Ab initio study on the deactivation of an H-SSZ-13 and H-SAPO-34 catalyst during the MTO process

Kristof De Wispelaere, Jeroen Van der Mynsbrugge, Bart De Sterck, Karen Hemelsoet, Michel Waroquier and Veronique Van Speybroeck
Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium

The depletion of oil reserves and the rapidly increasing demand for base chemicals such as ethylene and propylene initiated the quest for chemical processes based on alternative feedstock. Among these, the methanol-to-olefin process (MTO), using natural gas, coal or biomass as raw material, is one of the most important. MTO conversion occurs in acidic zeolites or zeotype catalysts. For industrial applications H-SAPO-34, which has a chabazite topology, shows the best performance and the highest selectivity toward light olefins.[1]

The generally accepted reaction mechanism for MTO is based on a hydrocarbon pool hypothesis, in which organic molecules (predominantly polymethylbenzenes) trapped within the anorganic zeolite framework act as co-catalysts. Methylation of the hydrocarbon pool species and subsequent olefin elimination are the key steps in the production of ethylene and propylene.[2] An important secondary effect of the presence of reactive methylbenzenes, is the formation of polycyclic aromatic compounds.[3] These large molecules are considered as coke, blocking the cages or channels, poisoning the active sites and finally deactivating the catalyst. Because the channels connecting the cages of H-SAPO-34 are narrow, polyaromatic molecules typically remain trapped inside the cages.[4] Coke formation increases with the acid strength of the catalyst, causing deactivation to occur faster in H-SSZ-13, the more acidic zeolite analogue of H-SAPO-34.[5]

In this contribution the activities of benzene, naphthalene, and phenanthrene toward methylation in H-SSZ-13 and H-SAPO-34 are compared based on theoretical calculations. This allows the assessment of the influence of the acid strength on the stability of these species and their tendency to lead to the formation of polyaromatics. Additionally, a possible route for the formation of peri-fused bicyclic compounds via isobutene, a commonly formed side-product in the MTO process, is proposed in an effort to investigate its contribution to the formation of deactivating species.

[1] Chen, J.Q., Bozzano, A., Glover, B., Fuglerud, T. and Kvisle, S., Catal. Today 106 (2005) 103.
[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] Hemelsoet, K., Nollet, A., Vandichel, M., Lesthaeghe, D., Van Speybroeck, V. and Waroquier, M., ChemCatChem 1 (2009) 373.
[4] Mores, D., Stavitski, E., Kox, M.H.F., Kornatowski, J., Olsbye, U. and Weckhuysen, B.M., Chem. Eur. J. 14 (2008) 11320.
[5] Bleken, F., Björgen, M., Palumbo, L., Bordiga, S., Svelle, S., Lillerud, K.-P. and Olsbye, U., Top. Catal. 52 (2009) 218.

E-mail: kristof.dewispelaere@ugent.be
www: http://molmod.ugent.be/