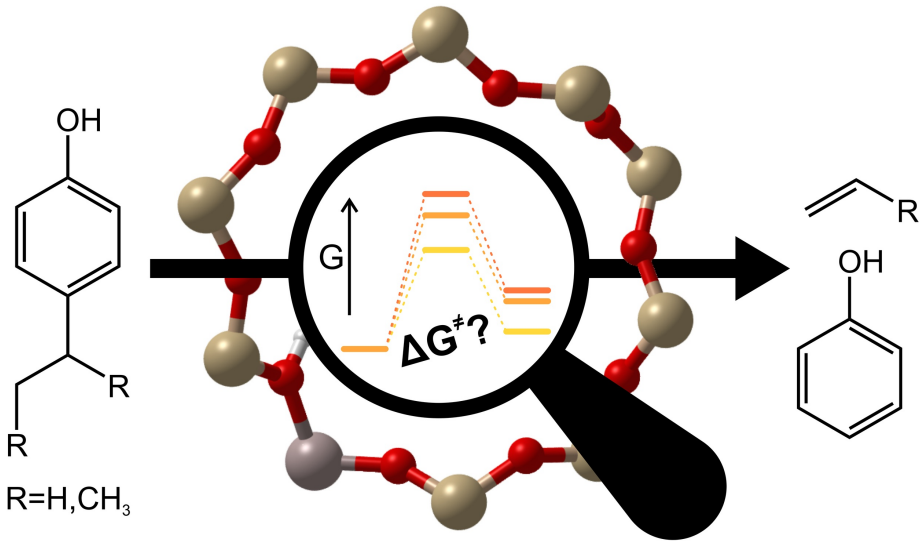
Theoretical insights into mechanism and reactivity of zeolite-catalyzed alkylphenols dealkylation

M. Bocus, Center for Molecular Modeling, Ghent University
V. Van Speybroeck, Center for Molecular Modeling, Ghent University
Y. Liao, B.F. Sels, Center for Sustainable Catalysis and Engineering, Katholieke Universiteit Leuven

It has recently been discovered that the H-ZSM-5 zeolite is able to catalyse the dealkylation of alkylphenols with high activity and selectivity [1-3]. This process is of particular interest as not only the products (phenol and olefins) have a high added value, but also because alkylphenols can be obtained in high yield from lignin depolymerization [4]. The development of this reaction represents therefore a key step in the production of commodity chemicals from renewable resources. However, many of its aspects, concerning the reactivity of different reagents and the reaction mechanism in particular, are still unclear. For instance, it has been noticed that 4-isopropylphenol is much more reactive than 4-n-propylphenol which is in its turn more reactive than 4-ethylphenol.

To better understand the differences in reactivity between those model reagents and, more in general, the reaction mechanism, we have investigated the reaction with dynamic and static periodic density functional theory calculations. Molecular dynamics (MD) simulations are particularly suited to assess the flexible behaviour and stability of the reaction intermediates in the zeolite pores at reaction conditions, by fully taking into account their mobility and entropic effects. With static calculations, on the other hand, we calculated the energetics of the transition states connecting such intermediates and explored which mechanisms are more likely to occur in the catalyst pores.From MD simulations, we determined that isopropylphenol forms more reactive intermediates than the other two reagents. For instance, we compared the length of the C-C bond that must be broken to achieve dealkylation and found it to be significantly longer for isopropylphenol than the other two molecules. This applies to all the possible intermediates that, based on similar reactions already investigated [5], might be formed in the zeolite channels. Moreover, the calculated reaction barriers for the plausible dealkylation mechanisms nicely follow the reactivity trend observed experimentally. Our hybrid static-dynamic approach has then allowed us to collect clear indications on the reasons which underlie the different reactivity of alkylphenols in the H-ZSM-5 catalyst.

Acknowledgement: Financial support was received from the EoS project BIOFACT and the European Union's Horizon 2020 research and innovation program (consolidator ERC grant agreement No. 647755 - DYNPOR (2015-2020)) and the Research Board of Ghent University.



[1] Danny Verboekend, Yuhe Liao, Wouter Schutyser, Bert F. Sels. (**2016**). *Green Chem.*, *1*, 297. DOI: 10.1039/c5gc01868d
[2] Yuhe Liao, Martin d'Halluin, Ekaterina Makshina, Danny Verboekend, Bert F. Sels. (**2018**). *Applied Catalysis B: Environmental*, *234*, 117. DOI: 10.1016/j.apcatb.2018.04.001
[3] Yuhe Liao, Ruyi Zhong, Ekaterina Makshina, Martin d'Halluin, Yannick van Limbergen, Danny Verboekend, Bert F. Sels. (**2018**). *ACS Catal.*, *9*, 7861. DOI: 10.1021/acscatal.8b01564
[4] W. Schutyser, T. Renders, S. Van den Bosch, S.-F. Koelewijn, G. T. Beckham, B. F. Sels. (**2018**). *Chem. Soc. Rev.*, *3*, 852. DOI: 10.1039/c7cs00566k
[5] Niels Hansen, Till Brüggemann, Alexis T. Bell, Frerich J. Keil. (**2008**). *J. Phys. Chem. C*, *39*, 15402. DOI: 10.1021/jp8036022