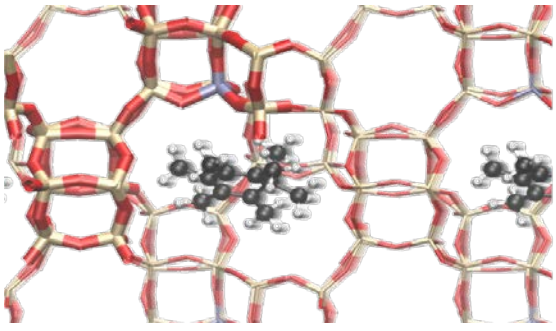
UV/VIS SPECTRA OF CARBONACEOUS METHANOL-TO-OLEFIN INTERMEDIATES USING TD-DFT COMBINED WITH MOLECULAR DYNAMICS

HEMELSOET Karen[A,B]; QIAN Qingyun[B]; DE WISPELAERE Kristof[A]; DE MEYER Thierry[A]; VAN YPEREN-DE DEYNE Andy[A]; WAROQUIER Michel[A]; WECKHUYSEN Bert[B]; VAN SPEYBROECK Véronique[A]

A) Center for Molecular Modeling (CMM); Ghent University; Technologiepark 903; Zwijnaarde; Belgium; *B) Inorganic Chemistry and Catalysis; Debye Institute for Nanomaterials Science; Utrecht University; Universiteitsweg 99; Utrecht; The Netherlands*
Contact: Karen.Hemelsoet@UGent.be

The optical absorption properties of (poly)aromatic hydrocarbons occluded in a nanoporous environment of chabazite topology are investigated. These compounds are an essential part of a working catalyst for the Methanol-to-Olefins (MTO) process[1]. To determine which organic species contribute to the experimentally obtained in-situ UV/Vis bands, a systematic series of polymethylated (poly)aromatics are analyzed by means of TD-DFT calculations on neutral and cationic species.

Static TD-DFT simulations on gas phase cationic compounds are performed to determine the influence of structurally different hydrocarbons on the absorption spectra; whereas the influence of the zeolitic framework is examined using supramolecular models within a QM/MM framework. Different functionals such as BLYP, B3LYP, CAM-B3LYP and M06-2X are tested for the TD-DFT simulations[2]. The effect of the zeolite leads to geometrical distortions of the (poly)aromatic compounds compared to the gas phase species and additionally may lead to mixing of framework orbitals with those of the hydrocarbons. However our simulations show that a molecular dynamics simulation study of the trapped organic species in the inorganic host is essential. During such simulation the flexibility is fully taken into account and the effect on the UV/Vis spectra is determined by performing TD-DFT calculations at various snapshots of the molecular dynamics run. This procedure allowed us to provide an energy absorption scale and to assign the various absorption bands determined from in-situ UV/Vis spectra to structurally different species.



KEYWORDS: TD-DFT, MOLECULAR DYNAMICS, UV/VIS, METHANOL-TO-OLEFINS

[1] V. Van Speybroeck, K. Hemelsoet, K. De Wispelaere, Q. Qian, J. Van der Mynsbrugge, B. De Sterck, B. M. Weckhuysen, M. Waroquier ChemCatChem 5 (2012) 173-184.
[2] C. Adamo, D. Jacquemin, *Chem. Soc. Rev.* 42 (2013) 845-856.