

Modeling Lewis acid catalyzed reactions in MOFs:

How to solve the challenges?

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Nowadays, Metal-organic frameworks (MOFs) attract increasing interest in catalysis. In this work, two MOFs containing Lewis acid sites (UiO-66 and Cu₃BTC₂) have been investigated for the citronellal cyclization (Figure 1). To clarify the reaction mechanisms, various theoretical approaches have been necessarily applied.

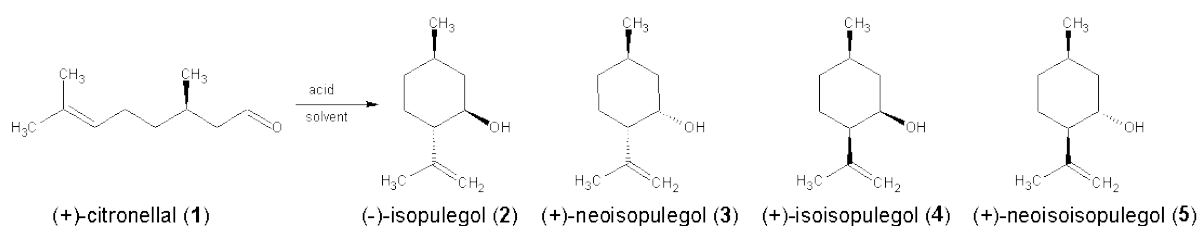


Figure 1. Four possible isomers from the citronellal cyclization

The electronic effects of linker substitution have been investigated on UiO-66 [1]. A cluster study support the experimental evidence that defect Zr sites inside the framework were responsible for the catalysis. In order to rationalize the electronic modulation of the active sites, molecular modeling calculations have been performed on extended clusters to prove the rate acceleration behavior of the UiO-66-NO₂ compared to the UiO-66.

Secondly, the product selectivity distribution has been determined for the citronellal cyclization on Cu₃BTC₂ [2]. We show the importance of a complete description of the catalyst environment, which can only be addressed by periodic calculations.

References

(1) Vermoortele, F., Vandichel, M., Van de Voorde, B., Ameloot, R., Waroquier, M., Van Speybroeck, V., De Vos, D. E., *Angewandte Chemie International Edition*, in press

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