Theoretical validation of a fully functional route to both ethene and propene formation for methanol-to-olefin conversion in H-ZSM-5

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To meet the ever increasing demand for oil-based chemicals in spite of waning oil reserves, the development of new technologies based on alternative feedstock is high on the agenda of both academic and industrial communities. One of the most promising emerging technologies is the methanol-to-olefin (MTO) process in acidic zeolites. Despite considerable efforts from both experimental and theoretical research, the reaction mechanism has proven to be extremely difficult to unravel. Experimental results advocate a hydrocarbon pool mechanism, in which organic centers inside the zeolite pores act as co-catalysts.[1,2] Recently, a complete such catalytic cycle has been studied from a combined theoretical and experimental viewpoint,[3] but it still fails to explain ethene formation witnessed in H-ZSM-5.[4] Polymethylbenzenes have been commonly regarded as the most important hydrocarbon pool species, independent of the employed zeolite. While this assumption still holds for zeolites with the BEA- or CHA-structure, recent experiments have shown that H-ZSM-5 (in which space is more limited, due to the MFI-topology) could be an important exception. Researchers found that the higher methylbenzenes, even though present, are virtually unreactive in the pores of H-ZSM-5. Recent experimental results, however, revived the old proposal of successive methylation and cracking reactions of C_{3+}-alkenes instead, providing a parallel route for the production of light olefins. In a more detailed study by Svelle et al. ethene appears to be formed solely from the lower methylbenzenes, while propene and higher alkenes would be formed from alkene methylations and interconversions. These observations led to the proposal of a complete dual cycle mechanism, consisting of two interconnected cycles: a polymethylbenzene cycle that yields predominantly ethene, and an alkene cycle that yields propene and higher alkenes.[5,6]

In this study, the C_{3+}-alkene cycle is modeled using quantum-chemical techniques to identify a complete low energy pathway, to verify whether olefin formation proceeds through this route and whether propene formation is indeed preferred. Since the proposed dual cycle might eventually allow control of the propene-to-ethene ratio, a thorough understanding and comparison of all elementary steps is of utmost importance.

References [1] Dahl, I.M., Kolboe, S., Catal. Lett. **20**, 329 (1993); [2] Haw, J.F., Song, W.G., Marcus, D.M., Nicholas, J.B., Acc. Chem. Res. **36**, 317 (2003); [3] McCann, D.M., Lesthaeghe D., Kletnieks P.W., Guenther D.R., Hayman M.J., Van Speybroeck V., Waroquier M., Haw J.F., Angew. Chem. Int. Ed. **47**, 5179 (2008) ; [4] Lesthaeghe, D., Horré, A., Waroquier, M., Marin, G. B., Van Speybroeck, V., Chem. – Eur. J. **15**, 10803 (2009); [5] Svelle, S., Joensen, F., Nerlov, J., Olsbye, U., Lillerud, K. P., Kolboe, S., Bjorgen, M., J. Am. Chem. Soc. **128**, 14770 (2006); [6] Bjorgen, M., Svelle, S., Joensen, F., Nerlov, J., Kolboe, S., Bonino, F., Palumbo, L., Bordiga, S., Olsbye, U., J. Catal. **249**, 195 (2007)