Cracking of \( n \)-butane over alkaline earth-containing HZSM-5 catalysts

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Received 10 June 2002; accepted 13 September 2002

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 \( \text{NH}_2 \)-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 carbonium 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\textsubscript{2}/Al\textsubscript{2}O\textsubscript{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
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 (N₂ and O₂) 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 (%) \[
\text{Conversion} = \frac{\text{subrate fed} - \text{unconverted substrate}}{\text{subrate fed}} \times 100 \quad (1)
\]

where substrate fed and unconverted substrate were measured in mol min⁻¹.

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

Yield (%) \[
\text{Yield} = \frac{(\text{product [mol min}^{-1}]) \times \text{carbon number of the product}}{(\text{subrate fed [mol min}^{-1}]) \times 4} \times 100 \quad (3)
\]

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SiO₂/Al₂O₃</th>
<th>M⁺/Al₂O₃</th>
<th>Surface area/m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>197</td>
<td>–</td>
<td>403</td>
</tr>
<tr>
<td>Mg-ZSM-5</td>
<td>200</td>
<td>2.2</td>
<td>377</td>
</tr>
<tr>
<td>Ca-ZSM-5</td>
<td>200</td>
<td>3.2</td>
<td>325</td>
</tr>
<tr>
<td>Sr-ZSM-5</td>
<td>206</td>
<td>3.8</td>
<td>330</td>
</tr>
<tr>
<td>Ba-ZSM-5</td>
<td>189</td>
<td>1.9</td>
<td>328</td>
</tr>
</tbody>
</table>

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 cm³ min⁻¹; N₂, 18.6 cm³ min⁻¹. (b) Catalyst, 1 g; 650 °C; n-butane, 5.5 cm³ min⁻¹; N₂, 11.5 cm³ min⁻¹. (c) Catalyst, 1 g; 650 °C; n-butane, 2.7 cm³ min⁻¹; N₂, 4.9 cm³ min⁻¹.](image-url)