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# SHAPE-SELECTIVE CRACKING OF OCTANES OVER PARTIALLY CATION EXCHANGED H-MORDENITE

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Cracking of octanes over H-Y, H-mordenite, and partially cation exchanged H-mordenite was carried out. It was found that the original reactivities of octanes were 3-methylheptane $>$ 2,2,4-trimethylpentane $\gg$ octane and in the case of H-mordenite the order changed to octane $\gg$ 3-methylheptane $>$ 2,2,4-trimethylpentane. By the partial cation exchange only 2,2,4-trimethylpentane reactivity was decreased with the ionic radius of exchanged cation.

This study is on shape selectivity of H-mordenite (H-M). The pore structure of H-M is composed of two dimensional channels, and its effective pore dimension is about 0.9 nm. It can be adjusted to smaller one by the partial exchange of cation with a suitable ionic radius. In the case of shape-selective disproportionation of xylene to form 1,2,4-trimethylbenzene (smallest isomer) over partially exchanged H-M by various cations, the selectivity for 1,2,4-trimethylbenzene formation depends on the ionic radius of exchanged cation$^{1,2)}$.

Csicsery$^{3)}$ and Burbidge et al.$^{4)}$ have reported the shape selectivity of Pt- or Pd-H-M in hydrocracking of paraffins; n- (and near-n-) paraffins are hydrocracked faster than the corresponding cycloparaffins, and in catalytic dewaxing of high boiling petroleum fraction n-paraffins and singly branched (mostly monomethyl) paraffins are selectively hydrocracked, although these results are not quantitative.

In this letter, we show quantitatively the shape selectivity for the cracking of three types of octanes (octane without branch, 3-methylheptane having a tertiary carbon, 2,2,4-trimethylpentane having a quarternary carbon) and the effect of the partial cation exchange on the shape selectivity.

H-M and H-Y zeolite were prepared by the conventional method. The partial cation exchange was carried out at 343 K by using Ca, Sr or Ba acetate aqueous solution. The cracking was carried out in a fixed bed type apparatus with a continuous flow system under atmospheric pressure. Nitrogen was used as a carrier gas (reactants/nitrogen = 1/3). The mixture of the reactants (3-methylheptane/octane = 1 or 2,2,4-trimethylpentane/octane = 1) was fed into the nitrogen stream by a microfeeder. After the catalyst was calcined at 873 K for 2 hours, the temperature was lowered to 673 K (reaction temperature) and then the reactants were input. The unconverted reactants during the initial 25 minutes were collected with a Dry Ice-acetone trap and analyzed by gas chromatography.

The life of H-M as a cracking catalyst was short because of coking-up. The cracking rate was found to be first order with respect to the partial pressure of the reactants. The first order rate constants for the cracking of octane ($k_n$), 3-methylheptane ($k_m$), and 2,2,4-trimethylpentane ($k_i$) over various catalysts were obtained from the mean conversions ($x_n$,$x_m$,$x_i$) in the initial 25 minutes. In table 1, the conversions and the selectivities ($k_m/k_n$, $k_i/k_n$) are shown together with the ionic radii of the cations. In the case of H-Y, whose effective pore dimension is large enough for the reactants to diffuse into the pore, the original reactivities of the reactants are maintained, i.e. the order of the original reactivities is $k_m > k_i \gg k_n$. In the case of H-M, the order changes to $k_n \gg k_m > k_i$. This fact means that the diffusion of the octane with a tertiary or quarternary carbon is inhibited and the diffusion of the octane without branch is not seriously inhibited. Namely, H-M itself has the shape selectivity for three types of paraffins. In the case of partially exchanged H-M by alkaline earth cation, $k_i/k_n$ decreases with the ionic radius, while $k_m/k_n$ does not change appreciably. The diffusion of 2,2,4-trimethylpentane, which has a quarternary carbon, is inhibited more than 3-methylpentane.

Thus, the parent H-M has the shape selectivity and the reaction of paraffin having a quarternary carbon can be controlled by partial cation exchange. The order of the reactivities on Ba-H-M is $k_n \gg k_m \gg k_i$ (4:2:1).

Table 1. Shape Selectivity of Various Catalysts

| Catalyst | Ionic Radius(nm) | Exchange Degree(%) | Conversion $x_m$* | $x_n$* | $k_m/k_n$ | Conversion $x_i$** | $x_n$** | $k_i/k_n$ |
|---|---|---|---|---|---|---|---|---|
| H-Y | —— | 80*** | 0.78 | 0.58 | 1.78 | 0.79* | 0.64* | 1.52 |
| H-M | —— | 96*** | 0.25 | 0.40 | 0.57 | 0.35 | 0.62 | 0.45 |
| Ca-H-M | 0.099 | 21 | 0.21 | 0.38 | 0.51 | 0.30 | 0.63 | 0.36 |
| Sr-H-M | 0.116 | 17 | 0.26 | 0.42 | 0.55 | 0.22 | 0.58 | 0.31 |
| Ba-H-M | 0.136 | 34 | 0.22 | 0.38 | 0.52 | 0.20 | 0.57 | 0.27 |

* Conversion at W/F = 25 g-h/mol-paraffins.
** Conversion at W/F = 45 g-h/mol-paraffins.
*** Exchange degree of proton.

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