

First principle kinetic studies of zeolite-catalyzed methylation reactions : Towards kinetic accuracy for rate constants

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The theoretical determination of rates of chemical reactions taking place in nanoporous materials remains a challenge, despite the rapid evolutions witnessed in the recent years in computational molecular modeling. The rate is governed by an energetic and entropic contribution, determining the activation energy and preexponential factor, respectively. In this contribution methylations of ethene, propene and butene by methanol over the acidic microporous H-ZSM-5 catalyst are studied by means of state of the art computational techniques, to derive Arrhenius plots and rate constants from first principles that can directly be compared with the experimental data. For these key elementary reactions in the methanol to hydrocarbons (MTH) process, direct kinetic data became available only recently [1]. At 350 °C apparent activation energies of 103, 69 and 45 kJ/mol and rate constants of $2.6 \cdot 10^{-4}$ mol/(g h mbar), $4.5 \cdot 10^{-3}$ mol/(g.h.mbar) and $1.3 \cdot 10^{-2}$ mol/(g.h.mbar) for ethene, propene and butene were derived, giving following relative ratios for methylation kethene:kpropene:k butene=1:17:50.

For the theoretical calculations, the topology of the material was taken into account by a cluster approach in which a finite cluster was cut from the periodic materials structure [2,3]. Dispersive interactions have been found to be very important to describe accurately the adsorbed states and thus also to describe “apparent kinetics”. The theoretically determined rate constants are in very good agreement with the experimental data : apparent activation energies of 94, 62 and 37 kJ/mol for ethene, propene and butene are found and relative ratios of methylation kethene:kpropene:k butene=1:23:763. The absolute values of the rate constants are very close to the experimental values and reach “kinetic accuracy” (deviations of less than a factor 10). The proposed method is computationally very attractive and can be applied routinely on reaction cycles applicable in heterogeneous catalysis. This is a huge step forward for theoretical predictions of zeolite-catalysed reactions and it shows that theoretical methods viable alternative to estimate kinetics of elementary reactions that cannot easily be monitored experimentally

[1] Svelle, S.; Rønning, P.O.; Olsbye, U.; Kolboe, S.; J. Cat., 234, 385-400 (2005); Svelle, S.; Rønning, P.O. Kolboe, J. Cat., 234, 115-123, (2004).

[2] 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. (2008), 47, 5179-518

[3] Van Speybroeck, V. et al., submitted to the Journal of the American Chemical Society.

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