Deactivation of the catalyst during the MTO process from a molecular modeling perspective

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Currently, the industrially important conversion process of methanol to olefins (MTO) forms a key process for the production of higher valued products that can easily be transported, such as ethylene and propylene. Methanol can be made from natural gas or coal via synthesis gas. Unraveling the underlying reaction mechanism of the complex MTO process has already shown to be very challenging. Recent ab initio calculations, in combination with experimental data, are in strong support of the "hydrocarbon pool model" as opposed to a direct (C-C coupling) route [1, 2]. The hydrocarbon pool has been described as a catalytic scaffold inside the zeolite building, consisting of polymethylbenzenes and their cationic derivatives.

The continued growth of these initially active carbonaceous species within acidic zeolites, such as H-ZSM-5 and H-SAPO-34, is an undesired side effect resulting from secondary reactions for which at present no computational data exist whatsoever. The presence of these large species – coke precursors - inside or at the external cups of the periodic structure leads to blockage of the pores or channels and ultimately to the deactivation of the catalyst. An improved in-depth understanding of the underlying reaction mechanisms of coke formation is therefore desperately needed. A main problem is the generally poor characterization of coke, despite the great number of techniques (gas chromatography, mass spectroscopy) that can be used for locating and identifying the deposits [3, 4]. Because of this, it is not clear whether benzenoid species consisting of 3 rings can already be regarded as coke as opposed to large aromatic species present in the hydrocarbon pool that still allow an active route.

Within this contribution possible reaction routes leading to the formation of naphthalene- and/or phenanthrene-like species are studied from theoretical viewpoint within various industrially relevant zeolite topologies. For each of these elementary steps reaction rates are evaluated based on energies and frequencies originating from reliable ab initio data. The latter were obtained by taking into account a large portion of the zeolites, as to be representative for the actual topology.

[1] Lesthaeghe D., Van Speybroeck V., Marin G. B. and Waroquier M., Angew. Chem. Int. Ed. 45 (2006) 1714.
[2] McCann D. M., Lesthaeghe D., Kletnieks P. W., Guenther D. R., Hayman M. J., Van Speybroeck V., Waroquier M. and Haw J. F., Angew. Chem. Int. Ed. 47 (2008) 5179.
[3] Bauer F., Karge H. G., Molecular Sieves, Springer Berlin Heidelberg, 5 (2007).
[4] Palumbo L., Bonino F., Beato P., Bjørgen M., Zecchina A. and Bordiga S., J. Phys. Chem. C 112 (2008) 9710.

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