

# Dehydrogenation of 1-Butene over Pt/SnO<sub>2</sub>-SiO<sub>2</sub> Catalysts in the Presence of Steam

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## 1. Introduction

The demand of 1, 3-butadiene (BD) has been increasing by motorization in Asia. The supply of BD will decrease, because ethylene source changes from naphtha to ethane. Therefore, the development of new processes for BD production is expected [1]. Recently, we focused on the simple dehydrogenation (SDH) of 1-butene, and found that Pt/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts having a high SnO<sub>2</sub> content showed a high activity and selectivity to BD.

In this study, we prepared the Pt/SnO<sub>2</sub>-SiO<sub>2</sub> catalysts and used for the 1-butene dehydrogenation. Moreover, the relationship between PtSn species and the performance of the catalyst was discussed.

## 2. Experimental

### 2.1. Preparation of the catalyst

SnO<sub>2</sub>-SiO<sub>2</sub> Supports were prepared by an impregnation method with SiO<sub>2</sub> (JRC-SIO-10) and an appropriate amount of an ethanol solution containing SnCl<sub>2</sub>. After the calcination of the supports at 550 °C, the precursors of the Pt catalysts were prepared by an impregnation method with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>. To obtain the Pt/SnO<sub>2</sub>-SiO<sub>2</sub> catalysts, the precursors were dried in an oven at 130 °C overnight and reduced at 550 °C in a H<sub>2</sub> flow.

### 2.2. 1-butene dehydrogenation

SDH of 1-butene was carried out using a fixed bed isothermal reactor. Prior to the reaction, the catalysts (0.50 g) were reduced for 1 h at the reaction temperature (600 °C). The molar ratio of the feed gas was 1-butene:He:H<sub>2</sub>O = 1:4:3 with the total flow rate was 99 ml/min.

## 3. Results and discussion

Fig. 1 shows the results of 1-butene SDH over five kinds of the Pt/SnO<sub>2</sub>-SiO<sub>2</sub> catalysts having different Sn/Pt molar ratios (1.1, 1.7, 2.3, 2.8, and 3.3). The catalysts with Sn/Pt=1.7-2.3

exhibited a higher BD yield and stability for 6 h compared to the other catalysts. Meanwhile, both the catalysts having higher and lower Sn/Pt ratios (Sn/Pt=1.1, 2.8 and 3.3) showed the serious deactivation.

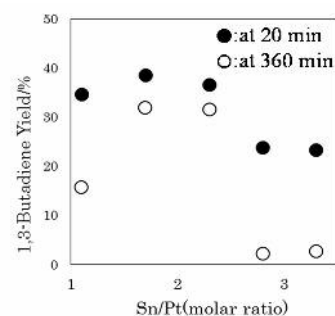


Fig. 1 1-Butene SDH over Pt/SnO<sub>2</sub>-SiO<sub>2</sub> catalysts.

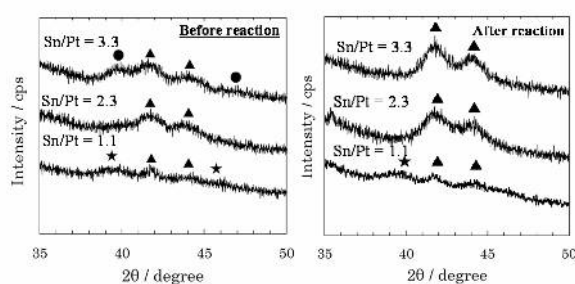


Fig.2 XRD pattern of fresh and used Pt/SnO<sub>2</sub>-SiO<sub>2</sub> catalysts.  
★:Pt<sub>3</sub>Sn or PtSn solid solution ▲:PtSn ●:PtSn<sub>2</sub>

Fig.2 shows the XRD patterns of the catalysts. The peaks of PtSn intermetallic compounds were observed in the patterns of the fresh and used catalysts with Sn/Pt=2.3 that showed the best performance in the 1-butene SDH. In the pattern of the catalyst with smaller Sn/Pt ratio (1.1), the Pt-rich phase (Pt<sub>3</sub>Sn and PtSn solid solution) was observed in addition to the PtSn intermetallic compounds. This Pt-rich phase is considered to cause the coking on the catalyst during the SDH, because that has strong adsorption ability for BD. On the other hand, PtSn<sub>2</sub> and PtSn were formed in the fresh catalyst (Sn/Pt=3.3) before the reaction. After the reaction, the peaks derived from PtSn<sub>2</sub> disappeared, and only peaks derived from PtSn was observed. This change was due to the oxidation of Sn in the PtSn<sub>2</sub> by steam. The active sites in the catalysts was covered with SnO<sub>x</sub> produced by this oxidation, which caused the deactivation.

## REFERENCES

- [1] J.J.H.B. Sattler, J. R.-Martinez, E. S.-Jimenez, B.M. Weckhuysen, Chem. Rev., 114, 10613-10653 (2014).