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EFFECT OF TITANIUM DIOXIDE PHOTOCATALYSTS ON HYDROGEN PRODUCTION FROM RAW BIOMASS

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Abstract

The rapid increase in global energy demand has led to the search for clean and sustainable energy sources. In recent years, the possibility of hydrogen production and utilization has become an area of interest. Efficient methods for hydrogen production must be developed for hydrogen to be a viable source of energy. Photocatalytic reforming using organic sacrificial agents is a popular area, with the majority of research focusing on the development of highly active photocatalysts for the process. This study aimed to investigate the potential of titanium dioxide (P25) and titanium tetraisoproxide (TTIP) photocatalysts on the photocatalytic reforming of glucose and Ipomea asarifolia leaves. Initially, the effect of varying glucose concentrations was investigated over different weights of bare TiO2 (P25) and titanium tetraisoproxide catalysts. It was found that an ideal glucose concentration of around 20 mg/L over 2g of both catalysts enhanced the rate of hydrogen production by many-fold, even though P25 was more active. No hydrogen was recorded for Ipomea asarifolia over the titanium tetraisoproxide catalyst. However, a considerable amount of H_2 was produced from the ipomea in the presence of P25.

Introduction

The extraordinary changes in the ecosystem due to the pollution of fossil fuels led to the evolution of alternative sources of greener energy, such as hydrogen (Idris, 2020) . Fossil fuels were the main source of energy for industries and transportation (David et al., 2019). Biodiesels have been considered eco-friendly compared to fossil fuels (Mazloomi and Gomes, 2012). Nevertheless, Regauskas *et al*. (2006) added that it is still not a preferable alternative fuel source due to its low cost effectiveness and complex preparation techniques. Hydrogen is the future fuel (Idriss, 2020). It is recognized as a cleaner and alternative fuel (Bowker et al., 2014). When combusted with oxygen, it is an energy carrier that can be used in internal combustion engines or fuel cells producing virtually no greenhouse gas emissions. The only significant emission is water vapor. Hydrogen production from water splitting has a big barrier due to the stability of water, and the reaction

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requires as much as 237 kJ/mol (Zheng et al., 2016). The pioneering research for about 6 decades ago by (Fujishima and Honda, (1972) had electrochemically decomposed water into hydrogen and oxygen in the presence of TiO_2 electrode. Photocatalytic reforming of biomass has been considered as one of the approaches to produce sustainable hydrogen to overcome the challenges associated with water splitting (Yang et al., 2006b). The water-splitting process in the presence of an organic component as a hole scavenger (Bowker and Jones, 2020), photocatalyst (Fujishima et al., 2000), and sunlight or solar simulator (Grätzel, 2001) has been described as a sustainable approach (Hutchings and Catlow, 2018).

As a photocatalyst, titanium dioxide has certain features, including an appropriate band gap (3.0-3.2eV) (Serpone, 2006) efficient light absorption (Diebold, 2003) nontoxic and chemically stable (Ohno et al., 2001). TiO2 has three major phases: anatase, rutile, and brookite (Lan et al., 2013). However, anatase and rutile are often used as photocatalysts (Ohno et al., 2001). Anatase has a tetragonal structure and a thermodynamically metastable phase with a bandgap of 3.2 eV. The rutile phase has a tetragonal structure and is stable at elevated temperatures with an energy band gap of ~3.0eV. Anatase -to-rutile phase modifications occur during heat treatment at approximately 900 K (Scanlon et al., 2013). Anatase-rutile is the most common form of TiO_2 (Zhang et al., 2014). The tendency of H_2 and O_2 to recombine to form water (surface back reaction) (Bisquert et al., 2002) could easily proceed and strongly compete with water splitting. However, such a reaction could be minimized by using organic molecules as sacrificial agents to serve as electron donors (h+ trapping) (Al-Mazroai et al., 2007). Also, Kawai and Sakata (1980) reported hydrogen production from biomass-derived molecules via a photocatalytic route, implying that alcohols and biomass-derived molecules are excellent suppressants of photogenerated holes (Colmenares and Luque, 2014).

Traditional photo-reforming of carbohydrate and alcohols undergoes simultaneous oxidation that leads to the formation $CO_2 + H_2$

$$(C_6H_{12}O_6)n + 6nH_2O \xrightarrow[TiO_2]{hv} 6nCO_2 + 12nH_2 \qquad 1$$

The photoreforming of the alcohol–water mixture occurs upon excitation due to absorption of photon when hv≥Eg, electrons are transferred from the TiO_2 VB into the CB, forming electron–hole pairs (e^-– h^+) (Linsebigler et al., 1995). The study conducted by Bahruji et al. (2011) in different alcohol–water mixtures over photocatalyst, has revealed that one of the factors for high yield of hydrogen production rates was the presence of α-hydrogen on the alcohols. The effect of chlorides on photocatalytic hydrogen production for glycerol-water mixtures has been thoroughly studied by Ahmad et al. (2023). These alcohols are classified as first-generation biofuels that are substantially derived from biomass resources, such as carbohydrates. The use of biomass-derived molecules for hydrogen production may compete with their use as food (Kawai and Sakata, 1980). However, considering the potential of heterogeneous catalysts such as TiO_2 (Rinsant et al., 2014) for the selective photocatalytic oxidation of glucose into high-valued organic compounds (Lathasree et al., 2004), it is important to consider the following: The main aim of this study was to assess and compare the rate of hydrogen production from glucose over P25 (TIO2) and titanium tetraisoproxide (TTIP) photocatalysts. This study aims to generate H_2 from raw biomass (*Ipomea asarifolia*) and glucose using TiO_2 (P25) and titanium tetraisoproxide (TTIP).

Materials and Methods

The TTIP titanium dioxide was synthesized by modifying the method (Nolan et al., 2009). Isopropyl alcohol, isopropyl alcohol, and nitric acid were purchased from Sigma Aldrich. 5 mL of titanium tetraisopropoxide was added to 95% mL of isopropyl alcohol. The mixture was then added to 900 ml of deionized water at pH1.5

(acidified with nitric acid) at pH 1.5. The solution was stirred at room temperature for 24 h until a transparent colloid formed. The colloidal solution was heated at 75-80°C for 6 h. The mixture was dried in air in furnace at 100°C for whole night to evacuate the alcohol, followed by calcination at 250°C. For the photocatalytic experiment, a variable amount of P25/TTIP catalysts and 50 mL of deionized water were placed in the reaction vessel and mixed with glucose as the sacrificial agent. The reactor was sealed with foil paper, and the solution was purged with argon under stirring in the dark to remove dissolved oxygen. After 30 minutes of purging . The reactor was illuminated using a 150 W xenon arc lamp, and the photocatalytic reaction was conducted for 3 h. However, to test the raw biomass, Ipomea leaves were washed at 50°C with water and then with methanol and dried overnight at 100°C. 0.2 g of washed and dried leaves was mixed with 50 ml H2O and 2g of P25 and TTIP at temperature of 60°C of the reaction vessel. The hydrogen generated in this study was analysed using gas chromatography. At interval of 30 minutes 200µL of gas sample was taken from the reaction vessel using a gas-tight syringe and injected into a Varian 3200 gas chromatograph equipped with a thermal conductivity detector and a 2 m long MS 13X column.

Results and Discussion

Figure 1 shows the XRD pattern of TTIP and P25. A major phase of anatase with very intense peak at 25.10°, 38.2°, 48.10°, 55.00 ° and 70.11°. However, minor peaks at 27.30 °, 36.78 ° and 42.10 ° were found to indicate the rutile phase. Not significant structural difference was observed between TTIP and P25 (Lan et al., 2013) reported that the addition of a dopant to TiO_2 would suppress the growth of particle size.

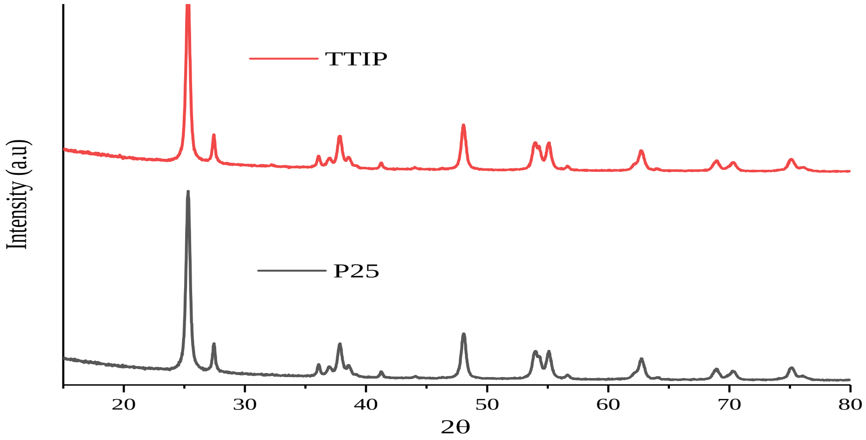

Fig.1. XRD patterns for 2g P25 and 2g titanium tetraisopropoxide (TTIP)

The synthesized TTIP catalyst displayed relatively similar peaks as P25. Fujishima and coworkers reported that the Degussa P25 is in the ratio of 1 rutile:3 anatase (Fujishima et al., 2008). The surface areas of P25 and TTIP were analyzed using the N2 adsorption technique. The P25 surface area was $59m^2/g$ and $67m^2/g$ was obtained from the TTIP. However, the relationship between the surface area and the rate of hydrogen evolution (Figure 2) proves that the activity of the TTIP with a high surface area is lower than that of the P25 with a lower surface area. This indicates that a high surface might not be a key attribute of a photocatalyst to enhance the reaction rate.

Photocatalytic hydrogen production

The hydrogen production profiles of the TTIP catalyst are shown in Fig. 2 and compared with the TiO_2 P25 photocatalyst, the same reactor system and operating conditions were applied in both cases. However, P25 titania shows significant activity under UV irradiation, which might be attributed to its crystallinity.

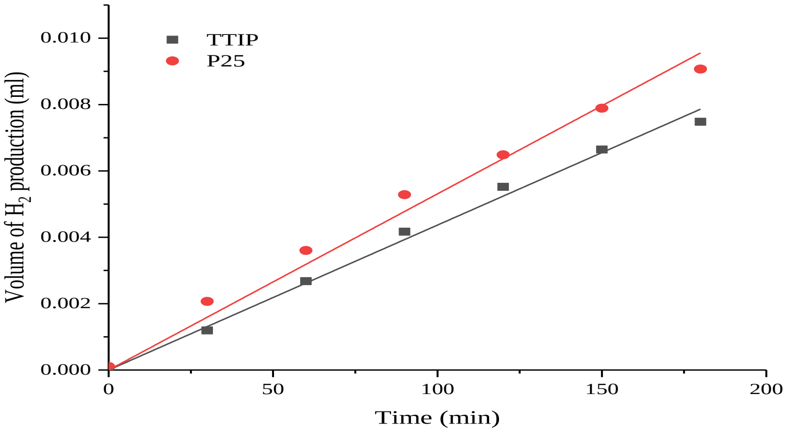

Fig.2. Comparison of hydrogen production (ml) between P25 and TTIP

The effect of the weight content on the P25 and TTIP was examined by varying the mass of both catalysts within the range of 0.5–3.0 g to identify the optimal mass for the best performance. Usually, there is an optimum mass toward enhanced photo activity, which varies depending on the shielding effect (Kondarides et al., 2008) on catalytic activity, and in the beginning, increases with increasing catalyst amount.

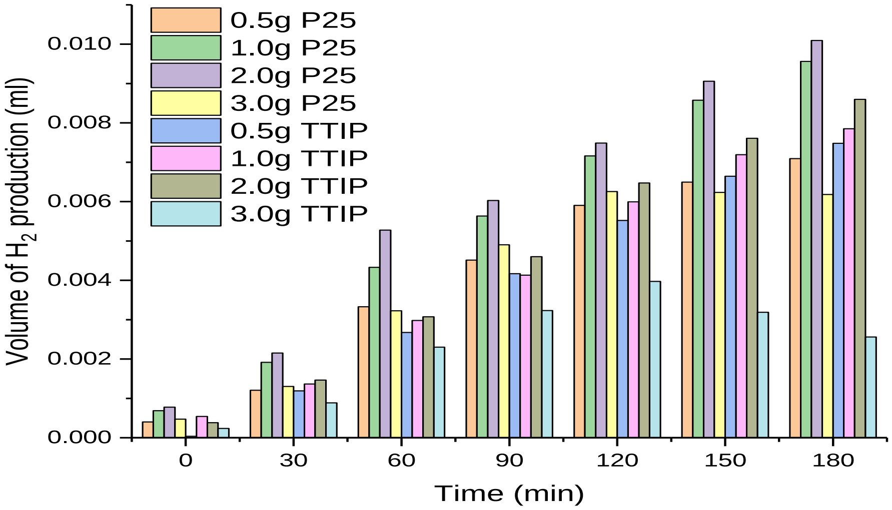

Fig.3. Effect of P25 and TTIP content on the production of photocatalytic hydrogen

A further increase in the amount normally decreases the overall photocatalytic activity of both P25 and TTIP catalysts. This fact has been attributed to shading effects caused by the excess charge that results in charge recombination (Leung et al., 2010). The results of hydrogen production under UV irradiation over photocatalysts are shown in Fig. 3. Compared to Fig. 2, TiO_2 and P25 have higher hydrogen production activity than TTIP that indicates the magnitude of the rapid recombination of the photogenerated electron–hole pairs is much higher in TTIP.

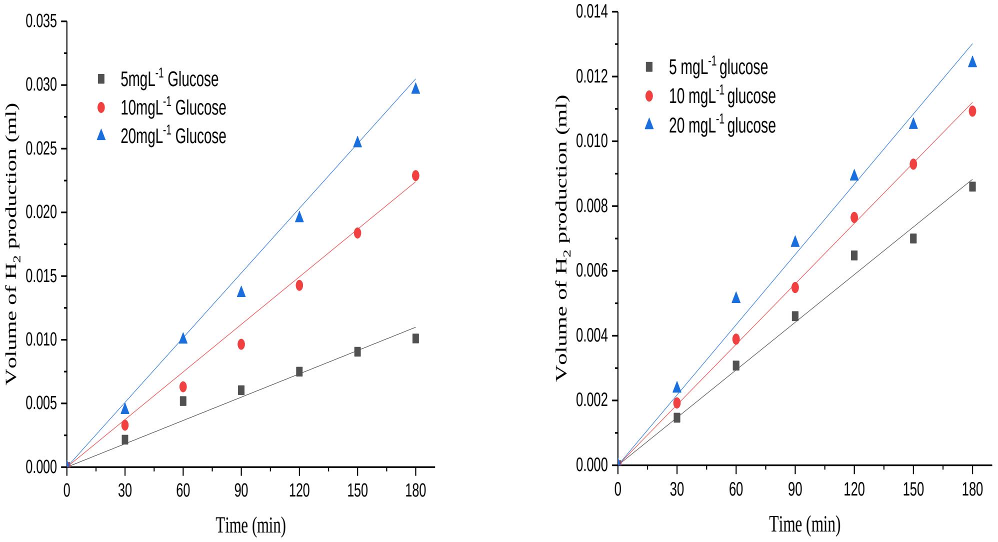

Fig.4. Effect of glucose content on photocatalytic hydrogen production for the (a) 2.0g P25 and (b) 2.0g TTIP catalysts

Figure 4 shows the hydrogen production (ml) as a function of irradiation time from a glucose/water mixture using a 2.0g P25 and TTIP catalysts. In the presence of glucose, hydrogen production is significantly higher than that from water alone, as shown in Figure 4. Glucose acts as a very efficient sacrificial agent, inhibiting the recombination of photogenerated electrons and holes (Tran and Kannangara, 2013) by providing a suitable alternative pathway for hole capture. It is not surprising that the volume of hydrogen increases with increasing glucose concentration. This implies that the scavenging power of glucose increases by increasing its concentration, which is in good agreement with the finding of Kawai and Sakata, (1980). The metal nanoparticles, with the pure TiO2 showing negligible rates similar to those observed in the absence of a sacrificial agent, are addressed below.

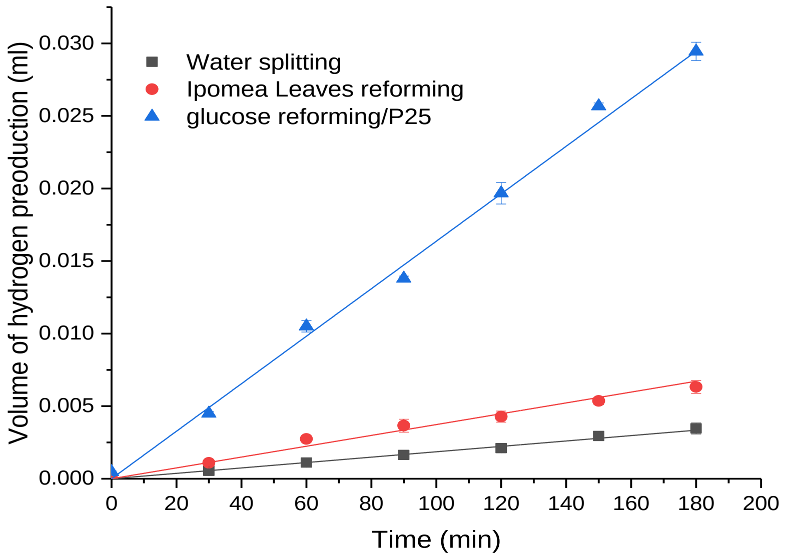

Fig.5. Hydrogen production from Ipomea asarifolia leaves (comparison with H_2 produced from water splitting and glucose over P25)

As shown in Figure 5, the amount of hydrogen produced for the photoreforming of Ipomea was approximately one-fifth as much as that for glucose in the presence of P25 and less than double of that obtained from water splitting. In photocatalytic water splitting over TiO_2 or other semiconductor materials, the absorption of a photon/light with an energy equal to or higher than the band gap (E_g = 3.1 eV (Yu et al., 2000) of the materials is the initial stage, as shown in equation 1. Subsequently, the initial step stimulates the promotion of an electron from the VB to the CB, followed by the formation of an electron–hole pair (Wu, 2018). The hydrogen generated from raw biomass is much higher than that of water splitting over bare P25. The small amount of hydrogen from water splitting was due to frequent recombination of electrons and holes.

Conclusion

In this study, we show that hydrogen can be generated from the photoreforming of glucose–water mixtures over TiO_2/P25 and titanium tetraisopropoxide catalysts. It is also evident that the Ipomea asarifolia leaf could serve as a suitable hole scavenger for enhancing hydrogen production via photoreforming over P25. No hydrogen was obtained from the raw biomass over the titanium tetraisopropoxide catalyst, which might be associated with its poor crystallinity.

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