Photocatalytic Transformations of Functional Groups of Organic compounds by Metal Loaded TiO_2

A

Thesis Submitted
In partial fulfillment of the requirements for the degree
M Sc (Chemistry)

Submitted by:
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I thank to all other faculty members and my friends for their help and motivation.

NIDHI GUPTA

Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"Study of Photocatalytic Functional Group Transformation of organic compounds by Metal Loaded TiO_2"**, in partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala, is my own work during the period of Jan to May 2009, under the supervision of Dr. Bonamali Pal. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala
Date: 10.6.09

Nidhi Gupta

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

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Dr. Susheel Mittal
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Certificate

This is to certify that the project entitled **"Study of Photocatalytic Functional Group Transformation by Metal Loaded TiO_2 Particles",** being submitted by Ms Nidhi Gupta in partial fulfillment of the requirement for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr. Bonamali Pal and that no part of this project has been submitted for the award of any other degree by me.

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Introduction

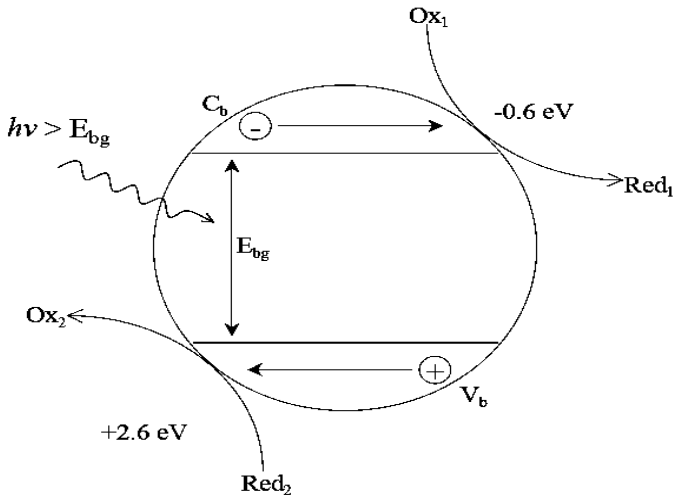
Photocatalysis[1,2]consists of the combination of photochemistry and catalysis and implies that light and a catalyst are necessary to generate or to accelerate a chemical transformation. Catalysts used in such reactions are called photocatalyst, such as chlorophyll in photosynthesis is a natural photocatalyst. Artificial photocatalyst are mainly semiconductor materials. In photogenerated catalysis the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs which reacts with adsorbed species, e.g., H_2O molecule and produces hydroxyl radicals ($OH^{\cdot}$) etc.

In 1972, Fujishimna and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes[3]. This discovery led to the invention of new field of heterogeneous photocatalysis[4]. The main focus of previous studies have been to investigate the principal applicability of photocatalysis systems for efficient treatment of water polluted with toxic substances and latter on quantum size effects on photoreactions for semiconductor nanoparticles have only been extremely studied[5].

Semiconductors are three-dimensional networks of ordered atoms. They have properties that are intermediate[6] between conductors and insulators. Their conducting power can be increased by a number of factors like increasing temperature, metal doping etc. At 0 K the lower energy levels, or valence band, are filled with electrons, while the conduction band consisting of the higher energy levels is unoccupied. Semiconductors typically exhibit band gaps in the range 0.3-3.8 eV. TiO_2 has a band gap of 3.2 eV and absorb light in UV region at 380-400 nm. An excited electron in the conduction band together with the resulting hole in the valence band forms an “electron-hole pair” and this property helps them in conducting photocatalytic reactions.

The main reason for the difference of semiconductors from metals and insulators is band gap. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors[7] there is a small gap between the valence and conduction bands that can be sometime thermally excited depending on magnitude of band gap energy.

- **Mechanism of Semiconductor Photocatalysis**[8,9,10]



When we irradiate TiO_2, the electron get excited from valence band to conduction band or can then either drop back down into the valence band resulting in recombination as heat, or it can react with other adsorbed species. Hole will oxidize the adsorbed species, such as organic compounds, water or hydroxyl ions.

$$TiO_2 + h\nu \rightarrow e^- + h^+$$
$$e^- + h^+ \rightarrow \text{heat}$$
$$h^+ + H_2O_{ads} \rightarrow {}^{\bullet}OH + H^+$$
$$h^+ + OH_{ads} \rightarrow {}^{\bullet}OH$$
$$h^+ + RH_{ads} \rightarrow {}^{\bullet}R + H^+$$

The electrons can also react with the compounds that are present in the solution such as oxygen and hydrogen peroxide. The electrons can be absorbed by the oxygen to form superoxide or it can react with oxygen together with hydrogen to create hydrogen peroxide. It can then react with hydroxyl radicals and hydroxyl ions.

$$e^- + O_{2ads} \rightarrow O_2^-$$
$$2e^- + O_{2ads} + 2H^+ \rightarrow H_2O_2$$
$$e^- + H_2O_{2ads} \rightarrow {}^{\bullet}OH + OH^-$$

All of these produced species are highly reactive. The electrons when combined with oxygen are stopped from dropping back to the valence band and prevent the electron-hole recombination[11]. This means that the hole and the electron have more time to react with species adsorbed to the catalyst. A lack of dissolved oxygen would hinder the reaction as

electron-hole recombination would occur far more readily, giving less time for the species to react. TiO_2 is highly active because the oxidation and reduction potential of valence band hole and conduction band electron, respectively, are appropriate for the most of the redox reactions.

Photocatalysis a preferred and more advanced technique than conventional organic synthesis due to following reasons[12]:

- In photocatalytic reactions, both oxidation and reduction occurs simultaneously on the photocatalyst particles but in conventional reactions we need different oxidizing agent and reducing agent.
- These redox reactions by e^- and h^+ leave no by-product that originated in the reductant and oxidant; this is in contrast to conventional redox reagents such as permanganate or lithium aluminum hydride to leave respectively, manganese ion or aluminum hydroxide after oxidation and reduction.
- Also in photochemical reactions there is not much need of solvents which are expensive and are difficult to dispose off. We generally use water but in conventional reactions many solvents are used.
- Photochemical reaction is a single step reaction, we can get our product just by mixing the reactant and irradiating them but conventional reactions are multi-step reactions.
- Photocatalytic reactions occur at ambient temperature and pressure so need not to maintain drastic conditions as required in conventional reactions.

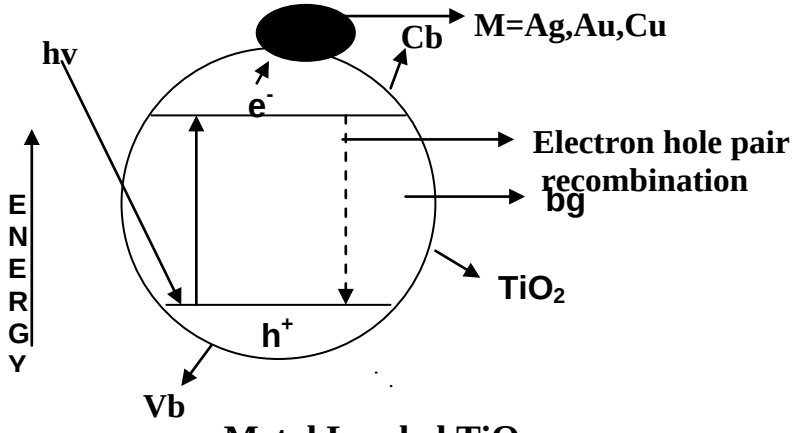
In-spite of having these many advantages these photocatalytic reactions have not been industrialized[13]. This is mainly because these reactions are less selective and also it is necessary to optimize the operating conditions for large scale use which is currently investigating.

❖ **Function of metal loading**

Metal Loading is mainly done in order to improve the photocatalytic activity of semiconductors. The photocatalytic activity of TiO_2 is observed to be poor in the absence of a metal. Generally a noble metal[14] like Au, Ag or Pt is added to the nanoparticle. A transition metal is loaded on the photocatalyst as a co-catalyst to enhance the rate of the photoreaction. The barrier height at the photocatalyst/noble metal interface of the

photocatalyst is lowered relative to that at the photocatalyst/solution interface, causing efficient charge separation of photogenerated electrons and holes thus avoid the recombination because electrons from the conduction band are taken up by the metal present on surface of semiconductor. Sathish *et al*[15]have reported that there is a direct correlation between the rates of hydrogen evolution and properties of the transition metal co-catalysts. Among Pt, Pd, Rh and Pt metal with higher redox potential and work function, and lower metal hydrogen bond strength was found to be the most favorable for hydrogen evolution activity. Without cocatalysts[16], photocatalysts show very poor performance and many of them do not function at all. The above scheme is shown below.

The absorption band of the metal ion-implanted titanium oxide was found to shift smoothly to visible light regions[17], the extent of the red shift depending on the amount and type of metal ions implanted with the absorbance maximum and minimum values always remaining constant. The photocatalytic reaction does not proceed under visible light irradiation ($\lambda > 450$ nm). However, visible light irradiation of the metal ion-implanted titanium oxide photocatalysts led to various significant photocatalytic reactions. The metal is present on the surface and thus has an electron rich region which can be attacked by a suitable electrophile. The molecule is susceptible to attack by oxidizing agents as well that will accept electrons from the surface and bring about oxidation. Based on the above principle we can change the selectivity and yield of the reaction products.

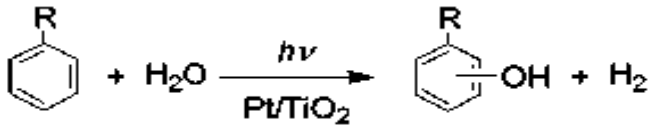


Metal Loaded TiO_2

Literature Review on the functional group transformation by TiO_2

Recently, scientist transformed many functional groups by using TiO_2. Some work was done by using metal loaded TiO_2 and the effect of loading of metal was examined. It soon became apparent that novel redox reactions of organic and other inorganic substrate could also be induced by band-gap irradiation of a variety of semiconductor particles of sizes ranging from clusters and colloids to powders and large single crystals**.** Following are few examples listed:

- **Photocatalytic hydroxylation of aromatic ring by using water as an oxidant in the presence of platinum loaded TiO_2:**[18]

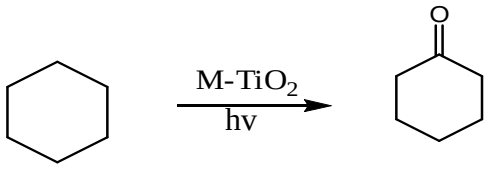


Hydroxylation of benzene was done by using water as an oxidant in presence of Pt loaded TiO_2. Same reaction can be performed by using different metal loaded TiO_2 to see the effect of other metals and yield of product given by them.

The primary photocatalytic oxidation of aromatic compounds containing an electron donating group (EDG) gives rise mainly to ortho and para mono-hydroxy derivatives while in the presence of a electron withdrawing group (EWG) all the mono-hydroxy derivatives are obtained. This opens a new green route for the synthesis of hydroxylated aromatic compounds. Moreover, in the presence of both an EDG and an EWG, as in the case of 4-chlorophenol and hydroxy-cyanobenzenes, the attack of the hydroxyl radical takes place only in the positions activated by –OH. A competing reaction pathway to total oxidation was also observed from the starting of the irradiation; this pathway was more important for compounds containing a EWG. This evidence can be explained by considering the strong interaction of these molecules with the TiO_2 surface. In fact, adsorption in the dark, measured for all the compounds, resulted to be significant only for molecules having strongly EWG's.[19]

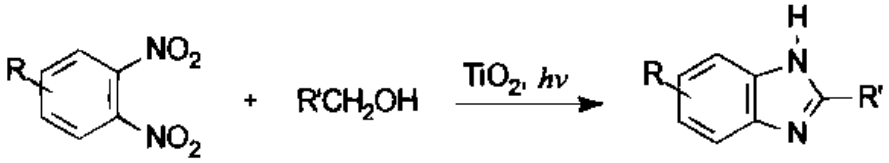
- **Oxidation of cyclohexane to cyclohexanone :**

The oxidation of cyclohexane by O_2 over native or chemically modified TiO_2 is thermodynamically acceptable. But it was reported that the rate at room temperature is impossibly slow without photo assistance, and at higher temperatures little oxidative selectivity is observed. High oxidative selectivity is attained with $Ti0_2$ photocatalysis, producing 83% cyclohexanone, 5% cyclohexanol, 12 % CO_2.[20]



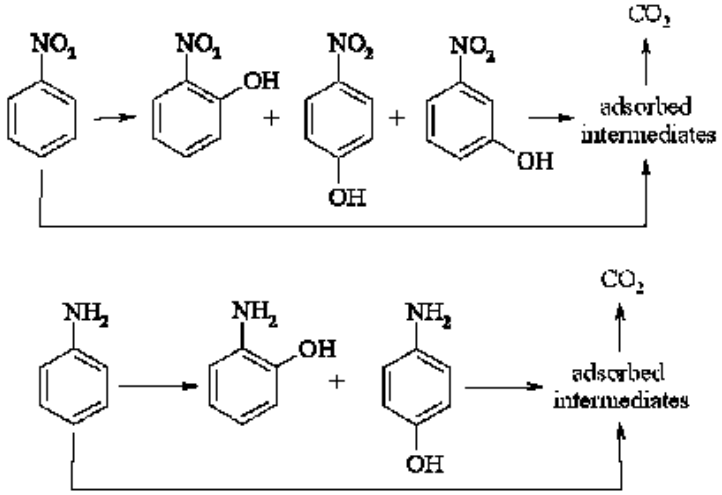
Cyclohexane Cyclohexanone

- **Synthesis of 2-Alkylbenzimidazoles via TiO_2-Mediated Photocatalysis from dinitro benzene derivatives:**[21]

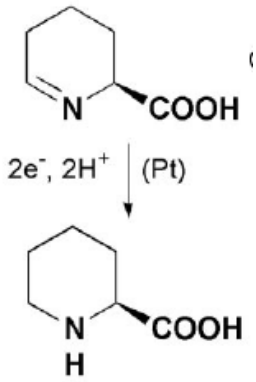


Cyclization of dinitro derivatives of benzene was done by using alkyl alcohol in the presence of TiO_2.

- **Photocatalytic Oxidation of Nitrobenzene and Phenylamine in aqueous suspension of TiO_2 yield CO_2.**[22]



- **Reduction of pyridine derivative into piperidine derivative by the electrons produced by TiO_2 loaded with Pt.**[23]



(S)-isomer

- TiO_2-photocatalyzed reduction of nitro benzene by loading Ag was also reported. Loading of Ag shows the increase in photocatalytic effect of TiO_2. Electrons on TiO_2 are easily captured by metal so that the species present get easily reduced.[24]

$$C_6H_5NO_2 \xrightarrow[hv]{Ag\text{-}TiO_2} C_6H_5NH_2$$

Objective

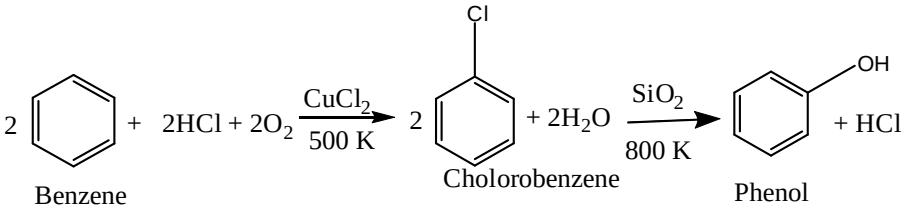
TiO_2 is known as the most important photocatalyst on account of its advantages over other materials, such as its higher activity, lower price and its chemical and photo resistance properties. One of this catalyst disadvantages is that the activity is still not high enough to be suitable for commercial application[25]. Its activity is enhanced by adding some transition metal dopants (Zn^{2+}, Fe^{3+},V^{4+}, Zr^{4+}, Mo^{6+}) or co-deposition of noble metal (Pt, Pd, Au, Ag) on TiO_2[26]. This phenomenon of metal deposition is called metal impregnation. Our main objective is to increase the activity of TiO_2 by metal loading and to increase the selectivity of organic functional group transformation.

❖ **Metal impregnation**[27]

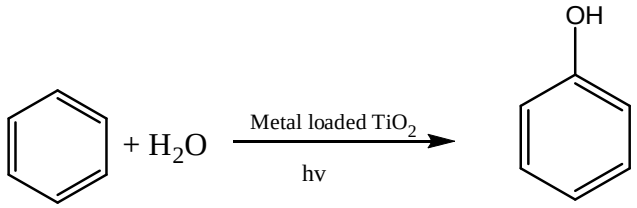
Metal ion impregnation: Depositing a metal on the surface of TiO_2 is called metal impregnation. A required amount of transition metal salt was dissolved in water and then was mixed well with the TiO_2 sol suspended in water. The mole ratio of metal salt to TiO_2 varies accordingly. The mixture was heated hydro thermally at 105 ˚C for 48 h. The solid was isolated by centrifugation, washed with water, and then dried in the oven. The structure of the metal-loaded TiO_2 was identified with X-ray powder diffraction (XRD).This method of synthesis of metal deposited TiO_2 is Post hydrothermal Synthesis.

Photodeposition: A required amount of transition metal salt was dissolved in water and then was mixed well with the TiO_2 sol. The mole ratio of TiO_2 to metal varies accordingly. Nitrogen gas was purged for 10-15 min. The mixture was irradiated with an UV light of wavelength of about 365 nm for 48 h. After photoirradiation, the solution was filtered and dried at 105 ˚C. This method of synthesis of metal deposited TiO_2 is Photo-assisted reduction/impregnation. We can also reduce the metal ion to elemental metal by adding equimolar amount of $NaBH_4$ as of metal salt present in solution.

We are interested in doing functional group transformation of organic compounds by photocatalytic method as it is a single step reaction and does not require harsh oxidizing and reducing agents as are required in conventional methods. Following is the conventional method of group transformation:

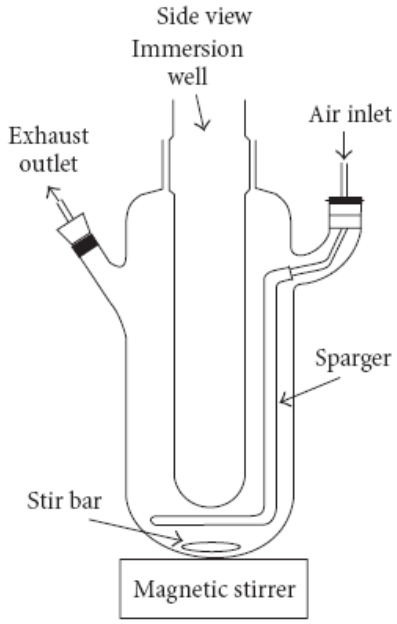


Photocatalytic method of group transformation:



Conventional method is more drastic than photocatalytic reaction as it require high temperature, pressure, complex catalyst and is a multi-step reaction where as photocatalytic reaction is a one step reaction thus Greener Reactions.

❖ **Photocatalytic Reactor**



The photoreactor[28]as two glass tubes arranged concentrically, one having a larger diameter than the other. The inner channel contains an elongated light source, a bulb radiating light outwardly. There are two openings at the top, one for water inlet and the other for water outlet. On the sides, there is an air inlet and an exhaust outlet. A long thin capillary on the air inlet side helps in homogenizing air with the reaction mixture under magnetic stirrer.

In the present case, the outer jacket of the reactor was removed and the sample is irradiated directly in a test tube surrounding the UV lamp. The test tubes were kept at a distance of 2 cm from light source. The whole set up was placed in a wooden box to prevent the UV exposure as a safety measure.

Experimental Section

The experimental works are divided in the following sections:

1. **Metal impregnation of catalyst**
2. **Photocatalytic test reaction of KI**
3. **Photocatalytic conversion of organic compounds**
    - **Oxidation of benzene to phenol.**
    - **Oxidation of Cyclohexanol to cyclohexanone.**

❖ **Metal impregnation on TiO_2:** 2g TiO_2 was weighed and 50 ml distilled water was added to it in a 250 ml beaker. The metals chosen for impregnation were: Fe, Au, Cu, Ag and Ni. Different weight percentages of these metals from a solution of their respective metal salts like $FeCl_3$, $HAuCl_4.xH_2O$, Cu $(NO_3)_2.3H_2O$, $AgNO_3$, Ni $(NO_3)_2$ were impregnated on TiO_2. Metal was impregnated in the reduced form (M^0) as well as in the oxidized form (M^{n+}). In order to impregnate metal in reduced state, solution of $NaBH_4$ was added to the solution above in equimolar amount as metal salt present. The catalysts thus prepared are filtered and dried at 500^o C in muffle furnace for a period of 5 h.

❖ **Photocatalytic test reaction of KI (formation of I_2 from KI):** The catalytic efficiency was tested with 200 mM aqueous solution of KI. The photocatalytic activity[29]as evaluated through the oxidation of I^- to I_2 as a model reaction. The absorbance peak of I_3^- appeared at 288 nm. Photocatalytic reaction is based on the following reaction:

$$2I^- \rightarrow I_2 + 2e^-$$

$$I_2 + I^- \rightarrow I_3^-$$

Reaction was done by taking following Catalyst:

✓ **Reaction of KI with commercial TiO_2 and Metal impregnated TiO_2:** 100 mg of each type of catalyst was added to 10 ml solution of KI in different test tubes and O_2 was purged in the solutions for a period of 10 min. The test tubes were capped with rubber cap and was wrapped with parafilm and kept in photoreactor under UV light for 2.5 h with constant stirring using a magnetic stirrer. The resulting filtered

solutions were analyzed by taking their UV spectra and also by titrating I_2 with 1mM sodium thiosulphate solution.

- **Photocatalytic conversion :**
  - **Oxidation of benzene to phenol:**

- ✓ **Effect of irradiation time on photocatalytic reaction using 10% Fe by weight of P-25 TiO_2:** 50 mg of metal impregnated catalyst, as prepared earlier was taken in different test tubes and 5 ml aqueous solution of benzene (1 µM) was added to it and O_2 was purged for a period of 10 min. The test tubes were irradiated under UV light (intensity of 10.4mW/cm^2) for different time periods viz. 30, 60, 90 and 120 min with constant stirring using a magnetic stirrer. After required time interval, resulting solutions are filtered with cellulose filter (0.22µm) and analyzed by UV spectra.

- ✓ **Effect of different metal ions having different concentration on photocatalytic reaction:** 50 mg of various weight percentages of metal impregnated catalyst, as prepared earlier were added to 5 ml aqueous solution of benzene (1 µM) in different test tubes and O_2 was purged in the solutions for a period of 10 min. The test tubes were irradiated under UV light (intensity 10.4 mW/cm^2) for 2 h with constant stirring using a magnetic stirrer .The resulting solutions are filtered with cellulose filter (0.22 µm) and analyzed by taking their UV spectra.

- ➢ **Oxidation of cyclohexanol into cyclohexanone[30] using different metal impregnated catalyst:** This alcohol was chosen as it gets easily oxidized due to its simple structure. 50 mg of various weight percentages of metal impregnated catalyst, as prepared earlier were added to 5 ml aqueous solution of cyclohexanol (1 µM) in different test tubes and O_2 was purged in the solutions for a period of 10 min. The test tubes were irradiated under UV light (intensity 10.4 mW/cm^2) for 1 h with constant stirring using a magnetic stirrer. The resulting solutions are filtered with cellulose filter (0.22 µm) and analyzed by taking their UV spectra.

Results and Discussion

- **Results of formation of I_2 from KI:** When 200 mM solution of KI along with various weight percentages of different metal loaded TiO_2 was irradiated for 2.5 h in UV light, different amount of iodine in their reduced as well as in their oxidized state are formed. This is because the activity of each metal-TiO_2 composites is different due to difference in their physicochemical and electronic properties. Following figure shows the amount of iodine formed by different catalysts.

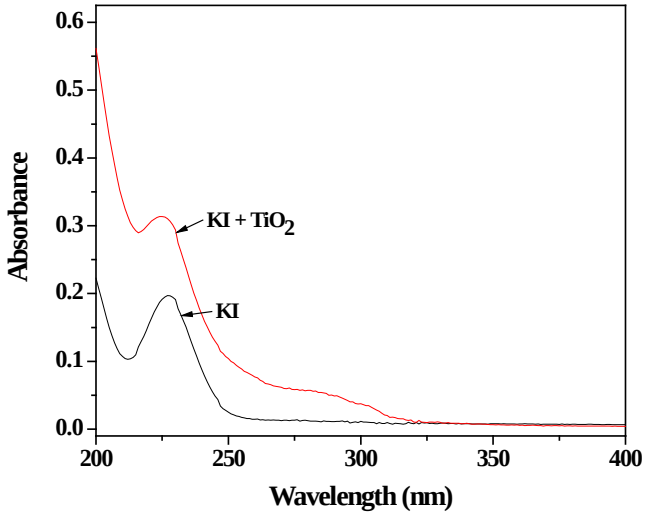


Figure1. Absorption spectra of 200 mM sol. of KI and KI+TiO_2

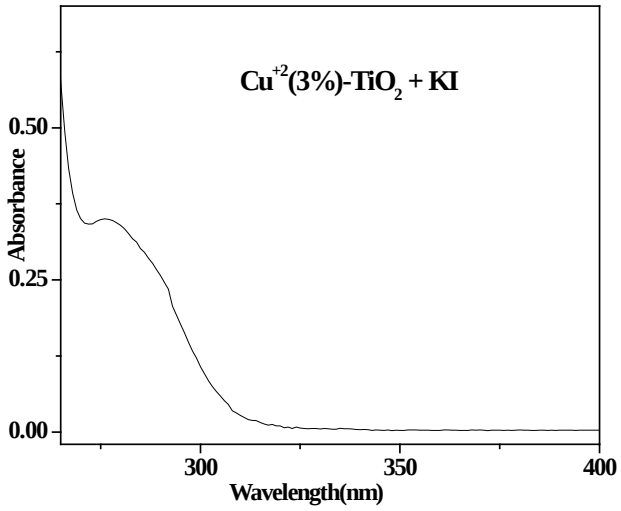


Figure2. Absorption spectra of 200mM KI+Cu^{+2} (3%) loaded TiO_2

The above spectra shows that the authentic sample of KI gives maximum absorption at around 227 nm but when reacted with TiO_2 this peak intensity gradually reduced along with formation of another peak with increasing absorption intensity at around 288 nm due to the formation of iodine. But when the same reaction was performed with metal ion loaded TiO_2 i.e. Cu^{+2}(3%)-TiO_2 then absorbance at 288 nm increases which correspond to increase in concentration of iodine, as absorbance is directly proportional to the concentration. This increase in absorbance proved the enhanced photoactivity of TiO_2 after loading metal ion on to it.

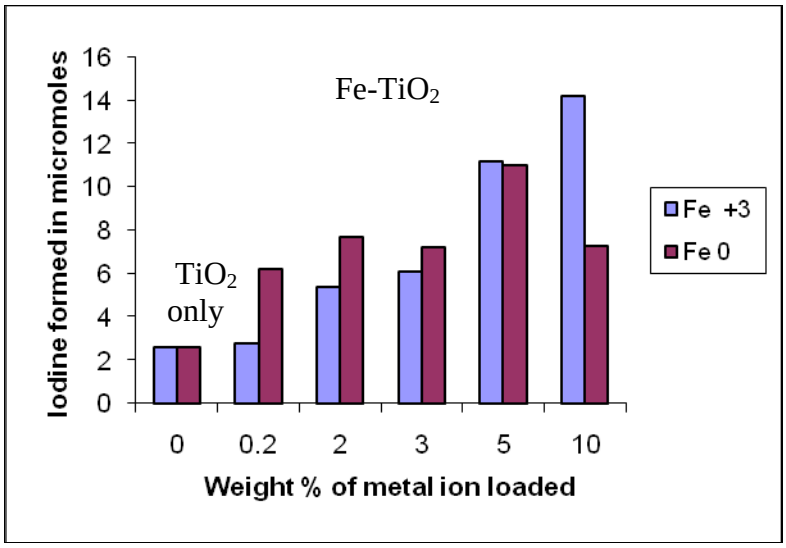


Figure3. The amount of iodine formed with Fe loaded TiO_2 having different weight % of metal ion (Fe^{+3} and Fe^0)

This figure show that amount of iodine formed by TiO_2 alone is less in comparison to amount formed by Fe loaded TiO_2. Amount of I_2 increases with increase in percentage of Fe^{+3} loading on TiO_2 in which 10 weight % loading of metal ion gave highest activity of iodine formation. When Fe^0 was loaded on TiO_2 this trend was not observed. Amount of I_2 increases up to 5 weight % metal ion and then decreases.

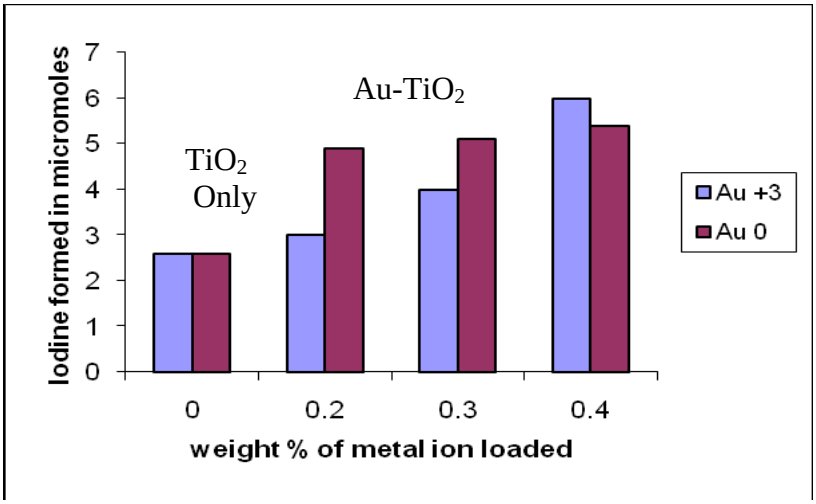


Figure4. The amount of iodine formed with Au loaded TiO_2 different weight % of metal ion (Au^0 and Au^{+3})

Above figure results that amount of iodine formed by TiO_2 alone are less in comparison to amount formed by Au loaded TiO_2. Amount of I_2 increases with increase in Au^{+3} loading

on TiO_2 in which 0.4 weight % loading of metal ion give highest activity of I_2 formation. When Au^0 was loaded on TiO_2, the activity almost double compared with pure TiO_2 and after that there is almost no effect upon further loading up to 0.2-0.3 wt % which gives more or less same amount of I_2.

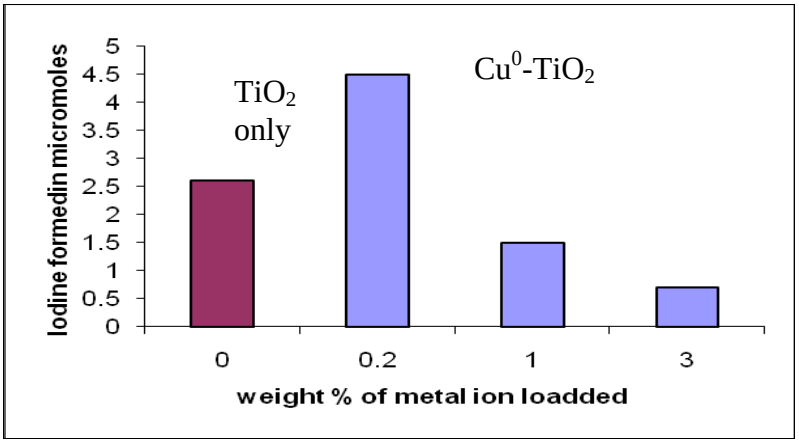


Figure5. The amount of iodine formed with Cu^0 loaded TiO_2 having different weight % of metal ion

From the above figure it was concluded that amount of iodine formed by TiO_2 alone is high in comparison to amount formed by higher weight percentages of Cu^0 loaded TiO_2. Amount of I_2 decreases with increase in Cu^0 loading on TiO_2 in which lowest weight percentage (0.2%) of metal ion is most active. Cu^{+2} loading on TiO_2 did not show much effect of I_2 formation as analyzed by UV spectra.

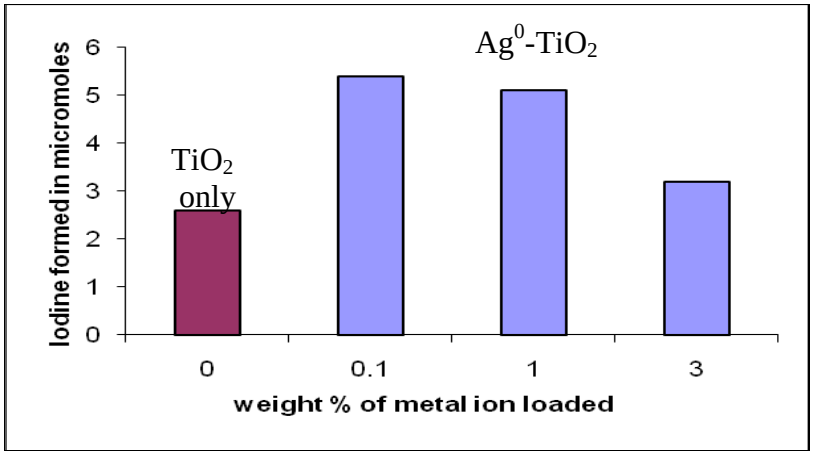


Figure6. The amount of iodine formed with Ag^0 loaded TiO_2 having different weight % of metal ion

It was concluded from the above figure that activity of TiO_2 is highly enhanced by Ag^0 loading. Amount of iodine formed by TiO_2 is less in comparison to Ag^0 loaded TiO_2 Amount of I_2 decreases with increase in Ag^0 loading on TiO_2 in which lowest weight percentage (0.1%) of metal ion is most active and decreases as Ag^0 loading on TiO_2 increases. Ag^+ loading on TiO_2 did not show any effect as found by UV spectra.

- **Table1. shows comparison of highly active M^{+n}& M^0-TiO_2 composites towards I_2 formation in 5 ml after irradiation of 2 hours.**

Metal loaded on TiO_2	**Amount of metal loading that gave highest activity**	**Amount of iodine formed in µmol**
Fe^{+3}	10.0	14.2
Fe^0	5.0	11.0
Au^{+3}	0.4	6.0
Au^0	0.4	5.4
Cu^0	0.2	4.5
Ag^0	0.1	5.4

From the above results it was concluded that

- ✓ In all cases activity of TiO_2 is highly enhanced after loading with M^{+n} and M^0.
- ✓ Different metal ion and neutral metal showed different activity. As in case of Fe-10 weight % of metal ion is highly active in Fe^{+3} where as 5 weight % of metal ion is highly active in Fe^0.

  • Difference in their (M^{+n}& M^0-TiO_2 composites) reactivity can be explained on their Fermi energy level which is changed compared with individual entity. When metal get loaded on TiO_2 then Fermi energy Level of metal and TiO_2 come to equilibrium.

  • Difference in their reactivity can also be explained due difference in surface area and charge transfer ability of M^{+n} or M^0-TiO_2. Photocatalysis is a surface phenomenon thus

efficiency of the reaction depends on the surface area of the catalyst. Metal modifies the surface of TiO_2 and thus its reactivity.

• Another reason may be their difference in electron capturing capacity of different metal ion. Different metal have different oxidation and reduction potential so they may modify the rate of electron transfer.

- ✓ Highest active weight percentage of metal ion is different in different cases due to the effect of metal, type and concentration of substrate.
- ✓ Metal ions like Ag, Cu show very little or negligible activity in their oxidized form.
- ✓ All three coinage metals-Cu, Ag, Au show same behavior in their M^0 state as they are present in same group of periodic table .Lowest weight percentage of metal ion is most active in all three cases.
- ✓ Activity of metal ion loaded TiO_2 increases as oxidation state of metal ion increases. Au^{+3} is the most active and Ag^+ is least active amongst Au^{+3},Cu^{+2} and Ag^+. With increase in oxidation state electron capturing capacity of metal ion increases thus increase the activity of TiO_2.

❖ **Functional group transformation reaction:**

➢ **Oxidation of benzene to phenol:** When aqueous solution of benzene (1µM) with M^{+n}& M^0 TiO_2 catalyst was irradiated in UV light then it get converted to phenol**.** The formation of product was confirmed by taking UV spectra of the product. Following are the absorption spectra of authentic sample of benzene and phenol.

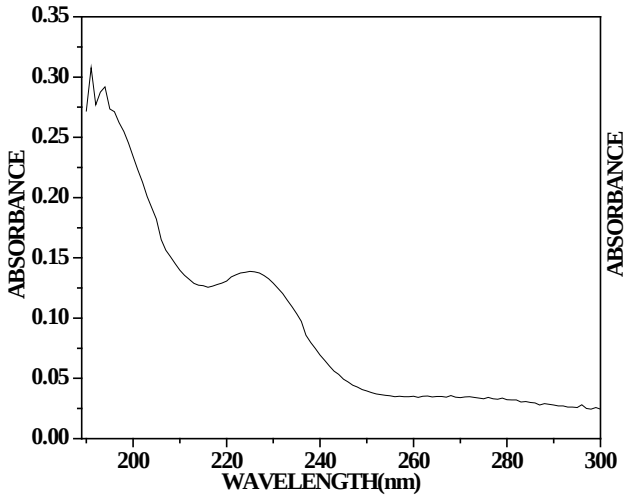


Figure 7. Absorption spectra of 1 µmolar aqueous sol. of benzene.

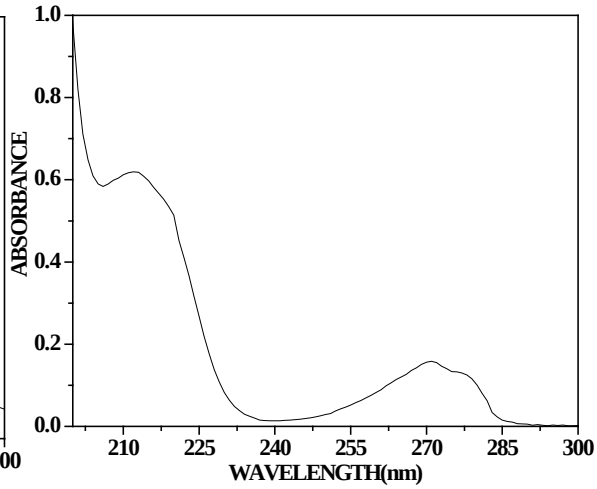


Figure 8. Absorption spectra of 100 µmolar sol. of phenol

- ✓ **Effect of irradiation time on photocatalytic reaction using 10% Fe -TiO_2 by weight:**

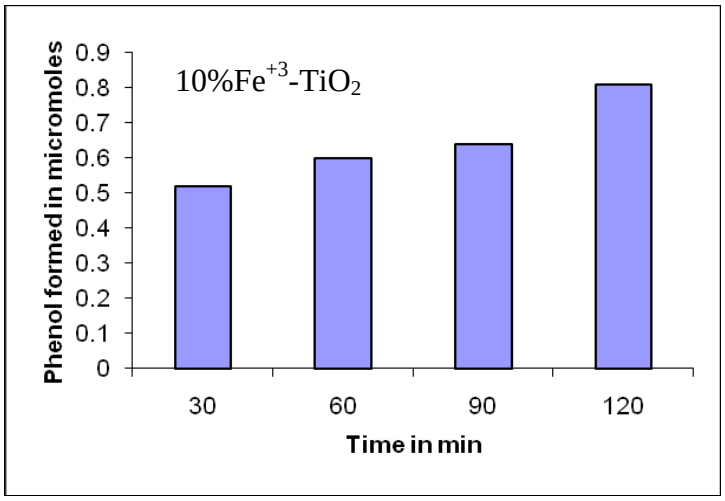


Figure 9. Amount of phenol formed with different irradiation time using highest active weight % of Fe^{+3} loaded TiO_2

Above graph results that amount of phenol increases as the irradiation time increases from 30 min to 120 min by keeping other parameters constant, like amount of catalyst, substrate concentration, temperature etc. This reveals that by increasing the irradiation time and controlling the reaction condition can increase the yield and selectivity of product.

- ✓ **Amount of phenol formed through oxidation of benzene by different metal impregnated catalyst in 5 ml reaction mixture after 2 hours light irradiation.**

Table2. Show amount of phenol formed with Fe^{+3}& Fe^0-TiO_2 with different weight percentage of metal ion

- Results obtained with different concentration of Fe (0.2%, 2%, 3%, 5%, 10%) by weight in its oxidized (Fe^{+3}) and reduced form(Fe^0):

Amount of phenol formed in µmol		
Weight %	**Fe^{+3}**	**Fe^0**
0.2	**0.064**	**0.068**
3	**0.193**	**0.129**
5	**0.280**	**0.335**
10	**0.774**	**0.332**

i. From above data it was concluded that Fe behaves differently in Fe^{+3} and Fe^{0} form. In this case Fe^{0} is more active than Fe^{+3}.

ii. Activity of Fe^{+3}-TiO_2 increases with increase in Fe^{+3} loading on TiO_2 in which 10% by weight of metal ion is highly active. Activity of Fe^{0} does not follow this fashion. Amount of phenol increases up to 5% (by weight) of metal ion and then decreases.

iii. By comparing the results of iodine formation and phenol formation with Fe^{+3} and Fe^{0}-TiO_2 it was concluded that activity of metal in both reactions follows exactly the same pattern.

- Reaction performed with different concentration of Cu (0.2%, 1%, 3%) by weight in its oxidized (Cu^{+2}) and reduced form(Cu^{0}):

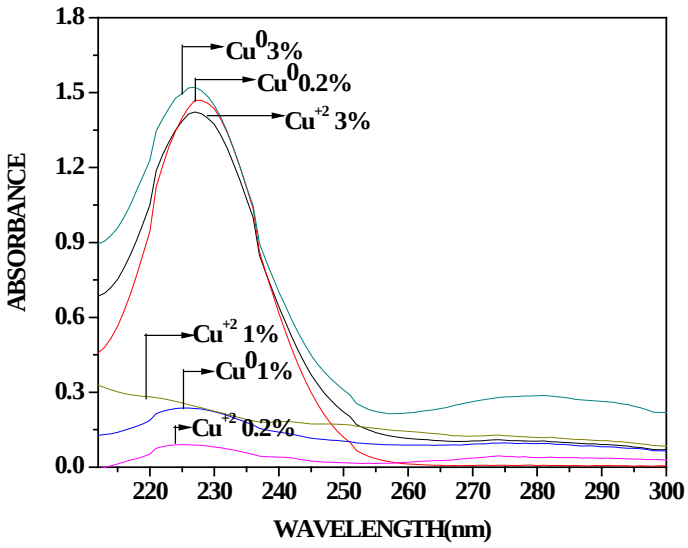


Figure10. Absorption spectra of benzene with different weight% of Cu^{+2}& Cu^{0}-TiO_2

It was concluded from the above spectra that amount of phenol increases with increase in loading of Cu^{0} on TiO_2 in which 3% Cu^{0}-TiO_2 is most active. Whereas Cu^{+2}-TiO_2 show random behavior.

- Reaction performed with various weight percentage of Ag (0.1%, 1%, 3%) in its oxidized (Ag^{+}) and reduced form(Ag^{0}):

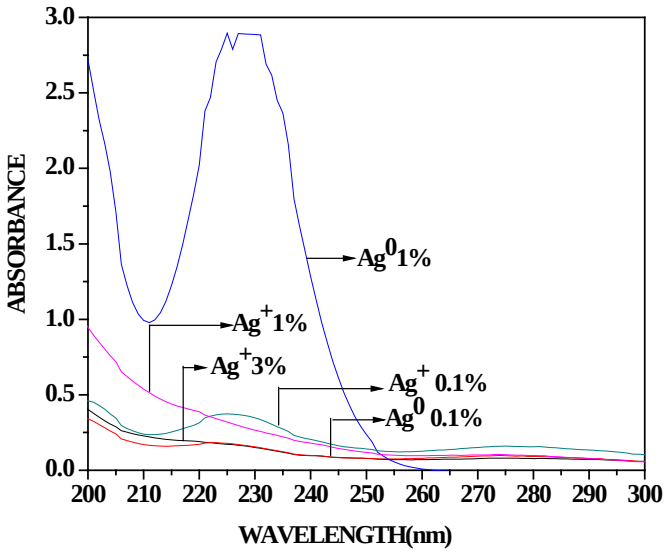


Figure11. Absorption spectra of benzene with different weight% of Ag^{+}& Ag^{0}-TiO_2

Above spectra results that amount of phenol increases with increase in loading of Ag^{0} on TiO_2 in which 1% Ag^{0}-TiO_2 is most active which results in 2.3 µmol of phenol which is the highest amount obtained after loading all other metals. From above spectra, it is clearly seen that further increase in weight percentage of Ag^{0} on TiO_2 will increase the amount of phenol. Whereas the activity of Ag^{+} do not follow this general trend. Activity of Ag^{+}-TiO_2 decreases with increase in loading of Ag^{+}.

Table3. Show amount of phenol formed with Au^{0}-TiO_2 with different weight percentage of metal ion

Amount of phenol formed in µmol	
Weight %	**Au^{0}**
0.2	**0.04**
0.3	**0.03**
0.4	**1.13**

i.Above table conclude that the amount of phenol formed by lower weight percentages of Au^{0} loaded TiO_2 (0.2% & 0.3%) was more or less same but

amount of phenol increases as loading of Au^0 increases on TiO_2. Further addition of Au^0 on TiO_2 may led to more phenol formation.

ii. Activity of Au^{+3}-TiO_2 found to be very less as no phenol was observed after the completion of reaction.

- **Table 4. Show comparison of highly active M^{+n}& M^0-TiO_2 composites towards phenol formation:**

Metal loaded on TiO_2	**Weight % of metal ion**	**Amount of phenol formed in µmol**
Fe^{+3}	**10**	**0.77**
Fe^0	**5**	**0.33**
Cu^{+2}	**3**	**1.12**
Cu^0	**3**	**1.22**
Ag^0	**1**	**2.30**
Au^0	**0.4**	**1.13**

From the above table following results were concluded:

i. Different metal show different activity.

ii. Different metal ion and neutral metal showed different activity.

As in case of Fe-10 weight % of metal ion is highly active in Fe^{+3} whereas 5 weight % of metal ion is highly active in Fe^0 but in case of Cu- same weight percentage of Cu^{+2} and Cu^0 is highly active.

iii. Ag^0-TiO_2 (1%) by weight is highly active amongst all the highly active M^{+n} and M^0-TiO_2 composites.

➢ **Oxidation of cyclohexanol to cyclohexanone:** Reaction of 1µM aqueous solution of cyclohexanol was done with various metal impregnated catalyst having different weight percentages of metal ion. That results in the oxidation of **cyclohexanol** to **cyclohexanone** along with some intermediates. Following results were obtained from the UV spectra of the resultant solution.

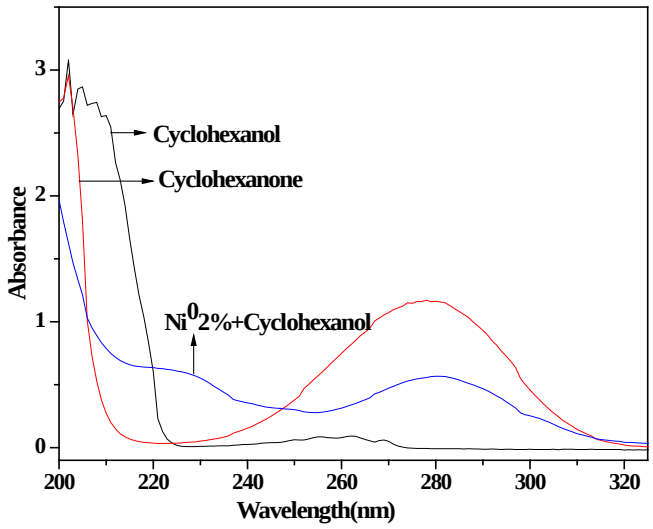


Figure12. Absorption spectra of cyclohexanol, cyclohexanone and cyclohexanol when treated with Ni^0(2%) -TiO_2

The above spectra shows that aqueous solution of cyclohexanol (1µM) give maximum absorption in the range of 180-190 nm, aqueous solution of cyclohexanone give maximum absorption at 275-280 nm. When same solution of cyclohexanol along with Ni^0-TiO_2 (2%) irradiated for 1 hr gave absorption peak in range of 275-280 nm indicating the formation of cyclohexanone. Difference in their reactivity can also be explained due difference in surface area of M^{+n} or M^0-TiO_2. We know that photocatalysis is a surface phenomenon thus efficiency of the reaction depend on the surface area of the catalyst. Metal modifies the surface of TiO_2 thus its reactivity. Metal change surface properties like porosity, active sites etc.

✓ **Reaction with different metal impregnated catalyst:**

• With various concentration of **Au (0.2%, 0.3%, 0.4%)** by weight in its oxidized **(Au^{+3})** and reduced form**(Au^{0}):**

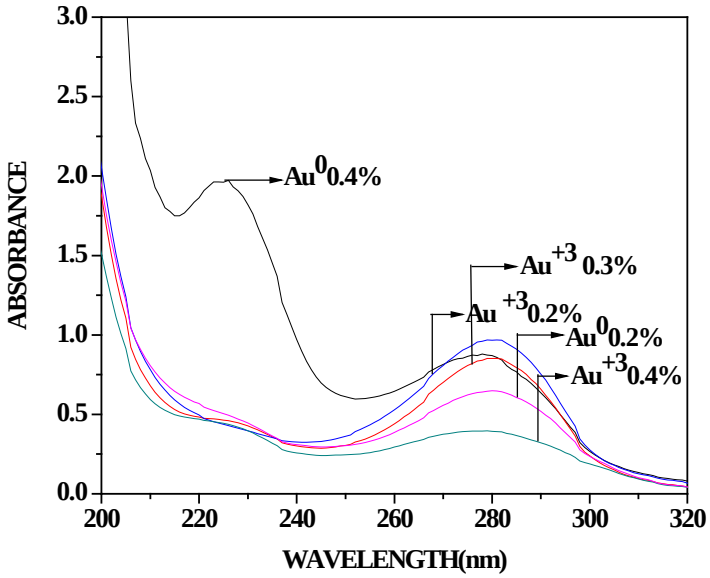


Figure13. Absorption spectra of 1 µM cyclohexanol when irradiated for 1 hr with various weight % of Au^{+3}&Au^{0}-TiO_2

Above UV spectra shows that amount of cyclohexanone formed decreases with increase in loading of Au^{+3} on TiO_2. 0.2% Au^{+3}-TiO_2 is the most active. Whereas the activity of Au^{0} show different behaviour. Up to 0.3% (by weight) of Au^{+3}-TiO_2 amount of cyclohexanol increases but 0.4% (by weight) of Au^{+3}-TiO_2 form intermediates like polyhydroxy compounds along with cyclohexanone with decreasing peak intensity at around 275 nm.

- Reaction performed with the highest active concentration of Ag ,0.1% in (Ag^{+}) and 3% in (Ag^{0}) form:

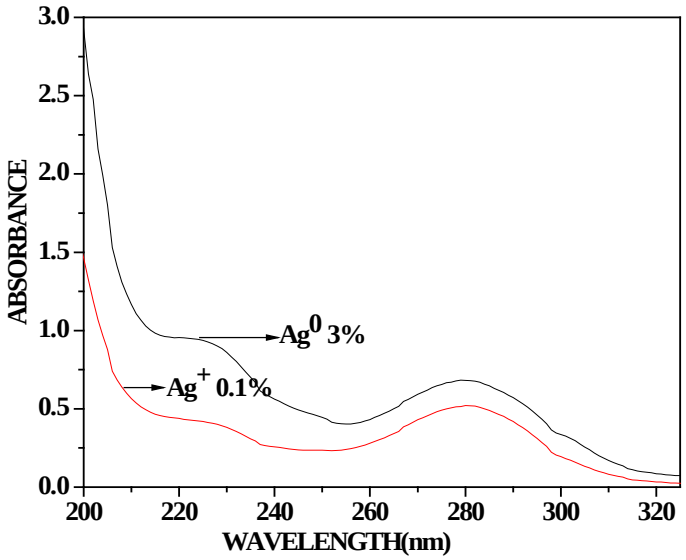


Figure14. Absorption spectra of cyclohexanol with Ag^{0}3% and Ag^{+}(0.1%)-TiO_2 after 1 hr irradiation

Above spectra shows that Ag^{0}-TiO_2 (3%) is more active as it form some polyhydroxy intermediates along with cyclohexanone.

Summary and Conclusion

It can be concluded that under the given laboratory conditions, TiO_2 alone shows very little catalytic activity but the combined effect of metal-TiO_2 composites show enhanced catalytic activity in the evolution of I_2 as well as in oxidation of benzene to phenol and cyclohexanol to cyclohexanone.

But different metal ion showed different activity as electron affinity and work function of different metal is different. Generally metal ion (M^{n+}) is more active than metal zero (M^0) due to more electron affinity of metal ion but in some cases M^0 is more active than M^{n+} due to the effect of metal, type and concentration of substrate.Ag^0, Fe^{3+} and Fe^0 gave highest results as were tested during our experiment.

Phenol and cyclohexanone are industrially important chemicals. There is a huge use of phenol as it is used by various pharmaceutical companies in making various drugs like aspirin. If its production can be done using alternative methods using sunlight, it will be highly economical and a green process. If we are able to carry out any organic functional group transformation in a single step reaction, it will be highly beneficial. All the above results show a promising route for the synthesis of compounds. We can increase the yield of product by changing various parameters like temperature, irradiation time, amount of catalyst and substrate concentration etc. In future we can see the effect of same metal in different oxidation state or the effect of same oxidation state of different metal. We can use other method of metal impregnation which can improve metal loading.

But in this field, not much research is being carried out at present because the conditions still need to be optimized. If research is advanced in this direction it will be highly revolutionizing. I found all the above results very interesting which motivates me for future research.

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