Monte Carlo simulation of complex isomerization. I. Effect of diffusivity on product selectivity

Jianguo Wang, Yongwang Li, Sonying Chen and Shaoyi Peng
Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

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A Monte Carlo method by which actual situations can be approached was developed. The complex isomerization A = B = C in a regular network was simulated, and the effects of intracrystalline diffusivities of molecules on the product selectivity were also investigated.

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

1. Introduction

The importance of zeolites as catalysts hardly needs to be emphasized. This, to a great extent, can be attributed to their shape selectivity. In spite of extensive research in the area and numerous applications of zeolite catalysts in industry for important reactions, such as xylene isomerization, toluene disproportionation, and alkylation of toluene with methanol, the nature of shape selectivity of these reactions is not well understood. A plausible explanation of para-selective phenomena can be based on the much higher intracrystalline diffusivity of para-xylene in relation to the other two isomers [1], and a quantitative theory of para-selectivity was presented [2]. But some reports showed that the diffusivity of para-xylene is only two to ten times higher than those of the other two isomers, and they believe that the para-selectivity is attributed to diffusivities, equilibrium adsorption constants and intrinsic rate constants of xylenes [3]. To study the nature of shape selectivity, investigating the surface acidic properties and channel structure of different modified zeolites separately in detail is of significance. Since all modifications, such as partial cation exchange, coke deposition, and impregnation with phosphorus and boron compounds, change both acidity and channel structure of zeolites at the same time, it is difficult to distinguish the contributions of diffusion, adsorption and intrinsic reaction in experiments. Theodorou and Wei [4] studied the diffusion and simple isomerization in a regular network using a Monte Carlo method. The result showed that this can be an efficient and self-consistent method for attacking problems of diffusion and reaction in zeolites. They did not consider the adsorption and the desorption of molecules. In fact, the most important difference between zeolites and other catalysts appears to be the absence of a free gas phase in the zeolite cavities. The gas phase terminates at the external surface of zeolite crystallites which contain the sorbed phase inside the channel.

In the present paper, considering the adsorption and the desorption of molecules at the border sites of the grid, a Monte Carlo method by which the actual situation can be approached was developed. The complex isomerization A = B = C was simulated, and the effects of intracrystalline diffusivities of molecules on the product selectivity were also investigated.

2. Assumptions and method

Some basic assumptions are used in addition to several original assumptions for the Monte Carlo method [4].

(1) The molecules which attach to the grid after the collision are free molecules. They can walk and react until they are adsorbed and change into the sorbed phase. Otherwise, they will stay at the same sites or exit the network.

(2) The product molecules can exit the network until they walk to the border of the network and desorb.

(3) The adsorption probabilities of all species are the same as well as the desorption probabilities.

(4) The intrinsic rate constants of the reaction in gas phase are the same.

The sequencing and coordination of events used in the Monte Carlo simulation is the same as in the paper of Theodorou et al. [4].

The results were treated with the following formulas:
global occupancy:

$$\Theta = (N_A + N_B + N_C + N_{A,ad} + N_{B,ad} + N_{C,ad})/(2N+1)^2 ,$$

Thiele modulus:

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

product selectivity:

$$S_B = N_{B,ex}/N_{C,ex} , \quad S_C = N_{C,ex}/N_{A,ex} ,$$

effectiveness:

$$\eta_A = N_{A,ex}/[k_0'(N_{B,ad} + N_{A,ad}D_A/D_B + N_{C,ad}D_C/D_B)] ,$$

$$\eta_B = N_{B,ex}/[k_0'(N_{A,ad} + N_{B,ex}D_B/D_A + N_{C,ex}D_C/D_A)] ,$$

where D_A, D_B, D_C are the effective intracrystalline diffusivities of species A, B, and C; k_0, k_0' are intrinsic rate constants of the reaction in gas phase and sorbed phase respectively; K_0 is the equilibrium adsorption constant; N is the grid size parameter; $N_{A,ex}$, $N_{B,ex}$, $N_{C,ex}$, denote the number of molecules of species A, B and C exiting the grid per step; $N_{A,ad}$, $N_{B,ad}$, and $N_{C,ad}$ are the numbers of molecules of sorbed A, B and C in the grid.

Table 1
Parameters employed in the simulations

Network dimension	21 × 21
Diffusivity matrices for A isomerization	$\mathbf{D}_1 = D_0\begin{vmatrix}1 & 0 & 1\\ 0 & 1 & 0\\ 0 & 0 & 1\end{vmatrix}$ $\mathbf{D}_2 = D_0\begin{vmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 10\end{vmatrix}$ $\mathbf{D}_3 = D_0\begin{vmatrix}1 & 0 & 0\\ 0 & 10 & 0\\ 0 & 0 & 1\end{vmatrix}$
for B isomerization	$\mathbf{D}_1 = D_0\begin{vmatrix}1 & 0 & 1\\ 0 & 1 & 0\\ 0 & 0 & 1\end{vmatrix}$ $\mathbf{D}_2 = D_0\begin{vmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 10\end{vmatrix}$ $\mathbf{D}_3 = D_0\begin{vmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 100\end{vmatrix}$ $\mathbf{D}_4 = D_0\begin{vmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1000\end{vmatrix}$
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 matrix	$\mathbf{K} = K_0\begin{vmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{vmatrix}$

3. Results and discussion

The complex isomerization A = B = C was simulated in a 21 × 21 network and parameters used in the simulations are listed in table 1.

3.1. A ISOMERIZATION

The dependence of the product selectivity S_B on the Thiele modulus ϕ for different $D_B : D_C$ was investigated (fig. 1). The results show that S_B is very high at lower ϕ and decreases with the increase of ϕ, and then toward a certain value when ϕ is

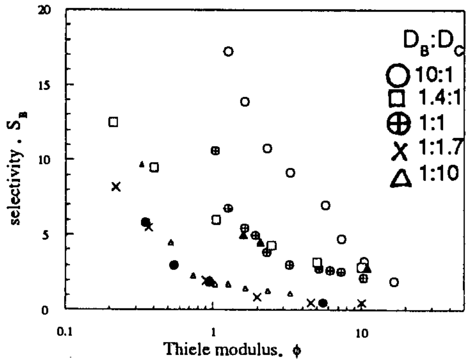

Fig. 1. Dependence of the selectivity of B on the Thiele modulus for different $D_B : D_C$. (□, X) continuous model [3]; (▲, ●) experimental [5].

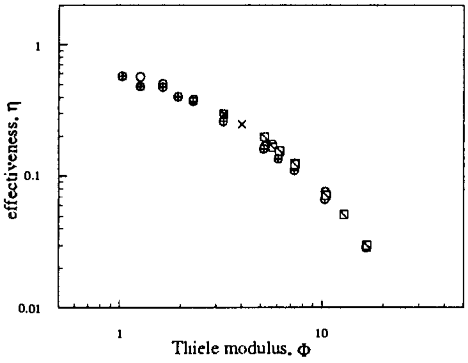

Fig. 2. Dependence of effectiveness on the Thiele modulus.

high enough. The selectivity S_B increases with the increase of $D_B : D_C$ at the same ϕ unless the ϕ is very high. This can be interpreted by conventional diffusion–reaction theory. When ϕ is lower, the reaction predominates over the diffusion so there is no diffusion resistance to mass transfer in the pores, the product B is not able to react further before it exits the pores. As ϕ increases, the diffusion of B is limited, the reaction rate $B \rightarrow C$ increases and the selectivity S_B decreases. When ϕ is very high, the effectiveness is very small as shown in fig. 2 and the reaction occurs at the border sites only, thus the effects of $D_B : D_C$ on selectivity disappear. Fig. 1 also shows that the simulation results are roughly consistent with the continuous model [3] and experimental results [5].

3.2. B ISOMERIZATION

Fig. 3 shows how the selectivity S_C is affected by $D_C : D_A$ and the Thiele modulus ϕ which is consistent with the results reported by McGreavy et al. [6]. S_C increases and then decreases with the increase of ϕ for all $D_C : D_A$ but $D_C : D_A = 1 : 1$, and $S_C \rightarrow 1$ when ϕ is very high for each intrinsic rate constant in

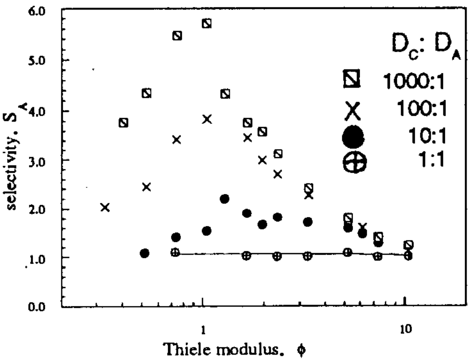

Fig. 3. Dependence of the selectivity of C on ϕ for different $D_C : D_A$.

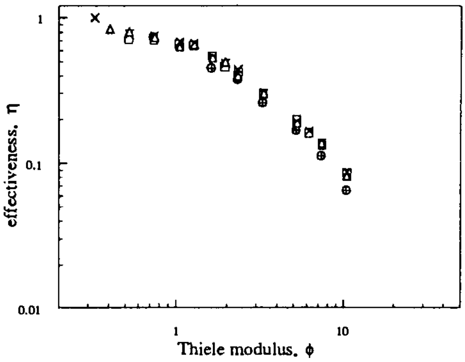

Fig. 4. Dependence of effectiveness on Thiele modulus.

the reaction is the same. The selectivity S_C also increases with the increase of $D_C : D_A$ at the same ϕ.

All above results show (1) increasing the difference of diffusivities of the species in reaction by proper modifications of catalyst, such as impregnation with some compounds, partial cation exchange, coke deposition, could improve dramatically the product selectivity; (2) the reaction should be operated under proper Thiele modulus in order to get a high para-selectivity.

4. Conclusions

The regularity of the selectivity on the Thiele modulus for the different ratios of diffusivity of species is consistent with the continuous theory and experiments. This shows that the Monte Carlo method developed in the present paper can be useful for studying the nature of shape selectivity and catalyst design though a quantitative consistence with experiments needs further study.

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