Catalytic conversion of hydrocarbons in zeolites from first principles*

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Abstract: The application of the density functional techniques to processes of the conversion of hydrocarbons in zeolites has been reviewed. The conversion of hydrocarbons over zeolites is an important industrial process. The microscopic steps of the conversion, however, are still not satisfactorily understood. In order to examine reaction pathways, both static and molecular dynamics density functional theory (DFT) calculations have been performed. Simulated structural and spectral properties compare reasonably with experimental data. Comparison of energies of physisorption and chemisorption indicates possible reaction channel of the conversion through the chemisorption at the specific O-sites of the zeolite.

INTRODUCTION

Zeolites are microporous aluminosilicates widely used as acid-base catalysts [1–4]. Industrial conversions using acid-base catalysts include processes like dehydration and condensation, cracking, isomerization, hydration, and hydrogenation [5]. Detailed mechanisms of the elementary steps, including initiation, propagation, and termination, are still unclear.

The wealth of experimental material has attracted the attention of theoreticians for decades. They simulate the whole spectrum of intrazeolite phenomena such as (1) diffusion of reactants into the zeolite, (2) physisorption (chemisorption) at the active site, (3) reaction of the conversion, (4) desorption, and (5) diffusion out of the zeolite. Methodologies of various levels of sophistication include simple force-field approaches as well as highly precise ab initio methods. The former are proven to characterize satisfactorily transport phenomena. Calculated diffusion coefficients obtained by means of classical molecular dynamics [6] with properly parametrized interatomic potentials reasonably compare with available experimental data [7,8]. Such methods, however, can be applied only to phenomena for which they are parametrized but cannot contribute to the understanding of reaction mechanisms. Contrary to the simple force-field treatment, the first-principles approach provides full understanding of chemical reactivity. Due to the rapid progress in the development of computer technologies, the ab initio technique is, in a relatively short period of time, maturing into a powerful tool for investigation of properties of rather complex materials.

Bonding in zeolites is traditionally investigated via the cluster approach. The cluster description of the acid sites in the zeolite is widely used to investigate the conversion of hydrocarbons [9–12]. A

disadvantage is the neglect of long-range interactions. This is overcome via the extension to a larger cluster which, however, leads to the increase of computer time. Periodical approaches, therefore, seem natural to mimic the bonding in crystals. The first attempts to simulate intrazeolite chemistry from first principles appeared only recently. Both Schwarz and coworkers [13] and Stich and coworkers [14] have investigated the behavior of water and methanol in sodalite [13], ferrierite, and ZSM-5 [14]. They show that simple phenomena, such as adsorption, and vibrational properties of small molecules are reasonably well characterized by ab initio molecular dynamics. The first attempts to mimic the complete conversion within the zeolite demonstrate an extremely high complexity of such a computational task [14,15].

The turnover frequencies of the conversion are measured on the scale of milliseconds [16,17], and the affordable time of the molecular dynamics simulation is measured only on the scale of picoseconds. We are, therefore, not trying to simulate any complete conversion but to perform short-time simulations of partial intrazeolite processes and phenomena. Upon gathering partial results, we accumulate pieces of the mosaic and enhance our understanding of the intrazeolite chemistry.

The simulations have been performed with the hexagonal structure of gmelinite. The adsorbed molecules are placed in the main channel extended along the c axis (Fig. 1). The first-principles calculations are based on the DFT using the generalized gradient approximation (GGA) for the exchange-correlation functional, the ultrasoft pseudopotentials and plane-wave basis, as implemented in the Vienna Ab-initio Simulation Package (VASP) code [18].
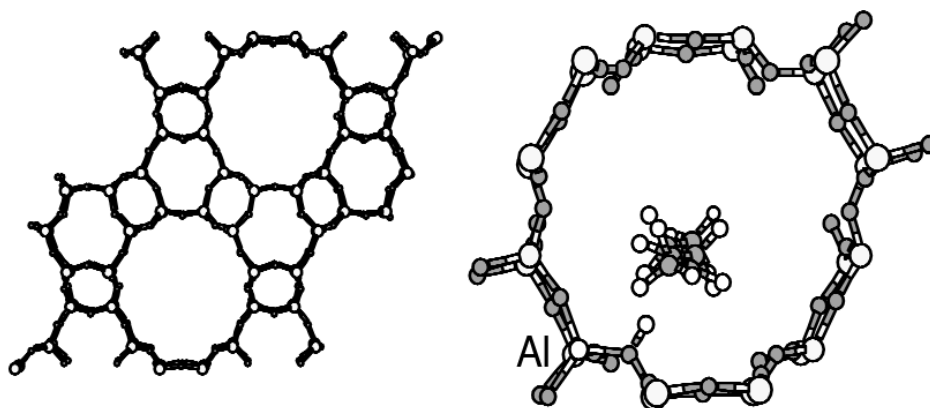

Fig. 1 Hexagonal structure of gmelinite (left), and the detail showing the typical position of the adsorbed molecule within the main channel of the zeolite (right). The molecule is placed at a short distance from the Brønsted acid site (~2.2 Å), and the active site is located at the O-atom neighboring the Al atom.

RESULTS AND DISCUSSION

The simulated intrazeolite processes and phenomena include relaxation of structures of both siliceous and Al/Si exchanged zeolite [19,20], the ion exchange [21], and adsorption of water [22–24] and benzene [25]. The study of the adsorption of paraffins [26], olefins [27], and protonized olefins [15] is complemented with the investigation of extra-framework aluminum particles [28].

The simulated structural and spectral properties reasonably agree with available experimental data. The paraffins adsorbed in zeolites are stabilized mainly through dispersion forces. Weak interactions at relatively large distance between atoms with nonoverlapping electron density, however, are difficult to treat within the DFT. The functionals currently used to approximate the exchange and correlation energy neglect most of the dispersion interactions. Figure 2 demonstrates the failure of DFT for the adsorption of saturated hydrocarbons in zeolites. In the diagram, the calculated energies of physisorp-
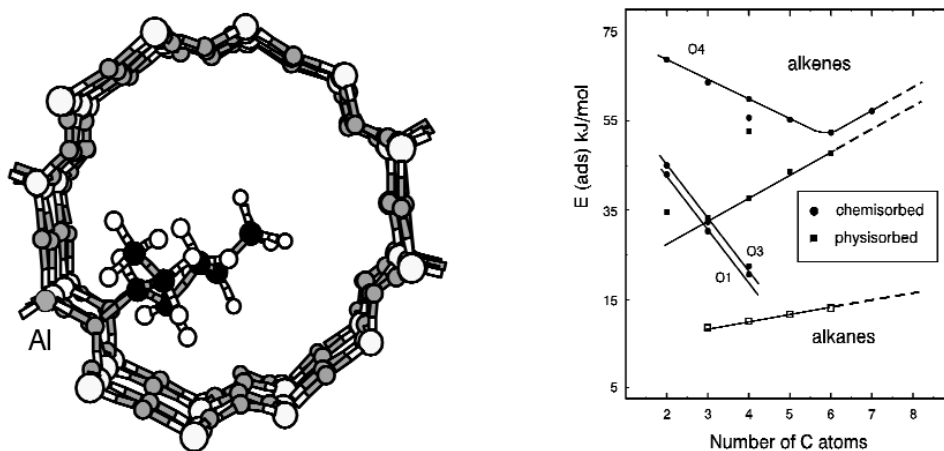
Fig. 2 The detail of the structure showing the connection of the chemisorbed alkene to the zeolite framework (left). The calculated adsorption energies of both physisorbed and chemisorbed species (right). The bonding to the O4-site is more favorable than that to the O1- and O3-sites and even more favorable than physisorption.

tion are compared for paraffins and olefins and complemented with energies of chemisorption. In zeolites with framework density similar to that of gmelinite, measured dependence of the heats of adsorption of olefins reasonably compares with our calculated line for the physisorption (Fig. 2). Measured heats of adsorption of paraffins are slightly higher [29]. Our calculated values, however, are due to the failure of DFT ~2.5 times smaller.

Displayed energies of chemisorption (Fig. 2) show that the zeolite O-sites are distinguished in two types. Chemisorption at the O1- and O3-sites is for smaller molecules slightly favored compared with physisorption, but disadvantaged for molecules longer than C3. The decrease of the energy of chemisorption with the length of the molecule is due to the deformation to the U-shape necessary for the formation of the effective O(zeolite)-to-C(molecule) covalent bond. The chemisorption at the O4-site, however, is the most favorable for molecules of all lengths. The calculated energies thus indicate possible reaction channel of the hydrocarbon conversion through the chemisorption at specific O-sites of the zeolite.

SUMMARY

First-principles short-term molecular dynamics simulations are applied to intrazeolite processes to investigate the catalytic conversion of hydrocarbons over zeolites. Simulated structural and spectral properties compare reasonably with experimental data. The failure is observed for the adsorption of paraffins due to the neglect ion of dispersion forces in DFT functionals. The comparison of energies of physisorption and chemisorption indicates a possible reaction channel of the conversion through the chemisorption at the specific O-sites of the zeolite.

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