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Fluidized-bed photocatalytic degradation of airborne styrene

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Abstract

Monomeric styrene, an aromatic compound present in many industries involved in the processing of fiberglass reinforced plastic products, is potentially carcinogenic. Based on current literature, studies on the breakdown of styrene via photocatalysis are limited. This study aims to develop suitable photocatalysts to be used in the mineralization of styrene. In particular, two specific objectives are of interest: first, the development of photocatalysts which are able to work under ultraviolet (UV) radiation and potentially visible/solar light irradiation; secondly, the design of an efficient fluidized-bed photoreactor. Preliminary work done using titania-based catalysts incorporated into a designed bench-scale UV photoreactor indicates that up to 80% of styrene can be degraded to water and carbon dioxide, based on an effective concentration (C_0) of 300 ppm.

Keywords: Titanium dioxide; Titania; Pillared clays; Photocatalysis; Styrene; Fluidized-bed

1. Introduction

Compounds like acetone, trichloroethylene and benzene are commonly used or produced in industries. Such substances, commonly termed volatile organic compounds (VOCs), have relatively low boiling points and tend to occur in liquid–vapour form in ambient conditions. Traditional forms of abatement of such compounds include the use of methods [1] which may produce waste products (if regeneration options are not available), or are energy intensive (thermal degradation or condensation).

Monomeric styrene, an oily volatile substance, is considered one of the most important materials used in the production of plastics and rubber. It is reported that the highest human exposure to styrene is found in the manufacture of fiberglass reinforced plastic (FRP) producers [2,3], including bathtub and spa units, vehicle parts, boats, septic and water tanks, kitchen surfaces and ducts for power supply lines. The health effects of being exposed to styrene are reported extensively [4], including its listing as being potentially carcinogenic. In Australia, the Occupational and Health Administration standard for exposure to styrene is 50 ppm (210 mg/m^3) [5] for an 8-h time weighted allowable (TWA), while in the US, the recommended ceiling exposure is 200 ppm (850 mg/m^3).

Photocatalysis (part of the group of technologies known as advanced oxidation processes or, AOPs) promises an exciting and alternative form of treatment to the use of common forms of air pollutant control. It is potentially renewable, and under well-engineered conditions, produces water and carbon dioxide as end products. The use of a photonic source to excite electrons to the conduction band in a semiconductor material like titanium dioxide (TiO_2), serves to create positive holes necessary for the oxidation of potentially toxic compounds, thus forming a basis for heterogeneous catalysis to occur in the solid-gaseous phase.

Monomeric styrene, commonly used in the production of its polymeric form to be used in food packaging, surfaces and water or septic tanks, is an aromatic compound possessing a sweet odour at relatively lower concentrations. Whilst the potentially toxic effects of exposure to styrene have been extensively documented, studies involving the degradation of styrene via photocatalysis are limited in current literature [6,7]. Work involving the photodegradation of a similar compound (α-methylstyrene) was also reported recently [8].

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This study reports the use of a fluidized-bed UV photoreactor incorporating a titania-pillared clay (TPILC) catalyst to degrade monomeric styrene in air. The activity of well-characterized Degussa P25 TiO_2, supported on silica gel, is also included as a comparison. On a per unit mass basis, the amounts of titania present in TPILC and the reference catalyst are 20% and 10%, respectively.

2. Experimental

TPILC was prepared via a modified sol–gel method, using titanium (IV) isopropoxide as precursor to the titania pillars in the final material. An inorganic surfactant, Tergitol, TS-9 was also introduced into the starting mixture. The final catalyst was sized using a disc-mill (Fritsch Pulverisette 13 Laboratory Disc Mill, Biolab Australia), to a suitable mean diameter of about 440 μm (determined by laser light diffraction using a Malvern Mastersizer 2000). The particle size distribution of the catalyst used in the fluidization process is presented in Fig. 1.

Degussa P25 TiO_2 particles were loaded onto silica gel (250–500 μm) via a simple dip coating-calcination process. The product from this is named SGP251CC. Information regarding preparation of the catalysts described is detailed elsewhere [9].

An annular photoreactor was designed and built to test the activities of the catalysts developed. Fig. 2 depicts a schematic of the experimental set-up and a detailed view of the reactor. The reactor is of effective height 35 cm and cylindrical diameter 4 cm. A UV source (Heraeus TNN 10/12, 12 W) emitting UVC radiation with a peak occurring at 254 nm was used as the excitation source, with styrene-laden air passing through the reactor. Flowmeters (Cole-Palmer) having glass/stainless steel floats were installed at positions 1, 2 and 3, as indicated in Fig. 2(a). The minimum fluidization velocity (U_{mf}) (assuming mean particle size of 400 μm and density 700 kg/m^3 for both catalysts) was calculated as approximately 0.90 cm s^{-1}, according to the method of Wen and Yu [10].

The concentrations of styrene in influent and effluent (C) gas were monitored via gas chromatography (GC-8A with flame ionisation detector, FID) equipped with a packed column (Hayesep D, 100/120, 10′) and subjected to a temperature programme from 180 to 290 °C (4 °C/min). Intermediates formed in the catalyst after photoreactions occurred were leached using solid–liquid extraction and identified using GC–MS (Shimadzu QP 5050 fitted with a Phenomenex Zebron ZB5-w 30 m × 0.25 mm × 0.25 μm).

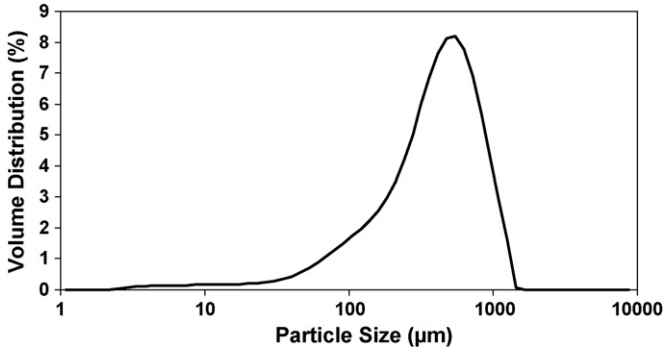

Fig. 1. Particle size distribution of TPILC based on volume distribution.

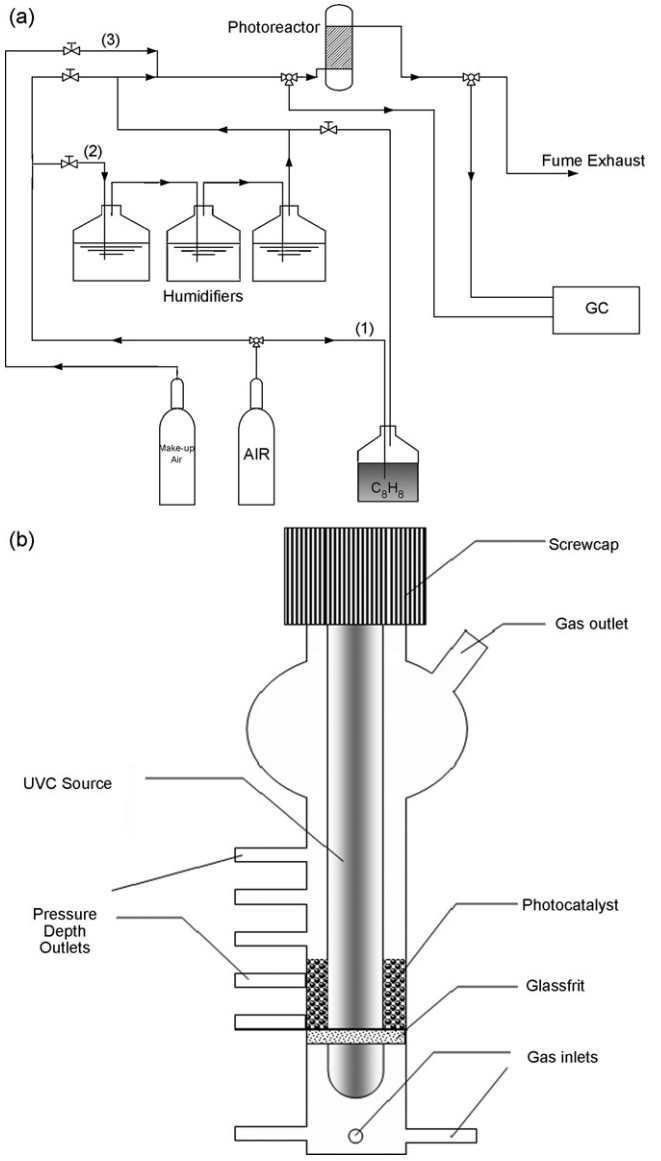

Fig. 2. (a) Schematic of experimental setup. (b) Detailed view of photoreactor.

3. Results and discussion

The photo-oxidation of airborne styrene was carried out using the earlier photoreactor described. The effects of flowrate (residence time) and relative humidity (RH) were investigated separately. In each experimental run, 2 g of catalyst was used. The reaction system was left to reach equilibrium in the dark before the UV source was turned on, thus ensuring that any changes in effluent concentrations of airborne styrene was not due to adsorption by the catalysts. Photolysis of styrene due to exposure to UV radiation was observed, in separate control experiments, to be negligible in all cases.

The concentration of styrene in the effluent stream was observed to decrease with the time of exposure to UVC

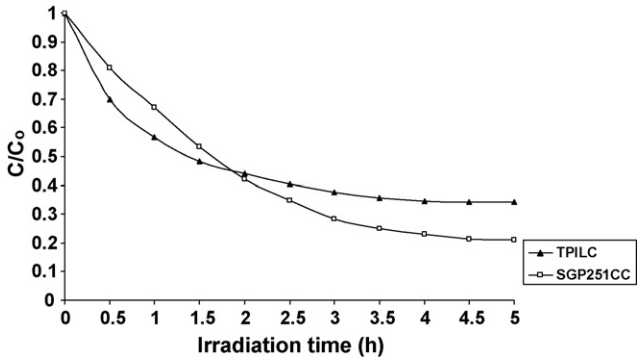

Fig. 3. Photocatalytic degradation of styrene (2 g catalyst, $C_0 = 300$ ppm, flowrate = 1.74 cm s^{-1}, RH = 0%).

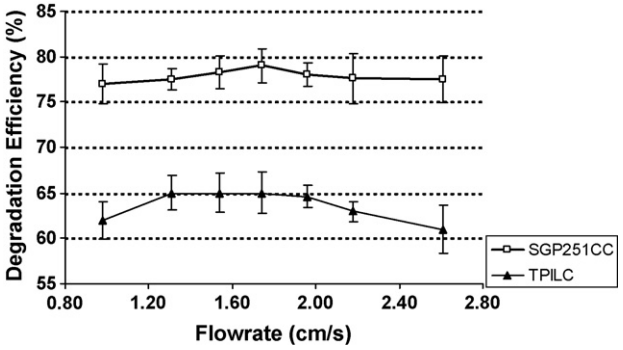

Fig. 5. Photocatalytic degradation of styrene under different flowrates (2 g catalyst, $C_0 = 300$ ppm, RH = 0%).

illumination. Fig. 3 shows typical data corresponding to degradation of airborne styrene under certain experimental conditions. The initial rate of degradation of styrene in the presence of SGP251CC is higher compared to TPILC. After about 1.8 h, the concentration of styrene in the effluent is similar ($C/C_0 = 0.46$) in both experiments. Five hours after the start of the photoreaction, the steady-state values of C/C_0 are 0.4 and 0.25 for TPILC and SGP251CC, respectively. This relatively long time required for the reaction system to reach steady-state, similarly observed in the photodegradation of carbonyl compounds [11] is likely to be due to progressive dilution of the gas mixture present in the freeboard volume of the reactor. Assuming a well-mixed freeboard volume (V_{FB}) of 250 cm^3, and a known volumetric flowrate of the influent/effluent gas stream (v), the space velocity (V_s), is described by

$$V_s = \frac{v}{V_{FB}} \quad (1)$$

Fig. 4 depicts the correlation between gas flowrate and dilution rate of the gas mixture in the freeboard volume of the photoreactor. As the flowrate of the influent gas mixture increases, the space velocity of the system increases linearly.

The effect of varying flowrate on the photodegradation of styrene was investigated. Based on the results presented in Fig. 3, and other experimental runs conducted in similar fashion (except for a change in flowrate in each run), the results are grouped and shown in Fig. 5. Generally, in these runs, the time required to reach steady-state was in the range of 4.5–5 h. The beds of catalysts were generally well-fluidized up to about 1.96 cm s^{-1}. Flowrates beyond this caused bubbles to be introduced into the bed. This would have decreased the contacting areas between the photocatalysts, reactants, and incoming photons of UV irradiation. On the other hand, mass transfer limitations may have been present, with the use of lesser than optimum flowrates. For SGP251CC, the optimum degradation efficiency occurs at 1.74 cm s^{-1}, whereas for TPILC, this optimum is achieved between a range of flowrates (1.31–1.74 cm s^{-1}).

The effect of RH on the degradation efficiency of styrene is shown in Fig. 6. The degradation efficiency of styrene for TPILC increases, as RH increases from 0 to approximately 2%. Beyond 2% RH, the efficiency decreases. For SGP251CC, the effect of increasing RH is not as well-pronounced, although a decrease in the efficiency of styrene degradation is observed at RH of more than 4%.

It is well known that the presence of water in photocatalytic reactions serve to create hydroxyl radicals [12] necessary for the oxidation of organic compounds. Studies involving the oxidation of various organic molecules indicate that the presence of water (RH) up to 50% may be used before deactivation of the related catalysts occurs [13,14]. In this study, it is likely that the different specific surface areas of the catalysts contribute significantly to the different responses to changes in RH. The Brunauer, Emmett,

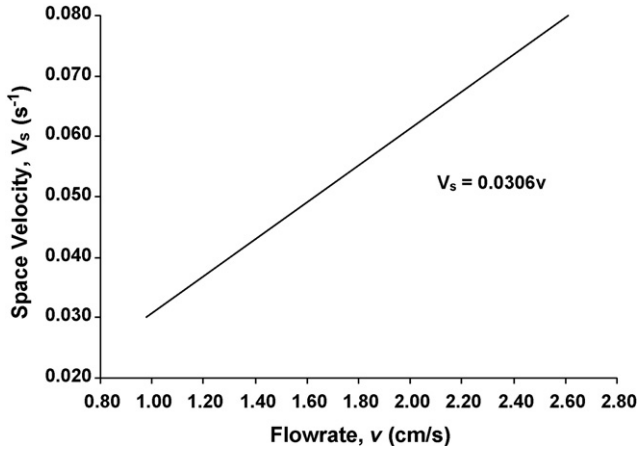

Fig. 4. Dependence of space velocity on inlet flowrate.

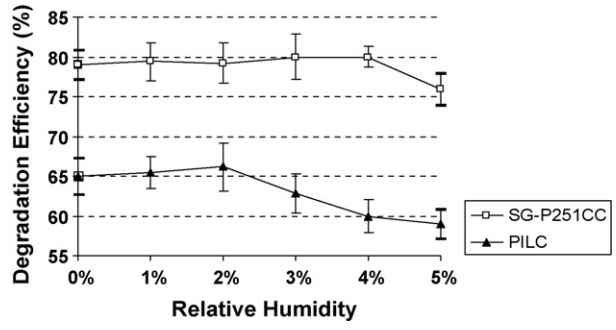

Fig. 6. Effect of RH on Degradation of Styrene (2 g catalyst, $C_0 = 300$ ppm, flowrate = 1.74 cm s^{-1}).

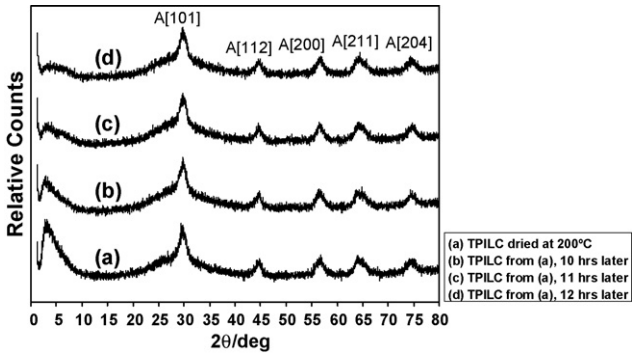

Fig. 7. In situ observation of the adsorption of moisture in TPILC based on X-ray diffraction.

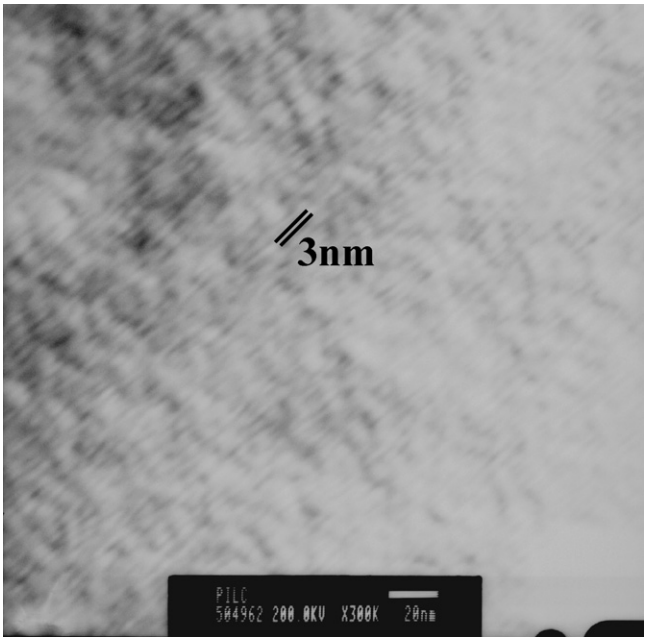

Fig. 8. Layered structure of TPILC as observed using transmission electron microsopy (TEM).

and Teller (BET) surface areas for TPILC and SGP251CC are 720 and 350 m^2/g, respectively. The increase in the degradation efficiency in using TPILC is likely to be due to further exfoliation of the titania-clay layers in increasing RH from 0 to 2%. This may have increasingly exposed the titania pillars to styrene molecules. Contradictorily, any increase in RH thereafter induces competitive adsorption of water over styrene molecules in the catalyst, thereby reducing the degradation efficiency of the system.

An additional investigation of the effect of moisture on TPILC was carried out, and is depicted in Fig. 7. In this study, a sample of TPILC was dried at 200 °C overnight and studied under in situ X-ray diffraction (Rigaku MiniFlex, Co Kα radiation) for up to 12 h at a room humidity level of 68%. Characteristic anatase peaks of titania (A) are observed, together with a 2θ-peak at approximately 3.4°, corresponding to a basal spacing of about 3 nm. This peak declines with time, indicating that the initially layered structure of the titania-pillared clay is continually exfoliated as moisture is adsorbed. This characteristic basal spacing is further observed in samples observed under transmission electron microscopy (Fig. 8).

In an attempt to deduce the resulting carbonaceous material after photocatalysis, intermediates in the spent photocatalysts (both SGP251CC and TPILC) were leached using methanol, and two main substances, namely, benzaldehyde and dimethylacetalbenzene (in similar amounts), were identified. A previous study [14] on the intermediates generated in the photocatalytic oxidation of toluene also identified benzaldehyde as one of the main intermediates.

4. Conclusion

Monomeric styrene of about 300 ppm concentration was photocatalytically degraded in a fluidized-bed reactor. The effects of varying flowrate and relative humidity based on two different catalysts (SGP251CC and TPILC) were investigated. Based on specific amounts of catalysts used (2 g), the amounts of titania present are approximately 20% and 10%, respectively. Although the silica-supported P25 catalyst presented higher degradation efficiency in all cases, arguably, TPILC is a better catalyst, based on actual amounts of titania present in the catalysts. It is also likely that the continual exfoliation of the layers of TPILC exposed the titania pillars further to the UVC irradiation employed in the reactor. The mechanisms and pathways leading to the formation of the intermediates (benzaldehyde and dimethylacetalbenzene) are at present not fully understood, and further work will be carried out, attempting to propose possible reaction pathways.

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