MODELING ELEMENTARY REACTIONS IN COKE FORMATION FROM FIRST PRINCIPLES

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Introduction

Thermal cracking of hydrocarbons is the simplest and oldest method for petroleum refinery processes and is considered as the main process for the production of light olefins such as ethene. The thermal cracking of hydrocarbons is known to proceed through a free radical chain mechanism. Radicals are mainly formed via C-C bond breaking and propagation occurs through abstraction and addition reactions. Decomposition of radicals by β-scission results in the desired gas-phase olefins. During this process, highly undesirable carbon-rich products are formed on the inner walls of the reactor giving rise to the formation of a coke layer. This coke layer has a negative influence on the efficiency of the cracking unit.

The process of coke formation is a complex phenomenon[1,2]. Initially coke is formed by a heterogeneous catalytic mechanism in which the properties of the inner tube skin play an important role. Once the metal surface is covered with coke the catalytic activity of the metal particles diminishes and a heterogeneous non-catalytic mechanism becomes important. The coke layer thus formed has a polynuclear aromatic character. Usually one focuses on the second process since the period of catalytic coke formation is very small with respect to the total run length.

In today's operation of a plant simulation models play a very important role. Recently a coking model based on elementary reactions was developed at the Laboratorium voor Petrochemische Techniek[3,4]. In view of the fundamental nature of the elementary steps considered such a model is of general applicability . One of the main challenges in the development of an accurate and broadly applicable model is the assignment of values for rate coefficients of the individual reactions occurring in the reaction network. The fundamental nature of the elementary steps considered allows the use of theoretical calculations to provide kinetic and thermodynamic data and to obtain microscopic insight in the basic reaction steps of the coke formation model. The elementary reaction steps that lead to incorporation of carbon atoms and growth of the coke surface can be divided in five classes of reversible reactions (cf. Fig. 1) :

- **(i)** Hydrogen abstraction reactions by gas phase radicals and reverse reactions
- **(ii)** Substitution reactions by radicals at the coke surface and reverse reactions
- **(iii)** Addition reactions of radical surface species to gas phase olefins and the inverse ß-scission of a radical surface species in smaller surface species and gas phase olefins
- **(iv)** Addition reactions of gas phase radicals to olefinic bonds in a surface species and the inverse decomposition of radical surface species to gas phase radicals and olefinic surface species
- **(v)** Cyclization of radical surface species and decyclization

Due to the increasing capabilities of computing power and optimization of numerical models it is now possible to perform high level ab initio calculations on systems of industrial importance. Kinetic parameters, such as the preexponential factor and activation energy, can be obtained by means of Transition State Theory (TST). The microscopic quantities are obtained by means of ab initio calculations In this work preference has been given to Density Functional Theory calculations, since this approach is computationally attractive for the larger structures that are involved in this work. This approach has been successfully applied to a variety of important chemical reactions.

In the first part of this paper, microscopic routes starting from benzene leading to the formation of naphthalene are investigated with the aim to identify important coke precursors and to obtain insight into the elementary reaction classes that determine the rate of coke formation. In the second part of the paper, larger polyaromatic clusters are considered in order to determine the influence of the coke matrix on the kinetics of the elementary reactions.

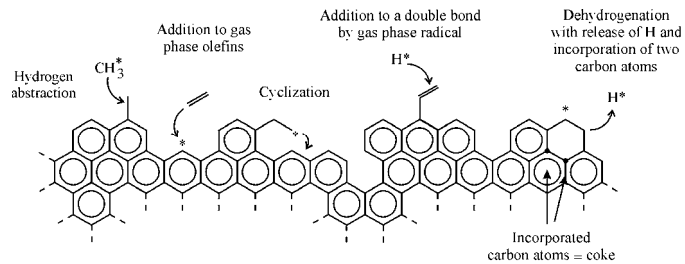

Figure 1. Radical elementary reaction steps leading to coke growth.

Microscopic pathways for the formation of naphthalene from benzene. In order to obtain microscopic insight into the elementary reactions leading to cokes, various pathways are studied starting from benzene that lead to the formation of naphthalene. For this study the coke layer is approximated by only one benzene ring. The composition of the process gas is an important factor in the coke formation A lot of work in this research field has been done by Kopinke et al., who performed tracer experiments with ^{14}C-labeled hydrocarbons added to straight run naphtha to establish structure-reactivity relations and relative coking rates for various types of hydrocarbons[5]. The most important coke precursors were found to be olefins and aromatics. Ethene has the lowest coking tendency of the olefinic hydrocarbons but its high concentrations in the gas phase, explains its large contribution to the coke formation in a thermal cracking unit. Propene shows similar properties. Ethyne is more reactive than ethene but appears in much smaller concentrations, limiting its contribution to coke formation. To investigate these earlier experimental findings all reaction routes with ethyne and ethene as typical coke precursors are taken into consideration (cfr. Fig. 2).

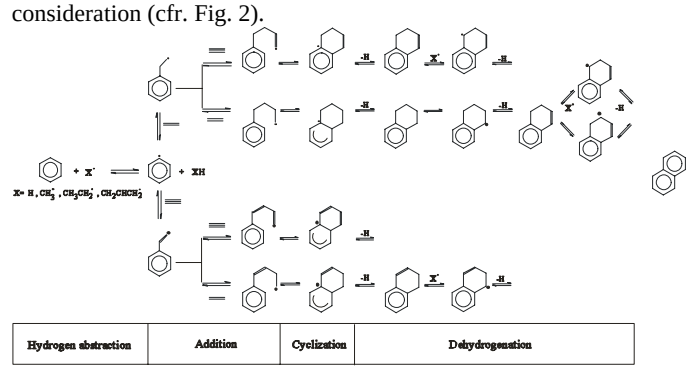

Figure 2. Radical elementary reaction steps leading to coke growth

The reaction sequence is initiated by hydrogen abstractions from benzene with gas phase radicals creating radical surface species. In turn these radicals react further with unsaturated gas phase components. Earlier experimental work indicated that hydrogen, methyl, ethyl and allyl radicals are very reactive in the coke

formation during thermal cracking[6]. Therefore all hydrogen abstractions in which the latter radicals are involved are taken into consideration. Based on the proposed reaction scheme. several conclusions concerning the coking tendency of gas phase components and the relative importance of the various reaction types can be drawn.

Influence of gas phase precursors on the coking rate. For all studied addition reactions with ethyne and ethene, both gas phase unsaturated components yield activation energies which are in the same order of magnitude, with respect to each other. The preexponential factor for reactions with ethyne is higher than for the corresponding additions with ethene, resulting in relative rate constants for additions to ethyne that are approximately twice as high as the ones for additions to ethene.

To estimate however the relative importance of both gas phase components as a coke precursor, their concentration has to be taken into account also. Gas phase concentration profiles were obtained from a simulation program, which is based on a detailed network of elementary reactions, developed at the Laboratorium voor Petrochemische Techniek[7,8]. The reactor geometry and the operating conditions are taken for a typical ethane cracking unit. The process gas temperature profile as a function of the axial reactor coördinate is shown schematically shown in fig. 3 and varies between 800 K at the reactor inlet to reach a coil outlet temperature of 1100 K.

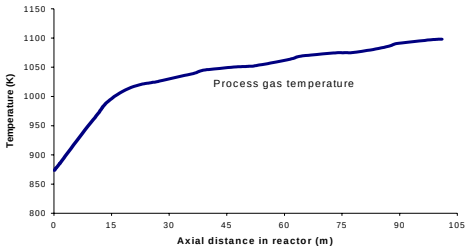

Figure 3. Temperature profile of the process gas along the reactor coil for typical ethane cracking conditions.

Typical concentrations of ethene and ethyne were obtained at the reactor inlet, in the middle of the reactor length and at the outlet the reactor. These values are presented in Table 1.

Table 1. Concentrations of ethyne and ethene at various axial reactor distances during ethane cracking .

Axial distance (m)	Ethene (mol/dm3)	Ethyne (mol/dm3)
1,09	$2.52\ 10^{-7}$	$1.51\ 10^{-15}$
44.02	$3.14\ 10^{-3}$	$3.90\ 10^{-6}$
100.96	$5.88\ 10^{-3}$	$5.35\ 10^{-5}$

Taking these concentrations into account, ethene shows the highest coking tendency despite its lower reaction rates. This result is in accordance with earlier reported experimental data[5]. However, at the higher temperatures prevailing in the last passes of the reactor, the coking tendency of ethyne becomes more important due to the smaller difference in concentrations between the two unsaturated hydrocarbons.

Relative importance to coke formation of the various reaction types. At second instance it is interesting to search for rate determining reaction steps along the reaction sequence going from benzene to naphthalene. Since the reaction network contains both bimolecular and unimolecular reactions, it is not possible to compare directly the rate constants of the elementary reaction steps. Again concentration profiles have to be taken into account to compare absolute rates of the various reaction steps. It is found that the initial hydrogen abstraction are relatively slow, due to the low concentration of the gas phase radicals. The individual rate constants however were found to be one of the highest in the total reaction network. The initially created radical surface species can further grow by means of various subsequent additions. The first addition of ethene or ethyne to the phenyl radical is characterized by a high rate constant. This can be explained by the reactivity of the phenyl radical. The subsequent additions are much slower and determine the coking efficiency. After the second addition all further reaction steps, i.e. the cyclizations and dehydrogenation, proceed very fast. Previous discussion reveals that the initial creation of surface species and the subsequent additions determine the coking efficiency of the reaction network.

Influence of the coke matrix on the kinetic parameters

The reaction network discussed in the previous section was based on the assumption that the coke surface could be approximated by only one benzene ring. It is however important to investigate the validity of this approximation. Therefore calculations were performed on larger polyaromatic compounds to establish the importance of the local environment of the active surface site in the coke formation.

Classification of PAHs based on Bond Dissociation Energies. A measure of the chemical reactivity of a site at an aromatic cluster is the bond dissociation energy (BDE) of the corresponding C-H bond. BDEs of all C-H bonds were calculated for the series of PAHs shown in fig. 4.

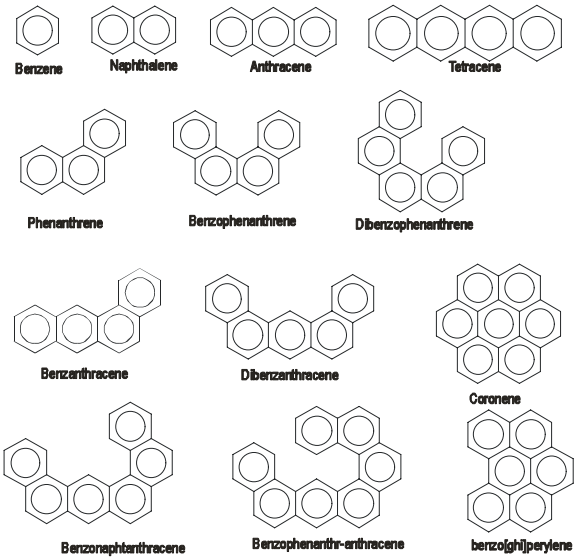

Figure 4. PAHs considered in this study

Based on the BDEs the C-H bonds in aromatic structures can be divided into four types with different reactivity, which can be related to the local structure around the site (Fig. 5). Similar conclusions were made by various other authors [9].

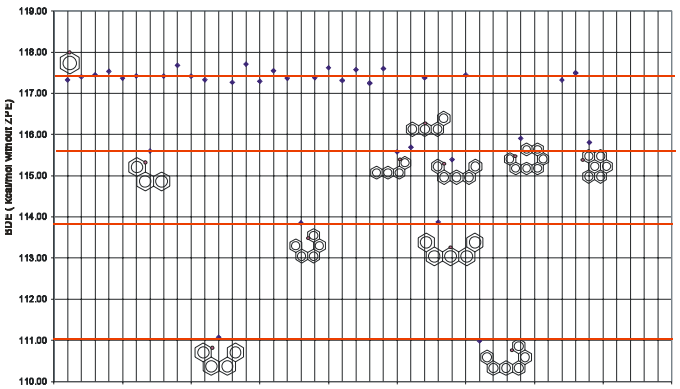

Figure 5. BDEs for a series of PAHs

The types of sites at the coke surface are defined based on their reactivity as well as on the structure of the local surroundings. Although benzene, naphthalene and anthracene have similar reactivities, they are retained as separate surface sites for further kinetic calculations due to their structural differences. This results in six different sites which are based on differences in local structure and/or on differences in chemical reactivity. The six different sites are named according to the smallest aromatic compound that exhibits the same local structure i.e. a benzene-like, naphthalene-like, anthracene-like, phenanthrene-like, benzophenanthrene-like and dibenzo(c,g)-phenanthrene-like site.

Kinetics of hydrogen abstraction reactions on PAHs. Attention is focussed on the influence of the local polyaromatic structure on the kinetic parameters of hydrogen abstractions reactions with a methyl radical. The latter reactions are known to determine the global coking rate. The kinetic parameters are determined for six different sites as introduced in the previous section. A conformational and vibrational analysis was performed for each of the reactants, products and transition states at the B3LYP/6-311G** level of theory. The resulting kinetic parameters, calculated in the temperature interval from 700 to 1100 K which is characteristic for thermal cracking, are given in table 2.

Table 2. Kinetic parameters (700-1100K) for hydrogen abstractions at PAHs

Hydrogen abstraction	Ea (kJ/mol)	A (m^3/mol.s)
at benzene-like site	79.68	$1.7\ 10^9$
at naphthalene-like site	81.82	$8.2\ 10^7$
at anthracene-like site	84.63	$2.4\ 10^8$
at phenanthrene-like site	85.94	$1.7\ 10^7$
at benzophenanthrene-like site	85.42	$4.8\ 10^6$
at dibenzo(c,g)-phenanthrene-like site	85.81	$4.5\ 10^6$

The microscopic calculations give insight into the factors that determine the kinetic parameters. The activation energy varies only slightly in terms of the local PAH structure. The small differences must be traced back to the steric hindrance between the attacking methyl radical and the polyaromatic structure. The frequency factor however varies largely with the number of aromatic rings involved in the polyaromatic structure. These variations must be traced back to the occurrence of skeletal vibrations in the larger PAH structures. For larger PAH structures more skeletal vibrations are present in the reactant structures and thus the PAH obtains a larger degree of conformational flexibility and a larger partition function. This results in smaller rates for hydrogen abstractions at larger polyaromatics. This is further illustrated by comparing absolute rates in the temperature interval which is typically encountered in an industrial cracking unit. The relative rates for hydrogen abstractions with a methyl radical at site X (X=naphthalene, anthracene, phenanthrene, benzophenanthrene) with respect to a benzene-like site are presented in fig. 6.

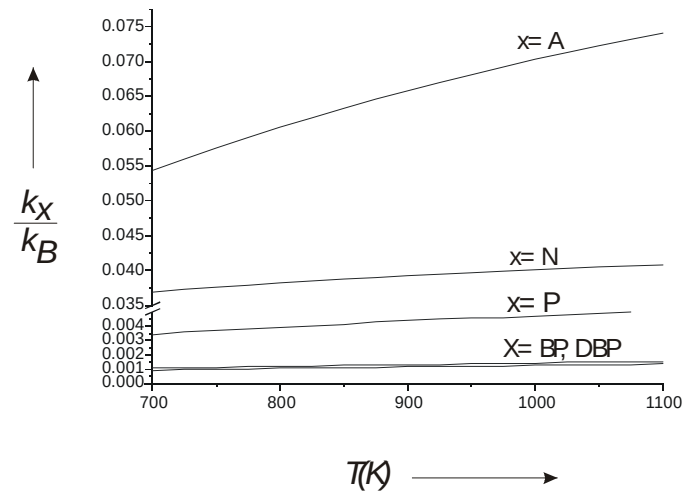

Figure 6. Rate constant for hydrogen abstractions with a methyl radical at site X, relative to the rate constant at the B site, as a function of temperature.

The initial creation of radical surface species predominantly occurs at the smaller clusters and preferentially at a benzene-like site.
For other elementary classes of the coke formation network, also a strong correlation was observed between the size of the PAH and the rate constants [10,11].

Conclusions

In this paper, various elementary reaction steps important for coke formation during thermal cracking of hydrocarbons are studied. In a first instance all elementary reaction steps of a reaction network starting from benzene and leading to naphthalene were studied. The importance of various gas phase components as coke precursors was evaluated by considering all reaction routes in which ethene and ethyne are involved. It was shown that, despite its lower reactivity in the various elementary steps, ethene is an efficient coke precursor due to its high concentration.. Although ethyne is more reactive, it contributes only significantly to coke formation at higher axial distances in the reactor. The theoretical calculations of the rate constants also reveal that the initial hydrogen abstractions and the subsequent addition occur at lower rates than cyclization and dehydrogenation reactions.

In a second instance, the kinetic calculations were extended to larger polyaromatics, to investigate the influence of the local environment of the coke surface on the kinetic parameters. A classification for the reactivity of PAH's based on BDE's was proposed. Four different classes of C-H bonds could be identified. Based on reactivity and local structural difference six types of active sites for coke growth were identified. The influence of the local environment of the active site on the kinetics was investigated by studying a series of hydrogen abstraction reactions. The latter reaction class was derived to determine the global coking rate of the reaction network. It was found that the rate constants can vary largely depending on the local structure of the polyaromatic surface.

Moreover at typical temperatures encountered during cracking, hydrogen abstractions preferentially occur at the smaller PAHs, such as benzene, naphthalene and anthracene.

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