(P13)

Selectivity prediction for the citronellal cyclization on Cu_3BTC_2: a comparison between extended cluster and periodic calculations

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In this work, the catalytic properties of the metal organic framework (MOF) Cu_3BTC_2 have been studied as catalyst. More in particular, the selectivity for the isopulegol isomers as products of the citronellal cyclization has been theoretically investigated (Fig. 1). Recently, this reaction was also studied to investigate the electronic effects of linker substitution on the lewis acid MOF UiO-66 [1].

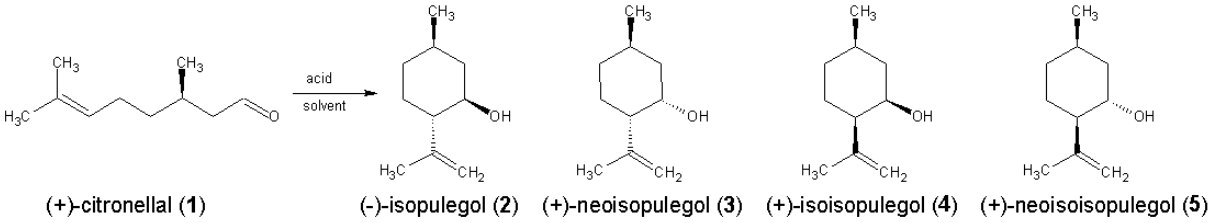

Figure 1. *Four possible isomers from the citronellal cyclization*

Theoretical approach

To find a plausible model for the citronellal cyclization (Fig. 1), we performed extended cluster and periodic calculations within DFT (Fig. 2).

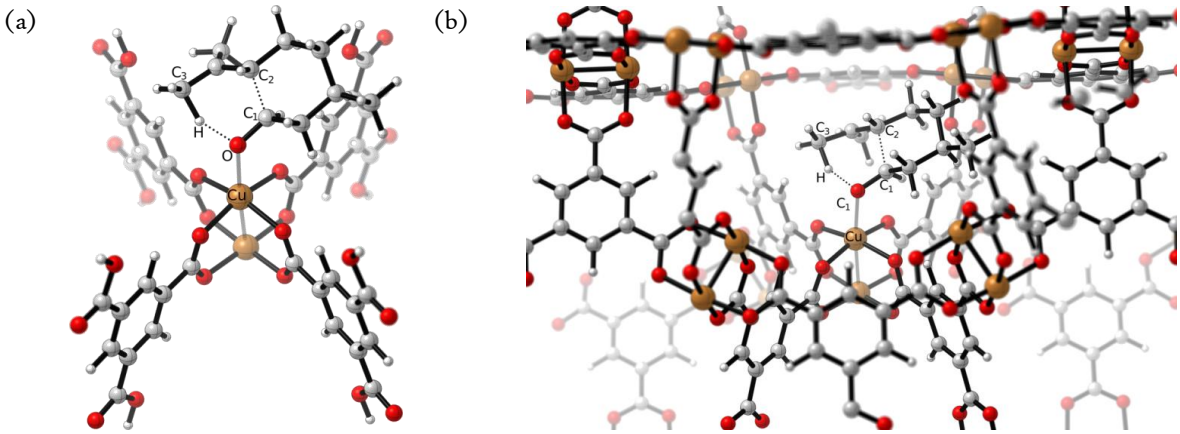

Figure 2. *Cyclization of citronellal towards isopulegol: (a) extended cluster, versus (b) periodic calculations*

All relevant reaction routes leading to the various isopulegol isomers are determined theoretically for each catalyst model (Fig. 2). We used Curtin Hammet`s principle, stating that only Gibbs free energy differences between the transition states are necessary to predict initial selectivities. Those selectivities could then be compared with experimental values obtained on highly pure Cu_3BTC_2 crystals [2]. In this work, we focus on the selectivity towards isopulegol (Fig. 3). For the extended cluster calculations, the transition states were optimized using an ONIOM-approach, with energy refinements at B3LYP/6-311+g(d,p)-D3, while the periodic calculations were performed at the PBE-D2 level, applying very robust optimization parameters.

Results and discussion

The experimental selectivity towards isopulegol drops when temperature raises. This general trend is reproduced by both theoretical approaches (Fig. 3). Some experimental data points at low citronellal conversion are also shown in Fig. 3. The selectivity in the periodic approach agrees well with the experimental behavior.

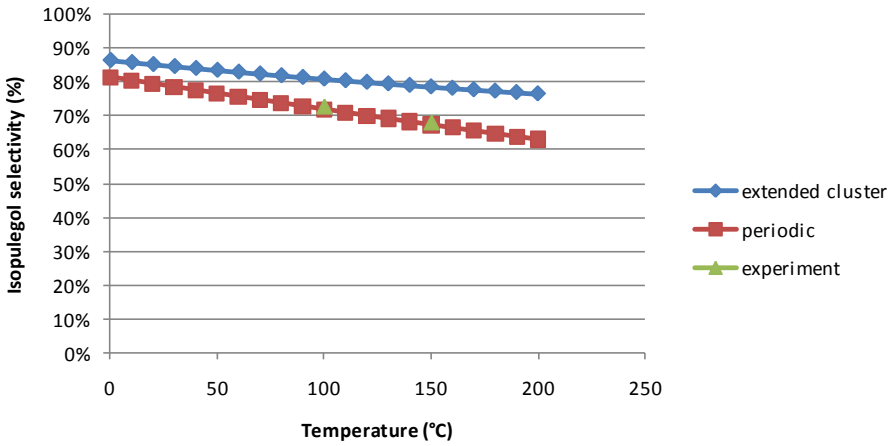

Figure 3. *Isopulegol selectivity in function of temperature.*

Conclusions

Relevant transition states are determined to have an accurate description of the citronellal cyclization on Cu_3BTC_2. The periodic calculations comprise a complete description of the catalyst environment by construction, which can not be fully covered by the extended cluster model. This might explain why only periodic PBE-D2 calculations are able to accurately predict the selectivity at various reaction temperatures.

Acknowledgements

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[2] Vandichel, M., Vermoortele, F., Cottenie, S., Devos, D.E., Waroquier, M., Van Speybroeck, V., submitted