Significance of pH measurements in photocatalytic splitting of water using 355 nm UV laser

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Abstract

The pH changes during the course of photocatalytic splitting of water significantly affect the band edges of the semiconductor and enhance or retard the rate of the splitting process. The effect of pH on photocatalytic activity in splitting of water over WO_3, TiO_2 (rutile) and NiO by using a monochromatic light source such as laser at 355 nm wavelength was studied for the first time. The mechanism of action of oxygen and metal ions (Fe^{3+} and Ag^+) as electron capture agents was investigated on the basis of pH changes under illumination. It was observed that the pH changes measured during the course of reaction provides a deep insight of different processes occurring simultaneously in photocatalytic systems.
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1. Introduction

The pH of a system is a measure of the concentration of H^+ ions and is considered as a valuable tool in evaluating the mechanisms of various inorganic and organic reactions. Heterogeneous photocatalysis is a developing field [1–14] in which the pH changes play a vital role when applied for water splitting. To oxidize water, the potential of valence band (V_{vb}) should be more positive than +1.23 V (H_2O/OH). The positions of both conduction and valence bands, in aqueous medium, are pH dependent and the change in the pH of the semiconductor/electrolyte system by one unit shifts the position of the flat-band potential (V_{fb}) of the semiconductor by 59 mV [1,3–5]. In other words, the change in the pH of the photocatalytic system shifts the position of valence band and conduction band edge, which in turn affects the ability of the

semiconductor to photo-oxidize or photo-reduce [15].

$$E_{vb} = E_{vb}^0 - 0.059\,pH \qquad (1)$$

$$E_{cb} = E_{cb}^0 - 0.059\,pH \qquad (2)$$

where E_{vb}^0 and E_{cb}^0 are the valence and conduction band potentials at zero pH.

The effect of "preset pH" on different processes especially photocatalytic degradation have been extensively studied and its impact on the mechanism of degradation have been discussed [16–24]. Various studies have been performed to investigate different processes under different pH values but less effort have been focused on measuring the pH changes during the course of a photocatalytic process and the effect of these changes on the processes occurring at the surface of the catalyst and bulk.

Keeping in view the significant effect of the shifting of the valence and conduction band edges due to pH changes during a photocatalytic process, the mechanism of photocatalytic splitting of water over WO_3, TiO_2 (rutile) and NiO by

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using a laser emitting at 355 nm wavelength has been studied in this paper for the first time. The pH changes under UV laser illumination were used for finger printing the action of oxygen and metal ions as electron capture agents, and the action of methanol as a hole-capture agent. It was observed that the pH changes measured during the course of reaction provides a deep insight of the processes occurring simultaneously in the photocatalytic splitting of water.

2. Experimental details

A schematic diagram of the experimental setup applied in this study is presented in Fig. 1, and is described in detail in earlier publications [25–28]. The pH changes in the solution during laser irradiation were measured using a pH meter that was calibrated by using the buffers of pH 4, 7 and 10. For pH measurements during water splitting, 300 mg of each catalyst (WO_3, TiO_2 and NiO) was suspended in 60 ml of doubly distilled water and exposed to a 355 nm wavelength laser beam generated by the third harmonic of a Nd:YAG pulsed laser (Spectra Physics Model GCR 250). All experiments were performed at an optimal laser energy of 100 mJ per pulse, as discussed in detail elsewhere [26]. Argon gas was initially purged through the solution to remove the dissolved oxygen. For the pH measurements during water-splitting studies in the presence of metal ions, a 10 ppm solution of each metal ion was prepared by dissolving the stoichiometric amounts of metal nitrates in $1000\,dm^3$ of doubly distilled water. For each experiment, 300 mg of the catalyst was suspended in 60 ml of the respective metal solutions. A 10 ppm concentration of each metal ion was chosen so as to minimize the optical effects such as self absorption by the metal ions. The pH measurement experiments in the presence of the hole capture agent (i.e., methanol) were performed by adding 10 μl of methanol in colloidal suspension of each catalyst. The pH changes in the presence of electron and hole capture agents

were performed by using 10 ppm solutions of the respective metal ions and 10 μl of methanol. To ensure reproducibility, all the experiments were performed in duplicate. All the experiments were performed at room temperature and atmospheric pressure.

3. Results and discussion

In this study, the role of pH changes during the course of illumination for the photocatalytic splitting of water over three catalysts, i.e., WO_3, TiO_2 and NiO has been investigated. The choice of the photocatalysts (WO_3, TiO_2 and NiO) was based on their stability in aqueous suspensions under laser illumination [27]. The laser photon energy of 355 nm (~3.5 eV) was in close agreement with the bandgap of semiconductor powders (2.8, 3.2 and 3.5 eV for WO_3, TiO_2 and NiO, respectively). The valence and conduction band edge potentials of WO_3, TiO_2 and NiO are +3.2, +2.70, +3.0 and +0.4, −0.4, −0.5 V, respectively [29–30].

When illuminated, H_2O splits into its components over the surface of a photocatalysts by donating the electrons to the photogenerated holes, with the formation of hydroxyl radicals ($OH^\bullet$) and H^+ ions as shown in Eqs. (1) and (2). This is possible when the valence band edge of the catalyst is positive than +1.23 V,

$$SC \xrightarrow{h\upsilon > E_g} SC(h_{vb}^+ + e_{cb}^-) \qquad (3)$$

$$H_2O + h_{vb}^+ \rightarrow H_2O^+ \rightarrow OH^\bullet + H^+ \qquad (4)$$
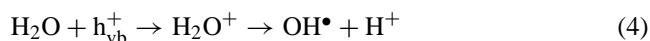
The combination of hydroxyl radicals produced because of water oxidation generates oxygen (Eq. (5)).

$$OH^\bullet + OH^\bullet \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (5)$$
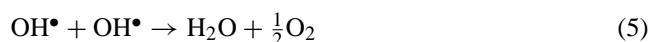
The capture of conduction band electrons by H^+ ions leads to the formation of hydrogen if the potential of the conduction
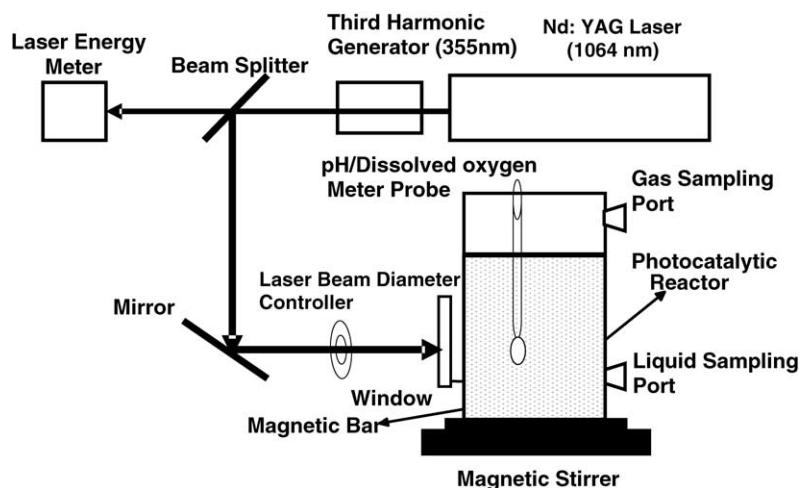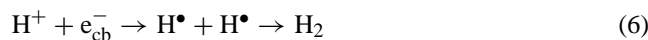

Fig. 1. Schematic diagram of the experimental setup for pH measurement applied for laser photocatalytic water splitting.

band edge of the semiconductor photocatalyst is negative than 0.0 V (Eq. (6)).

$$H^+ + e_{cb}^- \rightarrow H^\bullet + H^\bullet \rightarrow H_2 \tag{6}$$

Water splitting is a complex reaction due to the possibility of a number of side reactions that can occur at the surface of the catalyst and in the solution. The possibility of occurrence of these reactions and the effect of these side reactions on oxygen and hydrogen yields for individual catalysts can be estimated by measuring the pH changes during the course of reaction. The possible side reactions are the reduction of oxygen and the formation of HO_2 radicals (Eqs. (5) and (6)).

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \tag{7}$$

$$H^+ + O_2 + e_{aq}^- \rightarrow HO_2 \tag{8}$$
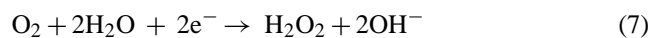
By examining the reactions given in Eqs. (3–8), it can be inferred that the reactions mentioned in Eqs. (4), (7) and (8) lead to a change in the pH while the rest of the reactions occur through free radical mechanisms. For the catalysts which do not have the conduction band edge suitable for the formation of H_2 (negative than 0.0 V), all the H^+ produced by the oxidation of water by valence band holes (positive than 1.23 V) will remain in the solution and lead to a decrease in the pH of the system. By contrast, for the catalysts which have the conduction band edges suitable for the conversion of H^+ ions to $H^\bullet$ radicals to form hydrogen, there is an equal probability for oxygen reduction (Eq. (7)) which increases the pH of the system.

The actual pH changes plotted as a function of time during the water-splitting process, in argon environment, over WO_3, TiO_2 and NiO are presented in Fig. 2. A decrease in the pH for WO_3 and an increase for TiO_2 and NiO can be observed. The decrease in the pH of the WO_3 system, from 4.77 to 1.65 over a period of 60 min, clearly indicates that all the H^+ ions that are produced as a result of the photocatalytic oxidation of water remains in the solution and in the absence of unsuitable
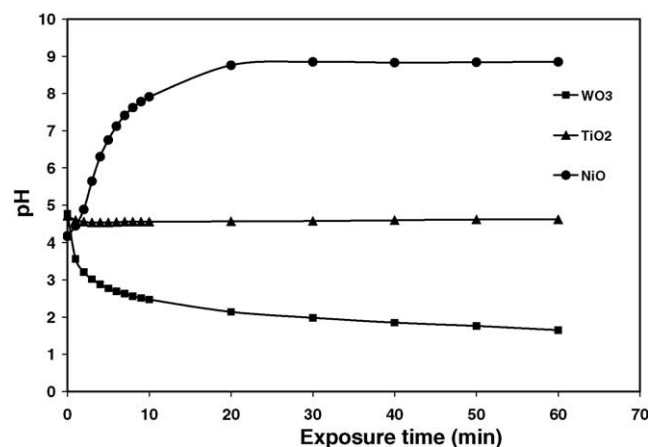

Fig. 3. Shift in the valence band (VB) edge of WO_3, TiO_2 and NiO with the change in pH as a function of time under 100 mJ laser illumination. using 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO, respectively. Shifting of valence and conduction band edges are calculated using Eqs. (1) and (2).

conduction band edge (+0.4 V), do not lead to the formation of hydrogen. As the amount of oxygen produced through Eq. (7) reaches to some appreciable limit in the solution, other processes such as the formation of HO_2 radicals (Eq. (8)), are activated causing a slow decrease in the pH. The comparison of the shifting of valence and conduction band edges, calculated by using Eqs. (1) and (2), with the change in the pH of the system with irradiation for WO_3, TiO_2 and NiO, are presented in Figs. 3 and 4. The shifting of valence band edge (Eq. (1)) from 2.81 to 2.95 V in the first 10 min and then to 3.00 V in 60 min, with the decrease in the pH of the system, enhances the extent of over potential associated with the oxidation of water over WO_3. This is another possible reason for the slow decrease in the pH during the period of 10–60 min. TiO_2 has highly suitable band edges both for the oxidation of water and reduction of H^+ ions. In the presence

Fig. 2. Comparison of pH changes at laser energy of 100 mJ using 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO respectively.
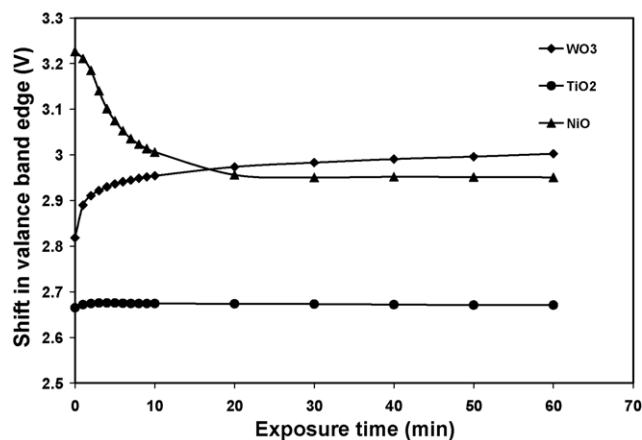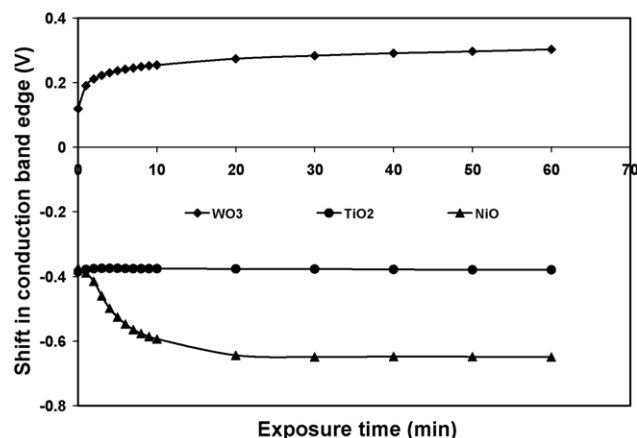

Fig. 4. Shift in the conduction band (CB) edge of WO_3, TiO_2 and NiO with the change in pH as a function of time under 100 mJ laser illumination using 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO, respectively. Shifting of valence and conduction band edges are calculated using Eqs. (1) and (2).
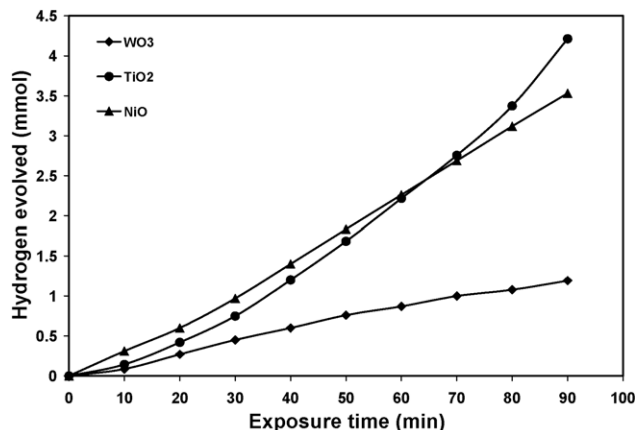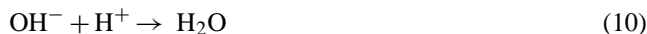
Fig. 5. Comparison of hydrogen production over WO_3, TiO_2 and NiO as a function of laser exposure time. Here, laser energy was 100 mJ per pulse and 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO was used.

of argon, there was a very mild increase in the pH of the system (Fig. 2) under irradiation of the TiO_2 suspension. On the other hand, a sharp increase in the pH of the system was observed during water splitting over NiO. A comparison of hydrogen and oxygen production over WO_3, TiO_2 and NiO is presented in Figs. 5 and 6. The hydroxyl ions serve as the additional source for the production of precursors, i.e., hydroxyl radicals, for oxygen production as well as a sink for H^+ ions as indicated below in Eqs. (9) and (10).

$$OH^- + h_{vb}^+ \rightarrow OH^\bullet \tag{9}$$

$$OH^- + H^+ \rightarrow H_2O \tag{10}$$

3.1. Oxygen as electron scavenger

Oxygen, in the dissolved form in aqueous heterogeneous photocatalytic suspensions, serves as an electron capture agent to form superoxide (O_2^-) radical either by captur-
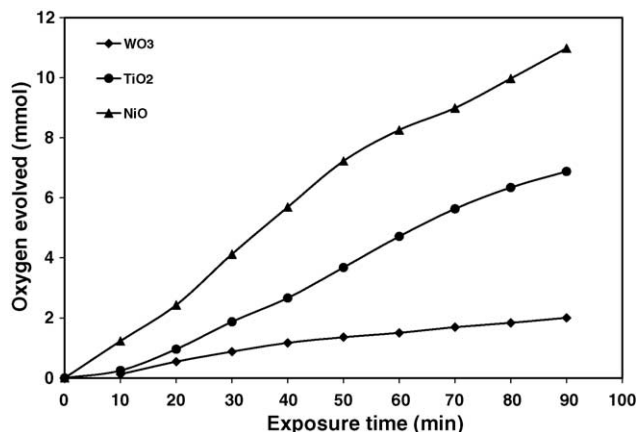

Fig. 6. Comparison of oxygen production over WO_3, TiO_2 and NiO as a function of laser exposure time. Here laser energy was 100 mJ per pulse and 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO was used.
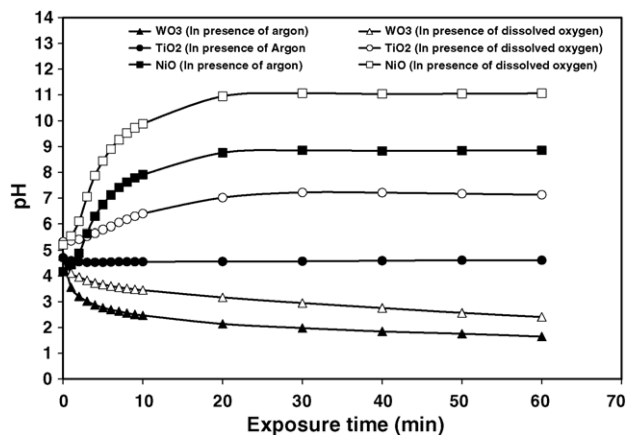

Fig. 7. Comparison of pH changes in argon and dissolved oxygen environment under laser illumination over WO_3, TiO_2 and NiO. Here laser energy was 100 mJ per pulse and 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO was used.

ing the conduction band electrons (e_{cb}^-) or aqueous electrons (e_{aq}^-).

The superoxide radicals can initiate a range of reactions depending upon the pH of the system. In acidic solutions, it reacts with H^+ ions to give HO_2 radicals, which may combine with each other to give H_2O_2 and O_2 [31].

In the presence of favorable conduction band edges, the reduction of oxygen or the formation of superoxide radicals proceed through the capture of conduction band electrons. This leads to the reduction of water (Eq. (7)) thus causing an increase in the pH of the system. A comparison of pH changes over WO_3, TiO_2 and NiO in the presence of argon and dissolved oxygen is presented in Fig. 7. Here, a decrease in the pH for WO_3 and an increase in the pH for both TiO_2 and NiO can be observed in the presence of dissolved oxygen as compared to argon. A less decrease in pH in the presence of dissolved O_2 clearly suggests that H^+ ions produced because of photocatalytic water oxidation (Eq. (4)) are consumed in the formation of HO_2 radicals. An increase in pH, for both TiO_2 and NiO, depicts that the extent of water reduction is quite high in the presence of dissolved oxygen compared to that in an argon environment. As both TiO_2 and NiO have suitable conduction band edges compared to the potential of water reduction (+0.03 V), dissolved oxygen serves as efficient electron capture agent.

3.2. Metal ions as electron scavengers

In this study, Fe^{3+} and Ag^+ were selected as electron capture agents and their action-mechanisms were established on the basis of the measurement of pH changes during the course of reaction over WO_3, TiO_2 and NiO. The reduction potentials of Fe^{3+}/Fe^{2+} and Ag^+/Ag^0 are +0.77 and +0.80 V, respectively [31]. All these reaction were performed in argon environment.

The comparison of normalized pH changes during the photocatalytic splitting of water in the presence of metal ions to
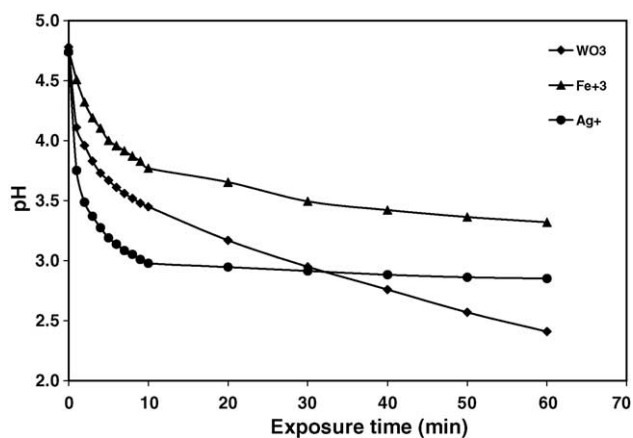
Fig. 8. Comparison of pH changes under argon environment in the presence of Fe^{3+} and Ag^+ over WO_3. Here laser energy was 100 mJ per pulse and 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO was used.

Fig. 9. Comparison of pH changes under argon environment in the presence of Fe^{3+} and Ag^+ over TiO_2. Here laser energy was 100 mJ per pulse and 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO was used.

that without metal ions over WO_3 is presented in Fig. 8. Here, an initial decrease in the pH can be observed in the presence of Ag^+ compared to that for pure WO_3. Ag^+ has a favorable reduction potential of +0.80 V compared to the conduction band edge potential of WO_3 and qualifies for serving as an electron scavenger. An initial decrease in the pH in the presence of Ag^+ establishes its behavior as an electron capture agent, but a stable value afterwards (higher than pure WO_3) predicts the consumption of Ag^+ as Ag^0 by capturing conduction band electrons.

Fe^{3+} also has a favorable reduction potential of +0.77 V, for the capture of conduction band electrons, but a slight decrease in the pH in the presence of Fe^{3+} ions compared to that of pure WO_3 was observed. One possible explanation for this effect based on pH changes is the regenerative behavior of Fe^{2+} formed due to conduction band electron capture by Fe^{3+} by the valence band holes in competition with water molecules that reduces the extent of water oxidation, and in turn reduces the formation of H^+ ions.

The comparison of normalized pH changes during the photocatalytic water-splitting process in pure and in the presence of metal ions, over TiO_2, is presented in Fig. 9. A substantial decrease in the pH of the system in the presence of Ag^+ compared to that for pure TiO_2 can be observed. This large decrease followed by a stable pH indicates that due to the non-regenerative behavior of Ag^+ ions, their concentration decreases with time and leads to a stable pH value. For Fe^{3+} ions, a mild increase in the pH of the system compared to that of pure TiO_2 was observed.

A substantial decrease in the pH of the system in the presence of both Ag^+ and Fe^{3+} as compared to pure NiO was observed. The comparison of normalized pH changes during the photocatalytic water-splitting process in pure and in the presence of metal ions over NiO is presented in Fig. 10. Apparently, this decrease in pH establishes the
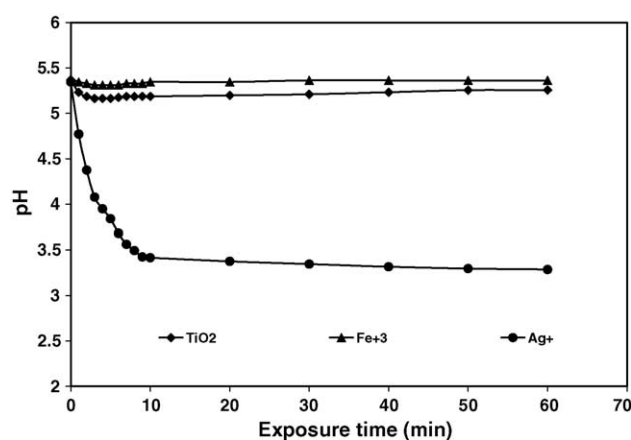
efficiency of both metal ions as electron capture agents by capturing the conduction band electrons, in competition with H^+ ions and O_2 and suggests an increase in the production of oxygen and decrease in the production of hydrogen. However, a reverse behavior was observed in H_2 and O_2 measurements [29]. As discussed earlier, the reduction of water over NiO leads to the increase in pH with the formation of hydroxyl ions in the system. These hydroxyl ions serve as precursors for oxygen production and as a sink to H^+ ions. The metal ions, besides serving as electron capture agents, react with hydroxyl ions forming $Fe(OH)_3$ and AgOH, thus reducing the pH of the system and enhancing the yield of H_2. As each Fe^{3+} consumes three hydroxyl ions compared to Ag^+ that consumes only one hydroxyl ion, the decrease in the pH is higher for Fe^{3+} as compared to Ag^+.
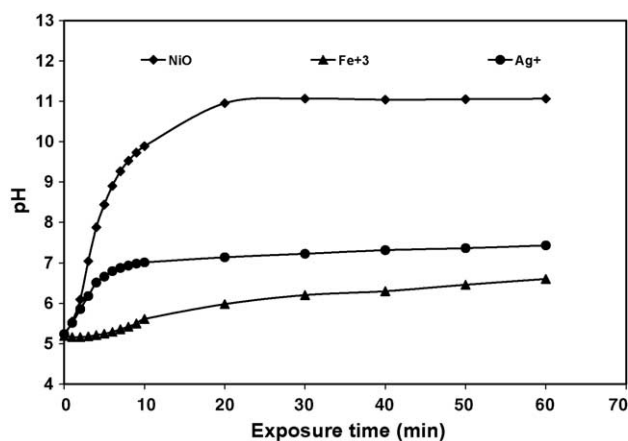

Fig. 10. Comparison of pH changes under argon environment in the presence of Fe^{3+} and Ag^+ over NiO. Here laser energy was 100 mJ per pulse and 300 mg of each catalyst with initial pH of 4.8, 4.75 and 4.2 for WO_3, TiO_2 and NiO was used.

4. Conclusions

The measurements of the pH changes along with the study of products during the photocatalytic splitting of water are essential since these changes give deep insight into the working and behavior of the catalyst under laser illumination. The role of the oxygen dissolved, as well as the oxygen produced, during the photocatalytic splitting process can be fully understood on the basis of pH measurements. The pH changes properly describe the mechanism and the function of dissolved metal ions as electron capture agents and methanol as a hole capture agent. The variation in the product yield can be well understood on the basis of pH changes under laser illumination.

Acknowledgements

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