

Diffusion limitation in the alkylation of benzene - A multiscale investigation

Niels Hansen^{1*}, Rajamani Krishna², Jasper M. van Baten², Alexis T. Bell^{3*}, and Frerich J. Keil¹

¹Hamburg University of Technology, 21073 Hamburg, Germany

²Van't Hoff Institute for Molecular Sciences, University of Amsterdam, 1018 WV Amsterdam, The Netherlands

³University of California, Berkeley, California 94720-1462, USA

*n.hansen@tu-harburg.de; *bell@cchem.berkeley.edu

Introduction

Gas-solid-reactions in porous media are taking place via a number of elementary steps that are (i) entrance of the reactants in the pore, (ii) multicomponent diffusion towards the active site, (iii) adsorption on the active site, (iv) reaction, (v) desorption of the products from the active site, and (vi) multicomponent diffusion of the products back to the bulk phase. In zeolite catalysis the kinetic diameter of reactants is often of similar size as the pore diameter. This leads to strongly confined reactants and/or products. When modelling these processes special care has to be taken of a proper description of the multicomponent diffusion combined with reaction kinetics. Both of these rate phenomena are strongly dependent on the pore topology and are unique for a certain zeolite. Due to the complicated nature of the diffusion process the real effectiveness factors for zeolite catalysed reactions are often smaller than those estimated by means of the conventional Thiele modulus [1].

In the present study all parameters describing the elementary processes adsorption, diffusion and reaction involved in the alkylation of benzene with ethene were obtained using theoretical approaches such as molecular simulations and quantum chemical calculations. These data were then used in a continuum model to simulate the overall activity of a H-ZSM-5 catalyst particle on the basis of which reactor simulations are performed in order to study and optimize operating conditions for this reaction.

Materials and Methods

The present study utilizes data from quantum chemical calculations carried out at the DFT and MP2 level with the QM-packages TURBOMOLE and VASP. Rate constants were calculated using transition state theory. Molecular dynamics simulations were performed with the DL_POLY code. For Monte Carlo simulations the BIGMAC code was used. A more detailed description of all methods employed can be found in references [2,3].

Results and Discussion

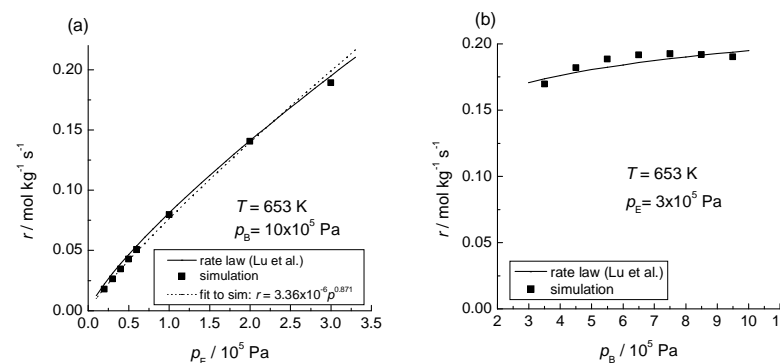
The performance of the proposed continuum model is evaluated by comparing simulation results to kinetic measurements reported in the literature. In the absence of diffusion limitation the model predicts an almost first order dependence of the reaction rate on the ethene partial pressure while the exponent 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 ethene are in good agreement with experimental data. For benzene the reaction order depends on the temperature and pressure range in which it is determined. 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. 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.

Significance

The present study uses for the first time a purely theoretical approach to obtain insights into a zeolite catalyzed reaction which are of both fundamental and practical relevance. On the fundamental level a new attempt is proposed to link results of quantum chemical calculations to a continuum model for reaction and diffusion. From the practical point of view the simulation results can be used to find optimized operation conditions for the alkylation and to guide experimental investigations of this reaction.

Figure 1. Simulated and experimental rates per unit mass of catalyst for the alkylation of benzene with ethane. (a) constant benzene partial pressure; (b) constant ethene partial pressure. The experimental data were calculated using the data of Lu et al. [4].



References

1. Baur, R., Krishna, R. *Chem. Eng. J.* 99, 105 (2004).
2. Hansen, N., Brüggemann, T., Bell, A. T., Keil, F. J., *J. Phys. Chem. C* 112, 15402 (2008).
3. Hansen, N., Krishna, R., van Baten, J. M., Bell, A. T. Keil, F. J. *J. Phys. Chem. C* in press.
4. Lu, M., Wu, Y., Zhu, Z., Sun, H., Chen, Q. *Petrochemical Technol. (China)* 30, 182 (2001).