Analysis of Diffusion and Reaction in the Alkylation of Benzene over H-ZSM-5 by Combining Quantum Chemical Calculations, Molecular Simulations and a Continuum Approach

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In the present study the framework of the Maxwell-Stefan (M-S) equations adapted to diffusion in zeolites, combined with an appropriate theory to describe multicomponent adsorption equilibrium is applied to the industrially relevant gas phase alkylation of benzene with ethane in order to get insights into how diffusional limitations affect the observed macroscopic behaviour of the reaction system. To make these simulations predictive as many parameters as possible needed to solve the system of differential equations are determined from molecular simulations, quantumchemical calculations, and transition state theory. A continuum model is proposed to calculate the intrinsic rate of reaction as function of the local concentration at the active sites that takes the unique pore structure of MFI into account.

The first step of the study was the elucidation of the reaction mechanism using density functional theory (DFT) on cluster models of the active site. For this purpose three different reaction mechanisms – two one-step schemes and on two-step scheme – were studied on three cluster models of progressively larger size. In the one-step schemes ethylene protonation and C-C bond formation occur simultaneously. The two-step scheme starts with the formation of a stable ethoxide intermediate which subsequently reacts with benzene to form the reaction product. As the present DFT functionals cannot describe van der Waals interactions accurately, activation energies obtained from DFT results were improved by single-point MP2 calculations. The calculated intrinsic activation energies of the one-step schemes are similar to the activation energy of the alkylation step in the two-step scheme. Numerical values of the MP2 corrected activation energies are in reasonable agreement with experimental data. The largest cluster (33 T-atoms) was found to stabilize protonated ethylbenzene as a stable intermediate [1].

We employ a MP2/DFT multilevel approach [2] to improve the rate coefficients obtained from DFT cluster calculations. This includes the re-optimization of all stationary points obtained with DFT cluster calculations within the full unit cell using plane wave DFT with periodic boundary conditions. Subsequent MP2 and DFT calculations on cluster models of increasing size cut out from the plane wave DFT-optimized unit cell are then used to estimate the missing dispersion interaction by fitting the difference between MP2 and DFT reaction energies to an analytical dispersion term. Moreover, the basis set incompleteness is accounted for by extrapolating MP2 energies obtained with basis sets of increasing size towards the complete basis set limit. Rate coefficients obtained in this way are more likely to be quantitative accurate than those obtained from DFT cluster calculations.

In order to parameterize the M-S equations, molecular dynamics (MD) simulations were carried out for pure ethane in MFI and for ethene-benzene and ethane-ethylbenzene mixtures at a variety of loadings and temperatures. The adsorption isotherms of all species have been obtained from Monte Carlo (MC) simulations in the grand canonical ensemble. For calculating mixture adsorption isotherms the Ideal Adsorption Solution Theory (IAST) [3] was used.

The performance of the proposed continuum model is evaluated by comparing simulation results to kinetic measurements reported in the literature. Experimental activation energies and turnover frequencies are in good agreement with simulated data. Moreover, the continuum model allows investigating separately the influence of (i) the mixture adsorption equilibrium, (ii) the pore architecture, and (iii) the degree of diffusion limitation on the macroscopic reaction orders. The adsorption equilibrium of ethane-benzene mixtures under the industrially relevant process conditions is the first important factor responsible for the difference in the macroscopic reaction orders with respect to ethane and benzene partial pressures. The pore architecture mainly affects the reaction order with respect to the benzene partial pressure. In the absence of diffusion limitation the model predicts an almost first order dependence of the reaction rate on the ethane partial pressure while the exponent associated with the benzene partial pressure is less than 0.5. Diffusion limitation considerably affects the reaction orders. The simulated values of around 0.8 for ethane are in gook agreement with experimental data. For benzene the reaction order depends on the temperature and pressure range in which it is determinded. It ranges from slightly negative to slightly positive values. The results of this study show that neither Langmuir-Hinshelwood expressions nor empirical power laws offer the flexibility to correlate kinetic measurements of this reaction over a wide range of partial pressures and temperatures. The main reason for this is the deviation from the assumptions in the meanfield approach. Moreover it is demonstrated that the effectiveness factors predicted from the continuum model are smaller than those calculated using the conventional definition of the Thiele modulus. The results have been published [4].

References

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