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Cracking of *n*-butane over alkaline earth-containing HZSM-5 catalysts

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The effect of alkaline earth modification on HZSM-5 was investigated by catalytic cracking of *n*-butane under non-oxidative and oxidative conditions. The yields of aromatic products were low compared with that obtained using the non-modified HZSM-5, and higher yields of ethylene and propylene were observed with Mg-, Ca-, and Ba-ZSM-5. The NH_3–TPD spectra of these catalysts show that the strong acid sites were transformed to weak acid sites. The dehydrogenation cracking was considered to occur at the acid sites modified with the alkaline earth elements because the ethylene/ethane ratio and the C_2/other products ratio were high using the alkaline earth-containing HZSM-5. It is suggested that the suppression of hydrogen transfer reaction and the stimulation of dehydrogenation cracking were the major cause of the improvement of olefin yield in the cracking.

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

1. Introduction

Light olefins such as ethylene and propylene are produced mainly by steam cracking (pyrolysis) of hydrocarbons in the current chemical industry. Ethylene and propylene can also be produced by the cracking of higher hydrocarbons using zeolite as a catalyst. However, the yield of olefins (ethylene and propylene) was reported to be lower than that obtained by steam cracking, because of the side reactions (aromatization or oligomerization) of the product olefins over the acid sites on the zeolite [1]. Moreover, hydrogen-transfer reactions between the reactant paraffin and the carbenium ion occur easily to produce more paraffin fractions [2]. In order to improve the yield of light olefins in the cracking of paraffinic hydrocarbons, it is important to suppress these side reactions over the acid catalysts.

It has been reported that MFI-type zeolites (HZSM-5) are suitable for olefin production by the cracking of paraffinic hydrocarbons. Over 40% yield of light olefin (ethylene + propylene) was reported using an alkaline earth-containing HZSM-5 [3,4]. One of the roles of the alkaline earth was believed to be a modification of acid characters of the HZSM-5 (weakening acid strength or reducing acid sites). Hydrogen-transfer reactions were reported to be suppressed by the alkaline earth modification [4].

On the other hand, Tao and coworkers reported an oxidative dehydrogenation cracking over alkaline earth-containing HZSM-5 catalysts [4,5]. They suggested that the hydrogen-transfer activity was inhibited and the dehydrogenation activity was promoted under the oxidative conditions, although the cracking mechanisms and the effect of modification elements were not clarified.

When using an alkaline earth-containing HZSM-5, we observed that the selectivities of cracking products at the initial stage of the reaction are different from those obtained using an HZSM-5 without modification [6]. It was suggested that dehydrogenation cracking could occur at the alkaline earth-modified acid site of the catalyst even under the non-oxidative conditions.

In this work, we investigated the cracking of *n*-butane by HZSM-5 catalysts containing various alkaline earths and investigated the effect of the modification with these elements on the selectivity of the cracking products. We have analyzed the data with regard to the ethylene/ethane ratio and the C_2/other products ratio and found that these ratios were increased using the alkaline earth-containing HZSM-5 as catalysts.

2. Experimental

The HZSM-5 samples were synthesized by a hydrothermal procedure followed by conventional ion exchange in 0.6 M HCl solution and calcined in air at 550 °C for 3 h. The SiO_2/Al_2O_3 ratio was *ca.* 200. The introduction of alkaline earths in the zeolites was done by the addition of carbonate salt of each alkaline earth (Mg, Ca, Sr, Ba) to the aqueous solution used for the

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synthesis of the zeolite [7]. The salt/Al ratio was 2.5 in the solution. The analytical compositions of the synthesized zeolite samples are presented in table 1. The catalysts were ground and sieved and the fractions that passed through an ASTM 200 mesh sieve were used for the reaction.

A quartz tube fixed-bed reactor (10 mm i.d.) with a thermocouple tube (4 mm o.d.) was used for *n*-butane cracking experiments. The reactant *n*-butane and the diluent gas (N_2 and O_2) were fed using thermal mass flow controllers. The partial pressure of *n*-butane was 0.33 atm and the overall pressure in the reactor was almost atmospheric. The details of the reaction procedure were presented in a previous paper [8]. Substrate conversion and product selectivity (carbon atom basis) were calculated as follows:

Conversion (%)

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

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

Selectivity (%)

$$= \frac{\begin{array}{c}(\text{product [mol min}^{-1}]\\ \times\, \text{carbon number of the product}) \times 100\end{array}}{(\text{converted substrate [mol min}^{-1}]) \times 4} \qquad (2)$$

Yield (%)

$$= \frac{\begin{array}{c}(\text{product [mol min}^{-1}]\\ \times\, \text{carbon number of the product}) \times 100\end{array}}{(\text{substrate fed [mol min}^{-1}]) \times 4} \qquad (3)$$

The first sampling of the product gas was done 15 min after the reactant feed started. During a typical run, subsequent samplings and analyses were done with 30 min sampling periods. The conversion and selectivity were stable during each run (*ca.* 5 h).

Table 1
Properties of catalysts.

Catalyst	SiO_2/Al_2O_3	M^a/Al_2O_3	Surface area/m^2g^{-1}
HZSM-5	197	–	403
Mg-ZSM-5	200	2.2	377
Ca-ZSM-5	200	3.2	325
Sr-ZSM-5	206	3.8	330
Ba-ZSM-5	189	1.9	328

[a] alkaline earth (Mg, Ca, Sr, Ba).

3. Results and discussion

Figure 1 shows the result of the cracking of *n*-butane using various HZSM-5 catalysts (non-modified and alkaline earth-modified). The non-modified HZSM-5 showed the highest activity, but a large amount of aromatic products (benzene, toluene, xylenes (BTX)) were obtained and the olefin (ethylene and propylene) yield was low.

The temperature needed for the cracking had to be higher with the alkaline earth-containing HZSM-5 than those for the non-modified because of the lower cracking activities of the catalysts. The yields of aromatic products were low compared to that obtained using the non-modified HZSM-5, and higher yields of ethylene and propylene were observed with Mg-, Ca-, and Ba-ZSM-5. It was reported [7] that the amount of strong acid site in HZSM-5 catalyst decreases with alkaline earth modification in the order of non-modified > Mg > Ca > Sr > Ba. In the present experiment, the order of the catalytic activity was somewhat different from those observed in the literature. The order of the cracking activity was non-modified > Mg ≫ Ca ~ Ba > Sr. The activity of Sr-ZSM-5 was the lowest among the catalysts used in these experiments, probably because of the unexpectedly high amounts of Sr introduced into the zeolite matrices (table 1).

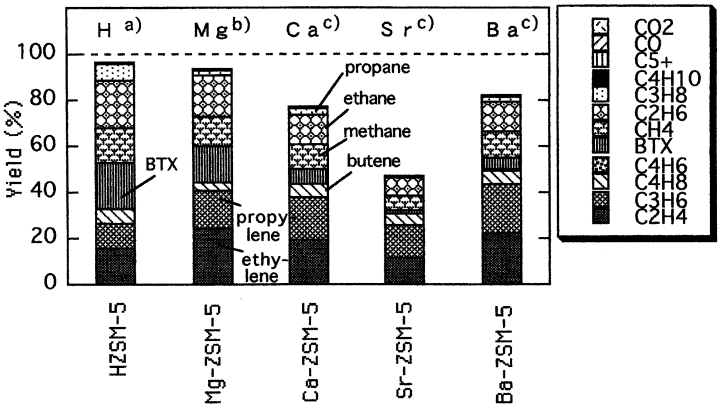

Figure 1. Product distribution in cracking of *n*-butane on alkaline earth-modified HZSM-5. (a) Catalyst, 1 g; 600 °C; *n*-butane, 8.2 cm^3 min^{-1}; N_2, 18.6 cm^3 min^{-1}. (b) Catalyst, 1 g; 650 °C; *n*-butane, 5.5 cm^3 min^{-1}; N_2, 11.5 cm^3 min^{-1}. (c) Catalyst, 1 g; 650 °C; *n*-butane, 2.7 cm^3 min^{-1}; N_2, 4.9 cm^3 min^{-1}.

It is obvious that hydrogen-transfer reactions were suppressed with the alkaline earth-containing HZSM-5 considering that the aromatic products are formed by hydrogen-transfer reactions between olefins [2]. This is consistent with the results observed in the reaction of methanol to olefins using the same kind of modified HZSM-5 catalysts [7].

The alkaline earth/Al ratios were 2.5 in each solution used for the synthesis of the catalysts. If the alkaline earth metal can only exist in the ion-exchange sites, the alkaline earth/Al ratio of the catalyst should be 0.5 (M/Al_2O_3 ratio = 1). However, the analytical M/Al_2O_3 ratios of the catalysts were much larger than 1.0 even after H^+ ion exchange and calcination (table 1). This indicates that the alkaline earth exists not only near the Al^- ion in the zeolite matrices but also in the silica phase as an alkaline earth metal silicate, which could be formed under hydrothermal conditions [7].

Figure 2 shows the NH_3-TPD spectra of the catalysts. The peaks at higher temperature, around 350 °C, decreased and those at lower temperature increased in the Ba-modified samples. The same kind of spectra were obtained from the Ca- and Sr-modified samples. This is considered to reflect a transformation of the acidic character from strong to weak by the introduction of the alkaline earths (Ca, Sr, Ba). On the other hand, with the Mg-modification, the peak profile was not drastically changed from that of the non-modified, although the higher peak decreased and the lower peak increased to some extent. These results are consistent with the results obtained in the reaction experiment.

The results in figure 1 were obtained using N_2 as a diluent gas (n-butane/N_2 = 1/2). In order to investigate the effect of oxidative condition on the reaction, we used O_2/N_2 gas as a diluent (n-butane/O_2/N_2 = 1/0.4/1.6). The results are shown in figure 3. The data of Sr-ZSM-5 were not collected because of the breaking of the quartz reactor during the experiment.

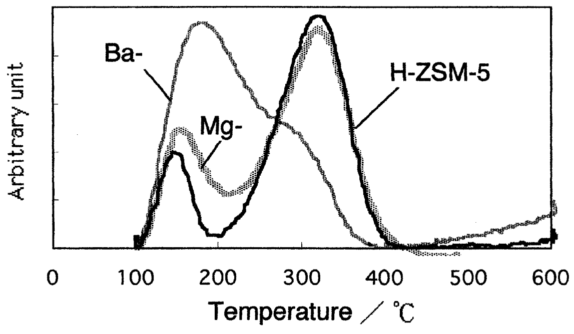

Figure 2. NH_3-TPD spectra of alkaline earth-modified HZSM-5. Pretreatment: He, 50 cm^3 min^{-1}, 773 K, 1 h; NH_3 adsorption: NH_3, 4 kPa, 373 K, 30 min and evacuated at 373 K, 1 h; Desorption: He, 50 cm^3 min^{-1}, 10 °C/min.

As shown in figure 3, oxygen had some effects on the product selectivities. The yield of aromatic products (BTX) decreased and combustion products (CO, CO_2) were generated over the HZSM-5 catalyst. The yields of the other products (ethylene, propylene, methane, ethane, propane) were not changed. With the alkaline earth-containing HZSM-5 (Mg-ZSM-5, Ca-ZSM-5, Ba-ZSM-5), the yield of aromatic products increased compared with the data in figure 1. This suggests that an oxidative dehydrogenation occurred over these catalysts. Also, the yield of ethane decreased and CO_x were generated. The yield of light olefin (ethylene and propylene) increased over the Ca-ZSM-5 catalyst with the oxidative condition, although the yield decreased over the Mg- and Ba-ZSM-5.

The activation energy of the cracking over the non-modified HZSM-5 was 125 kJ/mol. Although the activation energies over the other catalysts and those under oxidative conditions were not collected, they are considered to be almost the same because the conversions are not very different between oxidative and

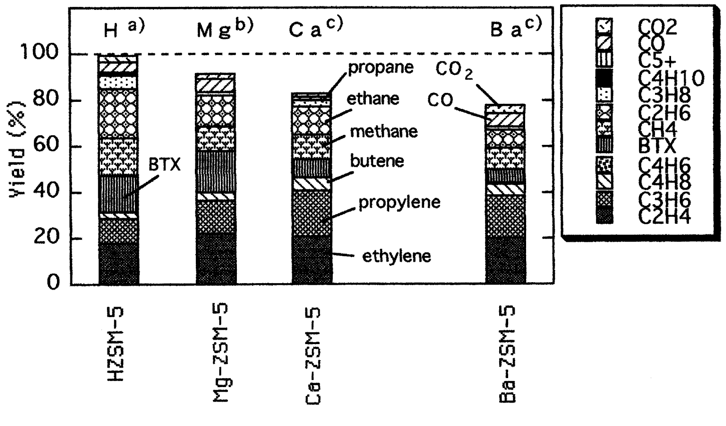

Figure 3. Product distribution in cracking of n-butane on alkaline earth-modified HZSM-5: (a) catalyst, 1 g; 600 °C; n-butane, 2.7 cm^3 min^{-1}; N_2, 4.3 cm^3 min^{-1}; O_2, 1.1 cm^3 min^{-1}. (b) catalyst, 1 g; 650 °C; n-butane, 5.5 cm^3 min^{-1}; N_2, 8.8 cm^3 min^{-1}; O_2, 2.2 cm^3 min^{-1}. (c) catalyst, 1 g; 650 °C; n-butane, 2.7 cm^3 min^{-1}; N_2, 3.9 cm^3 min^{-1}; O_2, 1.0 cm^3 min^{-1}.

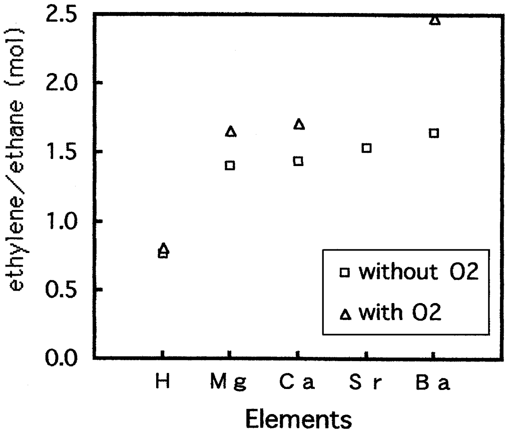

Figure 4. Ethylene/ethane ratio of cracking products obtained using various ZSM-5 catalysts.

non-oxidative conditions for each catalyst. This suggests that the rate-determining step is same under the conditions with or without oxygen and the cracking on the acid of the zeolite is rate-determining.

Figure 4 shows the ethylene/ethane ratio in the cracking product for each run. The ratio with the non-modified HZSM-5 (designated as "H" in figure 4) was a little under 1.0. According to the cracking mechanism proposed in the literature [9], the ratio should be equal to 1.0. The data under 1.0 suggest that hydrogen-transfer reactions occurred between the C_2 carbenium ion and the other hydrocarbons. On the other hand, the ratios obtained with the alkaline earth-containing ones (Mg, Ca, Sr, Ba) were all over 1.0 (around 1.4–1.7) even under the non-oxidative conditions. As we have already reported [6], these data suggest that dehydrogenation cracking occurred at the modified acid sites of the catalysts.

The generation of an acid site in the zeolite containing a metal cation is illustrated as figure 5 [10]. Considering the proposed mechanism of a cracking of paraffin over the acid site of zeolite *via* carbonium ion [9], the dehydrogenation cracking of *n*-butane could proceed as shown in figure 6. The dehydrogenation was considered to occur at the metal ion site. Under an oxidative condition, the ethylene/ethane ratios with the alkaline earth-containing ZSM-5 increased (figure 4), not because of the increase of the ethylene yield but because of the decrease of the ethane yield (figure 3). The fraction of the C_2 carbenium ion from the C_4 carbonium ion seemed to be oxidized further to CO and CO_2 as the alkaline earth-loaded site may have activity for combustion under an oxidative condition [11].

In contrast, propylene and butene formations could be explained as a conventional carbonium–carbenium ion mechanism only (figure 7) and the occurrence of oxidative dehydrogenation cracking was ambiguous. However, as mentioned above, the increase of BTX formation under the oxidative condition was considered to suggest the occurrence of oxidative dehydrogenation. The decrease of propylene and butene in the cracking products under the oxidative condition may be caused by the stimulation of BTX formation or combustion reactions of the intermediate carbenium ions.

The C_2/other products ratios are shown in figure 8 for each catalyst. The ratio increased with the increase of basicity of the alkaline earth elements [7]. The dehydrogenation cracking seems to occur more easily with the increase of basicity of the modification element. Under the oxidative condition, the C_2 ratio with the

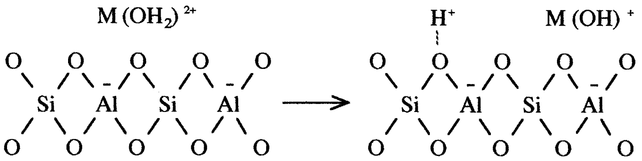

Figure 5. Generation of an acid site in the zeolite containing an alkaline earth cation. M: alkaline earth.

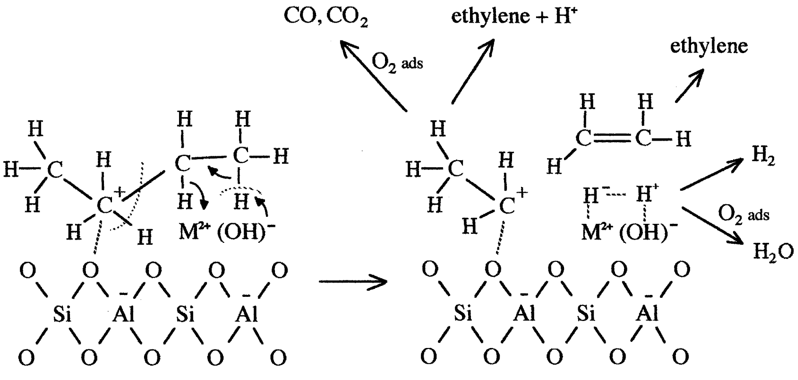

Figure 6. Tentative mechanism of dehydrogenation-cracking of *n*-butane. M : alkaline earth. $O_{2\,ads}$: adsorbed O_2 on the catalyst.

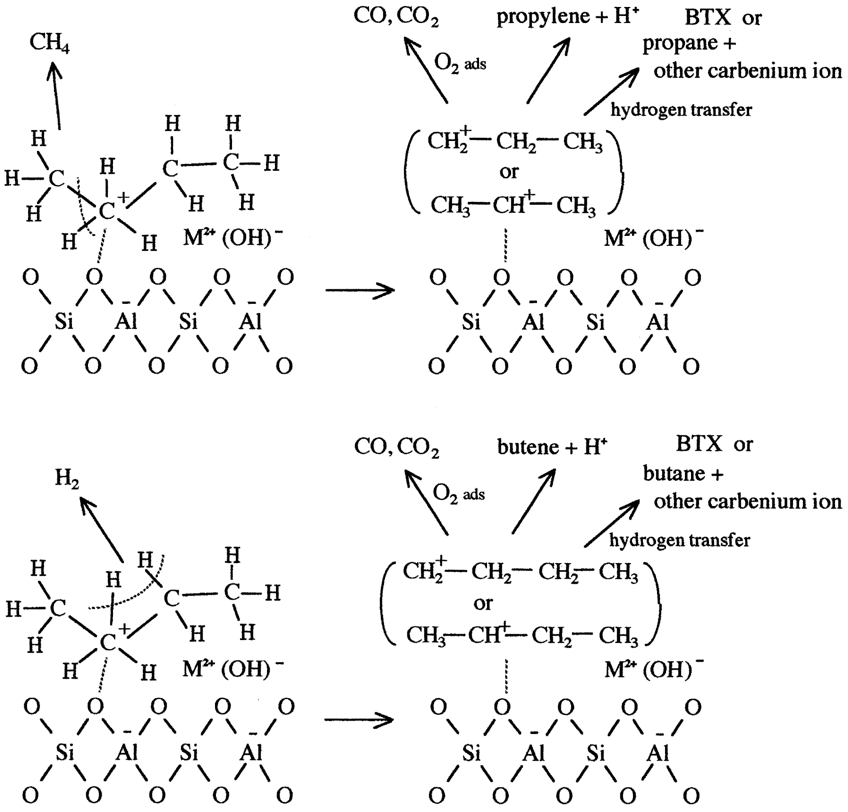

Figure 7. Formation of propylene and butene in the cracking over zeolite.

non-modified (H) increased because of the decrease of BTX, whereas the ratio with the alkaline earth-containing ones decreased according to the decrease of the yield of ethane. The smallest combustion products were observed with Ca-ZSM-5 even under oxidative condition.

From the above results, under the non-oxidative condition, it was found that Ba-ZSM-5 is most suitable for the production of light olefin (ethylene + propylene), whereas the Ca-containing ones seemed to be suitable under the oxidative condition.

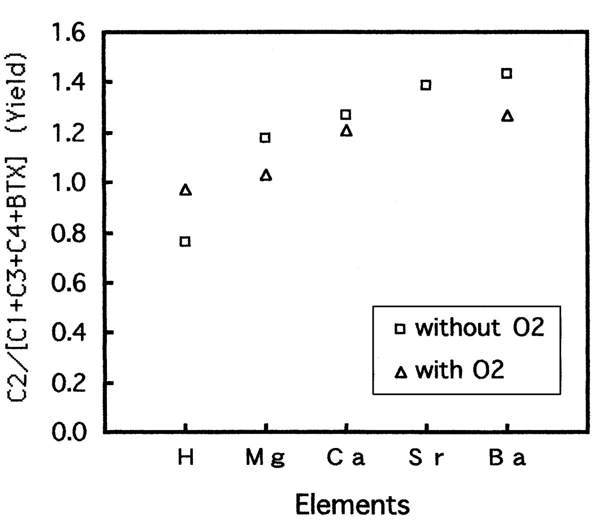

Figure 8. $C_2/[C_1 + C_3 + C_4 + \text{BTX}]$ ratio of cracking products obtained using various ZSM-5 catalysts.

4. Conclusions

In the cracking of *n*-butane using alkaline earth-modified HZSM-5 catalysts, the ethylene and propylene selectivities were improved compared with the non-modified HZSM-5, although the catalyst activities were lowered. The NH_3-TPD spectra of these catalysts showed that the strong acid sites were transformed to weak acid sites. When using the alkaline earth-modified HZSM-5, the ethylene/ethane and the C_2/other product ratios were higher than those obtained using the non-modified one. With Ba-ZSM-5, the highest yield of ethylene and propylene was obtained as the dehydrogenation cracking was stimulated with the modification. On the other hand, under an oxidative condition, the highest yield was obtained using Ca-ZSM-5. It was found that the control of the acid character and the dehydrogenation activity of the HZSM-5 catalyst is important for an improvement of the olefin yield.

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