Influence of a little containing dimethylsulfide on methane steam reforming over Pt/α-Al_2O_3 catalyst

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Abstract: Methane steam reforming (MSR) containing 10 ppm of dimethylsulfide (DMS) over Pt/α-Al_2O_3 catalyst was conducted. The decrease of the catalytic activity was caused by a reversible sulfur poisoning, the DMS adsorption on the reaction site, although the DMS in the feed gas caused sintering of Pt metal particles and carbon deposition. An apparent activation energy of the MSR over the catalyst was remarkably increased by containing the DMS in the feed gas. Therefore, the catalyst had the site capable of avoiding the sulfur poisoning, and the MSR proceeded over the reaction site even in the presence of the DMS.

Keywords: Methane steam reforming, Sulfur poisoning, Pt/α-Al_2O_3 catalyst.

1. Introduction

Methane steam reforming (denoted as MSR) has been extensively industrialized as a process to produce hydrogen from natural gas and the reaction has a possibility to be a core technology in the hydrogen society. Generally, Ni-catalyst is utilized for the reaction, but the Ni-catalyst is weakly resistant to sulfur species contained in natural gas, and it requires a desulfurization step as a pre-treatment. Our laboratory has investigated a catalyst with higher sulfur tolerance, in order to improve the efficiency of the MSR process. Among them, it was revealed that Pt/α-Al_2O_3 catalyst showed stable activity even in the presence of dimethylsulfide (denoted as DMS), which was one of sulfur species containing in natural gas[1]. In this report, we show several influences of a little containing DMS in the MSR on Pt/α-Al_2O_3 catalyst.

2. Experimental

1.0 wt.% Pt/α-Al_2O_3 catalyst was prepared by an impregnation method used diamindinitroplatinum as a precursor. All activity tests were conducted using a fix-bed flow reactor. The pre-treatment was conducted at 997 K for 30 min in 10%H_2/N_2 flow. The total flow rate was 325 mL min^{-1}, and the gas mixture was 3.1%N_2/27.7CH_4/69.2%H_2O/10ppmDMS in the reaction test at 997 K. The product was analyzed by a GC-TCD after passing an iced trap. The size of Pt metal particles was measured by a TEM (JEM-2100, JEOL), and the amount of carbon deposition was derived by a temperature programmed oxidation (TPO).

3. Results and discussion

First of all, a catalytic performance of Pt/α-Al_2O_3 for the MSR without the DMS was evaluated. The catalyst showed *ca.* 50 % of CH_4 conversion and stable MSR activity for 8 hrs. Compared with this result, the catalytic activity for the MSR containing the DMS decreased after 20 min of the reaction to 20 % of CH_4 conversion. For evaluating the decrease factor, the amount of carbon deposition on the catalyst was measured by the TPO, and the Pt particle size was observed by the TEM. Figure 1 shows the influence of the DMS contained in the MSR on the carbon deposition and the Pt sintering. The large amount of the carbon deposition was not detected until 4 hrs after the reaction start, and the sintering of Pt particles proceeded. On the other hand, after 4 hrs of the reaction start, a flame-retardant carbon (burned over 673 K) deposited. However, the catalytic activity was regenerated as shown in Figure 2, although these factor was irreversible. Then, we focused on the DMS adsorption on the catalyst, and investigated a regeneration behavior of the catalyst.

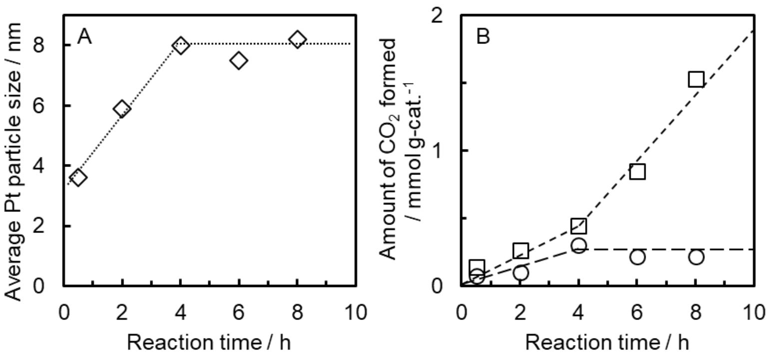

Figure 1. Influence of the DMS contained in the MSR on (A) the size of Pt metal particles, (B) the amount of carbon deposition (Circle: easy flammability carbon, Square: flame-retardant carbon (burned over 673 K)).

Figure 2 shows the regeneration behavior of the catalytic activity after 2 hrs of the MSR containing the DMS. The catalytic activity was regenerated by the conventional MSR without the DMS. The result indicated that the decrease of the catalytic activity was caused by the sulfur poisoning, which was a reversible DMS adsorption.

On the other hand, it was found that the catalytic activity for the MSR containing the DMS was stable, after the sulfur poisoning. This result suggested that a different reaction site was stably working even in present of the DMS. Figure 3 shows an apparent activation energy for the MSR with and without the DMS over Pt/α-Al_2O_3 catalyst. The apparent activation energy was 71.2 kJ mol^{-1} in case of without the DMS, but containing the DMS, the energy increased to 260.1 kJ mol^{-1}. These results indicated that the catalyst had two kinds of the reaction site for the MSR; one was main active site for the conventional MSR, which had a possibility to be poisoned by the DMS, the other was the active site with high activation energy barrier, which could avoid the sulfur poisoning.

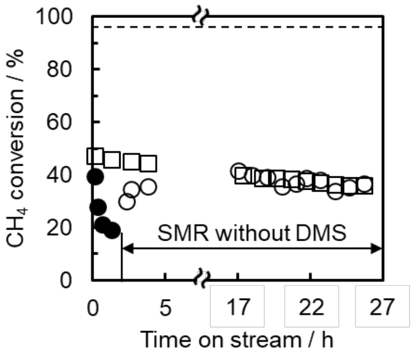

Figure 2. Regeneration behavior of the catalytic activity after the MSR containing the DMS. (Blank: without DMS, Filled: with DMS)

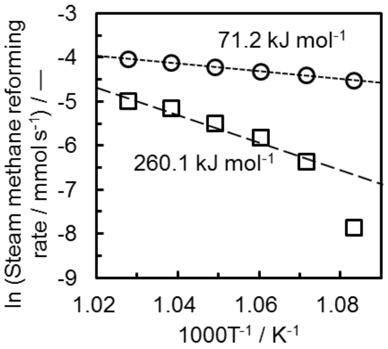

Figure 3. Apparent activation energy of the MSR with and without the DMS over Pt/α-Al_2O_3 catalyst. (Circle: without DMS, Square: with DMS)

4. Conclusions

Dimethylsulfide (DMS), which was one of the sulfur species in natural gas, caused the sintering of Pt metal particles and carbon deposition on Pt/α-Al_2O_3 catalyst in methane steam reforming (MSR). On the other hand, the catalytic activity could regenerate in the conventional MSR after the decrease caused by the DMS. And Pt/α-Al_2O_3 catalyst had two kinds of the active site; one that had high catalytic activity but was poisoned by the DMS, the other that could avoid the DMS poisoning but had high activation energy barrier.

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References

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