Mastering simultaneous reaction and diffusion through Single Event Microkinetic modeling of n-alkane hydroconversion on Pt/H-ZSM-5

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Introduction

The shape selective catalysis based on ZSM-5 zeolite has found widespread application (1,2) in refining and petrochemical industry since long time. The product distribution associated with hydrocracking and hydroisomerization processes on ZSM-5 are predominantly controlled by the pore geometry and component diffusion. The various aspects of diffusion inside ZSM-5 pore structure have been widely covered in the literature (1,3) in the absence of reaction. On the other hand, detailed kinetic models generally make use of a simple diffusion model. With the augmentation of computational power, molecular modeling tools like Monte Carlo simulations are popularly performed nowadays (3,4 and the references therein) considering both diffusion and reactions in a zeolite matrix though these methods are yet to be established in relevant time scales. To understand the simultaneous shape selectivity effects on diffusion and reaction in ZSM-5 in a fundamental way, the detailed modeling of both the aspects is required. In the present work, a kinetic model has been developed for *n*-alkane hydroconversion on Pt/H-ZSM-5 using the single event microkinetic (SEMK) methodology along with a detailed multi-component diffusion model. It accounts explicitly for the pore structure by distinguishing between physisorption of branched and non-branched alkanes. The pore connectivity enters into the model via its effect on the occupancy of the active sites in determining the values of the diffusion coefficients. The model is validated with n-hexane hydroconversion data on Pt/H-ZSM-5 catalyst and allows to describe the differences of the of the product distribution when compared to Pt/H-USY.

Procedures

The Pt/H-ZSM-5 catalyst used in the experiments is synthesized according to a recipe described elsewhere (5) having a Si/Al ratio of 137. The average crystal size is 0.5 µm. For catalytic testing, the zeolite powder is shaped into pellets and calcined ex-situ under flowing oxygen at 823 K for one hour. The catalyst was reduced with hydrogen at 673 K during 4 hours before experimentation. The n-hexane hydroconversion experiments are performed in a Berty type CSTR set-up by varying the feed flow rate at different temperature, pressure and H_2/HC values. The outlet product flow rates are determined from the GC analysis using methane as internal standard.

The estimation of the kinetic parameters is performed by minimization of the weighed sum of squares of the residuals between the observed and the calculated outlet flow rates. The ordinary least square (OLS) option of the ODRPACK- package version 2.01 is used for that purpose. The model responses for experiment i are calculated from the following molar balance equation for each component j of the reacting mixture except the feed component and hydrogen which are calculated through subsequent carbon and hydrogen balances:

$$F_{i,j} - F_{i,j}^{0} - R_{i,j} W_i = 0 \qquad [1]$$

The set of algebraic equations [1] is solved using the routine DNSQE obtained from the NETLIB software library (6).

SEMK model for hydroconversion on Pt/H-ZSM-5 catalyst

A widely accepted bi-functional reaction mechanism is followed (7). The concentration of physisorbed alkanes is calculated by the multicoponent Langmuir (MCL) expression for physisorption:

$$C_{P_i} = \frac{K_{L,i} C_{P_i}^{sat} p_i}{1 + \sum_{j=1}^{n} K_{L,j} p_j} \qquad [2]$$

The carbon number dependence of physisorption parameters for linear and branched alkanes, as reported by Denayer et al (8) for vapor phase physisorption at high temperature, is considered in the present work. The occupancy by individual species is calculated as:

$$\theta_i = \frac{C_{P_i}}{C_{P_i}^{sat}} \qquad [3]$$

The configurational diffusion inside the ZSM-5 pore network is most fundamentally described by the self diffusion. The self diffusion coefficient is assumed isotropic in the zeolite lattice and it is characterized by the activated jump of physisobed molecules between the channel and intersection sites. The frequencies of the activated jumps depend on the sorbate concentration as well as on the strength of the acid sites and the distribution between weak and strong sites as described by Coppens et al. (9). The mean field approximation which implies that the activated jumps are uncorrelated, is considered in developing the equations and results in a qualitatively good match with the Dynamic Monte Carlo studies (10). The concentration dependence of self diffusivity of a single component is thus calculated to be a function of 1) species occupancy, θ_i of different types of sites: channel (α) or intersection (βw / βs) determined from lattice representation; 2) fraction of strong sites (f) which is function of acid site concentration and depends on Si/Al ratio and 3) relative adsorption strengths on the sites (τ_s/τ_w), a function of sorption properties of the component. In a similar way, the self diffusion coefficient $D_{s,i}^{\theta}$ for other components can be calculated by considering the topology of ZSM-5 pore network as well as the lattice heterogeneity in a generalized way.

In the case of the multicomponent mixture a correlation exists between species of different mobilities which can be modeled by considering inter species diffusivity through the Stefan-Maxwell formulation as developed by Krishna et al (3). In the development of the model for a multicomponent mixture, it is assumed that the concentration dependency of the single component self diffusion coefficients still holds. Hence, the corrected diffusivity, $D_{c,i}$ for each component can be calculated from the single component self diffusion coefficient in a multicomponent environment (11).

$$\frac{1}{D_{s,i}^{\theta}} = \frac{1}{D_{c,i}} + \sum_{j=1}^{n} \frac{\theta_j}{D_{i,j}} \qquad [4]$$

D_{ij} is the inter species diffusivity between pair of components i and j and is calculated in the model as an extension of Vignes logarithmic interpolation formula for binary mixture (11).

$$D_{ij} = D_{c,i}^{\frac{\theta_i}{(\theta_i+\theta_j)}} D_{c,j}^{\frac{\theta_j}{(\theta_i+\theta_j)}} \qquad [5]$$

The set of non-linear equations [4] in $D_{c,i}$ are solved by hybrid powell method from NETLIB library to calculate corrected diffusivity for each component in multicomponent environment as a function of species occupancy. Although the corrected diffusivity and the inter species diffusivities should be calculated at each iteration for a given dependency of the surface concentration, it is found sufficient to calculate these diffusivities once for a set of representative surface concentrations.

The Stefan Maxwell formulation relates the component flux with the gradient of chemical potential, $\nabla\mu$ but it is much convenient to “factor out” the thermodynamic effect from the corrected diffusivity, $D_{c,i}$ and use the fluxes with concentration gradient (12):

$$[N] = -\rho[C^{sat}][B]^{-1}[\Gamma][\nabla\theta] \qquad [6]$$

Where, $[N]$ is the matrix of component flux, $[C^{sat}]$ is the diagonal matrix for the saturation concentration of the species, $[B]^{-1}$ is the inverse of drag coefficient matrix as calculated by eq. [7] in Stefan Maxwell formulation and $[\Gamma]$ is the matrix of thermodynamic factors calculated from adsorption isotherm (12). The product of $[B]^{-1}$ and $[\Gamma]$ gives the matrix for effective diffusion coefficients in a multicomponent environment which contains the correlation between diffusivities of individual species as discussed later in more details.

$$B_{ii} = \frac{1}{D_{c,i}} + \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\theta_j}{D_{ij}}$$

$$B_{ij} = -\frac{\theta_i}{D_{ij}}, \qquad i \neq j \qquad [7]$$

$$\Gamma_{ij} = \frac{\theta_i}{p_i}\frac{\partial p_i}{\partial \theta_j} \qquad i, j = 1, n \qquad [8]$$

The n-alkane hydroconversion reaction mechanism for Pt/H-ZSM-5 is considered in terms of “free carbenium ion chemistry” similar to that of Pt/USY, so the reaction rates of the rate-determining steps are expressed as follows (13):

$$r_{AS/PCP/\beta}(m_1, m_2) = \frac{C_t \frac{\sigma_{O_{i,j}}}{\sigma_{\neq}} \tilde{k}_{AS/PCP/\beta}(m_1, m_2)\tilde{K}_{isom}(O_{i,j}; O_r)\tilde{K}_{prot}(m_1)K_{deh}(P_i; O_{i,j})C_{P_i}^{sat}K_{L,i}\frac{p_i}{p_{H_2}}}{\left(1 + \sum_i K_{L,i}p_i + \sum_{i=1}^{npar}\sum_{j=1}^{nole_i} \frac{\sigma_{O_{i,j}}}{\sigma_{R_{i,k}^{+}}} \tilde{K}_{isom}(O_{i,j}; O_r)\tilde{K}_{prot}(m_1)K_{deh}(P_i; O_{i,j})C_{P_i}^{sat}K_{L,i}\frac{p_i}{p_{H_2}}\right)} \qquad [9]$$

The net rate of formation of an alkane P_i is calculated from the rates of formation and disappearance of the corresponding alkylcarbenium ions vide eq. [9] and the net rate of formation of alkenes directly formed via the β-scission reactions.

The concentration profile inside the crystallite is obtained by solving the species balance equations in unsteady-state:

$$[C^{sat}]\frac{\partial[\theta]}{\partial t} = -\frac{1}{r^s}\frac{\partial}{\partial r}\left(r^s[N]\right) + [R] \qquad [10]$$

$[N]$ is substituted from eq. [6], s is the particle shape factor (s=0, 1, 2, for slab, cylinder and sphere respectively) and $[R]$ is the column vector for the net production rate of n components, calculated as discussed above. The set of PDEs are discretized in the model at some pre-defined grid points along the diffusion length of the crystallite and the resulting ODEs are then solved by DVODE subroutine from NETLIB library till the steady state is reached. The net production rate for each component at the catalyst surface used in eq. [1] are obtained by computing numerical integration of the rates calculated at each grid points along the length of the crystallite.

Results and Discussion

The developed SEMK model has been applied for n-hexane hydroconversion on Pt/H-ZSM-5 catalyst. The multicomponent adsorption and diffusion, as described in previous section, are sufficient to model the observed shape selectivity phenomena in nC_6 hydroconversion. In contrast to heavier components, where the transition state shape selectivity is important, for n-hexane, the reactant and product shape selectivity is dominant.

The reaction network for nC_6 hydroconversion consists of 6 components, viz. 2 methyl pentane (2mp), 3 methyl pentane (3mp), 2,2 di methyl butane (2,2 dmb), 2,3 dimethyl butane (2,3 dmb) and n-propane besides the feed component. The reported values of the self diffusion coefficients in literature vary with the measurement techniques and experimental conditions used (14). So, it is important to use the diffusion coefficient values for different components measured by similar methods and conditions. In the present work, the self diffusion coefficients as measured by TEX-PEP method (14,15) for n-hexane, iso pentanes and n-propane are used. As there is no such measurement for dimethyl butanes, the values calculated by Post et al. (3) have been considered. A typical concentration profile inside the crystallite is shown in *Figure 1* which reflects the typical effects of the simultaneous occurrence of diffusion and reaction.

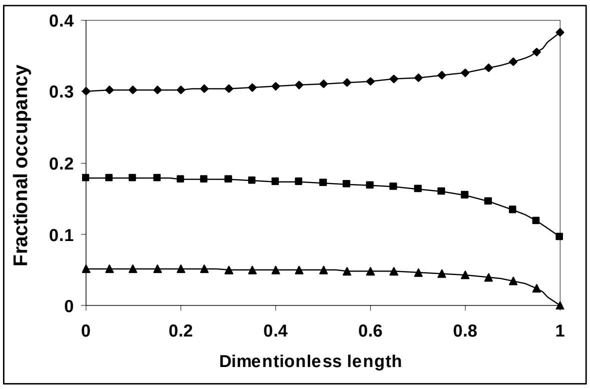

Figure 1: Concentration profile as a function of length of the ZSM-5 crystallite calculated by the SEMK model, vide eqs [2]-[8] at T = 503 K, P = 1.0 MPa, molar H_2/HC ratio = 50 and

W/F^0_{HC}: 96 kg-s/mol; feed composition : (nC_6 : 2mp: 3mp = 50: 20:30) ; symbols: (♦)nC_6, (■) 2mp, (▲) 2,2 dmb; crystallite length =0.5 µm

The correlation between diffusivities of different species is incorporated via the inter species diffusivity $Đ_{ij}$ through the matrix $[B]^{-1}$ as well as by the matrix of thermodynamic factor $[\Gamma]$ and illustrated through the concentration profiles shown in *Figure 2*. In absence of the correlation effects, the component diffusivities are independent of each other and the matrix $[B]^{-1}[\Gamma]$ vide eq. [6] takes the form of diagonal matrix in terms of the so-called "Fickian" diffusivites. In that case, as the fractional occupancy by nC_6 along the crystallite length is not influenced by the diffusion of other components in the mixture, at steady state, the occupancy by nC_6 inside the crystallite remains equal to its occupancy at the external surface as shown in *Figure 2(a)*. As a result, an increase in the net formation of the product species inside the crystallite is observed. The correlation between species diffusivities is found to be dominated by the matrix of thermodynamic factor $[\Gamma]$ as the concentration profiles are hardly changed vide *figure 2(b)* in absence of the inter species diffusivities.

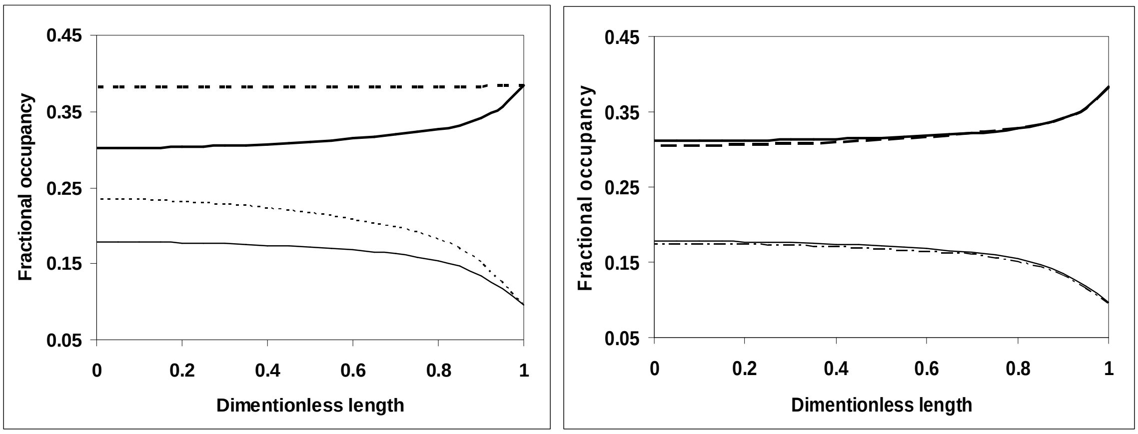

Figure 2: Concentration profile as a function of length of the ZSM-5 crystallite describing a) effect of correlation between component diffusivities, b) effect of inter species diffusivities calculated by the SEMK model, vide eqs [2]-[8] at T = 503 K, P = 1.0 MPa, molar H_2/HC ratio = 50 and W/F^0_{HC}: 96 kg-s/mol; feed composition : (nC_6 : 2mp: 3mp = 50: 20:30) ; lines: (full line) present model, (dashed line) in absence of the correlation between component diffusivities, (long-dashed line) present model in absence of the inter species diffusivity, i.e. $Đ_{ij} \rightarrow \infty$; (thick lines) nC_6, (thin lines) 2mp; crystallite length =0.5 µm

The dependency of diffusion coefficients on sorbate concentration is substantial which mainly affects the conversion rather than the product distribution, vide *Figure 3*.

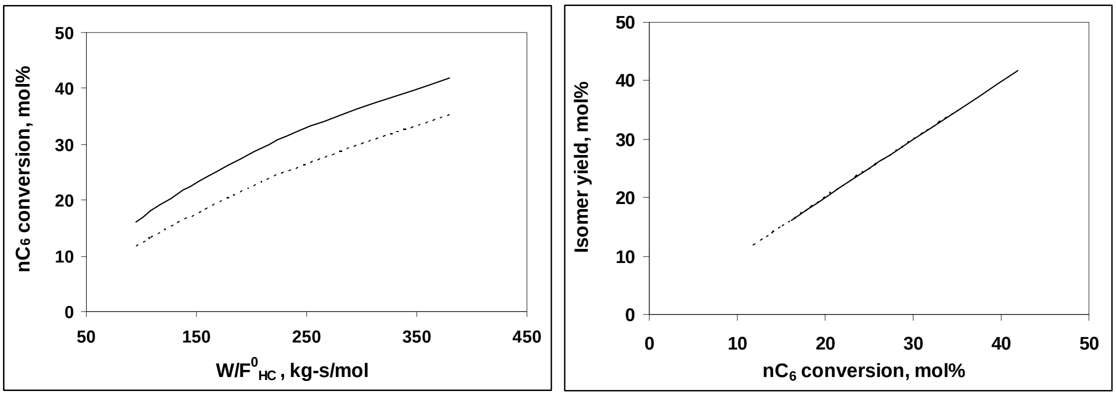

Figure 3: a) nC_6 conversion as a function of W/F_{HC}^{0} , b) total isomer yield as a function of nC_6 conversion calculated by the SEMK model, vide eqs [2]-[8] at T = 503 K, P = 1.0 MPa and molar H_2/HC ratio = 50; lines: (full line) strong dependence of the self diffusion coefficients on sorbate concentration, (dashed line) in absence of the concentration dependence

The nC_6 hydroconversion data on Pt/H-ZSM-5 catalyst at 503 K, pressure levels 2.0 and 3.0 MPa and molar H2/HC ratio 50, 75 and 100 at varying W/F_{HC}^{0} are used to estimate the model parameters through regression. In the present work, only protonation enthalpies for formation of secondary and tertiary carbenium ions are estimated while the activation energies corresponding to “free carbenium ion chemistry” and the self diffusion coefficients are taken from the literature (13-15). An estimated value of -67.41 ± 0.89 kJ mol^{-1} which is about 2.48 kJ mol^{-1} more negative compared to a reference USY catalyst are obtained for protonation enthalpy of secondary carbenium ion. As the dibranched isomers are practically absent in the experimental data, the protonation enthalpy for tertiary carbenium ions could not be estimated properly. Hence its value was taken equal to that of the reference USY catalyst (13). The parity diagrams for 2mp and 3mp vide *Figure 4* show a good fit of the experimental data within a band of 15%. Though the total isomer yield is well calculated by the model, the 2mp isomer selectivity is found to be slightly over predicted. The model calculations may be further improved by considering differences in physisorption parameters between individual isomers besides a consideration for the transition state shape selectivity which may already be taking place for nC_6 hydroconversion.

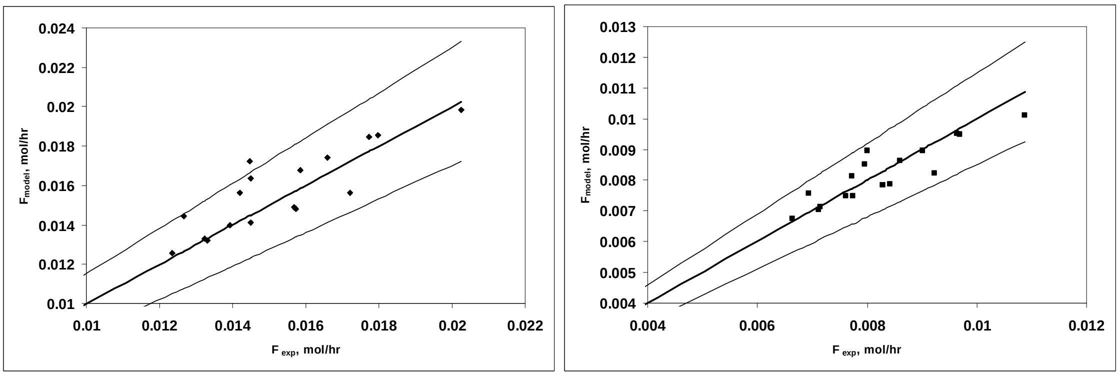

Figure 4: Parity diagrams for a) 2mp and b) 3mp flow rates calculated by the SEMK model with estimated parameters at T = 503 K, P = 2.0 and 3.0 MPa and molar H_2/HC ratio = 50,75 and 100; symbols: (♦)2mp, (■) 3mp; The calculated flow rates lies within a range of ± 15%

Conclusions

A kinetic model is developed for n-alkane hydroconversion on Pt/H-ZSM-5 catalyst combining a detailed multicomponent diffusion model and a reaction mechanism through application of the single event microkinetic approach. The concentration dependency of the diffusion coefficients in a multicomponent mixture is described in a consistent way in terms of single component self diffusion coefficient at zero occupancy. The nC_6 hydroconversion data can be well described by the model by estimating only the protonation enthalpies. The model can be used for understanding sorption and diffusion induced shape selectivity in hydroconversion on ZSM-5 zeolites and other medium pore zeolites having similar structure.

References

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