

PHOTO-EPOXIDATION OF CYCLOHEXENE IN GAS-PHASE

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Background: The production of alkenes as by-products of the oil industry, which poses a threat to public health and natural components of the environment. To prevent negative impacts, these volatile organic compounds (VOCs) must be converted into safe, useful products like epoxides. In addition, this process must be environmentally friendly and energy-efficient. Photoepoxidation of cyclohexene in the gas phase using H_2 and O_2 gases as redox agents can solve this problem. However, the effectiveness of the process must be studied. **Objectives:** The purpose is to investigate the effectiveness of using cyclohexene photocatalysis as an environmentally friendly, low-energy process for the production of epoxides in the gas phase using H_2 and O_2 gases as redox agents. It is also expected to obtain a low-cost, efficient process with the ability to control the reaction products. **Methods:** Titanium dioxide (TiO_2) and Titanium silicate (TS-1) were prepared using sol gel and wetness impregnation, and used as photocatalysts. **Results:** Stable production of cyclohexene oxide was achieved with the TS-1 while only total mineralisation to CO_2 was achieved with the TiO_2 . The kinetic analysis conducted here showed that the gas-phase reaction mechanism follows the Eley-Rideal mechanism. Gas-phase cyclohexene reacted directly with the intermediate formed through reaction between Ti base and the hydroperoxyl species, to produce cyclohexene oxide. Thus, this step was considered the rate-determining step. The effect of temperature was investigated at various partial pressures of individual gas reactant. An approximate value of 31 kJ/mol of activation energy was achieved. No epoxide was produced in the absence of H_2 under the experimental conditions studied here. Total mineralisation of cyclohexene to CO_2 was observed when O_2 was used alone in the system. **Conclusion:** The results obtained in this work revealed that utilizing H_2 and O_2 for various oxidation reactions at elevated temperatures is possible.

Keywords: photo-epoxidation; cyclohexene; Titanium silicate; hydrogen peroxide.

INTRODUCTION

Choice of oxidant during epoxidation reactions of alkenes is often seen as a challenge for this process. While molecular oxygen remains the ultimate oxidant, a lot has been done to minimise the total mineralisation through the use of other oxidants such as H_2O_2 , H_2O and in some cases, air. However, other factors such as the environmental hazards, selectivity of desired products and chemical costs come into play when the choice for the type of oxidant is made (Khomane et al., 2002). Among the most abundant and important organic products of the chemical industry are the alkenes. Due to heavy dependence on alkenes as key chemicals for the production of economically important polymers such as polyethylene and polypropylene, alkenes are produced in large quantities. As production of alkenes by the petroleum industries is on the increase, the quest to conserve natural resources is also on the increase, which makes it imperative to use such products as starting materials in other industrial processes.

Hydrogen peroxide has been used extensively for epoxidation of alkenes owing to the fact that it only produces water as a by-product (Khomane et al., 2002; Du et al., 1996; Zhao et al., 2008). Higher olefins such as 1-Hexene (C_6H_{12}) have been converted to their corresponding oxides using H_2O_2 (Du et al., 1996). Such reactions are typically performed in liquid phase using batch reactor setup, in which the overall reactivity of the catalyst can be influenced by the solvent used, which adversely affects the selectivity of products. Separation of product can also be a challenge (Du et al., 1996; Zhao et al., 2008; Pędzwiatr, 2018). The effect caused by solvent type can be due to its hydrophilic and hydrophobic interaction with the catalyst, oxidants and the alkene undergoing reaction (Pędzwiatr, 2018). However, reactions such as this, can also be performed in gas-phase with higher reaction rates, high selectivity and high reaction stability at higher operating temperature and pressure. Furthermore, it is possible to avoid leaching of the active sites, which is a typical challenge in liquid-phase when gas-phase is used.

In gas-phase, H_2O_2 can be directly produced by catalytic reaction of H_2 and O_2 in the presence of Au-doped Ti (Nguyen et al., 2014). The H_2O_2 is produced on the Au particles while the epoxidation reaction occurs on the Ti active sites. It was believed that the H_2O_2 was converted to the hydroperoxyl species on the nearby Ti sites in the form of Ti-OOH. However, most of the thermal alkene epoxidations have to use H_2O_2 as the main oxidant. The challenge in the use of H_2O_2 as an oxidant is to maximise the formation of epoxides without mineralisation of the alkenes (Nguyen et al., 2014; Ohno et al., 1998; Yoon et al., 2011). By using H_2O_2 in a gas-phase directly in the epoxidation process, the decomposition of alkenes can be minimised according to the report by Lousada et al. (2012). In another report by Ferrandez et al. (2013). An epoxidation rate of $10.5 \text{ kg}_{po}/(\text{kg}_{cat} \cdot \text{h})$ and selectivity of 90% was achieved when H_2O_2 vapour was used alongside Titanium silicate (TS-1) to convert propylene to propylene oxide.

During this investigation, kinetic study of cyclohexene was carried out with emphasis on the mechanism of gas-phase epoxidation using H_2 and O_2 to form hydroperoxyl species through photoexcitations over TS-1 photocatalyst. The direct epoxidation of alkene, using the co-reactants H_2 and O_2 and oxygen is highly selective over gold-titania based catalysts and has gained considerable attention in the past decade (Nijhuis & Weckhuysen, 2005). Although this catalytic reaction has been investigated extensively, the mechanism is still not well understood.

Hydroperoxyl formation can occur by protonating a superoxide radical (Shima et al., 2010). The supplied O_2 is adsorbed on the photocatalyst and is reduced by the photo-generated electrons to form superoxide radicals. The adsorbed H_2 is oxidised by the photogenerated holes and forming protons. This proton reacts with the nearby superoxide radicals to form hydroperoxyl species (HO_2^*), which was stabilized by attaching to the transition metal ion, Ti^{4+} and forming Ti-OOH (Li et al., 2014). The resulting Ti-hydroperoxyl (Ti-OOH) complex reacts with alkenes to form corresponding epoxide. Similar reactions in the literature show

that a number of oxidation pathways exist which inhibit the selectivity of cyclohexene oxide (Joshi et al., 2005; Sever & Root, 2013; Ojeda & Iglesia, 2009). In this work, an attempt was made to establish the mechanism for the photocatalytic epoxidation with H₂ and O₂ based on the kinetic measurements.

MATERIALS AND METHODS

Preparation of TS-1

TS-1 was prepared hydrothermally, through wetness impregnation using a modified procedure reported by Deng et al. (2013) and Zhang et al. (2017). The catalyst was prepared in stages described in the following subsections.

Sol-gel preparation

Sol-gel was prepared by hydrolysing tetraethyl ortho-silicate (TEOS, 98%) with 0.05 M hydrochloric acid (HCl, 32%) under magnetic stirring at room temperature. The mol ratio used was 1:4 of HCl:TEOS. Separately, titanium (IV) chloride (TiCl₄) and isopropyl alcohol (IPA) in a ratio of 15:2 of IPA:TiCl₄ were mixed, stirred and added dropwise to the silicate-acid solution under continuous stirring. The silicalite and Ti mixture were then mixed by adding the former in to the latter under stirring. The obtained sol was allowed to age for 1 h at room temperature.

Gelation

The prepared sol-gel from above was transformed to a solid cogel by dropwise adding 10 mL 20% solution of tetrapropylammonium hydroxide (TPAOH). However, the gel point obtained depends on the amount of base added. The product obtained was then dried in an oven at 60 °C overnight.

Wetness impregnation

The impregnated gel was transferred to a Teflon autoclave and heated at 120 °C under autogenous pressure for 24 h. The product was cooled at room temperature and the crystals were filtered using vacuum filter, washed with water and dried under ambient temperature. The final product was then calcined at 550 °C for 24 h in air. 87% yield of the final product was obtained based on the amount of TiO₂ and SiO₂ in the starting materials.

Characterization

XRD patterns were obtained using a Siemens powder X-500 diffractometer. SEM analysis of the synthesised TS-1 was performed using a Jeol-JSM 820 Scanning Electron Microscope. Elemental analysis was performed using a Leica Stereoscan 420 Energy Dispersive X-ray Spectroscopy. The surface area BET measurements were performed on JWK-B122 surface area and pore size distribution analyser 77 K.

Cyclohexene epoxidation reactions

The schematic for the gas-phase epoxidation kinetic studies is shown in Figure 1. The reactor consisted of a quartz tube plugged at both ends for inlet and outlet of reactants and products respectively. All photocatalytic reactions were performed in a flow system under various conditions. TS-1 and P25 TiO₂ were used as the catalysts. The catalyst was immobilised on glass beads. Hydrogen was supplied from a hydrogen generator and mixed directly with pure oxygen in a round bottomed flask that was stocked with quartz wool to ensure adequate gas mixing. The gas mixture was fed directly to the catalyst coated glass beads. Cyclohexene was admitted into the reactor in gaseous phase by placing liquid cyclohexene (5 mL) in a Dreschel bottle where nitrogen gas was used as a carrier gas to deliver gaseous cyclohexene into the reactor at a total flow rate of 1.4 ± 0.2 L/h controlled by rotameter. At this point, the concentration of cyclohexene was monitored through the FT-IR/GCMS tandem analysis. All standard reactions were performed under ambient conditions. The boiling points of cyclohexene and cyclohexene oxide are 83 °C and 130 °C, respectively. In order to minimise deposition of chemicals in transfer tube, all the connection tubes, particularly the outlet tubes, were shortened as much as possible. Upon attaining a steady state flow in the reactor, i.e. at adsorption desorption equilibrium, UVA lamps were turned on to initiate the photoreaction. Changes in concentration of cyclohexene as well as the products formed were monitored in a tandem FTIR-GCMS analysis. The outlet of the reactor was connected to the IR sampling cell with NaCl windows which was in turn connected to a modified GCMS auto-sampler. FTIR and GCMS data were collected every 3 min. This sampling frequency is restricted by the retention time of the targeted chemicals in the GC.

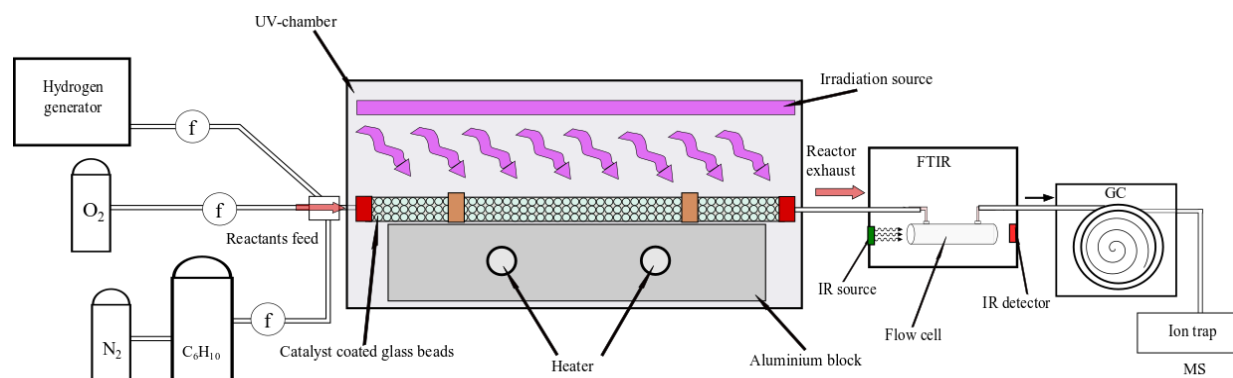


Figure 1. Experimental set up for gas-phase cyclohexene epoxidation with H₂ and O₂

The epoxidation products were separated using an Rxi-5Sil MS fused silica column with total length of 30 m. The inner diameter of the column is 0.25 mm while the film thickness is 0.25 µm. The column was engineered to be a low-bleed GC-MS column. The column was set at a pressure of 68.9476 kPa for the carrier gas and a constant temperature of 130 °C, similar to the boiling temperature of cyclohexene oxide. The gaseous mixtures were introduced to the GC through auto-injection at a fixed interval of 3 min. A carrier gas of helium was used at a flow rate of 100 ml/min. Data was collected for

at least 1 h under each set of conditions to allow attainment of steady state concentrations of the products. During the kinetic studies, the effect of partial pressure of individual reactant was studied. Since all reactants were delivered in gaseous phase there was no consideration to the possibility of condensation of reactants in transfer line when determining the partial pressures. In a typical photo-epoxidation reaction, the partial pressures of the reactants were: 3 kPa, 5 kPa and 20 kPa for cyclohexene, hydrogen and oxygen respectively. 5 mg of catalyst per 1 g of glass beads was found to be ideal for this reaction.

RESULTS AND DISCUSSIONS

TS-1 characterisation

The XRD pattern of the TS-1 sample prepared by the hydrothermal method is shown in Figure 2 in the 2θ ranging from 5 to 40° . The diffraction peaks at $2\theta = 7.8^\circ, 8.8^\circ, 23.1^\circ,$ and 23.9° match well with the characteristic MFI-type structure of TS-1. A typical silicate-1 exhibits an amorphous crystallite in its XRD pattern even if it contains low amounts of Ti. Depending on the content of Ti in the framework, TS-1 shows well defined diffraction peaks typical of MFI topological structure (Ren et al., 2004). The high crystals of TS-1 may be attributed to the linear increase in the unit cell parameter and volume relative to Ti content in the framework as suggested by some literature reports (Ren et al., 2004; Machado et al., 2015; Katkar et al., 2012). It can be seen in Figure 2 that the TS-1 synthesised during this study exhibited high phase purity, judging by the appearance of the characteristic peaks above.

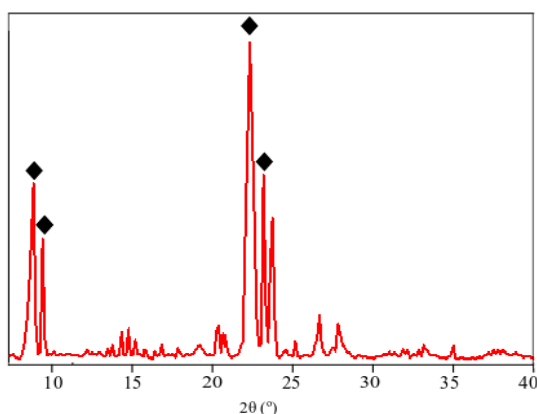


Figure 2. XRD pattern of TS-1

SEM image of synthesized TS-1 is shown in Figure 3. It has a particulate morphology with particles diameter of about 150 nm. Different morphologies of TS-1 have been reported in the literature. For instance, Zhao et al. (2008). reported a spherical morphology of nanosized crystallites without characteristic hexahedron configuration.

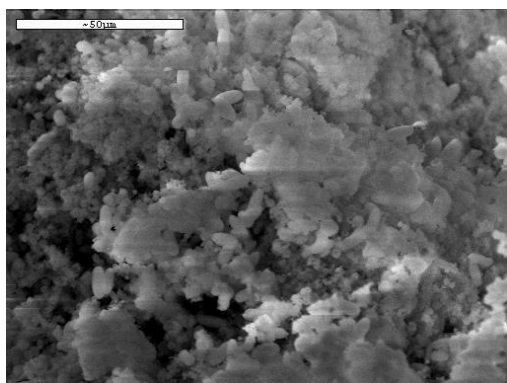


Figure 3. SEM image of synthesised TS-1 showing grain-like particles

To further verify the composition of the synthesised TS-1 in this work, EDX analysis was performed and the result shown in Figure 4. It can be seen that the composite consisted of Ti, Si and O. The additional peak with high intensity is ascribed to C, which was used as support material during the EDX analysis.

The atomic percentages of the constituent elements are given on the inset Table 1. These values agree with the ratio (2:1, Si:Ti) of the input chemicals during the synthesis of the catalyst, hence confirming the purity of the catalyst.

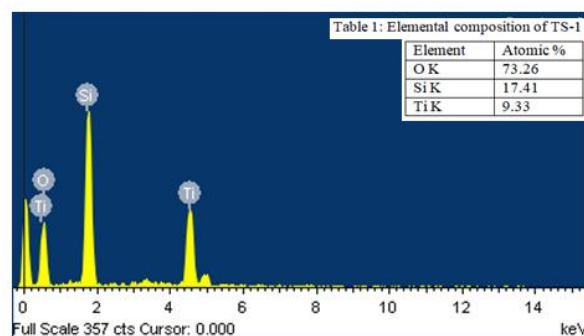


Figure 4. EDX showing elemental composition of the synthesised TS-1

Gas-phase cyclohexene epoxidation

One of the major challenges associated with using hydrogen peroxide in gaseous phase is its tendency to decompose under thermal condition. Studies on its decomposition rates show that the nature of the material used for the reaction plays a vital role on the rate of decomposition. Satterfield & Stein (1957). reported that the decomposition rate is higher when metals are used compared to when borosilicate or quartz. This knowledge was an advantage in this work as it provided the basics for the use of quartz tube packed with catalyst coated glass beads, hence the stability of the hydroperoxyl species was improved. In this work, hydroperoxyl species are expected to be formed on the catalyst as the product of the reaction between H_2 and O_2 . It is important that these hydroperoxyl species are able to react with cyclohexene as soon as it was formed, due to its limited lifetime. To verify that both H_2 and O_2 was responsible for the epoxidation of cyclohexene, studies were performed by altering the partial pressure of individual species during photoreaction. First, the partial pressure of O_2 was reduced by half while that H_2 was kept constant. It was not surprising to see that the conversion of cyclohexene decreased by 80% and zero conversion was achieved when no O_2 was supplied to the system. Without H_2 , total oxidation of cyclohexene was observed, as CO_2 was the main product and no epoxide was observed across the photocatalysts tested. This indicates that H_2 is responsible for the selectivity cyclohexene epoxidation while O_2 is responsible for the conversion of cyclohexene. It is also important to mention at this point that no reaction was observed in the absence of either catalyst or light.

To study the intrinsic behaviour of the catalyst, the reactants' stoichiometry should not limit the reaction under specific conditions of differential conversion (Ren et al., 2004). Therefore, it was of high significance to ensure that the hydroperoxyl species was constantly formed on the active sites of the catalyst for the production of Ti-OOH complex and subsequent conversion of cyclohexene (Machado et al., 2015; Katkar et al., 2012; Satterfield & Stein, 1957).

The conversions and selectivity of cyclohexene and products respectively were quantitatively determined. Turn over frequency (TOF) was determined according to the mole of cyclohexene oxide produced per mole of Ti per second and was used to represent the product formation rate. No epoxide was made under standard conditions of reaction with TiO_2 , and only CO_2 remained the dominant product with a selectivity of 96% while ketone and alcohol were formed with selectivity of 2.8 and 1.2% respectively.

TS-1 showed activity towards formation of cyclohexene oxide with selectivity of 38.1%. Unfortunately, the cyclohexene oxide selectivity obtained during this work was lower than the reported value in the literature. By Kwon et al. (2015) recorded up to 74.1% of cyclohexene oxide selectivity with their mesoporous TS-1. However, their experimental conditions were more complex than those used in this study. This group used temperature range between 120 and 160 °C at 50 ml/min, while a milder temperature ranging from 60 to 80 °C at 20 ml/min (1.4 L/h) was used in this study. Nevertheless, the use of O₂ and H₂ to generate in-situ reaction intermediates remains advantageous over the use of more expensive H₂O₂, which can also decompose easily resulting in undesirable products (Satterfield & Stein, 1957).

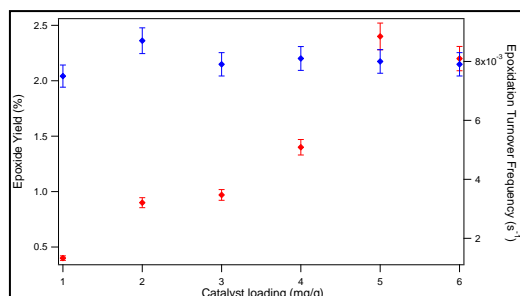


Figure 1. Cyclohexene oxide yield (red diamonds) and TOF (blue diamonds) under different catalyst (TS-1) loading

TS-1 was tested in different amounts to study the effect of catalyst loading on the photoepoxidation of cyclohexene. Figure 5 shows that the yield of cyclohexene oxide increased while TOF remained unchanged with increase in the catalyst loading. The highest yield for cyclohexene oxide was achieved at the optimal catalyst loading of 5 mg/g and the yield was reduced as the loading was increased to 6 mg/g. Meanwhile, the cyclohexene oxide yield decreased from 2.39% (at 5 mg/g) to 2.2% (at 6 mg/g). Such decreases could be related the increased diffusion path length as the thickness of the catalyst increases. The TOF is directly determined by the surface concentration of the hydroperoxyl. As TOF is independent of TS-1 loading, it suggests that the epoxidation happens on the surface of the TS-1 catalyst, so the thickness of the TS-1 film is not affecting the reactivity. The effective surface area can be increased by using smaller glass beads as supporting media. So, it is possible to increase the epoxide yield using smaller beads. It has already been established that the total beads surface area is inversely proportional to the radius of the beads. By reducing the radius by half, one can expect to double the yield. These results are in agreement with those reported by Kwon et al. (2015) in their cyclohexene epoxidation reaction over mesoporous TS-1. Contrary to the findings of Ferrandez et al. (2013) where they found the conversion is relatively independent of the amount of TS-1 used. They ascribed their observation to the limited amount of the H₂O₂ present in the system due to its rapid decomposition. In both examples, H₂O₂ was used as oxidant.

Stability

The stability test was performed by measuring the formation of cyclohexene oxide at the optimal catalyst loading of 5 mg/g up to 6 h of reaction.

Figure 6 show that a steady TOF was maintained with no sign of degrading, suggesting that the catalyst was remaining active. Contrary to the findings on Au-doped TiO₂ which was deactivated within a short period of reaction time, the TS-1 used in this work proved to be stable with no observable sign of deactivation over the period of the reaction. Although still a

subject of debate, the rapid deactivation in Au-doped TiO₂ is widely believed to be due to the generation of H₂O₂ which oxidizes surface Au atoms (Kwon et al., 2015).

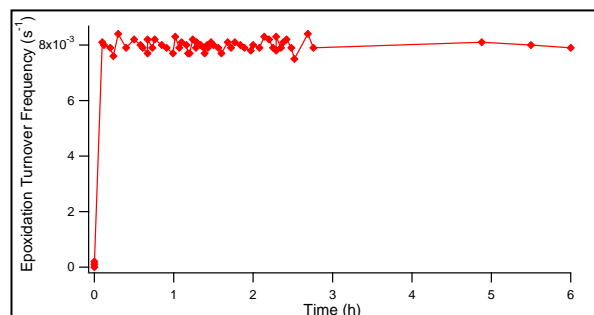


Figure 2. Gas-phase cyclohexene epoxidation turnover frequency over time with 5 mg of TS-1 and total flow rate of 2.8 L/h

By-products

During the gas-phase epoxidation of cyclohexene with hydroperoxyl radicals formed on Titanium silicate catalyst (TS-1), high selectivity towards cyclohexene oxide was observed. Only negligible amount of the ring-opening products, such as 1,2-cyclohexanediol was observed and so was not considered in determining the yield of epoxide. Ketone and alcohol were also formed only in small quantities. This observation agrees with reports on liquid phase reactions under similar conditions (Katkar et al., 2012; Kwon et al., 2015; Gao et al., 2011). Some reports suggested that epoxidation reaction proceed through a simple electrophilic oxygen transfer while others reported that an allylic oxidation proceed through a radical pathway (Du et al., 1996; Yoon et al., 2011). Similar observation was made by Klemm et al. (2012) in their study of propylene epoxidation over TS-1 catalyst and H₂O₂. The details of the epoxidation mechanism and competitive pathway for by-products will be discussed later.

Temperature effect

The dependence of the production rate of the epoxide on temperature was investigated in order to study the possible reaction mechanism and to evaluate the reaction activation energy. With light on, the reactor will reach a stable temperature of 335 K over a period of 1 h. The reactor temperature was then controlled by applying heat on a purpose-built aluminium block. This way, the maximum temperature of 433 K can be achieved. Here, we use TOFs for cyclohexene oxide to represent the reaction rates. A single set of reaction parameters showed a typical Arrhenius kinetics, as expected. However, adjusting the in-flow of reactants into the reactor resulted in different trends in the apparent activation energy. In general, by increasing the partial pressure of all reactants, including cyclohexene, H₂ and O₂, the reaction rates increase, as observed from Figure 7. All the Arrhenius curves show a negative gradient, which suggests a positive reaction energy barrier. However, by changing the cyclohexene partial pressure from 1 to 5 kPa, there was no significant change of the activation energy with an averaging value of 15.03 kJ/mol, shown in Figure 7a. On the other hand, for both H₂ and O₂, the changing of their partial pressure could affect the apparent activation energy, shown in Figures 7b and 7c. For H₂ gas, the change of the partial pressure from 2 to 6 kPa, the activation energy increases from 22.4 to 12.46 kJ/mol. Less effects on the activation energy was observed for O₂ gas pressure.

Such observation, suggests that the final step of epoxidation of cyclohexene is probably elementary single step, while the reaction of H₂ and O₂ are less simple and likely to involve multiple steps. In principle, it is impossible to have H₂ and O₂

directly reacting with cyclohexene on TS-1 surface under light illumination, since it involves the simultaneous collision of three chemicals on the same site on the solid surface.

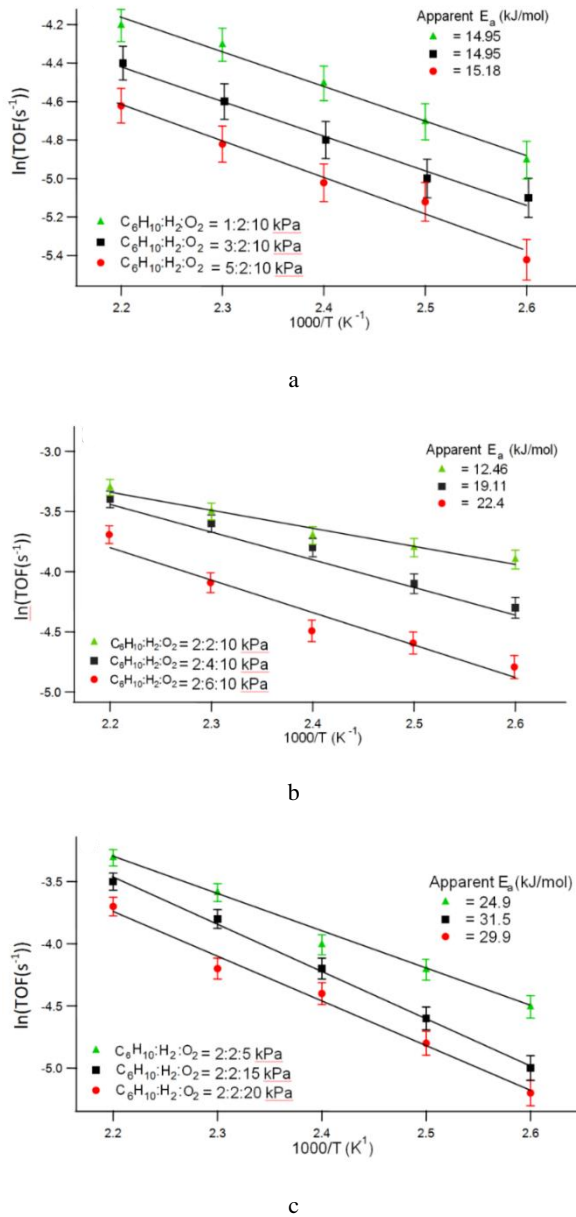


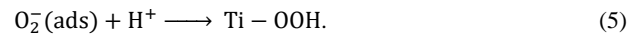
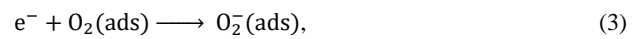
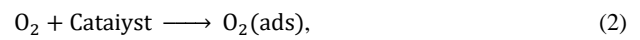
Figure 3. Temperature dependence of cyclohexene oxide production rate with different partial pressures of reactants over TS-1 photocatalyst loaded at 5 mg/g

Thus, as suggested from literature and described in the introduction of this work, H_2 and O_2 must be adsorbed on the TS-1 surface, dissociate and photocatalytically form the critical intermediate of hydroperoxyl species, OOH. The importance of hydroperoxyl in the epoxidation of alkenes on catalyst surface has been well established in the literature (Zhang et al., 2017; Katkar et al., 2012; Kwon et al., 2015). This species is assumed to be stabilized by attaching to the Ti cations, denoted as Ti-OOH. As such, the reaction kinetics is related to the partial pressure. The Arrhenius behaviour as a function of cyclohexene partial pressure suggests that cyclohexene can be oxidized by the formed Ti-OOH directly in a single step. So, it is likely that the reaction follows the Eley-Rideal mechanism in which an adsorbed chemical reacts with a gas-phase molecule. The adsorption of water on active sites of the catalyst is competing

with the formation of Ti-OOH. Increasing the reactor temperature however, would cause a decrease in the amount of water adsorbed consequently, increasing the number of sites available for the formation of hydroperoxyl species. Hence the TOF for cyclohexene oxide increased as the reaction temperature increased.

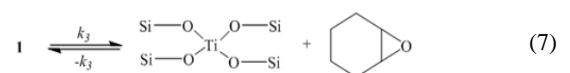
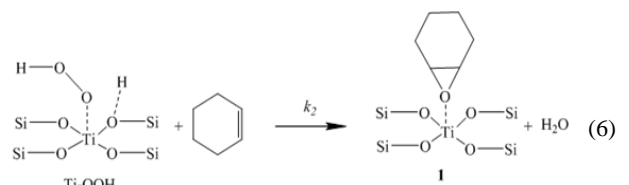
Reaction mechanism

The oxidation of alkenes to corresponding epoxides using a Ti-based catalyst and hydrogen peroxide is widely reported to proceed through two major pathways. First, the reaction between Ti site and the hydrogen peroxide species which results in the formation of a titanium-hydroperoxo complex (Ti-OOH) and secondly, the closer oxygen atom to the Ti in the Ti-OOH is transferred to the alkene resulting in the formation of the epoxide (Gao et al., 2011; Kwon et al., 2015; Li et al., 2008) as shown below:



In this work, the overall reaction begins by illumination and generation of photoexcited electrons (e^-) and holes (h^+) (Equation 1). O_2 is adsorbed on the surface of the catalyst (Equation 2). The adsorbed O_2 was then reduced to superoxide radical O_2^- (Equation 3). Meanwhile H_2 is oxidised to proton (Equation 4). Although it is difficult to confirm whether H_2 was adsorbed on the surface before oxidation, the result proton is very likely attached to the nearby O atoms in the silicate, forming OH groups, holding by the relative weak hydrogen bond. The proton will react with the superoxide radicals to form hydroperoxyl species, OOH attached to the Ti^{4+} metal ions (Equation 5). Obviously, without H_2 , the photoexcited hole (h^+) will oxidise the alkene instead which will lead to the fragmentation and mineralization of alkene, rather than epoxidation. In this work, no epoxide was formed in the absence of H_2 and no significant amount of alkene was observed to adsorb on the active site of the catalyst (perhaps due to its low BET surface area – $21 \text{ m}^2/\text{g}$). The structure of Ti-OOH intermediate is proposed in Equations 1 – 5.

The formed surface Ti-OOH complex reacted with gas-phase cyclohexene to form the cyclohexene oxide as shown in Equations 1 – 5. Therefore, the epoxidation of cyclohexene under our experimental conditions is an Eley-Rideal type. This result is similar to the liquid-phase epoxidation reported by Sever and Root (Ramakul et al., 2012) when they carried out a DFT study of the epoxidation of ethylene using a Ti-based catalyst in the presence of H_2O_2 . The desorption of the epoxide results in regeneration of the active sites, ultimately inducing a recycled competitive adsorption of water and hydroperoxyl species onto the active site. Proposed reaction mechanism for cyclohexene with Ti-OOH species shown in Equations 6 and 7:



Following the proposed mechanism, it is possible to establish the reaction kinetics. Here we assume the O₂ is adsorbed on the Ti⁴⁺ site while H₂ is attached to the SiO sites. So there is no direct competition for the adsorption of O₂ and H₂ on TS-1 surfaces. However, if element transition metals, such as Pd or Pt, are used, both O₂ and H₂ will adsorb on the same sites and directly react them to form water. It was also assumed that the redox of the adsorbed O₂ and H₂ are relatively efficient and are not rate limiting steps.

$$\theta_{O_2} = \frac{K_O P_{O_2}}{(1+K_O P_{O_2})}, \quad (8)$$

$$\theta_H = \frac{K_H P_{H_2}}{(1+K_H P_{H_2})^2} \cdot \frac{1}{[1+(K_H P_{H_2})^2]}. \quad (9)$$

Gases, such as O₂ and H₂, are normally weakly adsorbed on silicate surface, due to their non-polar nature (Ramakul et al., 2012). Hence at low gas pressure, the adsorption likely follows the Langmuir isotherm. The equilibrium is described in

$$r_e = k_e \theta_{Ti-OOH} P_C = \frac{k_e k_{OH} K_O P_{O_2}}{(1+K_O P_{O_2})(K_H P_{H_2})^2} \cdot \frac{1}{[1+(K_H P_{H_2})^2] P_C} = \frac{k_e k_{OH} K_O P_{O_2}}{(1+K_O P_{O_2})(K_H P_{H_2})^2} \cdot \frac{1}{[1+(K_H P_{H_2})^2] P_C P_{O_2}}, \quad (12)$$

where PC is the partial pressure of cyclohexene.

Here, it was also assumed that the formed epoxide will desorb from the site immediately without competitively disturbing the adsorption equilibrium of hydroperoxyl species. If this condition is not satisfied, significant amount of mineralization will happen and large quantity of CO₂ will be formed.

Equation 12 is a typical formula for the Eley–Rideal type reaction. It is clear, that for cyclohexene, the apparent rate constant is defined as:

$$k_C = \frac{k_e k_{OH} K_O P_{O_2}}{(1+K_O P_{O_2})(K_H P_{H_2})^2} \cdot \frac{1}{[1+(K_H P_{H_2})^2]}, \quad (13)$$

which is independent of P_C. Therefore, the calculated activation energy is independent of P_C, as we observed from the Arrhenius plots in Figure 7b. However, for O₂, the apparent rate constant is defined as:

$$k_O = \frac{k_e k_{OH} K_O P_{O_2}}{(1+K_O P_{O_2})(K_H P_{H_2})^2} \cdot \frac{1}{[1+(K_H P_{H_2})^2] P_C}. \quad (14)$$

It clearly demonstrated that the apparent rate constant is also affected by the O₂ partial pressure P_{O₂}. Therefore, the obtained activation energy can be a function of P_{O₂}, as we have observed from Figure 7c. Similar behaviour could be analysed for H₂, although its kinetics is more complicated, since it follows a dissociative adsorption.

CONCLUSION

A successful demonstration of epoxidation of cyclohexene over TS-1 and hydroperoxyl under UV illumination was achieved. Under the experimental conditions, no cyclohexene oxide was produced over TiO₂ even in the presence of H₂ and O₂. TS-1 produced cyclohexene oxide with high stability only when H₂ and O₂ were simultaneously present in the reaction system. No epoxide was formed in the absence of H₂. The gas-phase epoxidation of cyclohexene is believed to follow the same type of mechanism as that proposed for the liquid-phase reaction, known as the Eley–Rideal mechanism. The reaction between superoxide and hydrogen formed the hydroperoxyl which reacted with the Ti site of the catalyst to form the Ti-OOH complex. Other forms of active oxygen and peroxy

Equations 8 and 9, where θ_O and θ_H are the surface coverages for O₂ and H₂. P_{O₂} and P_{H₂} are the partial pressures for O₂ and H₂. K_O and K_H are the Langmuir constant for O₂ and H₂ on TS-1 surface. For H₂, a dissociative adsorption on the silicate is calculated. The reduced O₂ and oxidised H will react to form hydroperoxyl species. Assuming an equilibrium is reached with steady state concentration of Ti-OOH, its concentration can be expressed as:

$$\theta_{Ti-OOH} = k_{OH} \theta_O \theta_H, \quad (10)$$

where k_{OH} is the equilibrium constant for the formation of Ti-OOH, which includes the redox process and protonation of superoxide radicals. Equation 10 can be extended as:

$$\theta_{Ti-OOH} = \frac{k_{OH} K_O P_{O_2}}{(1+K_O P_{O_2})(K_H P_{H_2})^2} \cdot \frac{1}{[1+(K_H P_{H_2})^2] P_C}. \quad (11)$$

Therefore, the reaction rate for the epoxidation of cyclohexene can be described as:

species may be generated within the reaction system from the presence of O₂ and H₂, and as such, new reaction pathways resulting in the generation of different products may be possible. The effect of temperature and partial pressure was investigated, and the true apparent activation energy was determined to be 31.5 kJ/mol. The results obtained in this work provide the possibility of utilizing O₂ and H₂ for various oxidation reactions at elevated temperatures.

Author's statements

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