

CATALYTIC CRACKING ON FAU, MFI AND BIPOMS: EFFECT OF ACIDITY AND FRAMEWORK TOPOLOGY

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Summary

The use of zeolites in hydrocarbon conversion processes is based on their acid properties and their framework topology. The aim of this work was to develop a single event microkinetic model for catalytic cracking accounting for the effect of these catalyst properties on activity and selectivity. Cracking experiments using 2,2,4-trimethylpentane and methylcyclohexane have been performed over FAU, MFI and BIPOMs. Based on these results kinetic descriptors and catalyst descriptors are obtained via regression. The developed models can provide guidelines for catalyst design.

Keywords

rational design of catalysts, reaction path analysis, novel functional materials

Introduction

The widespread use of zeolites in oil refining industry is based on two main features: an adjustable Brønsted acidity generated by the presence of Al inside the framework and shape selective effects due to the particular framework topology with well-defined pore sizes and structures¹. Both catalyst properties can be tailored to the requirements of the process in question.

In fluid catalytic cracking heavy oil fractions are converted into valuable transportation fuels, typically gasoline, and light olefins. FAU zeolite is used for the production of gasoline, while MFI can be added as a co-catalyst to increase the yield of olefins, mainly propylene. The trend to process increasingly heavier feedstocks has driven catalyst researchers to design materials with larger pores than conventional zeolites to reduce diffusion limitations encountered by bulky molecules. One approach was to synthesize zeotype materials with a bimodal porous structure, BIPOMs². Aggregation of structured zeolite building units with MFI framework type in different ways leads to zeotype materials with MFI micropore system and different ordered mesopore systems.

The aim of the present work was to develop an accurate and flexible kinetic model that can describe the effect of acidity and framework topology on activity and selectivity in catalytic cracking. This model can be applied for process optimization by giving guidelines to design the most appropriate zeolite to meet the refiner's requirements. Model parameters are obtained via regression to experimental data.

Materials

Catalytic cracking experiments using model components have been performed over a series of five FAU and three MFI zeolites. Besides these commercially available zeolites, two newly developed zeotype materials with bimodal pore structure, BIPOMs, have been studied. These catalysts vary in Si/Al ratio (2.6 – 30 for FAU, 15 – 40 for MFI, 50 for BIPOMs), in the presence of EFAl and in framework topology. A suitable model component to study alkane cracking is 2,2,4-trimethylpentane, while methyl-cyclohexane is selected to study cycloalkane cracking.

Cracking has been studied in a recycle electrobalance reactor setup equipped with online gas chromatographic effluent analysis³. Reaction temperature was varied from 698 to 763 K, hydrocarbon partial pressure ranged from 3 to 15 kPa and a broad range of space times were applied to obtain a broad range of conversions.

Results and discussion

At equal experimental conditions, 2,2,4-trimethylpentane conversion is considerably lower on MFI than on FAU, while methylcyclohexane conversion is similar on MFI and FAU. This lower activity points to the occurrence of reactant shape selectivity effects caused by the slower diffusion of the bulky 2,2,4-trimethylpentane inside the MFI pores. Both BIPOMs display a cracking activity that is comparable to that of a commercial MFI with similar Si/Al ratio.

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The product distribution obtained in 2,2,4-trimethylpentane cracking on FAU over a conversion range from 1 to 70 mol% shows a peak at C₄, while on MFI C₁ – C₃ species are most abundant. On FAU the main reaction route is hydride transfer followed by β -scission, while on MFI protolytic scission is favored. This indicates that transition state shape selectivity plays a role too in 2,2,4-trimethylpentane cracking on MFI. Also in methylcyclohexane cracking different product distributions are obtained on FAU and MFI. Similarly, protolytic scission is favored on MFI over hydride transfer and β -scission on FAU.

These product distribution features can be used to easily identify large pore FAU or medium pore MFI type catalytic behavior of the BIPOMs. The catalytic cracking performance of one BIPOM is similar to FAU, while the other shows mixed FAU/MFI type behavior. This distinct behavior can be explained by different locations of the acid sites in the BIPOMs, due to different synthesis methods.

Within one framework type, the zeolite acid properties do not affect the product selectivities obtained for both reactants. However, the zeolite topology does influence the product selectivities due to the occurrence of shape selectivity effects. It can thus be stated that in catalytic cracking the zeolite acidity controls its activity, while the framework topology determines its selectivity.

Kinetic model

The thousands of reactions occurring during catalytic cracking of hydrocarbons can be classified into a limited number of elementary reaction families. The reaction network is generated automatically using a computer algorithm and includes protolytic scission, (de)protonation, β -scission/alkylation, hydride transfer and isomerization reaction steps^{4,5}.

To reduce the number of kinetic parameters, the single event microkinetic modeling methodology⁶ was applied. The single event rate coefficients thus obtained only depend on the reaction family and on the type (primary, secondary or tertiary) of the carbenium ion involved in the elementary reaction. This allows determining these rate coefficients using suitable model components. These single event rate coefficients are termed “kinetic descriptors”.

The influence of catalyst properties such as acidity and framework topology can be incorporated in the model by introducing “catalyst descriptors”.

Catalyst descriptors that account for acidity are for example the concentration of active sites, the protonation enthalpy^{7,8} and the activation energy⁹. In the model, the latter two catalyst descriptors are expressed relative to a reference catalyst. The effect of reactant shape selectivity occurring in MFI due to mass transfer limitations can be modeled by incorporating configurational diffusion. The diffusion coefficients are the necessary catalyst

descriptors. Transition state shape selectivity can be modeled by building in restrictions in the network generation code.

Conclusions

The influence of acid properties and framework topology on catalytic cracking activity and selectivity has been studied on FAU, MFI and BIPOMs. Based on the experimental data a kinetic model is developed including kinetic descriptors as well as catalyst descriptors.

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