Monte Carlo simulation of xylene isomerization over zeolite catalysts

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The isomerization reaction of xylene was simulated by means of the Monte Carlo method based on the experimentally observed parameters, including the diffusivity, equilibrium adsorption constant and intrinsic rate constant. The dependence of the product selectivity upon the Thiele modulus was examined and the results were satisfactorily consistent with those of the continuous model as well as the experiments. This suggests that the Monte Carlo method is helpful for investigating the nature of shape selectivity in zeolite-catalyzed reactions.

Keywords: xylene isomerization; Monte Carlo; simulation; shape selectivity; zeolite

1. Introduction

Xylene isomerization is an industrially important process which allows the conversion of the less useful meta-xylene into para and ortho isomers. Reactions catalyzed by ordinary catalysts produce the equilibrium distribution at 22% ortho-, 54% meta-, and 24% para-xylene [1]. However, shape selectivity has been observed on modified ZSM-5 catalysts which gives higher selectivity of para-xylene. A plausible explanation of this para-selectivity phenomenon was given based on the much higher intracrystalline diffusivity of para-xylene in relation to other isomers [2], and a quantitative model of para-selectivity neglecting the adsorption of molecules was presented [3]. Some authors reported that the intracrystalline diffusivity of para-xylene is only two to ten times higher than those of other isomers [4,5]. They believe that the para-selectivity is attributed to the diffusivity, equilibrium adsorption constant and intrinsic rate constant of molecules for the reaction occurring in sorbed phase, and a quantitative model considering the adsorption and desorption of molecules was presented [5]. Theodorou and Wei [6] studied the diffusion and simple isomerization reaction \( A \rightarrow B \) in a regular network by use of the Monte Carlo method. The results showed that the Monte Carlo simulation technique is an efficient and self-consistent method for attacking problems of diffusion and reaction in microporous solids, and it seems to be an approach particu-
larly suitable for understanding the structure--selectivity relationship in zeolite catalysis. Taking into account the characteristics of the adsorption, diffusion and desorption in zeolite catalysis, we previously developed a Monte Carlo model for the simulation of the diffusion and reaction in zeolites by which the complex isomerization reaction $A = B = C$ was simulated. The effects of the intracrystalline diffusivity and equilibrium adsorption constant of molecule on the product selectivity were investigated [7,8].

Here, xylene isomerization over zeolite catalysts was simulated by means of the Monte Carlo technique which accounts for the elementary processes of adsorption, diffusion, reaction and desorption in zeolites. The dependence of the product selectivity upon the Thiele modulus was examined, and the results were compared with those of the continuous model as well as the experiments.

2. Model

Some basic assumptions are used in addition to several original assumptions for the Monte Carlo method [6,7].

1) The zeolite crystal is modeled here as a finite, two-dimensional rectangular grid of intersecting channels.

2) The adsorption and desorption of molecules take place at border sites only, and the diffusion of sorbed molecules in the channel is modeled as a random walk process.

3) The reaction occurs in the sorbed phase.

The simulation method was described elsewhere [6,7].

For xylene isomerization, $o$-xylene = $m$-xylene = $p$-xylene, the results are calculated as follows:

- Global occupancy:
  \[ \Theta = \frac{(N_o + N_m + B_p + N_{o,ad} + N_{m,ad} + N_{p,ad})}{(2N + 1)^2}, \]  
  \[ (1) \]

- Thiele modulus:
  \[ \phi = N[k'_0/D_0(1 - \Theta)]^{1/2}, \quad k'_0 = k_0K_0, \quad D_0 = D_o, \]  
  \[ (2) \]

- Selectivity:
  - For $o$-xylene isomerization:
    \[ S_m = N_{m,ex}/N_{p,ex}, \]  
    \[ (3) \]
  - For $m$-xylene isomerization:
    \[ S_p = N_{p,ex}/N_{o,ex}, \]  
    \[ (4) \]
  - For $p$-xylene isomerization:
    \[ S_m = N_{m,ex}/N_{o,ex}, \]  
    \[ (5) \]

where the symbols are defined as follows: $D$ is the effective intracrystalline diffusivity; $k'_0, k_0$ are the reaction rate constants in gas phase and sorbed phase, respectively; $K_0$ is the equilibrium adsorption constant; $N$ the grid size parameter; $N_j$ the