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Effect of preparation method of colloidal platinum on performance of 12-tungstosilicate for photocatalytic hydrogen generation

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Abstract

Colloidal platinum nanoparticles, the co-catalyst for hydrogen evolution, were prepared using 12-tungstosilicate as photocatalyst by two methods in which photolysis and reduction reaction took place at the same time and at different time, respectively. For the former, H_2PtCl_6 was reduced directly to colloidal platinum under irradiation and 12-tungstosilicate would transfer into a new structure compound during the process. For the latter, 12-tungstosilicate was first photoreduced to heteropoly blue anion, and then the blue anion could reduce H_2PtCl_6 to colloidal platinum under no irradiation. The Pt particle size and reactivity of 12-tungstosilicate were characterized by UV–vis and cyclic voltammetry. Preparation methods affect markedly the Pt particle size and reactivity of 12-tungstosilicate so that the photocatalytic activity and stability for hydrogen evolution are different. The possible mechanism was discussed.

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Keywords: Photocatalysis; Colloidal platinum; 12-Tungstosilicate; Hydrogen

1. Introduction

From the viewpoint of solar energy conversion efficiently and obtaining regenerative hydrogen energy, photocatalytic production of hydrogen by water-splitting has been considered to be one of promising approaches. Many researches have been done to achieve the goal in this field [1–3].

In the present, photocatalysts used widely are inorganic semiconductors, including transition metal oxides (e.g. TiO_2) and sulfides (e.g. CdS). Polyoxometalates (POMs) [4] are other kind of photocatalysts. Semiconductor photocatalysts have been studied widely for photocatalytic H_2 generation, but polyoxometalates seldom [5,6]. The semiconductor photocatalysis is initiated by absorbing photons with concurrent generation of conduction band electrons and valence band holes at the same semiconductor particle. Thus, for semiconductor photocatalysis, addition of noble metals (e.g. Pt) is necessary to restrain photoinduced electron–hole recombination and lower overpotential for hydrogen evolution. The excitation of POMs induces a ligand (oxygen) to metal charge transfer (LMCT) with promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The charge transfer excited states of POM (POM^*) react with substrates to yield reduced POM (POM^-) and oxidized substrates as products. Because of the well-recognized electron holding ability [7] of excited POMs might make the POM-induced photoreductive processes quite different from those on semiconductor (e.g. TiO_2), where the electron accumulation is negligible under normal reaction conditions. Therefore, for POM photocatalysis, addition of noble metals is only used to lower overpotential for hydrogen evolution.

Akid and Darwent [5] reported using $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, $[FeW_{12}O_{40}]^{5-}$, $[CoW_{12}O_{40}]^{6-}$, $[H_2W_{12}O_{40}]^{6-}$ and colloidal platinum for photocatalytic production of hydrogen by water-splitting. Using polytungstates and colloidal platinum as photocatalysts, Rustamov et al. [6] studied the photocatalytic hydrogen evolution from water–organic solutions and discussed the mechanism of the photocatalytic reaction. Their results showed that colloidal platinum provided a surface for the lowering the activation energy of the reaction and acted

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as microelectrodes with a mixed potential determined by the photoreduced heteropoly anion/polyoxometalate and the H^+/H_2 couples.

Although the role of colloidal metals in photocatalytic hydrogen production in polyoxometalate systems was studied [5,6], the effect of the preparation method of colloidal metals on photocatalytic production of hydrogen by water-splitting has not been reported. Troupis et al. [8] prepared colloidal metal nanoparticles directly from aqueous solutions by using 12-tungstosilicate as both photocatalyst and stabilizer. The obtained colloidal was stable against aggregation for over 2 months. In this study, colloidal platinum nanoparticles were prepared by two methods. The photocatalytic activity and stability of two reaction systems were investigated comparatively and the possible mechanism was discussed.

2. Experimental

12-Tungstosilic acid ($H_4SiW_{12}O_{40}$), chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), anhydrous ethanol and nitric acid were of all analytical grade and were used without further purification.

The photocatalytic reaction was carried out in a Pyrex flask of about 170 ml with a flat window. The cell glass permits radiation to pass through when wavelength is over 300 nm. The 80 ml reaction mixture containing 7.4 mol l^{-1} ethanol and a given concentration of 12-tungstosilicate inside the cell was stirred up by a magnetic stirrer during the reaction. The pH value of the reactant mixture was adjusted to 2.4 by nitric acid. A 250 W high pressure Hg lamp was used as the light source. The platinum served as catalyst for H_2 evolution was prepared by methods ‘a’ and ‘b’. Nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen prior to irradiation. The top of the cell was sealed with a silicone rubber septum. The reaction was carried out at room temperature. The produced H_2 was analyzed on a gas chromatograph (TCD, N_2 as gas carrier, Zeolite 13× column).

Colloidal platinum was prepared by following methods, respectively. Method ‘a’: 80 ml aqueous solution containing a given concentration of 12-tungstosilicate and 7.4 mol l^{-1} ethanol (pH 2.4) was irradiated for 30 min so that a large amount of blue polyanion (heteropoly blue) was formed. Under stirring and no irradiation, a given volume of 1.93×10^{-3} mol l^{-1} H_2PtCl_6 was added quickly into the blue solution so that H_2PtCl_6 was reduced to Pt by the heteropoly blue immediately. Method ‘b’: a given volume of 1.93×10^{-3} mol l^{-1} H_2PtCl_6 was added into the reaction mixture solution (the same conditions as in the reaction section) before irradiation. After nitrogen was bubbled through the reaction mixture for 30 min, the photocatalytic reaction was carried out. The platinum was photoreduced in situ in the photoreaction for hydrogen evolution.

UV–vis absorption spectra of the sample solutions were determined on a Hitachi U-3310 Spectrophotometer. The electrochemical experiment was carried out on LK98BII Microcomputer-based Electrochemical Analyzer in three electrode system. The reference electrode, the counter electrode and the working electrode were a saturated calomel electrode (SCE), a platinum flake and a glassy carbon (GC) disc, respectively. The solution containing 1.0×10^{-3} mol l^{-1} 12-tungstosilicate, 7.4 mol l^{-1} ethanol and 0.97×10^{-5} mol l^{-1} H_2PtCl_6 was irradiated for 1 h. The supporting electrolyte was 1.0 mol l^{-1} NaAc–HAc. Before experimentation, the solution was bubbled with nitrogen for 15 min and this inert atmosphere was maintained in the electrochemical cell during the experiment.

In all the cases, the reproducibility of the measurements was at least ±10%.

3. Results and discussion

The photoreduction of H_2PtCl_6 to form Pt by methods ‘a’ and ‘b’ can be expressed as follows [5,8]:

$$[SiW_{12}O_{40}]^{4-} + h\nu \rightarrow [^{*}SiW_{12}O_{40}]^{4-} \tag{1}$$

$$2[^{*}SiW_{12}O_{40}]^{4-} + CH_3CH_2OH \rightarrow 2[SiW_{12}O_{40}]^{5-} + CH_3CHO + 2H^+ \tag{2}$$

$$4[SiW_{12}O_{40}]^{5-} + [PtCl_6]^{2-} \rightarrow Pt + 4[SiW_{12}O_{40}]^{4-} + 6Cl^- \tag{3}$$

The irradiation of 12-tungstosilicate with UV light induces formation of an excited state $[^{*}SiW_{12}O_{40}]^{4-}$ which can be reduced by ethanol. The produced heteropoly blue anion $[SiW_{12}O_{40}]^{5-}$ is very stable and can exist for long time in deaerated solution [7,8]. So for the method ‘a’, the photolysis reactions (1) and (2) and the reduction reaction of $[PtCl_6]^{2-}$ (3) took place at different time. However, for the method ‘b’, all the reactions occurred simultaneously in the reaction system.

Due to plasmon-resonance absorbance, there is absorbance for metal nanoparticles [9]. Luo et al. [10] studied the spectrum of the colloidal Pt and found that no absorption peaks for Pt particles could be observed in the range of 200–800 nm. However, they found that particle size could be determined by UV–vis absorption spectrum, which was consistent with result of TEM analysis. The absorbance increased linearly with increase of the number of the particles in the range of wavelength 300–500 nm, indicating that the size of Pt particles was homologous.

Fig. 1 shows the absorbance of colloidal Pt of various concentrations prepared by methods ‘a’ and ‘b’. From Fig. 1, one can be sure that the number of particle size increases linearly at lower Pt concentration; whereas the number does not increase and even decrease at the higher concentration, which can be attributed to that smaller Pt particles grow or aggregate into larger particles, and even precipitate from the solution. At higher Pt concentration for method ‘b’, black Pt precipitation could be observed after 1 h irradiation, which confirms above explanation.

From Fig. 1, one can also see that the number of Pt particles prepared by method ‘a’ is larger than that by method ‘b’, which can be explained as follows. The mechanism of colloidal metals synthesis has been studied in detail [11]. The common accepted mechanism suggests a two-step process, nucleation and the successive growth of the particles. In the first step, a part of the metal ions in solution was reduced by a suitable reducing agent. The atoms thus produced agglomerate to form small metal clus-

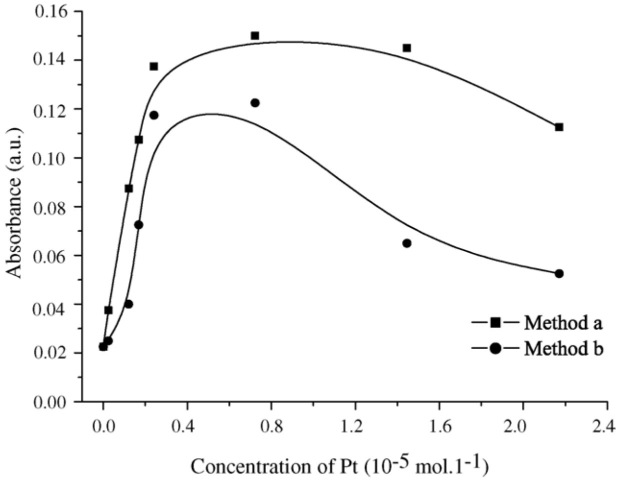

Fig. 1. Dependence of absorbance at 350 nm on the concentration of Pt. Reaction conditions: 80 ml reaction solution, 0.2×10^{-3} mol l^{-1} 12-tungstosilicate, 7.4 mol l^{-1} ethanol, pH 2.4, irradiation time 1 h.

ters and then formed crystallite in the second step. Moreover, in the process of preparation, the particle growth can be restrained effectively if the induction period for nucleation was reduced in the system of the reaction. For method ‘a’, the nucleation and crystal growth could be completed with in a few seconds due to a large amount of heteropoly blue anion as reducing agent, which restrained the particles growth effectively and the Pt particles were kept in small size [8]. But for the method ‘b’, Pt particles was formed in the process of the interaction between H_2PtCl_6 and a small amount of $[SiW_{12}O_{40}]^{5-}$ produced in situ so that the induction period for nucleation and growth period were prolonged. Therefore, the Pt particles of larger size were formed to decrease the number of the particles.

The produced colloidal Pt catalyst can scavenge heteropoly anion $[SiW_{12}O_{40}]^{5-}$ to evolve H_2 [6].

$$2[SiW_{12}O_{40}]^{5-} + 2H^+ \xrightarrow{Pt} 2[SiW_{12}O_{40}]^{4-} + H_2 \tag{4}$$

Thus, sufficient Pt particles can effectively promote H_2 evolution.

Fig. 2 shows the effect of the concentration of the colloidal Pt prepared by methods ‘a’ and ‘b’ on the rate of H_2 evolution. One can see that the concentration of colloidal Pt prepared by the two methods affect both the rates of photocatalytic H_2 evolution. In the absence of Pt, there was only trace amount of H_2. Low concentration of Pt can lead to dramatic increase in the rate of H_2 formation, which reaches a maximum value at 0.24×10^{-5} mol l^{-1} Pt and decreases at higher Pt concentration. From Fig. 2, one can also see that the rate of photocatalytic H_2 production for method ‘a’ is higher (by about 86%) than that for method ‘b’. In the range of 0.24–1.45×10^{-5} mol l^{-1} Pt, the rate of photocatalytic H_2 evolution does not change for method ‘a’, but that decreases gradually for method ‘b’. All changes of the rates shown in Fig. 2 are basically consistent with the changes of the number of colloidal Pt particles in Fig. 1, indicating that the number of the colloidal Pt particles does play a key role in H_2 evolution.

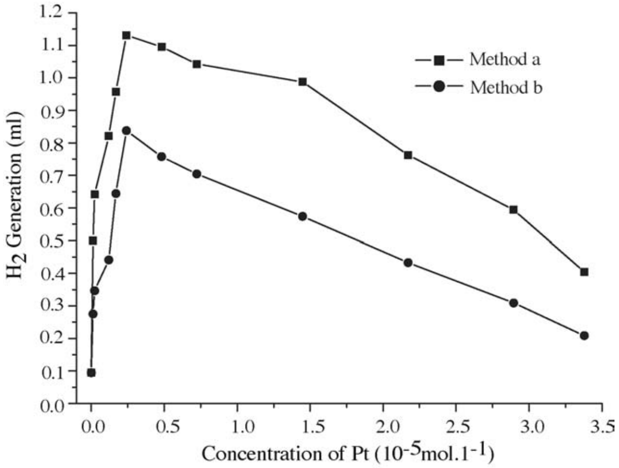

Fig. 2. Dependence of the rate of photocatalytic H_2 evolution on the initial colloidal Pt concentration. Reaction conditions as in Fig. 1.

Fig. 3 shows absorption spectra of two kinds of solutions after 1 h irradiation under N_2 atmosphere and pure 12-tungstosilicate. The reacted solutions were diluted with 7.4 mol l^{-1} ethanol by 2.5 times before the spectral analysis. One can see that the characteristic absorption peak of the 12-tungstosilicate solution with H_2PtCl_6 prepared by method ‘a’ at 263 nm is almost the same as that of pure 12-tungstosilicate solution of the same concentration, indicating the structure of 12-tungstosilicate remains unchanged. It is interesting that for the method ‘b’, the characteristic absorption peak of the reacted solution at 263 nm disappears. There are two absorption peaks at about 200 nm (very strong absorption peak and not showed in Fig. 3) and 260 nm for UV–vis spectra of polyoxometalates with 1:12 keggin structure, which can be assigned to $O_d \rightarrow W$, $O_{b,c} \rightarrow W$ transition, respectively. One cannot find characteristic absorption peak at about 263 nm for method ‘b’, which can be attributed to the structure of 12-tungstosilicate has transferred into a new structure. We are trying to determine the structure of the new heteropolyanion. The transformation could not be attributed to $[PtCl_6]^{2-}$ reacting

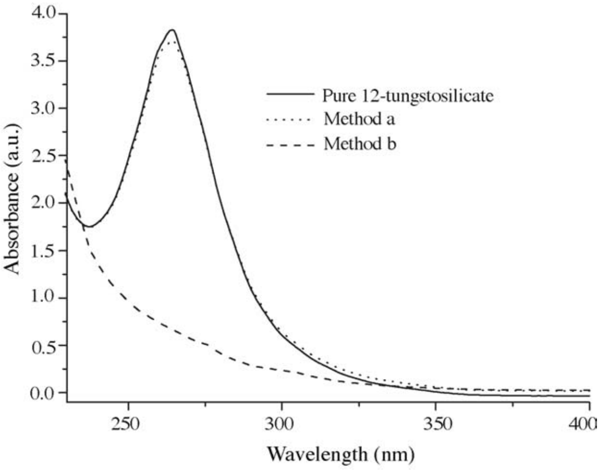

Fig. 3. Absorption spectra of the reacted solutions and pure 12-tungstosilicate, containing 0.24×10^{-5} mol l^{-1} colloidal Pt prepared by methods ‘a’ and ‘b’. Reaction conditions as in Fig. 1.

with $[SiW_{12}O_{40}]^{4-}$, because even when the ratio of concentration of $[PtCl_6]^{2-}$ to that of $[SiW_{12}O_{40}]^{4-}$ was 1/160, we could also observe complete transformation after 1 h irradiation. The transformation could not be observed under dark, under air atmosphere with irradiation and under irradiation without $[PtCl_6]^{2-}$, respectively. Therefore, one can speculate on that $[PtCl_6]^{2-}$ would catalyze the heteropoly blue (or 12-tungstosilicate) under irradiation to transfer into a new structure.

$$[SiW_{12}O_{40}]^{5-} \text{ (or } [SiW_{12}O_{40}]^{4-}\text{)} \xrightarrow{h\nu,\ [PtCl_6]^{2-}} \text{unknown polyoxometalate} \quad (5)$$

For method ‘b’, the reactions (3) and (4) should compete with reaction (5), because H_2 can be formed effectively. Because $[SiW_{12}O_{40}]^{5-}$ can reduce $[PtCl_6]^{2-}$ to produce Pt particles without forming the new POM under dark for method ‘a’, the excited state of $[PtCl_6]^{2-}$ ($[^*PtCl_6]^{2-}$) should play an important role in the transformation of 12-tungstosilicate in method ‘b’.

As shown in Fig. 2, the photocatalytic efficiency by the method ‘b’ is lower, which might be partly explained as follows. The new formed POM species would to some extent react with $[PtCl_6]^{2-}$ under irradiation or no irradiation not to produce Pt colloids necessarily (e.g. substituted by Pt) to decrease the number of the particles, which would also be a possible reason for poor photocatalytic efficiency by method ‘b’.

A typical cyclic voltammetry pattern of the reacted solution measured in 1.0 mol l^{-1} NaAc–HAc with two-step redox processes in the potential scan region, are shown in Fig. 4. Table 1 presents the data obtained from Fig. 4, where E_{pa}, E_{pc} and ΔE present the anodic peak potential, cathodic peak potential, and the difference of the E_{pa} and E_{pc}, respectively. The difference of the E_{pa} and E_{pc} for 12-tungstosilicate by method ‘a’ is 0.08–0.10 V and both E_{pa} and E_{pc} are independent of the potential scan rate in the range of 0.05–0.2 V/s, suggesting the quasi-reversible with two one-electron transfer processes. The two couples of redox waves are ascribed to the W(VI → V) process of the electron transfer [12]. The mechanism can be expressed as follows:

$$[SiW_{12}(VI)O_{40}]^{4-} + e^- \rightleftarrows [SiW_{11}(VI)W(V)O_{40}]^{5-} \quad (I\text{–}I') \qquad (6)$$

$$[SiW_{11}(VI)W(V)O_{40}]^{5-} + e^- \rightleftarrows [SiW_{10}(VI)W_2(V)O_{40}]^{6-} \quad (II\text{–}II') \qquad (7)$$

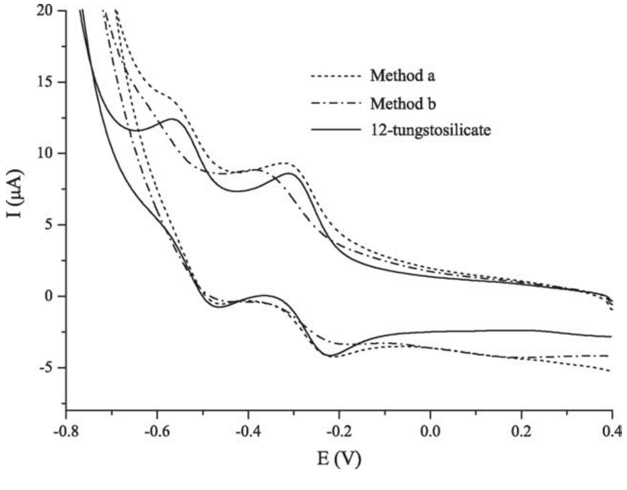

Fig. 4. Cyclic voltammometry of the reacted solutions and pure 12-tungstosilicate. Conditions: 1.0×10^{-3} mol l^{-1} 12-tungstosilicate; scan rate: 100 mV/s; supporting electrolyte: 1.0 mol l^{-1} NaAc–HAc; 0.97×10^{-5} mol l^{-1} H_2PtCl_6. Other reaction conditions as in Fig. 1.

Table 1
Cyclic voltammetry data for reacted solutions

System	Step	E_{pa} (V)	E_{pc} (V)	ΔE (V)
Pure 12-tungstosilicate	I–I′	−0.223	−0.310	0.087
	II–II′	−0.469	−0.560	0.091
12-Tungstosilicate with Pt by method ‘a’	I–I′	−0.223	−0.313	0.090
	II–II′	−0.468	−0.568	0.100
New tungstosilicate with Pt by method ‘b’		−0.219	−0.375	0.156
		−0.466	–	–

The wave shape and peak potential of the reacted solution by method ‘a’ are similar to that of pure 12-tungstosilicate, whereas that by method ‘b’ is different from pure 12-tungstosilicate, which also confirms that the keggin structure of 12-tungstosilicate is unchanged in the solution prepared by method ‘a’ and is destroyed by method ‘b’. For the new POM, there are two oxidation waves and one reduction wave. The difference of the E_{pa} and E_{pc} for one couple of the new POM is 0.156 V and its E_{pa} and E_{pc} are also independent of the potential scan rate in the range of 0.05–0.2 V/s, suggesting the quasi-reversible electron transfer process. There is not reduction wave for other redox couple, indicating the irreversible process.

The effect of concentration of the initial 12-tungstosilicate for the two methods on rate of H_2 formation is described in Fig. 5. As in the case of Fig. 2, the rate of H_2 evolution by method ‘a’ is also faster than that by method ‘b’. For both methods, low concentrations of initial 12-tungstosilicate can lead to dramatic increase in the rate of H_2 formation, and the rate reaches a plateau at ca. 1.0×10^{-3} mol l^{-1} initial 12-tungstosilicate. The rate of H_2 formation depends on incident light intensity and concentration of $[SiW_{12}O_{40}]^{4-}$ [5]. Therefore, when concentration of initial 12-tungstosilicate is over 1.0×10^{-3} mol l^{-1} for method ‘a’ or ‘b’, all available photons of incident light are absorbed completely by sufficient $[SiW_{12}O_{40}]^{4-}$ or the new POM species to produce a maximum number of Pt particles (via the reactions (1)–(3)), and so the rate reaches a plateau.

As shown in Fig. 5, at the lower initial concentration, the difference of H_2 formation rates between the two methods is smaller and smaller with decrease of initial $[SiW_{12}O_{40}]^{4-}$ concentration, which can be attributed to that concentration of produced $[SiW_{12}O_{40}]^{5-}$ by method ‘a’ is too low to reduce $[PtCl_6]^{2-}$ to Pt completely, and this effect should be much weaker for method ‘b’. Thus, difference of number of colloidal

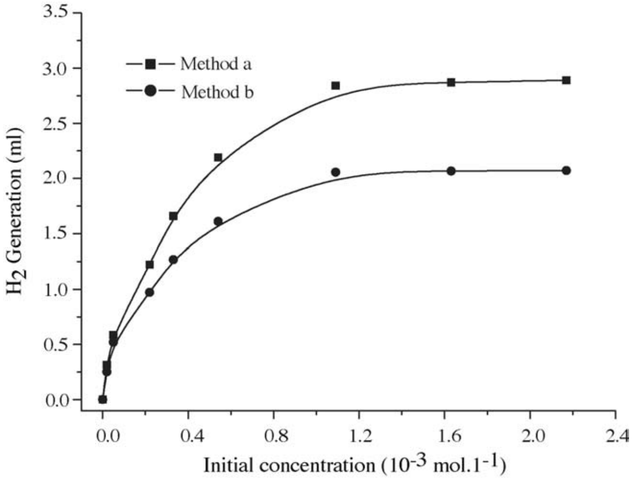

Fig. 5. Dependence of the rate of photocatalytic H_2 evolution on the initial 12-tungstosilicate concentration. Reaction conditions: 80 ml reaction solution; 0.24×10^{-5} mol l^{-1} H_2PtCl_6. Other conditions as in Fig. 1.

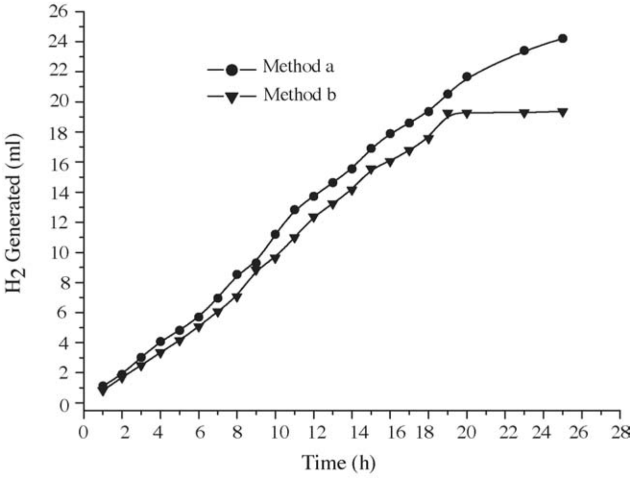

Fig. 6. Effect of preparation method of colloidal Pt on stability of photocatalytic H_2 generation. Reaction conditions: 0.24×10^{-5} mol l^{-1} colloidal Pt. Other conditions as in Fig. 1.

Pt between both methods decreases with the initial concentration decreasing.

For the method ‘b’, when the initial $[SiW_{12}O_{40}]^{4-}$ concentration was below 0.22×10^{-3} mol l^{-1}, all of 12-tungstosilicate were completely transformed into the new POM after 1 h irradiation; whereas over the concentration, only a part of 12-tungstosilicate were transformed. The higher the initial concentration is, the lower the transformation ratio is. After 1 h irradiation for method ‘b’, nitrogen was again bubbled through the reaction mixture for 30 min and the second irradiation (for 1 h) was carried out. In the first reaction, due to the transformation of 12-tungstosilicat into the new POM, H_2 formation was produced by the two POM species for all initial concentrations. But in the second reaction, H_2 formation was produced only by the new POM species at the lower initial concentration ($<0.22 \times 10^{-3}$ mol l^{-1}); whereas by both POM species over the concentration. The amount of H_2 formation at every responsive initial concentration (not shown in Fig. 5) in the second reaction is identical to that in the first reaction within experimental error, except a 14% decrease at 0.22×10^{-3} mol l^{-1} initial 12-tungstosilicate (just complete transformation at this concentration), suggesting the photoactivity of the new POM is very near to (a little smaller than) that of 12-tungstosilicate. This further confirms above explanation about H_2 evolution based on the number of Pt particles. The H_2 evolution by the new POM can be similarly expressed as follows:

$$\mathrm{POM} + h\nu \rightarrow \mathrm{POM}^* \qquad (8)$$

$$2\mathrm{POM}^* + \mathrm{CH_3CH_2OH} \rightarrow 2\mathrm{POM}^- + \mathrm{CH_3CHO} + 2\mathrm{H}^+ \qquad (9)$$

$$2\mathrm{POM}^- + 2\mathrm{H}^+ \xrightarrow{\mathrm{Pt}} 2\mathrm{POM} + \mathrm{H_2} \qquad (10)$$

Fig. 6 shows the effect of colloidal Pt prepared by methods ‘a’ and ‘b’ on stability of photocatalytic H_2 production. For colloidal Pt prepared by method ‘a’, the amount of photocatalytic H_2 production increases almost linearly during all irradiation time; whereas for colloidal Pt prepared by method ‘b’, it also increases almost linearly during first 19 h irradiation, but do not increase after this time, indicating that catalyst Pt particles would aggregate into larger particles after 19 h reaction. The result can be explained by that the colloidal Pt prepared by method ‘a’ is more stability than that by method ‘b’.

12-Tungstosilicate is a good stabilizer for Pt colloidal particles [8]. Based on the results from Figs. 6 and 1, one can speculate on that the new tungstosilicate as stabilizer should be worse than 12-tungstosilicate.

4. Conclusions

Both the states of colloidal platinum and performance of tungstosilicate affect photocatalytic efficiency and stability. The rate of the photocatalytic H_2 depends on the number of Pt particles. Using the colloidal Pt as catalyst prepared by method ‘a’, photocatalytic H_2 generation enhances by about 86% comparing with the Pt prepared by method ‘b’, which can be attributed to higher dispersivity and better stability. Moreover, the method ‘a’ reduces the period of the interaction time between H_2PtCl_6 and heteropolyanion so that the keggin structure of 12-tungstosilicate can be kept completely.

Acknowledgements

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