



Adsorption and diffusion of *n*-heptane and toluene over mesostructured ZSM-5 zeolitic materials with acidic sites

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ABSTRACT

In order to understand the effects of the surface acid sites in mesoporous zeolites on the adsorption and diffusion of hydrocarbons, the adsorption and diffusion of *n*-heptane and toluene (two C₇ hydrocarbons) over the mesoporous HZSM-5 zeolites (SiO₂/Al₂O₃ = 36) were investigated. The adsorption isotherms of two C₇ hydrocarbons over the mesoporous HZSM-5 zeolites showed the experimental data good fitting to dual-site Langmuir-Freundlich model (DSLFL) similar to mesoporous NaZSM-5. Henry's constants and the initial heats of adsorption displayed stronger interactions in HZSM-5 than in NaZSM-5, especially for *n*-heptane, due to the presence of surface acid sites. The influence of acidity to the adsorbate-adsorbent interactions decreases with increasing of the mesoporosity. The investigation on the diffusion of *n*-heptane and toluene in mesoporous HZSM-5 samples by the zero-length column (ZLC) method showed the strong interaction of adsorbates and HZSM-5 samples by effective diffusivity and activation energy. Moreover, the diffusions of adsorbates in zeolites were advanced with the introduction of mesopores in the zeolitic samples, though the dramatic influence of mesopore to diffusion is not arisen in mesoporous NaZSM-5, reflecting larger influence of acid sites on diffusion in mesoporous HZSM-5 samples.

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1. Introduction

Zeolites are microporous crystalline materials with high surface area, adsorption capacity, ion-exchange capacity and regular arrays of nanometer-sized channels and cages. The materials have been widely used on adsorption, separation and catalytic reactions in industrial processes. The uniform pore structures with one or more discrete sizes are endowed zeolites with three types of shape selectivity for product, reactant, and/or transition state, to favor the desired product in catalytic process and to avoid undesirable reactions [1,2]. Thereinto, one of the most commonly used zeolites is ZSM-5 with MFI type topology, and HZSM-5 is perhaps one of most famous and versatile solid-acid catalysts known due to tunable Si/Al ratios which lead to various acidity suited for a variety of catalytic reactions. In many processes of petrochemical industry and environmental technology, the zeolite HZSM-5 as catalysts and/or support materials is usually applied to displace conventional corrosive acidic catalysts to achieve benign endings [3].

The conventional ZSM-5 is an interesting catalytic material

because its medium pore size of ~0.55 nm and a pore network composed of straight and zigzag channels. However, the sole presence of microporous structure strongly retarded practical applications of zeolites in the reactions of larger molecules, because of the restriction of the intracrystalline accessibility and diffusion limitation of reactants and products. Therefore, different approaches have been employed to improve pore structure of ZSM-5 zeolitic materials for increasing catalytic performance. Introduction of mesopores into originally microporous zeolitic structures to form hierarchical systems with micropores and mesopores is considered one of the best strategies and has attracted increasing attention [4,5]. The bimodal porous networks combining advantages of microporous and mesoporous materials have significantly improved the transport properties of reaction molecules in zeolitic particles, and lowered diffusion restrictions for larger molecular species, and meanwhile still retained the activity of the acid sites within the zeolite microstructure [6–8]. In the past decade, two strategies, directly synthesis and post-synthesis, have been developed to obtain the mesoporous zeolitic materials [9]. In the post-synthetic route alkaline treatment-desilication is believed to be the most simple and effective for forming mesoporous structure in the zeolitic materials [10].

For any one catalytic reaction arising on zeolites, reaction molecules need first to diffuse to and then adsorb on the acid sites

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located within the micropores of the zeolites. Therefore, understanding the adsorption thermodynamics and diffusion dynamics of reactants is very necessary for understanding the reaction processes at the molecular level. Proverbially, the adsorption and diffusion behaviors of reactants and products in porous materials are strongly dependent on the pore structures and surface properties. Until now, a few work related to the adsorption and diffusion of hydrocarbons in zeolites with mesoporous structure have been reported [11–16]. Such as, by measuring the adsorption equilibrium data of *n*-heptane, toluene and oxylene on a semi-crystalline UL-ZSM-5 material (Si/Al = 100) with different micro- and mesoporosity, it was found that the adsorption capacities of the adsorbates increased with decreasing microporosity, while the adsorption affinity exhibited opposite trends [13]. The diffusion of *n*-heptane and toluene in the mesoporous zeolitic materials by the zero-length column (ZLC) method revealed the effective diffusivity values to be a few orders of magnitude higher than those in conventional microporous ZSM-5 sample, clearly indicating an advanced pore structure in the zeolitic material by the introduction of mesopores by partially crystallization of amorphous mesoporous silica-alumina materials [14]. However, the acid characteristics in the mesoporous zeolitic materials resulted in a decrease in the diffusivities and an increase in the diffusion activation energy of *n*-heptane and toluene due to the strong interaction between the C₇ hydrocarbons with surface acid sites [15].

In our previous paper, the adsorption and diffusion of *n*-heptane and toluene over mesoporous NaZSM-5 zeolites have explored the effects of the mesoporous structure in ZSM-5 zeolites [16]. Here, we report the adsorption and diffusion of *n*-heptane and toluene over corresponding mesoporous HZSM-5 zeolites. The main objective is to investigate the influence of acidity of the mesoporous HZSM-5 on the adsorption and diffusion of two C₇ hydrocarbons by comparing the different structure and surface properties between mesoporous HZSM-5 and NaZSM-5 zeolitic materials, to lay foundation for industrial applications of the mesoporous ZSM-5 materials.

2. Materials and methods

2.1. Preparation of the samples

Mesoporous ZSM-5 zeolites were prepared from the same starting HZSM-5 zeolite (SiO₂/Al₂O₃ = 36, crystal diameter 2 μm), according to the previous procedure given in Reference 16. Three consecutive ion exchanges were performed in 0.5 mol/L NaCl aqueous solutions at 303 K for 2 h or in 0.5 mol/L NH₄NO₃ solutions at room temperature for 3 h to obtain mesoporous Na- or H-form ZSM-5 zeolite samples. The ion-exchanged zeolitic samples were washed, dried and calcinated in air at 823 K, and coded NaZSM-5(1), NaZSM-5(2) and HZSM-5(1) and HZSM-5(2), respectively. The corresponding pure microporous ZSM-5 zeolites were coded NaZSM-5(0) and HZSM-5(0). The detailed preparation processes of the samples NaZSM-5(1) and NaZSM-5(2) were provided in the Supporting Materials.

2.2. Structural characterization

Powder XRD patterns of the zeolitic samples were recorded using a SHIMADZU XRD-6000 X-ray diffraction diffractometer operating at 40 kV and 30 mA selecting the Cu K_α radiation. Textural properties were determined by N₂ adsorption/desorption studies at 77 K on a Quantachrome NOVA 1200e gas adsorption analyzer. The specific surface area (*S*_{BET}) was obtained from the Brunauer–Emmett–Teller (BET) equation, and the micropore surface area (*S*_{mic}) and micropore volume (*V*_{mic}) were calculated from the *t*-

plot method. The mesopore volume (*V*_{meso}) was evaluated according to *V*_{meso} = *V*_{total} – *V*_{mic}, where *V*_{total} was derived from the amount of nitrogen adsorbed at *p/p*₀ = 0.99.

2.3. Adsorption isotherms measurements

The adsorption measurements of adsorbates on the zeolite surface were carried out using a Hiden Intelligent Gravimetric Analyzer (IGA-002), which contains a high sensitive microbalance with a weighing resolution of 0.1 μg. Prior to the adsorption measurement, the HZSM-5 sample of about 50 mg was loaded in the microbalance basket and then outgassed to 10^{–7} mbar and regenerated at 673 K for 8–10 h until no further weight loss was observed. To obtain the isotherms at a given temperature, the vapor of the adsorbate was gradually introduced into the ultrahigh vacuum system until the desired pressure value was obtained. Once the adsorption equilibrium was established, the vapor pressure was increased to the very next designed pressure. The weight as a function of pressure was continuously recorded under computer controlled. The isotherm measurements of *n*-heptane and toluene were taken in the pressure range 0–32 mbar over the temperature range 293–323 K and 308–338 K, respectively. Both of two adsorbates used in the present study were of GC grade (purity >99.9%).

2.4. Diffusion measurements

Diffusion studies of *n*-heptane and toluene on HZSM-5 samples were performed with ZLC technique. Before each run, the zeolitic sample of about 1–2 mg was sandwiched in two porous sintered discs and placed into the ZLC column. In order to eliminate impurities and moisture, the sample was first heated and activated at 573 K overnight. During the measurement, the adsorbent was initial equilibrated with a low relative pressure of adsorbates (0–0.00015), corresponding to the linear region of adsorption isotherms, followed by desorption with a high flow rate of He purge. The effluent concentration of the adsorbate was monitored by FID, desorption curve was recorded on the computer. Here the diffusion measurements of *n*-heptane (99.9% grade) and toluene (99.9% grade) were performed at 333 K, 353 K, 373 K and 353 K, 373 K, 393 K, respectively. Helium (purity >99.99%) was served as carrier gas and the flow rate was in the range of 80–100 ml/min. A purge flow rate of 80 ml/min was chosen as a standard flow rate for all the experiments. The data was analyzed using linear ZLC analysis of the desorption curves developed by Eic and Ruthven [17]. The ZLC model, for a linear system with uniform spherical particles, is given by:

$$\frac{c}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\beta_n^2 \frac{D_{\text{eff}} t}{R^2}\right)}{\left[\beta_n^2 + L(L-1)\right]} \quad (1-1)$$

where β_n is given by the roots of the equation

$$\beta_n \cot \beta_n + L - 1 = 0 \quad (1-2)$$

And

$$L = \frac{1}{3} \frac{FR^2}{KV_s D_{\text{eff}}} \quad (1-3)$$

where *F* is the interstitial gas velocity, *R* is the crystal radius, *K* is the dimensionless Henry's constant, and *D*_{eff}/*R*² is the effective diffusion time constant. By plotting ln(*c/c*₀) versus time, the effective diffusion constant (*D*_{eff}/*R*²) can be extracted based on the full range method.

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