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Full Length Article

Effect of pore confinement on the adsorption of mono-branched alkanes of naphtha in ZSM-5 and Y zeolites

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ABSTRACT

Branched alkanes are important parts of naphtha, and their conversions are related to the adsorption stabilities in the pore of zeolites. In this work, the adsorption stabilities of C7–C10 mono-branched alkanes in the pores of HY (ca. 0.74 nm) and HZSM-5 (ca. 0.55 nm) zeolites are investigated using DFT calculation. After excluding the effect of Brønsted acid by subtracting the adsorption energy on 8T cluster from the total adsorption energy, it is found that confinement effect plays an essential role in stabilizing mono-branched alkanes. With the increase in the carbon number of alkanes, there is gradual increase of adsorption energy on both HZSM-5 and HY zeolites. Moreover, in the narrow channel of HZSM-5 zeolite, the change of adsorption energy (ethyl-alkane < methyl-alkane < *n*-alkane) is completely different from that in the pore of HY zeolite (ethyl-alkane > methyl-alkane > *n*-alkane), which is mainly due to confinement effect rather than effect of Brønsted acid. Methyl-alkanes prefer to stay in the pore of HZSM-5, while ethyl-alkanes and propyl-alkanes are more likely absorbed in the pore of HY zeolite. By analyzing the total electron densities of adsorbates, it is concluded that only when there is a certain distance between zeolite fragment and the adsorbate and low electron density region occupies the remaining space of the pore, the confinement effect is the strongest.

1. Introduction

Nowadays, the petrochemical industry is facing a severe test in light olefins availability on account of increasing demand for light olefins derivatives (e.g. polypropylene). The traditional thermal cracking of naphtha to produce light olefins is not satisfactory to this increasing demand, because this process operated at high temperatures (>1073 K) requires enormous energy [1,2]. In comparison to thermal cracking process, catalytic cracking of naphtha [3,4] over solid-acid catalysts is more energy-saving and environment-friendly, which has been drawing the widespread attention. Compared with *n*-alkanes, the conversion of branched alkanes is overlooked in most cases through the ages, even though branched alkanes [5] account for almost 25% of naphtha and their conversion create a certain effect on catalytic cracking of naphtha.

To date, various pure and modified zeolites such as MFI, FAU, MWW, MOR and MSE types have been extensively investigated as cracking catalysts [6,7]. Among these zeolites, HZSM-5 and HY are widely used in petrochemical industry because of their various properties, such as high thermal and hydrothermal stabilities as well as their strong acidities [8,9]. It is reported that the different pore sizes lead to distinct reaction rates of branched alkanes by affecting the adsorption stabilities of reactants in the pore of zeolite [10,11]. Therefore, exploring the adsorption of mono-branched alkanes in zeolites is critical for the catalytic cracking reaction.

There are two factors [12,13] that affect the adsorption stabilities of mono-branched alkanes in zeolite pore, i.e., acid strength and pore confinement effect. Both experimental [14,15] and theoretical [16,17] results reported that the Brønsted site has an effect on the adsorption of alkanes. For example, the adsorption energy for *n*-hexane on HZSM-5 is 10 kJ/mol larger than that on siliceous ZSM-5 [14]. Besides the acid property, the pore confinement effect (pore size and its shape) is another important factor [18–20] in the adsorption of alkanes. It plays a key role in determining the strength of interactions between adsorbates and the zeolite fragment. The adsorption energies of dimethylamine caused by confinement effect [21] take up 20% and 30% in MFI and MOR, respectively. Furthermore, due to confinement effect, different cracking rates are observed to have a strong correlation with the pore size. The cracking rate [11,22,23] of *n*-alkane increases in the order HY < H-BEA < H-MOR < HZSM-5 < H-FER, which is in line with its adsorption stability. However, there were few reports about the confinement effect on the adsorption of mono-branched alkanes in

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zeolites. Therefore, it is highly desired to investigate the effect of confinement on catalytic cracking rate of branched alkanes.

The Density functional theory (DFT) calculations [24,25] on large zeolite clusters are known to be able describe the confinement effect between molecules and zeolite fragments. Recently, Zhao and Truhlar [26] have reported the new meta-hybrid density functional M06 series, which have a better average accuracy than the popular B3LYP hybrid functional for main-group and transition-metal thermochemistry and noncovalent interactions. In addition, the mGGA-M06-L function is comparable to MP2 calculations at a high basis set but at much more affordable computer times [27,28]. Moreover, the M06-L [29], included medium-range van der Waals forces, has been found to give the best performance in calculating the noncovalent interaction.

In this work, effect of acid strength and pore confinement on the adsorption of C7–C10 mono-branched alkanes of naphtha in ZSM-5 and Y zeolites we investigated using DFT calculation with mGGA-M06-L function. It was found that the adsorption stabilities of branched alkanes were higher with increasing side-chain length of alkanes in the pore of HY zeolite, while it had the opposite tendency in HZSM-5 zeolite. Moreover, the intrinsic reason for this phenomenon were further elucidated. By building 8T and 48T (66T) cluster models, which represented local and framework structure, respectively, the adsorption energy derived from acid strength and pore confinement effect were calculated. The confinement effect was the dominant factor in the adsorption of mono-branched alkane. This paper provides insights into the role of confinement effect on the adsorption of mono-branched alkanes with various side-chain length, which is of great significance to the screening of industrial catalysts for catalytic cracking of naphtha.

2. Models and methods

The density functional theory (DFT) calculation was performed with the program package DMol3 in Materials Studio (version 8.0) [30,31]. The meta-generalized gradient approximation (mGGA) with M06-L function [32,33] and double-numerical quality basis set with polarization functions (DNP) were used for all the atoms. The convergences of energy, gradient and maximal displacement were set as 10^{-5} Ha, 2.0×10^{5} Ha cm^{-1} (2.0×10^{-2} Ha nm^{-1}) and 5.0×10^{-4} nm, respectively.

It's known that the model should essentially be built large enough but finite [34]. The cluster size can apply multicenter spherical cutoffs ($r \geq 5$ Å) based on centers of the zeolite active site and the adsorbed molecule to within chemical accuracy (±1 kcal/mol) [35]. In this work, as shown in Fig. 1, we generated 66T HZSM-5 and 48T HY zeolite clusters from their lattice structures [36,37]. The 66T HZSM-5 cluster covers the intersection (5.1 × 5.5 and 5.3 × 5.6 Å) of zigzag pore channel and 10-membered ring straight channel. Silicon at the T12 position is replaced by aluminum to generate a Brønsted acid site. Schuring et al. [38] have reported that branched alkanes are preferentially sited in the intersection between the straight and zigzag channels. The 48T HY model covers the 12-membered-ring window (7.4 × 7.4 Å) connecting two supercages of faujasite. One aluminum atom is substituted for a silicon at T2 site to model a Brønsted acid site. Only the 8T active region of"$(SiO)_3SiOHAl(OSi)_3$" and the adsorbed molecule are allowed to relax while the rest of the structure is kept fixed at the crystallographic coordinates.

The 8T HZSM-5 and 8T HY cluster models, extracted from the crystalline structure of MFI and FAU, respectively, represent the local structure of the acid sites. The terminal Si atoms were saturated by H atoms. The acid strength can be theoretically simulated by changing terminal Si-H distances of zeolite model [39], because the variation of peripheral Si-H bond lengths will change the charge distributions of cluster model to further influence the acid strength of the bridging hydroxyl group (SiOHAl). In this work, we fixed the Si-H bond length of 1.47 Å and 1.85 Å in the model of HZSM-5 [40] and HY zeolite. The deprotonation energies (DPE) of acid site (1254.4 kJ/mol and 1164.6 kJ/mol) are almost in the range of the experimental values for HZSM-5 zeolite (1217–1255 kJ/mol) [41,42] and HY zeolite (1161–1166 kJ/mol) [43,44].

3. Result and discussion

3.1. The total adsorption energy of mono-branched alkanes in HZSM-5 and HY zeolites

The total adsorption energy can give an expression to the stability of the mono-branched alkane in the pore of zeolite. The value can be calculated through the formula given in Eq. (1). The $E_{zeolite}$ is the energy of zeolite cluster, and E_{alkane} is the energy of the alkane. $E_{alkane\text{-}zeolite}$ is the energy of alkane in the zeolite cluster.

$$E_{ads} = E_{alkane\text{-}zeolite} - E_{zeolite} - E_{alkane} \quad (1)$$

As shown in Fig. 2, the total adsorption energies have opposite trends on the same carbon number of mono-branched alkanes in HY and HZSM-5 zeolites: the adsorption energy in HY zeolite gradually climbs up with increasing side-chain length of alkanes indicating a more stable adsorption complex, while the adsorption energy climbs down sharply in the pore of HZSM-5 zeolite. For isomerides, the total adsorption energies of mono-branched alkanes increase by 3–9 kJ/mol per added-CH_2-group of side chain in the HY, which agrees well with the theoretical result [45]. However, towards isomerides in HZSM-5 zeolite, the total adsorption energies of *n*-alkanes are almost 20 kJ/mol larger than those of methyl-alkanes, which is consistent with the computational result [46]. The total adsorption energies of methyl-alkanes are nearly 60 kJ/mol larger than those of ethyl-alkanes, which coincides well with the experimental result [47]. Acid strength and pore confinement effect both have influence on the adsorption of mono-branched alkanes, but which one is the main factor causing the different trend need to be further explored.

In addition, the total adsorption energies of methyl-alkanes and *n*-alkanes in the HZSM-5 zeolite are larger than those in the HY zeolite. As can be seen in Fig. 2 and Table S1, the E_{ads} value of 4-methyl-heptane (−111.80 kJ/mol) in the HZSM-5 zeolite is 29.34 kJ/mol larger than that (−82.46 kJ/mol) in the HY zeolite. This indicates that methyl-alkanes and *n*-alkanes are absorbed more stable in the HZSM-5 zeolite. The total adsorption energies of ethyl-alkanes and propyl-alkanes in HY zeolite are much larger than those in HZSM-5 zeolite. The E_{ads} value of 3-ethyl-hexane (−89.54 kJ/mol) in the HY is 42.69 kJ/mol larger than that (−46.85 kJ/mol) in the HZSM-5 zeolite. Therefore, ethyl-alkanes and propyl-alkanes tend to exist in HY zeolite. What's more, the E_{ads} value of 4-propyl-heptane (24.30 kJ/mol) in HZSM-5 is positive value, meaning that it needs extra energy in the small pore.

3.2. Acid strength of Brønsted acid sites inside HZSM-5 and HY zeolites

The deprotonation energy (DPE) is a criterion to measure the intrinsic acid strength of zeolites. It is defined as the energy of removing the acidic proton to form an Brønsted acid site (Zeo-OH → Zeo-O^{-} + H^{+}). Smaller DPE value corresponds to stronger acid strength of the zeolite. It can be shown by the following formula given in Eq. (2), $E_{Zeo\text{-}OH}$ and $E_{Zeo\text{-}O^{-}}$ represent the energy of zeolite before and after the removal of proton, respectively. In addition to DPE value, the O—H bond length of acid site also can reflect the acidity of the zeolite. The longer bond length results in the easier to the removal of the proton and the stronger acidity. Therefore,