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Gas-phase Photocatalytic Oxidation of 1-Hexene Using Heterogeneous Semiconductor Materials

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Abstract

Photo-catalytic reactions have been carried out and proved to be conducted under mild conditions in contrast to several conventional industrial chemical processes, which involve the use of high amounts of temperature and pressure. In this work, an investigation of the photo-catalytic oxidation of 1-hexene was carried out using UVA-activated TiO_2, and coupled TiO_2/WO_3 to drive organic reactions. Different mol % of WO_3 ranging from 1-7mol% were used to monitor effect of coupling amount. The chosen photo-catalyst was immobilized on glass beads using an innovative *in-house* procedure. The immobilized catalyst was then used in a vapour-phase flow reactor designed for alkene photo-oxidation studies. It was possible to establish oxidation rates of 0.14±0.02 mmol/h for 1-hexene with TiO_2/WO_3 (1mol %). 1,2-epoxyhexane was successfully synthesized from 1-hexene achieving 15.9% conversion and 41% and 54% selectivity for the 1-hexene, 1,2-epoxyhexane and CO_2 respectively when H_2O/O_2 was used as oxidant. Selectivity of 96% and 97% for CO_2 were achieved with N_2 and O_2 respectively. No epoxide was formed with either N_2 or O_2 alone.

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Keywords: Alkene, Photo-catalysis, Flow reactor, Titanium dioxide, Glass beads

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1. Introduction

The epoxidation reaction of alkenes has seen a surge in interest for decades now owing to the enormous usefulness of the epoxides. With nearly 7.5 Mt of propylene oxide produced annually, it ranks among the top 50 list of important

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chemicals. Heterogeneous photocatalytic oxidation has been adopted by researchers due to its suitability for oxidising both organic and inorganic compounds. It only requires low temperature and pressure [1,2] and more interestingly, employs the use of inexpensive, readily available semi-conductor materials such as TiO_2, ZnO, ZnS, CdS, Fe_2O_3, and SnO_2.

Epoxidation of hexene in liquid phase have been studied using different catalysts and solvents in the presence of hydrogen peroxide as oxidant. Vongani and Tebello, [3] investigated the use of the derivatives of Gallium phthalocyanines (GaPc) and Indium Phthalocyanines (InPc) as catalysts to photo-oxidize 1-hexene. They obtained 1,2-epoxyhexane and 1-hexen-3-ol as the photocatalytic oxidation products. The conversion values of the reactant (1-hexene) and selectivity of the product (1,2-epoxyhexane) were generally higher for InPc derivatives. Similarly, Li *et al.* [4] carried out epoxidation of 1-hexene with hydrogen peroxide over nitrogen incorporated TS-1 zeolite. They found that methanol as a solvent had higher catalytic activity resulting in higher selectivity of epoxide compared to acetonitrile solvent. However, liquid-phase epoxidation of alkenes has been characterised by the challenge of product catalyst separation. Choice of suitable solvent is also problematic. This study reports a simple procedure for epoxidation of 1-hexene in gas-phase using TiO_2 and WO_3-coupled TiO_2 supported on glass beads. Our novel coating procedure produced a gas-phase photo-reactor with good catalyst-substrate contact as pre-treatment of the glass beads gave a homogeneous adhesion hence an even distribution of the catalyst within the reactor. TiO_2 was chosen as the benchmark photo-catalyst for this work considering that it is one of the most important and popular compounds for a multitude of applications; it is chemically inert, readily available and can easily be produced [5]. Photo-activation of TiO_2 with UVA can be achieved easily, a factor that enhanced its relatively high reported quantum efficiency. In order to prevent the need for lengthy characterisation of catalysts, P25 (Titanium (IV) oxide, 21 nm particle size) was used throughout this work for consistency, since it is often used as a “benchmark” in the literature due to its (relatively) well-defined structure as well as consistent photo activity.

The aim of this study is to achieve photo-oxidation of gas-phase 1-hexene with TiO_2 supported on glass beads using combination of H_2O/O_2 by a means of modified GC-MS auto-sampling procedure which allows easy tuning of the reaction parameters such as partial pressures of the reacting gases and instantly monitors effect on the reaction. This procedure give a more accurate results than the manual injection of gases into the analytical instruments thus, it is beneficial for kinetic studies.

During the present work it was possible to study the photocatalytic oxidation properties of a variety of nanostructured materials, which led to the development of highly efficient photocatalytic reactors for the photo oxidation of 1-hexene in gas phase. The development of the technologies presented here was performed in such a way as to ensure that their industrial applicability is retained and enhanced. Furthermore, in addition to the role of the reactants as photocatalytic oxidation agents, it was also possible to demonstrate the potential of the developed reactors as means of synthesizing organic precursors that are rare and novel, owing to the fact that the synthesized product exiting the reactor can directly react with another substance in tandem to yield new products.

2. Experimental

2.1. Catalyst support and immobilization

As it has already been established that dip-coating method of immobilizing catalysts has a number of drawbacks hence, less efficient, a new and reliable in-house technique was used for the first time throughout this work since the glass beads (soda-lime glass beads; 1.0-1.5mm diameter) were spherical. The glass beads were washed with acetone and then refluxed for 2 hours in 6M NaOH. This was done to increase the surface OH group density and consequently enhance catalyst adherence unto the beads. The glass beads were rinsed with deionised water until the washings were neutral, then rinsed with ethanol, dried with compressed air and accurately weighed to account for any loss in mass that could have resulted from the base treatment. They were then left in a rotating drum overnight with appropriate amounts of catalyst to give loadings of 1-8 $mg_{catalyst}/g_{beads}$, followed by a second weighing to check the catalyst loading.

2.2. 1-hexene oxidation reaction

The 1-hexene oxidation reaction was performed using a reactor similar to that used by Verbruggen *et al.* [6]; but was independently modified by adding extra lamps on the outside walls of the reactor tube. The reactor (**Figure 1**)

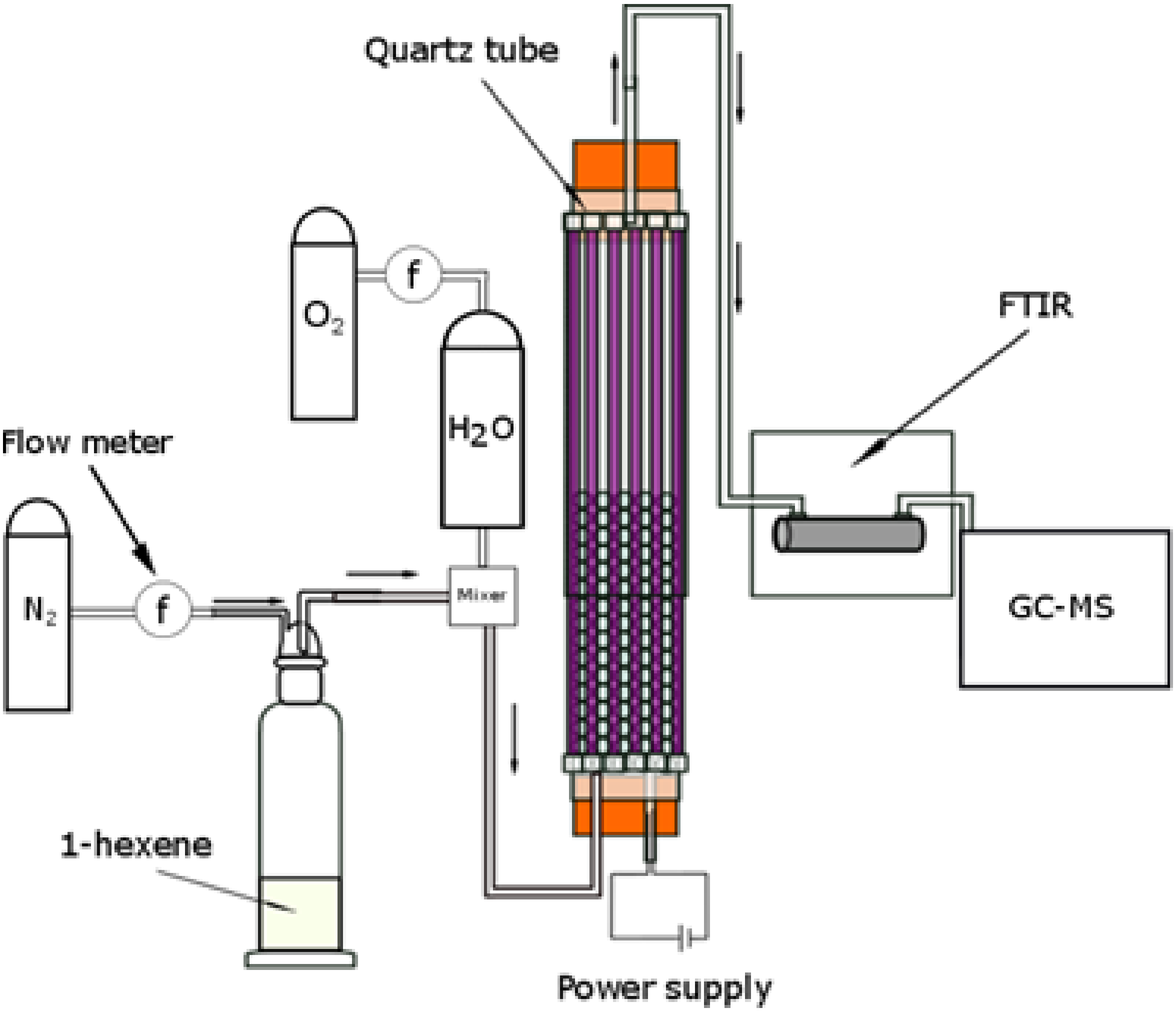

Figure 1. Flow reactor assembly

consisted of a quartz tube (400 mm length, 24/28 mm internal/external diameter) surrounded with 8 cold-cathode fluorescent UVA lamps (purchased from Xenta) each being; 305 mm long and 4.0 mm diameter. Another lamp was placed in the interior of the reactor tube making it a total of 9 lamps each having a peak intensity at 365.44 nm and 22.6 mW power output. Aluminium foil was wrapped around the reactor to maximize the UV radiation contact with the photo-catalyst. Catalyst coated glass beads were used to fill up the remaining space in the reactor tube. The dead reactor volume was calculated to be approximately 56 cm^3.The temperature of the reactor was measured and found to rise to a maximum of 62.4°C over 2.5 h, after which it remained constant.

In order to admit the 1-hexene in a gas-phase into the reactor, during the experiment, a known amount (5 ml) of the 1-hexene in liquid form was placed in a Dreschel bottle through which a continuous flow of N_2 gas, which served as a carrier gas at a flow rate range of 0.9-1.2 L/h, flown in an up-flow configuration to ensure adequate purging of the reactor with the 1-hexene. These steps were repeated prior to each run. In subsequent reactions, the N_2 gas was substituted with O_2 as the carrier gas and later O_2 and H_2O were simultaneously introduced into the reaction system. The length of the dip tube in the Dreschel bottle was adjusted in order to maintain constant concentration of the substrate (1-hexene) during the experiments.

After attaining a steady state flow through the photo-reactor, the lights were turned on and the reactor exhaust passed through a purpose-built, gas-phase flow cell which was built of a steel tube (130 mm length, 18 mm internal

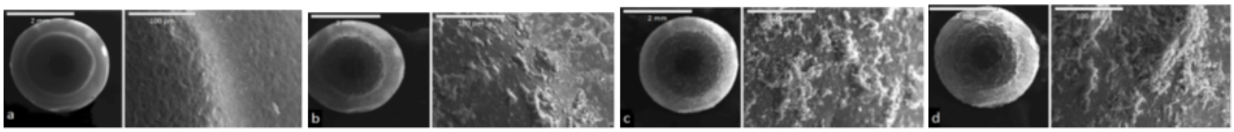

Figure 2. Glass beads coated with catalyst as observed under SEM. (a) 1 mg/g; (b) 3 mg/g; (c) 5 mg/g; (d) 7 mg/g

diameter) with inlet and outlet ports and NaCl windows. By monitoring the concentrations of some selected species, it was possible to gain insights on the photo-oxidation of 1-hexene by TiO_2 photo-catalysts in the gas stream.

A PerkinElmer Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the concentration of 1-hexene and the products of the reaction. The CO_2 peak area was measured between wavelength of 2390 and 2230 cm^{-1}. The 1-hexene peak was measured from 1695-1600 cm^{-1}. In order to establish reliability of procedure, a second peak was looked at from 3170-2820 cm^{-1} which is a common peak for the C-H stretch. This peak was also used to confirm the formation of epoxides as no other side products were observed. The detection limit for the FTIR was found to be approximately 3 μmol dm^{-3}.

A Varian CP-3800 gas chromatograph was used to separate the compounds and a Varian Saturn 2000 mass spectrometer was used to analyse the separated products. The column (Rxi-5Sil MS 30m x 0.25mm ID x 0.25um df). Various coating amounts ranging from 1-8mg of catalysts per gram of the glass beads were loaded onto the reactor separately and photo-catalytic efficiency measured.

In order to investigate the effect of modifying TiO_2 on the photo catalytic activity, various molar concentrations of WO_3 were added to the TiO_2 and the overall mixture coated on the glass beads.

Conversion and selectivity were defined as follows:

$$Conversion = \frac{Hexene_{initial} - Hexene_{final}}{Hexene_{initial}} x100(\%)$$

$$Selectivity = \frac{mol\ of\ Epoxide}{Hexene_{initial} - Hexene_{final}} \text{x } 100(\%)$$

3. Results and discussions

3.1. Catalysts immobilisation

Gas-phase photo-catalytic reactions are generally known to have advantages over liquid-phase systems which include higher operating temperatures consequently resulting in higher rates of reactions [7, 8]. Typically, a gas-phase, flow-type reactor affords the advantage of circumventing the catalyst/product separation problem. Flow rate/contact time can also be adjusted to yield different product ratios when required and continuous operation is possible [8]. Moreover, typical drawbacks of the liquid-phase such as leaching of the active site of the catalyst as well as choice of suitable solvent could be avoided in a gas-phase system [7]. Developing an efficient gas-phase photo-catalytic reactor requires the photo-catalyst immobilised on specific supports, the type of which influences the adsorption behaviour which in turn determines the decomposition rate of pollutants [2]. This was important in this work as it afforded the pressure build-up issues that are usually caused by non-immobilised photo-catalyst powders to be overcome while simultaneously enabling an effective and simple handling and use of the catalysts. As such, glass beads were used in this work due to their spherical shape (which afforded them high parking density), transparency to irradiation, high specific surface area, chemical stability and more importantly, their ability to bond strongly with TiO_2 without any negative effect to the reaction [1].

The Scanning Electron Micrograph (SEM) images of the catalyst immobilized showed a stable, well-dispersed and controllable catalyst loading (Figures 2). The base treatment initially carried out on the glass beads also led to a noticeably denser coating. Among the various catalyst loading amounts used, 1 mg/g was the most homogeneous. It was however, observed under SEM an increase in size of the aggregates of the catalyst as loading amount was increased.

Table 1. Hexene epoxidation tithe different catalysts and oxidants

Entry	Catalyst	Oxidant/ Carrier gas	Products	Conversion (%)	Selectivity (%)		TOF (s^{-1})
					CO_2	$C_6H_{12}O$	
1.	TiO_2 /5mgg^{-1}	Air	CO_2	4.4 ± 0.2	95	00	-
2.	TiO_2/5mgg^{-1}	O_2	CO_2	8.1 ± 0.4	98	00	-
3.	TiO_2/5mgg^{-1}	O_2, H_2O	CO_2, $C_6H_{12}O$	15.3 ± 0.1	57	38	0.004
4.	TiO_2/WO_3 99:1	Air	CO_2	4.8 ± 0.2	96	00	0.004
5.	TiO_2/WO_3 99:1	O_2	CO_2	9.4 ± 0.1	97	00	0.006
6.	TiO_2/WO_3 99:1	O_2, H_2O	CO_2, $C_6H_{12}O$	15.9 ± 0.2	54	41	0.009

3.2. Verifying reactions

To verify the reaction efficiency, 1-hexene oxidation with P25 and with coupled P25/WO_3 at different molar ratios was tested using three different oxidants/carrier gases: (1) N_2 (2) O_2 and (3) O_2/H_2O. In the case of N_2 and O_2 (cases 1 and 2), the partial pressure of each oxidant was set to be the overall partial pressure (20 kPa) of the reaction system as they both served as carrier gases throughout this work, while in the case of the mixture of H_2O and O_2, the pressures were set to be half of the final partial pressure in the reactor in order to minimise over saturation of the active sites of the catalyst. As expected, low conversions (4.4 % and 8.1% for N_2 and O_2 respectively) of 1-hexene were observed against the more than double the conversion in cases where H_2O was added as seen on Table 1. This shows that H_2O is an important component of this reaction due to the assumption that it supplies the catalyst a means of generating OH radicals which take part in the oxidation process. It is widely accepted that the two major mechanisms of formation of OH radicals involve the reaction of H_2O with $O_2{}^{-}$, which is formed as a result of electron attaching to O_2, and through hole-mediated reaction (oxidation) of adsorbed hydroxyl anions. (Hoffmann, 2008) [2].

Figure 3A was measured at room temperature using N_2 only, as the carrier gas. Upon attaining a steady flow of 1-hexene in the reactor the reactor was illuminated. The CH stretching band of =CH_2 groups at 3087cm^{-1} and the C=C at 1647cm^{-1} were used to identify 1-hexene [9]; CO_2 which was observed at 2380cm^{-1} appeared after 15min illumination and increased proportionately until steady state after ca. 1h of reaction time when no other changes were observed. This peak decreased sharply when the lights were turned off or in the absence of 1-hexene or catalyst confirming a clear photocatalytic effect. The CH_2 stretching modes were ascribed to the peaks at range 3000cm^{-1} and 2700cm^{-1} while those below 1500cm^{-1} were considered for bending vibration mode [10]; at 1415cm^{-1}, 1260cm^{-1} and 843cm^{-1} were all observed to increase in intensity as time of reaction increased while peaks at 1829cm^{-1}, 1647cm^{-1} and 994cm^{-1}were observed to decrease accordingly.

The photo-oxidation became stable and no other changes were observed after a reaction time of 1h. When H_2O was introduced to the system (Figure 3B), the peaks in the region between 3700 and 3000 cm^{-1} and those between 1700 and 1600 cm^{-1} were assigned to OH stretching and bending vibrations, respectively [11,12]. The increase in intensities of these bands with time is believed to be due to the gradual diffusion of H_2O molecules inside the pores of active site of the photo-catalyst.

The bands at 3087 and 1647 cm^{-1} gradually decreased in intensity and the former disappeared completely while the latter still remained after about 1h reaction time. Finally, the steady state spectrum of the epoxidation reaction was compared with that of a standard 1,2-epoxyhexane, the desired product, and both appeared to be similar, hence confirming the identity of the reaction products. In addition, the band at 1415 cm^{-1} was only observed for 1,2-epoxyhexane.

In order to study the intrinsic behaviour of catalyst within the reaction system, it is imperative that the reaction is performed under several conversion conditions rather than being limited by the stoichiometry of the reactants. In our work it became essential to verify that the partial pressure of H_2O/O_2 was constant throughout the reactor considering that different loading amounts of the catalyst were tested. Within our experimental conditions, the production of

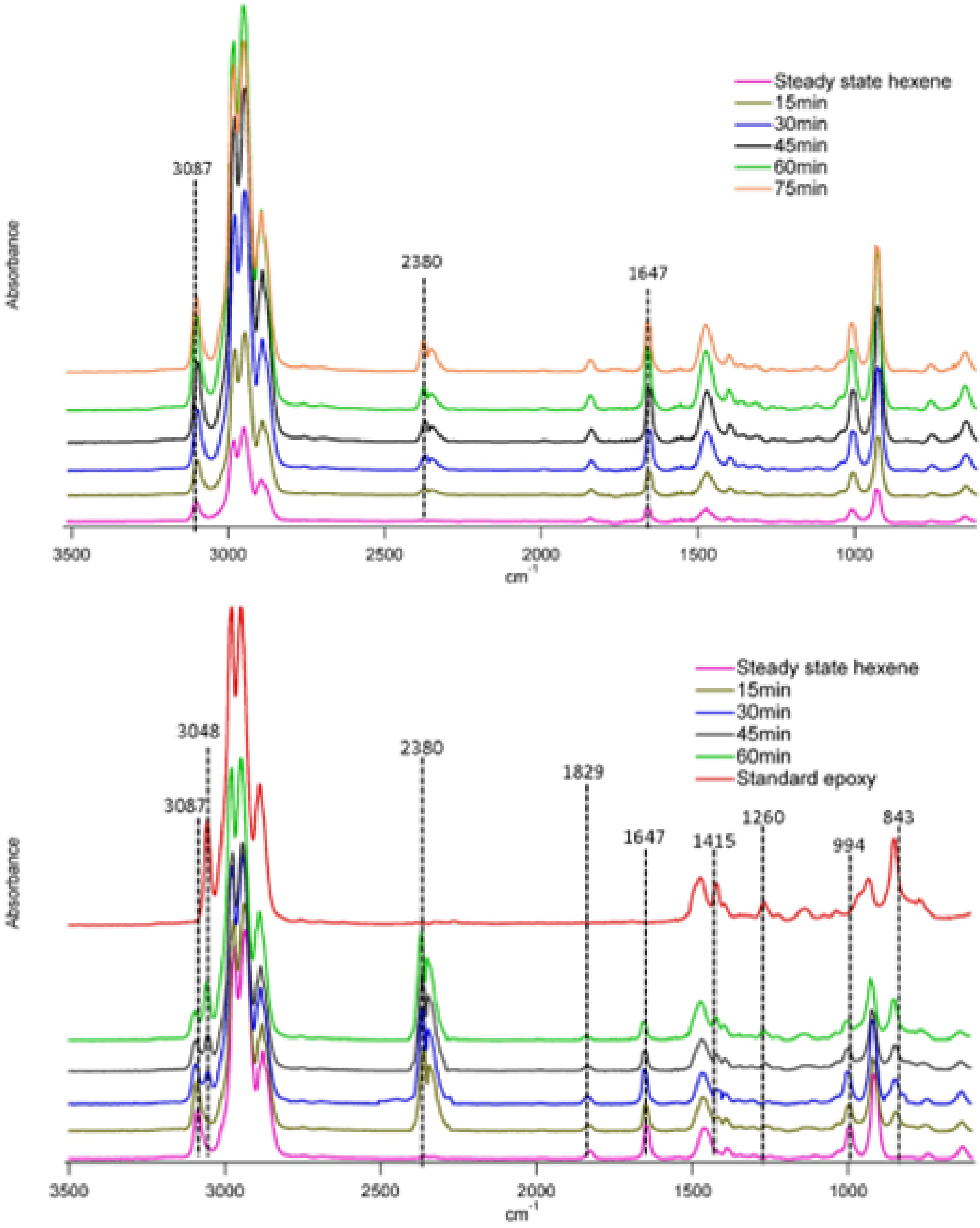

Figure 3. (A) IR Spectral of oxidation of 1-hexene; 5mg$_{TiO_2/WO_3}$/g$_{beads}$ (B) in the presence of O_2/H_2O

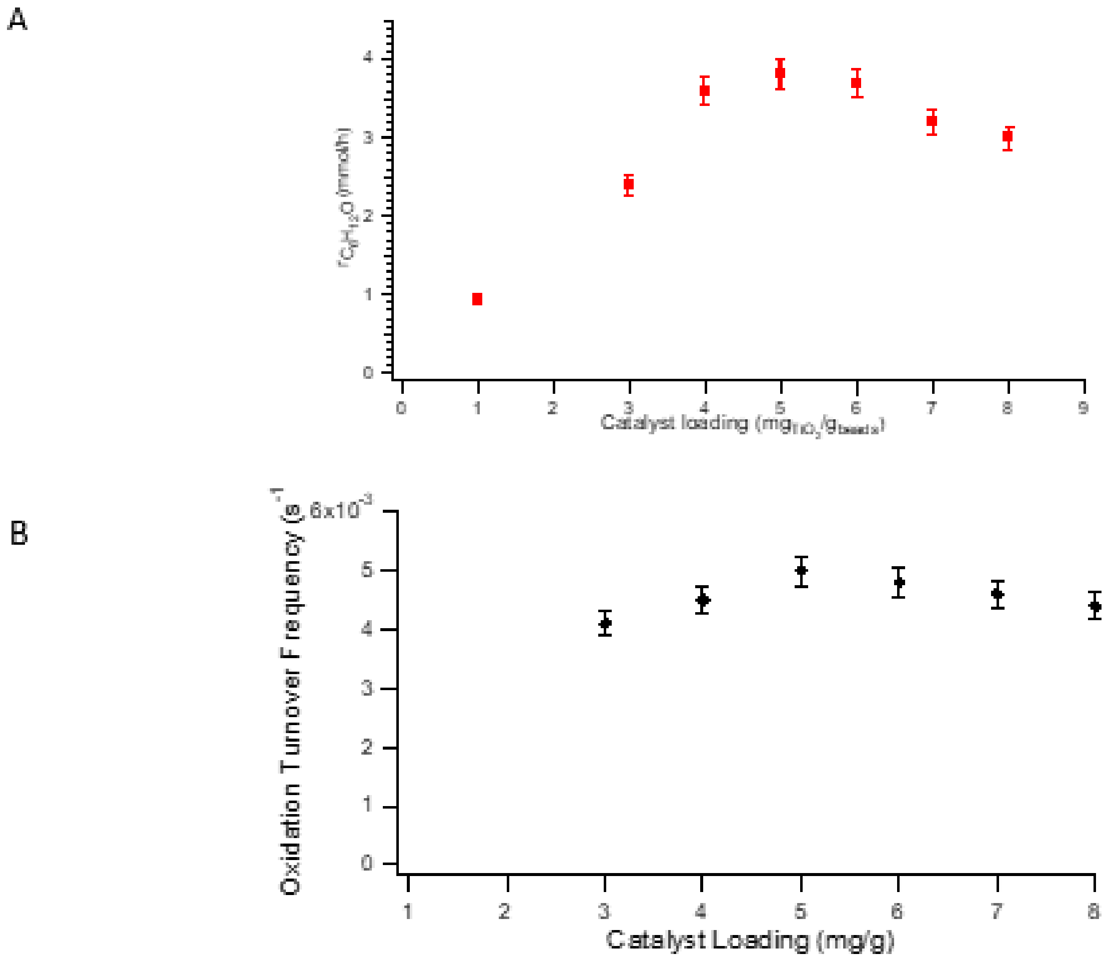

Figure 4. (left) Concentration of epoxy hexane per catalyst load and (A) 1-hexene epoxidation turnover frequency (taking as mol of epoxides produced per mol of Ti per second)

epoxide was observed to increase, first linearly until the catalyst loading reached 5mg/g then a decreasing pattern was observed beyond this loading amount (Figure 4A). Similarly, the turnover frequency (TOF) followed the same increasing and decreasing pattern as the catalyst loading amount increased (Figure 4B). This implies that the system was not limited by the partial pressure of H_2O/O_2 but by the excess loading of the catalyst since most of the active sites were not utilized as discussed in the next section. If the partial pressure of H_2O/O_2 had changed within the reactor, it would be expected then that the apparent TOF would decrease at least with one of the initial loading amounts (1-5mg/g). This result contradicts the findings of Ferrandez *et al.* [13]. where they observed that conversion was constant even at catalyst loadings above 10 mg, attributing their results to limited amount of H_2O_2 in the reaction system [13].

3.3. Effect of catalyst loading

Upon attaining steady state concentration of $C_6H_{12}O$ under UV illumination of the reaction system, the overall rate of $C_6H_{12}O$ production was established by combining the difference between the steady state $C_6H_{12}O$ concentrations in the presence and absence of UVa illumination, $[C_6H_{12}O]_{\Delta ss}$, with the flow rate, F, of the gas stream through the system (Equation1). This was determined for each reaction with different loading amounts. However, in this work consideration was made on the overall rate of $C_6H_{12}O$ production since it enables a better representation due to the effect of the gas stream flow rate over the absolute rise of $C_6H_{12}O$ concentration.

$$\underline{d}[C_6H_{12}O]/dt = F[C_6H_{12}O]_{\Delta ss} \quad (1)$$

The amount of catalyst loading has been reported to affect photocatalytic activity [13]. This was also observed in this work. Figure 4A shows the rate of $C_6H_{12}O$ production achieved during the photo-oxidation of 1-hexene using glass beads with different loading amounts of catalyst. It can be seen that the amount of $C_6H_{12}O$ produced increased proportionately as the loading amount of catalyst increased until a maximumrate of 3.87 ± 0.08 mmol/h for a catalyst loading of 5 mgTiO_2/g$_{beads}$was reached.

However, as the catalyst loading was increased to 6mg/g and above, the $C_6H_{12}O$ production rate was observed to decrease proportionately as in figure 4A. This observed trend can be attributed to an excessive catalyst loading on the glass beads. Indeed, one would expect that an increase in catalyst loadings would inevitably lead to an increase in photocatalytic activity owing to the fact that more active sites for the photo-oxidation of organics were introduced into the system. But the increased loadings also resulted in an increased UVa adsorption of each individual bead, hence, only the beads closest to the UVa lamp would become photo-active, consequently inhibiting the beads furthest from the light source. Moreover, due to the non-linear, flow pattern of the gas stream through the reactor, the inhibition of the outer beads results in a significant loss in 1-hexene photo-oxidation. Therefore, due to the above-mentioned effects, an optimal loading amount of 5mgTiO_2/g was established and adopted throughout this work.

3.4. Catalyst modification

In order to test the effect of modifying P25 catalyst on the photo-oxidation of 1-hexene, various molar concentrations WO_3 were physically added to P25 since WO_3 serves as an electron accepting species [14]; WO_3 has a suitable conduction band potential that allows the transfer of photo-generated electrons from TiO_2 resulting in an effective charge separation [14]; In addition, when a monolayer of WO_x species is formed on TiO_2 a significant increase in the surface acidity of TiO_2 can be achieved since WO_3 is 15 times more acidic than TiO_2 [15]; Figure 5 shows the effect of P25 modification on the concentration of 1-hexene. The coupled catalyst containing 1% mol WO_3 showed the highest photo-catalytic activity of up to 90% compared with the other samples. The increase in the photo-catalytic activity can be attributed to improved charge separation. As the loading amount of WO_3 increased to 3% mol or higher, the activity decreased. The reduced activity was attributed to the dilution effect of the non-photo-active WO_3 phase [14].

Upon doping TiO_2 with WO_3, the photo-generated electrons are transferred to the conduction band of WO_3 which lies lower than that of TiO_2, while the photo-generated holes accumulate in the valence band of the $TiO_2$to be scavenged by the oxidation process simultaneously, the photo-generated electrons migrate to the surface of the WO_3 effectively reducing bulk recombination [14]; Moreover, the increase in acidity of coupled TiO_2/WO_3 can lead to absorption of more hydroxyl groups and simultaneously more organic reactants on its surface which can result into an improved photo catalytic activity in comparison with pure TiO_2 photo catalyst.

The production of $C_6H_{12}O$ within our experimental conditions was stable throughout the period of this work and beyond as shown in Figure 6. This shows that the catalyst was not deactivated throughout the reaction and that the feeding of 1-hexene and the various oxidants was also steady.

3.5. Co-products

The gas-phase 1-hexene oxidation with H_2O/O_2 over the TiO_2 was selective toward CO_2 and epoxide as seen on Table 1. CO_2 is a core product of photo oxidation of organics in the gas-phase reaction due to higher reaction temperature. In the reaction for the formation of diol which is sensitive to the type of solvent used for the epoxidation of cyclohexene carried out by Guidotti *et al.* [16]; CO_2 was reported to be the major by-product when a Ti mesoporous SiO_2 system was used alongside H_2O_2. They also reported that while no ring-opening reaction took place in acetonitrile, a significant amount was observed in *tert*-butanol [16]. Although not much have been published on the gas-phase epoxidation of 1-hexene, it is widely accepted that the epoxidation of alkenescan occur through electrophilic oxygen transfer which comes from the *OOH species formed when water was introduced to the system. Reports of *OOH species formation by various researchers showed that the presence of noble metals such as Au is responsible for this reaction. Ojeda and Iglesia, [17], in their work on catalytic epoxidation of propene with Au/TiO_2 also confirmed the formation of OOH by Au clusters. However, allylic oxidation which follows a radical pathway has also been reported, although in some cases, only a negligible amount of products were observed. Kwon et al. [7] in their study on the vapor-phase cyclohexene epoxidation by H_2O_2 over mesoporous TS-1 observed that the allylic oxidation products

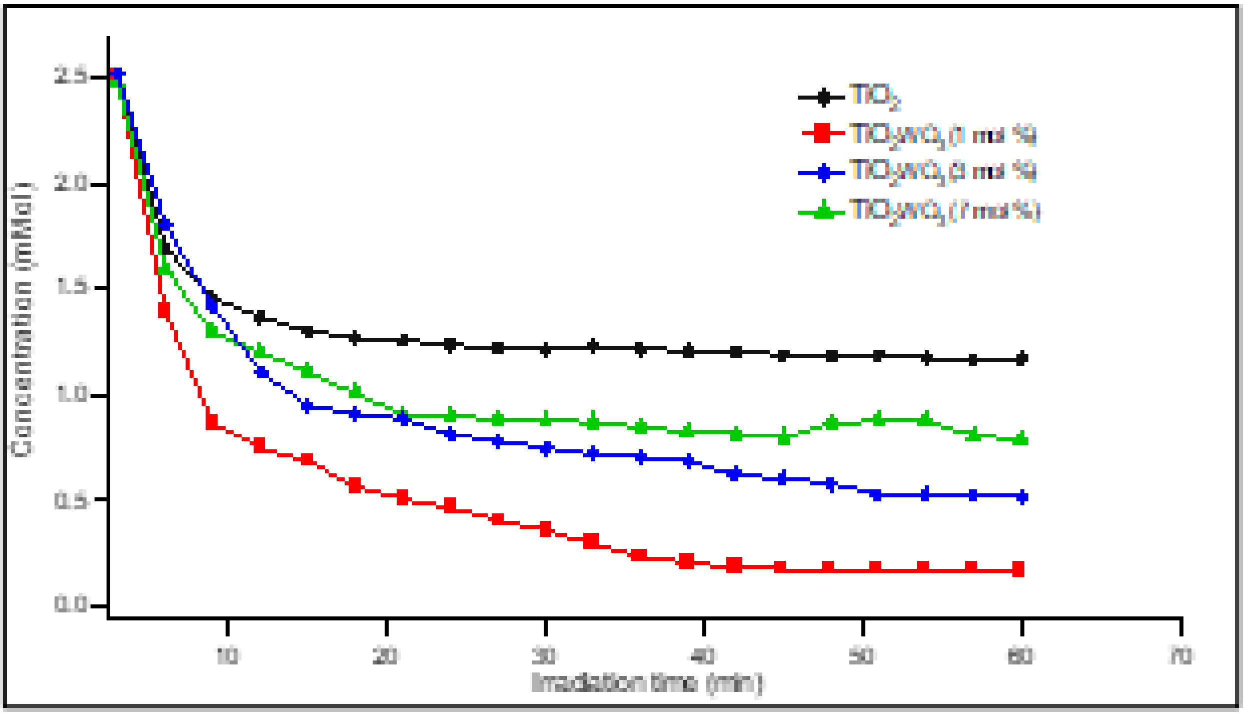

Figure 5. Effect of catalyst modification

were negligible which corresponds to the findings of Fan *et al* [18]; where they used various solvents to test Ti-based microporous zeolites (Ti-beta and Ti-MWW) to oxidise cyclohexene in a liquid-phase in the presence of H_2O_2 [7, 18].

3.6. Reaction mechanism

Photo-excited metal oxide catalysts are known to convert photo-energy to chemical energy through the generation of electron-hole pairs [19]. Such energetic species migrate to the surface of the semiconductor ultimately facilitating the generation of oxidative radicals through the transfer of charges between adsorbed molecules. In the presence of O_2 and H_2O, the photo-generated electron-hole pairs will generate the extremely active superoxide and hydroxyl radicals. One of the possible mechanistic routes is shown in the following equations:

$$O_2 + e^- \rightarrow O_2 \tag{2}$$

$$O_2^- + 2H_2O + e^- \rightarrow H_2O_2 + 2OH^- \tag{3}$$

$$H_2O - e^- \rightarrow [H_2O^+] + H_2O \rightarrow H_3O^+ + OH \tag{4}$$

It can be seen that the transfer of an excited electron to O_2 to form a superoxide radical (Equation 2), can in the presence of H_2O convert to hydrogen peroxide including *OOH, HOO^-, OH (Equation 3), by either reduction or hydrolysis process. Simultaneously, the holes can also directly oxide H_2O to generate hydroxyl radicals. The epoxidation of alkenes with *OOH species using Ti-based catalysts is widely accepted to proceed in two steps: firstly, the interaction between the Titania active site and the OOH species resulting in the formation of Ti–OOH and secondly, the formation of epoxides through the transfer of the proximal oxygen from Ti–OOH to the alkene [20].

Lin and Frei, [21], in their FTIR study of the epoxidation of olefins with TS-1 in the presence of H_2O_2, identified Ti–OOH to be an active intermediate during the reaction. In accordance with the literature, the reaction was proposed to be Eley–Rideal type since no measureable adsorption of alkene was detected on the catalyst active site [20].

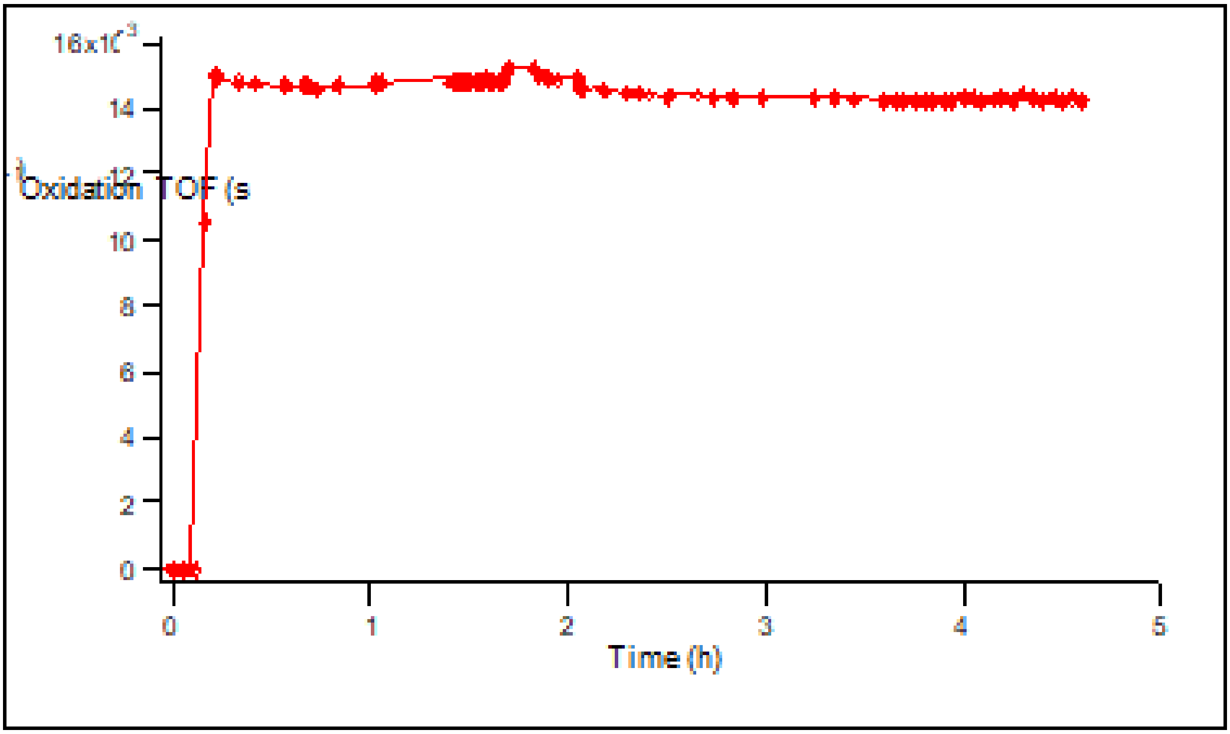

Figure 6. Oxidation turnover frequency over time for the gas-phase oxidation of 1-hexene

However, in this work, it is propose that the formation of epoxide occurred through a reaction similar to the second step, i.e. the reaction between alkene and Ti-OOH. This step is therefore considered the rate-determining step (RDS).This however, contradicts the proposal of Wells *et al.* [22], in their DFT studies of epoxidation of propylene on defective Titania sites in TS-1, where they proposed that the formation of Ti-OOH, the first step, is the RDS. The hydroxyl radicals generated in equation 3 can be responsible for dehydrogenation of alkene leaving the carbon atoms to react with the superoxide to form CO_2.

4. Conclusion

The photo-oxidation of gas-phase 1-hexene with TiO_2 supported on glass beads using combination of H_2O/O_2 has been achieved. Within our experimental conditions, the formation of products was stable throughout the reaction period implying that there was a good contact between the reacting species and the catalyst. The catalyst immobilisation method was simple to implement and used a highly active, commercially available photo-catalyst (Aeroxide® P25) to achieve excellent adherence stability for the lowest loading, which has promising industrial implications. The glass beads used, also instituted the homogeneity within the reactor. No catalyst deactivation was observed within the reaction period, although a slight colour change of the catalyst was noticed but the overall activity was not abated. This colour change has been observed by a number of researchers and is believed to be due to carbon depositions. CO_2 was the major product observed when N_2 and O_2 were used as carrier gases. However, when H_2O was added, epoxide was formed with high selectivity. To the best of our knowledge, the gas-phase oxidation of 1-hexene with H_2O/O_2 has not been reported.

4.1. Recommendation

It is propose from this study that the gas-phase and liquid-phase epoxidation of alkenes are identical as they both exhibit the Eley–Rideal type mechanism in which the RDS is the reaction involving the Ti–OOH and the physisorbed

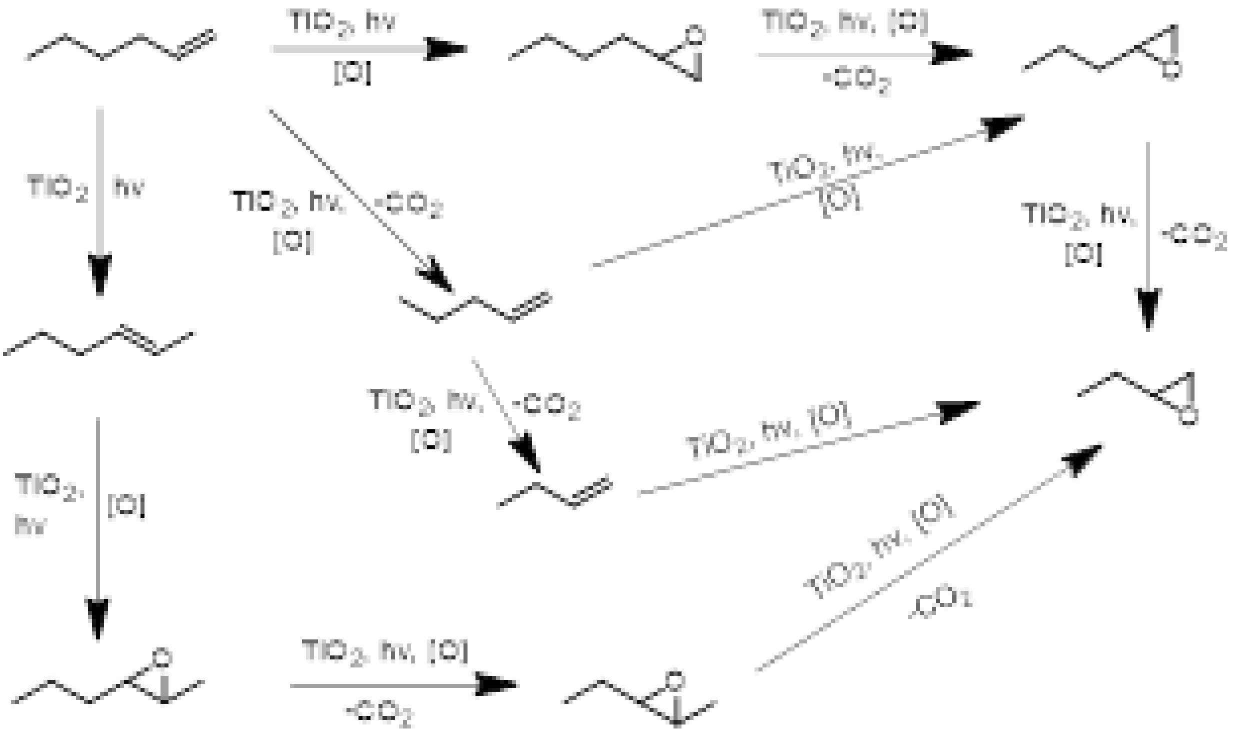

Figure 7. Scheme 1: Schematic of some of the many potential mechanistic photo-oxidation routes of 1-hexene with molecular oxygen

alkene.

In this study, it was propose that the contributions of H_2O to the reaction system are two-fold. First, it served as a source of generating hydroxyl radical through oxidation by the photo-generated holes and secondly, it reacts with the superoxide, a product of reduction of O_2 by the photo-generated electrons.

This work may provide routes to unachievable chemical syntheses as it offers a simple, tuneable, energy efficient, cost-effective alternative to several multi-step complex reactions. More importantly, it can be performed at standard temperature and pressure.

Further studies could be carried out to elucidation other reaction products and their reaction path ways

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