Dehydrogenative cracking of *n*-butane over modified HZSM-5 catalysts

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Dehydrogenative cracking reaction of *n*-butane was studied using HZSM-5 catalyst modified with various metal oxides. Alkaline earth (magnesium), transition metal (cobalt) and rare earth (lanthanum) elements are used for the modification. The selectivity of the products was studied at low conversion ($\lesssim 20\%$). Methane, ethane, ethylene, propylene, butenes and butadiene were the main products. With the use of the cobalt- or magnesium-containing HZSM-5, dehydrogenative cracking was observed and the selectivity of ethylene was much larger than that of ethane. On the other hand, the selectivity of ethylene and ethane were almost the same in the reaction using the lanthanum-containing HZSM-5. It is considered that the cobalt- and magnesium-loaded sites on HZSM-5 played an important role in the dehydrogenative cracking.

KEY WORDS: HZSM-5; butane; cracking; cobalt; dehydrogenation; ethylene; propylene; olefin.

1. Introduction

Light olefins such as ethylene and propylene are industrially produced *via* steam cracking of ethane or higher hydrocarbons (*e.g.*, naphtha). Olefins can also be produced by cracking catalyzed using a solid acid such as zeolite, though the yield of olefins (ethylene and propylene) is reported to be lower than that obtained by steam cracking.

We have been investigating cracking of *n*-butane using modified HZSM-5 catalysts (metal oxide-loaded or ion exchanged with a metal ion) and found that the selectivity of the products was significantly affected by the modification.

In order to increase the selectivity of olefin, some researchers examined the oxidative dehydrogenative cracking of light alkanes using modified HZSM-5 [1]. In this study, we examined non-oxidative cracking of *n*-butane by HZSM-5 catalysts modified with alkaline earth (magnesium), transition metal (cobalt) and rare earth (lanthanum) elements and investigated the effect of the modification with these elements on the selectivity of the cracking products and the possibility of dehydrogenative cracking for light olefin production.

2. Experimental

2.1. Catalyst

HZSM-5 samples were synthesized by a hydrothermal procedure [2] followed by conventional ion exchange in 0.6 M HCl solution, then calcined in air at 550 °C for 3 h. The SiO_2/Al_2O_3 ratios of the HZSM-5 were 69 and 200 (designated as HZSM-5(69) and HZSM-5(200), respectively).

The metal-ion modified form of HZSM-5 (Co-ZSM-5, La-ZSM-5) was prepared by an ion exchange procedure using an aqueous solution of metal salt ($Co(NO_3)_2 \cdot 6H_2O$, $La(CH_3COO)_3 \cdot 1.5H_2O$, respectively) and HZSM-5(69). The samples were dried at 120 °C for 8 h and calcined at 600 °C for 5 h. The magnesium-containing HZSM-5 (Mg-ZSM-5) was prepared by a hydrothermal procedure [3]. The SiO_2/Al_2O_3 ratios of the Mg-ZSM-5 were 197.

Cobalt oxide-loaded HZSM-5 (5%Co/ZSM-5) was prepared by impregnation using an aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution and HZSM-5(200). The loading amount of the cobalt was calculated on the basis of weight as cobalt metal. Thus, "5%Co/ZSM-5" catalyst contains 5 wt% of Co as the metal for the weight of the HZSM-5(200) support.

The catalysts were ground and sieved and the fractions that passed through an ASTM 200 mesh sieve were used for the reaction.

2.2. Cracking of n-butane

A small-scale quartz tube reactor (2.1 mm i.d.) with a ceramic heater was used for the cracking experiment. The temperature of the reactor was measured at the outer surface of the reactor tube. The amount of the catalyst used for the reaction was 1.5–10 mg for each run. The catalyst powder was diluted with quartz sand (100–180 mesh) and then loaded in the reactor. The catalysts

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were pretreated in the reactor at the reaction temperature (600 or 650 °C) under a flow of O_2/He gas (10 $cm^3\,min^{-1}$, 20 vol% of O_2) for 1 h and the gas was changed to N_2/He gas (10 $cm^3\,min^{-1}$, 20 vol% of N_2), then, after 5 min, *n*-butane (0.5 $cm^3\,min^{-1}$) was added to the N_2/He gas stream and the reaction started.

The outlet gas of the reactor was sampled by an on-line sampling loop, and the products were analyzed by an on-line gas chromatograph. The sampling of the product gas was done 3 or 4 min after the substrate feed started. It was confirmed that the composition of the gas phase in the experimental apparatus (from the reactor through the sampling loop) was totally renewed within 3 min.

Substrate conversion and product selectivity (carbon atom basis) were calculated as follows:

$$\text{Conversion}(\%) = \frac{(\text{substrate fed} - \text{unconverted substrate})}{\text{substrate fed}} \times 100 \quad (1)$$

where substrate fed and unconverted substrate were measured in mol min^{-1}.

$$\text{Selectivity}(\%) = \frac{(\text{product}\,[\text{mol min}^{-1}] \times \text{carbon number of the product}) \times 100}{(\text{converted substrate}\,[\text{mol min}^{-1}]) \times 4} \quad (2)$$

Methane, ethane, ethylene, propane, propylene and butenes were detected as the cracking products. Hydrogen was not quantitatively measured in this experiment. The yield of the aromatic products such as benzene, toluene and xylenes was negligible (<1%) under the experimental conditions employed here.

3. Results and discussion

3.1. Cracking of n-butane using non-modified HZSM-5

In order to investigate the earlier stage of the cracking, a short contact time cracking condition was employed so that the conversion of *n*-butane was low ($\lesssim$20%). The conversion of *n*-butane was almost zero without a catalyst (0.2–0.4%, only with quartz sand at 600–650 °C).

Figure 1 shows the results using HZSM-5(69) or HZSM-5(200) as the catalyst. The product gas samples were collected within 4 min after the reaction started. It was confirmed that the conversions and selectivities were almost unchanged at 10 min after the sampling. The reaction proceeded catalytically as the TON of the reactions was about 6 and 20 (based on Al in the catalysts) for HZSM-5(69) and HZSM-5(200) respectively, at 10 min after the reactions started. Methane, ethane, ethylene and propylene were detected as the main products. It was observed that the selectivities of $C_1 + C_3$ (methane + propylene), C_2 (ethane + ethylene) and C_4 (butenes) were equal to each other, and the selectivity of ethane and ethylene was almost equal. From these results, it is considered that *n*-butane is cracked *via* three passes: (1) methane and propylene, (2) ethane and ethylene, (3) hydrogen and butene, and that these three passes occurred with equal probabilities. This

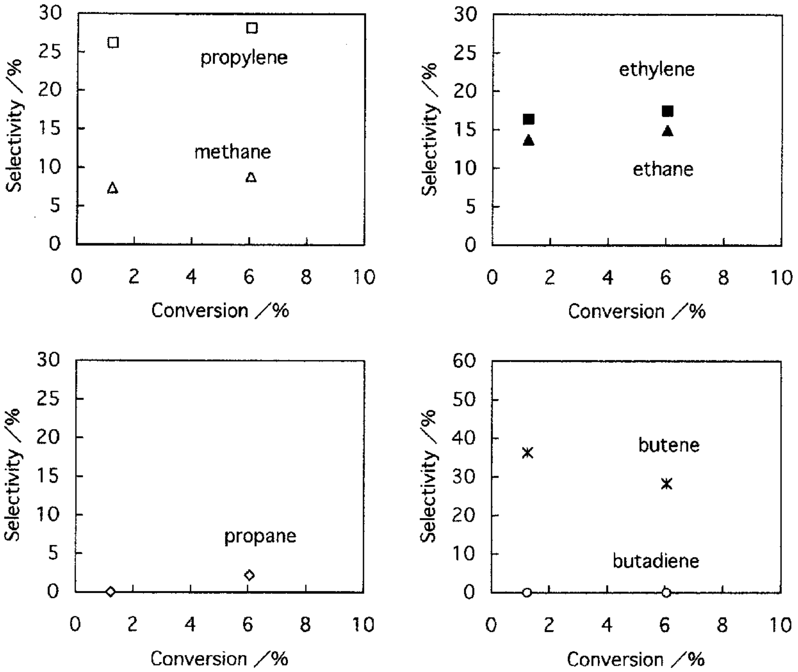

Figure 1. Distributions of products in cracking of *n*-butane catalyzed by HZSM-5. Catalyst: HZSM-5(69), 1.5 mg (conversion, 6.1%); HZSM-5(200), 2.5 mg (conversion, 1.2%). Reaction conditions: temperature, 600 °C; *n*-butane, 0.5 $cm^3\,min^{-1}$; He, 8 $cm^3\,min^{-1}$; N_2, 2 $cm^3\,min^{-1}$.

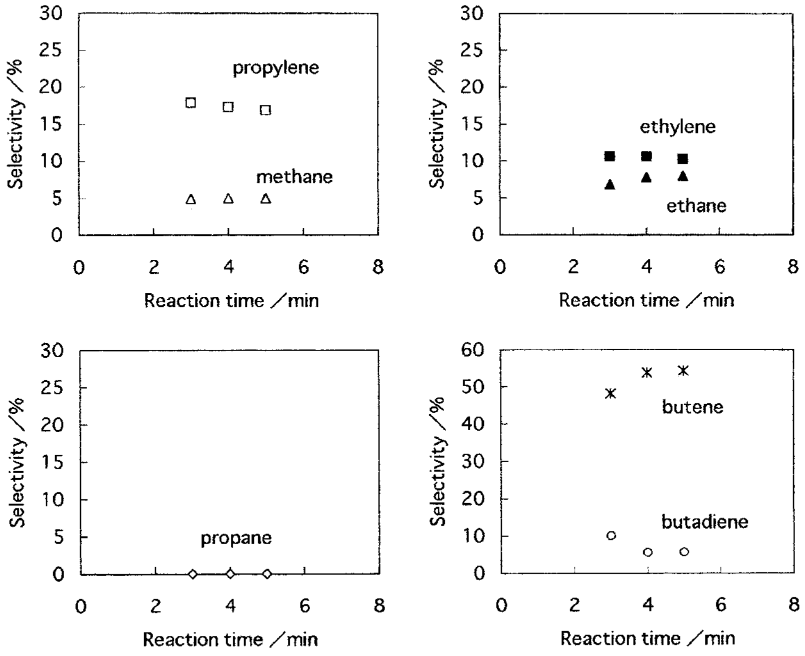

Figure 2. Distributions of products in cracking of n-butane catalyzed by Co-ZSM-5. Catalyst: Co-ZSM-5, 2.0 mg (conversion 5–6 %).

observation is consistent with the results reported in the literature [4]. From the results shown in figure 1 and in the above literature, we consider that the initial cracking selectivities are not affected by the SiO_2/Al_2O_3 ratio of the zeolite catalysts.

3.2. *Cracking of* n*-butane using modified HZSM-5*

With the use of the modified HZSM-5, the product compositions were different from those obtained by HZSM-5. The results are shown in figures 2–5. With Co-ZSM-5 catalyst (figure 2), the selectivity of butene was enhanced, which is considered to be due to the dehydrogenation activity of cobalt in the catalyst. A higher selectivity of ethylene was obtained using 5%Co/ZSM-5 as the catalyst (figure 3).

The results using La-ZSM-5 are shown in figure 4. Comparing the data with those obtained using non-modified HZSM-5, it is considered that lanthanum does not affect the initial cracking selectivity.

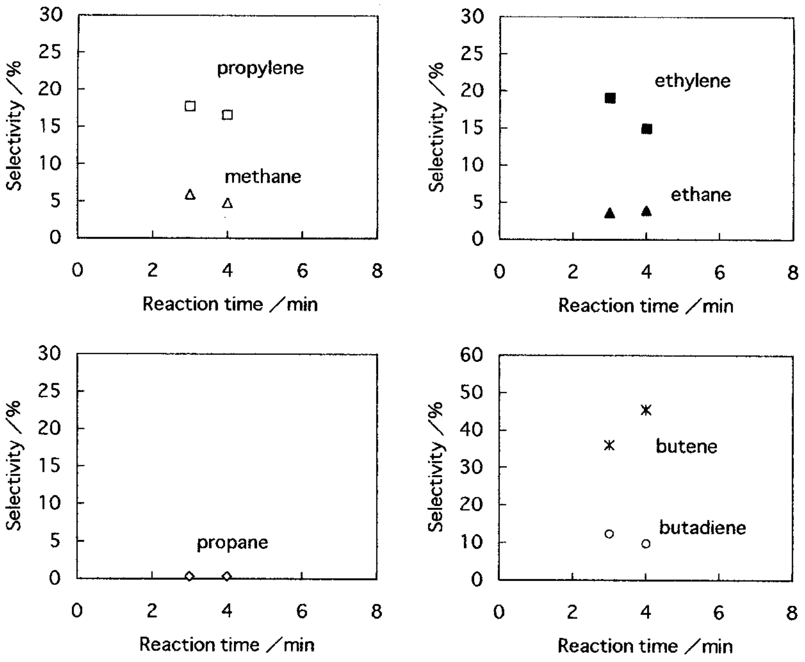

Figure 3. Distributions of products in cracking of n-butane catalyzed by 5%Co/ZSM-5. Catalyst: 5%Co/ZSM-5, 1.9 mg (conversion ~20%).

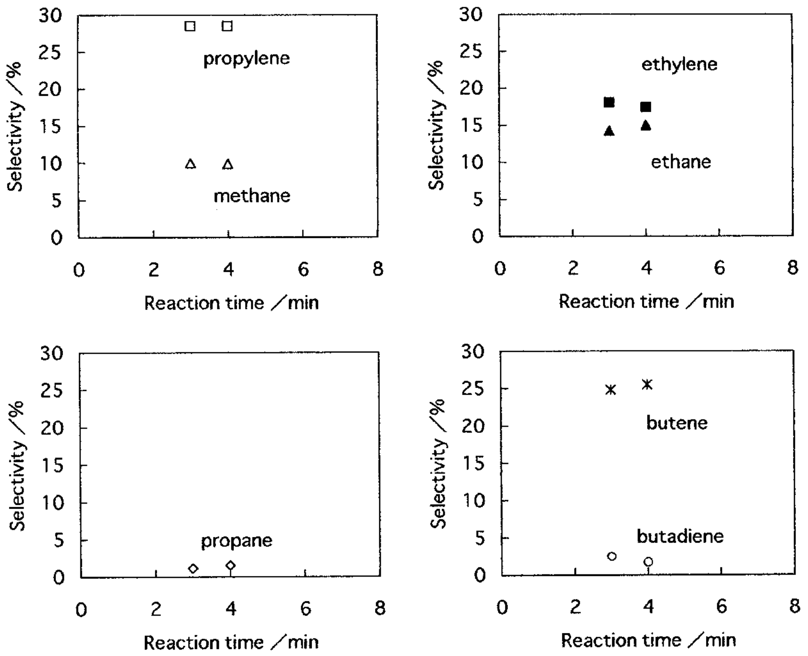

Figure 4. Distributions of products in cracking of *n*-butane catalyzed by La-ZSM-5. Catalyst: La-ZSM-5, 2.1 mg (conversion 2–3%).

With the use of Mg-ZSM-5, the ethylene selectivity was much larger than ethane (figure 5), suggesting that a different cracking mechanism is involved in the reaction using Mg-ZSM-5.

Figure 6 shows the plots of selectivity *versus* conversion which were obtained using Co-ZSM-5 and 5%Co-ZSM-5. From these data, it is considered that the dehydrogenation of butane to butene is enhanced over the cobalt-containing catalyst, and that butene is cracked to ethylene as the reaction proceeds:

$$\text{C–C–C–C} \xrightarrow{-\text{H}_2} \text{C–C=C–C} \tag{3}$$

$$\begin{aligned}\text{C–C=C–C} &\xrightarrow{\text{H}^+} \text{C–C}^+\text{–C–C} \longrightarrow\\ &\text{C}^+\text{–C–C–C} \longrightarrow\\ &\text{C=C} + \text{C}^+\text{–C} \xrightarrow{-\text{H}^+}\\ &\text{C=C} \times 2\end{aligned} \tag{4}$$

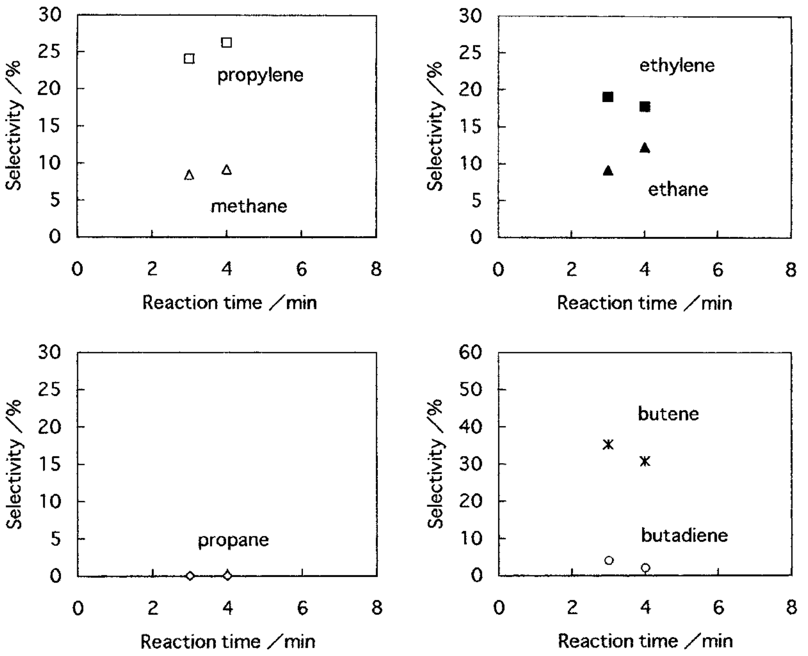

Figure 5. Distributions of products in cracking of *n*-butane catalyzed by Mg-ZSM-5. Catalyst: Mg-ZSM-5, 2.5 mg (conversion 2–4%).

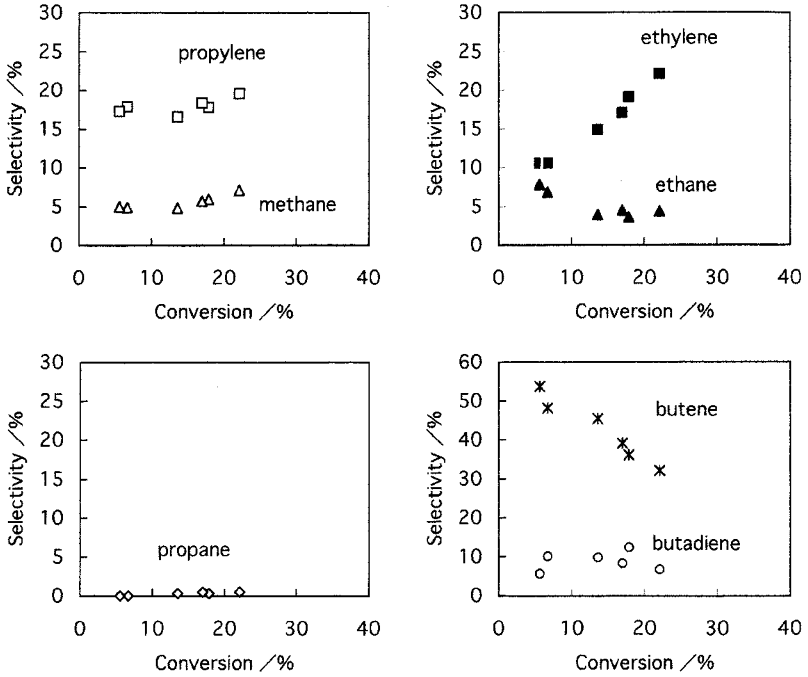

Figure 6. Distributions of products in cracking of *n*-butane catalyzed by Co-ZSM-5 and 5%Co/ZSM-5.

On the other hand, with the use of Mg-ZSM-5, the selectivity of ethylene was much larger than ethane although the conversion was lower (1–4%). The enhanced butene formation was not observed. Though the mechanism of enhanced ethylene formation on Mg-ZSM-5 is not clarified, the possibility is suggested that dehydrogenative cracking of butane occurred at the Mg ion-exchanged site in the ZSM-5.

We have reported that the yield of ethylene and propylene was improved in the cracking of *n*-butane using La-loaded HZSM-5 [5]. We have observed the suppression of olefin adsorption property of La-loaded HZSM-5 as the amount of loaded La increased, and concluded that the suppression was the main reason for the higher yields of ethylene and propylene [6]. Olefins (ethylene, propylene and butene) are inclined to react further on an acid catalyst into aromatic or heavier products. Loaded lanthanum can suppress the olefin adsorption and the bimolecular reaction of olefins is considered to be inhibited on the catalyst. From the result presented here, lanthanum on ZSM-5 does not have any effect on the initial cracking selectivity. This result is informative data for analyzing the previous results.

Table 1
Distribution of products in cracking of *n*-butane at high feed concentration

Time on stream (min)	35	65
Conversion (%)	93.8	93.6
Selectivity (%)		
Methane	13.1	13.3
Ethane	17.3	17.4
Ethylene	24.3	23.7
Propane	2.7	2.7
Propylene	16.2	15.7
Butene	3.9	3.7
Butadiene	0.2	0.2
BTX	15.4	16.5

Reaction conditions: temperature, 650 °C; *n*-butane, 32 vol%; N_2, balance; total gas flow rate, 17 cm^3 min^{-1}; catalyst, 1.0 g (Mg-ZSM-5).

Although the above results are all based on low feed concentration (mostly ~10%) and short time-on-stream, the enhanced ethylene selectivity was also observed on higher feed concentration (up to ~30%) and longer time on stream (over 60 min). The data are shown in table 1. As shown in table 1, the formation of aromatics (BTX: benzene, toluene, xylenes) becomes large at high feed concentration. In order to improve the yield of olefins, it becomes essential to suppress the formation of aromatics at high conversion and at high feed concentration.

By the results presented here, it is suggested that a higher yield of ethylene and propylene could be obtained with the use of an appropriately designed catalyst containing Co, Mg and La.

4. Conclusions

During the cracking of *n*-butane using modified HZSM-5, it was observed that the initial selectivity of products was different from those obtained by HZSM-5. Dehydrogenation of butane was enhanced on cobalt-containing HZSM-5 catalyst and the product butene further cracked to ethylene as the reaction proceeded.

With the magnesium-containing HZSM-5, the selectivity of ethylene was high although at low conversion. A different mechanism of cracking from those with the cobalt-containing catalysts was suggested with Mg-ZSM-5. On the other hand, the initial cracking selectivity obtained using the lanthanum-containing HZSM-5 was almost equal to the non-modified HZSM-5. The improved olefin yield obtained using the lanthanum-loaded HZSM-5 previously reported in the literature was proved not to be contributed from the initial cracking selectivities over the catalyst.

It is considered that dehydrogenative-cracking is a possible alternative process for olefin production from alkanes using an appropriately designed catalyst.

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