Using Elementary Reactions To Model Growth Processes Of Polyaromatic Hydrocarbons Under Pyrolysis Conditions Of Light Feedstocks

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Steam cracking or pyrolysis of hydrocarbons remains one of the simplest and oldest petroleum refinery processes and is considered as the main production source of light olefins such as ethylene and propylene. These species form key products in modern chemistry. Simultaneously with the cracking processes, the formation of a carbonaceous residue (or coke) on the inner walls of the reactor tubes has been observed. The presence of this carbon-rich structure is highly undesirable as the coke layer leads to a higher pressure drop over the reactor and an increased heat-transfer resistance. The coke growth mechanism consists of different stages: initially coke is formed by a heterogeneous catalytic mechanism involving the metal tube skin of the cracking reactor. Once the surface is covered with a thin filamentous layer a heterogeneous non-catalytic process takes over, resulting in a graphite-like structure. In particular circumstances (at very high temperatures or using heavy feedstocks) a homogeneous, non-catalytic mechanism is also observed. It is reported that for the temperature intervals relevant in the steam cracking units, the second mechanism is the most important. Due to its graphite-like characteristics, the coke layer can be modeled as a network consisting of aromatic rings with varying carbon/hydrogen ratio. The overall cracking and coke formation processes are known to proceed through a complex cascade of free radical reactions. Due to this complexity, simulation models have become essential tools in today's operation plant. Recently, the effect of radial gradients (for the temperature as well as molecular and radical concentrations) on the global coking rate was investigated using a 2-dimensional reactor model [1] and the correspondence with experimental data was shown to be satisfying.

In order to study the growth of the coke layer, a model based on elementary reactions was proposed [2]. The main advantage of such a model is the fundamental nature of the elementary steps and consequently its general applicability. In the particular model, five classes of reversible reactions can be distinguished: hydrogen abstraction; substitution; gas phase olefin addition to radical surface species; gas phase radical addition to olefinic bonds; and cyclization. The complexity of the mechanism prohibits a complete experimental investigation and therefore, ab initio modeling techniques are applied to provide reliable kinetic data about important reaction steps. Several of the distinct reactions have already been examined using advanced ab initio methods (an overview is given in ref. [3]). In particular, the recently developed hybrid BMK functional as well as composite methods (using post-Hartree-Fock energies) have been proven successful for the important class of hydrogen abstraction reactions [4,5]. The former method is generally preferred for systems of (moderately) large size since density functional theory (DFT) provides an excellent cost-to-performance ratio.

To identify the elementary reaction classes that determine the global coking rate, microscopic routes that start from benzene and lead to naphthalene have been investigated. It is found that initial hydrogen abstraction reactions (with or without assisting radicals) and final dehydrogenation reactions are decisive. Overall, the concentrations of the involved species are found to be crucial to verify the most possible reaction pathway. In this light, the low concentration of available gas phase radicals (e.g. methyl radical) strongly influences the observed low rate constants of the bimolecular abstraction reactions. In this work, two new routes are proposed and thoroughly investigated using high-level DFT-methods. One route starts from the benzene molecule, whereas in the other route the focus lies on toluene and its derivatives. Intrinsic as well as modified reaction rate constants for the elementary steps in both schemes are presented.

The influence of the local polyaromatic structure on the kinetics of the hydrogen abstraction reactions is studied by performing calculations on larger polycyclic structures. Hydrogen abstractions at aromatic structures involving six-membered rings and leading to aryl and benzyl radicals (in the case of the benzene, toluene route, respectively) have been examined. In the first case, this has revealed six types of possible reactive site at the coke surface, with the local polyaromatic structure strongly influencing the reaction kinetics [5]. Overall, we find that hydrogen abstraction preferentially occurs from the surface sites of smaller PAHs, such as benzene and naphthalene.

References

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