Ab initio study of the growth of fused bicyclic species within a zeolite-type catalyst: the influence of confinement and material composition

Karen Hemelsoet, Arno Nollet, Veronique Van Speybroeck and Michel Waroquier
Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium, karen.hemelsoet@ugent.be

Introduction

In the search for greener and cheaper manufacturing routines for the key chemical compounds ethylene and propylene, the conversion process of methanol to olefins (MTO) is becoming more and more vital. Methanol can be made from natural gas or coal via synthesis gas. The transformation to the smaller olefins occurs over microporous solid acids, such as zeolites and zeotype materials. ZSM-5 and SAPO-34 are currently the most applied representatives in industry. Other materials however also show promising product distributions [1]. Unraveling the underlying reaction mechanism of the complex MTO process has already shown to be very challenging. 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 [2,3]. The hydrocarbon pool has been described as a catalytic scaffold inside the zeolite building, consisting of polymethylbenzenes [4] or alkenes [5] and their cationic derivatives.

The continued growth of these initially active carbonaceous species within the channels and pores of the periodic structure is an undesired side effect resulting from secondary reactions, leading to blockage and ultimately to the deactivation of the catalyst. It is however not clear whether larger aromatics should be regarded as passive coke or rather as hydrocarbon pool species that still allow an active route. Theoretical calculations can provide important insights regarding this activity behavior. In order to model the growth process of aromatic species, methylation reactions at fused bicyclic species are examined by means of advanced computational methods. A protonated high-silicon zeolite with chabazite topology [6] is compared with its silicoaluminophosphate analogue (SAPO-34), allowing to study the influence of material composition and the comparison with experimental data [7].

Methodology

Two-layered computations were performed on a periodic porous structure with the CHA-topology. A large 46T or 96T cluster for the pure silicon and SAPO, respectively (with the active site represented by a 8T high level region) was applied. The models were constructed using Zeobuilder [8]. In order to quantify the dispersion or van der Waals contributions, the b3lyp-d approach, using damped interatomic potentials of the form C_6R^{-6}, was utilized. A kinetic analysis was performed using transition state theory as implemented in the TAMkin program, which is a post-processing toolkit [9].

Results and discussion

The reaction scheme consists of two normal methylation steps, followed by an *ipso*-methylation leading to the formation of a trimethylnaphthalenium ion (Fig. 1(a)). These gem-methylated species can form the onset of an olefin-producing route such as the sidechain mechanism. The stabilizing effect of the zeolite framework on carbenium ions leads to a stepwise methylation behaviour: a relatively slow methyl addition is followed by a much faster deprotonation (Fig. 1(b)).

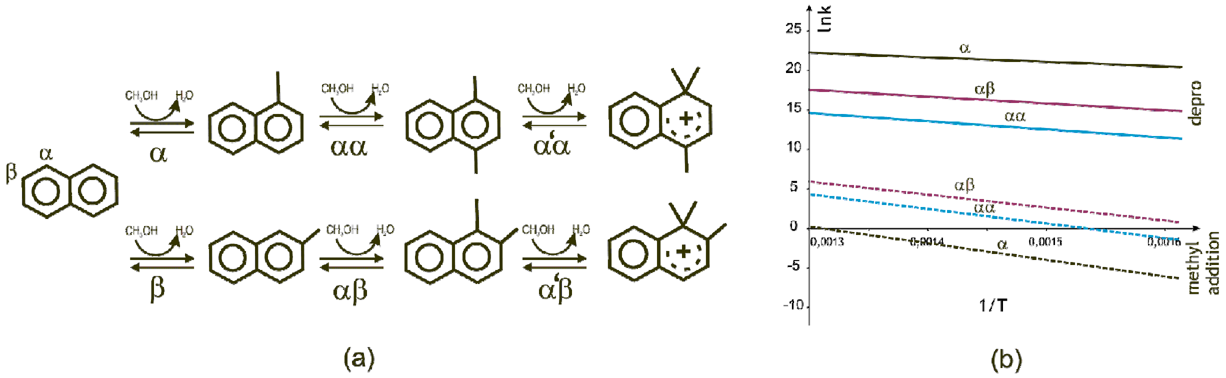

Figure 1. Methylation scheme (a) and calculated rate coefficients (b) for the protonated aluminosilica chabazite catalyst.

The initial methylation is found to be the hardest, and the position of the electrophilic attack (α versus β) is also important. In the case of the β-methylation, the large organic compounds are pushed out of the chabazite cage. The dispersion contributions to the energy barriers amount to approximately 20 kJ/mol in the case of methyl additions, whereas they are of course much smaller for the deprotonations [6]. For the SAPO-34 catalyst, the reactions barriers and energies are substantially shifted as compared to the more acidic pure silicon counterpart.

Conclusions

It is shown that the growth of fused bicyclic compounds within a chabazite cage is still feasible, although the reactions are slower compared to benzenic compounds. The transition states are subject to framework limitations. Van der Waals corrections are shown to be substantial; however the general trend is maintained. The material composition is an important, but not crucial parameter for the investigated reaction mechanism.

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