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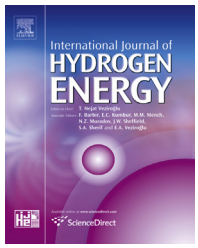

Hydrogen production via decomposition of hydrogen sulfide by synergy of non-thermal plasma and semiconductor catalysis

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ABSTRACT

Direct H_2S decomposition induced by plasma with an aid of alumina-supported metal sulfide semiconductors (ZnS/Al_2O_3 and CdS/Al_2O_3) for the production of hydrogen was investigated in a dielectric barrier discharge (DBD) reactor. Effects of specific input energy (SIE), feed flow rate, metal sulfide loading, and added hydrogen on the performance of H_2S decomposition were studied. With the aids of ZnS/Al_2O_3 and CdS/Al_2O_3, full conversion was obtained at reasonably low energy costs. The 100-h test runs indicated that both ZnS/Al_2O_3 and CdS/Al_2O_3 were stable in the course of H_2S decomposition. A supported metal sulfide solid solution ($Zn_{0.4}Cd_{0.6}S/Al_2O_3$) exhibited higher performance than ZnS/Al_2O_3 and CdS/Al_2O_3, achieving full conversion at a reduced energy cost. The mechanism of the plasma-induced H_2S decomposition with an aid of a semiconductor catalyst was tentatively proposed.

1. Introduction

Hydrogen sulfide (H_2S) is a highly toxic contaminant, which is in a variety of natural and man-made sources including gas industries and oil refineries [1]. H_2S is corrosive, and a major source of acid rain when oxidized in the atmosphere [2]. As a consequence, H_2S must be detoxified, in general, by the Claus process, in which H_2S is partially oxidized to produce elemental sulfur and water. On the other hand, H_2S has been regarded as a potential hydrogen source, because the dissociation energy required to split H_2S is lower than that of H_2O, CH_4, and NH_3 [3]. Such an approach for producing hydrogen is especially important in oil industry, where a huge amount of hydrogen is consumed in hydrotreating units to produce clean engine fuels whereas H_2S is produced as the major byproduct.

Several approaches have been investigated to split H_2S into its constituent elements, including catalytic decomposition [4], thermal diffusion [5], and thermochemical method [6], electrochemical method [7], photochemical method [8], and plasma method [9]. A comparative analysis of the economics showed that thermal decomposition and plasma methods are more promising than other ones because they involve lower

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energy consumption [6,10–12]. H_2S decomposition is endothermic, favored at high temperatures. Moreover, limited by thermodynamic equilibrium, the conversion in H_2S decomposition is, substantially low even at >1000 °C [6]. In the thermal catalytic decomposition approach, conventional catalysts are not effective for H_2S thermal decomposition probably due to elevated operating temperatures and high reactivity of H_2S with metal species. On the other hand, non-thermal plasmas have an advantage over the thermal processes in enhanced conversion due to its non-equilibrium feature [13–17]. In plasma, there exist both strong electric field and spatially distributed photons. Our recent investigation indicated that both electric field and plasma-generated photons were able to excite semiconductor catalysts to generate hole–electron pairs, which significantly enhanced the conversion in plasma-induced H_2S decomposition [18].

In the present paper, the non-thermal plasma-catalyst hybrid process was investigated extensively, and the possible pathways in H_2S decomposition by the plasma-catalyst hybrid approach were tentatively proposed.

2. Experimental

2.1. Catalyst preparation

Al_2O_3-supported CdS, ZnS and $Zn_{0.4}Cd_{0.6}S$ were used as the semiconductor catalysts. The supported metal sulfides were obtained by sulfiding the supported metal oxides at 400 °C for 180 min in a 10% H_2S/Ar flow (80 mL/min). Al_2O_3-supported metal oxide precursors were prepared by an impregnation procedure from their salts and Al_2O_3. A loading level of 10 wt% oxide precursor was chosen for each catalyst, unless otherwise specified. $Cd(NO_3)_2{\cdot}4H_2O$ (99.0%, Sinopharm Chemical Reagent Co., Ltd.) and $Zn(NO_3)_2{\cdot}6H_2O$ (99.0%, Sinopharm Chemical Reagent Co., Ltd.) were used. For example, 10 wt% CdO/Al_2O_3 was prepared as follows: γ-Al_2O_3 extrudes (surface area: 270 m^2/g, Fushun Research Institute of Petroleum and Petrochemicals, China) were crushed and sieved to 40–60 mesh. 4 g $Cd(NO_3)_2{\cdot}4H_2O$ was dissolved in 15 mL de-ionized water. 15 g γ-Al_2O_3 particles were added to the resulting solution, which were kept at room temperature for 8 h. Then the mixture was dried at 120 °C for 12 h, followed by calcination at 450 °C for 5 h.

2.2. Plasma-induced H_2S decomposition

The non-thermal plasma was generated at atmospheric pressure by dielectric barrier discharge (DBD). A high-voltage generator (CTP-2000K; Corona Laboratory, Nanjing, China) was applied to supply a voltage (peak-to-peak voltage) from 0 to 15 kV with a sinusoidal waveform at a frequency of about 10 kHz. The DBD reactor mainly consists of a quartz tube and two electrodes (Fig. 1). The high-voltage electrode was a stainless-steel rod, which was installed along the axis of the quartz tube and connected to the generator. The grounding electrode was an aluminum foil, which was wrapped around the quartz tube and was connected to ground by a wire. Al_2O_3-supported semiconductor catalyst was placed into the gap between the quartz tube and the high-voltage electrode. The discharge power (the power applied to the reactor) of about 0–6 W was calculated using the Q-V Lissajous diagram, which was measured by a digital oscilloscope. The reactor was immersed in an oil bath, which was kept at 120 °C to allow the generated sulfur to leave the catalyst bed in the form of liquid drops and to prevent sulfur deposition on the catalyst surface. A flow of feed gas (7.5–20 vol% H_2S in Ar) was passed through the catalyst bed while a high-voltage was applied to discharge the gas to form a non-thermal plasma. The effluent was passed through a saturated NaOH solution trap to remove unreacted H_2S, and the hydrogen content was analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector. At 100% conversion, the effluent was rechecked with lead acetate test paper.

In H_2S decomposition, only H_2 and S are produced, without any other byproduct. Therefore, H_2S conversion (X_{H_2S}) is equivalent to H_2 yield (Y_{H_2}):

$$X_{H_2S} = Y_{H_2}\frac{A_E}{A_0} \times 100\%$$

Where A_E is the H_2 peak area in the chromatogram of the effluent, A_0 is the H_2 peak area at full H_2S conversion.

The area of the Lissajous diagram measures the energy dissipated in the discharge during one period of the voltage. The charge was determined by measuring the voltage across the capacitor of 0.47 μF connected in series to the ground line of the plasma reactor [19]. The discharge power was calculated from the product of the area of charge–voltage parallelogram and the frequency of discharge (10 kHz). Specific input energy (SIE, J/L), which measures the energy input in the plasma process, was calculated by:

$$SIE = \frac{P}{V}$$

where P is the discharge power (W), and V is the gas flow rate (L/s).

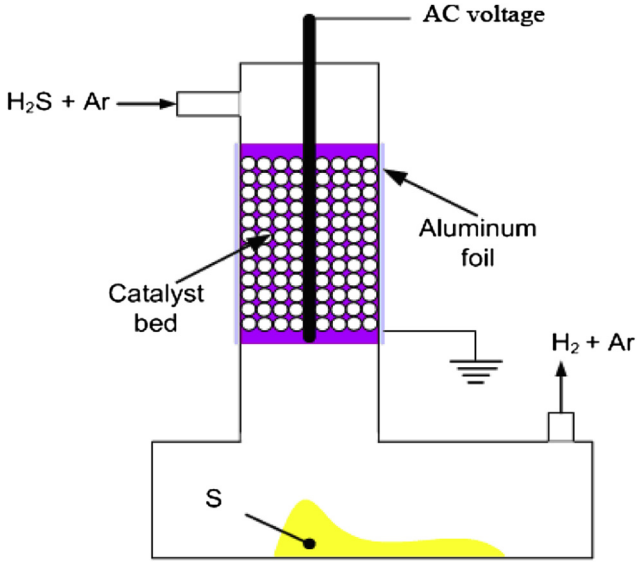

Fig. 1 – Schematic diagram of the DBD reactor for semiconductor-catalyzed H_2S decomposition.