

CeO₂ and CeO₂/MgO catalysts for steam and dry CH₄ reforming under the influence of high concentrations of H₂S

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Abstract: Steam and dry reforming of CH₄ is a key technology for H₂ production. In order to diversify the source of CH₄ gas for H₂ production, catalysts with tolerance against high concentrations of H₂S are necessary. We studied CeO₂ catalysts under the influence of H₂S. As a result, pure CeO₂ exhibited high and stable catalytic activity even in the presence of 2000ppm H₂S. No impurity phases containing Ce₂O₂S or coking were observed after the reaction test. In addition, CeO₂/MgO exhibited comparable activity to CeO₂ with a small amount of CeO₂. Detailed discussion will be presented in an on-site presentation using data of XAS, TPR, and DRIFT studies.

Keywords: H₂S, Steam and dry reforming, CeO₂ catalyst

1. Introduction

Steam and dry reforming of CH₄ is a key technology to industrially produce H₂. Although conventional processes use Ni catalysts to perform the reactions, those catalysts are vulnerable to H₂S even if the concentration of H₂S is as low as 1 ppm. Therefore, it is necessary to remove H₂S from the feed CH₄ gas before subjecting it to the catalysts. In contrast, there are several industrially available CH₄ gases that contain a lot of H₂S. For example, the H₂S concentration of biogas produced by methane fermentation reaches more than 2000 ppm. A comparable concentration of H₂S is also contained in coke oven gas generated as a by-product of the steel industry. Catalysts with tolerance against such high concentrations of H₂S will diversify the source of CH₄ gas and increase the processing options to produce H₂.

Several research groups reported that CeO₂ exhibits high catalytic activity for steam CH₄ reforming under the influence of H₂S.¹ They showed the higher catalytic activity of CeO₂ catalysts under the influence of 500ppm H₂S than with no H₂S. However, it was also reported that CeO₂ reacted with 1000ppm H₂S to form Ce(SO₄)₂ and Ce₂O₂S during the steam reforming reaction, which caused the deactivation of the catalysts.

Here, we performed a further study on CeO₂ catalysts for CH₄ reforming under the influence of H₂S. As a result, we found that CeO₂ of high purity exhibits high and stable catalytic activity even under the influence of 2000ppm H₂S.² In addition, CeO₂/MgO exhibited comparable activity to CeO₂ with a small amount of CeO₂.³

2. Experimental

Pure CeO₂ (Catalysis Society of Japan, JRC-CEO-2) was heated at 800°C in air for 5 h. The calcined sample was used as the CeO₂ catalyst. CeO₂/MgO catalysts were prepared by the impregnation method. The as-achieved Mg(OH)₂ (Wako Pure Chemical, >99.9%) was decomposed to MgO at 800°C in air. The achieved MgO support was suspended in an acetone solution of Ce(NO₃)₃·6H₂O (Kanto Kagaku, >98.5%) and dried in air. Then, the samples were dried at 110°C and calcined at 800°C for 5 h. The samples were denoted as CeO₂/MgO catalysts. The molar ratio between CeO₂ and MgO of CeO₂/MgO was 5: 95.

The catalytic activity of the catalysts was evaluated by the steam CH₄ reforming reaction (CH₄ + H₂O → CO + CO₂ + H₂ (not balanced)) and dry CH₄ reforming reaction (CH₄ + CO₂ → 2CO + 2H₂) with a flow reactor at atmospheric pressure. All of the catalysts were subjected to the reaction tests without any pretreatment. The gas composition was CH₄: 25%, H₂O or CO₂: 25%, and H₂S: 0-2000 ppm, with N₂

making up the balance. The total amount of gas flow was 100 cm³/min, of which the space velocity was 60,000 cm³/h.gcat. Typically, the reactions were performed at 800°C for 1–20 h. The gas composition of the outlet gas from the reactor was determined with a gas chromatograph.

3. Results and discussion

The steam and dry CH₄ reforming reaction test results of CeO₂ are shown in Fig. 1(a). The CeO₂ catalysts exhibited higher CH₄ conversion in both the steam and dry reforming in the presence of H₂S than the reaction with no H₂S. No impurities containing Ce(SO₄)₂ or Ce₂O₂S were observed in XRD after the reaction test. In addition, thermogravimetric analysis detected no coking after the reaction. All of the experimental results showed the high and stable catalytic activity of CeO₂ under the influence of high concentrations of H₂S. There are two points worthy of note here. The first point is that CH₄ reforming proceeded faster in the dry reforming condition than in the steam reforming condition. We deduced that CeO₂ surfaces are terminated by OH under the influence of H₂O, which would retard the breakage of the C-H bond. This hypothesis was supported by a study of the reaction rate. The steam reforming reaction rate depended on the partial pressure of H₂O at negative order. The second point is the dependence of CH₄ conversion on the concentration of H₂S. The higher the H₂S concentration, the higher the activity exhibited by the catalyst. The relationship between CH₄ conversion in the steam reforming and H₂S concentration was formulated by a Langmuir plot; therefore, we supposed that the surface with adsorbed H₂S has higher activity than a clean surface.

In order to reduce the usage of the rare earth CeO₂, we prepared CeO₂-supported catalysts with various supports. The steam and dry CH₄ reforming reaction test results of CeO₂/MgO are shown in Fig. 2. The catalytic activity of CeO₂/MgO was comparable to that of CeO₂ in spite of the large difference in the amount of CeO₂ in the catalysts. Transmission electron microscope observation showed large dispersion of CeO₂ particles even after the reaction test. This result suggests that higher dispersion of CeO₂ is one of the origins of the high catalytic activity of CeO₂/MgO.

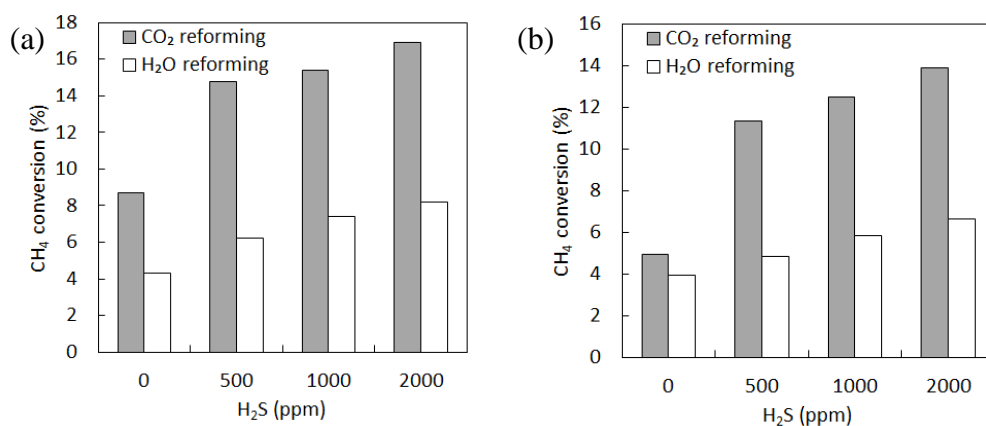


Figure 1. Dependence of CH₄ conversion on H₂S concentration for (a) CeO₂ catalysts and (b) CeO₂/MgO

4. Conclusions

Steam and dry CH₄ reforming reaction proceeded on CeO₂ of high purity and CeO₂/MgO catalysts even in the presence of 2000ppm H₂S. The existence of H₂S accelerated the reactions in both the steam and dry reforming. The CeO₂ and CeO₂/MgO catalysts exhibited a comparable CH₄ conversion rate in spite of the large difference in CeO₂ content. Detailed discussion related to the effect of H₂S will be presented in an on-site presentation using experimental data of XAS, TPR, and DRIFT studies.

References

1. N. Laosiripojana, S. Charojrochkul, P. Kim-lohsoontorn and S. Assabumrungrat, *J. Catal.*, 2010, **276**, 6–15.
2. Japanese patent application JP2017-057485, (2017).
3. Japanese patent application JP2017-118796, (2017).