ABSTRACT

The aim of the study is to photogenerate hydrogen from organic compounds and water. In this attempt, molecular photocatalytic systems as well as semiconductor photocatalytic systems were studied. In the case of molecular photocatalytic system, photoactive species are employed to bring about unfavorable oxidations and reductions. In semiconductor photocatalytic systems, photogenerated electrons and holes are utilized to bring about the above oxidations and reductions. Photolysis experiments were carried out in 300 cm^3 cylindrical reactor with a 400 W medium pressure mercury lamp.

Copper (II) chloride was found to catalyze photogeneration of hydrogen from aqueous solutions of ethanol. It was observed that at a given concentration of ethanol, the hydrogen evolution rate increases and then decreases with increase in concentration of $CuCl_2$. The optimum [$CuCl_2$] being 0.01 M and this value is nearly independent of the ethanol concentration. It was also noticed that at a given concentration of $CuCl_2$, the hydrogen evolution rate increases and then decreases with increase in concentration of ethanol for all values of [Cu^{2+}], the H_2 evolution rate becomes maximum when ethanol concentration = 25% v/v.

Ethanol or methanol and water mixtures containing copper (II) sulfate are found to liberate hydrogen upon UV irradiation with partial reduction of copper sulfate to metallic copper. It was seen that mixing ratios of alcohol and water affects the reaction rate.

Fe^{3+} ion was found to photocatalyse dehydrogenation of alcohols. The reaction rate depends on anionic species present in the photolysate and the degree to which they form complexes with Fe^{3+}. Anion species such as Cl^-, ClO_4^- and SO_4^{2-} were chosen to study their effects on hydrogen generation rate. The highest quantum yield was obtained when the anion in the solution is Cl^-. It was seen that, pH of the medium, and $[Fe^{3+}]$ affect the hydrogen photogeneration rate. Reaction mechanism for the above process is discussed.

An aqueous tetrahydroxostanante(II) ion, was found to liberate hydrogen with concomitant oxidation to tetrahydroxostanante(IV) ion upon irradiation. It was observed that the reaction rate increases with increasing pH and then decreased. Reaction mechanism is discussed.

Samarium(III) and europium(III) ions are found to photocatalyse the photogeneration of hydrogen from aqueous solutions of alcohols. The reaction rates are found to increase in the order propan-2-ol > ethanol > methanol. Eu^{3+} is slightly more active than Sm^{3+} in photogeneration of hydrogen. A significant increase in the hydrogen photogeneration rate was observed when chloroplatinic acid is present in the solution.

An aqueous suspension of iron (III) phosphate ground with TiO_2 found to liberate molecular oxygen with reduction of iron(III) phosphate to iron (II) phosphate. The formation of iron(II) phosphate leads to photogeneration of hydrogen with its concomitant oxidation.