

Public summary of PhD-thesis of Roderigh-IJsbrand Rohling

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Optimizing nanoreactors for sustainable feedstock for next-generation plastics

Biomass is an appealing alternative source for the depleting fossil resources for the production of aromatic compounds, which are intermediates for the production of plastics. In this theoretical study, we elucidated the Diels-Alder Cycloaddition(DAC)/Dehydration(D) reaction mechanism to obtain aromatics from biomass-derived furanics and ethylene, using zeolite-based catalysts. We significantly improved the conventional description of the zeolite catalyst model and were able to add important refinements to the current zeolite-reactivity theory.

Ideally, chemicals produced from biomass should directly be compatible with existing petrochemical processes. This approach circumvents new major capital investments. A group of such ideal chemicals are aromatic compounds, which are important intermediates for the production of polymers applied in plastics.

A promising route for biomass-based production of aromatics is the DAC/D reaction of biomass-derived furanics with ethylene, with a zeolite as catalyst. Furanics are the starting point as they can easily be obtained from biomass. The first DAC reaction step is a much used reaction that gained the discoverers the 1950 Nobel Prize. Zeolites are molecular sieves which can catalyze chemical reactions within their molecularly sized pores. However, the reaction mechanism and factors determining the zeolite activity in the conversion of bio-derived furanics to aromatics were not understood yet.

This dissertation provides insight into these by using the computational quantum chemical modelling method 'density functional theory'. In our work, the chemical description of the actual catalyst was improved by accounting for the high active site density in the zeolite, as opposed to conventional modelling efforts that focus on a single active site only.

We studied the DAC/D reaction of 2,5-dimethylfuran with ethylene to produce the aromatic para-xylene over alkali-exchanged faujasite zeolites. The results show that the cooperative action of multiple closely packed active sites in the zeolite lowers reaction barriers as compared to the conventional isolated active site model. We performed microkinetic computer modelling simulations to predict the catalyst reactivity trend, which was confirmed by experiments. Crucially, we found that the studied catalysts are highly active, as opposed to the existing hypothesis, which disregards these catalysts.

Furthermore, we discovered that the improved DAC reactivity is caused by confinement of the reactants, interacting with multiple active sites in the zeolite pores via electrostatic interactions. The sites collaborate to pre-organize the reactants and push them together such that the molecules are properly aligned to react.

Additionally, we varied the furanic compounds by changing their composition. Conventional DAC theory states that such changes affect the DAC reaction speed. However, the changing chemical properties did not affect the reaction energetics when the reaction takes place within the zeolite. Rather, a lock-and-key like fit on the multiple active sites by the reactants and additional pre-organization of the reactants govern the reaction energetics.

We used molecular dynamics simulations to study the effect of reactant confinement in zeolite catalysts at elevated temperatures on the activation entropy – which is a measure for the loss of

molecular mobility. The results indicated that the activation entropy is reduced upon a concomitant increase of reactant confinement.

Our findings illustrated the key role of multi-site cooperativity and confinement of the chemical reactions taking place in zeolite catalysts. The conventional DAC-reactivity theory does not hold when the complex reaction environment within the zeolite catalyst is taken into account. A paradigm shift is required in computational zeolite modelling. As compared to conventional modelling efforts using greatly reduced models, models with an improved description of the zeolite should be used, although they are computationally more demanding.

Title of PhD-thesis: Theory of Lewis Acid Zeolite Catalysis for the Conversion of Biomass-Derived Furanics - On the Effect of Multi-Site Cooperativity and Confinement. Supervisors: Emiel J.M. Hensen, Eindhoven University of Technology. Co-Supervisor: Evgeny A. Pidko, Delft University of Technology