

# Effects of Reaction Conditions on Hydrogen Production of Fe Complexes Catalyst in Photocatalysis System

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**Abstract:** Fe thiolate complexes Fe(bpy)(pyS)<sub>2</sub> (M) were synthesized, the properties of complexes were characterized by <sup>1</sup>H-NMR and MS and the effects of reaction conditions on catalytic performance had been studied. The results of catalytic performance implied that when 5% triethylamine was used as electron donor, 2.0 mM fluorescein was used as photosensitizer and the catalyst content was 2.5 μM, the hydrogen production of M reached 89.6 μmol/h after reacted for 15 hours.

## 1 Introduction

With the continuous emission of carbon dioxide, greenhouse effect are intensifying [1-3]. In the past few years, noble metal complexes were used as catalysts in the hydrogen production, such as Pt, Pd and Rh [4-9]. It is economical that unsustainable noble metals could be replaced with some inexpensive metals. Recently, a kind of noble-metal-free catalyst [Co(dmgh)<sub>2</sub>] had been reported for hydrogen production, the H<sub>2</sub> evolution of 150 TON was observed [10].

In this paper, a new noble-metal-free complex Fe(bpy)(pyS)<sub>2</sub> (M) was synthesized. The properties of complexes were characterized by <sup>1</sup>H-NMR and MS, 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<sub>2</sub> atmosphere with standard Schlenk techniques. Solvents were dried with 4 Å molecular sieves and distilled prior to be used according to the standard methods. Pyridine-2-thiol (pySH), 2,2'-bipyridine, 1,10-bipyanthroline hydrate, Cobalt nitrate hexahydrate, Manganese acetate tetrahydrate, sodium metal, fluorescein (FI) and triethylamine (TEA) were purchased from Aldrich and used without further purification.

### 2.2 Synthesis of Fe(bpy)(pyS)

Fe(bpy)(pyS)<sub>2</sub> (M) was synthesized as Fig. 1. The solution of 2,2'-bipyridine (1.0 g, 6.4 mmol) in 10 mL of acetonitrile was added slowly to the solution containing FeCl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub> (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 was added 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 (M1) was collected by suction filtration. The products were stored under atmosphere without protection from water and oxygen.

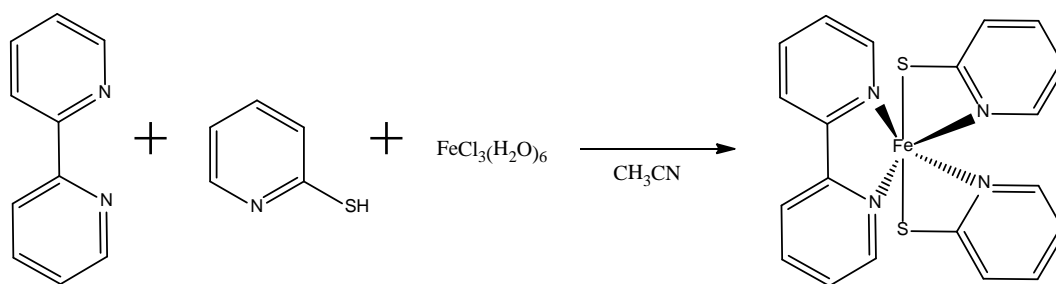


Fig. 1 The synthetic routes of M

The yield of M1 was 1.7 g (74%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 20 °C):  $\delta$  8.7, 8.18, 7.48 ppm. ESI MS:  $m/z$  432.02 (expected), 432.02 (found). Elem. Anal. Calculated: C, 55.56; H, 3.73; N, 12.96; Found: C, 55.54; H, 3.76; N, 12.95.

### 2.3 $^1\text{H-NMR}$ Spectra

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

### 2.4 Mass Spectra

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

### 2.5 Evaluation of Performance of Photocatalyst for Hydrogen Production

The 0.04 mM photocatalysts was placed in the mixed solution containing ethanol/ $\text{H}_2\text{O}$  (1:1<sub>v/v</sub>, 120 mL), 2.0 mM Fland TEA (5% v/v). The above mixed solution was placed in an inner irradiation quartz cell (250 mL) and protected from light before use. The pH values of the solutions were measured with pH meter and adjusted to 11.6 by adding HCl or NaOH. The photocatalysis system were kept at 25 °C. The cell were irradiated with a 500 W Xe lamp and the produces were analyzed with an on-line TCD gas chromatograph (GC-9800). During the irradiation process, 0.5 mL methane was used as the internal standard gas, and the amount of hydrogen was calculated according to the amount of methane.

## 3 Results and Discussion

The results of previous studies indicated that the main influencing factors on performance of photocatalytic system for hydrogen production were electron donor, photosensitizer and catalyst content. In this paper, the effects of electron donor, photosensitizer and catalyst content on performance of catalyst M were investigated and the optimum conditions for hydrogen production were determined.

### 3.1 The Effects of Electron Donor on the Performance of Catalyst M for Hydrogen Production

Catalyst M (0.04 mM) and fluorescein (2.0 mM) were added to the reactor, ethanol/water (V/V, 1:1) mixed solution was used as solvent of photocatalysis system. In the process of the reaction, pH value was 11.6, light intensity, stirring speed and temperature remained constant for 15 h. The effects of two electron donor triethylamine and triethanolamine (two electron donor content was 5%) on catalytic performance were investigated and the experimental results were showed in Fig. 2.

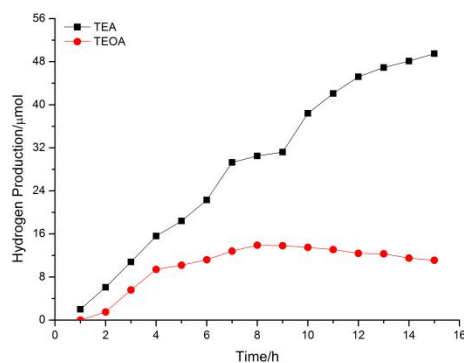


Fig. 2 Effects of electron donor on the performance of catalyst M for hydrogen production

The results of Fig. 2 indicated that when electron donor was triethylamine, catalyst M presented the best catalytic performance and the hydrogen production reached 49.5  $\mu\text{mol}$  after reacted for 15 h. When triethanolamine was used as electron donor, the catalytic performance of M was significantly decreased and hydrogen production of M decreased after reacted for 12 h, which indicated the deactivation of catalyst. Therefore, in this reaction system, triethylamine was the suitable electron donor.

### 3.2 The Effects of Electron Donor Contents on the Performance of Catalyst M for Hydrogen Production

In addition, the effects of electron donor contents (1.25%, 2.50%, 3.75%, 5%) on the catalytic performance of this reaction system were investigated respectively and the experimental results were showed in Fig. 3.

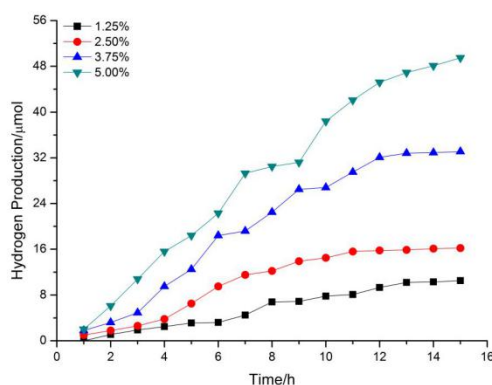


Fig. 3 Effects of electron donor contents on the performance of catalyst M for hydrogen production

Fig. 3 displayed that with the increasing of triethylamine contents from 1.25% to 5%, the amounts of hydrogen production were increased gradually. When the triethylamine content was 5%, catalyst M showed the best catalytic performance. When the triethylamine content decreased to 1.25%, the amount of hydrogen production was reduced to 8.9  $\mu\text{mol}$  after reacted for 15 h. Therefore, the suitable triethylamine content was 5%.

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

The effects of photosensitizer (fluoresce in, eosin B and rose red impurity oxygen anthraquinone) on performance of catalyst M were investigated and the experimental results were showed in Fig. 4.

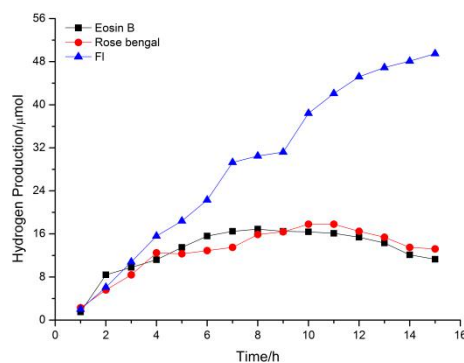


Fig. 4 Effects of photosensitizer on the performance of catalyst M for hydrogen production

Fig. 4 presented that when fluoresce in was used as photosensitizers, hydrogen production reached the highest. But when the photosensitizer was eosin B or rose red, hydrogen production decreased obviously and when the reaction time was 11 h, the hydrogen production of catalyst decreased which indicated the deactivation of catalyst. Therefore, in this photocatalytic system, fluoresce in 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 fluoresce in (0.25 mM, 0.50 mM, 1.0 mM, 2.0 mM and 2.50 mM) were investigated and optimized. The effects of photosensitizer contents on photocatalytic performance of catalyst were studied and the experimental results were showed in Fig. 5.

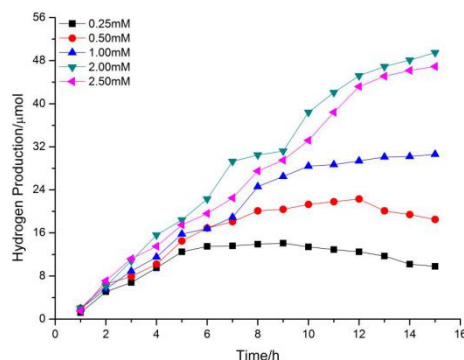


Fig. 5 Effects of photosensitizer contents on the performance of catalyst M for hydrogen production

Fig. 5 showed that with the gradual increasing of fluoresce in contents in this system, the amount of hydrogen production increased accordingly first and then decreased. When the content of fluoresce in was 2.0 mM, the hydrogen production reached the highest. After reacted for 15 h, hydrogen production of catalyst M was 49.5  $\mu\text{mol}$ . The above results determined that the optimal content of photosensitizer fluoresce in was 2.0 mM.

### 3.5 The Effects of Catalyst Contents on the Performance of Catalyst M for Hydrogen Production

The effects of catalyst contents (2.5  $\mu\text{M}$ , 5.0  $\mu\text{M}$ , 10.0  $\mu\text{M}$ , 20.0  $\mu\text{M}$  and 40.0  $\mu\text{M}$ ) on the photocatalytic hydrogen production were studied and the experimental results were showed in

Fig.6.

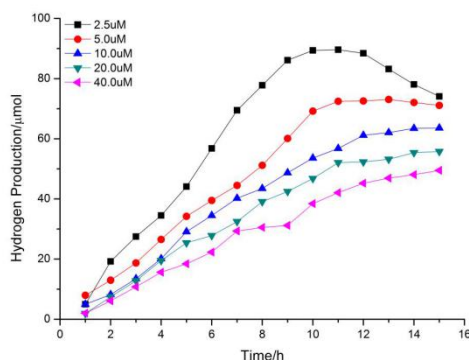


Fig. 6 Effects of catalyst contents on the performance of catalyst M for hydrogen production

The results of Fig. 6 indicated that with the reduction of catalyst contents, hydrogen production increased gradually. When the content of catalyst M was 40.0  $\mu\text{M}$ , hydrogen production reached 49.5  $\mu\text{mol}$  after reacted for 15 h. When the content of catalyst M was decreased to 2.5  $\mu\text{M}$ , hydrogen production reached 89.6  $\mu\text{mol}$ . Therefore, the optimal content of catalyst was 2.5  $\mu\text{M}$ .

## Conclusions

Thiolate complexes  $\text{Fe}(\text{bpy})(\text{pyS})_2$  (M) had been synthesized and the performances of complexes M were studied. The results indicated Fe-balt thiolate complexes M was active for light-driven hydrogen production in aqueous/organic mixtures and the hydrogen production of M was 89.6  $\mu\text{mol/h}$  after reacted for 15 hours when 5% triethylamine was used as electron donor, 2.0 mM fluorescein as photosensitizer and the catalyst content was 2.5  $\mu\text{M}$ .

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