Effects of metal oxide addition to PtSn/MgO-Al_2O_3 catalysts on activity for *n*-butane dehydrogenation in the presence of steam

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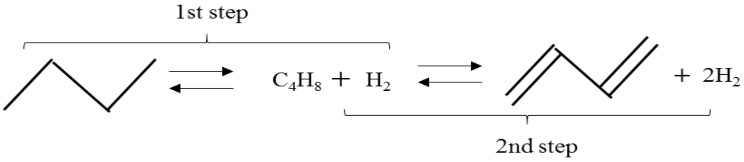
Abstract: Influence of metal oxide (La_2O_3, CaO, or ZnO) addition to PtSn/MgO-Al_2O_3 was investigated in *n*-butane dehydrogenation. The highest *n*-butane conversion was obtained over ZnO-doped catalyst. The PtSn/ZnO-MgO-Al_2O_3 catalysts were prepared with different Zn content (0, 0.12, 1.2, 2.4, 5.1, or 9.0 wt %), and the 2.4 wt% Zn-doped catalyst showed the highest activity (68.0 % initial conversion).

Keywords: *n*-butane dehydrogenation, PtSn catalysts, metal oxide addition

1. Introduction

1,3-Butadiene (BD) is a raw material of ABS resin and synthetic rubber. The demand of BD has been increasing by motorization in Asia. However, the supply of BD will decrease because ethylene source changed from naphtha to ethane. Therefore, development of a new process of BD production is expected. Recently, we focused on *n*-butane simple dehydrogenation by two-steps dehydrogenation (Scheme 1) and found that PtSn/MgO-Al_2O_3 catalysts showed a high activity and selectivity for dehydrogenation from *n*-butane to butenes. For practical use, we have to increase the catalytic activity and decrease coke formation. Addition of metal oxide (La_2O_3, CaO, or ZnO) to supported Pt catalysts is known to improve its activity for propane dehydrogenation[1-3)]. In this study, we prepared PtSn/M_xO_y-MgO-Al_2O_3 (M: La, Ca, or Zn) catalysts and evaluated the performance of these catalysts for the 1st step of the *n*-butane dehydrogenation.



Scheme 1 Dehydrogenation from *n*-butane to 1,3-butadiene.

2. Experimental

MgO-Al_2O_3 (Mg/Al=0.5) support preparation

The MgO-Al_2O_3 support was prepared from γ-Al_2O_3 (Neobead-GB, 20-60-mesh) and a $Mg(NO_3)_2$ aqueous solution by a two-step impregnation method. After the impregnation, the support was dried at 130 ºC overnight, calcined at 300 ºC for 1 h and 550 ºC for 2 h, and finally calcined at 800 ºC for 4 h.

PtSn/M_xO_y-MgO-Al_2O_3 (M: La, Ca, or Zn) catalyst preparation

Pt/MgO-Al_2O_3 was prepared from the support and a H_2PtCl_6 aqueous solution by an impregnation method, and followed by drying at 130 ºC overnight and calcination at 550 ºC for 3 h. Sn was introduced on Pt/MgO-Al_2O_3 with a $SnCl_2$ ethanol solution in the same manner as the Pt addition. Finally, metal oxide was added using an aqueous solution of corresponding metal nitrate by an impregnation method.

n-butane dehydrogenation

The dehydrogenation of *n*-butane was carried out using a fixed-bed isothermal reactor. Prior to the reaction, the catalyst (0.50 g) was reduced with H_2 for 1 h at the reaction temperature (550 ºC). A molar ratio of the feed gas was *n*-butane: He: H_2O = 1: 4: 3 with the total flow rate 99 mL min^{-1}.

3. Results and discussion

Fig.1 shows the initial and final conversion of *n*-butane using the catalysts modified by different metal oxide (La_2O_3, CaO, or ZnO). The ZnO-doped catalyst exhibited the highest conversion (initial, 66.2 %; final, 54.2 %). The conversion of *n*-butane obtained by the La_2O_3-doped catalyst (initial, 60.4 %; final, 47.7 %) was slightly higher than that obtained by the PtSn/MgO-Al_2O_3 catalyst (initial, 58.8 %; final, 45.4 %). The PtSn/CaO-MgO-Al_2O_3 catalyst showed the lowest initial conversion (52.8 %). The high activity of the PtSn/ZnO-MgO-Al_2O_3 catalyst might be due to increasing Pt dispersion by addition of ZnO[3].

Table 1 shows selectivity to butenes + 1,3-butadiene ($S_{initial}$ and S_{final}), deactivation values (ΔX), and the amount of coke deposition (D_{coke}). The selectivities to butenes + 1,3-butadiene were 95-97 % for all tested catalysts, and no significant change was observed during the dehydrogenation. Both the PtSn/MgO-Al_2O_3 catalyst and the La_2O_3-doped catalysts showed almost same deactivation values, which was slightly lower than that obtained by the ZnO-doped catalyst. When the PtSn/CaO-MgO-Al_2O_3 catalyst was used, the deactivation value was remarkably low with a small amount of the coke formation compared with the PtSn/MgO-Al_2O_3 catalyst.

Table 1 Results of *n*-butane dehydrogenation over M_xO_y-modified PtSn/MgO-Al_2O_3 catalysts.

Catalyst	ΔX[a)] (%)	$S_{initial}$ (%)	S_{final} (%)	D_{coke} (wt%)
PtSn/ZnO-MgO-Al_2O_3	18.1	95.5	96.6	2.0
PtSn/La_2O_3-MgO-Al_2O_3	21.1	95.2	95.9	2.0
PtSn/MgO-Al_2O_3	22.7	95.5	96.3	1.7
PtSn/CaO-MgO-Al_2O_3	12.7	96.8	96.8	0.6

a) $\Delta X = (X_{initial} - X_{final})/ X_{initial} \times 100$

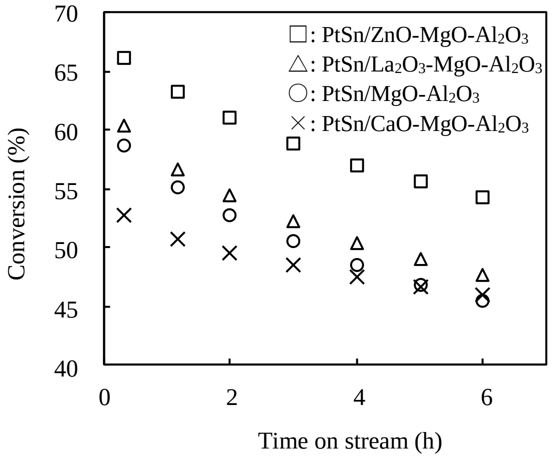


Figure 1 *n*-Butane dehydrogenation over PtSn/M_xO_y-MgO-Al_2O_3 (M_xO_y: 0.7-0.9 wt%) catalysts.

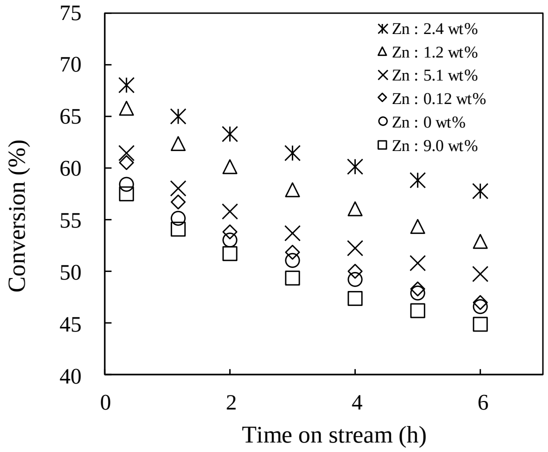


Figure 2 *n*-Butane dehydrogenation over PtSn/ZnO-MgO-Al_2O_3 (Zn : 0, 0.12, 1.2, 2.4, 5.1, and 9.0 wt%) catalysts.

The addition of ZnO to PtSn/MgO-Al_2O_3 catalysts effectively improved the catalytic activity for *n*-butane dehydrogenation. Six catalysts containing different amount of Zn (0, 0.12, 1.2, 2.4, 5.1, and 9.0 wt%) were used for the dehydrogenation. Fig.2 represents the catalytic performance of those catalysts. The *n*-butane conversion increased with the increasing content of Zn from 0 to 2.4 wt%. These facts might be attributable to increase the Pt dispersion of the catalysts with increasing Zn content. Meanwhile, the conversion decreased with the increasing Zn content at the range from 2.4 to 9.0 wt%. Excess amount of ZnO was not improved the activity.

4. Conclusions

The PtSn/M_xO_y-MgO-Al_2O_3 (M: La, Ca, or Zn) catalysts were used for the dehydrogenation of *n*-butane in the presence of steam. The ZnO-doped catalyst exhibited the highest activity among the tested catalysts, owing to the increasing Pt dispersion. The highest catalytic activity (initial conversion = 68.0 %) was obtained at the Zn content of 2.4 wt% without decreasing selectivity to butenes and 1,3-butadiene.

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