Photocatalytic decomposition of H_2S to Produce H_2 over ZnO/ZnS Composite Photocatalyst

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Introduction

H_2S is a type of by-product obtained from oil refinery, natural gas processing and other chemicals production. Till now, the well-established Claus process has been applied to deal with H_2S. It involves partial oxidation of H_2S to sulfur and water where hydrogen is wasted. If hydrogen can be recycled from H_2S instead of being directly oxidized into water, an immense amount of H_2 would be regenerated. The photocatalytic decomposition H_2S to H_2 over semiconductor photocatalysts is considered as a process to convert solar energy into fuels and the process requires less energy than the photodecomposition of water[1].

The schemes of a solar photocatalytic particle-based process for H_2 and sulfur recovery from H_2S have been suggested[2]. However, there is a demand for a highly efficient photocatalyst for the photoproduction of H_2. Single component semiconductors, such as CdS and TiO_2, usually could not obtain high photoefficiency and high activity for H_2 production. But the composite photocatalysts could give rise to an interparticle electron transfer (IPET) which could enhance the rate of H_2 production when mixed semiconductors contact intimately [3]. This intimate contact can also be called as microheterojunction formed between two semiconductors. In this paper, composite ZnO/ZnS photocatalyst was prepared and applied to the photocatalytic decomposition of H_2S to produce H_2. The activity for H_2 evolution was better than that of the pure ZnS or ZnO. The configuration model was suggested to explain the improvement of activity.

Materials and Methods

0.04 mol of $Zn(NO_3)_2$ was dissolved in 300 mL of distilled water. The H_2S gas (8 mL/min) was bubbled through the $Zn(NO_3)_2$ solution for 2 hours and the ZnS sol system was formed. The 5% ammonia was added into the system for adjusting the pH value to 7 and the white precipitate appeared. The precipitate was separated from the solution by centrifugation, dried at 95 ℃, ground to fine particles in mortar, calcined at 350 ℃ for 5 hours, and the yellowish ZnO/ZnS semiconductor photocatalyst was obtained.

The X-ray diffraction (XRD) analysis was carried out on a Rigaku D/MAX-3B X-ray diffractometer, equipped with Cu Kα radiation. The diffuse reflectance of UV-Vis spectra were obtained on Shimadzu UV-2450 spectrophotometer and converted from reflection to absorption by Kubelka-Munk method. The morphology of photocatalyst was investigated by a field emission scanning electron microscopy (SEM, JSM-6480) at 20 kV .

Photocatalytic decomposition of H_2S to produce H_2 was conducted in an outer-irradiation reactor with 500 W xenon lamp as the irradiation source. The photocatalyst powder (50 mg) was suspended in 100 mL mixed solution of Na_2SO_3 and Na_2S or NaOH aqueous solution saturated by H_2S. The amount of H_2 gas evolved was determined using gas chromatography (GC-9790, Fuli, China; GDX column, TCD, N_2 carrier).

Results and Discussion

As shown from the photocatalytic decomposition of H_2S in Fig. 4, the H_2 evolution rate over ZnO/ZnS is 3.67 mmol/g·h, higher than that over pure ZnO (0.69 mmol/g·h) or ZnS (1.54 mmol/g·h) in the aqueous solution of 0.35 mol/L Na_2S and 0.25 mol/L Na_2SO_3. Fig.5 shows the average H_2 evolution rate during 7 hours from H_2S photodecomposition over ZnO/ZnS in the 0.25 mol/L Na_2SO_3 and NaOH (with different concentration) alkaline solution saturated by H_2S. It is obvious that the H_2 evolution rate in alkaline solution is higher than that in the aqueous solution. As the NaOH concentration is 2.0 mol/L, the highest average H_2 evolution rate is 4.42 mmol/g·h. Its probable reason is that at this concentration, the ZnO/ZnS photocatalyst is more stable and the concentration of hydrogen ions is more suitable for H_2 generation. Compared with Na_2S and Na_2SO_3 mixture solution, when NaOH concentration is between 1.0 mol/L and 3.0 mol/L, the H_2 evolution rate is a little higher. It can be considered as a successive H_2 production process through successive H_2S absorption by the alkaline solution in the hydrodesulfurization plant.

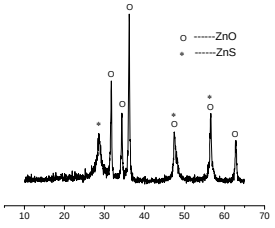

Fig.1 XRD pattern of ZnO/ZnS

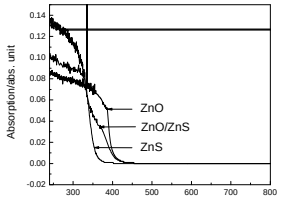

Fig.2 UV-Vis spectra of ZnO/ZnS

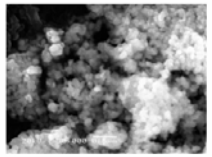
Fig.3 SEM micrographs of ZnO/ZnS

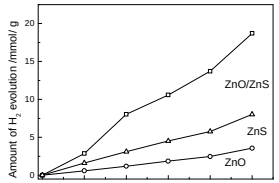

Fig.4 Catalytic activity of ZnO/ZnS

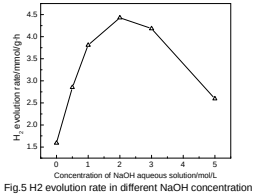

Fig.5 H2 evolution rate in different NaOH concentration

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