P76

First principle study on the kinetics of zeolite-catalyzed methylation reactions

Jeroen Van der Mynsbrugge, Michel Waroquier and Veronique Van Speybroeck
Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium

Catalytic conversion of methanol to light olefins (MTO) over acidic zeolites is currently one of the most prominent alternatives to traditional crude oil cracking processes for the production of ethene and propene. Despite many research efforts from both experimental and theoretical groups, the underlying reaction mechanisms have been under debate for decades. [1] Instead of following direct C-C coupling routes, MTO conversion was found to proceed through an indirect hydrocarbon pool mechanism. [2] The hydrocarbon pool consists of a variety of aromatic and aliphatic compounds acting as co-catalysts inside the zeolite pores. Depending on the characteristics of the zeolite material, polymethylbenzenes or alkenes are the predominant hydrocarbon pool species. [3] Repeated methylation of the hydrocarbon pool compounds and subsequent elimination and/or cracking reactions lead to the formation of light olefins. Theoretical studies identified several olefin-producing catalytic cycles and showed that methylation reactions are generally the rate-determining steps in the MTO-process. [4,5]

As it is very difficult to obtain experimental kinetic data on individual reaction steps, there is an ongoing interest in accurate determination of barriers and rate constants using theoretical methods. [6] Focusing on methylation reactions of hydrocarbons present inside the zeolite pores during MTO-conversion, the current study uses quantum chemical calculations on extended cluster models to obtain reaction barriers and rate constants that are comparable to experimental data. The balance between accuracy and computational efficiency signifies this approach as an important step toward routine ab initio prediction of rate constants in heterogeneous catalysis.

[1] Stocker, M., Micro. Meso. Mater., 29 (1999) 3
[2] Lesthaeghe, D., Van Speybroeck, V., Marin, G.B., Waroquier, M., Angew. Chem. Int. Ed. 45 (2006) 1714
[3] Olsbye, U., Bjørgen, M., Lillerud, K.-P., Kolboe, S., Catal. Today 106 (2005) 108
[4] McCann, D.M., Lesthaeghe, D., Kletnieks, P.W., Guenther, D.R., Hayman, M.J., Van Speybroeck ,V., Waroquier, M., Haw, J.F., Angew. Chem. Int. Ed. 47 (2008) 5179
[5] Lesthaeghe, D., Van der Mynsbrugge, J., Vandichel, M., Waroquier, M., Van Speybroeck, V., ChemCatChem (2010) DOI: 10.1002/cctc.201000286
[6] Van Speybroeck, V., Van der Mynsbrugge, J., Vandichel, M., Hemelsoet, K., Lesthaeghe, D., Ghysels, A., Marin, G.B., Waroquier, M., J. Am. Chem. Soc. (2010) in press

E-mail: jeroen.vandermynsbrugge@ugent.be
www: http://molmod.ugent.be