26d Single Event Kinetic Modeling of Complex Catalytic Processes

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The feedstocks processed in petroleum refining and in many petrochemical operations generally consist of homologous series of hydrocarbon families like paraffins, olefins, naphthenes and aromatics. These series each contain a large number of components, extending in a typical vacuum gas oil e.g. from C15 to C40.Each of these components leads to complicated reaction pathways. Because of this complexity, but also because of incomplete chemical analysis, the kinetic modeling of these processes was based until recently upon reduced networks consisting of a small number of reactions between pseudo-components or lumps, defined more by physical than by chemical properties. The rate coefficients of such models depend on the feed composition, so that extensive and costly experimentation is required when the feedstock is changed. As the feedstocks evolve towards greater complexity and as operational criteria become more severe the reaction model has to be more realistic, contain more lumps and more rate parameters ... Where is the limit? Is this really the way to go? The approach taken in the presentation is totally different. The model retains the full detail of the reaction pathways of the individual feed components and reaction intermediates. It is expressed in terms of elementary steps, e.g. on acid catalysts: the shift of a methyl group or the scission of a C-C-bond. These steps only involve moieties of the molecule and can occur in various positions of one and the same molecule. The number of types of elementary steps which are possible for hydrocarbons reacting on a given catalyst is much smaller than the number of molecules in the reacting mixture. Assigning a unique rate coefficient to a certain type of elementary step would be an excessive simplification, however: the structure of reactant and product also contributes to the value of the rate coefficient. The reduction of the number of parameters to a tractable level is possible only through a fundamental modeling of the rate coefficient itself, based upon transition state theory and statistical thermodynamics and accounting for the evolution of the potential energy. Such an approach leads to parameter values which are invariant with respect to the feedstock composition and has become possible through the computer generation of the network of elementary steps and the availability of advanced quantum chemical software. More specifically the talk deals with the kinetic modeling of processes catalyzed by acids and involving carbenium- and carbonium ions. Industrial examples are: catalytic reforming, catalytic cracking, hydrocracking, alkylation, isomerization and the conversion of methanol into olefins In certain cases (catalytic reforming, hydrocracking) the acid catalysts are loaded with metals which have a (de)hydrogenation function and produce olefinic intermediates which are more reactive on the acid sites than the saturated compounds. That does not affect the approach because the metal content is sufficiently high to ensure that the rate determining step is still associated with steps occurring on the acid sites of the catalyst. This permits an entirely general kinetic approach, applicable to all the processes mentioned above. The approach will be illustrated by means of the Methanol-to-Olefins process, that permits the full application of the concepts advocated here. After that a process with complex feedstock, like the catalytic cracking of oil fractions will be dealt with.