



Research Paper

Theoretical study of olefin protonation reactions confined inside mordenite zeolite by energy decomposition analysis

Benteng Song^a, An-Ya Lo^b, Jiqing Wang^{a,*}^a College of Life Science and Chemistry, Hunan University of Technology, Zhuzhou 412008, China^b Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taiwan

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ABSTRACT

The protonation reactions of ethene, propene and isobutene confined inside 8-MR and 12-MR pore structures of mordenite (MOR) zeolite are theoretically studied in order to reveal the origin of different catalytic activity. It is found that the higher activity of propene in 8-MR pore comes from the better fit of dimensional sizes compared to small ethene and bulky isobutene; while in case of large 12-MR pore, the reactivity is enhanced with the increase of molecular size. The interaction energy for the transition state is further investigated by energy decomposition analysis (EDA) method. Two physical properties are shown to highly contribute to the stability of transition state species: the charge property of adsorbed molecules related to the electrostatic interaction and the orbital overlap between adsorbates and zeolite framework involved in the orbital interaction. By using principal components analysis, the major role of electrostatic and orbital interactions in the apparent activation energies were also observed.

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1. Introduction

Compared to conventional homogeneous catalysis, zeolite catalysts have been extensively applied in both the fundamental studies and industrial applications for conversion of hydrocarbons on the basis of their special characteristics such as environmentally friendly properties, non-corrosion and non-pollution to the environment, and advantageous for product separation and reuse during the catalytic process [1–3]. It is possible to obtain various active sites, e.g., Brønsted and Lewis acid sites on zeolites undergoing dealumination or ion exchange of zeolites. It is generally accepted that these active sites initiate catalytic reactions *via* proton transfer or hydride abstraction [4,5]. Thus, it has been predicted that the catalytic activity of zeolite acid catalysts are strongly dictated by the acidic strength. Interestingly, it was found that the alkane activations (e.g., alkane hydrogen exchange and cracking) are significantly correlated with the acidic strength of zeolite catalysts [6], usually the stronger acidity the advanced reaction activity. However, with respect to Beckmann rearrangement (BR) over catalyst zeolite [7], it demonstrates that weak acid exhibits the highest conversion and product selectivity in the case of the molecular size of confined species is comparable to the dimension size of zeolite

pore, as the cyclohexanone oxime confines inside MFI-type zeolites (Si-, B- and Al-ZSM-5), the decreased conversion of oxime upon increased acid strength was found, that is, the Si-ZSM-5 zeolite with a relatively weak acid strength could facilitate the BR reactivity. These findings enable us to conclude that zeolite confinement effect imposed by their pore structures is another crucial factor that may affect the catalytic reactivity for a specific reaction process [8–10].

It is well-known that the pore confinement effect can be qualitatively described by electrostatic interactions and vdW dispersion interactions between adsorbed molecules and zeolite frameworks, which usually leads to a lower activation barrier, resulting in a higher catalytic reactivity. To the best of our knowledge, the quantitative analysis for the contributions of each component on the species stabilization and reactivity has not been systematically investigated. The host-guest interactions in zeolite-catalyzed systems are far from being fully understood. In recent years, the energy decomposition analysis (EDA) method begins to attract much more attention, which decomposes energy into four components (*i.e.*, electrostatic interaction, dispersion interaction, orbital interaction and Pauli repulsion interaction), allowing us to understand the difference of catalytic reactivity when adsorbed molecules confined inside zeolite pores in more detail. Based on the EDA calculations, Bell and co-workers have thoroughly studied the isomerization of glucose to fructose over metal-substituted (Sn, Ti, Zr, V, Nb, *etc.*) BEA zeolite. They found that the Sn and Zr sites correspond to the lowest barriers in contrast to other active sites, which could be ascribed

* Corresponding author.

E-mail address: wjqwh2006@163.com (J. Wang).

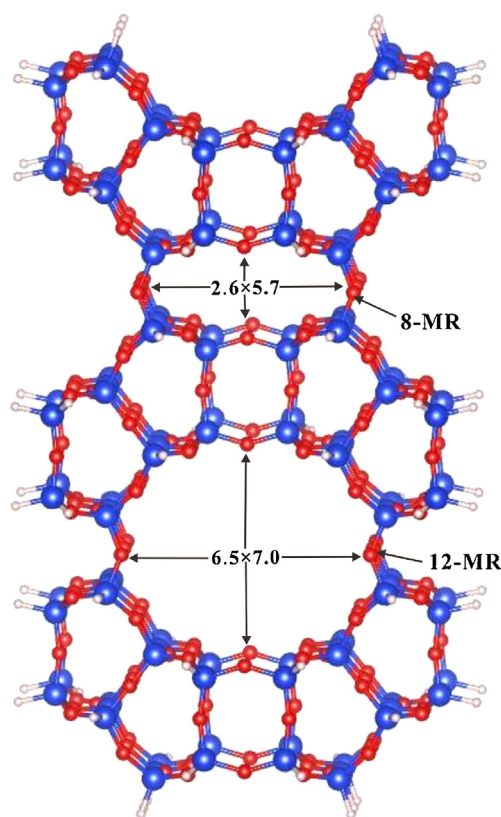


Fig. 1. Framework structure of mordenite zeolite with dimensional sizes of 8-MR channel (upper) and 12-MR channel (bottom).

to different effects. For the Zr active sites with large radius, which is highly polarizable so that there is a low energy penalty associated with geometric distortion; while the Sn sites can stabilize the transition state through electrostatic interactions [11]. Subsequently, the highly catalytic activity of Zr and Sn has been further demonstrated through the 4-(Hydroxymethyl)benzoic acid synthesis from ethylene and 5-(hydroxymethyl)furoic acid catalyzed by BEA zeolites [12].

The protonation reaction is the elementary step in many olefin-participation acid-catalyzed reaction, such as dimerization, oligomerization of olefins, double bond isomerization and formation of active species (cocatalytic hydrocarbon pool) in the MTO conversion [13–15]. The protonation mechanism of olefinic hydrocarbons on zeolite catalysts has been extensively investigated by using solid-state NMR [16,17] and IR spectroscopy [18,19]. As shown in Scheme 1, a weakly hydrogen-bonded complex (π complex) is first formed when an olefin adsorbs on a Brønsted acid site of zeolite. Then, *via* a carbenium ion-like transition state (TS), the transfer of an acidic proton from the zeolite to the olefin leads to the formation of alkoxy species.

It is illustrated that the different pore local environment has a significant effect on the reaction activity [7,20,21]. It is noteworthy that 8-MR and 12-MR channels are typical structures in the various zeolite catalysts. For example, AEN, DOR, EAB, FER, NAT zeolites contain 8-MR channels, while AFI, BEC, EON, IFR and MOZ zeolites include large 12-MR channels. Fortunately, Mordenite (MOR) zeolite possesses large, ellipsoidal 12-membered ring channels (12-MR: free aperture $6.5 \times 7.0 \text{ \AA}^2$) and compressed eight-membered ring channels (8-MR: free aperture $2.6 \times 5.7 \text{ \AA}^2$) (see Fig. 1) [22], it can accommodate not only small molecules but also the relatively bulky molecules, so that this provides a model to investigate the confinement effect derived from 8-MR and 12-MR

of zeolite frameworks. Therefore, we select MOR zeolite as a model to investigate the influence of pore confinement effect on olefin protonation reaction. In the present study, we have analyzed the energy parameters of olefin protonation reaction (ethene, propene and isobutene) confined inside MOR zeolite in forms of π complex, transition state and alkoxy species using 112T and 76T cluster models representation of the 12-MR and 8-MR structures to capture the pore confinement effect. The analysis of activation barrier for olefin protonation within these channels is in very good agreement to that observed experimentally. Using energy decomposition analysis (EDA) for the interaction energy of the transition state structures, two descriptors of stabilizing TS structures were identified. Owing to the fact that TS is carbocation-like complex, the first descriptor is the net charges on adsorbed molecules, which largely correlates with the magnitude of the electrostatic stabilization between adsorbates and zeolite framework. The second descriptor is the orbital overlap between two fragments, which correlates closely with the strength of the orbital interactions. Subsequently, the principal component analysis (PCA) reveals that both electrostatic and orbital interactions are highly important in the protonation reactions (the formation of transition state *via* π complex).

2. Theoretical methods

2.1. Computational model

In this work, all of the optimized structures are derived from the previous work [20]. Mordenite has an orthorhombic unit cell which consists of 8-MR ($2.6 \times 5.7 \text{ \AA}^2$) and 12-MR channels ($6.5 \times 7.0 \text{ \AA}^2$) [22]. 112T (1Al + 111 Si) and 76T (1Al + 75 Si) cluster models were used to represent the 12-MR and 8-MR zeolite structures, respectively (see Fig. 2).

The program package Amsterdam density functional (ADF) 2014.01 was used for the interaction between adsorbed olefins and zeolite framework by means of the EDA method (see below). In this work, all ADF calculations were carried out using the triple- ζ polarized (TZP) Slater-type all-electron basis set. The local spin density approximation of Vosko–Wilk–Nusair (VWN) [23] augmented with the nonlocal spin density of Becke–Perdew (BP) [24,25] generalized gradient approximation (GGA) was employed for the exchange–correlation functional [26]. This level provides very good results for the interaction between adsorbate and zeolite framework in zeolite-catalyzed reactions [27]. Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA) [28,29]. A frozen-core approximation up to the 1s orbital for O atoms and the 2p orbital both for Si and Al atoms was used. Meanwhile, the dispersion-corrected term was introduced to describe the noncovalent interactions, which was crucial to describe the host-guest interactions. The molecular charges of organic fragments were calculated using natural bond orbital (NBO) analysis [30].

According to the activation strain model that a fragment approach to understand chemical reactions, in which the height of reaction barrier is described and understood in terms of the original reactants [31,32], the potential energy (E) of the substrate-catalyst complex for each state is defined as the summation of strain energies (E_{strain}) associated with deforming the individual reactants and the actual interaction energies (E_{int}) between the deformed reactants, *e.g.*, $E = E_{\text{int}} + E_{\text{strain}}$. The interaction energy E_{int} can then be decomposed into the following physically relevant components.

$$E_{\text{int}} = E_{\text{es}} + E_{\text{Pauli}} + E_{\text{oi}} + E_{\text{disp}}$$

where the E_{es} term corresponds to the classical Coulomb interaction between occupied molecular orbitals of the strained fragments

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