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Computer generation of a network of elementary steps for coke formation during the thermal cracking of hydrocarbons

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Abstract

The methodology for developing a detailed network for coke formation during thermal cracking of hydrocarbons is described. Coke is represented as an aromatic structure. Coke growth is described by elementary reactions between surface species and the components present in the gas phase. The elementary reactions can be divided into five classes of reversible reactions: hydrogen abstraction, substitution, addition by gas phase radicals, addition to gas phase olefins and cyclization. The complete network for coke formation during ethane cracking contains over 14,000 reaction steps between 2400 reaction components, the latter being determined not only by the surface species but also by their local environment. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal cracking of hydrocarbons; Coke formation; Reaction network; Network generation

1. Introduction

Thermal cracking of hydrocarbons is one of the main processes for the production of olefins. The feed, ranging from light gases over naphthas to gasoils, is cracked in tubular coils suspended in a fired rectangular furnace. The heat required for the endothermic reactions is provided via radiation burners in the sidewalls or long flame burners in the bottom of the furnace. During the thermal cracking a carbonaceous residue is deposited on the inner walls of the reactor coils leading to an enhanced resistance against heat transfer and an increased pressure drop over the reactor. To retain the same conversion and selectivity an increase of the heat input is required. Applying a higher coil inlet pressure allows keeping the coil outlet pressure imposed by the separation section constant. Once the external tube skin temperature has reached its allowable maximum or once the pressure drop has become too high, the unit is taken out of operation for decoking, in which the coke is burned off with a controlled air/steam mixture.

Many efforts have been done in the development of reaction networks for the thermal cracking itself [1–13]. Besides simplified global networks, more detailed models based on elementary reactions have been developed. A simulation of the reactions inside the coils of a thermal cracking unit can provide information on the effects of changing feed properties or alternative operating conditions on the thermal cracking product distribution [14]. Since the coke formation has an important negative influence on the operation of the unit, it is important to have a rigorous coking model that is able to predict the coke formation correctly.

The coke formation in thermal cracking units is a complex phenomenon. In the initial stage, coke is formed through a catalytic mechanism, in which the properties of the tube skin material play an important role [15]. Once the metal surface is covered with coke, a heterogeneous non-catalytic mechanism dominates [16]. Literature data point out that the coke layer is mainly of a graphitic nature with a dense structure near the inner walls and a less dehydrogenated interface with the gas phase [17]. Upon reaction of gas phase radicals with the surface of the coke layer radical surface species are created, which in their turn can react with unsaturated components from the gas phase. The amount of radicals on the coke surface is determined by the temperature and the composition of the surrounding gas phase and in particular by the concentration of radicals in the gas phase [18–20]. The composition of the gas phase is therefore an important factor in the coke formation.

At the operating conditions prevailing in industrial cracking units, the period of catalytic coke formation is negligible with regard to the run length [21]. The modeling of the coke formation is therefore focused on the heterogeneous, non-catalytic mechanism. Up till now, semi-empirical models have been developed that can predict the coke formation for a limited range of feed stocks [21–24]. A model based

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on elementary reactions should have a wider applicability. The present contribution describes a fundamental approach to the modeling of the heterogeneous non-catalytic coke formation rather than the semi-empirical ones used up till now. Such an approach has been applied successfully in modeling the deposition of diamond like carbon layers [25], as well as of polycrystalline silicon [26].

The present paper describes the development of a model for the coke formation based on elementary reactions between process gas components and the macroradical coke surface. Neither the process gas species nor the surface species are lumped. Instead for each component the specific reaction possibilities are incorporated in the model as such. This implies that the kinetic parameters are independent of the feed stock [27,28]. In addition, the elementary reactions in the model can be divided into a number of classes such as hydrogen abstraction reactions and decomposition reactions. Within each class a reference reaction is chosen. The kinetic parameters for a reaction are then related to those of the reference reaction of the same class via structural contributions [9,10]. These contributions are defined based on the structural properties of the radicals involved in the reaction. Only a limited number of different types of radicals have to be distinguished. This approach guarantees a reduced number of kinetic parameters.

In the model that is developed, radical surface species are formed through hydrogen abstraction by gas phase radicals. These radical surface species can add to olefins from the gas phase leading to a growth of the surface species. Cyclization and dehydrogenation lead ultimately to incorporation of carbon atoms or coke.

The process gas mixture of the thermal cracker contains a lot of components that can react with the surface through different mechanisms. It is clear that the complete network is quite complicated. Generation of such a large network of elementary reactions by hand is practically not feasible. An automatic generation program is written allowing the construction of a coking network based on the characteristics of the surface species and the gas phase components. Matrices represent the surface species and the gas phase components and the reactions are carried out by performing mathematical operations on these matrices [27,28]. As the emphasis is put on taking into account as much as possible the detailed radical chemistry, the resulting network contains several hundreds of surface species involved in more than thousand elementary reactions. Although such numbers are still tractable, there are methods to limit the size of such networks [29–32], but this is beyond the scope of the present paper.

This paper outlines in detail the methodology followed for developing fundamental models for coke formation during thermal cracking of hydrocarbons. Simulation of an industrial thermal cracking coil based on such a model allows to calculate the amount of coke formed during the run based on the simulated process gas conditions and the process gas–coke interface temperature. A model developed along the lines described in this paper taking into account all important gas phase coke precursors should be capable of predicting the coke formation for different feeds in an industrial reactor.

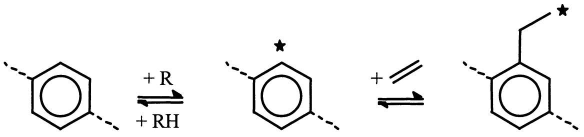


Fig. 1. Examples of surface species in the coking model.

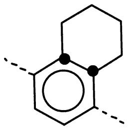


Fig. 2. Cyclic surface species: sites occupied are indicated with a filled circle (●).

2. Representation of the coke surface

Coke formation takes place at the surface of the coke layer. The coke layer is represented by a flat polyaromatic structure consisting of conjugated benzene rings. Upon reaction with gas phase components different surface species are formed at the coke surface as shown in Fig. 1. Each sp^2 carbon atom on the coke surface has two bonds attached to the coke lattice. The dangling bond is called a site. The total concentration C_t of sites is given by

$$C_t = \sum_{i=1}^{N} n_i C_i \tag{1}$$

$[C_t]$ mol sites/m^2 coke surface, $[n_i]$ mol sites/mol surface species i, $[C_i]$ mol surface species i/m^2 coke surface, with N the number of surface species distinguishable at the coke surface, n_i the number of sites occupied by the surface species and C_i the concentration of the surface species. For most surface species n_i is equal to one. In case of a cyclic surface species as shown in Fig. 2 n_i is equal to two. Based on the surface area per site a concentration of 2.0×10^{-5} mol sites/m^2 graphitic coke surface can be deduced.

3. Coke growth reactions

The growth of the coke layer is realized by the incorporation of carbon atoms in the coke layer by elementary reactions. Upon release of H, the two labeled carbon atoms in Fig. 3 are completely surrounded by aromatic rings and, hence, incorporated. Simultaneously two surface species are formed.

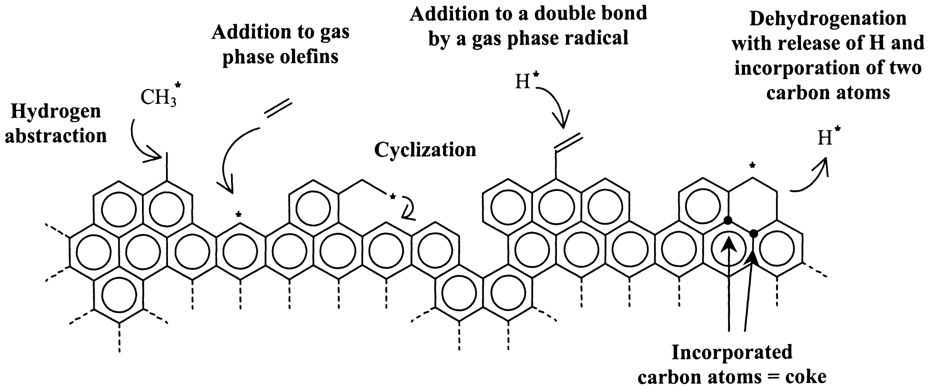


Fig. 3. Radical elementary reaction steps leading to coke growth.

The elementary reactions in the coke formation network can be divided into five classes of reversible reactions:

1. Hydrogen abstraction by gas phase radicals and reverse reactions.
2. Substitution by radicals at the coke surface and reverse reactions.
3. Addition of a radical surface species to a gas phase olefin and the inverse β-scission of a radical surface species in a smaller surface species and a gas phase olefin.
4. Addition of a gas phase radical to an olefinic bond in a surface species and the inverse decomposition of a radical surface species to a gas phase radical and an olefinic surface species.
5. Cyclization of a radical surface species and decyclization.

Cleavage of a C–C bond or a C–H bond is not incorporated in the reaction network due to the high activation energy accompanied with this reaction with regards to that of competing reactions in the coke formation network.

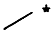
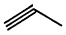
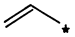
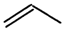
Recombination of radical surface species with radicals from the gas phase is not considered either. The radical surface species are likely to react with gas phase olefins first due to their high concentration compared to that of the radicals, which deviate from each other by approximately an order 10^5–10^6. Moreover at the higher process gas–coke interface temperature the reactions will be activated in favor of the addition of the radical surface species to gas phase olefins resulting in a larger increase in addition rate compared to the recombination rate.

As the β-scission of C–H functions to form a double bond has a high activation energy compared to the cyclization step, no additional β-scission is accounted for if cyclization is possible.

As only six member rings are considered in the coke layer, only those reactions that can lead directly to six member rings upon ring closure are taken into account.

From the preceding discussion it follows that radicals guarantee the (re)generation of the radical surface species necessary for a growth of the coke layer. As the number of gas phase components determines to a large extent the complexity of the model, a judicious choice of gas phase coke precursors is important. Literature data regarding the relative reactivity of the coke precursors towards coke formation are the key factor in this choice. Based on the proposed elementary reactions, it is clear that paraffins and naphthenes, which have a saturated structure, do not lead directly to coke since they are likely to crack first. This is in agreement with literature data [33]. Olefins, diolefins and alkynes which show an unsaturated character and which are present in considerable amounts in the cracking reactor at the prevailing high temperatures, are known to lead to coke [33]. Also the aromatics, which show a strong analogy with the coke, may play a significant role [34]. Based on considerations regarding concentration level in thermal cracking units and reactivity of the gas phase components the precursors summarized in Table 1 are retained within the model. During thermal cracking of light feed stocks mainly ethene and propene are formed. Due to their high concentration these components are important coke precursors. Also ethyne and propyne are known to lead to coke. Among the radicals hydrogen, methyl, ethyl and allyl are found to be very reactive in the coke formation during thermal cracking [18]. The vinyl radical, which is known to be a reactive radical, is not considered in the coke formation network due to its low concentration in the process gas mixture during thermal cracking of light feed stocks. In case of heavier feed stocks other gas phase components may be important in the coke formation and may need to be accounted for in the network.

Table 1
Gas phase coke precursors important in coke formation during ethane cracking

Radicals	Unsaturated hydrocarbons
H	
CH$_3$	
	
	

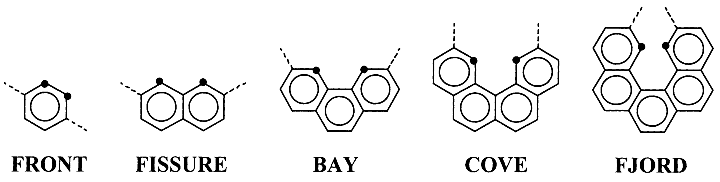


Fig. 4. Clusters at the coke surface: associated surface species marked with a filled circle (●).

It should be stressed that most of the elementary reactions mentioned above also occur in the gas phase. Hence, their kinetic parameters can be determined from those of the corresponding gas phase reactions provided the presence of a solid as reactant or product is accounted for in an appropriate way [35]. Literature data and quantumchemical calculations lead to the conclusion that the reactivity of a surface species at the coke surface is mainly determined by the local structure around the species and less on the underlying coke matrix. Rates of reactions of surface species located at a large aromatic structure are similar to those of small aromatics.

4. Generation of the network for coke formation

4.1. Clusters, ensembles of clusters and reaction components

The formation of a new ring is a necessary step in the reaction path leading to the incorporation of carbon atoms. The minimum number of carbon atoms required for the cyclization depends on the number of surface carbon atoms located between the surface species involved in the latter. In that context and in the assumption of a flat polyaromatic structure only five clusters can be distinguished on the surface as shown in Fig. 4. The nomenclature is similar to the one used by Cyvin and Gutman [36]. The minimum number of carbon atoms, which have to be added in order to allow the formation of a new ring, decreases from 4 to 0 going from left to right in Fig. 4. Note that the ring is formed between the two surface species located at the same cluster.

Note that for each cluster the number of carbon atoms incorporated ultimately in the coke layer is equal to the number of carbon atoms on the coke surface between the two surface species between which an additional ring is formed. Hence, ring closure does not necessarily lead to the incorporation of the same number of carbon atoms, instead the growth of the coke layer depends on the cluster at which the ring is formed. This requires that a surface species has to be defined together with the cluster it is located on. Actually, as each surface species is located at two neighboring clusters, it has to be defined together with an ensemble of two clusters (EOC). The total number of ensembles of clusters is equal to the number of combinations of five clusters in pairs of two increased by five pairs of identical clusters. This results in the consideration of 15 EOCs during the generation of the network for coke formation. Each surface species has to be considered in combination with these EOCs. Such a combination is called reaction component.

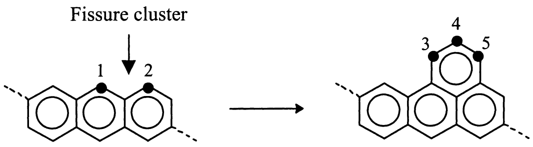


Fig. 5. Generation of new surface species upon ring formation at a fissure cluster.

A particular reaction component can result from three processes. First, it can be formed or disappear via the reactions enumerated in Section 3, i.e. involving only the surface species and not the corresponding EOC. Second, it can originate from the incorporation of carbon atoms in the coke layer. Fig. 5 shows the formation of three reaction components. Note that compared to the original reaction components 1 and 2 both the type of surface species and the EOC can have changed. In the example shown in Fig. 5 only the EOCs have changed. Third, the particular reaction component can be the result of changes in the corresponding

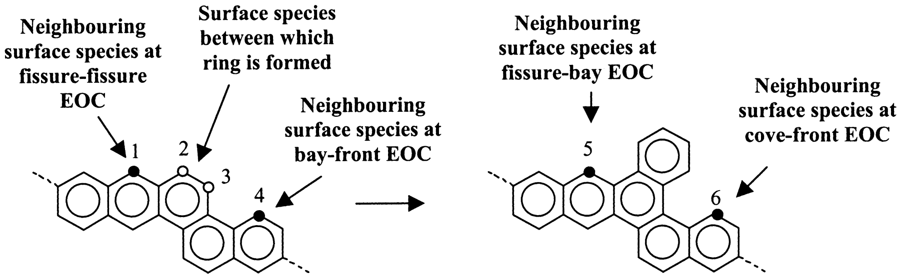


Fig. 6. Formation of a ring between surface species marked with an open circle (○) change in EOCs of neighboring surface species marked with a filled circle (●).

EOC by incorporation of carbon atoms at a neighboring individual cluster, i.e. without involving the surface species itself. This possibility is illustrated in Fig. 6 for the reaction components 5 and 6.

4.2. A typical reaction path

Fig. 7 shows the reaction paths from ethene, propene, hydrogen radicals and methyl radicals as coke precursors starting from a surface species at a front-bay ensemble leading to the incorporation of two carbon atoms and the generation of two new surface species. This individual network involves 10 reaction components. Hydrogen abstraction from reaction component 1 generates a radical reaction component 2, which can add to ethene and propene yielding larger reaction components 3 and 7. If ring closure to a six member ring is possible, the reaction components will react with the neighboring surface species located at the bay-front ensemble to form 4 and 8. β-scission of reaction components 3 and 7 to form a double bond is not accounted for as cyclization is possible. Dehydrogenation results in an aromatic ring. The dehydrogenation proceeds in two steps: a hydrogen abstraction leading to 5 and 9 and a β-scission with release of a hydrogen radical and formation of two incorporated carbon atoms and two new reaction components. The rate of coke formation through the reaction mechanism as depicted in Fig. 7 is given by

$$r_{\mathrm{C}} = 2k_{\mathrm{d,tnb,H}}C_5 + 2k_{\mathrm{d,snb,H}}C_9 \tag{2}$$

where $k_{\mathrm{d},i,j}$ is the rate coefficient for decomposition of a radical type i to a radical type j, $[k_{\mathrm{d},i,j}]$ 1/s, tnb the tertiary naphtheno-benzyl radical, snb the secondary naphtheno-benzyl radical.

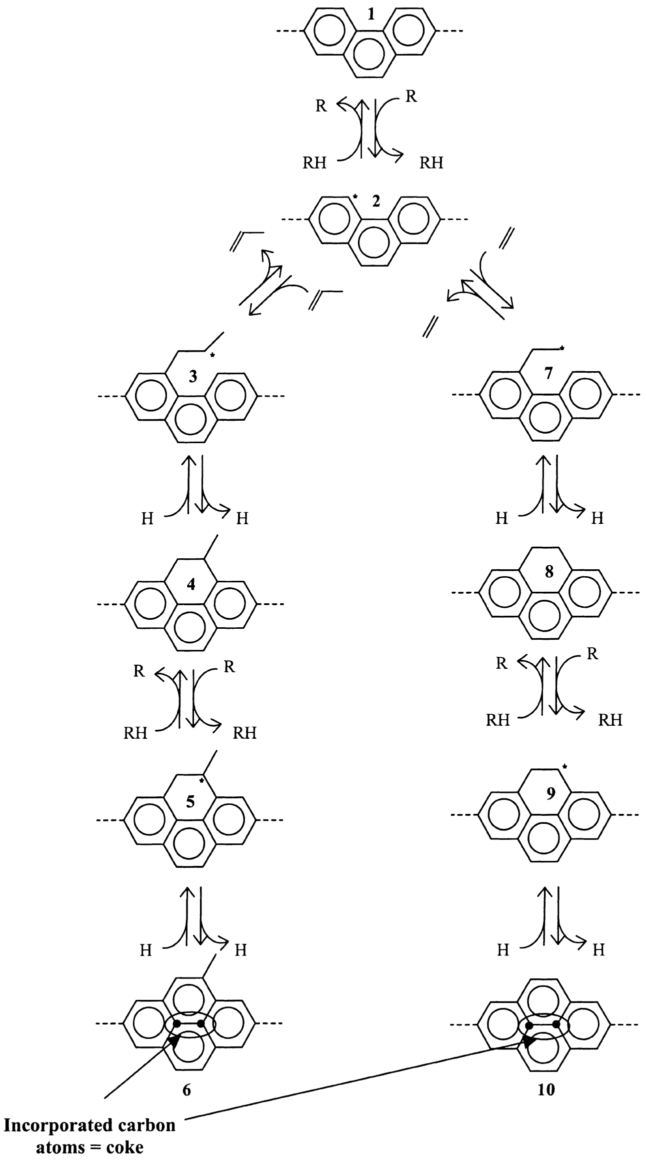


Fig. 7. Reaction paths for coke formation from a surface species at a front-bay EOC.

To obtain the concentrations of reaction components 5 and 9 the balances for all reaction components can be solved applying the pseudo-steady state assumption to the latter and taking into account that the total concentration of sites is constant (Eq. (1)).

4.3. Generation of a complete network

The generation of the complete network has to be based upon the description of the coke surface in terms of reaction components. Each reaction component can react via two networks associated with ring formation at each cluster in the EOC centered around the surface species corresponding to the reaction component. This reduces the generation of the complete network to that of the generation of the networks for the five individual clusters.

Fig. 8 shows a flow sheet of the generation of the complete network. First, the network for each EOC is generated from the networks for the two composing clusters starting from the surface species around which the clusters are centered. For some EOCs the formation of a ring at one of the clusters is not possible. In case a fjord cluster is combined with a front, a fissure or a bay cluster only ring closure at the fjord cluster is accounted for. Ring closure at the other member of the EOC leads to a non-flat coke surface, which cannot be identified with one of the five possible clusters, as shown in Fig. 9. If a cove or a fjord cluster is combined with a fjord cluster, a helix is formed and ring closure is prohibited by overlap of the rings as shown in Fig. 10. In the reactions leading to incorporation of carbon atoms the newly formed reaction components need to be identified. In Fig. 5, reaction components 3 and 4 can be immediately identified upon ring closure at the fissure–fissure EOC. The nature of reaction component 5 depends on the cluster that is located to the right of the fissure cluster at which the ring is formed. Similar considerations hold for reaction components 5 and 6 in Fig. 6. For example, the nature of 5 depends on the cluster that is located to the left of reaction component 2. The complete identification of such reaction

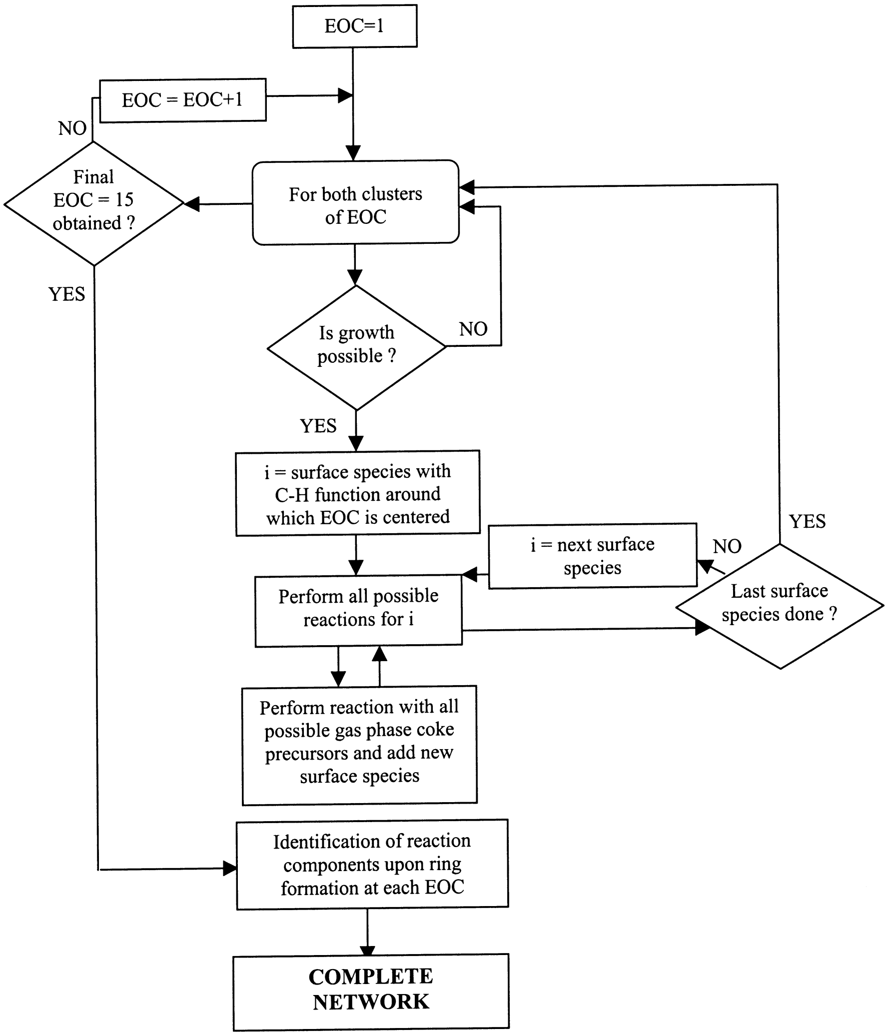


Fig. 8. Schematic representation of the generation of a complete network for coke formation.

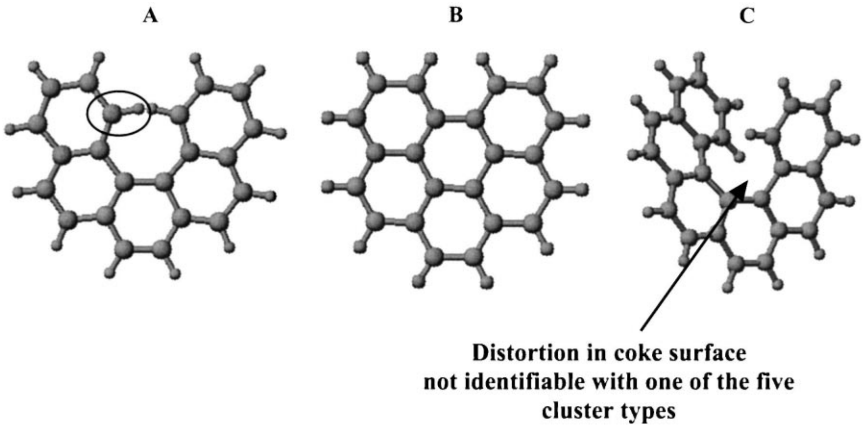


Fig. 9. Ring closure at a front-fjord EOC: (A) front-fjord EOC and associated surface species; (B) ring closure at fjord cluster; (C) ring closure at front cluster.

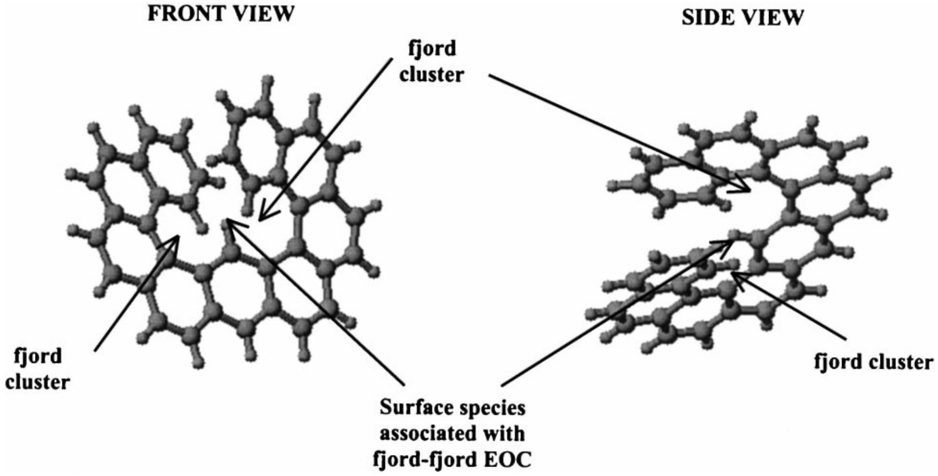


Fig. 10. Fjord-fjord EOC: formation of a helix leads to overlag of rings.

components occurs after the generation of the networks for all the EOCs.

Fig. 11 illustrates the generation of a network for a fissure cluster. A number of classes are defined each representing a specific type of surface species: paraffinic, radical, olefinic, cyclic, ... The generation starts with the surface species consisting of a C–H function at the cluster. All possible reactions are performed storing new products in the appropriate classes. If all reactions for this surface species are investigated, the first surface species in the next class is

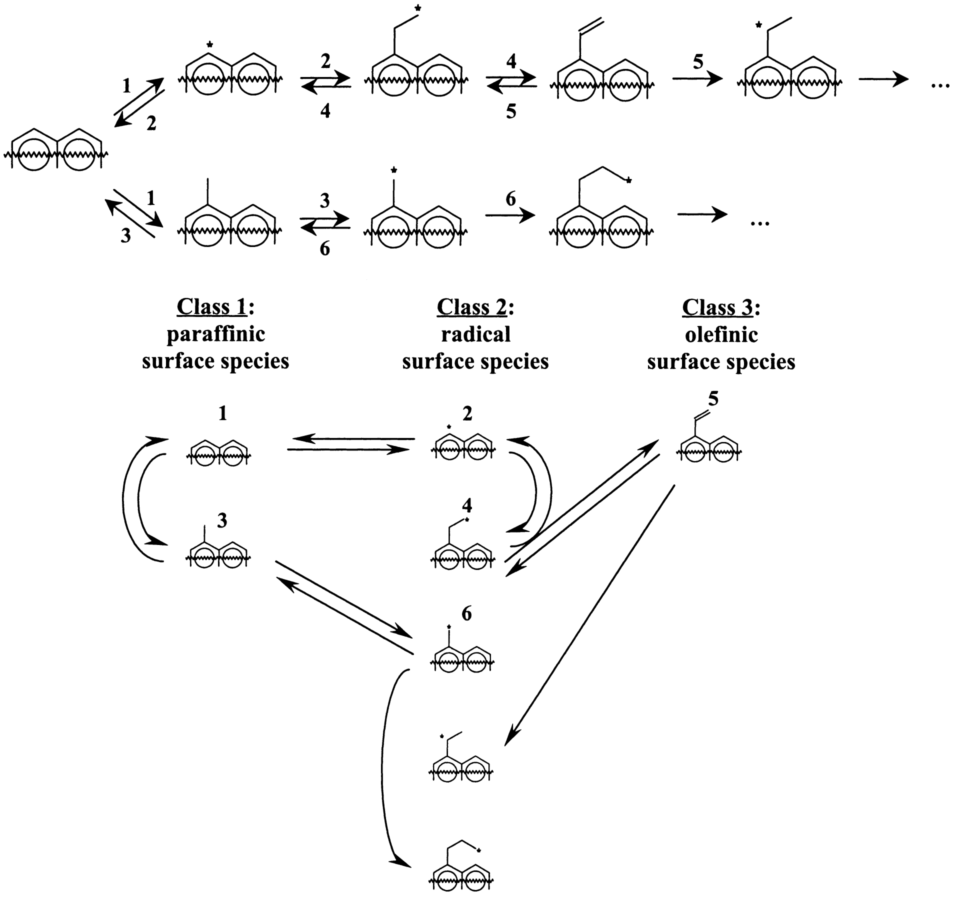
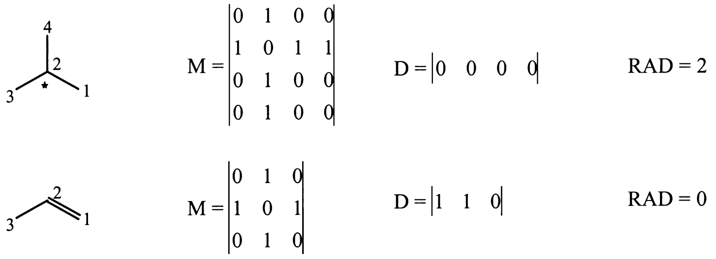


Fig. 11. Generation of the network for a fissure cluster.



$$M = \begin{vmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{vmatrix} \qquad D = \begin{vmatrix} 0 & 0 & 0 & 0 \end{vmatrix} \qquad RAD = 2$$

$$M = \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix} \qquad D = \begin{vmatrix} 1 & 1 & 0 \end{vmatrix} \qquad RAD = 0$$

Fig. 12. Characteristics of *i*-butyl radical and propene.

considered. Again all possible reactions are performed and the corresponding new products are stored. All classes are successively considered. The procedure starts again with the first class and the first surface species that has not yet been used to start a generation. This sequence is repeated until all surface species in all classes have been used. Performing the reactions and identification of the products is based on binary relation matrix principles.

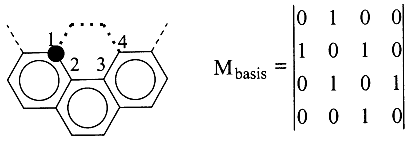
4.4. Generation of a network corresponding to a cluster based on binary relation matrices

The combination of the variety in possible elementary reactions and the large number of gas phase components and of reaction components leads to a network containing a large amount of elementary reactions. In contrast to previous work [21–24] developing such a network by hand is practically not feasible. A suitable alternative is an automatic generation along the lines followed for the generation of a network for the thermal cracking of naphtha feedstocks [27].

4.4.1. Principles of the method

The automatic generation program is based on the concept of the binary relation matrix [27,28,37,38]. A further refinement of the binary relation matrix is the Bond and Electron matrix approach as discussed by Broadbelt et al. [39].

The basic principle is that every chemical structure can be represented by a graph [40–42]. This graph can be translated into a binary relation matrix. Each element in the binary relation matrix M represents a bond in the chemical structure. An element m_{ij} equal to one indicates a bond between carbon atoms i and j. The number of elements 1 in a row or a column indicates the degree of substitution by non-hydrogen atoms, i.e. the primary, secondary or tertiary nature of the carbon atom. In case of a radical or an olefin the binary relation matrix alone is not sufficient to elucidate the structure of the hydrocarbon species and a number of other variables are necessary for complete identification. A scalar RAD indicates the position of the radical carbon atom in the structure and the double bond is defined by a vector D containing a 1 at the positions of the double bonded carbon atoms. Fig. 12 shows the characteristics for the *i*-butyl radical and for propene.



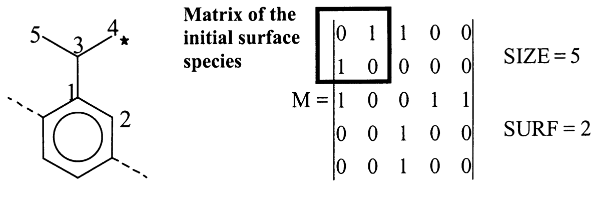
$$M_{\text{basis}} = \begin{vmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{vmatrix}$$

Fig. 13. Surface species at a bay cluster (●) and corresponding basic matrix.

4.4.2. Binary relation matrices for the surface species

Only the carbon atoms located at the coke surface take part in the coke formation reactions. The other carbon atoms in the cluster do not participate in the reaction. It is thus not necessary to take the complete structure of the clusters into account for the definition of the binary relation matrix of the surface species located at the clusters. Fig. 13 shows an example of a surface species, at carbon atom 1, at a bay cluster and the corresponding binary relation matrix. Between carbon atoms 1 and 4 a ring can grow. Two additional carbon atoms are necessary to close the ring. The binary relation matrix of a surface species without branches at a particular cluster is therefore a $n \times n$ matrix with n the number SURF of carbon atoms corresponding to the C–H functions of the cluster and the carbon atoms, incorporated in the coke surface, in between. The first row or column corresponds to the position at which the ring starts to grow. These binary matrices form the basis of the reaction network.

For a surface species with a branch the dimension SIZE of the binary relation matrix is equal to the sum of the number of carbon atoms in the branch and the number of carbon atoms SURF corresponding to the initial surface species without branches located at the same cluster. Fig. 14 shows an example of a branched surface species at a front cluster and its corresponding binary relation matrix.



$$M = \begin{vmatrix} \boxed{\begin{matrix} 0 & 1 \\ 1 & 0 \end{matrix}} & \begin{matrix} 1 & 0 & 0 \\ 0 & 0 & 0 \end{matrix} \\ \begin{matrix} 1 & 0 \\ 0 & 0 \\ 0 & 0 \end{matrix} & \begin{matrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{matrix} \end{vmatrix} \qquad \begin{matrix} SIZE = 5 \\ SURF = 2 \end{matrix}$$

Fig. 14. Binary relation representation of a branched surface species at a front cluster.

Table 2
Codes for carbon atoms used in the label formulation

Code	Nature of carbon atom
0	Carbon atoms at the polyaromatic surface carrying a free electron
1	Carbon atoms at the polyaromatic surface
2	Cyclic carbon atom participating in a double bond and carrying a free electron
3	Cyclic carbon atom participating in a double bond
4	Cyclic carbon atom carrying a free electron
5	Cyclic carbon atom
6	Radical acyclic double bonded carbon atoms
7	Acyclic double bonded carbon atoms
8	Radical paraffinic carbon atoms
9	Paraffinic carbon atoms

Each mathematical operation performed on a binary relation matrix has to preserve the first n = SURF rows or columns corresponding to the n = SURF carbon atoms incorporated in the coke surface.

4.4.3. Label formulation of the surface species

Storing the matrices, defining each surface species and the corresponding cluster at which it is located, demands large memory capacities. Hence, a compact label formulation is developed, which characterizes unambiguously the species. Characteristic elements of a hydrocarbon species are for instance the degrees of substitution by non-hydrogen atoms of the carbon atoms in the structure. The double bonded carbon atoms, the radical position, as well as the presence of a ring are also important factors determining the structure, which are defined by codes as shown in Table 2. The label consists therefore of two vectors, one containing the degrees of substitution by non-hydrogen atoms belonging to the structure and one containing the codes of the carbon atoms in the structure [28]. Note that the codes implicitly define the surface carbon atoms, the radical position and the double bonded carbon atoms. The dimension of the vectors of the label defines the size of the species.

The above labeling codes do not yet guarantee the uniqueness of the label, since the carbon atoms in the branches can be numbered differently. This problem is circumvented by introducing a number of priority rules [28]:

- the carbon atoms belonging to the cluster are considered first in the label;
- the longest branch (main branch) including the initial cluster carbon atoms is traced;
- along the main branch, the secondary branches are treated in increasing order of the branch point carbon atom number;
- the secondary branches are treated similar to the main branch;
- if equal branches are encountered, the codes of the equally placed carbon atoms along both branches are checked. In case of a difference between the codes of the carbon atoms at the same position, the branch with the carbon atom with highest code is dealt with first;
- if the equal branches have the same codes, the degrees of substitution by non-hydrogen atoms belonging to the structure of the successive carbon atoms along the branches defines their order;
- if no decision can be made based on the above considerations, both branches are symmetrical and the order may be determined arbitrarily.

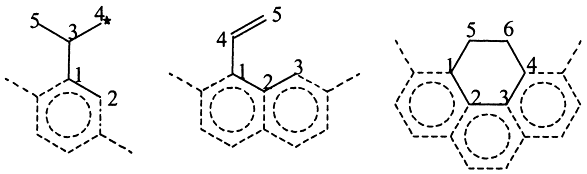
Fig. 15 shows some examples of labels. In the automatic generation, the binary relation matrices are transformed into the label formulation for storage, and vice versa. Due to the unique label no double counting of the species is encountered.

4.4.4. Transformation of the chemical reactions into mathematical operations

Each reaction can be transformed into a mathematical function operating on the binary relation matrix of the reacting surface species. These mathematical operations alter the values of the different variables defining the chemical structure. As an example the addition of a radical surface species to ethene is shown in Fig. 16. In contrast with previous work [27,28], the mathematical operations have to preserve the first n rows corresponding to the carbon atoms residing in the coke surface.

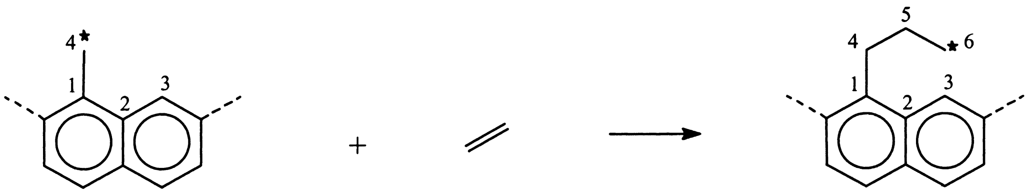
5. Complete network for coke formation during steam cracking of ethane

The more coke precursors are incorporated into the coke formation model, the larger the number of surface species and of reaction steps in the network for coke formation



Degree of substitution:	2 1 3 1 1	2 2 1 2 1	2 2 2 2 2 2
Codes:	1 1 9 8 9	1 1 1 7 7	1 1 1 1 5 5

Fig. 15. Labels of surface species and corresponding cluster.



$$M = \begin{vmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix} \qquad M_{\text{olefin}} = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} \qquad M' = \begin{vmatrix} 0 & 1 & 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{vmatrix}$$

$$D = \begin{vmatrix} 0 & 0 & 0 & 0 \end{vmatrix} \qquad D_{\text{olefin}} = \begin{vmatrix} 1 & 1 \end{vmatrix} \qquad D' = \begin{vmatrix} 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

$$\text{RAD} = 4 \qquad \text{RAD}' = 6$$

Fig. 16. Addition of a radicalar surface species to ethene.

becomes. The number of surface species is restricted by the assumption that the coke layer consists of aromatic rings and only those reactions are taken into account that can lead to closure to six member rings. In Fig. 17, for instance the reaction components 2, 4 and 6 are not taken into account.

In Table 3, the number of reaction steps and of surface species in the networks for coke formation generated for each cluster are shown as a function of the radical species taken into account in the generation. As an olefin only ethene is considered. The radicals participate in substitution reactions, abstraction reactions and addition reactions. The number of surface species and of reaction steps increases monotonically for each supplementary radical taken into account in the model. The largest increase in number of reaction steps and of surface species is caused by the consideration of the methyl radical. Upon addition of the other radicals this effect slightly decreases. Substitution and addition by methyl leads to other surface species than can be formed in case only hydrogen is considered.

In Table 4, the influence of the type of olefin on the number of reaction steps and of surface species in each network is summarized. As gas phase radicals the hydrogen, the methyl, the ethyl and the allyl radical are taken into account. The large increase in number of reaction steps and of surface species coupled with propene as a reacting olefin is explained in Fig. 18. Upon addition of propyne to a radical surface species (2) a vinyl radical (3) is formed which is highly reactive and will rapidly add to another unsaturated molecule (4). In case propene is added a secondary radical (7) is formed which can, besides addition to gas phase olefins (9), also decompose with formation of a double bond (8). The radical character of surface species (8) is re-established by addition of a gas phase radical. It is clear that addition of a methyl, ethyl or allyl radical will result in surface species different from those in the networks for coke formation from ethyne and propyne.

Table 5 summarizes the number of reaction steps and of surface species in the networks generated for each cluster in case the number of olefins considered in the model for coke formation is gradually increased. Again the hydrogen, the methyl, the ethyl and the allyl radical are chosen as gas phase radicals involved in the coke formation. The large increase coupled with propene is again visible. From Tables 4 and 5 it follows that the number of surface species and of reaction steps in case all olefins are considered together is not the same as the sum of numbers of surface species and of reaction steps for the olefins separately. This is due to the interaction of both olefins in the network for coke formation. Fig. 19 illustrates this. If as well ethene as ethyne is present also surface species such as 9 can be formed which is not the case if only one olefin is taken into account.

The network for an ensemble of clusters is obtained by assigning a network to each of the two clusters in the EOC starting from the surface species around which the EOC is centered. For a fissure-bay ensemble of clusters the network consists of the combination of the network for a fissure cluster and that for a bay cluster. After elimination of reaction components with the same structure the network for the fissure-bay EOC contains 1288 reaction steps and 233 reaction components. Combination of all networks corresponding with the 15 EOCs results in the complete network containing 14,268 reaction steps and 2422 reaction components. The approach based on elementary reactions guarantees, however, a reduced number of kinetic parameters as discussed earlier.

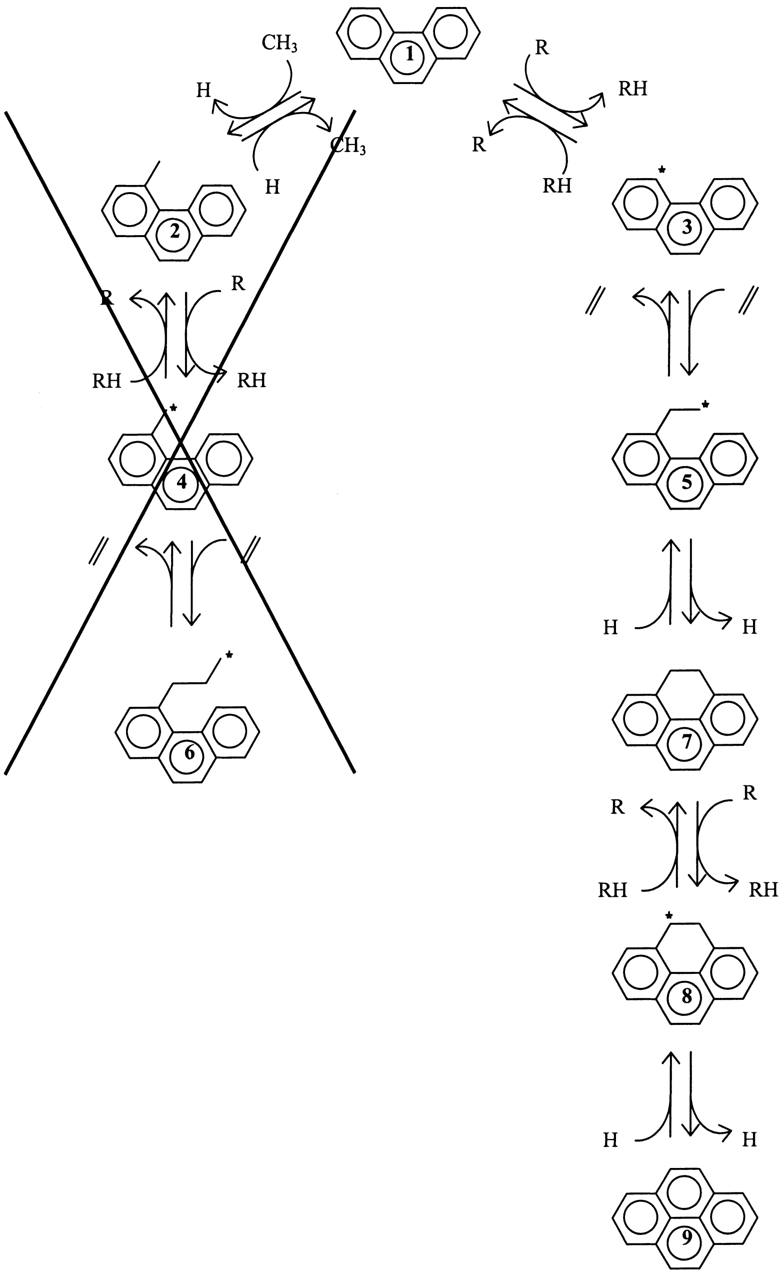


Fig. 17. Examples of reaction paths considered and omitted in the coke formation network.

Table 3
Number of reaction steps and of surface species in the networks generated for each cluster: influence of number and of type of gas phase radicals

Cluster	C_2H_4, H		C_2H_4, H, CH_3		C_2H_4, H, CH_3, C_2H_5		C_2H_4, H, CH_3, C_2H_5, C_3H_5	
	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps
Front	18	47	31	120	44	225	57	362
Fissure	19	45	40	137	50	222	51	274
Bay	6	13	6	19	6	25	6	31
Cove	8	18	15	46	18	69	21	96
Fjord	2	3	2	5	2	7	2	9

Table 4
Number of reaction steps and of surface species in the networks generated for each cluster: influence of the type of olefin

Cluster	C_2H_2, H, CH_3, C_2H_5, C_3H_5		C_3H_4, H, CH_3, C_2H_5, C_3H_5		C_3H_6, H, CH_3, C_2H_5, C_3H_5	
	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps
Front	4	15	8	24	207	1330
Fissure	7	32	10	44	135	737
Bay	3	12	4	14	24	135
Cove	6	29	6	29	32	141
Fjord	2	9	2	9	2	9

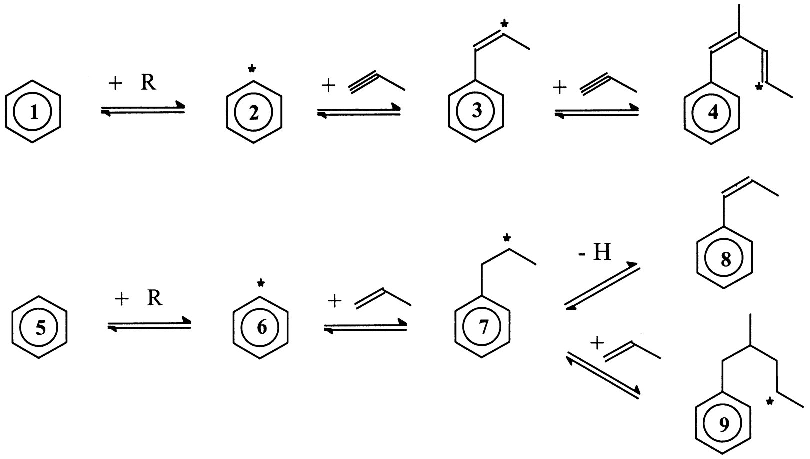


Fig. 18. Differences in reaction paths from propyne and propene.

Table 5
Number of reaction steps and of surface species in the networks generated for each cluster: influence of the number of olefins

Cluster	C_2H_2, C_2H_4, H, CH_3, C_2H_5, C_2H_3		C_2H_2, C_2H_4, C_3H_4, H, CH_3, C_2H_5, C_2H_3		C_2H_2, C_2H_4, C_3H_4, C_3H_6, H, CH_3, C_2H_5, C_2H_3	
	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps	Number of surface species	Number of reaction steps
Front	62	389	109	623	345	2151
Fissure	56	298	82	408	213	1162
Bay	7	35	9	41	26	145
Cove	21	96	21	96	33	146
Fjord	2	9	2	9	2	9

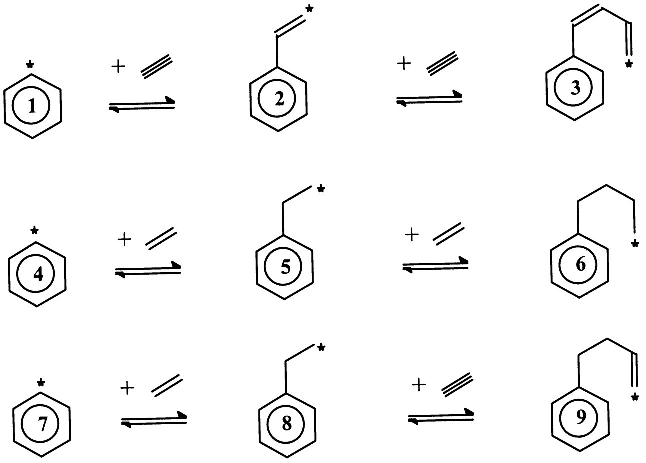


Fig. 19. Reaction paths in the coke formation from ethyne and ethene.

6. Conclusions

The complex mechanism of coke formation can be described based on elementary reactions between surface species and the coke surface. The coke layer is represented by a flat aromatic structure, which is activated by interaction with gas phase radicals. In case of ethane cracking hydrogen, methyl, ethyl and allyl radicals are the most important in that respect. For heavier feed stocks other gas phase components may also contribute significantly to the coke formation. Ethyne, ethene, propyne and propene contribute to the growth of the coke layer by elementary reactions which can be divided into five classes of reversible reactions: hydrogen abstraction, substitution by gas phase radicals at the aromatic surface, addition of gas phase radicals to the double bonds in surface species, addition of radical surface species to gas phase olefins and cyclization. The number of carbon atoms incorporated in the coke layer depends on the local environment of a surface species. This local environment can be described in terms of only five clusters. Each surface species is located at two clusters, an ensemble of clusters. The combination of both surface species and ensemble of clusters, a so-called reaction component, has to be considered when generating the network of elementary reactions. At each of the clusters in the ensemble a ring can be formed starting from the surface species corresponding to the EOC. The network for each individual cluster can be generated based on binary relation matrices. The complete network for coke formation can than be derived from these networks for the individual clusters. The identification of the reaction components formed upon ring closure and the determination of the change in ensemble of clusters upon ring formation at neighboring clusters are hereby essential.

For other processes, in which aromatics formation plays an important role such as in soot formation in combustion and fullerenes formation, the presented approach can be very useful and the corresponding network can be easily generated.

In case of ethane cracking the generated network contains over 14,000 reaction steps between about 2400 reaction components. The obtained network can be used to describe the coke formation during thermal cracking. The kinetics for the reactions can be obtained from those of analogous gas phase reactions taking into account the presence of the solid coke surface. This approach based on elementary reactions can be used for the development of a model for coke formation during the thermal cracking of a variety of feedstocks taking into account the corresponding significant coke precursors in the gas phase.

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References

[1] F.O. Rice, J. Am. Chem. Soc. 53 (1931) 1959.
[2] A. Kossiakoff, F.O. Rice, J. Am. Chem. Soc. 65 (1943) 590.
[3] W.D. Clark, S.J. Price, Can. J. Chem. 48 (1970) 1059–1064.
[4] K.M. Sundaram, G.F. Froment, Ind. Eng. Chem. Fundam. 17 (3) (1978) 174–182.
[5] W. Tsang, Int. J. Chem. Kin. 10 (1978) 599.
[6] J.A. Moens, G.F. Froment, J. Anal. Appl. Pyrol. 3 (1982) 187.
[7] E. Ranzi, M. Dente, S. Pierucci, G. Biardi, Ind. Eng. Chem. Fundam. 22 (1983) 132.
[8] P. Kumar, D. Kunzru, Ind. Eng. Chem. Proc. Des. Dev. 24 (1985) 774–782.
[9] P.A. Willems, G.F. Froment, Ind. Eng. Chem. Res. 27 (1988) 1959.
[10] P.A. Willems, G.F. Froment, Ind. Eng. Chem. Res. 27 (1988) 1966.
[11] Q. Chen, G.F. Froment, J. Anal. Appl. Pyrol. 21 (1991) 27–50.
[12] Q. Chen, G.F. Froment, J. Anal. Appl. Pyrol. 21 (1991) 51–77.
[13] Y. Xiao, J.M. Longo, G.B. Hieshima, R.J. Hill, Ind. Eng. Chem. Res. 36 (1997) 4033–4040.
[14] P.M. Plehiers, G.C. Reyniers, G.F. Froment, Ind. Eng. Chem. Res. 29 (1990) 636–641.
[15] J.L. Figueiredo, Erdöl und Kohle-Erdgas-Petrochemie 42 (7/8) (1989) 294–297.
[16] M.J. Bennet, J.B. Price, J. Mater. Sci. 16 (1) (1981) 170–188.
[17] F.D. Kopinke, G. Zimmerman, B. Ondruschka, Ind. Eng. Chem. Res. 26 (11) (1987) 2393–2397.
[18] G.F. Froment, Fouling of heat transfer surfaces by coke formation in petrochemical reactors, in: E. Sommerscales, J.G. Knudsen (Eds.), Fouling of Heat Transfer Equipment, Hemisphere Publ. Corp., 1981.
[19] L.F. Albright, J.C. Marek, Ind. Eng. Chem. Res. 27 (5) (1988) 755–759.
[20] G.F. Froment, Rev. Chem. Eng. 6 (4) (1991) 295–328.
[21] G.C. Reyniers, G.F. Froment, F.D. Kopinke, G. Zimmerman, Ind. Eng. Chem. Res. 33 (11) (1994) 2584–2590.
[22] K.M. Sundaram, G.F. Froment, Chem. Eng. Sci. 34 (1979) 635–644.
[23] K.M. Sundaram, G.F. Froment, AIChE J. 27 (1981) 946–951.
[24] M. Pramanik, D. Kunzru, Ind. Eng. Chem. Proc. Des. Dev. 24 (1985) 1275.
[25] M. Okkerse, M.H.J.M. de Croon, C.R. Kleijn, H.E.A. van den Akker, G.B. Marin, J. Appl. Phys. 84 (11) (1998) 6387–6398.
[26] W.L.M. Weerts, M.H.J.M. de Croon, G.B. Marin, J. Electrochem. Soc. 145 (4) (1998) 1318–1330.
[27] P.J. Clymans, G.F. Froment, Comp. Chem. Eng. 8 (2) (1984) 137–142.
[28] E. Vynckier, G.F. Froment, in: G. Astarita, S.I. Sandler (Eds.), Kinetic and Thermodynamic Lumping of Multicomponent Mixtures, Elsevier, Amsterdam, 1991, pp. 131–161.
[29] L.J. Broadbelt, S.M. Stark, M.T. Klein, Ind. Eng. Chem. Res. 34 (1995) 2566–2573.
[30] D.J. Klinke, L.J. Broadbelt, AIChE J. 43 (7) (1997) 1828–1837.
[31] R.G. Susnow, A.M. Dean, W.H. Green, P. Peczak, L.J. Broadbelt, J. Phys. Chem. A 101 (1997) 3731–3740.
[32] M.J. De Witt, D.J. Dooling, L.J. Broadbelt, Abstr. Pap. Am. Chem. Soc. 218, 27-Fuel, Part 1, (1999).
[33] F.D. Kopinke, G. Zimmerman, G.C. Reyniers, G.F. Froment, Ind. Eng. Chem. Res. 32 (1) (1993) 56–61.
[34] F.D. Kopinke, G. Zimmerman, G.C. Reyniers, G.F. Froment, Ind. Eng. Chem. Res. 32 (11) (1993) 2620–2625.
[35] M. Frenklach, H. Wang, Phys. Rev. B 43 (1991) 1520–1545.
[36] S.J. Cyvin, I. Gutman, Kekulé Structures in Benzenoid Hydrocarbons, Lecture Notes in Chemistry, Vol. 46, Springer, Berlin, 1988.
[37] D.M. Himmelblau, Bischoff, K.B., Process Analysis and Simulation, Wiley, New York, 1968.
[38] A. Calusaru, G. Volanschi, Int. Chem. Eng. 26 (3) (1986) 428.
[39] L.J. Broadbelt, S.M. Stark, M.T. Klein, Chem. Eng. Sci. 49 (1994) 4991–5010.
[40] A.T. Balaban, Chemical Applications of Graph Theory, Academic Press, London, 1976.
[41] N. Trinajstic, Chemical Graph Theory, CRC Press, Boca Raton, FL, 1983.
[42] R.B. King, D.H. Rouvray, Stud. Phys. Theor. Chem. 51 (1987) 575.