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on Fundamental and Applied Aspects of
Physical Chemistry

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CONTENT

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HYDROGEN PRODUCTION FROM GLYCEROL PHOTO-REFORMING OVER PT/N-DOPED TITANATE PHOTOCATALYSTS

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ABSTRACT

Conversion of sunlight energy via photocatalytic water splitting and photo-reforming of renewable biomass organic derivates has been increasingly utilized for hydrogen production. Photocatalytic processes have been used due to their sustainability, environmental-safety, and effectiveness. Pt/N-doped titanate photocatalysts were synthetized via alkaline hydrothermal treatment, followed by Na^+/NH_4^+ ion exchange, impregnation and gaseous reduction. The activities of the photocatalysts were tested for hydrogen production via photocatalytic reforming of glycerol under simulated solar irradiation. The improved hydrogen production from photo-reforming of glycerol was attributed to the anatase active phase and surface area which enhanced the adsorption of glycerol onto the surface of catalysts; metallic Pt suppress the electron/hole recombination by trapping the photo-generated electrons; reduced band gap by incorporation of N into lattice of TiO_2.

INTRODUCTION

Overcoming fossil fuel dependence in energy sector is great challenge in a last decade, regardless of increased use of alternative energy sources such as solar, wind, hydropower and geothermal energy. Hydrogen presented as efficient energy vector in utilization of sunlight, due to its high energy density and abundance from renewable sources. One of proposed strategies for efficient, environment friendly and reliable hydrogen production is photocatalytical water splitting. [1]

Among semiconductors fulfilling requirements for hydrogen production (valence band more positive than the O_2/H_2O redox couple, conduction band more negative than H_2O/H_2 redox couple and resistance to photocorrosion) TiO_2 have been extensively studied in relation to H_2 production from water or biomass derivates. [2] However, bare TiO_2 showed solar to hydrogen efficiencies under 5% which is limiting the industrial implementation of process. Different strategies are applied for improvement of efficiency for solar-light responsive photocatalysts.

Surface modification of TiO_2 with high work function metal cocatalyst (e.g., Pd, Au, Pt) suppress electron-hole pair recombination by forming Schottky junctions and accepting electrons from conduction band of TiO_2 to reduce hydrogen ions to molecular hydrogen. Doping of non-metals such as nitrogen extend absorption in visible light region of TiO_2 materials and allow improved separation of photo generated charge carriers. Sacrificial hole scavengers are commonly used for improvement of hydrogen production by directly reacting with positive holes, or intermediate $^{\bullet}OH$ radicals, thus reducing recombination of hole-electron pairs, while scavengers undergo rapid and irreversible oxidation. Different factors influence hydrogen photocatalytic production from alcohols: a) titania phase composition and morphology, b) the choice of metal, c) alcohol oxidation potential, d) presence of hydrogen atoms in alpha positions with respect to hydroxyl group, e) byproducts generated in reaction. [3], [4]

The predominant byproduct of biodiesel production yields glycerol, which has led to waste disposable issues. Photo-reforming of glycerol in hydrogen production processes is one of proposed possibilities for developing sustainable and economically viable biodiesel production.

The aim of the study was to evaluate the efficiency of Pt/N-doped titanate photocatalysts for H_2 production from glycerol–water mixtures as well determining optimized concentration of glycerol at

ambient conditions which may provide an efficient and low-cost method for the production of renewable hydrogen.

METHODS

Titanate nanotubes were synthesized by a hydrothermal method, as previously reported by Kasuga et al. In this work, 4 g of the P25 TiO_2 were mixed with 250 mL of 10 M NaOH solution in a Teflon-lined autoclave at 150 ℃ for 24 h. Sodium titanate was vacuum filtered, and precipitate was redispersed 4 times in 2 M NH_4NO_3 solution for 24 h, to ensure complete ion-exchange reactions. Titanate photocatalyst loaded with Pt were synthetized by impregnation method using H_2PtCl_6 aqueous solution. Final catalysts were obtained by reduction in H_2 flow (8.5 mL/min) at 500 ℃ for 60 min (temperature rate 5℃/min). The photocatalytic activity of the prepared catalysts was tested towards the hydrogen production via photocatalytic water splitting/alcohol reforming process under simulated solar light. The photocatalytic tests were performed at 25 ℃ in a photocatalytic reactor equipped with standard reaction vessel, quartz immersion well and 100 W mercury-vapor lamp. Prior to each test reaction mixture consisting of 125 mg of photocatalyst, different concentration of aqueous glycerol solution was placed in a reaction vessel and purged for 45 min with Ar flow to remove oxygen from the suspension. The concentration of hydrogen in effluent gas was analyzed with a constant time interval sampling by gas chromatograph.

RESULTS AND DISCUSSION

The photocatalytic activity of synthesized photocatalysts were evaluated under simulated solar light in glycerol-water mixtures at ranging alcohol concentration from 0.2 mol/L to 1.6 mol/L. Glycerol, byproduct of trans-esterification of oils in biodiesel production, was selected as renewable sacrificial agent, due to removing rapidly and irreversibly photogenerated holes, or oxidants such as ˙OH radicals.

Effect of glycerol concentration on hydrogen production activity over 0.5 wt% Pt/N-doped titanate catalysts is shown in Fig. 1. Addition of small amount of glycerol (0.2 mol/L) shows a very good improvement in hydrogen production activity. With increasing glycerol concentration up to 0.8 mol/L, an increase in the hydrogen production is observed with maximal rate of 15 mmol/gh. With further increase of glycerol concentration (1.6 mol/L), the hydrogen production activity is decreasing.

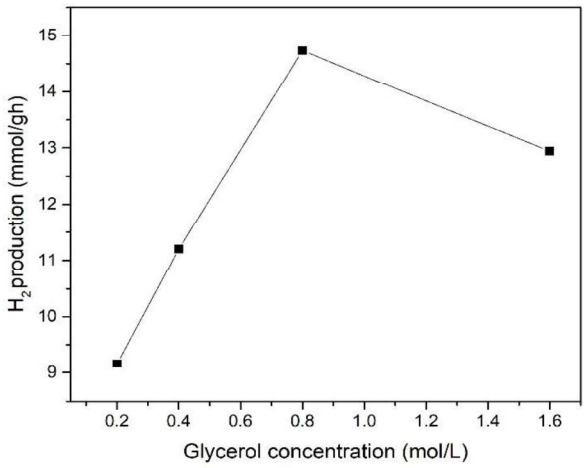

Figure 1. Effect of glycerol concentration on hydrogen production activity over 0.5 wt% Pt/N-doped titanate photocatalysts.

XRD pattern of N-doped titanate photocatalyst (presented in Fig. 2) showed anatase phase as main crystallite phase which attributed to improved photocatalytic activity.

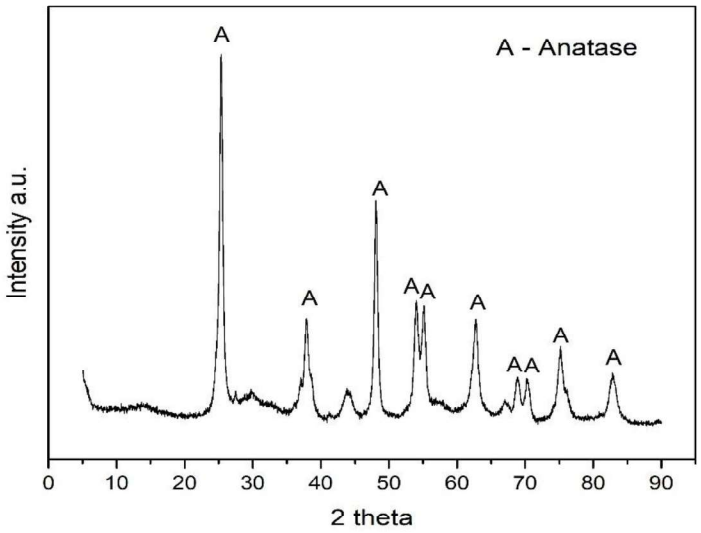

Figure 2. XRD pattern of N-doped titanate photocatalyst.

Parameters that could influenced the optimum alcohol concentration for the glycerol-water mixture are viscosity and generated intermediates. At higher concentrations of glycerol solution become viscous which has effect on transport of reactants and products to and from the photocatalyst surface.

During glycerol photo-reforming a large number of intermediates can be formed such as acetic acid, acetaldehyde, glyceraldehyde, acetol, carbon dioxide, carbon monoxide, methanol, ethanol, glycolaldehyde, acetone and acrolein which already have been reported in the literature. Proposed mechanism involves the oxidation of glycerol to glycolaldehyde and formic acid and the secondary oxidation of glycolaldehyde to formic acid and formaldehyde followed by the simple photocatalytic oxidation of formic acid and formaldehyde to CO_2. [5]

The photocatalyst surface is progressively covered by strongly adsorbed reaction intermediates and molecular fragments that restrict to some extent adsorption of compounds from the liquid phase, which could explain drop in hydrogen production rate.

Presence of metallic Pt is crucial in overcoming high H_2 overpotential, while N doping enabled improved sunlight harvesting, showed in DRS results where bandgap of N-doped titanate photocatalyst is red-shifted to 2.6 eV compared to TiO_2.

CONCLUSION

In this work Pt/N-doped titanate photocatalysts were successfully synthetized and their photocatalytic activity was accessed towards hydrogen production under simulated solar light. The results showed that use of glycerol as biodiesel waste product enhanced photocatalytic activity compared to H_2 production from pure water. Parameters influencing the optimum alcohol concentration for the glycerol-water mixture were solution viscosity and great number of photogenerated intermediates that restrict to some extent adsorption on catalysts surface. Metallic Pt were crucial in supressing electron/hole recombination.

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