EFFECTS OF MOLECULE STRUCTURE AND PORE SIZE ON MECHANISMS FOR ZEOLITE-CATALYZED HYDROCARBON CRACKING

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Abstract

The mono-molecular and bi-molecular cracking of short alkanes (linear C2—C4, isobutane, JP10, and adamantane) in medium and large pore zeolites (framework types MFI, BEA, MOR, and FAU), as well as on a model Al/SiO2 surface, is investigated using dispersion-corrected, periodic density-functional theory. The intrinsic barriers of the various reactions are found to be rather similar for the same reactants in different framework environments, and the differences in apparent barriers originate mostly from the adsorption enthalpy differences. Electronic effects (e.g., branching) affect the barriers in accordance with the rules of carbenium ion chemistry.

Keywords

Microporous catalysts, Protolytic cracking, Classical cracking, Hydride transfer, Beta scission.

Introduction

Catalytic cracking is a cornerstone process for current petroleum refineries. Its various forms, such as fluid catalytic cracking and hydrocracking, are the major routes through which transportation fuels and lubricants are made. (Meyers, 2003) More recently, the endothermic nature of cracking is also being explored as an effective route for heat removal and temperature control in supersonic aircraft engines. (Luo et al., 2014) In all these applications, nanoporous solid acids such as zeolites are often used as the catalysts, whose unique pore / channel systems afford the potential for a precise control of reactivity and selectivity through different degrees of "solvation" of the reactants and products, as well as transition states. In this work, we use dispersion-corrected, periodic density-functional theory to investigate the mono-molecular and bi-molecular cracking mechanisms of short hydrocarbons in various zeolites and on a model Al/SiO$_2$ surface, and discuss the effects of the reactant structure, alkoxide

structure, and framework confinement on the resulting activation energies. The results provide a foundation for the use of more cost effective methods to screen different zeolite pore topologies and to investigate how one can control the product selectivity by varying the temperature and reactant distributions, ultimately a step towards the rational catalyst design and optimization.

Mono-molecular Cracking

Also known as the protolytic mechanism, proposed by Haag and Dessau in 1984, mono-molecular cracking of alkanes is believed to be the dominant mechanism for alkane cracking at low reactant coverage, at low conversions, and within strong confinement of microporous catalysts. The protolytic route also initializes the cracking of pure alkane feeds and provides the initial carbenium ion species, and establishes a link between solid-acid catalyzed

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reactions with solution-phase super-acid chemistry. The protolytic mechanism occurs by a proton from a Brønsted acid site attacking a C—C bond and the formation of a 3-atom-centered carbocation, the carbonium transition state, which collapses to release a shorter alkane and a surface bound carbenium ion, or rather an alkoxide in most cases (Kotrel et al., 2000).

The structure of the carbonium transition states resembles two carbenium ions formed with the cleavage of the C—C bond by the proton, and the stability of the two quasi carbenium ion species can be used to understand the variation of activation energies with respect to changing reactant structures and different cracking modes.
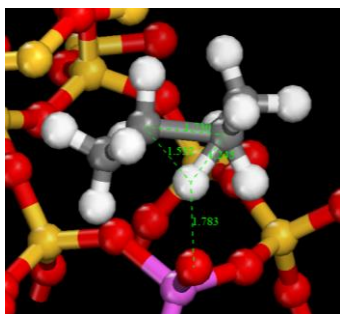

Figure 1. Transition-state structure of protolytic cracking at the middle C—C bond of n-butane in zeolite MFI.

Bi-molecular Cracking

Known as the classical mechanism, bi-molecular cracking involves the chain reactions of carbenium ion intermediates, in particular the hydride transfer from reactant hydrocarbon molecules to an alkoxide that is to be released as an alkane, and subsequent β-scission of the newly-formed alkoxide. These surface-bound carbenium ion species can also undergo skeletal isomerization to form more stable isomers, oligomerize with alkenes to produce longer chain hydrocarbons, dehydrogenate to alkenes and aromatics, etc. The classical mechanism is thought to be dominant at high reactant coverage and more spacious porous catalysts (Corma and Orchilles, 2000).

The trends of activation energies for hydride transfer and β-scission with varying reactant and alkoxide structures can be similarly understood in terms of the stability of the quasi carbenium ion species involved. The transition state geometries for both hydride transfer and β-scission are bulkier than those encountered in mono-molecular cracking, and can induce a higher reaction barriers with more confined catalyst environments, such as in medium-pore zeolite MFI.

Conclusions

We have performed a computational study using dispersion-corrected, periodic density-functional theory. Both the mono-molecular and bi-molecular cracking of short alkanes (linear C2—C4, isobutane, JP10, and adamantane) are investigated, and zeolites with medium to large pore sizes (framework types MFI, BEA, MOR, and FAU) and a model Al/SiO2 surface are examined. It is found that dispersion is critical in understanding the chain-length dependence and framework effects of the activation energies. In particular, the apparent activation energies decrease with carbon number and framework confinement, while the intrinsic activation energies for the various reactions (protolytic cracking, hydride transfer, and β-scission) exhibit a much weaker dependence on either factor. Electronic effects (e.g., branching) affect the barriers in accordance with the rules of carbenium ion chemistry. Bulky transition states (with respect to the channel dimensions of the zeolite catalyst) can deviate from these general trends.
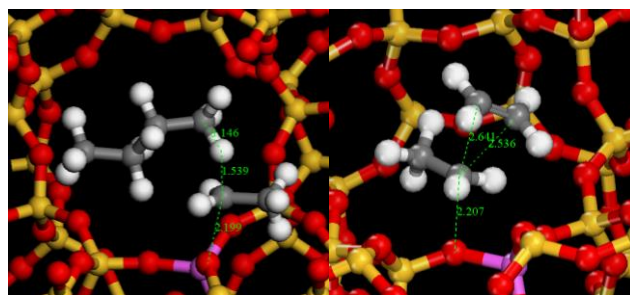

Figure 2. Transition-state structures of classical cracking in zeolite MFI, showing the hydride transfer from n-butane to ethoxide to release ethane (left) and subsequent β-scission of the newly-formed n-butoxide to form an ethane and an ethoxide.

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