

Quantifying the relative importance of the elementary steps involved in the cracking of (cyclo)alkanes via a microkinetic analysis

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Introduction

The catalytic cracking of hydrocarbons is known to be a complex process because of the huge number of elementary reactions and species involved. A detailed analysis of products spectra only supplies a limited view of how the cracking of the feedstock has taken place and, hence, a microkinetic analysis is needed. Fundamental kinetic models such as Single-Event MicroKinetics (SEMK) have been successfully utilized for modeling acid catalyzed process in general and catalytic cracking in particular [1]. SEMK is based on the free carbenium ion chemistry and requires a very detailed computed network involving a large number of species and elementary steps. The latter belong to a relatively limited number of reaction families, e.g., (de)protonation, β -scission, alkylation, isomerization and hydride transfer [2]. This work reports on the application of a SEMK to quantify, in relative terms, the importance of the elementary steps involved in the cracking of three (cyclo)alkanes, via a contribution analysis.

Materials and Methods

The experimental cracking of (cyclo)alkanes, i.e., n-decane, methylcyclohexane and n-butylcyclohexane, admixed with 1-octene, was performed in a fixed bed TEOM[®] reactor on a REUSY equilibrium catalyst. 1-Octene was added to enhance coke formation allowing studying cracking and coking in a further stage. The reaction was performed at 693-753 K, 9-47 kg_{cat}/(mol)⁻¹ and inlet partial pressure of 26.6 kPa for (cyclo)alkanes and 4.8 kPa for 1-octene [3]. The reactor was operated in the integral regime and in the absence of concentration and thermal gradients and exhibited a plug flow and an isobaric behavior. Thermal cracking was negligible. The kinetic model parameters required for the calculation of the reaction rates were estimated via a non-isothermal regression of the obtained experimental data in the absence of coking [2]. As the number of species in the SEMK network is enormous, some relumping is introduced to the model. The lump selection is defined by the observed products and accounts for the carbon number and the branching degree for acyclics and only the carbon number for cyclics. The contribution analysis is based on integral contribution factors which are defined as the ratio of the rate of (dis)appearance of a certain lump through a given elementary step to the total rate of (dis)appearance of that lump at a certain position inside the reactor [4].

Results and Discussion

(Cyclo)alkane conversions ranged from 8 to 70 % with n-butylcyclohexane exhibiting the highest reactivity and n-decane the lowest. The cracking of n-decane mostly produced alkanes and alkenes, whereas that of methylcyclohexane and n-butylcyclohexane yielded alkanes and alkenes together with cycloalkanes, cycloalkenes and aromatics. The relative amount of these types of hydrocarbons depends on the operating conditions, in

particular, on temperature. This is caused by the different values of the activation energies of the various reaction types. The contribution factors are also temperature dependent. Those computed at 753 K and 15.5 kg_{cat}/(mol)⁻¹ has been taken as reference in this work.

n-Decane is converted to the same extent, 27 %, to methylnonanes via PCP-isomerization and to linear decenes via deprotonation, while the remaining n-decane conversion, 46 %, occurs via protolysis. The latter reaction is only important for initiating the cracking and does not take place at all on branched n-decane isomers or other cracked products. Branched n-decane isomers are highly susceptible to PCP-isomerization exhibiting the largest rates of disappearance, in particular, the transformation of mono to dimethyl branched and di to trimethyl branched. The relative ratio β -scission to PCP-isomerization for methylnonanes is rather small, e.g. 99 % isomerizes to dimethyloctanes. The C₃-C₇ fraction is mostly formed out of di and tribranched species via β -scission showing that highly branched hydrocarbons are very susceptible to this reaction. Linear C₆-C₉ carbenium ions produced via n-decane protolysis isomerize to branched ions and then undergo β -scission to C₃-C₆ species.

50% of the converted methylcyclohexane is transformed into methylcyclohexene while 30% has undergone ring-contraction to dimethylcyclopentanes. The remaining 20% has lead to ethylcyclopentane through ring contraction and cyclohexane via protolysis. Dimethylcyclopentanes are more than three times more rapidly formed than ethylcyclopentane. Endocyclic β -scission almost exclusively occurs on the formed dimethylcyclopentanes yielding methylhexenes. The latter isomerize to dimethylpentenes, which are the source of the C₃-C₄ fraction formed through β -scission. The cycloalkenes formed via deprotonation not only undergo ring contraction and ring-opening, as was described for cycloalkanes, but also transform to cycloalkadienes. 25% of the methylcyclohexenes conversion yields the corresponding cycloalkadienes, which are practically fully converted to toluene. Protolysis participates in the conversion of methylcyclohexane, dimethylcyclopentanes and ethylcyclopentane but not in the reconversion of ring-opening products or lighter cracked products.

Dealkylation prevails over ring-opening when cracking n-butylcyclohexane, however, not to the expected extent. The former reaction is responsible for about 22% of the n-butylcyclohexane conversion, while endocyclic β -scission contributes to about 17%. The acyclic products produced via exocyclic β -scission and endocyclic β -scission are mostly branched ones showing that more stable carbenium ions formed via isomerization are required in order for β -scission to occur, as was also observed for n-decane and methylcyclohexane. Ring-opening products formed out of n-butylcyclohexane crack in the same way to what has been described for n-decane. Cycloalkenes formed from n-butylcyclohexane can reconvert to cycloalkanes, undergo ring-opening and dealkylation, and deprotonate to cycloalkadienes, which are practically fully converted to A₁₀ aromatics. Protolysis has also some participation, around 8 %, in the initial conversion of n-butylcyclohexane.

Significance

This work presents how experimental work and modeling techniques can be combined to determine how the catalytic cracking of hydrocarbons takes place.

References

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