SINGLE EVENT MICROKINETICS OF (CYCLO)ALKANE CRACKING ON Y AND ZSM-5 ZEOLITES

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Fluid catalytic cracking of hydrocarbons is one of the most important acid catalyzed processes in present-day oil refining [1]. The C-C bonds present in the feedstock, usually vacuum gas oils or residues, are broken in order to obtain gasoline and light alkenes. For the production of gasoline the main active component of an industrial catalyst is Y zeolite, while ZSM-5 can be added to increase the yield of light alkenes [2].

The widespread use of zeolites in hydrocarbon conversion processes is based on their tailor-made acid properties and on their particular framework topology. The goal of this research is to develop an accurate and flexible kinetic model that can account for the influence of these catalyst properties on activity and selectivity. Therefore, the cracking of model compounds over a series of commercially available Y and ZSM-5 zeolites varying in acid characteristics and in framework topology has been studied under a wide range of operating conditions. A suitable model component to study alkane cracking is 2,2,4-trimethylpentane, while methylcyclohexane is selected to study cycloalkane cracking.

Catalytic cracking experiments have been carried out in a recycle electro-balance reactor set-up equipped with online gas chromatographic effluent analysis using i-octane and methylcyclohexane. A series of five (US)Y zeolites with Si/Al ratio 2,6-30 and three ZSM-5 zeolites with Si/Al ratio 15-40 have been investigated allowing the evaluation of the influence of Si/Al ratio and of the presence of EFAl for two different framework topologies and for two different reactant structures.

Under the conditions studied the most abundant cracking products of 2,2,4-trimethylpentane over the (US)Y zeolites are isobutane, isobutene, n-butenes and propylene. On the ZSM-5 zeolites, methane, ethane, ethylene, propylene and propane are detected in the largest quantities. Methylcyclohexane cracking on (US)Y mainly yields isobutane, propane, n-butenes, propylene, isopentane and toluene, while on ZSM-5 propane,

propylene, toluene, xylenes and ethylene are formed. This indicates that distinct cracking reaction mechanisms occur on (US)Y and on ZSM-5.

It was observed that the hydrocarbon cracking activity of the zeolites studied was influenced by the acid properties. Enhanced catalyst activity was noticed when EFAl was present. However, within one framework type product selectivities were found to be independent of the acid properties. This shows that the catalyst activity is controlled by its acid properties while the catalyst selectivity is determined by its framework topology.

A kinetic model based on carbenium ion chemistry that includes the thousands of reactions occurring during catalytic cracking of hydrocarbons is developed. To reduce the number of kinetic parameters, the elementary steps are grouped into a limited number of reaction families [3] and the elementary rate coefficients are decomposed into a so-called "single event" contribution [4] and a symmetry contribution related to the structure of the reacting species. The single event rate coefficient thus obtained only depends on the reaction family and on the type (primary, secondary, tertiary) of the intermediate involved in the elementary step. This allows estimating these rate coefficients based on experimental data acquired from suitable model components.

The effect of the catalyst properties is incorporated in the model by introducing a limited number of catalyst descriptors accounting for the acid characteristics and the framework topology. Catalyst descriptors are for example the amount of acid sites, the protonation enthalpy [5, 6] and the activation energy [7]. In the model, the latter two catalyst descriptors are expressed relative to a well-known reference catalyst.

A single event microkinetic model for catalytic cracking of alkanes is developed. Combining transition state theory and statistical thermo-dynamics allows calculation of the pre-exponential factors. Activation energies and catalyst descriptors have been estimated by regression to experimental data. The model describes the observed trends adequately.

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