Effects of Metal Ions on H_2 Generation during Photolysis of Suspended TiO_2 in Aqueous Systems

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Abstract: Nowadays, photocatalysis is being applied as a promising technique for decontamination, purification, deodorization, etc. of polluted air and wastewaters. This technique attempts also to generate renewable and non-polluting fuels utilizing various carbon and hydrogen sources. In this context, studies on photo-catalytic generation of H_2 using 0.1% w/v TiO_2 photo catalyst as a suspension in water was carried out using 350 nm light. This was explored further in presence of various metal ions such as Ag^+, Cu^{2+}, Fe^{2+}, Au^{3+} and V^{5+} at different ambient such as air and CO_2, in presence of a hole scavenger (2-propanol and formic acid). H_2 yields in CO_2-purged systems as analyzed in GC-TCD were reasonably higher, and increased further when metal ions were added into the systems. Based on H_2 yields, HCOOH was found to be a more supportive hole scavenger as compared to 2-propanol in metal ions containing systems. Besides the formation of low to high concentrations of various gaseous products, nanoparticles of gold, silver and copper were also observed as photolysis products. This indicated that the presence of both reduced metal ions and their *in-situ* generated nanoparticles at various stages either in the free/unbound and/or associated with TiO_2 photocatalyst in aqueous systems, together play a significant role in enhancing the H_2 yields.

Keywords: H_2, TiO_2, hole scavenger, photolysis, metal ions, nanoparticles.

1. INTRODUCTION

The generation of H_2, a photolysis product through the photo catalytic effect of semiconductor in presence of water is well known [1-4]. Fujishima and Honda have highlighted their interests on heterogeneous photocatalysis when they successfully split water into hydrogen and oxygen in the presence of TiO_2 [4]. After their success, the research on heterogeneous photocatalysis has been enhanced tremendously all over the world. The primary step in TiO_2 photocatalysed oxidation has been understood with the formation of both hydroxyl radicals ($^\bullet OH$) and super oxide radical anions ($O_2^{\bullet-}$) [5-8] through several reactions as presented below:

$$TiO_2 \xrightarrow{\ h\upsilon\ } h^+ + e^- \qquad (1)$$

$$h^+ + H_2O \longrightarrow {}^\bullet OH + H^+ \qquad (2)$$

In presence of air,

$$e^- + O_2 \longrightarrow {}^\bullet O_2{}^{\bullet-} \qquad (3)$$

Hence, $^\bullet OH$ (E^o = 2.72 V) [9] a strong oxidizing and $O_2^{\bullet-}$ (E^o = -0.33 V) [10] a weak reducing species are generated from the above-mentioned photocatalytic redox processes. In absence of oxygen, $^\bullet OH$ radical, a strong oxidant and e^-, a strong reductant are the reactive species generated during photolysis of TiO_2

[11, 12] in water containing systems. In the presence of an $^\bullet OH$ or h^+ scavenger, it is possible to use TiO_2 system for photo-reduction processes, similarly in presence of an e^- scavenger, the system can be made favorable for oxidation reaction. During these conversion processes the respective product yields increases.

Earlier we have carried out the photo-reduction of CO_2 in the presence of TiO_2 as suspension in water at room temperature and under normal atmospheric pressure with and without 2-propanol (a hole scavenger) under diverse ambient conditions [13-16]. In continuation to the previous work, the photocatalytic studies on chemical reduction of CO_2 were carried out in two different ambient such as Air and CO_2, using TiO_2 suspended aqueous solutions both in presence and absence of 2-propanol/formic acid. In our previous experiments TiO_2 catalysts of 0.1% (w/v) amount as suspension in water has been found adequate for maximum yields of the photolytic products [13], therefore these experiments were carried out employing 0.1% (w/v) TiO_2. The two different ambient such as air (aerated or air saturated) and CO_2-purged systems were chosen because in earlier study in presence of 2-propanol, the highest yields of methane was observed as a reduction product of carbon dioxide. The significant yield of methane has been explained therein with the active role of *in-situ* CO_2 (generated due to mineralization of a part of 2-propanol) in free radical induced reduction reactions. The yields of CH_4 in both CO_2-purged as well as aerated systems were comparable [13]. This work was explored further in the presence of various metal ions (such as Ag^+, Au^{3+},

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Cu^{2+}, Fe^{2+} and V^{5+}) to realize their effects on photo-catalytic products. Moreover, H_2 formation during the photolysis of methanol-water (ratio 50:50) systems containing Pt, Pd, RuO_2 or rhodium complex - TiO_2 mixed photo catalyst was known, wherein the nature of catalyst play a significant role to increase H_2 yields [3]. The objective of this work is to investigate an effective way for enhancement of products yields if any, during transformation of CO_2 employing heterogeneous photocatalysis. The observed high yields of H_2 intending us to draw attention to the metal ion effects under the study, which is discussed in this communication.

2. EXPERIMENTAL

TiO_2 (anatase, -325 mesh) from Aldrich was used as received. A quartz cell of 16.5 ml capacity having a gas purging inlet and a gas sampling port as employed in previous studies was used for photo-irradiation with 350 nm light using Rayonet photoreactor. Photon flux used for irradiation was $5x10^{15}$ photons cm^{-2} sec^{-1}. The amount of solution used for photolysis was 5 ml. High purity (≥98%) $HAuCl_4$, $AgNO_3$, $FeSO_4$, $CuSO_4$, and $NaVO_3$ were used respectively for Au^{3+}, Ag^+, Fe^{2+}, Cu^{2+} and V^{5+} sources. The gaseous samples were analyzed offline by GC-TCD (Gas Chromatograph-Thermal Conductivity Detector, Model: GC 8610, supplied by Thermo Fisher Scientific India Ltd.) similarly as done previously [13-16] with Molecular Sieve 5A column of 5 ft length with diameter 1/4 inch using carrier N_2 15 mL min^{-1}, oven at $32°C$ (isotherm), TCD at $200°C$ and applied bridge voltage was 8.0 V. The yield of a particular product was estimated by comparing peak intensities of sample chromatogram at specific retention time with the chromatogram obtained for standard samples. CO_2 gas used was of high purity (>95%) available from Indian Oxygen. The CO_2

purged/saturated solutions (10 min purging time) were photo-irradiated at room temperature and normal atmospheric pressure after proper sealing with stopper and 500 µl gaseous sample was taken from the septum port attached therein for GC analysis. The estimated yield values of H_2 obtained in GC-TCD have an error of ±10%.

After the gas phase products analysis, the photo-irradiated samples were filtered using membrane filter (Ultipor ®N_{66} ®Nylon 6.6 membrane 0.45 µm from Pall Life Sciences) and the residues were characterized by X-ray diffraction (XRD) analyses. The XRD measurements were carried out with Philips diffractometer (Model: X'Pert PRO, supplied by PANalytical, Netherland) using Ni filtered Cu K_α radiation of 1.54 $A°$. The residues on membrane filters were loaded in sample holder directly for the measurement at ambient room temperature. Silicon standard was used for zero angle correction prior to actual measurements. The crystallite sizes of the metal particles formed were estimated from the broadening of the X-ray diffraction peaks using Scherer's formula [17, 18].

3. RESULTS AND DISCUSSION

Table **1** shows the yields of H_2 observed in photo-irradiated aqueous solutions containing 0.1% (w/v) TiO_2 suspension in presence and absence of various above-mentioned metal ions at two different ambient (air and CO_2) after 2 hr photo-irradiation. Under the present study, the yields of H_2 in metal ions containing systems listed in Table **1** were found to be higher in contrast to the yields obtained in plain TiO_2 systems (24 µL in CO_2-purged systems) under identical conditions. Herein the CO_2 purged systems behave both as deoxygenated as well as e^--scavenging

Table 1: The Yields of H_2 (in µl) Obtained after 2 hr Photolysis of 0.1% w/v TiO_2 Suspended in Water in Presence and Absence of Various Metal Ions (1 mM) at Different Ambient

Systems	Photolytic Yields			
	Air		CO_2	
	Color	[H_2]	Color	[H_2]
TiO_2	no	1.80	no	24.2
TiO_2 + Ag^I	no	0.00	black	45.8
TiO_2 + Cu^{II}	no	0.00	red	34.1
TiO_2 + Fe^{II}	no	0.70	no	27.1
TiO_2 + Au^{III}	no	1.20	pink	64.2
TiO_2 + V^V	no	0.00	purple	70.6

Table 2: **The Yields of H_2 (in μl) Obtained after 2 hr Photolysis of 0.1% w/v TiO_2 Suspended in Water in Presence and Absence of Various Metal Ions (1 mM) at different Ambient Containing 0.5 M 2-Propanol**

System	Photolytic Yields			
	Air		CO_2	
	Color	[H_2]	Color	[H_2]
TiO_2	no	nd	no	35.7
TiO_2 + Ag^I	blackish	1.25	blackish	64.2
TiO_2 + Cu^{II}	reddish	48.0	reddish	60.6
TiO_2 + Fe^{II}	no	0.5	no	57.1
TiO_2 + Au^{III}	pinkish	94.9	pinkish	295.3
TiO_2 + V^V	green	0.0	purple	60.6

systems. In aerated systems, the yields of H_2 remain low because of the presence of oxygen, which reacts with photo-generated e$^-$ yielding H_2O_2 through HO_2 (reaction 5). Interestingly, a significant change in color of the experimental solutions containing Au^{3+}, Cu^{2+}, Ag^+ in CO_2-purged systems was noticed after photo-irradiation in contrast to aerated systems where such change in matrix color was not observed.

In the same way, the yields of H_2 obtained during photo-irradiated aqueous solutions containing 0.1% (w/v) TiO_2 suspension and 0.5 M 2-propanol (a hole scavenger) in presence of various metal ions (1 mM) at air and CO_2 ambient after 2 hr photo-irradiation are listed in Table **2**. The H_2 yields in CO_2-purged systems were convincingly higher as compared to the systems containing TiO_2 but without 2-propanol otherwise under identical conditions. Under this condition, the color of the solutions containing Au^{3+}, Ag^+ and Cu^{2+} were changed to pink, black and red respectively after photolysis.

Concurrently, the yields of H_2 obtained during photo-irradiated aqueous solutions containing 0.1%

(w/v) TiO_2 suspension and 0.5 M formic acid (HCOOH), another hole scavenger in absence and in presence of various metal ions (1 mM) at two different ambient (air, and CO_2) after 2 hr photo-irradiation are tabulated in Table **3**. Interestingly, in CO_2-purged systems, like in 2-propanol systems (Table **2**), the H_2 yields obtained were higher. Moreover, H_2 yields in these systems were even higher than those listed for 2-propanol systems containing particular metal ions under analogous experimental conditions. Compared to all metal ions systems the H_2 yields in Cu^{2+} and Au^{3+} systems were found to be higher.

In addition, the changes in colors of the metal ions containing TiO_2 suspended aqueous systems during/after photolysis demonstrate an interesting observation, which are more prominent in CO_2-purged systems. For example as listed in Tables **1** to **3** in all Ag^+ containing systems, the color of the initial whitish (due to TiO_2 suspension) aqueous systems changed into blackish white after photolysis. The black color turned over is due to the formation of silver nanoparticles through subsequent reactions of Ag^o (a primary photo reduction product of Ag^+) with solute Ag^+

Table 3: **The Yields of H_2 (in μl) Obtained after 2 hr Photolysis of 0.1% w/v TiO_2 Suspended in Water in Presence and Absence of Various Metal Ions (1 mM) at different Ambient Containing 0.5 M Formic Acid**

System	Photolytic Yields			
	Air		CO_2	
	Color	[H_2]	Color	[H_2]
TiO_2	no	1.8	no	48.0
TiO_2 + Ag^I	blackish	1.3	blackish	55.7
TiO_2 + Cu^{II}	no	77.0	reddish	339.6
TiO_2 + Fe^{II}	no	7.2	no	104.6
TiO_2 + Au^{III}	pinkish	500.0	pinkish	1265.0
TiO_2 + V^V	green	0.9	violet	102.0

ions. Similarly, copper and gold ions containing systems also lead to the colors of their respective metal nanoparticles after photolysis (see Tables **1-3**). It will be interesting to include at this juncture that in case of iron(II) ions no change in color was observed under any of the above-mentioned experimental conditions. This is possibly due to *i)* the reduced Fe(II) species (Fe^+ and / or Fe^0) interact with the matrix within generating different products such as complex ions/compounds, H_2, etc. and as a consequence the reduced Fe(II) species oxidized back to the parent metal (Fe(II)) ions. *ii)* The iron nanoparticles does not absorb in the UV-vis wavelength region, which supports the previous observation on the reduction of Fe(II) ions in 2-propanol that did not show any absorption [19]. Similarly, in V^{5+} systems under photolysis light green and purple color changes were noticed in aerated and CO_2-purged systems containing either 2-propanol or HCOOH respectively. The color change in V^{5+} systems is as a consequence of the formation of various reduced vanadium species (mainly V^{3+} and V^{2+}) [20] but not due to the vanadium nanoparticles formation. In formic acid systems, HCOOH reacts with hole generating reducing radical $^•$COOH, which reduces solutes available within. Similarly in 2-propanol systems $(CH_3)_2C^•OH$ radical supports reduction reaction.

For characterization of the materials developed therein due to photolysis, the photo- irradiated samples were filtered using membrane filter. Photographs of the

samples recorded before and after photo-irradiation along with the residues on membrane filters after filtration are shown in Figure **1**. The residue materials on the membrane filters were characterized by XRD analysis.

Figure **2** shows the X-ray diffraction patterns of TiO_2 and various metal/TiO_2 materials developed on membrane filters along with the XRD pattern observed due to blank membrane filter. XRD spectra recorded for the residue of photolysis samples (containing TiO_2 in presence and absence of different metal nanoparticles including various reduced metal ion species) were identical with respect to the distinct peaks at 2θ values of 20.3^o and 23.9^o (see Figure **2**) for TiO_2 along with some additional peaks depending on the nature of metal ions used for photolysis. For example if we look at the spectrum labeled 3 we find two strong peaks at 2θ values of 37.7^o and 43.9^o, which is identical to those reported earlier for metallic gold [21, 22] whereas in Ag^+ containing system it gives a peak at 2θ values of $\sim38.0^o$ (spectrum labeled 6) referring Ag metal [23]. It is noticed that, the XRD spectra of TiO_2 in Figure **2** remain unaffected in Cu^{2+}, V^{5+} and Fe^{2+} containing systems, which is probably due to weak/no XRD signals for metallic particles formed if any during photolysis. Based on the XRD peak line broadening, the particle size of the metal nano-particles for the sample containing gold and silver were calculated using Scherer's formula [17, 18] to be ~10 nm and ~7 nm respectively. It is important to note that the average
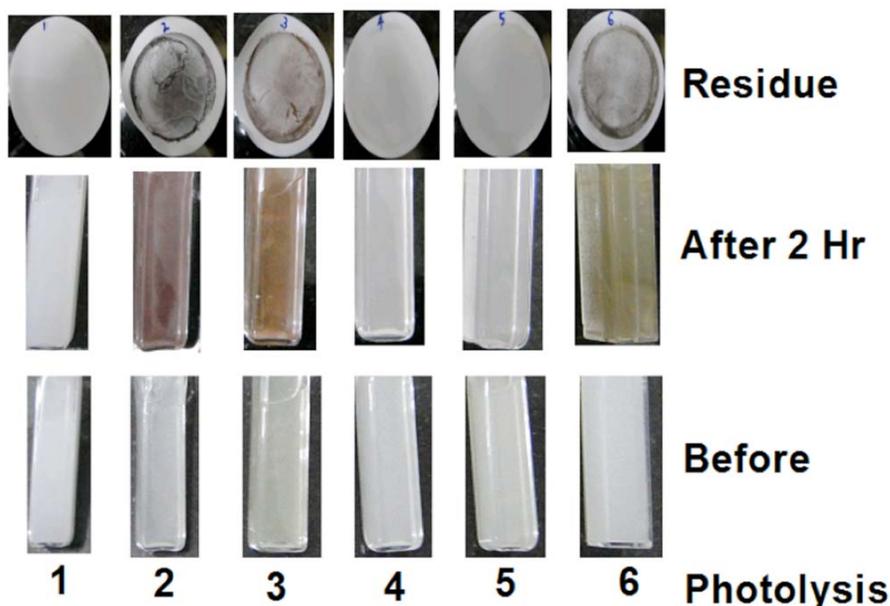
Figure 1: Photographs of the samples before and after photo-irradiation and the residues obtained after filtration of experimental solutions in water containing 1: only TiO_2; 2: TiO_2 with Cu^{2+}; 3: TiO_2 with Au^{3+}; 4: TiO_2 with Fe^{2+}; 5: TiO_2 with V^{5+}; and 6: TiO_2 with Ag^+ after 2 hr photolysis. (Systems: CO_2-purged, 0.1% TiO_2 suspension, metal ions 1 mM with 1 M 2-propanol).

size of TiO_2 particles employed in the study was 100 nm.
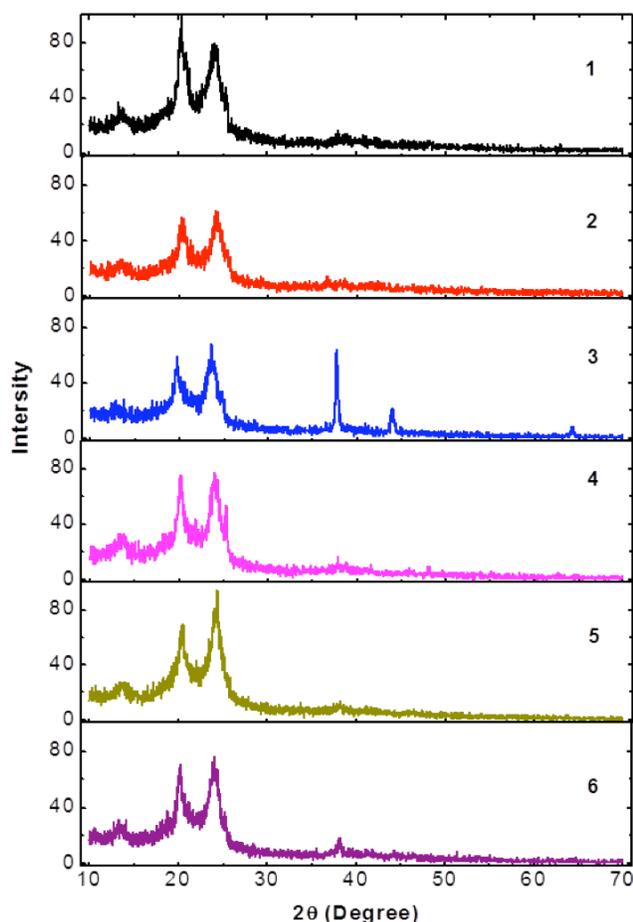
Figure 2: XRD patterns of residues of the filtration of photo-irradiated samples obtained after 2 hr photolysis. 1: only TiO_2; 2: TiO_2 with Cu^{2+}; 3: TiO_2 with Au^{3+}; 4: TiO_2 with Fe^{2+}; 5: TiO_2 with V^{5+}; and 6: TiO_2 with Ag^+. Systems: CO_2-purged, 0.1% TiO_2, metal ions 1 mM with 1 M 2-propanol).

The following reactions are proposed based on the results obtained during the experiments:

In aerated (in presence of O_2) systems, besides reaction (3) the additional reactions taking place are:

$$O_2^{\bullet-} + H_3O^+ \longrightarrow HO_2 + H_2O \tag{4}$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{5}$$

$$e^- + H_3O^+ \longrightarrow H + H_2O \tag{6}$$

$$H + O_2 \longrightarrow HO_2 \tag{7}$$

In CO_2-purged systems,

$$2e^- + 2H^+ \longrightarrow H_2 \tag{8}$$

$$e^- + CO_2 \longrightarrow CO_2^{\bullet-} \tag{9}$$

$$H + H \longrightarrow H_2 \tag{10}$$

$$CO_2^{\bullet-} + CO_2 + e^- \longrightarrow CO + CO_3^{2-} \tag{11}$$

$$CO_2 + e^- \longrightarrow CH_4 \text{ (multi steps reactions via CO formation)} \tag{12}$$

$$2CO_2^{\bullet-} + 2H^+ \longrightarrow (COOH)_2 \xrightarrow{TiO_2} 2CO_2 + H_2 \tag{13}$$
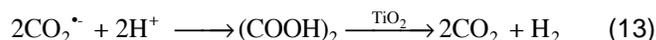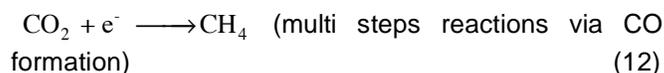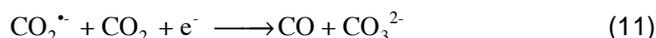
In presence of M^{n+} ions

Reactions related to reduction of metal ions, the initial reduced metal ions species are:

$$M^{n+} + CO_2^{\bullet-} \longrightarrow M^{(n-1)+} + CO_2 \tag{14}$$

$$M^{n+} + e^- \longrightarrow M^{(n-1)+} \tag{15}$$

$$M^{n+} + H \longrightarrow M^{(n-1)+} + H^+ \tag{16}$$

Likewise free radical induced reduction reactions of metal ions and initially generated reduced metal ions intermediate species sustained reduction reaction till they end with final metal nanoparticles formation. For example as discussed above, in the case of uni-charge metal ions (Ag^+), which reduced to silver atom (Ag^o) initially, later it produces silver nanoparticles through subsequent reactions as mentioned below:

$$Ag^+ + CO_2^{\bullet-} \longrightarrow Ag^0 + CO_2 \tag{17}$$

$$Ag^+ + e^- \longrightarrow Ag^0 \tag{18}$$

$$Ag^+ + H \longrightarrow Ag^0 + H^+ \tag{19}$$

$$Ag^0 + Ag^+ \longrightarrow Ag_2^+ \tag{20}$$

$$Ag_2^+ + Ag^+ \longrightarrow Ag_3^{2+} \tag{21}$$

$$Ag_2^+ + Ag_2^+ \longrightarrow Ag_4^{2+} \tag{22}$$

$$Ag_2^+ / Ag_3^{2+} / Ag_4^{2+} + e^- / H / CO_2^{\bullet-} \longrightarrow Ag_2 / Ag_3^+ / Ag_4^+ \tag{23}$$
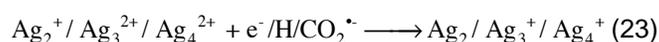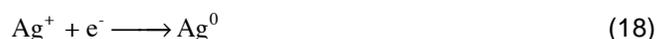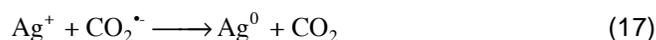
Finally, these reactions lead to the formation of silver nanoparticles.

In this process the growth of silver nanoparticles (Ag_n) takes place through nucleation (reactions 20-22) followed by reduction reactions (reaction 23) [24]. Similarly, in gold and copper systems, the nanoparticles generations through various reduced

metal ions are well known [25, 26]. However, oxygen in the aerated systems obstructed the formation of nanoparticles by scavenging reducing free radicals (e^-) as well as by reacting with intermediate reduced metal ions species. Moreover, in presence of a hole scavenger (2-propanol or HCOOH), the nanoparticles formation even in aerated systems was favorable following different chemistry although O_2 scavenges photogenerated e^- partly/fully, the reactions predominate under such conditions are:

In presence of 2-propanol or HCOOH,

$$h^+ + (CH_3)_2CHOH \longrightarrow (CH_3)_2C^\bullet OH \text{ (OR1)} + H^+ \quad (24)$$

$$2(CH_3)_2C^\bullet OH \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad (25)$$

$$h^+ + HCOOH \longrightarrow {}^\bullet COOH \text{ (OR2)} + H^+ \quad (26)$$

$$M^{n+} + (CH_3)_2C^\bullet OH/{}^\bullet COOH$$
$$\longrightarrow M^{(n-1)+} + (CH_3)_2CO/CO_2 + H^+ \quad (27)$$
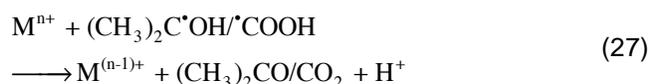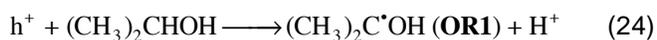
Organic radicals (**OR1** and **OR2**) ($(CH_3)_2{}^\bullet COH$ and ${}^\bullet COOH$) contribute in product yields generating through reduction reactions because of their high reduction potential values ($E^o(CH_3)_2{}^\bullet COH/(CH_3)_2CO$, $H^+ = -1.7$ V) and ($E^o({}^\bullet COOH/CO_2$, $H^+ = -1.9$ V) [27].

In aerated system, CO_2 generated *in-situ* through mineralization of organic substances.

$$\textbf{OR1/OR2} + O_2 \longrightarrow CO_2 \text{ (mineralization reaction)} \quad (28)$$
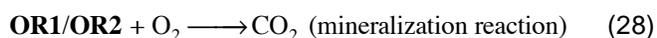
Even in aerated systems $(CH_3)_2C^\bullet OH/{}^\bullet COOH$ can reduce M^{n+} to metal nanoparticle through reactions similar to 20-23 and 27.

Acetone was also observed as other photolytic product along with H_2 during photolysis of 2-propanol in TiO_2 suspended aqueous systems. Under the present study, we have focused only on H_2, which was generated possibly through the reactions 8, 10 and 13. As the photolysis time is limited to 2 hr, the formation of CH_4 was observed to be low. In CO_2-purged system, H_2 formation takes place on the surface of semiconductor photo-catalyst during photolysis through reaction 13.

As discussed earlier, the yield of H_2 in CO_2-purged system has been decreased after 2 hr of photolysis, on the other hand, the yields of CO and CH_4 remain low up to 2 hr of photo-irradiation time but later (beyond 2 hr photolysis) their yields increase [15]. In the present study we have restricted to 2 hr photolysis to explore H_2 yields only with the manipulation of various inputs to the systems such as different metal ions and various hole scavengers onto the desire experiments. H_2 generation has been reported in photocatalytic reduction of CO_2 on TiO_2 (0.5 g/80 ml) suspension in aqueous solution containing 4 M methanol and the yield was enhanced on metal powder addition [28] exhibiting the significance of metal in reduction processes. Moreover, the decrease in H_2 production in photocatalytic reduction of CO_2 (high pressure) in presence of 0.2 N NaOH has been explained previously due to the formation of hydrocarbons [29], supports also the photolysis time limitation.

It is noteworthy to include that from the previous study on the photo-degradation or decomposition either of 2-propanol or formic acid in absence of TiO_2 at 350 nm experimental light to H_2 was negligible [13, 14, 16]. This was reconfirmed by carrying out separate photolysis experiments on 0.5 M 2-propanol and 0.5 M HCOOH in aqueous solutions in absence of TiO_2 before doing the desired experiments, wherein no H_2 and CH_4/CO_2 were observed as photolysis products. This indicates that no direct photolysis of 2-propanol/HCOOH was leading to H_2 generation under the present experimental conditions.

On comparison of the H_2 yields obtained in two different systems namely with and without 1 mM metal ions in 0.5 M 2-propanol containing 0.1% TiO_2 suspension in water at two different ambient (air and CO_2) conditions as listed in Tables **1** & **2**, we find that in CO_2-purged systems the yields of H_2 were high in presence of metal ions. There is a significant difference in H_2 yields between aerated and their respective CO_2-purged systems. This was happened due to the presence of 2-propanol, a hole scavenger, which resists hole – e^- recombination (reverse of reaction 1 which is very fast 10 - 100 ns [5, 30]) by reacting with photo-generated hole. The hole has been considered as an ${}^\bullet OH$ radical or surface attached ${}^\bullet OH$ radical generated in TiO_2 photolysis (reaction 2) under aqueous matrix [1, 11, 31]. The ${}^\bullet OH$ radical reaction with 2-propanol is very fast as observed in condensed media. (${}^\bullet OH + (CH_3)_2CHOH \rightarrow (CH_3)_2C^\bullet OH + H_2O$; $k_{bimol} = 1.9 \times 10^9$ M^{-1} s^{-1}) [32]). The presence of 2-propanol and its high concentration (0.5 M) together make the system more favorable towards reducing condition by rapid scavenging ${}^\bullet OH/h^+$, subsequently allowing photo-generated e^- to react with $H_3{}^+O$ (reaction 6) yielding more H_2. In absence of 2-propanol the yield of H_2 after 2 hr photolysis was observed to be

low in contrast to the high yield in the system containing 2-propanol (see Table **1**). The observed low H_2 yield is due to the pronounced recombination reaction (reverse of reaction 1) in absence of any added hole scavenger. This agrees well with the opinion suggested earlier [13, 33, 34] about the requirement of a hole scavenger for the enhancement of yields of the reduction reaction products. Also in the systems containing oxygen (in aerated systems), no yield of H_2 was observed in absence of 2-propanol in contrast to low H_2 yields in its presence. In this case O_2 present (0.2 mM) in aerated systems was enough to scavenge the photo-generated e^- through reaction 3 preventing reaction 8 to contribute H_2 formation. This way O_2 present in the system acts as an e^- scavenger. In aerated systems, in the presence of 0.5 M 2-propanol (having efficient h^+ scavenging properties), a small fraction of e^- contributes in reduction reactions resulting a low H_2 yield other than its scavenging reaction due to O_2. Different yields of H_2 in the presence of different metal ions reveal that the active participation of various intermediates starting from reducing metal ions to sub-nano and nanometric metal particles in reduction reactions. This is because these intermediates posses different redox potentials [35].

The following interpretations were therefore made: the photo-generated holes during photolysis of metal/TiO_2 are trapped by metal nanoparticles and metal ions. Metal nanoparticles being in the metallic form, acquire positive charge due to trapping of hole (formation of M^+ ion) and subsequently reduced by photo-catalytically generated e^- where metal/TiO_2 behaves as an improved recombination center. This reduces a fraction of hole concentration to interact with 2-propanol/HCOOH molecule for oxidation, resulting a low yield of oxidation products like CO_2 in metal/TiO_2 surfaces as compared to the plain TiO_2 systems. As reported earlier, the gold caped TiO_2 i.e. Au/TiO_2 system has been elucidated as recombination center due to presence of Au, in which, the formation of Au^I as well as its reduction to Au^o take place [36, 37]. During the process, the net loss of both photo-generated e^- and h^+ is more due to the recombination center, which is generated during continuous photolysis. In the presence of gold ions and nanoparticles on or over TiO_2, because of the consumption of photo-generated e^- (through $H_3O^+ + e^-$ reaction generate more H_2), its counterpart h^+ is available for the oxidation of organic compounds resulting in CO_2, which on surface reduction leads to CO, and the overall process is enhanced in Au^{III} and/or Au/TiO_2 systems due to the charge accumulating capacity [36.37] of the metal (Au) present in the modified photo-catalyst. In this case, water plays a significant role for photo-catalytic properties of Au/TiO_2. Nevertheless, in metal ions systems, after formation of metal nanoparticles (as soon as color appears) the systems behave as both metal doped as well as metal ions containing systems, wherein both metal ions and its nanoparticles play
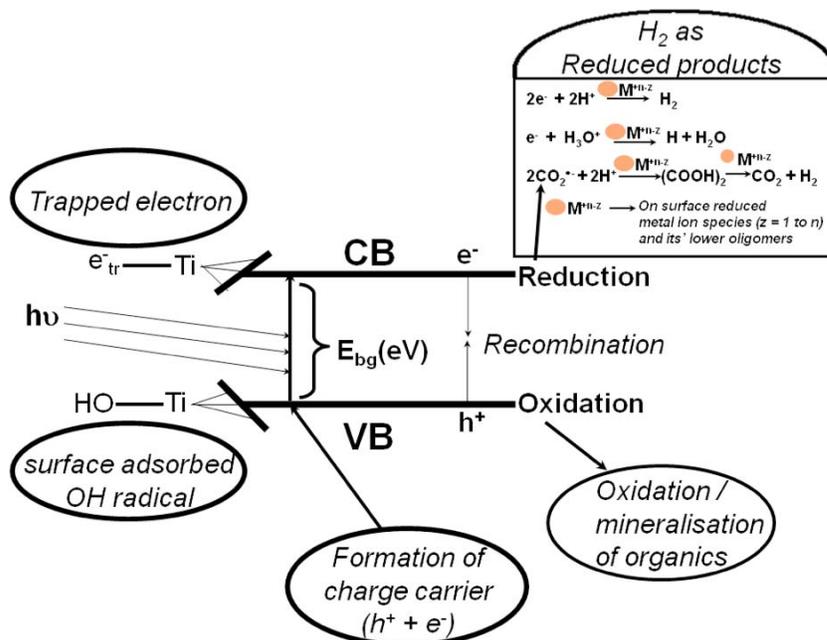
Figure 3: The H_2 formation mechanism during photolysis of TiO_2.

significant role in H_2 formation. This happens only when the photolysis is kept on, because after photolysis (photo-light off conditions) the colors of nanoparticles remain steady, indicating the negligible contribution of H_2 formation due to thermal reaction of the nanoparticles. It is noteworthy to include that the active role of various intermediates starting from reduced metal ions/metal atom to oligomers/small aggregates of sub-nano or nano sized metal particles is significant in H_2 formation because of different redox potentials, which is size dependent [38]. The difference in H_2 yields observed in various metal ions systems is probably due to the dissimilarities in the reactivity of various forms of metal ions produced in photolysis, as they have various redox potentials. Overall photo-catalytic processes and H_2 formation explained above are summarized in Figure **3**.

4. CONCLUSIONS

Under photo-catalytic reduction in CO_2 (deoxygenated) and aerated (oxygenated) systems using TiO_2 suspension in water with and without various metal ions such as Ag^+, Au^{3+}, Cu^{2+}, Fe^{2+} and V^{5+} in presence of 2-propanol or formic acid as a hole scavenger lead to the formation of H_2. The H_2 yields were more in all systems except aerated systems. The presence of both metal ions and its *in-situ* generated nanoparticles at various stages either in free state and / or associated to TiO_2 photocatalyst, together play a significant role in the generation of high yields of H_2. In addition, the color of the matrix changes in gold, silver and copper systems during photolysis may possibly lead to the development of significant/different materials for the production of fuel and/or the useful products utilizing solar light.

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