Photocatalytic oxidation of different aliphatic carboxylic acids by TiO_2 catalyst

A

Dissertation Submitted

In partial fulfillment for the award of the degree of

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IN

CHEMISTRY

By

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(301202008)

Under the Guidance of

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Certificate

This is to certify that the project entitled "**Photocatalytic oxidation of different aliphatic carboxylic acids by TiO_2 catalyst**" being submitted by Manpreet Kaur, Roll No. 301202008 in partial fulfillment of the requirements for the award of degree of **Master of Science in Chemistry**, in School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Ranjana Prakash and Dr. Bonamali Pal. This project has been submitted for the award of any other degree or certificate in this or any other university by me.

18/7/14

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Candidate's Declaration

I hereby declare that the work which is being presented in the dissertation entitled "**Photocatalytic oxidation of different alliphatic carboxylic acid by TiO_2 catalyst**" in the partial fulfillment of the requirements for the award of the degree of **Masters of Science in Chemistry**, School of Chemistry & Biochemistry (SCBC), Thapar University, Patiala, is an authentic record of my own work during the period of six month from January to July 2014, under the supervision of Dr. Ranjana Prakash and Dr. Bonamali Pal. I have not submitted the matter embodied in this dissertation for the award of my other degree.

Place: Patiala

Date: 18/7/14

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This is to certify that the above statement given by the candidate is correct and true to the best of our knowledge.

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Life at Thapar University would be unforgettable for me throughout my life because I was blessed to spend it with my friends. I thank them all for their great company.

Words fail me to express my thanks to my family for their selfless sacrifice, encouragement and heart full blessing that continue to enlighten my life.

At last, I express my special thanks to almighty God for blessing me with strength and wisdom to complete this project successfully.

Manpreet Kaur

Manpreet Kaur

Date: 18/7/14

Place: Patiala

Dedicated to

My Parents and Guides

God, my guides, my parents, my husband Er.Amrik Singh who taught me the basics of life.

Thank you all for being with me in all odd and pleasing times.

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ABSTRACT

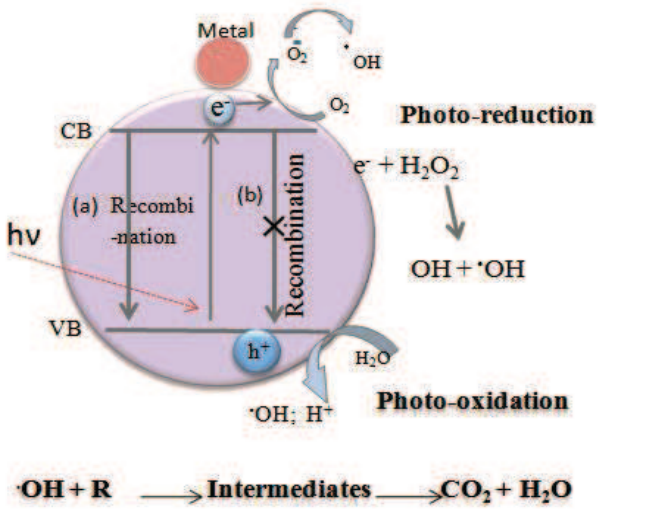
Among advanced oxidation processes, heterogeneous photocatalysis is a potential method based on UV/titanium dioxide for degradation of various recalcitrant chemical compounds. The dissertation work puts forward a method of UV based photocatalytic degradation (PCD) of long chain carboxylic acids, by bare and metal-doped TiO_2. The evolution of carbon dioxide was analyzed using gas chromatography and volumetric acid-base titration method. The degradation studies using Ag-TiO_2/UV system indicate enhanced degradation rate by metal doped system when compared to bare TiO_2. In addition, increase in chain length of carboxylic acids significantly influenced the degradability of the compounds with reduced degradation on increase in chain length. During photocatalytic degradation process, complete oxidation of acids lead to formation of CO_2. The rate of CO_2 formation was dependent on carbon chain length and irradiation time with requirement of longer duration of irradiation for acids with longer carbon chain. This study can be helpful for designing photocatalytic reactors for removal of acids from industrial wastewaters and other effluents.

Keywords: Heterogeneous photocatalysis; carboxylic acids; gas chromatography; carbon chain length.

1. Introduction

Carboxylic acids are classified as weak organic acids with at least one carboxyl group and are frequently formed as intermediates from the incomplete organic species degradation [1, 2]. Their derivatives like phthalic acid, benzoic acid and its nitro- chloro-, derivatives are mostly found in the waste water of pharma industries, dyes and paint industries, petrochemicals, pigment industries [3-5]. These organic acids are non-biodegradable which can be harmful to the environment. In recent years, photocatalytic degradation (PCD) of these aliphatic carboxylic acids and aromatic acids such as acetic acid, humic acid, benzoic acid, polycarboxylic acids, salicylic acid, etc. from sewage water using TiO_2/UV method has been reported [6-11]. The advantages of PCD by TiO_2 over conventional treatment techniques are its lower cost, mild operating conditions, non-toxicity, no harmful byproducts, chemical inertness, degradation of a broad range of organic pollutants [12, 14].

Upon photoactivation with a photon of energy equal to or greater than the band gap (3.2 eV) of TiO_2 semiconductor a positive hole (h^+) is created in the valence band and electrons (e^-) in the conduction band (**Scheme 1**). The photoexcited electrons (e-) and holes (h+) induce reduction and oxidation of the chemical substrates adsorbed on the surface of photocatalyst, converting photonic energy into chemical energy [15]. The hole can also produce



Scheme 1 Mechanism for the TiO_2 mediated photodegradation of pollutants.

hydroxyl radicals while coming in contact with water and the electron can reduce O_2 to generate powerful oxidizing superoxide ions and hydroxyl radicals [16-19]. On the other hand, in the absence of charge traps or scavengers, recombination occurs between the conduction band (CB) electrons and valence band (VB) holes and photonic energy dissipates as heat.

The phocatalytic activity of TiO_2 can further be improved by loading metals on it. Nobel metals such as Cu, Pt ,Au ,Ag ,Pd and Rh, etc. deposited on TiO_2 surface act a co-catalyst, causing efficient charge separation of photogenerated electrons and holes. This fact prevents the recomination and thereby, improves the photoactivity of TiO_2, the extent being depending upon the electron affinity, charge transfer ability, Fermi energy and particle size of the metals [20-22]. When metal gets loaded on TiO_2, the Fermi energy level of metal and TiO_2 come to equilibrium. This equilibration takes place due to the movement of electrons from species with higher reduction potential to species with lower reduction potential [23]. Metal which have lower reduction potential than TiO_2 are preferred, more and more electrons get transfer to the metal and further to the reacting species.

This creates future scope of research interest to load different metals on TiO_2 and study photo-degradation of various carboxylic acids with varying chain length. Herein, we report the photodegradation of carboxylic acids viz. formic acid, glacial acetic acid, propionic acid, butanoic acid, n-valeric acid, 2-ethylhexanoic acid with bare and Ag loaded TiO_2 nanoparticles.

2. Literature Review

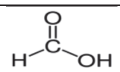
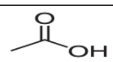
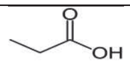
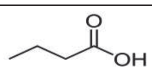
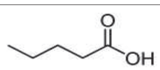
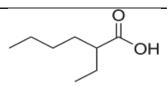
Much work has been done in past by various scientists on degradation of aliphatic and aromatic carboxylic acid. But till date, there are no reports available in the literature about the effect of carbon chain length of saturated aliphatic acids and their photo-activity by metal loaded TiO_2. Some of the literature related to the present study has been cited below:

Photocatalytic decomposition of aromatic and aliphatic acid in irradiated TiO_2 has been carried out by Gandhi et al [24]. Heterogeneous photocatalytic reactions of organic acids and water have been studied by Sakata et al [25]. The kinetics of photocatalytic degradation of aliphatic carboxylic acids in an UV/TiO2 suspension has been carried out by Chen et al [26]. The correlation between photocatalytic oxidation performance and chemical/physical properties of indoor volatile organic compounds has been studied by K. Yu, et al [27]. Minero et al. have reported the photocatalytic degradation of benzoic acid using TiO_2 particles as photo-catalyst under UV irradiation [28]. Heterogeneous photocatalytic decomposition of benzoic acid and adipic acid on Pt/TiO_2 powder has been approved by Izumi et al [29]. Photodegradation of salicylic acid in aqueous phase by using TiO_2 / UV System deliberated by Djouder et al [30]. Franch et al. studied the Fe (III) photocatalyzed degradation of low chain carboxylic acids implications of the iron salt [31].

3. Research Gap

Although, widespread research has been done on the photo-oxidation of a variety of carboxylic acids using various metal oxides, yet few reports exist for the degradation of acid using TiO_2. Some of these acids cause irritation to the eyes, skin or mucous membrane, allergic action and respiratory tract system. It is used by petrochemical, pharma, paints, dyes, paints and pigments industries, which is harmful for the human health due to their adverse effect. It is worthy to mention here that most of the acids were degraded using mostly active P25-TiO_2 . However, metal loaded TiO_2 for the degradation of carboxylic acid and effect on their carbon chain length, has not been studied yet. Thus, use these following six carboxylic acids were considered for their degradation study and following objectives is defined.

Table 1: Comparative photooxidation rate of various carboxylic acids under same condition (20 Mm concentration and 50 mg P25-TiO_2 and Ag-TiO_2)

Acids	Molecular Structure	No. of Carbon atom	Mol.Wt (g/mol)	Rate of CO_2 Formation by P25-TiO_2 (μmol)	Rate of CO_2 Formation by Ag-TiO_2 (μmol)
Formic acid		C1	46.02	60	65
Glacial acetic acid		C2	60.05	63	68
Propionic acid		C3	74.08	71	78
n-Butanoic acid		C4	88.11	65	71
n-Valeric acid		C5	102.13	74	80
2Ethylhexanoic acid		C6	134.21	52	59

4. Objectives

1. To study and compare the photocatalytic degradation of alliphatic carboxylic acids (formic acid, glacial acetic acid, propionic acid, butanoic acid, n-valeric acid and 2-ethylhexanoic acid) by bare P25-TiO_2 and Ag deposited TiO_2 catalyst.

2. To study the effect of varying chain length on the rate of degradation of aliphatic carboxylic acids.

5. Experimental work

5.1 Material and methods

Formic acid (HCOOH), glacial acetic acid (CH_3COOH), propionic acid (C_2H_5COOH),butanoic acid(CH_7COOH),n-valeric acid (C_4H_9COOH) and 2-ethylhexanoic acid($C_7H_{15}COOH$), methanol(CH_3OH), Sodium hydroxide (NaOH),oxalic acid($C_2H_2O_4.5H_2O$),silver nitrate ($AgNO_3$) were purchased from Loba Chemie, India. Nitrogen (99.999%) gas was obtained from BOC India Ltd. Commercially available P25-TiO_2 was gifted by Degussa Corporation, Germany with an average particle size of 30 nm and surface area of 50 m^2 gl^{-1}. De-ionized distilled water was used during the experiment.

5.2 Silver (Ag) photodeposition onto TiO_2

Metal loaded titania (P25-TiO_2) was synthesized through metal photodeposition method on the surface of TiO_2 using an aqueous solution of metal salts (silver nitrate, 0.01M) in the subsequent steps. Firstly, 1 wt % $AgNO_3$ was prepared in 10 ml de-ionized water. In a typical experiment, 100 mg of titania was mixed with 4ml de-ionized water to 4ml iso-propanol by adding required amounts (1 wt %) of prepared metal salts solution in a test tube. Then the argon gas was purged for 15-20 minutes to create inert atmosphere in a solution mixture. It was magnetically stirred under the UV-irradiation for 2-3 hr. After stirring, centrifuged it for 2-3 times and were washed with methanol. This was dried in an oven at 100ºC for half an hour. The dried solids were ground with pestle mortar. Sample thus obtain were abbreviated as: Ag-P25-TiO_2.

5.3 Photocatalytic activity

The comparative photocatalytic activity of bare and metal deposited titania was evaluated by taking 50 mg catalyst, 5 ml (20mM) aqueous solution of various carboxylic acids into a test tube under UV light (125 W Hg arc, 10.4 mW/cm^2) irradiation for different time interval. After that, the samples were then collected at regular time intervals (30 min) then analyzed by gas chromatography and volumetric analysis titration method.

5.4 GC analysis

In a typical experiment, after 30 min of UV-light exposure 1 ml of gaseous mixture from the reactant vessel (gas tight test tube) solution was injected with the help of micro-syringe into gas chromatography (NUCON-5765) using Propak–Q column. Nitrogen was used as a carrier gas with a flow of 30ml/min through capillary column and thermal conductivity detector (TCD). Column oven was maintained at 30^{o}C while injector and detector were at 70 and 80^{o}C, respectively. The thermal conductivity detector was also used, based upon Wheatstone bridge network. Its main application is for the detection of those substances (mainly permanent gases and water) that cannot be detected with the FID.

5.5 Titration method

The studies were performed using aqueous solutions of various organic acids. For this purpose,100 ml acid solution of different acids (20 mM) were magnetically stirred separately in presence of bare and metal impregnated catalyst Ag-TiO_2 (50 mg). Thereafter, the solution were collected after regular time intervals (30 min) and then volumetric titration was done with 0.1 N NaOH followed by standardization with oxalic acid (0.1 N). Phenolphthalein was used as indicator.

6. Results and Discussion

6.1 Effect on formic acid concentration during photodegradation

The effect on formic acid concentration has been studied in a range between 2, 10 and 20 mM for a constant TiO_2 dosage (50mg) during PCD.

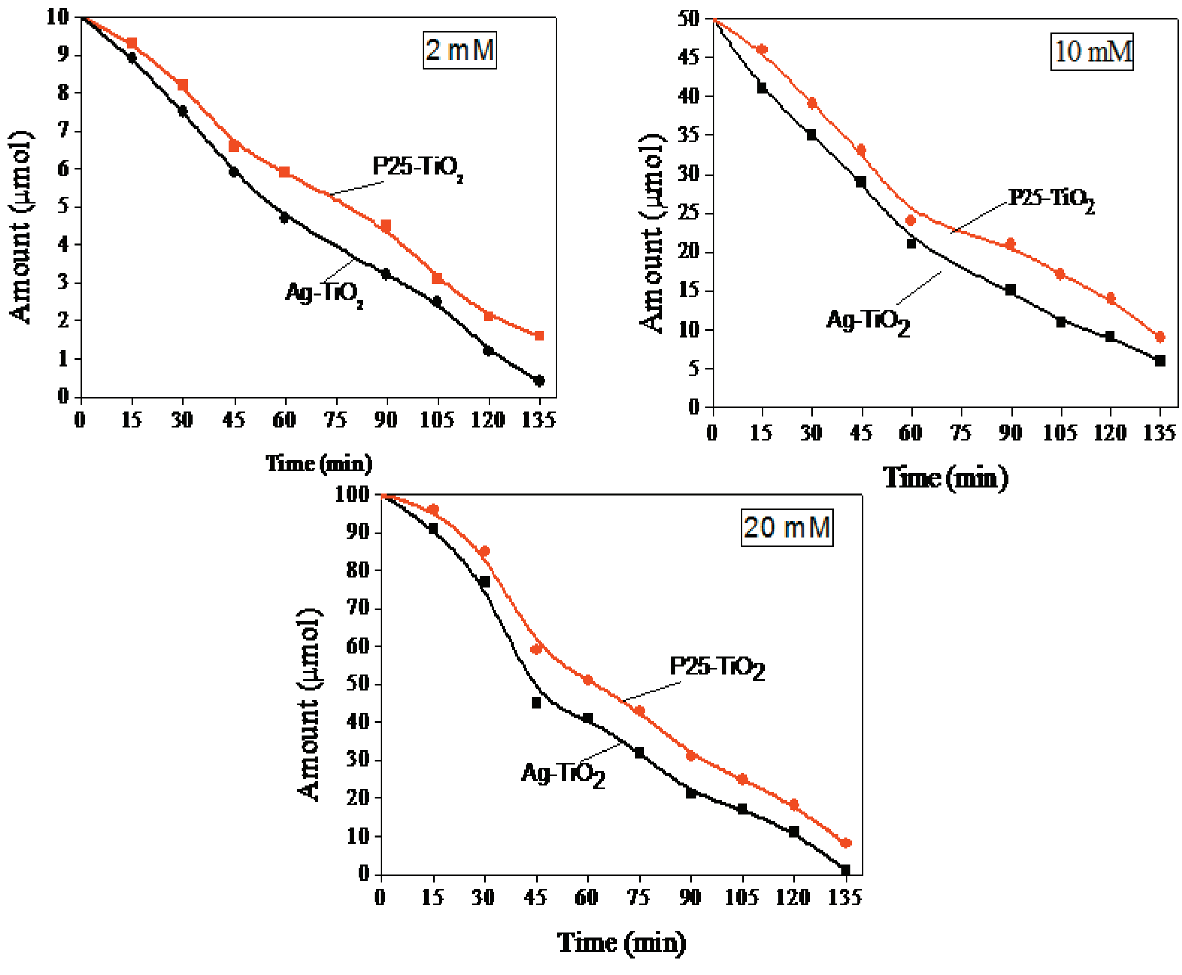


Figure 1. Photocatalytic degradation of different concentrations of formic acid (2 , 10 and 20 mM) by bare TiO_2 and Ag- TiO_2.

It is clearly evident from the results that adsorption decreased with increase in the concentration of acid (2, 10, 20 mM). This decrease might be due to the attractive interactions among positive charge on catalyst and negative charge on carboxylic acids. Subsequently, the attractive interactions between catalyst surface (P25-TiO_2 and Ag-P25-TiO_2) become less causing decrease in its adsorption. It is vividly seen from the above graphs that at 20 mM concentration formic acid degraded completely (Fig 1), whereas on the flipside, acid is not oxidized completed at other concentration. Hence, from above conclusion 20 mM was taken as optimized concentration for PCD of different acid.

6.2. Impact of photodegradation on evolution of CO_2 and concentration

Relative effect on metal loading on TiO_2 has been studied as shown in figure 2. As for the photocatalysis, adsorption of the substrate is the beginning stage which elucidates the highest photocatalytic rate. After deposition of Ag metal onto catalyst, not much difference was evident in their photo activity ascribing to a small difference in their redox potential. This process is done by gas chromatography and volumetric analysis for evaluating the carbon dioxide emission and concentration of following carboxylic acids in micromole term. Hence, by comparing the graphs, it can be concluded that with increase in the amount of carbon dioxide, the acid concentration decreases. However, long chain acids (n-valeric acid and 2-ethylhexanoic acid) were not degraded completely due to their bulky structure that causes higher interaction among them and presence of certain intermediate during degradation process.

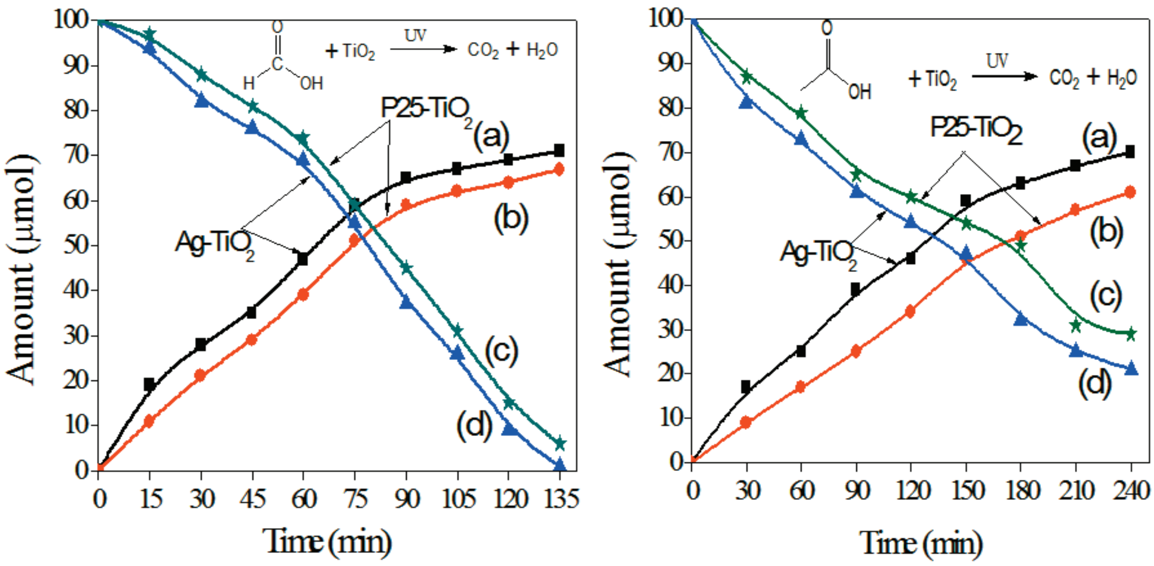


Figure 2: Photodegradation of aqueous suspension of formic acid and glacial acetic acid: CO_2 produced by **(a)** P25-TiO_2 **(b)** Ag-TiO_2 and concentration by **(c)** P25-TiO_2 **(d)** Ag-TiO_2

It is evident from the comparative graph of both formic acid and glacial acetic acid concentration and amount of CO_2 that with increase in evolution of CO_2, concentration of both acids decreases gradually with different time interval. Concentration of formic acid decrease upto 6 μmol and 1 μmol using Ag-TiO_2 and TiO_2, respectively during irritation time of 135 minutes. On contrary, the extent of acetic acid concentration decreases marginal i.e., 24 μmol and 30 μmol with both catalysts upto 240 minutes, respectively (Fig 2). Carbon-dioxide emission during photocatalytic degradation of formic acid using Ag-TiO_2 and P25-TiO_2 is 65 μmol and 60 μmol, correspondingly. And for acetic acid it is 68 μmol and 63 μmol respectively. These acids oxidized easily because of their smaller size and no intermediate involve in it, as predicted from their concentration and CO_2 evaluations.

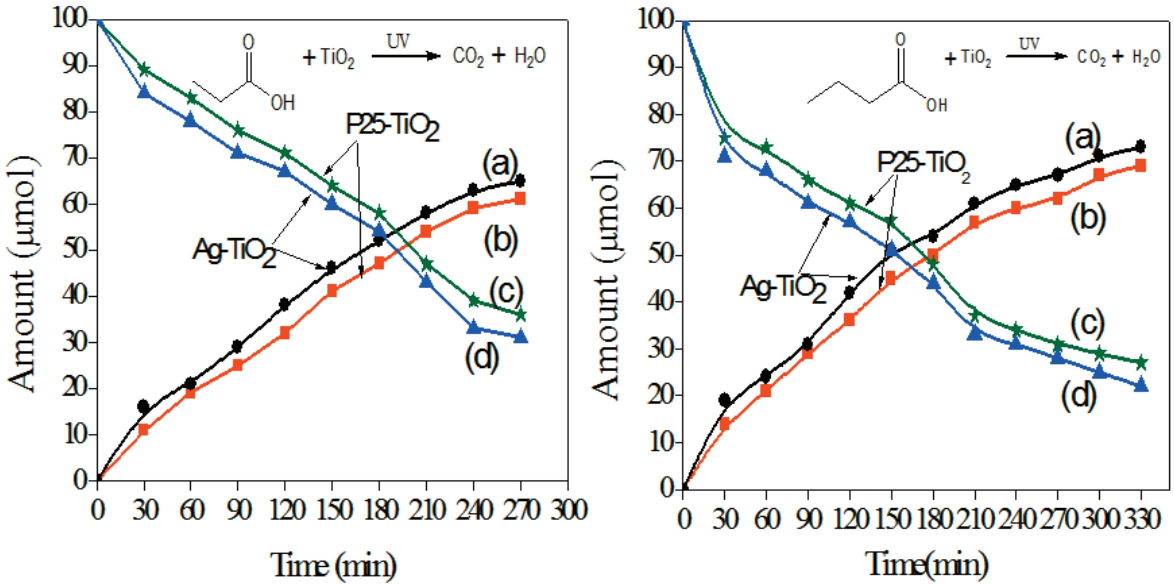


Figure 3: Photodegradation of aqueous suspension of propionic acid and butanoic acid: CO_2 produced by **(a)** P25-TiO_2 **(b)** Ag-TiO_2 and concentration by **(c)** P25-TiO_2 **(d)** Ag-TiO_2

Likewise, these graphs elucidate the concentration profile of the degradation of propionic acid and butanoic acid. Their amount of CO_2 increase during oxidation with respect their concentration decreases. Concentration of propionic acid decreased upto 37 µmol and 31 µmol while carbon-dioxide evolved is 78 µmol and 71 µmol using Ag-TiO_2 and TiO_2, respectively. On contrary, butanoic acid concentration decreased about 25 µmol and 32 µmol with both catalysts, respectively (Fig 3) and its CO_2 emitted as 71 µmol and 65 µmol respectively. It was clearly evident that butanoic acid evolved more CO_2 in degradation method it was expected to be due to presence of 1 ml methanol to make it soluble and facilitate its degradation more than propionic acid.

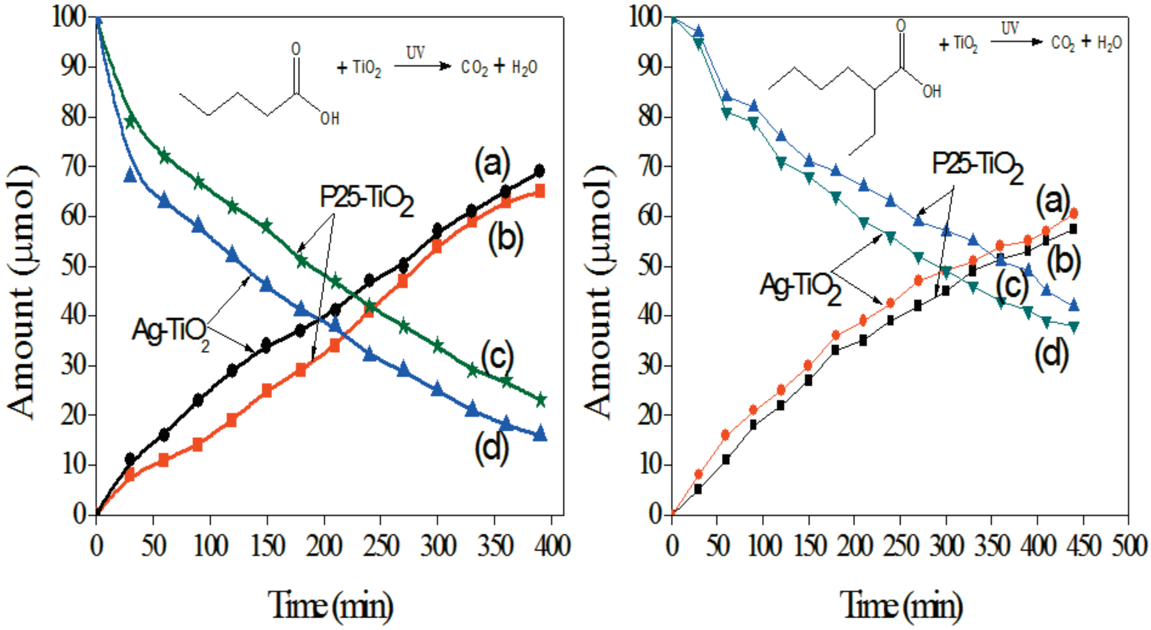


Figure 4: Photodegradation of aqueous suspension of n-Valeric and 2-ethylhexanoic acid: CO_2 produced by **(a)** P25-TiO_2 **(b)** Ag-TiO_2 and concentration by **(c)** P25-TiO_2 **(d)** Ag-TiO_2

Similarly, n-valeric acid and 2-ethylhexanoic acid showed a huge difference in their photoreactivity. Amount of CO_2 released during photo degradation of 2-ethylhexanoic acid was less than the n-valeric acid during oxidation with respects their concentration. Concentration of n-valeric acid decreased upto 31 µmol and 20 µmol with TiO_2 and Ag-TiO_2 while carbon-dioxide evolved is 80 µmol and 74 µmol using TiO_2 and Ag-TiO_2, respectively (Fig 4). This is due to addition of 3.5 ml methanol to solubilize the aqueous solution and accelerate its oxidation rapidly. Besides, 2-ethylhexanoic acid concentration decreased to about 47 µmol and 39 µmol and CO_2 evolution was 59 µmol and 52 µmol via Ag-TiO_2 and TiO_2, respectively.

Hence, the difference in photocatalytic efficiency dependent on the nature, charge of the metal on the catalyst and concentration and nature of given substrate is observed.

6.3 Effect on carbon chain length

It can be concluded from following graph that as the number of carbon atom in acids increase, a gradual increase in the formation of CO_2 during photocatalytic degradation was observed as analyzed by gas chromatography. All acids of 20 mM concentration was irridated for different time period for their degradation by bare TiO_2 and Ag- TiO_2. Acids wih shorter carbon chain (formic acid, glacial acetic acid, propionic acid, butanoic acid) degrade easily without any interference of intermediates. However, this trend is not observed in case of 2-ethylhexanoic acid. This may be due to the formation of some interemediate compounds and large molecular size of acid which is not degraded completely. Due to incomplete oxidation, some of intermediate photo-products are produced during photodegradation process which may gradually degraded to CO_2 over longer time period.

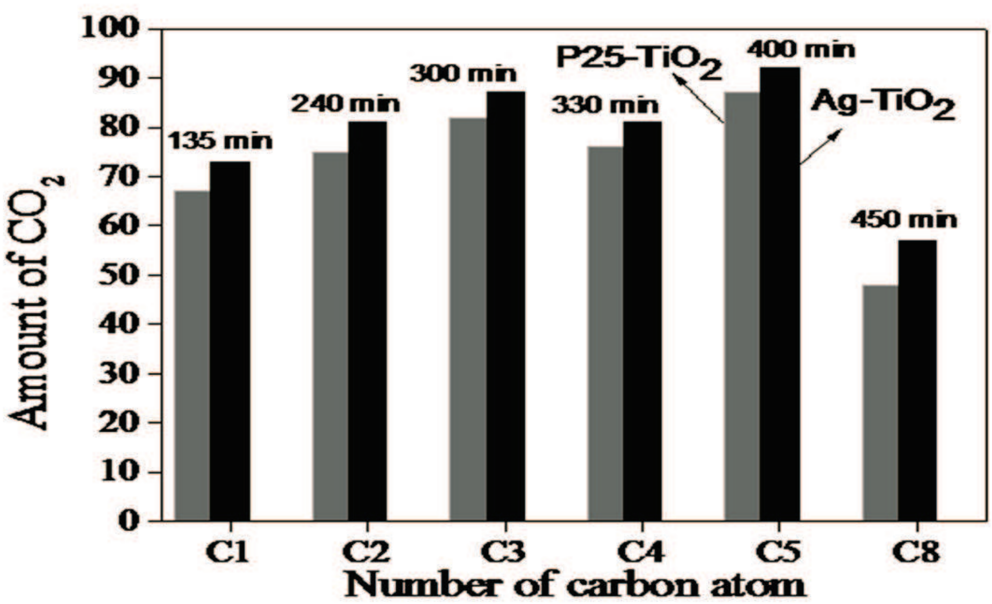


Figure 5 : Effect of carbon chain length of carboxylic acids during PCD by bare and metal loaded TiO_2.

Amount of carbon dioxide increases with the size of molecule indicating the effect of molecular size on degradation process. It also revealed that for larger acids, longer irriadation time is required as shown in (Fig .5) for their complete oxidation to CO_2. Moreover, it is also found that Ag-loaded TiO_2 enhance the photocatalytic activity of various acids as compared to bare TiO_2.

6.4 General mechanistic pathways trend of PCD of some carboxylic acids

Based on the result,it was observed that TiO_2 catalyzed photoctatalytic degradation of carboxylic acids follows two pathways. The first pathway involves, Photo Kolbe's decarboxylation of carboxylic acid followed by reaction of ●OH radical (hydroxylation). Whereas, in another path hydroxylation is followed by Kolbe's decarboxylation were observed (Fig.6). The mechanistic routes of some carboxylic acids are as follow:

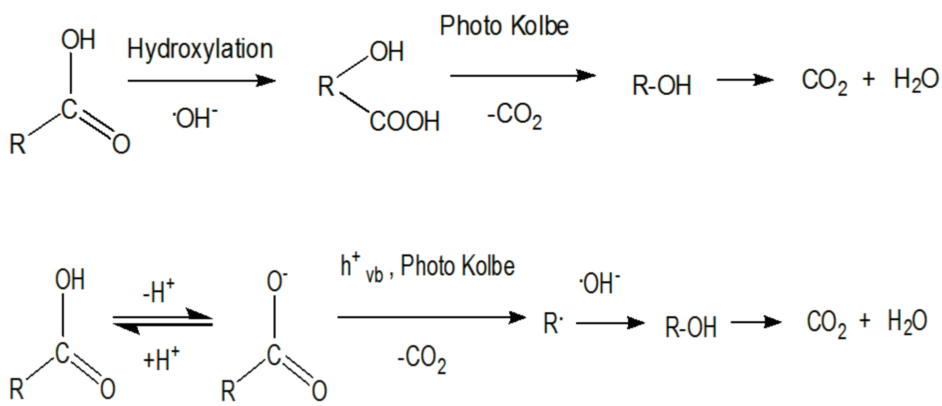


Figure 6: Generalized mechanistic routes for PCD of carboxylic acids

This reaction states that reaction conditions and the nature of substituents present in carboxylic acid chooses the mechanism of PCD.

7. Summary and Conclusion

In summary, photodegradation behaviour of acids as a function of their concentration and carbon chain length has been evaluated. Results showed that 20 mM concentration was the optimum concentration to get adsorbed on 50 mg catalyst completely for small carboxylic acid. Although, P25-TiO_2 has higher surface area, Ag deposited on P25-TiO_2 having less surface area showed enhanced in photodegradation rate. Photocatalytic experiments were carried out to completely oxidize small carboxylic acids and Ag doped metal on TiO_2 led to drastically improve the photodegradation rate. It is due to the presence of Ag on P25-TiO_2 because of strong attraction between acid and catalyst. As concentration decreased, there is increase in the amount of carbon dioxide evolved via PCD analyzed by gas-chromatography. Thereby, the study concludes as number of carbon chain length increases, there is increase in amount of CO_2 with decrease in concentration of acids. This study can be helpful for designing the photocatalytic reactor for complete oxidation of various fatty acids which may be present in industrial effluents and various other toxic materials.

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