

## Microkinetic Model Construction with Significant Parameter Estimation

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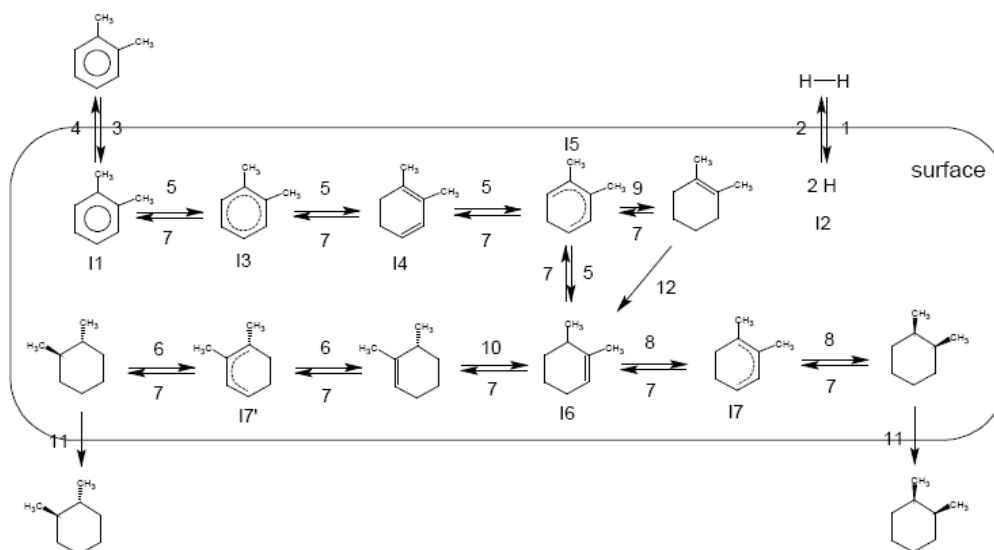
Microkinetic models allow accounting fully for the chemistry of a corresponding process by including all possible elementary steps. However, there are still challenges to be dealt with regarding the construction of such complex networks in general and the determination of a large number of parameters in particular [1]. By working with an in-house software tool, the so-called  $\mu$ kinetic engine ( $\mu$ KE), significant advances have been made in the development of a generic methodology for microkinetic model construction. The step-wise incorporation of additional detail and corresponding model parameters in the considered reaction network rather than the immediate evaluation of complex networks and correspondingly high number of adjustable parameters are essential for an efficient network construction and significant parameter determination.

The methodology has been applied to the gas phase hydrogenation of o-xylene hydrogenation on a Pd catalyst with experimental data acquired from high-throughput experimentation [2]. The assessment of data on other catalysts is straightforward and allows comparing the obtained parameter values and, hence, the interpretation of the reaction mechanism on each of these catalysts. To describe the reaction network with a power law model, only 2 steps are necessary. By adding o-xylene adsorption, the network expands to 4 steps in total and step-by-step a reaction network including 27 steps is obtained [Figure 1]. From a certain degree of detail onwards, the model fitting does not significantly improve anymore and, hence, it becomes practically impossible to significantly estimate all parameters. Transition state theory in combination with appropriate assumptions on changes in degrees of freedom of the species involved in the reaction can be used to calculate values for the pre-exponential factors. Further reduction of the number of parameters to be eliminated by regression can be achieved by using quantumchemically calculated reaction

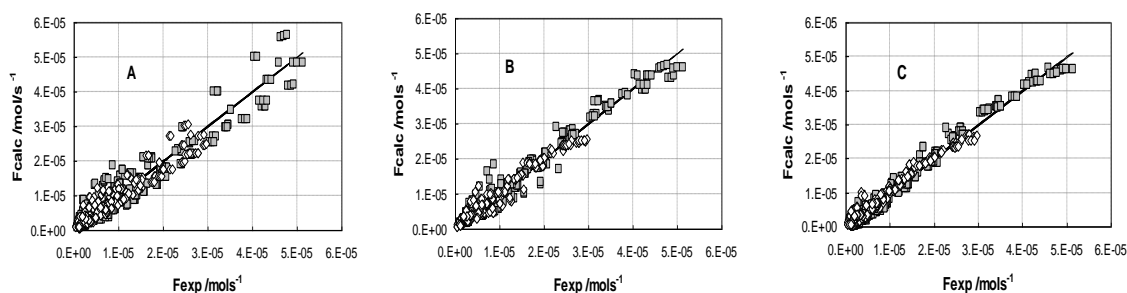
enthalpies or activation energies [3]. In this way, the fitting finally obtained is very good [Figure 2] maintaining physico-chemical meaningful values for the estimated parameter values.

## References

- [1] W.H. Green, Adv. Chem. Eng., v32, 2007.
- [2] G. Morra, A. Desmartin-Chomel, C. Daniel, U. Ravon, D. Farrusseng, R. Cowan, M. Krusche, C. Mirodatos, Chem. Eng. J., 138(1-3) (2008) 379.
- [3] M. Saeys, M.-F. Reyniers, J.W. Thybaut, M. Neurock, G.B. Marin, J. Catal., 236 (2005) 129.



**Figure 1:** Microkinetic reaction network showing the different reaction intermediates (I) and elementary steps involved in o-xylene hydrogenation.



**Figure 2:** Parity diagrams of the cis (◇) and trans (▣) isomer outlet molar flow rates using a power law model (A), a LHHW model including o-xylene hydrogenation (B) and a microkinetic model (C).