The role of polyaromatics in coke growth processes

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Polyaromatic hydrocarbons (PAHs) are known to be crucial intermediates leading to the formation of carbonaceous deposits in various industrial processes. These deposits, or coke, are highly undesirable and a detailed understanding of the underlying reaction mechanism can aid coke inhibition. This contribution will deal with coke growth during two applications, i.e. during thermal cracking and during heterogeneous catalysis. The emphasis will be on new insights due to the use of recent advances in density functional theory (DFT), such as the inclusion of dispersion corrections to standard DFT functionals and further assessment of the time-dependent DFT (TD-DFT) framework to simulate electronic excitations.

As a first topic, stacking interactions between phenyl substituents of a phosphorus-containing coke additive on one hand and the polyaromatic coke surface on the other will be discussed [1]. We recently reported that these dispersive π-π stacking interactions play a non-trivial role in hindering further stacking among coke surfaces during a thermal cracking process of heavy feedstocks. A small and a large compound, i.e. benzene and ovalene, are compared as a model structure for the aromatic coke surface. The coke growth reaction mechanism during thermal cracking consists of a cascade of radical reactions, of which the initial hydrogen abstraction or radical addition reactions are the most important.

The second topic is the assessment of recent DFT functionals to calculate transition energies of a series of (neutral and cationic) PAHs within the framework of TD-DFT. The reliable prediction of excited state-related properties of large π systems was previously shown to be problematic, since unsystematic and strongly size dependent errors were obtained using standard DFT functionals such as B3LYP and BP86 [2]. Comparison between theoretical and experimental electronic spectra of protonated linear PAHs reveal the importance of the charge-transfer character of the excited state [3]. Our interest in these electronic transitions stems from the availability of experimental UV/Vis spectra for the coke growth during the methanol-to-olefins process, in which methanol is converted to light olefins using an acidic zeolite type catalyst. This coke growth is due to a series of reactions involving cationic compounds, and methylation reactions are expected to be essential [4].

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