# Monte Carlo simulation of xylene isomerization over zeolite catalysts

J.G. Wang, Y.W. Li, S.Y. Chen and S.Y. Peng

*Institute of Coal Chemistry, Chinese Academy of Sciences, PO Box 165, Taiyuan 030001, PR China*

Received 21 October 1993; accepted 1 March 1994

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 = 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:

$$\Theta = (N_o + N_m + B_p + N_{o,\mathrm{ad}} + N_{m,\mathrm{ad}} + N_{p,\mathrm{ad}})/(2N+1)^2 , \tag{1}$$

Thiele modulus:

$$\phi = N[k_0'/D_0(1-\Theta)]^{1/2}, \quad k_0' = k_0 K_0, \; D_0 = D_o , \tag{2}$$

selectivity:

for *o*-xylene isomerization: $S_m = N_{m,\mathrm{ex}}/N_{p,\mathrm{ex}}$ , (3)

for *m*-xylene isomerization: $S_p = N_{p,\mathrm{ex}}/N_{o,\mathrm{ex}}$ , (4)

for *p*-xylene isomerization : $S_m = N_{m,\mathrm{ex}}/N_{o,\mathrm{ex}}$ , (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

Table 1
Parameters employed in the simulations [5]

| | |
|---|---|
| Network dimension | $21 \times 21$ |
| Diffusion matrix | $\mathbf{D} = D_0 \begin{vmatrix} 1.0 & 0 & 0 \\ 0 & 1.4 & 0 \\ 0 & 0 & 2.4 \end{vmatrix}$ |
| Reaction rate constant matrix | $\mathbf{k} = k_0 \begin{vmatrix} 2.0 & -1.0 & 0 \\ -2.0 & 2.0 & -2.0 \\ 0 & -1.0 & 2.0 \end{vmatrix}$ |
| Equilibrium adsorption constant matrix | $\mathbf{K} = K_0 \begin{vmatrix} 1.0 & 0 & 0 \\ 0 & 1.2 & 0 \\ 0 & 0 & 16.4 \end{vmatrix}$ |

number of molecules of gaseous species $j$ in the grid; $N_{j,\mathrm{ex}}$ the number of molecules of species $j$ exiting the grid per simulation step; and $N_{j,\mathrm{ad}}$ the number of molecules of sorbed species $j$ in the grid.

## 3. Results and discussion

Xylene isomerizations are simulated in a $21 \times 21$ network and the parameters employed in the simulations are listed in table 1.

The dependences of the product selectivities of meta-xylene upon Thiele modulus $\phi$ for ortho- and para-xylene isomerizations are shown in figs. 1 and 2, respectively. The results show that the product selectivity $S_m$ is very high at lower Thiele modulus and decreases rapidly with the increase of $\phi$, and then approaches a cer-

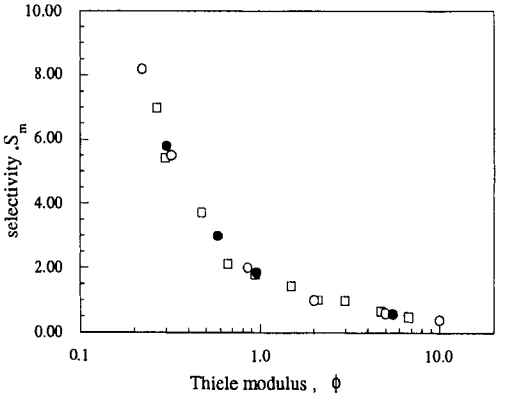


Fig. 1. Dependence of the selectivity of meta-xylene upon the Thiele modulus for ortho-xylene isomerization. (○) Continuous model [5]; (●) experimental [9]; (□) present work.

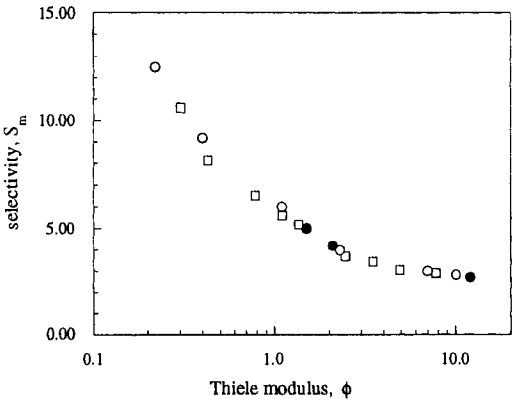


Fig. 2. Dependence of the selectivity of meta-xylene upon the Thiele modulus for para-xylene isomerization. (○) Continuous model [5]; (●) experimental [9]; (□) present work.

tain value when $\phi$ is high enough. This can be interpreted by conventional diffusion–reaction theory. When $\phi$ is lower, the reaction is not diffusion controlled, the product meta-xylene cannot be subjected to further reaction before it leaves the pores. As $\phi$ increases, the diffusion of meta-xylene is limited, the secondary reactions (meta- → ortho- and meta- → para-) take place distinctly and the selectivity $S_m$ decreases.

Fig. 3 shows how the selectivity of para-xylene $S_p$ changes with the Thiele modulus. $S_p$ approaches 1 at lower Thiele modulus and increases with the increase of $\phi$ and then approximates a certain value when $\phi$ is high enough.

Referring to figs. 1, 2 and 3, it can be seen that the results are satisfactorily consistent with those of the continuous model [5] as well as the experiments [9]. This suggests that the Monte Carlo model can be used to approach the diffusion and

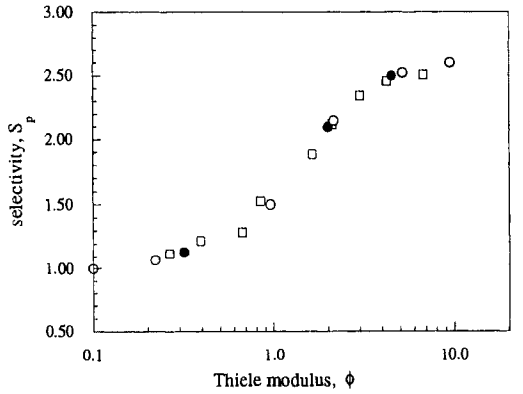


Fig. 3. Dependence of the selectivity of para-xylene upon the Thiele modulus for meta-xylene isomerization. (○) Continuous model [5]; (●) experimental [9]; (□) this work.

reaction in zeolite catalysts, and the shape selectivity is attributed to the diffusivity, equilibrium adsorption constant and the intrinsic rate constant of xylenes. As it is known, bot the equilibrium adsorption constant and the intrinsic rate constant are related to the surface acidity of zeolites and the intracrystalline diffusivity of molecules is pore structure dependent, therefore, the shape selectivity of the reactions is the result of the channel structure and the surface acidity of zeolite catalysts.

## 4. Conclusions

As is seen above, the application of the Monte Carlo method for investigating the elementary processes of adsorption, diffusion, reaction and desorption of molecules in zeolites is suitable. It can be used to examine the effects of adsorption, diffusion and reaction rate parameters, especially to examine the effects of the modifications of zeolites such as coke deposition, pore entrance deactivation upon the reaction performance. Thus, it is helpful for investigating the nature of shape selectivity in zeolite catalysis.

## Acknowledgement

The authors are grateful for the financial support of the National Natural Science Foundation of China.

## References

[1] R.H. Allen and L.D. Yats, J. Am. Chem. Soc. 83 (1961) 2799.
[2] W.T. Mo and J. Wei, Chem. Eng. Sci. 41 (1986) 703.
[3] J. Wei, J. Catal. 76 (1982) 433.
[4] K. Hashimoto, T. Masuda and Y. Hariguchi, J. Chem. Soc. Japan 3 (1989) 575.
[5] W.G. Liang, S.Y. Chen and S.Y. Peng, J. Catal. (China) 5 (1991) 369, 400.
[6] D. Theodorou and J. Wei, J. Catal. 83 (1983) 205.
[7] J.G. Wang, Y.W. Li, S.Y. Chen and S.Y. Peng, Catal. Lett. 24 (1994) 395.
[8] J.G. Wang, Y.W. Li, S.Y. Chen and S.Y. Peng, 93' ZMPC, 1993, 8, Japan.
[9] L.B. Young et al., J. Catal. 76 (1982) 418.