Hybrid effect of the activated carbon and the CuO catalyst on vegetable oil steam reforming

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Abstract

This study aims to utilize of bio material to produce green hydrogen energy through hybrid of the activated carbon and the CuO catalyst in vegetable oil steam reformer. The experiment was done in the atmospheric pressure steam reformer. The results show that activated carbon and CuO individually performs the same trend in producing hydrogen. Their combination accelerates hydrogen production. This indicates that heat energy makes CuO alters the electron density around the reactant by combining the van der Waals force with the induction due to electron jump in its narrow ban gap. Therefore, CuO activate effectively the polar water (H_2O) molecules. More energy is needed to alter the electron in stable large molecule triglyceride of vegetable oil. On the other hand, the activated carbon does it by combining the van der Waals force with the induction due to delocalized of the pi electrons travelling between carbon atoms in the graphite structure. Consequently, only the nonpolar triglyceride molecules are attracted while the polar H_2O are repelled by hydrophobic force. Thus, larger energy is needed to activate electrons in H_2O. When they are combined, the CuO works only on H_2O while activated carbon does only on triglyceride which is highly effective.

Keywords: Activated carbon, CuO catalyst, hybrid effect, steam reforming of vegetable oil, hydrogen.

Introduction

The significant increase in hydrogen demand is due to the technological advancements in the fuel cell industry. Steam reformer (SR) is mostly applied for hydrogen production in industry [1][2] though it releases the highest emission. This is because of many reasons such as industry has the most extensive experience in this technology, lowest process temperature, and best H_2/CO ratio [3].

Hydrogen is produced mostly from catalytic SR of natural gas and oil-derived naphtha [3-5]. Up to now, almost 95% of the world's hydrogen is being produced from fossil fuel based feed stocks. The CO_2 emission from this process has great impact to the global warming. Renewable resources based technologies for hydrogen production are attractive options for the future due to carbon neutral nature of these technologies with lesser effects to the environment.

Rioche et al. [6] have reported the successful use of model compounds as well as crude bio-oil as feedstock for catalytic SR towards hydrogen production, by using noble metal-based catalysts supported on alumina or on ceria–zirconia materials. The latter support leads to higher H_2 yields compared to alumina-supported catalyst.

Bio-fuels such as ethanol, glycerol and buthanol have been reformed to hydrogen and carbon dioxide [7-11]. Moreover, hexadecane, long chain hydrocarbon, has been reformed into hydrogen over a Rh/CeO_2 catalyst in microchannels [12]. This suggests that large and long chain vegetable oil is potential for hydrogen production as a green energy. However, large chain triglyceride molecule of vegetable oil consumes substantial heat energy because its boiling point is high. Even, when vegetable oil contact with water at high temperature they undergo hydrolysis reaction that break vegetable oil into glycerol and fatty acids [13]. This reaction also consumes additional heat energy. Therefore, performance of SR for large molecule vegetable oil should be improved.

In fact, most of SR utilizes catalyst from semiconductor. The polar nature of semiconductor is more suitable for polar fuel like methanol or very short hydrocarbon. In contrast, large molecule vegetable oil is usually nonpolar. However, our preliminary study [14] has successfully produced hydrogen from vegetable oil by using SR with CuO catalyst though the production rate is small and heat energy consumption is high.

The large molecule triglyceride vegetable oil and the high energy consumption problems could be solved by improving catalyst performance with environmental friendly material. This paper proposed the use of activated carbon (AC) combining with semiconductor catalyst in SR. Since AC is assemblies of defective graphene layers

[15], it has two characteristics, one is as an adsorbent which is good for catalyst, and the other as inductor for its very mobile electron due to delocalized pi electron in graphite lattice which is empowering the catalyst. The hybrid effect of the AC and the CuO catalyst on vegetable oil steam reforming reaction is discussed. The goal of the study is to increase the utilization of bio material for producing green energy with more efficient energy consumption.

Research concept

The concept of more effective and efficient SR for large molecule vegetable oil is explained in **Figs 1 to 3**. **Fig. 1** shows induction of water and vegetable oil by CuO to react producing H_2. The CuO is a p-type semiconductor with a narrow band gap of 1.2 eV. When it is heated, the electron in valence band becomes more energetic and tends to jump to the conductive band. As a result the conductive band tends to be more negatively charged while the valence band leaved by electron tends to be more positively charged [16]. Consequently, the CuO tends to have positive and negative charges. Thus, it activates more effectively polar molecule of water. The vegetable oil on the other hand is weakly activated because it is usually nonpolar [17] so that the number of electron which is unstable in the double bond of unsaturated fatty acids of vegetable oil is very few. The reaction of strong activated water and weak activated vegetable oil produces small number of hydrogen.

In contrast, as shown in **Fig. 2,** AC which is assemblies of defective grapheme layers is highly porous and the graphite structure gives it very large surface area which is nonpolar and hydrophobic [15]. For that reason, AC works more effectively on large triglyceride molecule. The hexagonal carbon chain structure in the graphite lattice makes electron to be delocalized generating magnetic field that induced strongly the van der Waals force in vegetable oil so that it is strongly activated. On the other hand, water which is polar molecule tends to be repelled away by hydrophobic force and therefore is weakly activated by the magnetic field. Similar with that in **Fig. 1,** the reaction of strong activated vegetable oil and the weak activated water produces small number of hydrogen.

When the effect in CuO **(Fig. 1)** and that in AC **(Fig. 2)** are combined, as shown in **Fig. 3** the CuO activates more effectively on H_2O for it is polar molecule with additional energy from repelling hydrophobic force from AC and at the same time AC activates more effectively only on triglyceride due to surface force and induction force from delocalized pi electron. This hybrid effect accelerates reforming reaction. However, the AC tends to capture the H_2 gas [18] that hampers the adsorption of triglyceride molecule giving lower H_2 production rate. Addition of more AC to the CuO could overcome the hydrogen adsorption by the AC. Therefore, the hybrid effect boosts the hydrogen production rate efficiently.

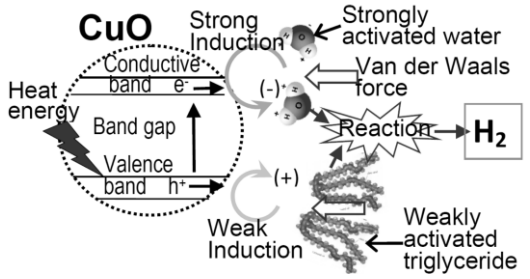

Fig. 1. Induction of water and vegetable oil by CuO to react producing H_2

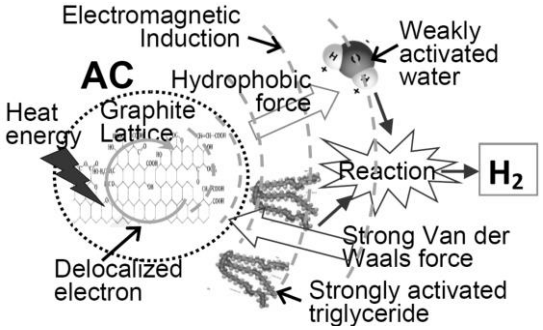

Fig. 2. Induction of water and vegetable oil by Activated Carbon (AC) to react producing H_2

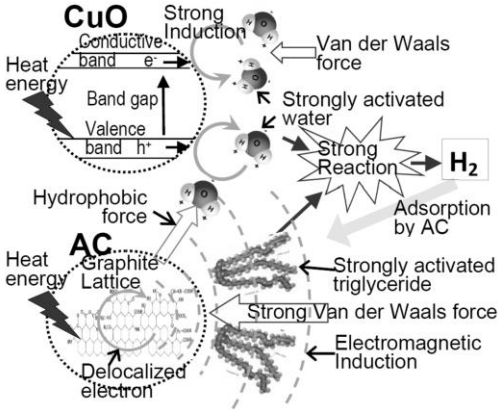

Fig. 3. Induction of water and vegetable oil by combined Activated Carbon and CuO to react producing H_2

Experimental

Steam reformer was constructed by three glass tubes, a reactor, and an H_2 gas collector as shown in **Fig. 4**. The first and the second glass tube were boilers. The third glass tube is a heated mixing chamber. They were heated by methanol flame. Vegetable oil and water were feed from separate infuse into boiler. The vegetable oil to water ratio was set as 3:1.

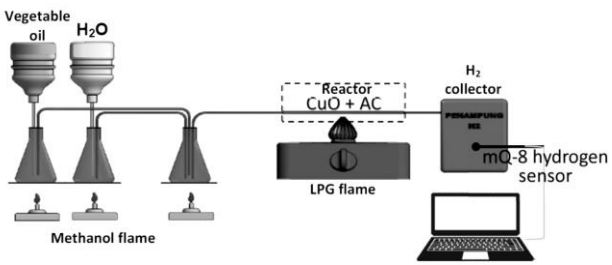

Fig. 4. Experimental apparatus.

The fuel vapor and steam were mixed and further heated at the third glass tube before flowing into reactor tube filled with CuO and AC. The reactor was heated with LPG flame to reach the appropriate temperature for reaction at the catalyst. The reaction temperature at the catalyst was set at 250ºC. The hydrogen produced in the reactor was flowing into H_2 collector. The hydrogen production in the collector was measured by mQ-8 hydrogen sensor. The sensor was calibrated with pure H_2 gas. The measurements were done during transient reforming reaction. The hydrogen signal was digitized by AD converter before it was recorded into computer memory.

The catalyst used in this study was LTS 302 composed by CuO=38-42 (wt%), ZnO=40-45 (wt%), and Al_2O_3=8-10 (wt%). The steam/gas ratio is ≥ 0.35 and the operating temperature range is 180-260 ºC. Though the CuO/ZnO catalyst is used the role of ZnO in this system remains unclear [19] despite the efforts made to elucidate its role [20-24]. Therefore only the role of CuO is discussed in this study because the active site is on the surface of CuO.

The AC for this experiment was produced from coconut shell. The coconut cell was dehydrated at 170ºC and then was carbonized at 400ºC-600ºC. The carbon was activated at 800ºC-1000ºC by flowing CO_2 gas. The ratio of CuO : AC was 0:1, 1:1, 1:3, and 0:1.

Results and discussion

Fig. 5 consistency of data and the dependency of the hydrogen production on the catalyst mass thermal energy storage. **Fig. 5a** shows that the measurement of hydrogen production with CuO:AC of 1:3 has good consistency. This suggests that the data in this experiment is in reasonably reliable.

Fig. 5b shows that doubling the number of catalyst delays the hydrogen production. This means that the larger number of catalyst consumes more energy to give the same effect to the hydrogen production. From this phenomenon, it can be concluded that the CuO needs certain number of energy to make the electron jumps across its energy band gap.

As shown in **Fig. 6a,** the hydrogen production from CuO without AC starts from around 800 s. The delay in production shows that the catalyst needs time to collect heat energy to energize electron jumping across the energy band gap. In other word, CuO need high heat energy to make the lip electron energetic enough to activate vegetable oil readily to react with water producing hydrogen. The activated carbon shows almost the same ability as CuO in producing hydrogen. It also need time to collect heat energy to make delocalized pi electrons travelling between carbon atoms in the graphite structure becomes more energetic inducing and activating more water in the reactant mixture. When the AC is added to CuO with the same ratio, i.e., CuO:AC of 1:1, the hydrogen is produced in relatively short time. This indicates that the combined AC - CuO give good effect on the hydrogen production though they are different type

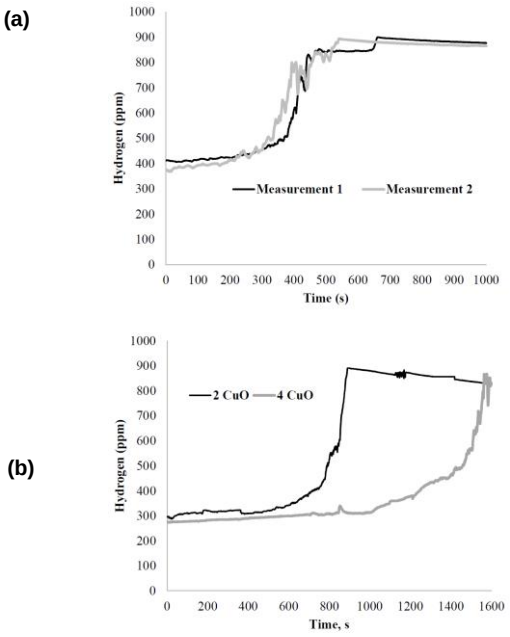

Fig. 5 (a) Measurement consistency. (b) Relation of hydrogen production to catalyst mass thermal energy storage

and therefore has different way to activate the reactant. The CuO is semiconductor, so it activates vegetable oil and water when the electron lip across the energy band gap. Since the electron lip makes positive and negative charges [16], so it activates more polar water than nonpolar vegetable oil. The vegetable oil is weakly induced by attraction of van der Waal force. On the other hand, the AC is assemblies of defective graphene layers which is highly porous and the graphite structure gives it very large surface area which is nonpolar and hydrophobic[15]. Therefore, the delocalized pi electron in the graphite lattice activated stronger vegetable oil than water because water is repelled by hydrophobic force while vegetable oil is attracted and induced stronger by van der Waals force and magnetic field, respectively. The combination of CuO and AC give good effect because they could share action separately at the same time. AC acts effectively on vegetable oil while CuO works more effectively on polar water. In this hybrid state, water gets addition energy from the hydrophobic force from AC that favors reaction. However, the production rate soon drops as the time elapse. This is due to the fact that AC is highly porous so it becomes good adsorption for H_2[18] that hamper the activation by induction on vegetable oil. By increasing the number of AC, that is CuO:AC=1:3, the hydrogen production increases though the production time is slightly longer. This is due to the fact that the large number of AC can overcome adsorption of H_2 but the higher heat energy is need to heat larger mass of AC.

It can be seen from **Fig. 6b** that the production rate of hydrogen by individual CuO, AC, and combined CuO-AC is nearly the same suggesting that the use of biomaterial in SR as a catalyst is possible for substitution of conventional catalyst material. In addition, the thermal power consumption can be reduced for shorter heat energy accumulation time.

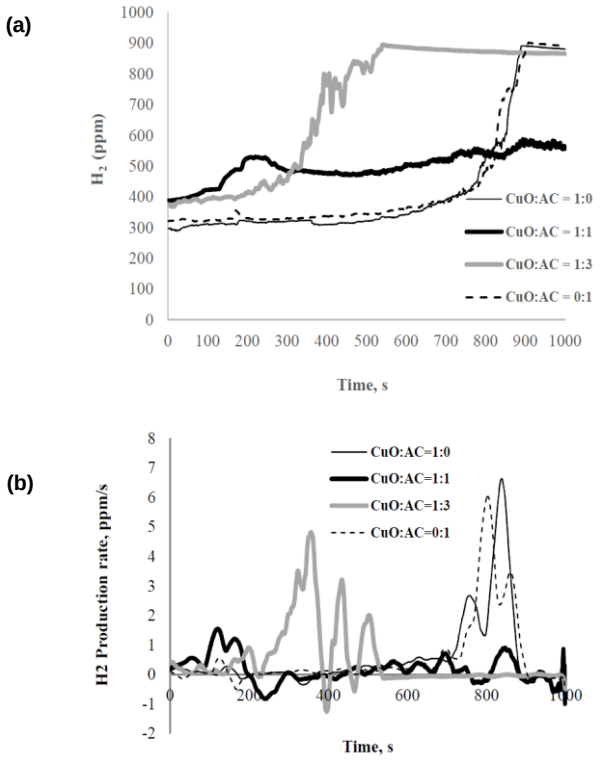

Fig. 6. (a) Hydrogen production at various ratio of CuO:AC, (b) hydrogen production rate.

Conclusion

The CuO and activated carbon individually give the same hydrogen production rate with long delay because larger heat energy is needed by both electrons in semiconductor CuO to lip across the energy band gap and in graphite lattice to delocalize. The reforming reaction is induced by these electron motions.

Combining activated carbon and CuO makes the reforming reaction starts much faster. The activated carbon attracts and induces only the nonpolar triglyceride molecule and repels the H_2O by hydrophobic force due to delocalized of the pi electrons travelling between carbon atoms in the graphite structure. The CuO attracts water molecules and alters the electron density around them due to electron jump in its narrow band gap. The hydrophobic force favors the water activation by CuO. This hybrid action accelerates reforming reaction. However, the activated carbon tends to adsorp the H_2 gas that hampers the attraction of triglyceride molecule giving lower H_2 production rate. The adsorption of H_2 gas in the activated carbon becomes less dominant at larger number of activated carbon giving higher H_2 production rate though the reaction delay becomes slightly longer due to higher heat energy required by the larger mass of activated carbon. This suggests that the bio material could be utilized more for producing green energy in steam reformer with lower thermal energy consumption.

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