Effect of regeneration process through coke combustion and reduction on catalytic activity during *n*-Butane dehydrogenation over PtSn/CeO_2 catalysts

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Abstract: The CeO_2-supported PtSn catalysts were prepared and tested for the *n*-butane dehydrogenation with the regeneration process (coke combustion and reduction) of the used catalyst. The activity of the prepared catalysts did not decrease even after 3 cycles of the dehydrogenation-regeneration process at 550 ˚C. In the XRD measurement of the catalysts used for those process, the diffraction peaks derived from Pt and/or PtSn species were not observed. These results indicated that the CeO_2 support suppressed the sintering of the Pt particles.

Keywords: *n*-butane dehydrogenation, PtSn catalysts, Reaction-regeneration process.

1. Introduction

Motorization in Asia has been increasing demand of 1, 3-butadiene (BD) as a raw material of synthetic rubber. The increase of the BD supply is difficult in Japan, because some naphtha crackers stopped in recent years. From those backgrounds, the development of new route for BD production is expected$^{1)}$.

Recently, we proposed the simple dehydrogenation (SDH) process of *n*-butane to produce 1,3-butadiene by two steps (Fig.1). In this process, we found that PtSn/MgO-Al_2O_3 catalysts showed a high activity and selectivity during the *n*-butane dehydrogenation to butenes (1st Step) but the activity dramatically decreased during the regeneration process (calcination and reduction) to remove cokes formed on the catalyst, owing to sintering of the Pt particles at high temperature. Therefore, we have to achieve the suppression of the sintering for practical use.

To improve the sintering, in this study, we prepared PtSn/CeO_2 catalysts and used these catalysts in *n*-butane dehydrogenation, because the CeO_2 support inhibited the Pt sintering$^{2)}$.

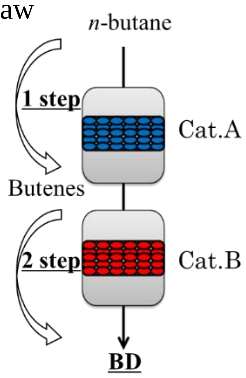

Fig.1 Production of 1,3-butadiene by 2 step dehydrogenation of *n*-butane.

2. Experimental

2.1. Preparation of the PtSn/CeO_2 catalysts (Pt: 1wt%, Sn: 2-4 wt%)

A CeO_2 support (JRC-CEO-3, S.A.: 80 m^2 g^-1) was supplied from the Catalyst Society of Japan. The PtSn/CeO_2 catalysts were prepared by a following sequential impregnation method. First, Pt/CeO_2 catalyst was prepared from CeO_2 and a H_2PtCl_6 aqueous solution by an impregnation method. After the impregnation, the product was dried overnight and then calcined at 550 ˚C in air for 3 h. Second, Sn was introduced on the calcined Pt (O)/CeO_2 with a $SnCl_2$ ethanol solution in the same manner. Finally, the PtSn/CeO_2 catalyst was prepared by calcination and reduction of the precursor at 550 ˚C in H_2 flow for 3 h.

2.2. *n*-Butane dehydrogenation

n-Butane dehydrogenation was performed using a fixed-bed isothermal reactor. As a pretreatment, the catalyst (0.30 g) was reduced for 1 h at the reaction temperature (550 ˚C) and then treated with steam for 30 min. The molar ratio of the feed gas was *n*-butane: He: H_2O = 1:4:3 with the total flow-rate of 99 ml/min.

2.3. Regeneration process

To investigate the catalyst life, we conducted the following reaction-regeneration cycle. After the dehydrogenation at 550 °C for 6 h (1st cycle), the used catalyst was regenerated by coke combustion in a flowing 2% O_2 (50 mL/min) at 550 °C overnight, reduction in 40 %H_2 (50 mL/min) at 550 °C for 1 h, and treatment with steam for 30 min. The experiment was carried out for 3 cycles of the dehydrogenation-regeneration process.

3. Results and discussion

Before investigating the thermal stability of the PtSn/CeO_2 catalysts, a suitable Sn content was examined. Fig.2 shows the results of *n*-butane SDH over three PtSn/CeO_2 catalysts having different Sn contents (Sn: 3, 4, and 6 wt%).

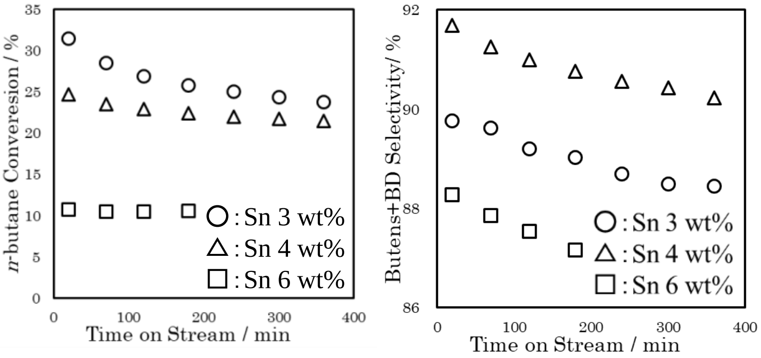

Fig. 2 *n*-butane SDH over PtSn/CeO_2 catalysts.

The catalyst containing 3 wt% Sn showed the highest initial conversion. The selectivity to C4 (butenes + BD) was about 90 %. Although the catalyst containing 4 wt% Sn showed lower initial activity than the catalyst containing 3 wt% Sn, the deactivation rate of the catalyst containing 4 wt% Sn was significantly moderate with the highest selectivity to C4, and the final conversion was nearly the same as that obtained by the catalyst having 3wt% Sn. The further addition of Sn (6wt %) showed the lower activity and selectivity.

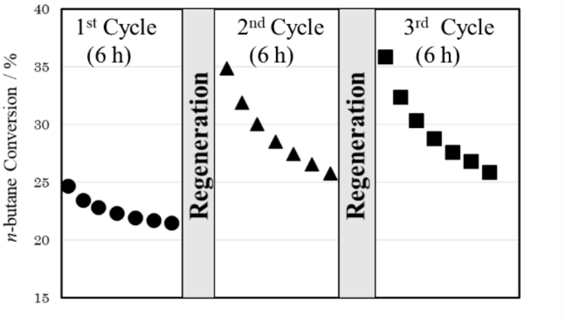

Fig.3 *n*-butane dehydrogenation reaction-regeneration cycle.

Fig.3 shows the results of the *n*-butane dehydrogenation-regeneration cycle over the PtSn/CeO_2 (Sn: 4 wt%) catalyst. At the 2nd cycle, the conversion increased compared to that at 1st cycle. This might be due to the exposure of the Pt surface covered with CeO_x which formed by a partial reduction of the CeO_2 support. During the catalyst preparation, the catalyst precursor was highly reduced (100 % H_2 for 3 h), whereas the pre-reduction at the beginning of the 2nd cycle was performed in 40% H_2 for 1 h. At the 3rd cycle, the conversion was the almost same as that of the 2nd cycle.

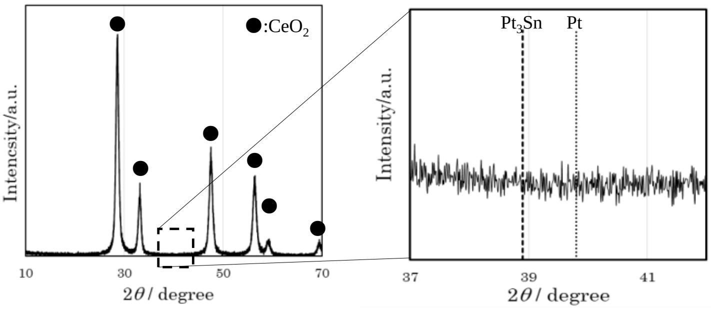

Fig.4 XRD patterns of the used PtSn/CeO_2 catalysts.

Fig.4 shows the XRD patterns of the used catalyst after the 3rd cycle. In the XRD patterns, only the peaks derived from CeO_2 were observed, and the peaks derived from Pt spices were not detected even after the 3 cycles of the dehydrogenation-regeneration process. These results suggested that the Pt particles on the CeO_2 support did not sinter in this dehydrogenation-regeneration cycle.

4. Conclusions

The PtSn/CeO_2 catalyst having 4 wt% of Sn showed the highest selectivity and stability during the dehydrogenation for 6 h. Additionally, this catalyst also showed the high stability for the regeneration process and no sintering of the Pt particles was observed.

References

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