[Letter]

Oxidative Cracking of *n*-Butane over BiOCl Catalyst

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Oxidative cracking of *n*-butane to lower olefins over BiOCl catalyst has been investigated. BiOCl catalyst shows particularly high olefins selectivity and suppresses deep oxidation reactions extremely. 52 % yield of C₂–C₄ olefins was achieved at 625°C.

1. Introduction

Oxidative catalytic cracking of higher paraffins to lower olefins would be an informative reaction to investigate the feasibility of catalytic converting of naphtha to lower olefins. Previously, we have reported that the catalytic performances of rare earth oxides in the oxidative cracking of *n*-butane to lower olefins were similar to those observed in oxidative coupling of methane (OCM) reaction¹⁾. On the other hand, a layered-structure BiOCl catalyst also shows high catalytic activity, high selectivity to C₂-hydrocarbons, and exceptionally large C₂H₄/C₂H₆ ratio in the OCM reaction^{2)–4)}. We then expect that the BiOCl catalyst has an oxidative cracking activity as well as a high oxidative dehydrogenation activity in the oxidation of *n*-butane. In this paper, we report the catalytic performance of the BiOCl catalyst in the oxidative cracking of *n*-butane.

2. Experimental

BiOCl catalyst, which is commercial product (Wako Pure Chemical Ind., Ltd.), was pressed, crushed, and sieved to the particle size of 75–150 μm. The BET surface area of the catalyst was 6.3 m²/g. The oxidative cracking of *n*-butane over the BiOCl catalyst was carried out at atmospheric pressure in a conventional fixed-bed continuous-flow reactor. The catalyst (3.0 g) was diluted with inert quartz particles and mounted in the middle of the reactor. To minimize the extent gas-phase reactions, the volume in the reactor except for catalyst was packed with the quartz particles. The reaction conditions were as follows: *T*=500°C–650°C, *n*-C₄H₁₀/O₂/N₂=2/8/40 cm³/min. The products of the reaction were separated with the columns of PEG-1500, MS-5A, SP-1700, Shimalite Q, Porapak Q, Porapak N, and Porapak QS, and analyzed by an on-line gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector and a flame ionization detector. N₂ in the feed was used as an internal standard for calculations of conversion and selectivity. The conversion and selectivity were calculated based on the amount of reacted *n*-butane. The carbon balances were nearly 100 %.

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3. Results and Discussion

The result of the catalytic performance of the BiOCl catalyst is summarized in **Table 1**. The conversion of *n*-butane increased with increasing the reaction temperature and reached about 93 % at 650°C, at which temperature oxygen conversion was about 50 %. The conversion of *n*-butane without catalyst was about 10 % at 650°C at most. As shown in **Table 1**, ethylene, propylene, butenes, butadiene, carbon monoxide, and carbon dioxide were always the major products and small amounts of methane was observed. Any oxygen and chlorine inserted products were not detected. Oxidative dehydrogenation and combustion were major reactions at 500°C; above 600°C oxidative cracking reaction began to be significant. The selectivity to CO_x increased at high temperatures, suggesting that consecutive oxidation reactions occurred at the high temperatures. The yield of C₂–C₄ olefins reached 52 % at 625°C, and then decreased above this temperature.

The BiOCl catalyst shows a rather high olefins selectivity and suppresses deep oxidation reactions extremely, as compared to the rare earth oxide catalysts¹⁾ for the oxidative cracking of *n*-butane and to the V-Mg oxide catalyst⁵⁾ for the oxidative dehydrogenation of *n*-butane. The V-Mg oxide catalyst shows a rather high selectivity to dehydrogenated products in the oxidative dehydrogenation of *n*-butane, i.e., 51 % selectivity to butenes plus butadiene at 63 % conversion of *n*-butane at 600°C, whereas overall C₂–C₄ olefins selectivity of this catalyst is smaller than that of the BiOCl catalyst. On the contrary, the BiOCl catalyst has oxidative cracking activity to produce ethylene and propylene as well as oxidative dehydrogenation activity, in particular at high reaction temperatures. This flexibility in products distribution is the characteristic feature of this catalyst compared to the V-Mg oxide catalyst.

Table 1 Catalytic Performance of BiOCl Catalyst in the Oxidative Cracking of *n*-Butane ^{a)}

Temperature (°C)	Conversion (%)		Selectivity (%)						
	<i>n</i> -C ₄ H ₁₀	O ₂	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	C ₄ H ₆	CH ₄	CO	CO ₂
500	3.6	1.9	6.2	9.5	32.7	20.9	0.0	6.5	23.9
550	15.5	6.6	16.8	11.3	33.3	15.8	0.4	5.5	16.9
600	50.7	19.0	28.3	10.1	19.9	15.1	0.9	7.1	18.5
625	78.6	33.7	30.1	8.7	11.1	16.5	1.4	10.2	22.0
650	93.3	49.6	30.0	6.0	4.1	11.6	2.4	16.9	29.0

^{a)} Data were collected within 1 h reaction. Reaction conditions: catalyst weight 3.0 g, *n*-C₄H₁₀/O₂/N₂=2/8/40 cm³/min.

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Keywords

Naphtha, Olefin, Oxidative cracking, *n*-Butane, Bismuth oxychloride catalyst