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H2S decomposition was examined in the gas and liquid phases over TiO2 photocatalyst. In the gas phase reaction, H2 was obtained using TiO2 as a photocatalyst. After the photocatalytic reaction, the color of TiO2 changed from white to yellow. SEM-EDS results revealed that sulfur was present on the TiO2 surface. H2 evolution rate was remarkably higher in the liquid phase reaction than in the gas phase reaction. Thus, liquid phase reaction is optimal to obtain H2 from the decomposition of H2S. Ethanolamine as a solvent of H2S underwent little photocatalytic decomposition. TiO2 photocatalyst has high potential for use in a new H2 recycling process in the petroleum industry.

Keywords
Hydrogen sulfide, Decomposition, Hydrogen production, Titania

1. Introduction

Hydrodesulfurization (HDS) of organic sulfur compounds is one of the most important processes to produce clean fuels in the petroleum industry1). Toxic H2S is formed in the tail gas of the HDS reaction, which can be captured in amine medium. After separation, the H2S can be decomposed into S and H2O (Claus reaction), as shown in Eq. (1). Consequently, the hydrogen (H2) added in the HDS process finally reacts with O2 to form H2O. Therefore, the petroleum industry has claimed the development of a new and environmentally friendly H2S treatment process.

Decomposition of H2S (Eq. (2)) over sulfide catalysts has been widely studied2),3). This reaction needs high temperatures (above 500 °C) to produce H2.

\[ 2H_2S + O_2 \rightarrow 2S + 2H_2O \quad (1) \]

\[ H_2S \rightarrow S + H_2 \quad (2) \]

Photocatalytic decomposition of H2S depends on a liquid–solid reaction system, especially an aqueous solution of Na2S4). However, H2S dissolved in amines has not been used as a reactant to produce H2, and gas–solid decomposition of H2S has not been extensively investigated4).

Metal sulfides, such as CdS, have been used as a photocatalyst for the decomposition of H2S to produce H23),4). However, photodissociation of these catalysts was induced by endogenous oxidation by holes (h+)3). In general, TiO2 is a low-cost material with appropriate band gap energy5). Thus, TiO2 is often used as a photocatalyst.
However, TiO$_2$ photocatalyst is not active for H$_2$S decomposition. Practical requirements suggest that photocatalytic decomposition using TiO$_2$ should be investigated with H$_2$S amine solution and gaseous H$_2$S as the reactant.

The present study investigated H$_2$ formation from the decomposition of H$_2$S in the gas and liquid phases over TiO$_2$ photocatalyst to assess the potential for a H$_2$ recycling system for the petroleum industry.

2. Experimental

Titanium dioxide (TiO$_2$) powders consisting of the anatase phase were obtained from Fuji Titanium Industry Co., Ltd. (TIO-2, 18 m$^2$/g) and Furukawa Co., Ltd. (TIO-9, 300 m$^2$/g).

Gas phase reaction: a film of TiO$_2$ particles on a slide glass was prepared with titania powder (1 g) suspended in water (500 µL) and Triton-X100 (20 µL), then the film was dried in air followed by calcination at 110 °C for 10 min. After calcination, the photocatalyst sample in the test tube (for the photocatalytic activity test) was purged free of air with argon gas. Then 5 mL of 5 vol% H$_2$S–N$_2$ gas was injected into the test tube.

Liquid phase sample: H$_2$S ethanolamine solution was obtained by passing a flow (30 mL/min) of 5 vol% H$_2$S–N$_2$ gas through an ethanolamine for 30 min. TiO$_2$ powder (50 mg) was suspended in the solution, and photo irradiated with stirring.

Photo irradiation and photocatalytic activity: photo irradiation was performed using a 400 W xenon arc lamp (Eagle Industry Co., Ltd., CX-04E, R300-3J) equipped with a cold mirror to decrease the heat from the lamp or a 400 W high pressure mercury lamp. The amount of H$_2$ gas formed was measured using a gas chromatograph (Shimadzu Corp., GC-8A) equipped with thermal conductivity detector (TCD).

Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) observation was carried out using a JSM-6380A/EX-54175JMU (JEOL Ltd.).

3. Results and Discussion

Figure 1 shows the decomposition of H$_2$S in the gas phase over TiO$_2$ photocatalyst. The H$_2$ evolution rate was estimated from the linearly fitted slope. TIO-9 photocatalyst showed 4.4 times higher H$_2$ evolution rate than TIO-2 photocatalyst. The photocatalytic reaction should occur on the surface of the catalyst, so the surface area strongly affects activity. Thus, the high H$_2$ evolution over TIO-9 can be explained by higher surface area (300 m$^2$/g). Furthermore, H$_2$ evolution rate hardly changed after reaction for 24 h over both catalysts.
After the reaction, the color of TIO-9 changed from white to bright yellow, as shown in Fig. 2. This indicates that sulfur was deposited on these catalysts during H₂S decomposition in the gas phase. However, the H₂ evolution rate over TIO-9 did not decrease with longer reaction time. The same trend was also observed for the TIO-2 catalyst with smaller surface area. Thus, no deactivation of these catalysts was observed under these reaction conditions.

The S content of the TiO₂ catalysts after the reaction is one of the most important factors to determine the chemical equation for this reaction. H₂S decomposition was carried out using TIO-9 under mercury lamp irradiation. SEM-EDS observation revealed that a slight amount of S (ca. 0.19 µmol) was deposited on TIO-9 catalyst after reaction for 20 h. Since the S content was very low, EDS analysis was not suitable to determine the S content. On the other hand, the amount of S was close to that of formed H₂ (0.15 µmol). Even if the EDS data includes large errors, these results suggest that H₂ was formed by the decomposition of H₂S, as shown in Eq. (2).

H₂S ethanolamine solution was used for photocatalytic decomposition to develop a H₂ recycling system for use in the petroleum industry. Table 1 shows the decomposition of ethanolamine and H₂S ethanolamine solution in the liquid phase under UV irradiation with and without TIO-2 photocatalyst. Little H₂ was formed from ethanolamine with and without H₂S (0.58 µmol/h and 0.41 µmol/h) in the absence of TIO-2 photocatalyst. No H₂ formation was observed under the unirradiated condition. Therefore, photocatalyst hardly decomposed ethanolamine to form H₂ (0.0 µmol/h). In contrast, significant H₂ evolution rate was observed (2.0 µmol/h) in the photocatalytic decomposition of H₂S dissolved in ethanolamine. These results indicate that H₂ formation from H₂S decomposition preferentially occurred compared to ethanolamine decomposition.

Figure 3 shows the photocatalytic decomposition of H₂S in the liquid phase. No CO₂, CO, or N₂ were observed in the gas phase. The H₂ evolution rate over TIO-9 photocatalyst was remarkably higher than that over TIO-2 photocatalyst. This trend was similar to that obtained in the gas phase reaction. Furthermore, the H₂ formation rate of TIO-9 photocatalyst (25 µmol/h) was about 350 times greater in the liquid phase reaction compared to that in the gas phase reaction (about 0.071 µmol/h). These findings indicate that the concentration of H₂S in the liquid phase was remarkably higher than that in the gas phase.

The amount of H₂ evolution linearly increased with longer reaction time over the TIO-2 photocatalyst, indicating that H₂ production rate was constant over the photocatalyst. The amount of H₂ evolution also increased linearly with longer reaction time from 0 to 3 h over the TIO-9 photocatalyst. However, the H₂ evolution rate was lower from 3 to 4 h.

Table 1  H₂ Evolution Rate from H₂S Decomposition in the Liquid Phase at Various Reaction Conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>UV</th>
<th>Ethanolamine</th>
<th>H₂S-ethanolamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIO-2</td>
<td>On</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Off</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Without</td>
<td>On</td>
<td>0.58</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Fig. 3  H₂ Evolution during Photocatalytic Decomposition of H₂S in the Liquid Phase Using TIO-2 (●) and TIO-9 (■)
After the reaction, the color of the ethanolamine solution turned from pale green into yellow (Fig. 4), showing that sulfur, formed from H₂S decomposition, was dissolved in the ethanolamine. Therefore, the photocatalytic activity of TiO₂ would be little affected by deposition of sulfur species even after H₂S decomposition. The lower H₂ formation rate from 3 to 4 h over TIO-9 photocatalyst can be explained by high H₂S conversion.

H₂S is weakly acidic to form protons (H⁺) in basic solution. Ethanolamine acts as a weak basic material. Therefore, H₂S dissociates to form H⁺ and HS⁻ in ethanolamine solution, as shown in Eq. (3). The H⁺ ions react with electrons (e⁻) to form H₂ (Eq. (4)). On the other hand, since a uniform yellow solution without precipitation was obtained after the liquid phase reaction (Fig. 4), sulfur species formed were dissolved in the ethanolamine solution. Therefore, HS⁻ was oxidized with a hole (h⁺) into disulfide ion (S₂²⁻)⁴⁺, as shown in Eq (5).

\[
\text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^- \quad (3)
\]
\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (4)
\]
\[
2\text{HS}^- + 2\text{h}^+ \rightarrow \text{S}_2^{2-} + 2\text{H}^+ \quad (5)
\]

The color of TIO-9 changed from white to light yellow after the gas phase reaction (Fig. 2), implying that solid state sulfur was deposited on the surface of the TiO₂ photocatalyst.

4. Conclusions

H₂ is formed from H₂S decomposition using TiO₂ photocatalyst under UV irradiation in both the gas phase and in the liquid phase. Ethanolamine was little decomposed photocatalytically in the liquid phase. H₂ formation rate in the liquid phase was remarkably higher than that in the gas phase. TiO₂ photocatalyst has high potential for H₂ recycling systems in the petroleum industry.

References