out into the above mentioned reactor. The 2-CEPS solution was prepared by dissolving the required amount of 2-CEPS in ethanol (from Merck). The variation of the 2-CEPS concentration versus time was monitored with different phases of TiO_2 (anatase, rutile, mixture of 80% anatase/20% rutile and bulk) with a constant catalyst amount (0.15 g) and 1 mL of water. The reactor temperature was maintained constant at 25°C for all experiments. Samples were collected at regular intervals for subsequent analysis. The Samples were filtered with 0.2 μm micro-filters and then centrifuged to remove the particles prior to the analysis.

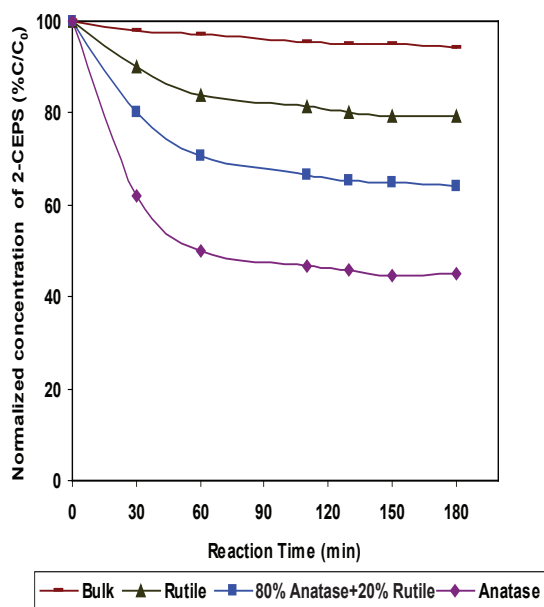


Figure 2: Catalytic detoxification of 2-CEPS with TiO_2 $[2\text{-CEPS}]_0 = 50 \text{ mg/L}$; $[\text{TiO}_2]_0 = 0.15 \text{ g}$

2.4. GC and GC-MS analysis

The VARIAN SATURN 3400CX gas chromatography equipped with FID detector and 10% OV- 101 CWHF 80/100 packed column (2 m length, 1.8 in i.d.) was used to determine the concentration of 2-CEPS. GC operating conditions for 2-CEPS was as follows: injector temperature 250°C, column temperature programming 100°C (2 min) at 10°C/min–250°C (5 min), carrier gas helium at flow rate of 10 mL/min. The GC–MASS

analyses were performed by VARIAN SATURN 4D GC coupled to a DB 5 mass spectrometer and 0.1 micron capillary column (30 m length, 0.25 mm i.d.). GC operating conditions for products was as follows: injector temperature 250°C, column temperature programming 50°C (2 min) at 8°C/min–100°C (5min) at 20°C/min–250°C (2 min), carrier gas helium at flow rate of 10 mL/min.

3. RESULTS AND DISCUSSION

3.1. Effect of Catalysis

The detoxification activity of 2-CEPS was tested with prepared nano- TiO_2 . The influence of catalyst on detoxification of 2-CEPS was done with different phases of nano- TiO_2 , i.e. anatase, rutile and mixture of anatase/rutile. Results are presented in Figure 2. It can be seen that the reactivity of anatase phase of nano- TiO_2 with 2-CEPS was significant. However, the higher activity of anatase compared to the other phases is due to its higher specific surface area. In fact, a higher surface area induces a higher number of accessible active sites and consequently leads to the better reactivity. According to numerous reports, the activity of the anatase phase of TiO_2 for the purification of various pollutants is, in general, much higher than that of rutile. There was explained that the rutile phase is calcined at higher temperature and cause the particle size to be increased and subsequently the specific surface area to be decreased. Thus, in the rutile phase, the specific surface does not play any role [19]. Inspection of the 2-CEPS reaction with anatase profile in Figure (2) shows that the reaction rate is rapid initially but decline at longer times. The fast reaction is attributed to facile liquid spreading through the pores across fresh, unreacted surface. Spreading stops once the liquid achieves its volume in the pores; the reaction cases, too, once the surface is consumed with product.

3.2. Effect of Photocatalysis

The photocatalytic reaction starts with the

adsorption of 2-CEPS on the surface of TiO_2 catalyst. The effect of photocatalytic reaction is shown in Figure 3. It is shown that concentration of 2-CEPS decreases sharply with anatase and a mixture of 80% anatase/20% rutile and then slowed. Nearly 65% and 85% of 2-CEPS was eliminated after irradiation for 3 h with anatase and a mixture of 80% anatase/20% rutile, respectively, as shown in Figure 3.

Under the same experimental conditions, one could observe that initial degradation was negligible with rutile and bulk TiO_2 , and the degradation was very slow. This was possibly due to the slow diffusion rate of 2-CEPS and also the deactivation of active sites on the catalyst [20]. The junction created by the two semiconductors (80% anatase/20% rutile) helps the charge-carriers separation. It means that the carriers created in the rutile part do not rise up photoactivity as in the pure phase. The rutile phase of mixture of 80% anatase/20% rutile plays only the role of charge separator and provides sites for oxidation [21]. The strength photodegradation of anatase and mixture are mainly due to the surface hydroxyl species as they are the strong decomposing agents [20].

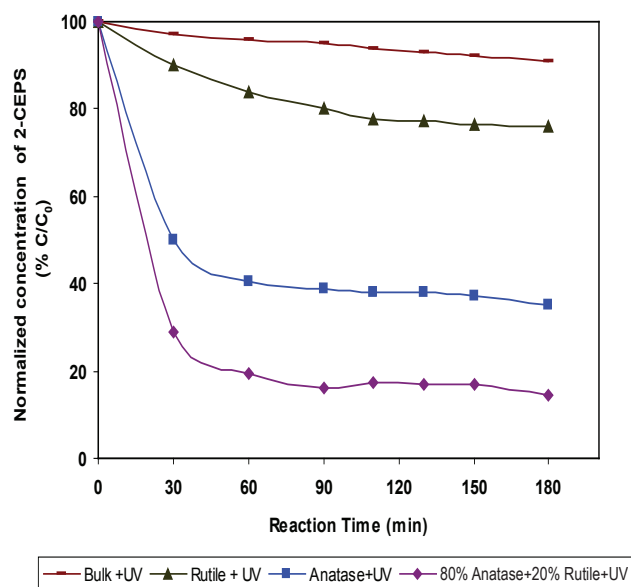


Figure 3: Photocatalytic detoxification of 2-CEPS with TiO_2
 $[2\text{-CEPS}]_0 = 50 \text{ mg/L}$; $[\text{TiO}_2]_0 = 0.15 \text{ g}$

3.3. GC and GC-MS results

The reaction mixtures were analyzed by GC-MASS for the characterization of reaction products. Data illustrates the formation of several products as (2-hydroxyethyl) phenyl sulfide, (2-ethoxyethyl) phenyl sulfide and vinyl phenyl sulfide with retention times 6.33, 6.66 and 8 minutes, respectively (Figure 4). Furthermore, the MASS data confirms them (Figure 5).

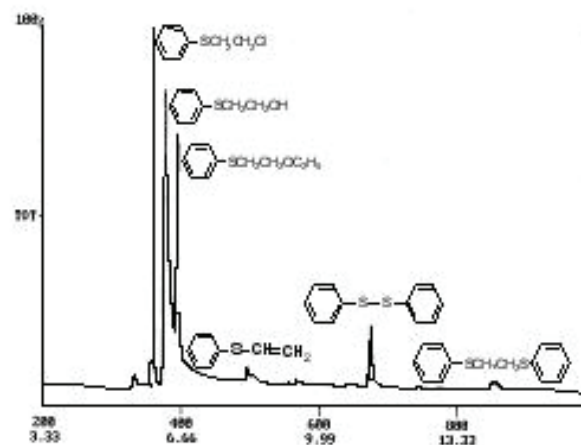


Figure 4: The GC-MS spectrum of products

Also, the band appeared at the end of GC-MS diagrams could be attributed to some probable impurities in 2-CEPS (about 5% or less). Figure 5(a) shows the m/z values at 77, 123, 154, indicating the formation of (2-hydroxyethyl) phenyl sulfide ($m/z=154$), with high molecular stability. The other fragmentations are: C_6H_5 ($m/z=77$), $\text{C}_6\text{H}_5\text{S}$ ($m/z=109$), $\text{C}_6\text{H}_5\text{SCH}_2$ ($m/z=123$), $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2$ ($m/z=137$). Unlike, $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2$ ($m/z=137$), $\text{C}_6\text{H}_5\text{S}$ ($m/z=109$) are not stable. Figure 5(b) shows the m/z values at 109, 123, 137, 182, indicating the formation of (2-ethoxyethyl) phenyl sulfide by relative stability. The other fragmentations are: $\text{C}_6\text{H}_5\text{S}$ ($m/z=109$), $\text{C}_6\text{H}_5\text{SCH}_2$ ($m/z=123$), $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2$ ($m/z=137$). The Figure 5(c) shows the m/z values at (109,137) that indicating the formation of protic vinyl phenyl sulfide ($m/z=137$) and $\text{C}_6\text{H}_5\text{S}$ ($m/z=109$). This is emphasizing the role of hydrolysis reaction in the decontamination of stimulant HD thereby rendering it non-toxic.

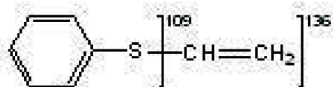
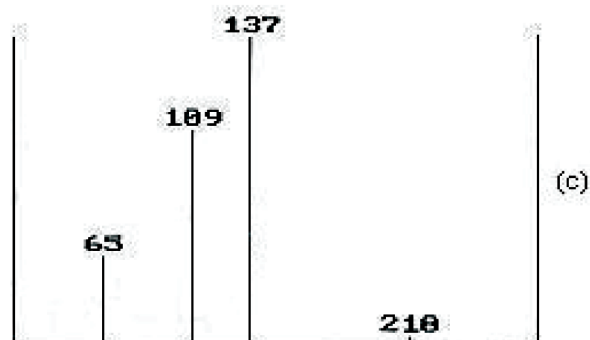
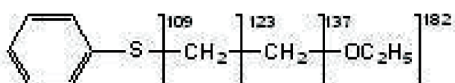
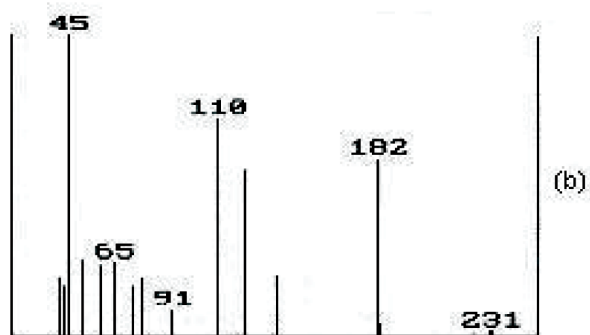
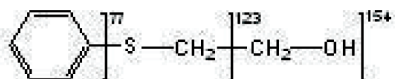
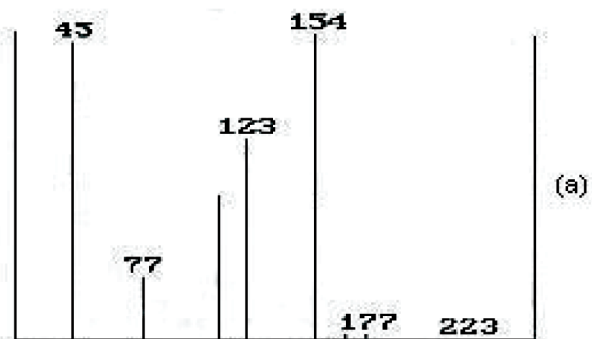


Figure 5: Mass spectra of [a: (2-hydroxyethyl) phenyl sulfide, b: (2-ethoxyethyl) phenyl sulphide, c: vinyl phenyl sulfide].

4. COCLUSION

The catalytic and photocatalytic decontamination of 2-CEPS was studied with anatase, rutile, mixture of 80% anatase/20% rutil and bulk TiO_2 . The photocatalytic activity for the detoxification of 2-CEPS was higher than catalytic activity, especially for anatase and mixture of 80% anatase/ 20% rutile.

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