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Comparison of Photocatalytic Hydrogen Production from Glycerol and Crude Glycerol Obtained from Biodiesel Processing

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Abstract Photocatalytic hydrogen generation from aqueous solutions of glycerol and crude glycerol (byproduct of biodiesel manufacturing) were compared using Pt/TiO_2 and CuO_x/TiO_2 catalysts. Glycerol solutions generated more H_2 than crude glycerol solutions, with the H_2 generation rate approximately 2.5 times higher for Pt/TiO_2 and approximately 4 times higher for CuO_x/TiO_2. Pt/TiO_2 produced more H_2 than CuO_x/TiO_2, with a ratio nearly 2.5 times higher for glycerol and nearly 3.5 times higher for crude glycerol. Ion exchange of crude glycerol solutions to replace Na^+ with Li^+ or K^+ had little impact on reactions with CuO_x/TiO_2 whereas ion exchange with Li^+ moderately reduced reaction rates with Pt/TiO_2. An anti-foam agent reduced foaming problems associated with higher concentrations of crude glycerol but itself degraded. The addition of 0.4 mM NaH_2PO_4 reduced the H_2 generation rate by nearly 60 % whereas the presence of 0.4 mM NaCl, 0.4 mM $NaNO_3$ or 0.2 mM Na_2SO_4 reduced the H_2 generation rate by only 10–20 % over the course of the reaction.

Keywords Photocatalytic · Photocatalysis · Hydrogen · Biodiesel · Glycerol

1 Introduction

Global biodiesel production experienced a nine-fold increase between 2004 and 2009, with the total 2009 production reaching nearly 5 billion gallons [1]. Feedstocks for biodiesel production include vegetable oils, both edible and nonedible oils, waste frying oils and animal fats. Biodiesel can be manufactured using an acid- or base-catalyzed reaction with an alcohol. The predominant process uses base with methanol to remove the fatty acid chains from a triglyceride molecule and produce three alkyl esters (biodiesel) and a glycerol molecule [2]. The base-catalyzed reaction is faster than the acid-catalyzed reaction, although it is less suitable for oils with considerable free fatty acid content [3].

Increased biodiesel production is accompanied by increased glycerol production, and development of suitable uses for the crude glycerol will help the economic feasibility and sustainability of the biodiesel industry [4]. Depending on the oil feedstock, the glycerol yield from transesterification using sodium methylate and methanol ranged from about 8 to 22 % of the initial oil mass, with waste vegetable oil producing the largest glycerol fraction [5]. The crude glycerol contains unreacted methanol and base, and may contain soaps that could be converted to free fatty acids under acid conditions. Purification of the crude glycerol by filtration, chemical treatment, distillation and ion exchange can improve its value, but is a costly option for small-scale producers [5].

Recent studies on crude glycerol utilization have focused on conversion to valuable products [6] or extraction of additional fuel value [7–9]. Several papers have addressed the production of H_2 from deoxygenated aqueous glycerol solutions using noble metals on TiO_2 [10, 11] or copper oxides on TiO_2 (CuO_x/TiO_2) [12–14]. This report will present the challenges that arise from using these catalysts with crude glycerol derived from biodiesel production for photocatalytic H_2 production, compared to the use of chemically pure glycerol.

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2 Experimental Methods

CuO_x/TiO_2 and Pt/TiO_2 catalysts were prepared from copper(II) nitrate hemihydrate and tetraamine platinum(II) chloride (Aldrich) solutions in ethanol. A slurry of the aqueous solution and TiO_2 (P25 provided by Degussa or purchased from Sigma Aldrich) was dried in an open beaker on a shaker table, ground, and calcined at 450 °C in air for 6 h. The CuO_x/TiO_2 and Pt/TiO_2 catalysts contained 1.25 wt% metal. The catalyst metal loading and mass were selected based on H_2 production in preliminary reactions performed in stoppered flasks.

Reactions were performed at atmospheric pressure and 40 °C using a 500 mL three port Pyrex® round bottom flask containing 250 mL of solution combined with 585 mg of catalyst. For certain runs, EnviroGem® AD01 surfactant (Air Products) or Surfynol® MD-20 defoamer (Air Products) was added to reduce foaming. The mixture was sonicated for 45 min in the reaction flask to disperse the catalyst. Argon was bubbled through the solution for approximately 4 h prior to the reaction to deoxygenate the system. Photoreactions were performed using UVA-340 lamps (Q-Lab) and a radiometer was used to measure an incident light intensity of 5.1×10^{-5} Einstein/m^2 s. Argon flow was continued during the reaction and a sampling valve delivered 500 μL of gas to a 5890 GC equipped with a Shin Carbon RT column and TCD detector. Gas samples were analyzed every 15 min for the first 4 h of reaction and every 30 min thereafter. After the reaction, solution pH was measured, formaldehyde (HCOH) concentration was determined using Nash's method [15], and Cu^{2+} ion concentration in the solution was determined using an Orion ion-specific electrode or inductively coupled plasma calibrated with standard solutions.

Glycerol (>99.0 %) was purchased from Sigma. Crude glycerol was obtained from an on-campus biodiesel pilot plant that generates biodiesel from used cooking oil. The crude glycerol layer from the NaOH-catalyzed transesterification reaction, containing NaOH, methanol, and water, was distilled in the pilot plant to recover methanol. The direct use of these distillation bottoms in photoreactions lead to problems with foam generation from the residual soaps. To remove any soap, water and concentrated H_2SO_4 were added to the distillation bottoms to adjust the pH to approximately 3. This converted the soaps to free fatty acids that were decanted from the crude glycerol.

The sodium and water content of the crude glycerol was determined by Intertek using ICP emission spectroscopy and Karl Fisher titration, respectively. The effect of sodium content on H_2 generation from glycerol solutions was studied by adding NaOH solid to the solutions with subsequent pH correction with 0.1 M HCl to obtain a pH of approximately 6 before reaction.

Experiments were also performed with crude glycerol after ion exchange with Amberlite 252 synthetic resin (Rohm and Haas) to remove the Na^+ ions. The sodium-form resin was exchanged with dilute H_2SO_4 and then used to exchange Na^+ ions from a 1.04 wt% crude glycerol solution. The sodium content of the solution before and after ion exchange was tested. Since ion exchange lowered the solution pH below the target initial value of 6, the pH was adjusted before reaction with 1 M LiOH or KOH and the effect of the various cations on reaction rate was compared.

Acid pretreatment of the distillation bottoms from the biodiesel plant introduces additional anions into the glycerol. The impact of these anions on H_2 production was studied by adding Na_2SO_4 (Sigma Aldrich), $NaH_2PO_4{\cdot}H_2O$ (Mallinckrodt), $NaNO_3$ (Fisher) or NaCl (Spectrum) to glycerol solutions. To maintain a constant cation effect, the salts were all added to give 10 ppm Na in the reacting solution.

3 Results and Discussion

3.1 Comparison of H_2 Generation from Glycerol and Crude Glycerol

All glycerol solutions used in this work were 0.1 M. Crude glycerol contained 11.5 wt% water and 0.66 wt% Na, and had a golden brown color which was associated with unidentified contaminants in the used cooking oil. Since the exact composition of the crude glycerol was unknown, corrections were only made for the water content, and a 1.04 wt% crude glycerol solution was considered comparable to the 0.1 M glycerol solution. The 1.04 wt% crude glycerol solutions had an average sodium content of 62 ppm.

The H_2 production rates from pure water and solutions of glycerol and crude glycerol are compared in Fig. 1. Pt/TiO_2 reacted with pure water to give a peak H_2 generation rate of 1 μmol/L min which gradually dropped to a steady 0.1 μmol/L min. The H_2 production rate from water with CuO_x/TiO_2 was significantly lower, close to the detection limit of the system. Glycerol generated more H_2 than crude glycerol, with the H_2 generation rate approximately 2.5 times higher for Pt/TiO_2 and approximately 4 times higher for CuO_x/TiO_2. Pt/TiO_2 produced more H_2 than CuO_x/TiO_2, with a ratio nearly 2.5 times higher for glycerol and nearly 3.5 times higher for crude glycerol. For all cases, the H_2 generation rate was fairly stable over the 20 h reaction period. High H_2 production correlated with a significant drop in pH from an initial target value of 6.0 to values as low as 3.5.

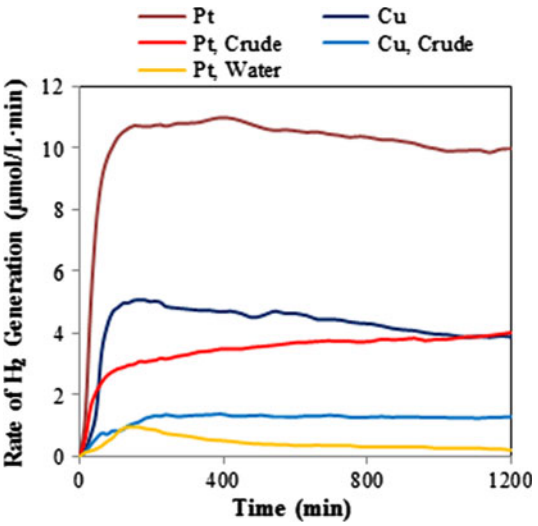

Fig. 1 H_2 generation rates from the photoreaction of glycerol (0.1 M) and crude glycerol (1.04 wt%), with 1.25 wt% Pt/TiO_2 and 1.25 wt% CuO_x/TiO_2

HCOH was also identified as a reaction product. For reactions with CuO_x/TiO_2, the measured HCOH concentrations ranged from 3.5 to 8.5 mM, and the molar ratio of H_2/HCOH formed after 20 h of reaction was nearly constant at a value of 0.65. Reactions with Pt/TiO_2 gave a range of H_2/HCOH ratios, with values close to 0.65 for conditions that gave lower H_2 generation rates and values as high as 3.5 for conditions that gave higher H_2 generation rates.

The stability of copper on CuO_x/TiO_2 was monitored by measuring the concentration of Cu^{2+} in the post-reaction solution. The measured concentration of Cu^{2+} in the solution was used with the calculated wt% loading of copper in the pre-reaction catalyst to determine the percentage of copper leached during reaction. Copper leaching ranged from 30 to 60 % and was comparable for the glycerol and crude glycerol solutions. The loss of copper was associated with the photoreaction, since no copper leaching was observed without illumination and/or H_2 generation. Copper leaching may be responsible for the reduction in H_2 generation rate over the duration of the reaction. One reaction with CuO_x/TiO_2 and glycerol was run for 65 h and showed a gradual decrease in H_2 generation to 50 % of the initial maximum with 60 % of the copper in the fresh catalyst leached into the solution.

3.2 Effects of Defoamer on H_2 Generation

Foam did not form with glycerol solutions; however, foaming was problematic with crude glycerol solutions. In some cases, dense foam formed on top of the reaction mixture, blocking light absorption and delaying the release of gaseous products or causing erratic H_2 generation. Foaming was more significant with CuO_x/TiO_2 than Pt/TiO_2 and increased with wt% crude glycerol. Therefore, the effects of Surfynol MD-20 defoamer and EnviroGem AD01 surfactant on the photoreaction were investigated.

Preliminary studies showed that MD-20 did not significantly reduce foaming and hindered reaction rates due to catalyst agglomeration. AD01 successfully reduced foaming without negatively impacting catalyst dispersion and was used in subsequent studies. As shown in Fig. 2a, the addition of 500 or 1,000 mg of AD01 to the crude glycerol reaction with CuO_x/TiO_2 nearly doubled the H_2 production rate. However, three separate trials with CuO_x/TiO_2 in pure water showed that the presence of defoamer increased the H_2 production rate from nearly undetectable to approximately 1 μmol/L min, comparable to the increase in H_2 production from crude glycerol solutions with the addition of defoamer. Figure 2b shows the addition of defoamer increased H_2 production from glycerol solutions, with the difference in H_2 generation rates again comparable to the rate of H_2 generation from water with defoamer.

The effects of higher crude glycerol concentrations were studied using Pt/TiO_2 because it appeared to be less affected by foaming. As seen in Fig. 3, the enhanced H_2 production from a 5.2 wt% crude glycerol solution with the addition of defoamer is again comparable to the increase in H_2 production from water with the addition of defoamer. The results for both catalysts suggest that the enhanced H_2 production in the presence of AD01 arises from breakdown of the defoamer. This is supported by the detection of formaldehyde in the products from reaction of water with defoamer. Figure 3 also includes a curve labeled 'heavy foam' which illustrates the erratic H_2 generation that can be observed when foam forms.

3.3 Effect of Cations on H_2 Generation

The presence of Na^+ in crude glycerol was identified as a potential cause of the lower H_2 generation rates. Two types of experiments were performed to study the impact of cations on the photoreaction: (1) addition of NaOH to glycerol with pH adjustment using 1 M HCl and (2) ion exchange to remove Na^+ from crude glycerol with pH adjustment using LiOH and KOH. Since the initial solution pH impacts the photoreaction rate, it was necessary to introduce the additional ions to return the solution pH to approximately 6. Figure 4 shows the reduction in H_2 production from glycerol with Pt/TiO_2 with the addition of Na^+ and Cl^-. The addition of 62 or 134 ppm Na^+ gave similar behavior, with a more gradual increase in H_2 production and a long-time H_2 generation rate approximately 70 % of that for chemical glycerol. For 278 ppm Na^+, the H_2 generation rate dropped to nearly that of the crude glycerol case, confirming that the addition of charged

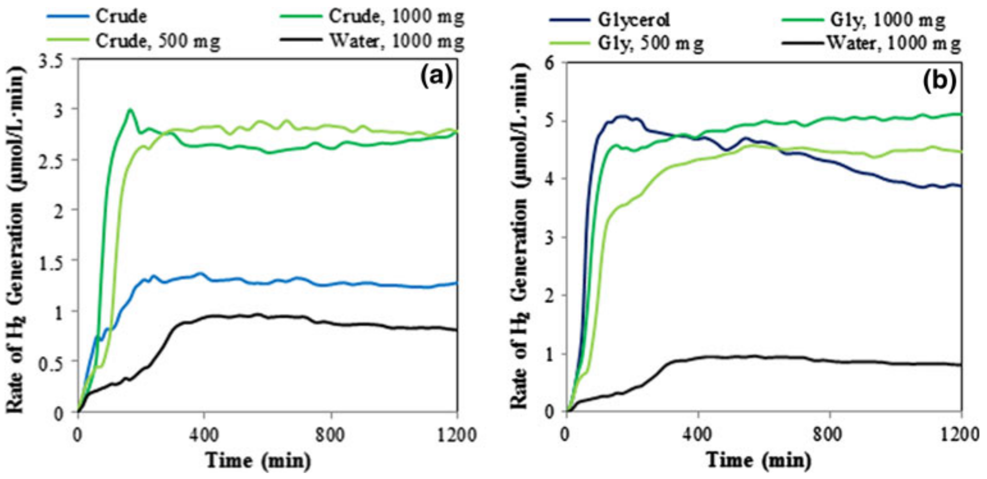

Fig. 2 H_2 generation rates from the photoreaction of crude glycerol and glycerol using 1.25 wt% CuO_x/TiO_2 and the addition of 500 or 1,000 mg of AD01. **a** Reaction of 1.04 wt% crude glycerol with defoaming agent, **b** reaction of 0.1 M glycerol with defoaming agent

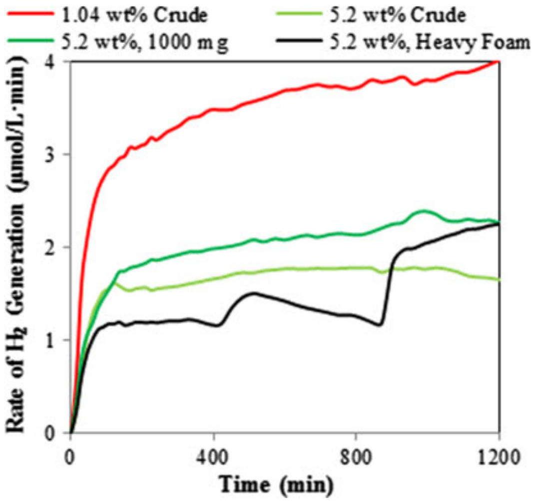

Fig. 3 H_2 generation rates from the photoreaction of 1.04 and 5.2 wt% crude glycerol using 1.25 wt% Pt/TiO_2 and the addition of 500 or 1,000 mg of AD01

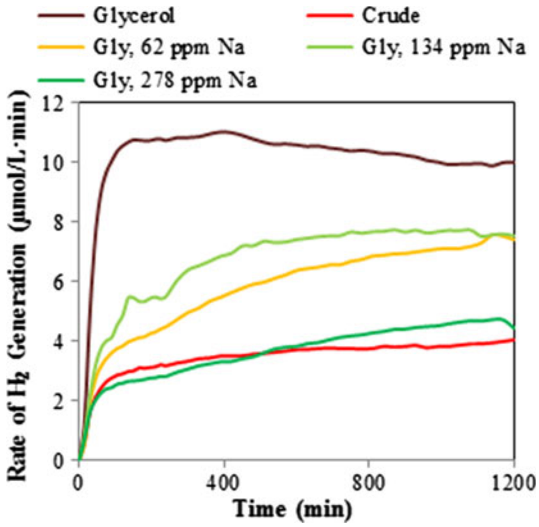

Fig. 4 H_2 generation rates from the photoreaction of glycerol using 1.25 wt% Pt/TiO_2 and the addition of sodium

species in solutions negatively impacts the photoreaction. HCOH analysis was not performed for runs involving ion exchanged cation, since the impact of these additional components on the assay was uncertain.

Amberlite 252 synthetic ion exchange resin was used to reduce the Na^+ content of 1.04 wt% crude glycerol solutions from 62 ppm to approximately 10 ppm. To restore the desired initial solution pH, small amounts of LiOH or KOH salts were added. The H_2 production rates from CuO_x/TiO_2 with the ion exchanged crude glycerol solutions were similar to that for the original sodium-containing crude glycerol. For Pt/TiO_2, the H_2 production rate from the K^+ exchanged crude glycerol solution was similar to that for the original crude glycerol, however, the rate for the Li^+ exchanged crude glycerol solution was slightly lower. This suggests that residual Na^+ from the transesterification catalyst is not necessarily the cause for the lower reaction rates of crude glycerol.

3.4 Effect of Anions on H_2 Generation

Acid pretreatment of crude glycerol to remove free fatty acids can introduce the anions of mineral acids into the crude glycerol. To test the effects of various anions, they were added as sodium salts to photoreactions with glycerol and Pt/TiO_2 at a fixed Na^+ concentration of 10 ppm. Figure 5 shows that H_2 generation was reduced by the addition of any sodium salt, with 0.4 mM NaH_2PO_4 having a stronger inhibiting effect than either 0.4 mM NaCl, 0.2 mM Na_2SO_4 or 0.4 mM $NaNO_3$. At earlier times, the presence of Cl^-, SO_4^{2-} and NO_3^- reduced H_2 generation by approximately 20 % compared to pure glycerol, with their impact decreasing slightly over time as the H_2 generation rate from pure glycerol slowly drops. In this work, phosphate was added as the monobasic sodium salt, NaH_2PO_4 to best match the ionic form present at the reaction conditions. Addition of 0.4 mM NaH_2PO_4 reduced the average reaction rate by 60 %. The variation in H_2

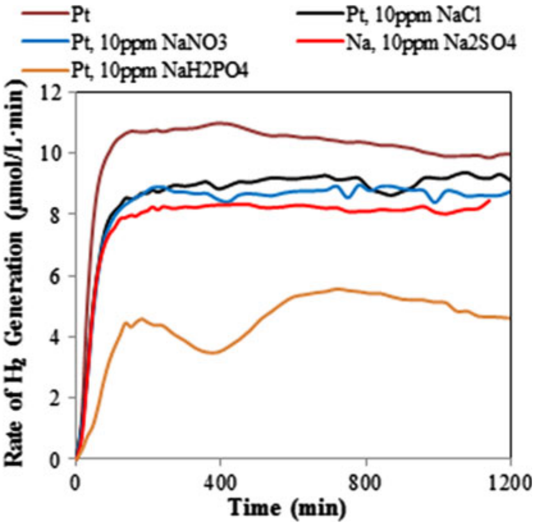

Fig. 5 H_2 generation rates from the photoreaction of glycerol using 1.25 wt% Pt/TiO_2 and the addition of various sodium salts

production rate for solutions containing NaH_2PO_4 was reproducible and thought to be related to changes in the solution pH during the reaction. Reactions with chloride, sulfate and nitrate produced H_2 and CO_2 in ratios similar to that of glycerol, however, reactions with $H_2PO_4^-$ gave nearly double the H_2/CO_2 ratio, with some H_2 possibly coming from the anion. HCOH analysis was not performed for runs involving sodium salts, since the impact of these additional components on the assay was uncertain.

These results are consistent with Matthews' report [16] that millimolar concentrations of Na_2SO_4 or Na_3PO_4 reduced photocatalytic oxidation rates of phenol, ethanol and 2-propanol with TiO_2 by 20–70 %, and confirm the lower H_2 production, shown in Fig. 1, for crude glycerol containing sulfate ions. Matthews found that higher concentrations of NaCl were needed to significantly reduce the reaction rate and $NaNO_3$ at concentrations up to 0.1 M had little effect on reaction rates. They demonstrated that the data was best modeled with a Langmuir–Hinshelwood kinetic model, with the assumption that the inorganic anions and solutes compete for adsorption at oxidizing sites on the catalyst surface. The adsorbed anions can be oxidized to radical anions, which could subsequently oxidize solute. In this work, millimolar concentrations of any salt reduced reaction rates, indicating that the metal-loaded TiO_2 catalyst is more sensitive to ionic strength of the solution than TiO_2.

4 Conclusions

An understanding of the impact of impurities present in crude glycerol from biodiesel production is important in developing realistic utilization options. Photocatalysis is one possible means to recover further value from the crude glycerol. Therefore, photocatalytic H_2 generation from crude glycerol and glycerol aqueous solutions and the impact of impurities were investigated. Glycerol solutions generated more H_2 than crude glycerol solutions, with the H_2 generation rate approximately 2.5 times higher for Pt/TiO_2 and approximately 4 times higher for CuO_x/TiO_2. Pt/TiO_2 produced more H_2 than CuO_x/TiO_2, with a ratio nearly 2.5 times higher for glycerol and nearly 3.5 times higher for crude glycerol. HCOH production was proportional to H_2 production under most reaction conditions. Higher concentrations of crude glycerol suffered from foaming and defoamers may be ineffective or degrade under the reaction conditions. The replacement of Na^+ for Li^+ or K^+ in the crude glycerol did not significantly impact H_2 generation rates. Millimolar concentrations of NaCl, Na_2SO_4 or $NaNO_3$ in glycerol solutions reduced the H_2 production rate by approximately 20 %, whereas similar concentrations of NaH_2PO_4 reduced the reaction rate by nearly 60 %. These results can be explained by competitive adsorption between the anions and oxidizing sites on the catalyst surface. Future research on biodiesel reaction chemistries and feedstocks should include consideration of their impact on the quality and value of the glycerol byproduct.

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