

Identification of Carbonaceous Compounds in H-SAPO-34: a Combined TDDFT and In-situ Spectroscopy Study

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In this contribution carbonaceous compounds formed during the methanol-to-olefins (MTO) process in H-SAPO-34 are identified by means of advanced molecular modeling techniques. Vertical excitation energies provide initial good approximations for optical absorption spectra and are calculated by means of cost-efficient time-dependent DFT (TDDFT). Structurally different charged aromatics with varying number of aromatic rings and methyl substituents correspond to distinct absorption bands and an assignment scale is introduced. Special attention is given to the influence of the chabazite topology, comparing gas-phase results with those of the species present in an H-SAPO-34 cluster. The TDDFT results are then used to assist the interpretation of the experimental UV/Vis data. In particular a new analysis procedure is presented which enables to derive activation barriers of formation of crucial reaction intermediates based on the time evolution of experimental in-situ UV/Vis spectra.^[1]

Introduction

Zeolites or zeotype materials are among the most valuable of inorganic materials, finding extensive use in a wide variety of applications, such as catalysis, in separations, as ion exchangers, and as adsorbents. The combination of theory and experiment is crucial to elucidate the structure-activity relation of these nanoporous materials. To date, hybrid QM/MM (and often QM/QM) computations have emerged as the method of choice for treating local electronic events in large molecular systems.^[2] Our specific interest lies in the methanol-to-olefins (MTO) process, which is a prominent technology to bypass crude oil as a fundamental feedstock.^[3] The methanol conversion occurs over protonated zeolitic materials via the hydrocarbon pool (HP) reaction mechanism, in which organic reaction centers, such as aromatics and alkenes, present in the zeolite pores act as co-catalysts. The continued growth of the initially active HP species ultimately leads to blockage of the pores and hence deactivation of the catalyst material. Thus far, little information is available about the reaction mechanism leading to these large polyaromatics and it is therefore very important to identify possible reaction intermediates. This can be achieved using different spectroscopic techniques. Due to the large and conjugated nature of the (poly)aromatic HP compounds and coke precursors we are interested in, UV/Vis spectroscopy is the most suitable tool.

Computational and experimental details

Two-layered computations were performed on large finite clusters containing 44T atoms, representative of HP compounds present in a chabazite (CHA) topology. Electronic energies were calculated using the B3LYP-D approach to account for the crucial dispersion contributions. Vertical excitation energies were obtained using the same level of theory with TDDFT. In addition, the long-range corrected CAM-B3LYP functional was also tested.

In-situ UV/Vis experiments were performed using H-SAPO-34 (58 x 58 x 58 μm) zeolite crystals, placed on the heating stage of an in-situ cell while exposed to a stream of methanol vapour at the reaction temperature range of 500 - 600 K.

Results and discussion

Figure 1(a) shows the assignment bar resulting from TDDFT computations on gas-phase charged intermediates. The structurally different HP compounds show absorption at various, distinct wavelengths. Comparison with experimentally available data reveals that the B3LYP functional performs well for these charged species, opposed to the series of neutral compounds for which the CAM-B3LYP results turn out to be superior. The influence of the CHA pore is shown to shift the excitation energies with up to 50 nm in case of strong deformation of the HP compound due to the zeolite confinement. However, in the majority of the cases the gas-phase data provide a reasonable approximation and can be used to assign peaks of experimental UV/Vis spectra. In Figure 1(b) the HOMO and LUMO orbitals of the hexamethylbenzenium ion in H-SAPO-34, contributing to the absorption at 400 nm, are depicted. Finally, the TDDFT results are used to correlate theoretically determined methylation barriers with the growth of the specific absorption bands in experimental UV/Vis spectra (Figure 1(c-d)).

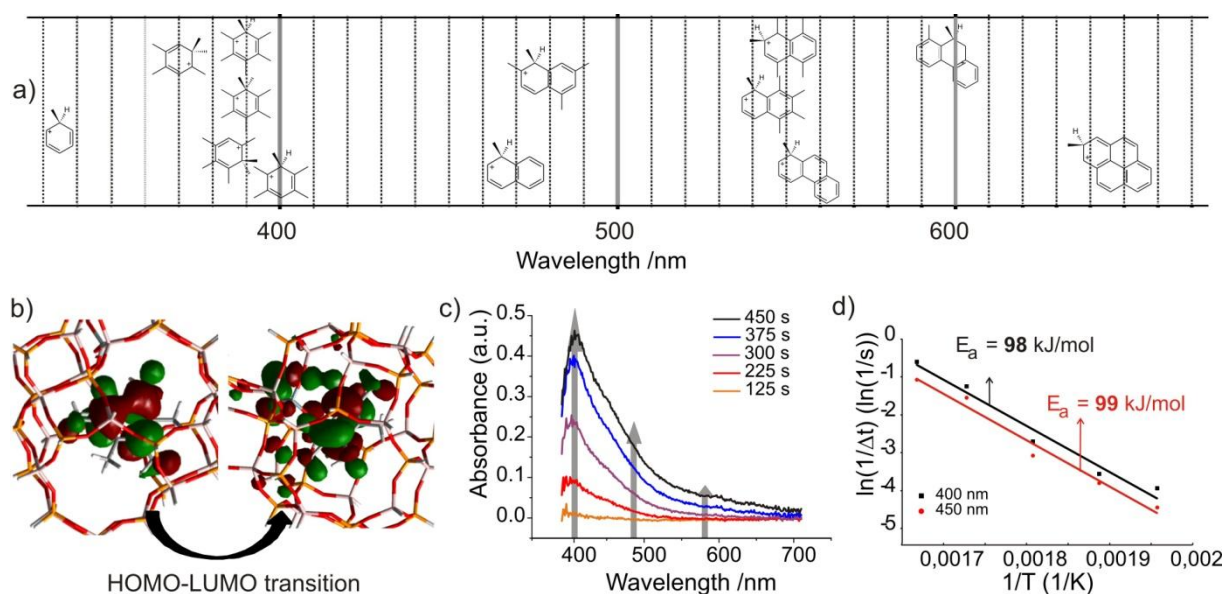


Figure 1. a) First vertical excitation energies of gas-phase charged HP compounds, calculated using B3LYP/DGTZVP TDDFT. b) Illustration of molecular orbitals involved in the excitation of the hexamethylbenzenium cation in H-SAPO-34. c) Time-resolved UV/Vis spectra taken during MTO reaction over H-SAPO-34 at 553 K. d) Arrhenius plots derived from the temporal evolution of the various bands in the temperature interval 500-600 K.

Conclusions

The electronic excitation of a variety of - both neutral and charged - carbonaceous compounds in H-SAPO-34 are computed using TDDFT, providing insight into experimental UV/Vis spectra. The confinement can lead to substantial changes in the absorption wavelengths.

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References

- [1] Van Speybroeck, V., Hemelsoet, K., De Wispelaere, K., Qian, Q., Van der Mynsbrugge, J., De Sterck, B., Weckhuysen, B. M., Waroquier, M., *Angew. Chem. Int. Ed.*, submitted.
- [2] (a) Svelle, S., Tuma, C., Rozanska, X., Kerber, T., Sauer, J., *J. Am. Chem. Soc.* 131 (2009), 816; (b) Van Speybroeck, V., Van der Mynsbrugge, J., Vandichel, M., Hemelsoet, K., Lesthaeghe, D., Ghysels, A., Marin, G. B., Waroquier, M., *J. Am. Chem. Soc.* 133 (2011), 888.
- [3] (a) M. Stocker, M., *Microporous Mesoporous Mater.* 29 (1999), 3; (b) Haw, J.F., Song, W.G., Marcus, D.M., Nicholas, J.B. *Acc. Chem. Res.* 36 (2003), 317.