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Photocatalytic Producation of Hydrogen from Aqueous Methanol Solution over Pt/TiO_2-Cu_2O Under Visible Irradiation

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Pt/TiO_2-Cu_2O photocatalysts were prepared in the experiments. For these complex oxides, morphology, structure, composition and optical properties were investigated by HRTEM, XRD, ICP and UV-visible techniques, respectively. In addition, in the absence of oxygen, the photocatalytic generation of H_2 from methanol over Pt/TiO_2-Cu_2O under visible light was studied and the effects of Pt content and composition of catalyst on photocatalytic activity were elucidated. The result showed Pt was deposited on the surface of TiO_2-Cu_2O in a clustered manner with particle size of 5-20 nm. When Pt content reached 1 wt. %, such catalyst exhibited highest photocatalytic activity. After the catalyst of 1 % Pt/5 % TiO_2-Cu_2O used for 7 times, the photocatalytic activity in the generation from aqueous methanol of hydrogen remained relatively stable. The catalyst of Pt/TiO_2-Cu_2O photocatalytic generation of hydrogen from methanol solution achieved through the photo-generated electron of e^- reduction of H_2O to produce H_2. As a result, 327 µmol H_2 was obtained after 3 h.

Keywords: Photocatalysis, TiO_2-Cu_2O, Methanol, Photocatalytic Producation of H_2.

INTRODUCTION

Hydrogen as an ideal non-polluting green energy,has attracted a wide spread attention in the development of new energy sources. However, the traditional method of hydrogen generation consume energy and the cost is high. Therefore, it limits the spread and application of hydrogen energy. In the 1970s, researchers found that, using TiO_2 single crystal electrodes could break down water to get hydrogen and made it possible to use solar energy for hydrogen production. If achieved hydrogen generation through photocatalytic decomposition of water and make it possible to industrialize, there may solve the energy problems completely. Therefore, researches on the photocatalytic generation of hydrogen have development prospects. However, H_2 and O_2 produced by photoexcitation on the same semiconductor particles can not easily be separated. So the electron donor, such as lower alcohol, was added to the reaction system to generate H_2[1-8]. Due to the higher hydrogen content, simple production of raw materials, methanol attracted great interests[2,5-8]. Studies on photocatalytic decomposition of methanol were mostly aqueous methanol liquid phase reaction system and under anaerobic condition. Compared to the aerobic condition, the anaerobic condition has the following advantages. Firstly, the electron acceptor of H^+ (or $H^\bullet$) in anaerobic condition get electrons as more and faster as possible and emit hydrogen. While in aerobic condition, oxygen will compete for electrons with the H^+ (or $H^\bullet$) and inhibit the reaction. Secondly, aerobic reaction needs to add oxygen constantly in practical applications. Meanwhile, hydrogen generated by the aerobic reaction will contain a certain amount of oxygen and that must be isolated by a certain devices before being used as fuel. Hydrogen generated by the anaerobic reaction could used directly as a fuel in addition to a small amount of inert gas in the beginning[4].

At present, Pt/TiO_2 catalyst used more in photocatalytic generation of hydrogen[3,4,9-12]. Nano TiO_2 has a very good light stability. When loading the platinum, it can gather and transfer electron and promote the desorption reaction of the reduction of light water. Many studies showed that the effect of loading platinum on TiO_2 was better than other precious metals, but Pt/TiO_2 can only be excited in the ultraviolet region. Solar energy in the ultraviolet region's share is only about 4 % of the total energy.Therefore, the utilization rate of solar energy is low. Cuprous(I) oxide Cu_2O can split water to produce H_2 and O_2 under visible light irradiation[13]. However, report about the photocatalytic generation of hydrogen from methanol using nano Cu_2O as catalyst is little. Senevirathna *et al.*[8] doped with a small amount of Cu_2O in TiO_2 (1 wt. % TiO_2) as photo catalyst and used it catalyze aqueous methanol solution to produce hydrogen under visible light. However, due to the low levels of Cu_2O, hydrogen generation rate is much lower than the UV irradiation condition.

This paper immersed K_2PtCl_4 in complex oxide of nano TiO_2-Cu_2O, then reduced by formaldehyde and loaded Pt on TiO_2-Cu_2O and preparated photocatalyst of Pt/TiO_2-Cu_2O. So far, such photocatalytic system has not been reported in the literatures. In addition, using the technologies of ICP, XRD, HRTEM and UV-visibleible diffuse reflectance to characterize the composition, structure, morphology and light absorption properties of Pt/TiO_2-Cu_2O composite photocatalyst in the experiments. Furthermore, A tungsten lamp was used as light source, the experiments investigated the catalytic performances for Pt/TiO_2-Cu_2O photocatalytic generation of hydrogen from aqueous methanol under visible light irradiation in anaerobic condition. The effect of Pt loading and catalyst composition on the reaction of photocatalytic generation of hydrogen from aqueous methanol solution was also investigated.

EXPERIMENTAL

Preparation of Pt/5 % TiO_2-Cu_2O catalyst: Weighed 0.2 g of 5 % TiO_2-Cu_2O into the surface of the dish[14], then add 0.3 mL of 0.014 g/mL K_2PtCl_4 solution, impregnation and natural drying. An excess of formaldehyde was reduced by heating for 1 h and then filtered. Washed with 400 mL of distilled water and finally with a small amount of anhydrous alcohol 2 to 3 times. The sample was then placed in a vacuum oven and dried for 2 h at 80 °C.

Using Shimadzu XRD-6000 type of X-ray diffraction (XRD, Cu target, K_α ray, $\lambda = 1.5418$ Å, voltage 40 kV, current 35 mA), JEOL JSM 2100 type of high resolution transmission electron microscopy (HRTEM, operating voltage 200 kV), T-1901 type of Diffuse reflectance UV-visible spectroscopy (with $BaSO_4$ as reference powder, scan range 230-800 nm), IRIS Intrepid full spectrum of direct-reading ICP spectrometer (Thermo Electron) type of inductively coupled plasma emission spectrometry (ICP-AEC) characterized the samples of catalyst.

Photocatalytic generation of hydrogen from aqueous methanol solution: Fig. 1 showed the schematic apparatus for photocatalytic generation of H_2 from aqueous methanol solution over Pt/TiO_2-Cu_2O. Firstly, measuring 60 mL of 12.5 % aqueous methanol solution in grinding mouth glass jar and adding 0.060 g photocatalyst. Then drumming N_2 for 40 min. to remove oxygen in the solution. Afterwards, stuffed with duct plugs and stirring to react sufficiently under irradiation of 250 W tungsten lamp. Hydrogen was derived from the catheter and the hydrogen collection process with displacement of water in laboratory. The gas was verified with fuel. Formaldehyde in the solution after the reaction was determined by acetylacetone spectrophotometry.

RESULTS AND DISCUSSION

Characterization of catalysts: Fig. 2 was the XRD patterns of 1 % Pt/5 % TiO_2-Cu_2O catalyst. Fig. 2 showed the diffraction peak of Cu_2O and no diffraction peak of Pt. ICP analysis showed that, the sample of 1 % Pt/5 % TiO_2-Cu_2O contained 0.92 wt. % of Pt. The results showed that Pt was highly dispersed in TiO_2-Cu_2O. Fig. 2 showed no diffraction peak of TiO_2 which indicated that TiO_2 was also highly dispersed in Cu_2O[14].

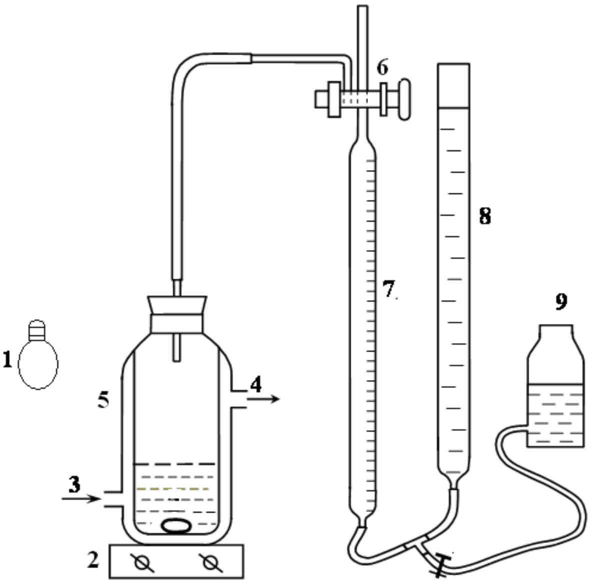

Fig. 1. Schematic apparatus for photocatalytic generation of H_2 from methanol over Pt/TiO_2-Cu_2O (1) tungsten lamp, (2) magnetic stirrer, (3) and (4) inlet and oudet of isothermal water, (5) reactor (6) 3-way valve, (7) graduated tube, (8) leveling tube and (9) water bottle

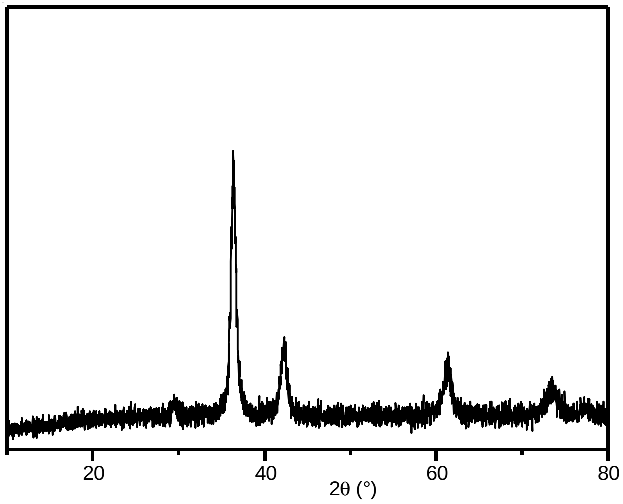

Fig. 2. XRD patterns of 1 % Pt/5 % TiO_2-Cu_2O

Fig. 3 showed HRTEM image of 1 % Pt-loaded on 5 % TiO_2-Cu_2O. Fig. 3 indicated that platinum deposited on the surface of TiO_2-Cu_2O in a clustered manner. The particle size of platinum cluster was unequal, between 5 and 20 nm.

Fig. 4 showed UV-visible diffuse reflectance spectra of 1 % Pt/5 % TiO_2-Cu_2O catalyst. It indicated that the catalyst of 1 % Pt/5 % TiO_2-Cu_2O was excited at 609 nm and that could play a photocatalytic role under visible light irradiation.

Coordinating role of each component in the catalyst in the reaction of hydrogen generation: The experiments compared the catalytic activity of 1 % Pt/5 % TiO_2-Cu_2O, 1 % Pt/Cu_2O and 5 % TiO_2-Cu_2O catalysts in photocatalytic generation of hydrogen from aqueous methanol. Fig. 5 showed the hydrogen yields for various photocatalyst systems. This showed that there was no gas generation in the absence of a catalyst. When adding the catalysts, the reaction system generate gas.

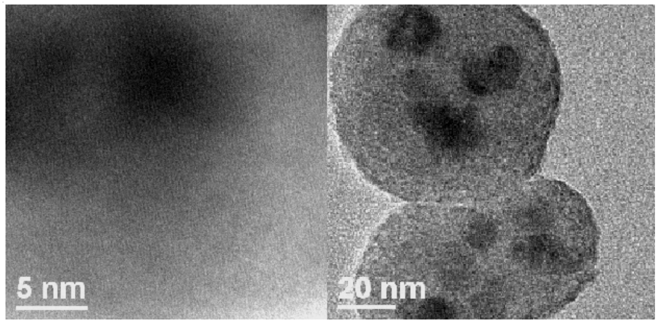

Fig. 3. HRTEM image of 1 % Pt-loaded on 5 % TiO_2-Cu_2O. The dark dots are platinium cluster

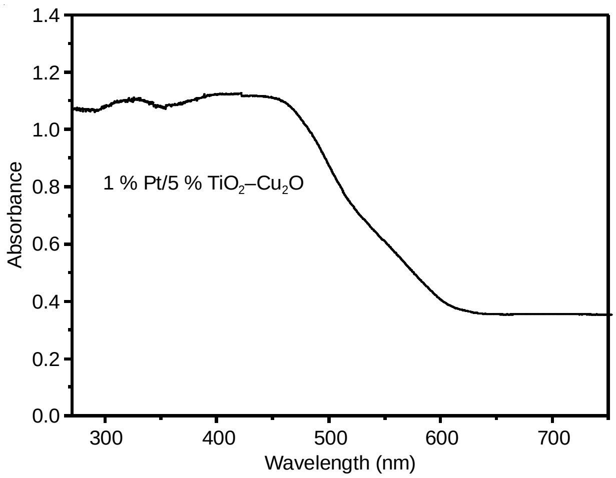

Fig. 4. UV-visible diffuse reflectance spectra of 1 % Pt/5 % TiO_2-Cu_2O

The gas was derived from the catheter, lit with a blue flame and accompanied by a slight crackling sound. That proved the production gas was hydrogen. Compared to the catalyst of 1 % Pt/Cu_2O, the hydrogen production rate of 1 % Pt/5 % TiO_2-Cu_2O catalyst was higher. After the composites of Cu_2O and TiO_2 under visible irradiation, Cu_2O was transferred to TiO_2 by photo-excited electrons. Thus inhibited the composites of photo-generated electron and the hole and improved the utilization of photo-generated electrons. The photocatalytic activity of 1 % Pt/5 % TiO_2-Cu_2O and 1 % Pt/Cu_2O catalysts were higher than the activity of 5 % TiO_2-Cu_2O catalyst. That indicated loading Pt was critical to photocatalytic production of hydrogen. On the one hand, the overpotential of hydrogen in the metal platinum was low and was easy to remove. On the other hand, platinum is an effective electron acceptor. That could gather and transmit eletrons and inhibit the composites of photogenerated electron and hole pairs, improve photocatalytic efficiency.

Effect of Pt loading on the catalytic activity: Fig. 6 showed the hydrogen yields for 5 % TiO_2-Cu_2O with different Pt loadings. It showed that the catalytic activity was the highest when the Pt loading was 1 wt. %. researches suggested that platinum had the optimal deposit amount[10,15]. When the Pt loading was excessive, the surface of photocatalyst was covered with too much metallic particles. That caused the effective area of the catalyst by light irradiation was reduced and the number of electron-hole pairs generated by photoexcitation was also reduced. Finally, photocatalytic activity of the catalyst decreased.

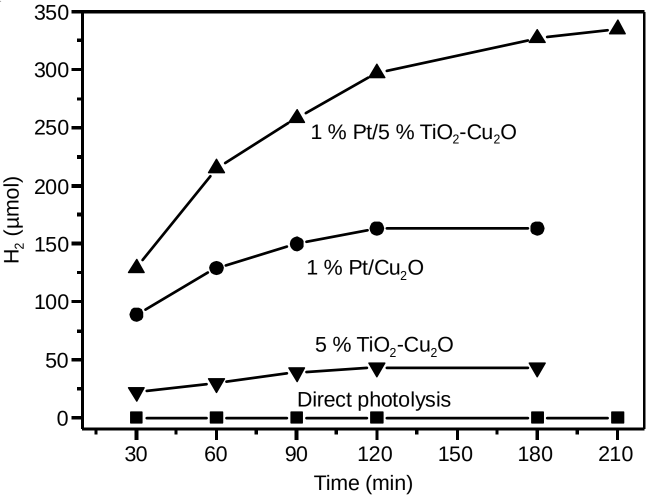

Fig. 5. Hydrogen yields for various photocatalyst systems. 60 mg of the catalyst suspended in 60 mL of 12.5 % aqueous methanol

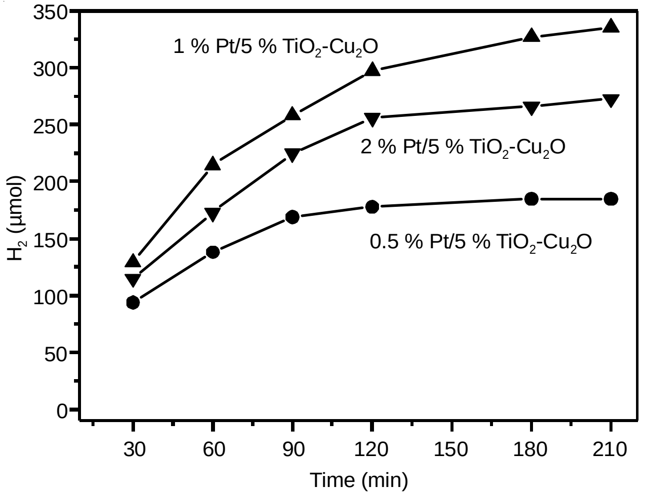

Fig. 6. Hydrogen yields for 5 % TiO_2-Cu_2O with different Pt loadings. 60 mg of the catalyst suspended in 60 mL of 12.5 % aqueous methanol

Effect of repeated times of the catalyst on hydrogen production rate: Fig. 7 showed the repeated times of reaction effect on the activity for the photocatalyzed dehydrogenation of methanol. In the experiments, 60 mg of the 1 % Pt/5 % TiO_2-Cu_2O catalyst was suspended in 60 mL of 12.5 % aqueous methanol. The reaction time was 3 h, then passing into N_2 for 40 min and then reacted 3 h again. In the process of reaction, adding some amount of methanol. This operation was repeated seven times. Fig. 7 also showed that the catalytic activity of photocatalytic generation of hydrogen from methanol remained relatively stable after the catalyst of 1 % Pt/5 % TiO_2-Cu_2O used 7 times under anaerobic conditions.

Mechanism of photocatalytic generation of hydrogen from aqueous methanol solution: Acetylacetone spectrophotometry was used to measure the aqueous solution of methanol after the reaction and found the formaldehyde generation. Therefore, we speculated photocatalytic production of hydrogen from aqueous methanol solution of Pt/5 % TiO_2-Cu_2O followed the reaction:

$$h\nu + Cu_2O \rightarrow e^-(CB\ Cu_2O) + h^+(VB\ Cu_2O) \rightarrow e^-(Pt) + h^+(VB\ Cu_2O) \quad (1)$$

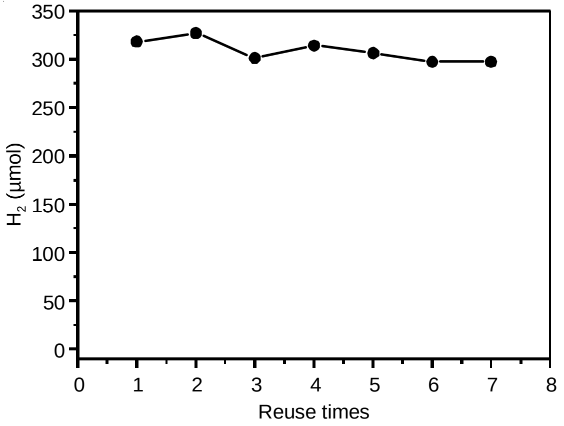

Fig. 7. Repeated times of reaction effect on the activity for the photo-catalyzed dehydrogenation of methanol. 60 mg of 1 % Pt/5 % TiO_2-Cu_2O suspended in 60 mL of 12.5 % aqueous methanol

$$\text{or} \quad \rightarrow e^-(\text{CB } TiO_2) + h^+(\text{VB } Cu_2O)$$

$$\rightarrow e^-(Pt) + h^+(\text{VB } Cu_2O) \qquad (2)$$

$$e^-(Pt) + H_2O \rightarrow H_2 + 2OH^- \qquad (3)$$

$$h^+(\text{VB } Cu_2O) + CH_3OH \rightarrow HCHO + H^+ \qquad (4)$$

Cu_2O was excited when visible light to Cu_2O. The electronic of valence band transition to the conduction band, formed photo-generated electron of e^- and hole of h^+. A part of photo-generated electron in Cu_2O transferred to the surface of Pt directly (eqn. 1). Another part of photo-generated electron transferred to the conduction band and then transferred to the surface of Pt (eqn. 2). The transfer of e^- to Pt reduced to H_2O and generated H_2 (eqn. 3). The h^+ in the valence band of Cu_2O oxidized methanol to formaldehyde (eqn. 4).

Taking 10 mg/L of formaldehyde solution 50 mL, adding 0.05 g of 1 % Pt/5 % TiO_2-Cu_2O catalyst. Then the nitrogen was passed into the solution for 40 min to remove the oxygen. The 250 W of tungsten lamp was used as the light source. The experiments measured the change with time in the degradation of formaldehyde. Fig. 8 showed the photocatalytic degradation of formaldehyde on 1 % Pt/5 % TiO_2-Cu_2O of catalyst under the anaerobic condition.

Fig. 8 showed that formaldehyde could not been degraded under the anaerobic condition. That indicated the formaldehyde in the solution was not further oxidized to CO_2 after 1 % Pt/5 % TiO_2-Cu_2O of catalyst photocatalytic generation of hydrogen from aqueous methanol solution. Researches suggested that[2-4], in the process of generation of hydrogen by catalyzing the low carbon alcohol, the photocatalyst taking TiO_2 as main body could further oxidized aldehydes to CO_2. This might be due to the oxidation ability of h^+ in the valence band of TiO_2 was more strong than the h^+ in the valence band of Cu_2O

Conclusion

The experiments immersed K_2PtCl_4 in the composite oxides of nanoTiO_2-Cu_2O and used the method of reducing formaldehyde. Platinum was loaded onto TiO_2-Cu_2O and prepared the photocatalyst of Pt/TiO_2-Cu_2O. HRTEM image showed that platinum deposited on the surface of TiO_2-Cu_2O in a clustered manner. The particle size of platinum cluster was unequal, between 5 and 20 nm. Tungsten lamp was used as light source. In the absence of oxygen, the experiments investigated the catalytic properties of different catalysts catalytic reforming of aqueous methanol solution and generation of hydrogen under visible light irradiation. The results showed that a synergistic effect was between Pt, TiO_2 and Cu_2O. The optimal Pt loading was 1 wt. %.

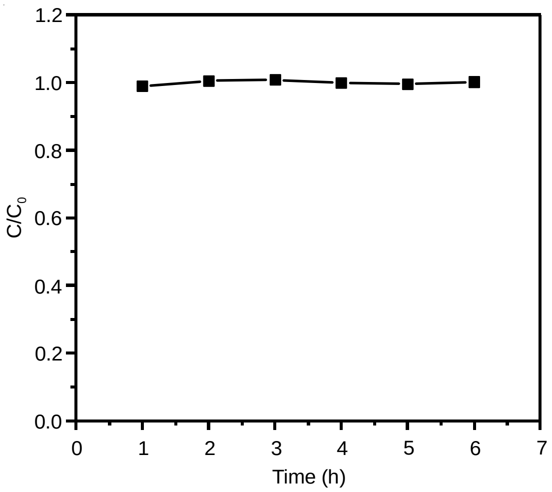

Fig. 8. Photocatalytic degradation of formaldehyde on 1 % Pt/5 % TiO_2-Cu_2O of catalyst under the anaerobic condition

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