

## Gas Phase photocatalysis application on Photooxidation of 2 Chloropropane

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### ABSTRACT

Most industrial chemical processes require large amounts of heat and pressure, whereas photocatalytic reactions may be carried out at room temperature and ordinary pressure. This study focuses on using UVA-activated TiO<sub>2</sub> to drive organic processes in order to examine the latter. In this research, Glass beads were immobilized with TiO<sub>2</sub> using a unique technique called gyratory induced adhesive coating. The catalyst was subsequently immobilized and employed in a gas phase flow reactor designed for experiments on the oxidation of 2-Chloropropane (2-CP).

**Keywords:** Gas phase photocatalysis, Photooxidation, UVA-activated TiO<sub>2</sub>, Gyratory induced adhesive coating, 2-Chloropropane (2-CP)

### INTRODUCTION

The concerns of energy security and climate change have accelerated the development of more energy-efficient devices in many spheres of society in recent years. By 2050, it is expected that the chemical industry's global energy consumption, which accounted for 7% of global energy output in 2011, would have doubled to over 40 EJ (1 EJ =  $1 \times 10^{18}$  J) (Elzinga *et al.*, 2014). Therefore, one crucial step in reducing our CO<sub>2</sub> emissions is the creation of more effective chemical syntheses.

High pressures and temperatures are necessary for many significant chemical processes, even when a catalyst is present (Nguyen *et al.*, 2013). Alternatively, photocatalytic processes can occur at standard temperature and pressure and require considerably milder energy sources (the sun is typically seen as a viable possibility) (Nair *et al.*, 2019). This provides low-cost, low-energy substitutes for typical synthetic reactions.

### MATERIAL AND METHODS

#### Catalyst Immobilisation

#### Dip Coating

Silica gel beads was investigated as a catalyst support first due to their high surface area and low cost. To prevent breaking when exposed to water, the beads was hydrated by 72 hours of exposure to water vapour in an evacuated desiccator.

To separate the particles, a suspension of P25 (25.0 g/L) and sodium dodecyl sulphate (SDS) (1.50 g/L) was sonicated (Rezende *et al.*, 2016). A sample of hydrated silica gel and glass beads was immersed in the solution, drained, and dried for 2 hours under vacuum at 80°C. They were also calcined for 1 hour at 550 °C; lower temperatures did not completely eliminate the SDS residue (as demonstrated by a beige/brown discoloration), whilst higher temperatures would have resulted in particle sintering and anatase conversion to rutile (Li *et al.*, 2013).

### Gyratory-Induced Adhesive Coating (GIAC)

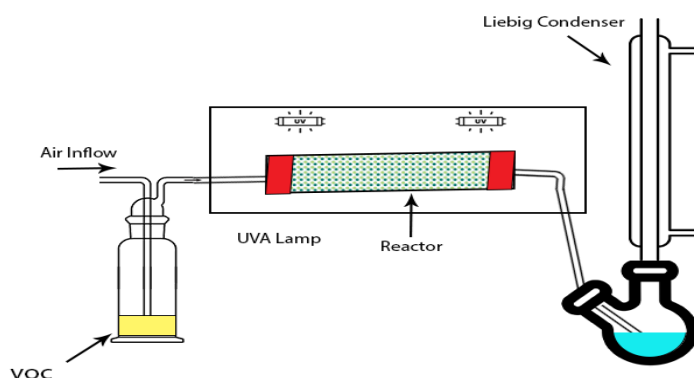
Mechanical ball milling is an effective method for grinding and de-aggregating crystalline materials (Achimovicová and Baláz, 2015). Due to the fact that the glass beads was spherical, this gave an appealing alternative particle separation strategy.

The glass beads were cleaned with acetone and ethanol before being refluxed in 5 M NaOH for 30 minutes to enhance the surface OH group density and promote catalyst adhesion (Christopher *et al.*, 2015; Singh *et al.*, 2011). The glass were rinsed with deionized water until the washings are neutral, washed again with acetone, compressed air dried, and precisely weighed ( $\pm 0.5$  mg). They were then be placed overnight in a rotating drum with suitable quantities of P25 to yield loadings of 1, 3, 5, and 7 mg/g, followed by a second weighing to confirm the catalyst loading. A small sample of base-treated and untreated beads will be coated with P25 (0.3 mg/g) using this procedure to assess the significance of the base treatment.

### Flow Reactor Design

A gas-phase flow reactor was used. The reactor was designed separately, although it was subsequently discovered to be comparable to that of Verbruggen *et al.* (2011).

The reactor (**Figure 1**) was made out of a quartz tube (400 mm length, 24/28 mm internal/external diameter) The reactor's tube area was filled with immobilized catalyst, and each end was sealed with a rubber bung. The rubber bungs were rebuilt with steel tubing (6 mm external diameter) to provide adequate gas inlet/outlets (sealed with glass wool) and (airtight) light connection to an external circuit. To contain the radiation, the reactor was encased with aluminum foil. VOCs were introduced at regulated flow rates through the headspace vapour of a Dreschel container. The dead reactor volume will be estimated to be around 56 cm<sup>3</sup>.



**Figure 1.** Flow reactor assembly with reactor tube exposed for illumination purposes and solvent trap

### Chloropropane (2-CP) oxidation

Flow reactor was assembled with the cold trap at the end of the line to capture oxidation product. After reaction, the trap was sealed and allowed to warm to room temperature, and the contents analysed. 2-chloropropane peak was present.

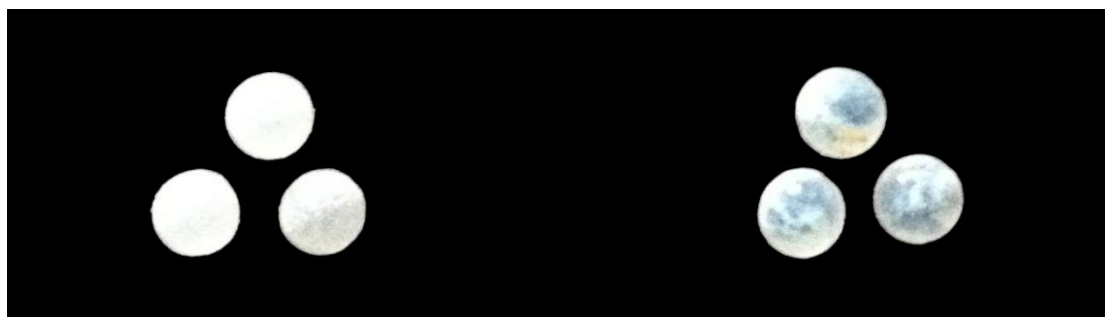
## RESULT AND DISCUSSION

### Catalyst Immobilisation

Two methods of catalyst immobilisation used were dip coating and GIAC method. The GIAC method gave a much more stable, well-dispersed and controllable catalyst loading than the dip-coating method (Figure 2 and 3), so GIAC was used for the remainder of this work. The GIAC-coated beads, 1 mg/g was the most homogeneous loading amount; larger aggregates of the catalyst formed as loading was increased. Dip-coating gave a less homogeneous loading with denser clumps of catalyst.



**Figure 2.** Glass beads coated using the GIAC method. Left to right: loadings of 0, 1, 3, 5 and 7



**Figure 3.** Comparison of glass beads coated using the GIAC (left) and dip-coating (right) methods.

The GIAC method (Left) shows a much more homogeneous loading than dip coating (Right).

A 1 mg/g loading had excellent adherence stability to the glass beads and a scratch test conducted on the beads has no visible loss of catalyst. Meanwhile, negligible amounts of  $\text{TiO}_2$  remained in the GIAC apparatus after the 3 mg/g and 5 mg/g coatings were performed, some catalyst would detach from the beads upon handling. A significant amount of catalyst remained in the apparatus after the 7 mg/g coating. Mechanical abrasion between a finger and thumb would remove much of the catalyst from the >1 mg/g loaded beads; the coatings were similar physically to the 1 mg/g loading. The 1 mg/g loading was the most suitable for repeated handling and usage due to its mechanical abrasion resistance therefore making it the most industrially relevant. 1 mg/g loading however, is the least active of the loadings tested towards acetone decomposition. The 7 mg/g loading was also not

the most active, indicating that the coating's opacity becomes an issue at this point.

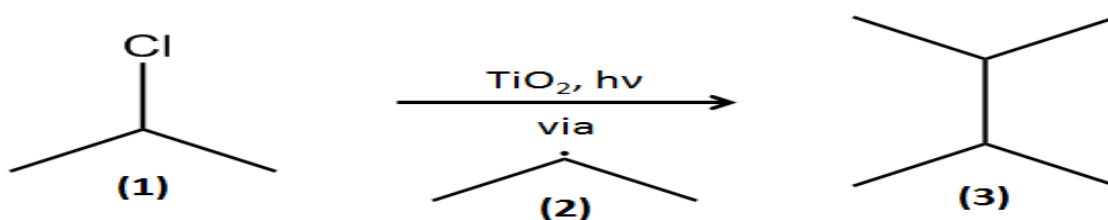
Overall, the 7 mg/g was unacceptably unstable while the 1 mg/g loading showed undesirably low activity when used in the present reactor setup. The 3 and 5 mg/g loadings were comparable with intermediate stability; the latter was used in the remainder of this work due to its greater activity.



**Figure 4.** Gyrotory Induced Adhesive Coating Method

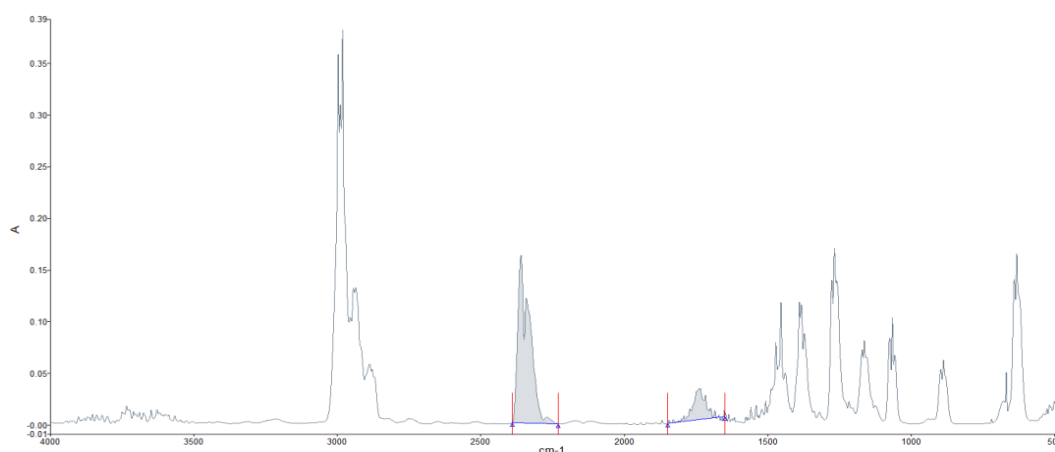
### 2-Chloropropane (2-CP)

It is well documented that, during photooxidation of chloroorganics, Cl is often abstracted first (Tan *et al.*, 2017; Uzun *et al.*, 2021). This experiment was initially conducted in an attempt to effect the following reaction:

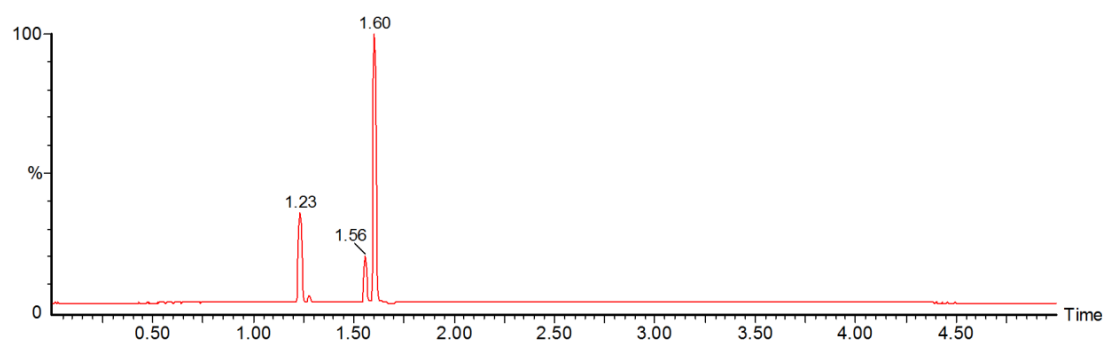


**Scheme 1.** Proposed photocatalytic Cl abstraction from 2-chloropropane and subsequent dimerization of the resultant isopropyl radical.

This led to CO<sub>2</sub> and carbonyl peaks in the FTIR spectra (Figure 5), and a cold trap was used to trap the reaction products. The resulting Chromatogram (Figure 6) showed a peak for acetone, as well as air, water and 2-CP, indicating partial oxidation and confirming the carbonyl peak in the IR spectrum. Unfortunately, no peak was observed for (3). The photooxidation of 2-CP is therefore unlikely to involve intermediate (2) or, if it does, the concentration was too low for any appreciable concentration of (3) to form during the reaction.

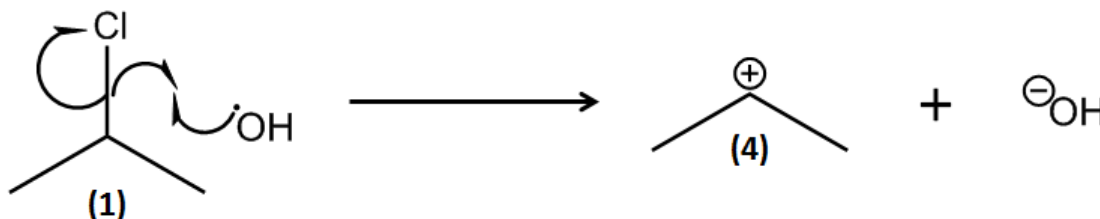


**Figure 5.** Typical FTIR spectrum during 2-CP photooxidation. CO<sub>2</sub> asymmetric stretch and Carbonyl stretch peaks are highlighted (2390 – 2230 cm<sup>-1</sup> and 1850 – 1650 cm<sup>-1</sup>, respectively).



**Figure 6.** Chromatogram of the cold-trapped 2-CP photooxidation exhaust vapour.

Air (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>) eluted after 1.23 minutes; acetone peak at 1.56 minutes; 2-CP peak at 1.60 minutes. However, the carbon backbone of the compound was left unchanged upon conversion to the major oxidation product (acetone), concurrent with the higher rate of abstraction of Cl than C. It also hints that the reaction proceeds, in part, via either radical (2), or the Cationic form. The latter seems more likely due to the electronegativity of Cl, a possible Mechanism is shown in Scheme 2. Again, the data here shows the reactor is capable of partial VOC oxidation (Marotta *et al.*, 2010).



**Scheme 2.** Possible mechanism for the initial photodegradation step of 2-CP, where the ·OH Species is formed.

## CONCLUSION

A gas-phase, flow-type photoreactor was successfully designed and put into use in this work. Additionally, a new, complementary catalyst immobilization technique called GIAC was created. The highly active, readily accessible photocatalyst (Aeroxide® P25) was employed in the immobilization approach, which was very easy to put into practice. The lowest loading required to ensure excellent adherence stability has encouraging industrial implications. The immobilization method's photoactivity may also be enhanced (without compromising this stability) by using smaller glass beads with a higher packing density and surface area. Photocatalytic breakdown of 2-chloropropane was effectively accomplished. And the reactor developed here may serve as a foundation for the development of residential, commercial, and industrial air purification systems in the near future. The potential of this reactor for significant synthetic chemical transformations was also successfully proven by the capability of partial photooxidation. The main benefit in this case is that the only energy source used was UVA radiation from a low-power, cool Cathode fluorescent light. Further evidence was obtained for the relatively rapid rate of the initial Cl abstraction step during the photooxidation of organic molecules containing Chlorine. Additionally, a straightforward pathway for converting a chlorocarbon functionality to a ketone was shown. Hopefully, our effort will prove to be a significant first step towards a more effective and sustainable future for the world's chemical sector.

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