Synthesis of a Novel ZnMoS₄ Photocatalyst and Its Performance for Photocatalytic Production of Hydrogen

Huirong LIANG, Guanjie LIU, Yaojun ZHANG, Liejin GUO*  
State Key Laboratory of Multiphase Flow in Power Engineering,  
School of Energy and Power Engineering, Xi’an Jiaotong University, 710049, Xi’an, China.  
* To whom correspondence should be addressed. Phone: +86-29-82663895. Fax: +86-29-82669033.  
Email address: lj-guo@mail.xjtu.edu.cn

ABSTRACT:
The production of hydrogen by photocatalytic decomposition of water using zinc tetrathiomolybdate catalyst was studied. Zinc tetrathiomolybdate catalyst was prepared by coprecipitation and hydrothermal method based on ZnSO₄ and self-prepared [NH₄]₂MoS₄ crystal. It was characterized by XRD, XRF, BET and UV-Vis spectra. The photocatalytic activities of the catalysts were ascertained by the production of hydrogen in an aqueous Na₂S-Na₂SO₃ solution under the ultraviolet and visible light irradiation. It was observed that the photocatalysts showed the visible-light photocatalytic activity, and the ZnMoS₄ photocatalyst prepared under hydrothermal condition for about 24h had the highest activity.

KEYWORDS: photocatalytic; hydrogen; water splitting.

1. Introduction

Hydrogen energy is a better choice in the name of its many virtues. Photocatalytic hydrogen production from water using solar energy is a challenging and interesting topic of research. Photocatalytic water splitting is a kind of technique for the conversion of photon energy into chemical energy. Hydrogen directly produced in this process has received much attention as a potential application for clean energy.

Since the report of Fujishima and Honda on water splitting using TiO₂ photocathode [1], numerous attempts have been made on the development of new semiconductor photocatalysts for efficient water splitting [2-10]. To this day, many semiconductors such as TiO₂, SrTiO₃, CdS, NaTaO₃ [10], K₂La₂Ti₃O₁₀ [11], and LnTaO₄ [12] have been studied for water splitting, but these catalysts are only active under UV light and their efficient utilization of solar energy is limited. Therefore, the development of visible-light-driven photocatalysts for water splitting is an important research target. Some metal oxides [13-15] and (oxy)sulfides [16-19] are studied as active photocatalysts for H₂ and O₂ evolution from aqueous solutions containing suitable electron acceptors and donors under visible light irradiation.

In the present study, we have prepared zinc tetrathiomolybdate photocatalysts, and their photocatalytic activities were evaluated by the decomposition of water accompanied with sacrificial electron donor under the ultraviolet and visible light irradiation.

2. Experimental

2.1 Preparation of the photocatalysts

Zinc tetrathiomolybdate photocatalyst was synthesized by coprecipitation and hydrothermal methods based on ZnSO₄ and self-prepared [NH₄]₂MoS₄ crystal. The hydrothermal temperature was 413K, while the hydrothermal time was 0-72h. Five samples were prepared in this paper.

2.2 Characterization

The crystal phases of the prepared samples were determined by X-ray diffraction (XRD) with Cu Kα rays (Rigaku, DM-X 2400, wavelength 1.5408 Å). UV-Vis diffuse reflection spectra were obtained by a spectroscopy (HITACHI UV4100). Elemental Analysis was conducted on Bruker S4 PIONEER X-ray fluorescence spectrometer (XRF), using Ru
target and 4KW maximum power. BET surface area of zinc tetrathiomolybdate nanoparticles was obtained by using a surface area analyzer (Beckman Coulter SA3100 plus instrument). The powder was first outgassed to remove the humidity and volatile adsorbents on its surface under vacuum at 373 K for 2 h before starting the analysis to determine the surface area.

2.3 Photocatalytic hydrogen production

Photocatalytic reduction of water under the ultraviolet light irradiation was performed in an inner-irradiation reaction cell. 0.1 g of powder photocatalyst suspended in 300 mL aqueous solution of 20%(v/v) ethanol with a magnet stirring. The optical system used for the reaction consisted of a 300 W high-pressure mercury lamp, which focused the light into the reaction cell and a water jacket to keep the reactor temperature constant at 25 °C by cooling water. The visible-light reaction was carried out in a Pyrex reaction vessel with a Xe lamp equipped with a cut-off filter (\(\lambda \geq 420\) nm). The gas evolution was determined in situ by gas chromatography with a TCD detector (NaX zeolite column, nitrogen as carrier gas).

3. Results and Discussion

3.1 Characterization of the catalysts

Figure 1 shows X-ray powder diffraction patterns of the prepared ZnMoS₄ photocatalysts. The diffraction peaks of the sample for 48h have the highest intensity. That is, the catalyst for 48h has the best crystal form. The intensity of the photocatalyst for 24h is a little lower than 48h. The sample for 0h isn’t treated by hydrothermal method. It has no diffraction peak, and it is amorphous solid.

Table 1 shows the specific surface area of the prepared ZnMoS₄ photocatalysts. It is observed that the catalyst for 48h has the biggest specific surface area. The specific surface area of the photocatalyst for 24h is approach to that of 48h. The sample without hydrothermal treat has the smallest specific surface area.

XRF elemental analysis results indicate that the prepared sample is our object product, ZnMoS₄.

UV-Vis diffuse reflectance spectra of the prepared ZnMoS₄ photocatalysts are shown in Figure 4. All of the ZnMoS₄ photocatalysts exhibit strong absorption in the UV and visible region. The amorphous ZnMoS₄ sample shows the weakest adsorption among the
five samples.

3.2 Photocatalytic activities of the catalysts

Table 2 is the rate of hydrogen production of the five samples under visible light. The catalyst for 24h has the best visible-light photocatalytic activities. The variation of the H₂ production efficiency under visible-light irradiation is the same as that of UV light.

4. Conclusion

The novel ZnMoS₄ photocatalysts are prepared by coprecipitation and hydrothermal treat methods based on ZnSO₄ and self-prepared [NH₄]₂MoS₄ crystal. They exhibit excellent adsorption of visible light. It is found that the synthesized catalysts show the better photocatalytic activities of hydrogen production by water splitting in the presence of sacrificial reagent as electron donor under visible light irradiation. The catalyst prepared for 24h shows the highest efficiency of H₂ production.

Acknowledgements

The authors thank the Ministry of Science and Technology of China providing for the financial support of the National Natural Science Foundation of China (No. 50521604 and 90210027).

References


