



The role of spatial constraints and entropy in the adsorption and transformation of hydrocarbons catalyzed by zeolites



Tomáš Bučko^{a,b,*}, Jürgen Hafner^c

^a Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská Dolina Ilkovičova 6, SK-84215 Bratislava, Slovakia

^b Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84236 Bratislava, Slovakia

^c Fakultät für Physik and Center for Computational Materials Science, Universität Wien, Sensengasse, Wien 1090, Austria

ARTICLE INFO

Article history:

Received 30 October 2014

Revised 10 April 2015

Accepted 19 April 2015

Available online 15 May 2015

Keywords:

Acidic zeolites

Protolytic cracking

Ab-initio molecular dynamics

Diffusion

Entropy effect

ABSTRACT

The competing influences of enthalpy and entropy on the adsorption and transformation of hydrocarbon molecules in zeolites have been investigated using dispersion-corrected density-functional theory in combination with advanced statistical-mechanical techniques. At the example of propane in protonated mordenite, it is demonstrated that while enthalpy favors adsorption in the narrower side pockets (SP) due to the stronger interaction with the framework, the loss of entropy is smaller for molecules in the wider main channel (MC). At ambient and elevated temperatures, the free energy favors adsorption in the MC (in agreement with experiment) and diffusion to the SP is an activated process. On the other hand, the free energy of activation for monomolecular cracking is lower for Brønsted acid (BA) sites in the SP, if the reactant is already located there. Cracking at a BA in the MC is a simple one-step reaction but as the SP is accessible to molecules only via the MC, cracking at a BA site in the SP is possible only after overcoming the barrier for diffusion from the MC to the SP. Thus, the difference in the free energies of adsorption in the MC and the SP increases the effective free-energy of activation for the reaction in SP and the reaction in the MC is favored. This result contradicts the interpretation of recent experiments on hydrocarbon transformations catalyzed by mordenite-containing BA sites and Na⁺ counterions in varying proportions. This experimental interpretation is based on the assumption that Na⁺ counterions preferentially replace BA sites located in the SP. This assumption has been critically examined using ab-initio calculations and found to be inconsistent with our theoretical predictions. It is demonstrated that the experimentally observed decrease of the reaction rate with increasing Na⁺/H⁺ ratio arises from the strongly attractive nature of the Na⁺ counterions, which makes the approach of the reactant to the BA site more difficult and reduces the reaction rate. We suggest that our results on the competing influence of enthalpy and entropy arising from the confinement of the reactant in cavities of different diameters have general validity for the adsorption and acid-catalyzed reactions of hydrocarbon molecules in zeolites with a complex framework structure.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Materials based on zeolites belong to the most important catalysts, and a detailed knowledge of various aspects of the processes determining their catalytic activity is required for improving existing or designing new applications. We have shown in a series of computational studies [1–4] that entropy plays an important role at various stages of chemical processes taking place in zeolites –

* Corresponding author at: Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská Dolina, SK-84215 Bratislava, Slovakia.

E-mail addresses: bucko@fns.uniba.sk (T. Bučko), juergen.hafner@univie.ac.at (J. Hafner).

from affecting the activation barriers to inducing new reaction mechanisms – and the importance of this effect is now documented also in number of other theoretical studies [5–8]. We have shown that alkanes such as propane and isobutane do not form stable adsorption complexes with Brønsted acid (BA) sites at reaction temperatures (300–800 K) and the work needed to bring the reactant molecules sufficiently close to the active site was recognized as an important contribution to the free energy of activation [1]. These results are a consequence of the fact that the specific interaction of the reactant with the BA site is responsible only for a small part of the adsorption energy, while the overwhelming contribution comes from the non-bonding interactions of the molecule with the atoms forming the inner wall of the zeolitic cavities [4,9].

The fact that the framework structure of zeolites or other microporous materials affects their performance as a catalyst or as a molecular sieve is well documented: perhaps the best known example is the shape selectivity where the size and geometry of the channels imposes spatial constraints on the molecules that react or are formed during the catalytic reactions [10–14]. The shape selectivity is understood to be mainly of enthalpic nature, i.e., its origin is the short-range repulsive interactions between reactant and zeolite framework [14].

The important role of the interactions between molecular adsorbates and the zeolite framework also explains why saturated molecules such as alkanes are more strongly bound in zeolites with narrower cavities. Savitz et al. [15], for instance, have shown that the heat of adsorption of methane in a series of zeolites with one-dimensional channels surrounded by 10-, 12-, and 14-membered rings (TON, MTW, UTD-1) varies from -27 kJ/mol to -14 kJ/mol with increasing effective diameter of the channel. Another experimental confirmation of this trend has been reported in Refs. [16,17], where the heat of adsorption of propane, butane, pentane, and hexane in protonated TON, FER, MFI, and MOR has been shown to increase with framework density. However, the influence of the pore structure on the adsorption properties is more complex in zeolites with a framework structure with large and small cavities accessible to adsorbates. For MOR, it was shown [18] that alkanes are adsorbed only in the large main channel (MC), but not in the smaller side pockets (SP), see Fig. 1. This would mean that the adsorption is determined not only by the enthalpy, but by a delicate balance between the enthalpy and entropy of adsorption. The smaller loss of entropy upon adsorption in the larger cavities favors a location of the adsorbates in the larger pores.

In contrast to these results, it has recently been suggested [21–24] that Brønsted acid (BA) sites located in the smaller side-pockets of MOR show a significantly larger activity for the monomolecular conversion (cracking, dehydrogenation) of alkanes than acid sites located in the larger main channels. This suggestion was based on the analysis of the reaction rates in Na-free H-MOR samples and partially Na-exchanged H-MOR, and led to the surprising conclusion that the loss of entropy is lower for reactions taking place in the smaller side-pockets. This is in direct contradiction of what is needed to explain the results of the adsorption studies. Gounder and Iglesia [22,23] attempted to explain this surprising result by the assumption that both the adsorbed molecules and their monomolecular transition states are only partially

contained within the SP's and protrude in the main channel. The interpretation of the reaction rates measured on Na-H-MOR samples is based on the assumption that the Na^+ counterions preferentially replace the H^+ sites in the center of the SP's and that the distribution of Na^+ does not change as a function of temperature. The assignment of the location of the Na^+ cations to the SP's is based on the conventional interpretation of the infrared (IR) spectra. The intensity distribution of the antisymmetric OH stretching modes [25] in the range from about 3550 to 3650 cm^{-1} is slightly asymmetric and may be fitted by two bands, a high-frequency (HF) mode at $\sim 3612\text{ cm}^{-1}$ and a low-frequency (LF) mode at $\sim 3585\text{ cm}^{-1}$. The HF mode was assigned to BA sites in the larger MC because its intensity decreases upon adsorption of large molecules such as pyridine which cannot enter the smaller SP. However, a detailed theoretical analysis [26,27] of the IR spectra has demonstrated that the OH stretching frequencies of BA sites in both the larger and smaller cavities show rather broad and overlapping distributions instead of a single characteristic frequency.

In this work, we present a fundamental analysis, based on first-principles density-functional calculations (including corrections for dispersion forces) combined with advanced statistical-mechanical simulations, of the effects of confinement and of the interplay between enthalpy and entropy on the adsorption and transformation of alkanes in zeolites, concentrating on propane in MOR. The paper is organized as follows: in Section 2, the methodology and the computational details used in this study are described. The hypotheses underlying the identification of BA sites in different locations in terms of the IR spectra and the energetics of different positions of the Na^+ cations are discussed in Section 3.1. The enthalpic and entropic aspects of propane adsorption in main channel and side pockets of MOR are analyzed in Section 3.2. The influence of confinement on the free energy of activation for cracking is explored in Section 3.3, discussion of the most important results is given in Section 4, and some more general implications of our results are discussed in Section 4.1.

2. Theory

2.1. Electronic structure calculation

Periodic density-functional calculations have been performed using the VASP code [28–31]. The Kohn–Sham equations have been solved variationally in a plane-wave basis set using the projector-augmented-wave (PAW) method of Blöchl [32], as adapted by Kresse and Joubert [33]. The PBE exchange–correlation functional in the generalized gradient approximation proposed by Perdew et al. [34] was used. The D2 correction of Grimme [35] has been applied to account for dispersion interactions not included in density-functional theory. This approach was shown to improve predictions on structure, energetics, and elastic properties of wide range of materials where dispersion forces play an important role [36]. As shown by Göltl et al. [9], the PBE-D2 approach predicts reasonable adsorption energies (compared to experiment and advanced quantum-chemical calculations) for alkanes in protonated acidic and Na-exchanged zeolites.

Brillouin-zone sampling was restricted to the Γ -point. In the static calculations, a plane-wave cutoff energy of 400 eV was used and the relaxations were terminated when all forces acting on atoms were smaller than 0.01 eV/\AA . Harmonic vibrational frequencies were computed using a finite-difference approach, and the anharmonicities were determined by solving the one-dimensional Schrödinger equation for the potential sampled along the direction of the harmonic eigenvectors using the program ANHARM [37].

In the ab-initio molecular dynamics simulations, the plane-wave cutoff energy was set to 311 eV , the convergence

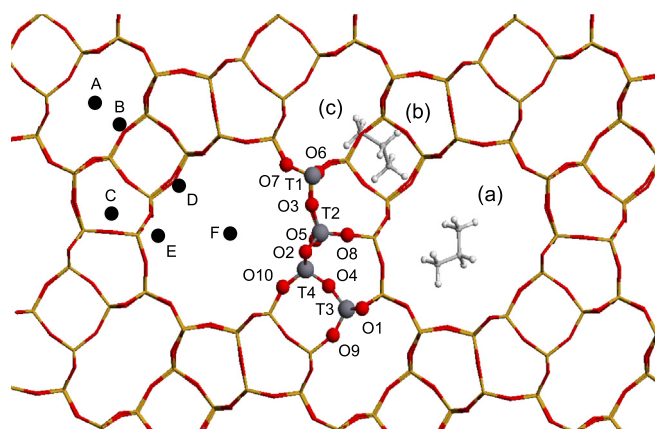


Fig. 1. Crystal structure of mordenite, projected along the c -direction, with propane adsorbed in the main channel (a), and a side pocket (b). According to our molecular simulations, location of propane in the small channel (c) is not stable and the molecule diffuses spontaneously to the side pocket at temperatures close to or higher than room temperature. The labeling of the tetrahedral (T) and oxygen (O) sites of the framework follows Ref. [19]. The possible locations of extra-framework cations classified by Mortier (Ref. [20]) are labeled by capital letters (A to F).

Download English Version:

<https://daneshyari.com/en/article/60793>

Download Persian Version:

<https://daneshyari.com/article/60793>

[Daneshyari.com](https://daneshyari.com)