Thiolate Complexes Catalyst in Noble-Metal-Free System for Light-driven Hydrogen Production

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Abstract: In this paper, Fe thiolate complexes Fe(phen(pyS)$_2$ (M) were synthesized and the properties of complexes were characterized by ^{1}H-NMR and MS. The effects of reaction conditions on performanceof Fe thiolate complexes Fe(phen(pyS)$_2$had been studied. The results of catalytic performance implied thatwhen 2.0 mMfluorescein was used as photosensitizer, ethanol/water was used as solvent and its volume ratio ofethanol/water was1:1, catalyst M showed the highest catalytic performance and hydrogen production was 115.6 μmol/h after reacted for 15 h.

1 Introduction

Hydrogen, a environment-friendly energy source is widely used for which could reduce emissions of greenhouse gases[1-3], and photocatalytic H_2 evolution has been considered as a suitable way by visible light irradiation[4]. Usually, a typical photocatalytic system includes a photosensitizer, a catalystand a sacrificial electron donor. In this system, homogeneous photocatalysts are very attractive in visible-light-driven hydrogen generation and it is a suitable method.

In most cases, metals such as platinum, rhodium, ruthenium and palladium are excellent choices in the photocatalytic multi-component systems because of their higher catalytic activity, but the expensive price limits their application[5-11]. So we should look for less expensive catalytic centers to replace them, such as cobalt and iron.

In this paper, a new noble-metal-free complexFe(phen)(pyS)$_2$ (M) was synthesized. The properties of complexes were characterized by ^{1}H-NMR and MS and the effects of reaction conditions on catalytic performance had been studied.

2 Experimental

2.1 Reagents and Instruments

All reactions were carried out under N_2 atmosphere with standard Schlenk techniques. Solvents were dried with 4Å molecular sieves and distilled prior to be used according to the standard methods. Pyridine-2-thiol (pySH),1,10-bpyanthroline hydrate, Cobalt nitrate hexahydrate, Manganese acetate tetrahydrate, sodium metal, fluoresce in (Fl) and triethylamine (TEA) were purchased from Aldrich and used without further purification.

2.2 Synthesis of Fe (bpy)(pyS)

Fe(phen)(pyS)$_2$ (M) was synthesized as Fig. 1.The solution of 1,10-bpyanthroline hydrate (1.3 g, 6.4mmol) in 10mL of acetonitrile was added slowly to the solution containing $FeCl_3(H_2O)_6$ (1.7 g, 6.4 mmol) in 80 mL of acetonitrile over 30 min. The color of the above solution changed from light violet to dark violet. Then a solution containing pySH (1.42 g, 12.9 mmol) and TEA (2.2 mL, 16.0 mmol) in 30 mL of acetonitrile wasadded to above mixed solution slowly over 1 h. The solution turned brown, and a brown precipitate formed after stirring for another 8 h. The product (M) was collected by suction filtration. The products were stored underatmosphere without protection from water and oxygen.

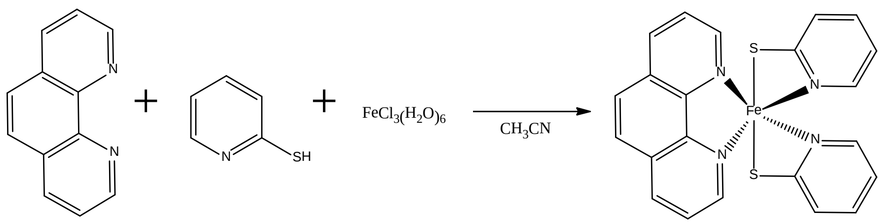

Fig. 1 The synthetic routes of M

The yield of M was 1.2 g (50%). ^{1}H-NMR (CDCl3, 20 °C): δ 8.73, 8.25, 7.6 ppm. ESI MS: m/z 456.02 (expected), 456.02 (found). Elem. Anal. Calculated: C, 57.90; H, 3.53; N, 12.28; Found: C, 57.91; H, 3.52; N, 12.24.

2.3 ^{1}H-NMR Spectra

^{1}H-NMR spectra were collected on Varian INOVA 400NMR spectrometer.

2.4 Mass Spectra

Mass spectra were performed by electro spray ionization (ESI) on HP 1100 MSD instrument.

2.5 Evaluation of Performance of Photo Catalyst for Hydrogen Production

The 0.04 mM photo catalysts was placed in the mixed solution, which contained ethanol/H_2O ($1{:}1_{v/v}$ 120 mL), 2.0 mM Fland TEA (5% v/v). The mixed solution was place in an inner irradiation quartz cell (250 mL) which should be protected from light before use. The pH values of solutions were adjusted to11.6 by adding HCl or NaOH measured with meter. The photo catalysis system were kept at 25 °C. The cell were irradiated with a 500 W Xe lamp and the produces were analyzed with gas chromatograph (GC-9800).

3 Results and Discussion

The results of previous studies displayed that the main influencing factors on performance of photo catalytic system for hydrogen production were solvent and photosensitize of this system. In this paper, the effects of pH value and solvent of the system on the performance of catalyst M were investigated and the optimum conditions for hydrogen production were determined.

3.1 The Effects of solvents on the Performance of Catalyst M for Hydrogen Production

Fluoresce in (2.0 mM), catalyst (0.04 mM) and triethylamine (5%) were added to the reactor. In the reaction, the intensity of light, temperature and stirring speed remained constant for 15 h. The effects of different solvents (ethanol/water, methanol/water, acetonitrile/water, ethanol, water) on catalytic performance of catalyst M were investigated and experimental results was shown in Fig. 2.

Fig. 2 indicated that the catalytic performance of catalyst M was obviously affected by the type of solvents in this system. When the solvent of this system was ethanol/water, the catalyst showed the best catalysis performance and the hydrogen production was 112.9 µmol after reacted for 15 h. When the solvent was acetonitrile/water or pure water, catalyst M showed poor catalytic performance. The results were mainly because that the interaction between solubility and electrostatic of solvent had a great influence on hydrogen production. In this system, the role of ethanol was to improve the solubility of catalyst and fluorescence but could not provide proton, the proton was provided by water. The above analysis determined that the suitable solvent for catalytic system was ethanol/water.

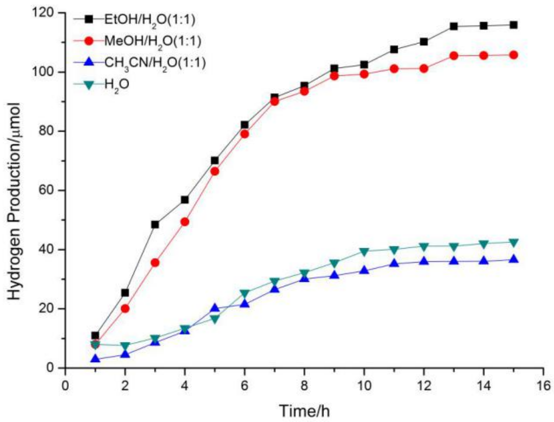

Fig. 2 The effects of solvents on the performance of catalyst M for hydrogen production

3.2 The Effects of Different Ratio (Ethanol/Water) on the Performance of Catalyst M for Hydrogen Production

The effects of different ratio (ethanol/water) on the performance of catalyst M for hydrogen production were presented in Fig. 3.

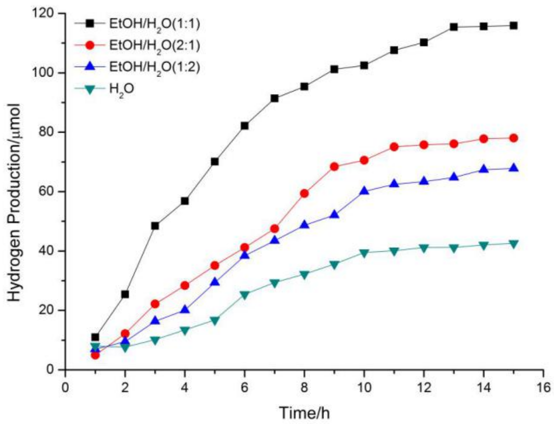

Fig. 3 The effects of different ratio (ethanol/water) on the performance of catalyst M for hydrogen production

Fig. 3 presented that when the volume ratio of ethanol/water was 1:1, catalyst M showed the best catalytic performance. When the volume ratio was 2:1 or 1:2, the catalytic performance of catalyst decreased significantly. Therefore, the optimal volume ratio of ethanol/water in thid reaction system was 1:1。

3.3 The Effects of Photosensitizer on the Performance of Catalyst M for Hydrogen Production

Catalyst M (0.04 mM) and different photosensitizer (2.0 mM) were added to the reactor,ethanol/water (V/V, 1:1) mixed solution was used as solvent of photo catalysis system. In the process of the reaction, pH value was 11.6, light intensity, stirring speed and temperaturemained constant for 15 h. The effects of different photosenxitizer ((fluoresce in, eosin B and rose red impurity oxygen anthraquinone)) on catalytic performance were investigated and the experimental results were showed in Fig. 4.

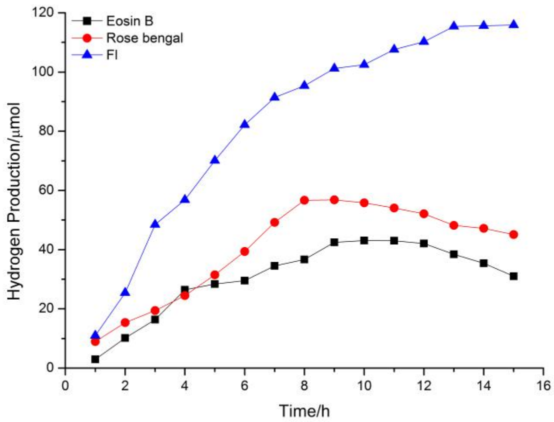

Fig. 4 Effects of photosensitizer on the performance of catalyst M for hydrogen production

Fig. 4 indicated that when photosensitizers of this reaction system was fluorescein, the performance of catalyst M reached the highest when the reaction time was 11 h. But when the photosensitizer was eosin B or rose red, hydrogen production decreased obviously. Therefore, in this photocatalytic system, fluorescein was the suitable photosensitizer.

3.4 The Effects of Photosensitizer Contents on the Performance of Catalyst M for Hydrogen Production

On the basis of above, the contents of photosensitizer fluorescein (0.25 mM, 0.50 mM, 1.0 mM, 2.0 mM and 2.50 mM) were investigated. The effects of photosensitizer contents on photocatalytic performance of catalyst M were studied and the experimental results were showed in Fig. 5.

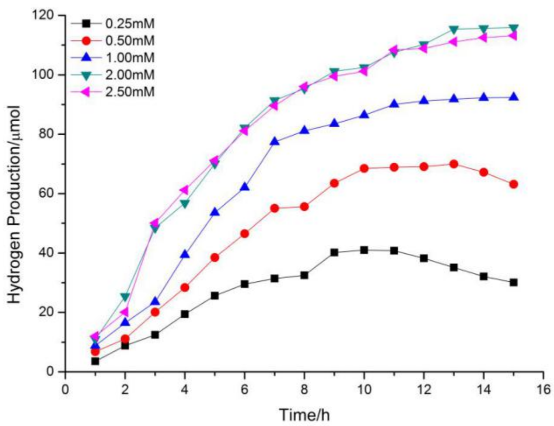

Fig. 5 Effects of photosensitizer contents on the performance of catalyst M for hydrogen production

Fig. 5 showed that with the increasing of fluorescein contents in this reaction system, hydrogen production increased accordingly first and then decreased. When the content of fluorescein was 2.0 mM, the hydrogen production reached the highest and after reacted for 15 h, hydrogen production of catalyst M reached 115.9 μmol. The above results determined that the optimal content of photosensitizer fluorescein was 2.0 mM.

4 Conclusions

Thiolate complexes Fe(phen)$(pyS)_2$ (M)has been synthesized and the effects of reaction conditions on performances of complexes M were studied. The results indicated Febalt thiolate complexes M are active for light-driven hydrogen production and thehydrogen production of M was 115.6μmol/h after reacted for 15 hourswhen fluorescein was used as photosensitizer and its optimal content was 2.0 mM, ethanol/water was used as solvent and its volume ratio ofethanol/water was1:1.

Acknowledgments

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