Photocatalytic Oxidation of Cycloalkanols to Cycloalkanones by TiO_2 Catalyst

A

Thesis Submitted

In partial fulfilment of the requirements for the degree

M.Sc. (Chemistry)

Submitted by:

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15th July 2010

Acknowledgement

I wish to express my deep sense of gratitude to my guide Dr. Bonamali Pal for his guidance and support in doing my project work.

I take immense pleasure in thanking to Prof. Susheel Mittal for approving me for this project.

I thank to all the research scholars for their valuable assistance.

I also thank to the laboratory staff for their timely help.

Finally, yet importantly, I would like to express my heartiest thanks to my beloved parents for their blessings, my friends for their help and wishes for the successful completion of this project.

Pooja Bansal

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Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"Photocatalytic Oxidation of Cycloalkanols to Cycloalkanones by TiO_2 Catalyst"** in partial fulfilment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of Jan to July 2010, under the supervision of Dr. Bonamali Pal. My thesis has not previously formed the basis for award of any degree, diploma, or other similar title or recognition.

Patiala

Date: 15.07.2010

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

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Certificate

This is to certify that the project entitled "**Photocatalytic Oxidation of Cycloalkanols to Cycloalkanones by TiO_2 Catalyst**" being submitted by Ms Pooja Bansal in the partial fulfilment of the requirement for the award of the degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried under the supervision of Dr. Bonamali Pal and no part of this project has been submitted for award of any other degree by me.

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Introduction

Photocatalysis: The term "photocatalysis" was introduced in early 1930s. Photo means light and catalysis is the process of increasing the rate of reaction in presence of a substance without involving it. So, photocatalysis is a process which uses light to activate the rate of a reaction in the presence of a substance called photocatalyst. A photocatalyst decreases the activation energy and photo induced processes (particles with strong oxidation and reduction ability) occur with suitable light energy absorption by the catalyst.

Substrate + light + catalyst $\longrightarrow$ Products + catalyst

Semiconductors are mainly used as artificial photocatalyst in comparison to chlorophyll as natural photocatalyst. Semiconductors are class of crystalline solids with electrical conductivity between that of a conductor and an insulator. Semiconductor materials are the foundation of modern electronics, including radio, computers, telephones, and many other devices. In semiconductors, current can be carried either by the flow of electrons or by the flow of positively charged holes resides in the conduction and valence band of the material respectively. The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap between the two bands and energy difference between these two bands is called band gap energy which is the elementary difference among conductors, semiconductors and insulators.

In 1972, Fujishima and Honda discovered the photocatalytic water splitting on TiO_2 electrodes and extensive research was carried out regarding TiO_2 photocatalysis and credited as a most promising photocatalyst due its characteristic properties like nontoxicity, low cost, easy availability etc. [2] .TiO_2 exist in three morphological forms: anatase, rutile and brookite. All three of these types have different activity due to their differences in the crystal structure and surface properties. Both the anatase and rutile have a tetragonal crystal structure with anatase unit cell having higher volume occupied as compared to rutile [1]. The anatase and rutile form posses a band gap of 3.2 eV and 3.02 eV with the absorption edge at 386 nm and 416 nm, respectively. The anatase form has been found to have higher photocatalytic activity compared to rutile. The reason for higher activity may be due to: **(i)** ***Higher Fermi Level*****:** Anatase has higher Fermi level over the rutile by 1.0 eV. This leads to lower oxygen affinity and presence of a high level of hydroxyl groups on the anatase surface. **(ii)** ***Indirect Band Gap*****:** The anatase posses an indirect band gap while the rutile has direct band gap. In a direct band gap material, minimum in the conduction band coincides with the maximum in the valence band, resulting in the early return of electron to the valence band. This enables the excited electron to stabilise at the lower level in the conduction band itself leading to

longer life and greater stability. **(iii) *Excitation electron mass*:** Anatase possesses wider absorption gap. Hence, it is proposed that excitation electron mass of the outer shell in the anatase may be lower than in case of rutile. This may explain higher mobility of electrons in the anatase compared with rutile structure [3].

Mechanism of Photocatalysis: When semiconductor photo catalyst like titanium dioxide (TiO_2) absorbs ultraviolet (UV) radiations with energy equal to or less than the band gap energy of a photocatalyst, the electron is photoexcited to the conduction band (cb) from the valence band (vb) and therefore, creating the negative-electron (e-) and positive-hole (h+) pair in the cb and vb, respectively. After that the photogenerated charge carriers in the bulk diffuse to the surface of photocatalysts and takes part in oxidation-reduction reactions of the surface adsorbed species. The highly oxidising positive-hole breaks apart the water molecule to form hydroxyl radicals and photoelectron takes part in reducing action. Figure. 1 shows various photo induced processes occur during irradiation of photo catalyst.

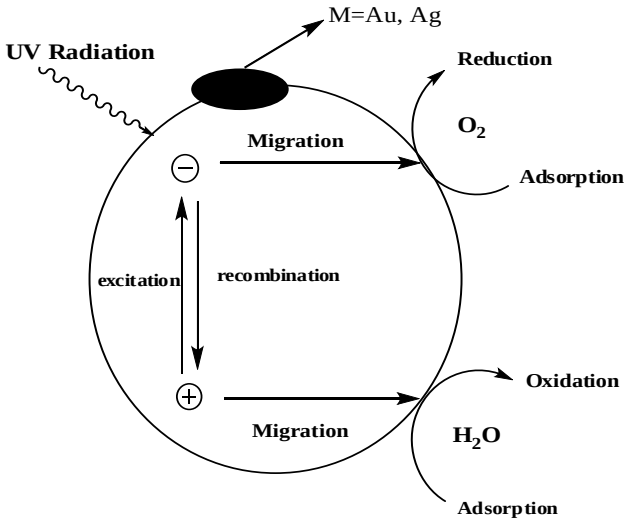


Fig. 1. Mechanism of photocatalytic action [4]

$$TiO_2 + hv \longrightarrow e_{cb}^{--} + h_{vb}^{+} \longrightarrow \text{recombination}$$

$$h^{+}_{vb} + H_2O \longrightarrow HO^{\bullet} + H^{+}$$

$$h^{+}_{vb} + D \longrightarrow TiO_2 + D^{+}$$

The electrons can be adsorbed by oxygen to form superoxide radical or it can react with oxygen along with hydrogen to create hydroxyl radicals and ions

$$e_{cb}^{--} + A \longrightarrow TiO_2 + A^{-}$$

$$e_{cb}^{--} + O_2 + H^+ \longrightarrow TiO_2 + HO_2^{\bullet} \rightleftharpoons O_2^{\bullet --} + H^+$$

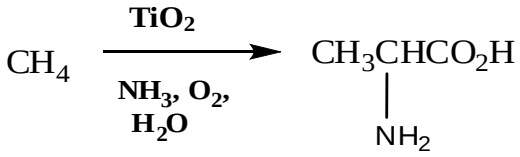
All the species produced are very reactive. The electrons when combined with oxygen are stopped from dropping back and thus recombination is prevented. This means they have more time to react with the reactant species. Reactivity of TiO_2 can further be increased by adding metal ion on it which prevents electron-hole pair recombination as discussed below [5].

Function of Metal Loading: TiO_2 has large band gap (3.2 eV) and it requires the use of UV light (340-390 nm) to be photoactivated. The large band gap and low quantum yield of TiO_2 prevent it from practical applications. In order to increase the photocatalytic activity, doping/ or deposition of metal ions/ metal onto TiO_2 have been extremely studied. Noble metals, such as Ag, Au, Pt, and Pd deposited on a TiO_2 surface, could enhance the photo catalytic efficiencies because they act as an electron trapper and slow down the recombination rate of electron-hole pair. The properties of TiO_2 have been modified by selective metal loading to extend the absorption spectrum to the visible light. One of the important parameters that affect the metal loading is the standard redox potential of the metal involved. Only those species with reduction potential much more positive than the conduction edge (0.1 eV) can be photo reduced on the surface of TiO_2. Trapping of the photogenerated electrons by oxidant species like Cu^{2+} or Fe^{3+} is possible as their redox potential values are + 0.34 V and + 0.77 V, respectively in relation with the flat band potential of the TiO_2 [5,6]. There are number of metal ions, e.g., Pt^{+4}, Au^{+3}, Ag^{+}, Pd^{+2}, and Rh^{+3} etc are easily reduced/deposited on the TiO_2 surface and showed tremendous increment in TiO_2 photo activity in many reactions.

Literature Review

TiO_2 as a photocatalyst has many applications, because of its high chemical stability, non toxicity and excellent degradation for organic pollutants. It has sterilisation effect for bacteria, fungi, pest infestation etc. Its superhydrophillic nature leads to self cleaning property and recently another use is organic functional group transformation due to its suitable redox capability. Irradiation with light of wavelength higher than 350 nm of deaerated mixtures of nitrobenzene in cyclohexene and TiO_2 or WO_3 or CdS [7] powder leads to the reduction of the nitro-compound to nitrosobenzene [8], azobenzene and azoxybenzene [9] etc. TiO_2 photocatalytic redox combined synthesis of pipecolinic acid from lysine is reported [10] in which the optical purity and selectivity is highly depends on the nature and reductive power of TiO_2 or CdS. There are many investigations on TiO_2 catalysed photoreduction of nitroaromatics to aniline with selectivity higher than 40% is obtained. Examples include which showed promising scope for organic synthesis are, e.g., TiO_2 photocatalytic oxidation of cycloalkanols to 2-Alkylbenzimidazoles [11] , cycloalkanones [12], synthesis of 2-methylpiperazine [13], photocatalytic epoxidation of styrene, hydroxylation of aromatic ring, Nitrobenzene and Phenylamine [14] and photocatalytic selective oxidation of 4-Methoxybenzyl and aromatic alcohols to aldehydes.

Meera et al [15] oxidized toluene with 1wt% cerium loaded TiO_2. The intermediate products are benzaldehyde, benzoic acid and benzyl alcohol, cresol and p-toluqinone which finally get converted to harmless CO_2 and water. Oxidation of toluene takes place on the methyl group and proceeds in the following reaction chain: toluene→ benzyl alcohol→ benzaldehyde→ benzoic acid → CO_2. Xinyong Li [16] examined the photocatalytic selective epoxidation of styrene by molecular oxygen over highly dispersed TiO_2 nanoparticle species on silica. P-25 Degussa TiO_2 samples show high selectivity for photocatalytic mineralization of styrene into CO_2. TiO_2/SiO_2 nanoparticles exhibit higher selectivity for styrene oxide and lower selectivity for benzaldehyde and CO_2. Bard and co-workers [17] shown that amino acids are produced upon near-UV irradiation of a platinized TiO_2 photocatalyst in contact with a KCN/ NH_3/H_2O mixture.



Photocatalytic Oxidation of Alchols/ Aldehydes to Ketones was studied by Paul et al. Benzaldehyde oxidation with TiO_2 was studied. While that occur the positive charge of the hole is transferred to the alcohol producing a radical cation .The alcohol then reacts with the superoxide producing the ketone and hydrogen peroxide.

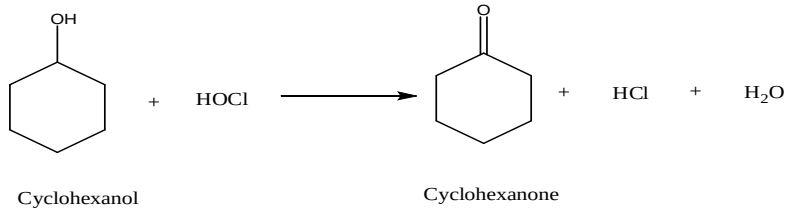
TiO_2 photocatalytic dehydrogenation of 2-propanol [26] was also studied. The alcohol first undergoes dissociative adsorption at the semiconductor. The alcohol then undergoes abstraction of a second hydrogen through reaction with a positive hole. Omima et al [18] studied the photocatalytic oxidation and degradation of alcohols namely cyclohexanol, cycloheptanol and cyclopentanol catalysed by TiO_2 and other semiconductor particulates have been studied. The effect of different parameters such as nature of catalyst, solvent, time, and oxidant was also studied. The primary photocatalytic oxidation products are the corresponding cycloalkanones with high percentage conversion and selectivity. Harvey et al. [19] studied photocatalytic oxidation of liquid propan-2-ol to propanone using suspensions of TiO_2 irradiated with filtered UV radiation.

Objective

It has been found that photocatalytic oxidation of organic compounds completely degraded to CO_2 and H_2O via many useful intermediates compound formation during longer exposure of light irradiation. Sometimes these important intermediate compounds are very hard to synthesize by conventional processes. As a result, if we control the oxidation step by changing the experimental parameters, e.g., light exposure time, solvent, surface modified TiO_2, metal additives and hole trapping agent, we may get the desired products of higher selectivity and yield. In this context, our aim is to do the partial oxidation of various cycloalkanols, namely cyclopentanol, cyclohexanol and cycloheptanol into corresponding ketones by photocatalysis using TiO_2 and metal loaded TiO_2. Complete oxidation of cycloalcohols results in CO_2 but our objective is to control the intermediates which are of commercial importance, formed during this process by doing partial oxidation. The effect of illumination time, nature and amount of catalyst is studied to increase the yield and selectivity of intermediates formed throughout the reaction. Effect of nature of the catalyst is studied by loading different weight percentage of different metal ions like Au, Ag and their respective nanoparticles on TiO_2. Metal loading is done by Photodeposition method. We are interested in doing photocatalytic reaction as it does not require toxic solvents as in conventional synthesis and it is a single step reaction. Photocatalysis take place at ambient temperature and pressure and oxidation and reduction reactions take place simultaneously.

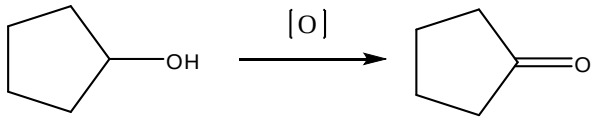
Conventional Synthesis of Cycloketones

(i) Cyclohexanone from Cyclohexanol:



Cyclohexanol is oxidised to its respective ketone by the use of hypochlorous acid /Cr_2O_3/Pb $(OAC)_4$ which are very corrosive to skin. Also oxidation byproducts, metal ion of Cr(VI), Pb^{+4} toxic in nature.

(ii) Cyclopentanone from Cyclopentanol:



Cyclopentanol cyclopentanone

The synthesis was carried out with Jones reagent, which is a mixture of concentrated sulphuric acid (H_2SO_4) and sodium dichromate ($Na_2Cr_2O_7$). Effects of sodium dichromate were found to inhibit reproduction and growth in Daphnia magna, a crustacean.

Photocatalysis is preferred over conventional synthesis: We are interested in doing photocatalytic reaction as it does not require toxic solvents as in conventional synthesis and it is a single step reaction. Photocatalysis take place at ambient temperature and pressure and oxidation and reduction reactions take place simultaneously leaving no toxic by-products.

Experimental methods and Materials

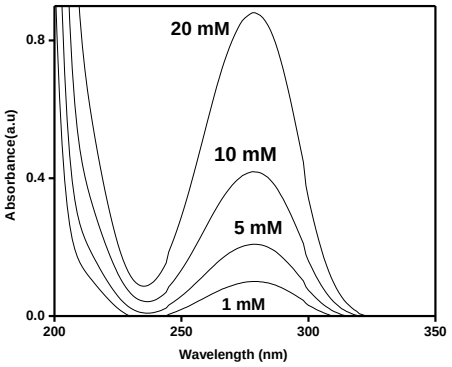
. Materials used in experiment were purchased from commercial resources and were used without any further purification. Cycloalcohols were purchased from Sigma-Aldrich and metal salts were purchased from loba-chemie and TiO_2 (P-25) was given as gift sample by Degussa company from Germany.

(i) Metal loading on TiO_2 by Photodeposition method: Metals like Au and Ag were loaded on TiO_2 by irradiating (10.4 mW/cm^2, 1-2 h) the test tube containing 5 ml of 50% methanol along with the requisite amount of metal salt solution from their respective salts like $HAuCl_4.xH_2O$ and $AgNO_3$ in 50 mg TiO_2 in N_2 purged solution. Then it is centrifuged, washed with water and dried and use for photocatalytic reaction.

(iii) **Photocatalytic Conversion of Cycloalkanol:** 50 mg metal-deposited TiO_2 catalyst was taken in test tubes and 5 ml aqueous solution of the cycloalkanols under study (20 mM) was added to it. The test tubes were irradiated under UV light (10.4 mW/cm^2) for different time periods (2-10 h) with constant stirring by using a magnetic stirrer. After the specified time interval the resulting solutions are filtered with cellulose filter (0.22 µm) and analysed by UV-Visible spectrophotometer and HPLC using C18 ODS column with 1:1 of methanol and water as mobile phase and the detecting range of cyclohexanol and cyclohexanone is 190 nm, cyclopentanol and cyclopentanone is 205 nm, and cycloheptanol and cycloheptanone is 254 nm.

Results and Discussion

Oxidation of Cyclohexanol and Cycloheptanol: Oxidation of cyclohexanol (20 mM) and cycloheptanol (20 mM) by using TiO_2 and metal loaded TiO_2 results in the formation of their respective ketones which were analysed by UV-Vis spectroscopy. Following figures showed the UV spectra of authentic sample of cycloketones.



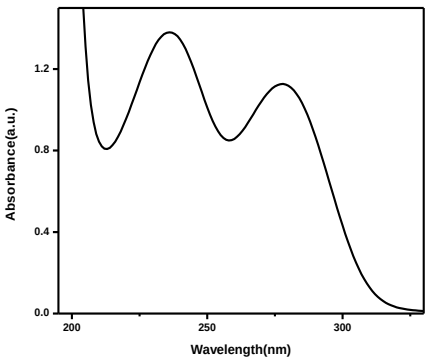


Fig. 1 Calibration curve of 20 mM cyclohexanone

Fig. 2 UV spectra of 20 mM Cycloheptanone

Fig.1 shows the calibration curve (UV spectra) of the cyclohexanone of different concentrations at λ_{max} of 280 nm. Absorption spectra of 20 mM cycloheptanone results in the appearance of two peaks at 235.5 nm and 278 nm as shown in Fig. 2. But in the present case we measure absorbance peak at 278 nm for analysing the reaction products.

Amount of cycloketones formed during irradiation of 100 mM aqueous suspension of 50 mg TiO_2 at different time intervals is shown in Fig. 3. Amount of cyclohexanone formed is increased with irradiation time 2 to 4 h. After 4 h irradiation, cyclohexanone formed is

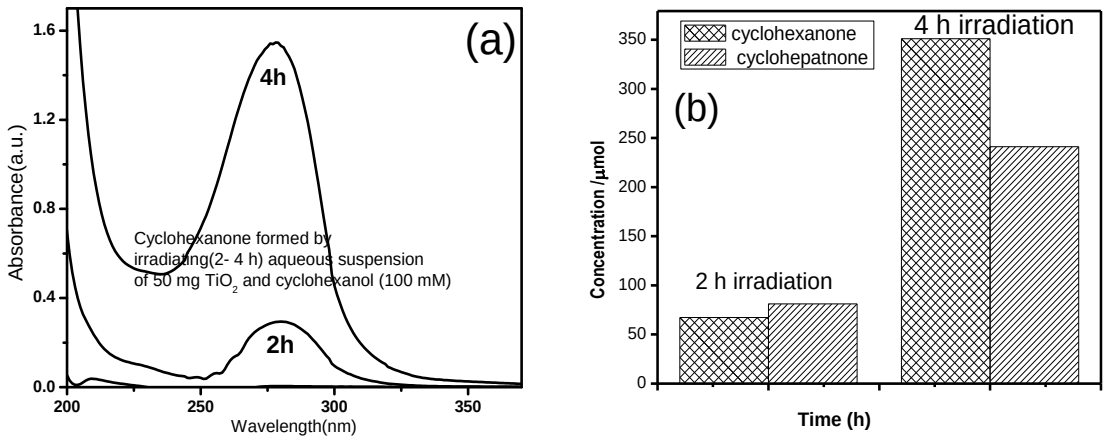


Fig. 3 Cycloketones formed by TiO_2 during 2-4 h irradiation (a) UV spectra (b) amount of products

considerable amount in comparison to cycloheptanone. It is interesting to note that 340 and 250 µmol of cyclohexanone (selectivity around 60 %) and cycloheptanone (selectivity 50 %) are produced by photocatalytic oxidation, respectively, from 500 µmol of corresponding cycloalcohols during 4 h irradiation. The lower yield of cycloheptanone may be explained by the fact that due to high ring strain-unstability in cycloheptanol that gets degraded to CO_2 very fast paralleled to ketone formation. When these cycloalcohols are irradiated for 2 h by using TiO_2 with addition of 100 µl Au nanoparticles (SP band 528 nm, size 4-8 nm) then, the amount of cycloheptanone formed is almost equal to the amount formed by the use of bare TiO_2 which signifies that the Au loading on TiO_2 does not improve the photoactivity. It was found that the anodic oxidation potential of the cyclohexanol is (+0.85V) which is less positive than the oxidation potential of hole (+2.35V), meaning that photocatalytic oxidation of cyclohexanol is thermodynamically possible. When cyclohexanol (100 mM) is irradiated more than 4 h results in the formation of higher amount of ketone but there is a shift in the λ_{max} when illumination time increases up to 8 h as shown in Fig. 4 which may be due to dihydroxylation occuring during photoreaction.

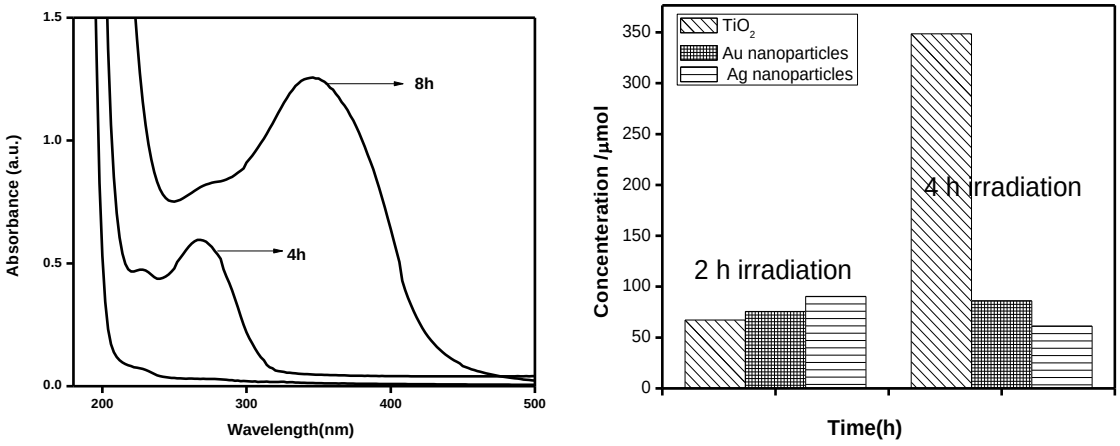


Fig. 4 (a) UV spectra of cyclohexanone formed at different irradiation time (b) Amount of cyclohexanone formed by bare and metal nanoparticles added TiO_2 during 2 and 4 h light exposure

Fig 4b showed the amount of cyclohexanone formed is always higher by bare TiO_2 in comparison to Au (size 4-8 nm) and Ag (5-10 nm) nanoparticles loaded TiO_2 during 2 and 4 h light irradiation. This can be explained on the basis of the fact that metal nanoparticle favour the reduction reaction as thermal catalyst along with the oxidation by positive holes though the reduction products are not verified.

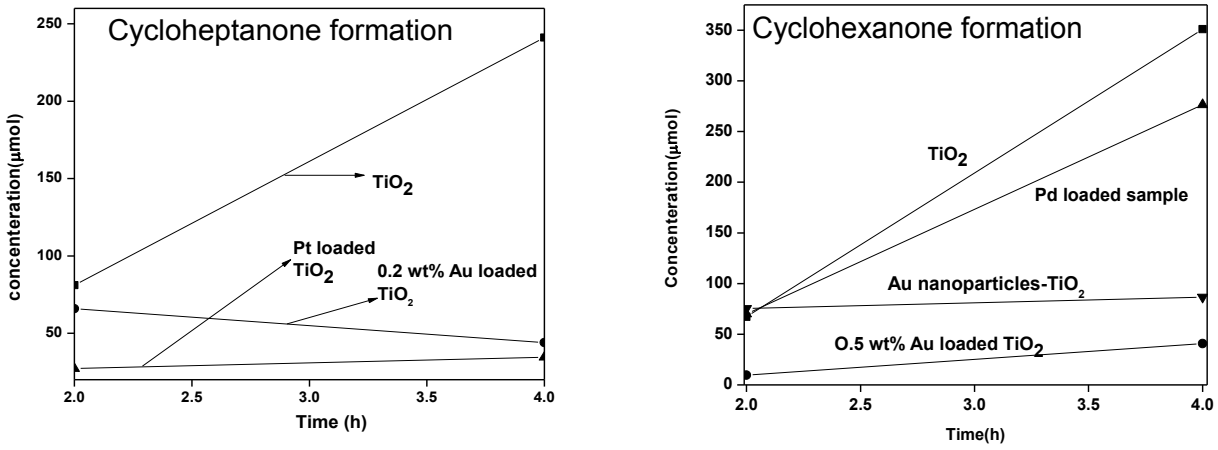


Fig. 5 Amount of Cycloheptanone and Cyclohexanone formed by various metal loaded TiO_2 and metal nanoparticles added to TiO_2

From the above figures it is clear that amount of the cycloheptanone and cyclohexanone is always high with bare TiO_2 compared with metal loaded TiO_2 which again confirmed that metal loading does not improving the photooxidation which is opposing the conventional beneficial function of metal loading in accelerating the photocatalytic activity.

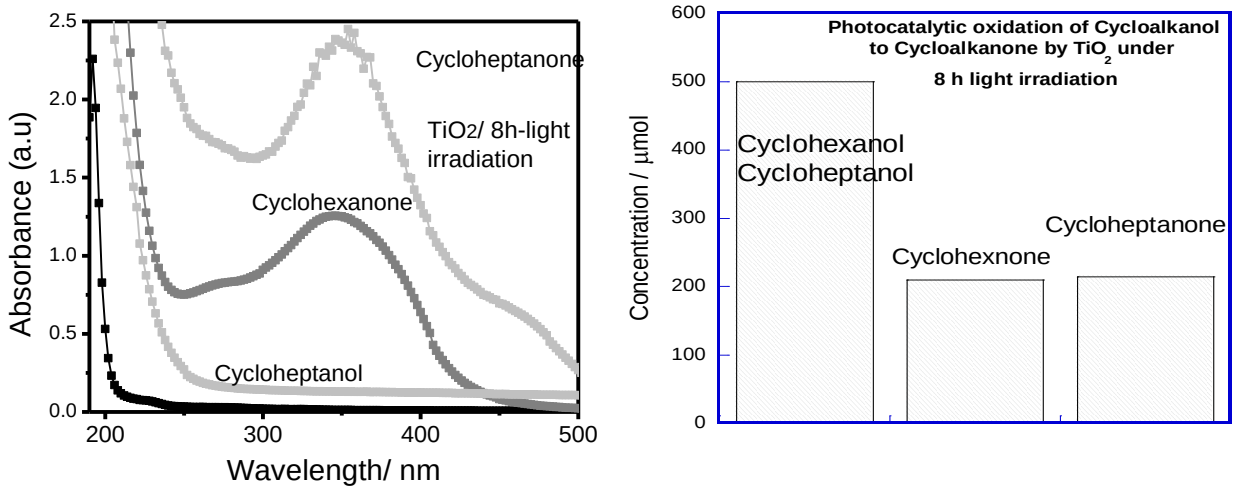


Fig. 6 Amount of cycloketone formed by Bare TiO_2 during 8h irradiation

It can be seen that significant amount of cycloheptanone and hexanone formed after 8 h light irradiation and almost 50 % products yield are obtained which may increase further for longer light exposure time. There are also some unidentified intermediates, such as n-heptanoic acid, 1-4 Cyclohexanedione, 2-hydroxy cycloheptanone etc. observed in HPLC chart due to photocatalytic hydroxylation which can be converted to desire products by suitable surface modification of TiO_2 and other reaction parameters.

Oxidation of Cyclopentanol: Photocatalytic oxidation of cyclopentanol was also studied by irradiation of aqueous suspension of 50 mg TiO_2 and 5 ml (20 mM) cyclopentanol solution.

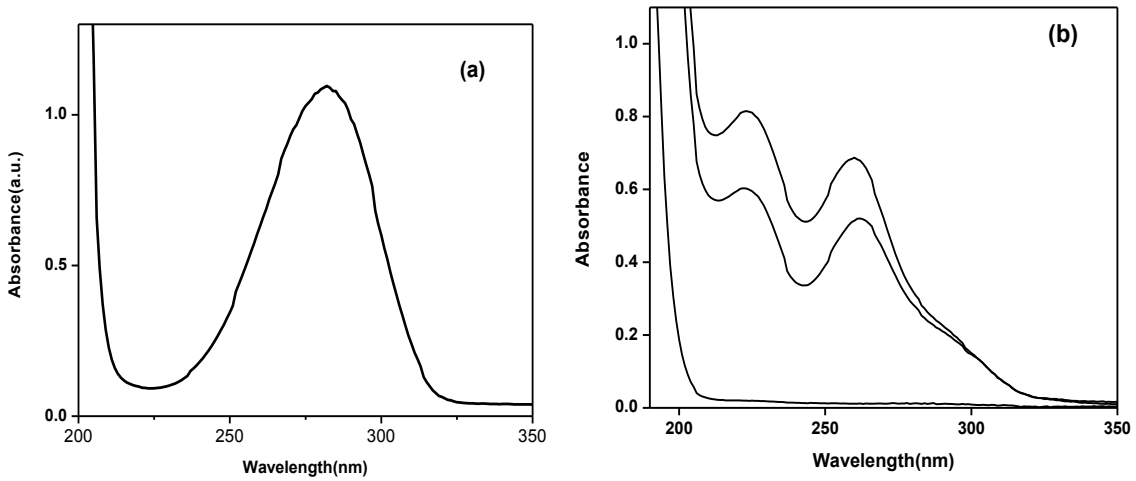


Fig. 7 (a) UV spectra of authentic Cyclopentanone (20 mM) (b) Absorption spectra of the photoirradiated cyclopentanol with bare TiO2 after 2 and 5 h.

The fig.7 (a) shows that the authentic peak of cyclopentanone comes at 280 nm. Fig. 7(b) shows that the peak (259 nm) is not corresponding to that of cyclopentanone (280 nm) when the reaction mixture was irradiated with bare TiO_2 for 2 and 5 h and absorbance of the peak is increasing after 5 h irradiation. This means that any intermediate product of cyclopentanol oxidation like n-pentanoic acid, Cyclopentyl pentanoate etc. is forming instead of cyclopentanone. The cyclopentanone oxidation was also carried out by increasing its initial concentration (100 mM) and irradiation time upto 8 h with 50 mg TiO_2. It has been found that (figure-8) instead of cyclopentanone, other products of different absorption at 264 and 367 nm are forming during longer UV illumination which may be due to n-pentanoic acid or 4-Pentenal formation as reported although that was not quantitatively analysed presently [18].

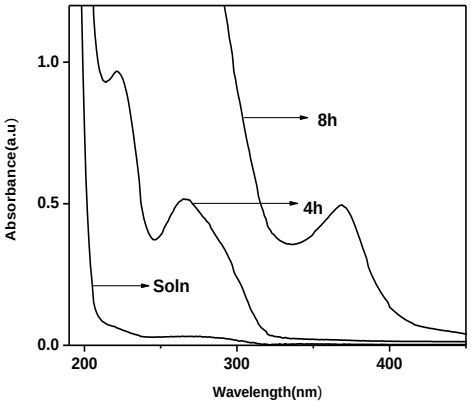


Fig. 8 Absorption Spectra of cyclopentanol photooxidation reaction after 8h irradiation with bare TiO_2

Summary and Conclusions

Our aim was to increase or improve the yield of the oxidation product i.e ketone from the selected cycloalkanols. Some papers reported high conversion (70-90 %) yield with as high as 85% selectivity during longer photooxidation reaction of 20 h UV irradiation over bare TiO_2 suspension with high intense (450W) light. We have done this research work with the aim to decrease the photo-oxidation reaction time by surface modified TiO_2 with various metal/ nanoparticles loading. Instead of complete oxidation which leads to the complete mineralization, we have tried to do the partial oxidation of the selected cycloalkanols so that the required ketonic products can be obtained.

Various metal loading and nanoparticles addition to the TiO_2 does not affect much to the yield which is in contradiction to the conventional results. In our case the photoconversion of cycloalkanol to cycloketone is always high with bare TiO_2 as reported and metal loaded TiO_2 or by nanoparticles addition does not gave any significant improvement. The reason probably the metal acts as thermal catalyst that leads to the other reduction products. The product which has been oxidised by photoirradiated TiO_2 gets reduced by the metal. So oxidation and reduction gets balanced and the net result is that there is no increase in the activity. Metal acts as dual catalyst, both as thermal catalyst and co-catalyst. In case of bare TiO_2, the activity is always higher irrespective of the ring structure of the selected cycloalkanols. It has been found that the photooxidation products of cyclopentanol is always differ than the cyclohexanol and cycloheptanol oxidation which probably due to their different alicyclic ring structure/stability. In our case the yield is around 50-60% in only 4-8 h irradiation. We have also tried other catalyst like WO_3 and ZnO etc. but the yield is not very good. Other parameters like changes in the TiO_2 particles size, surface modification, control of irradiation wavelengths and suitable solvent should be optimised for higher oxidation efficiency.

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