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Theoretical Estimation of Intracrystalline Diffusivity of Olefins in MTP Catalyst

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Highlights

- Intracrystalline diffusivities of olefins were estimated by Gas Translational model.
- Selectivity of propylene increases with temperature.
- Minimum ethylene ratio obtained is 2.29.
- Mobility of light olefins is highly restricted by protons.

1. Introduction

HZSM-5 is microporous crystalline catalyst being used in methanol to propylene (MTP) process to produce light olefins from methanol. This process is highly selective depending on the zeolite topology and molecular-lattice interactions within micropores. Product distribution in MTP is delineated by kinetic and diffusion process. Kinetics of this process and olefin selectivity were discussed elsewhere [1-2] in detail.

Wang et al. [3] presented the MD simulation study of ethylene and propylene in MFI, CHA, BEA and FAU zeolites within temperature range 673-873K. He found that temperature has pronounced effect on the self-diffusivity ratios of ethylene to propylene in small diameter microporous zeolites (CHA). Effective and self-diffusion coefficients in binary component system and in multicomponent systems were investigated by Masuda and Krishna separately [4,5]. But molecular interaction within intersections and channels is still ambiguous. Though Xiao and Wei [6] found Intracrystalline diffusivity of n-paraffins, cyclo-paraffins and aromatics and explained molecular interactions within ZSM-5 intersections and channels.

In this paper, we will make theoretical calculations of $C_{2=}$ - $C_{7=}$ olefins diffusion coefficients through ZSM-5 zeolite. Effect of temperature and molecular diameter will be demonstrated as well. In our work, we will follow methodology of Xiao and will try to investigate that if molecule-proton interactions are neglected then what will be the effect on intracrystalline diffusivities.

2. Methods

To address olefin diffusivities, Gas Translational model (GT model) is used. This model assumes that molecules retain their gaseous identity at higher temperatures. This method was developed by Xiao et al. and it predicts that only oxygen-olefin interactions are dominant. Larger olefins reside most of the time in intersections while that of lighter ones in channels. Mathematical form of this model is:

$$D=(1/Z)\,(\sqrt{(8KT/\pi m)})\,\alpha\, e^{[-E/RT]}$$

Where, K, m, α and Z are Boltzmann constant, molecular mass, channel length and coordination number of HZSM-5 respectively.

Activation energy is determined by 12-6 Lennard Jones model. Though this model does not predict the desorption activation energy well but still its estimated values are in good agreement.

3. Results and discussion

Diffusion coefficients of $C_{2=}$ - $C_{7=}$ olefins were estimated theoretically within temperature ranges and plotted against molecular diameters, as indicated in the Figure 1. For the tested molecules, the higher the diffusivity, the lower the activation energy. In microporous zeolites, molecule-lattice interactions are dominant as compared to that of molecule-molecule interactions. The intracrystalline diffusivity for ZSM-5 is related to the molecular velocity, zeolite structural parameters, and the energy barrier the molecules has to overcome during hoping as stated in GT model. Difference in diffusivities of olefins having same minimum kinetic diameter is due to different molecular lengths and interactions inside intersection. As molecular diameter increases, the attractions increase up to an extent and then decrease. But in the case of butene having higher kinetic diameter as compared to other olefins diffusivity is still high. The reason is that 1-butene has ability to deform itself due to which its affinity to the pore wall increases. Diffusivities of ethylene and propylene are very high due to their lower activation energies, 1.4093 and 5.9579 KJ/mole respectively. Since the mobility of olefins is highly affected by the presence of protons, that’s why their activation energies found by Lennard Jones potential are low as compared to desorption activation energies. It was also observed that influence of temperature on the selectivity of propylene in ZSM-5 is obvious and ethylene to propylene ratio is in good range with that of found by Wang et al. at given temperatures.

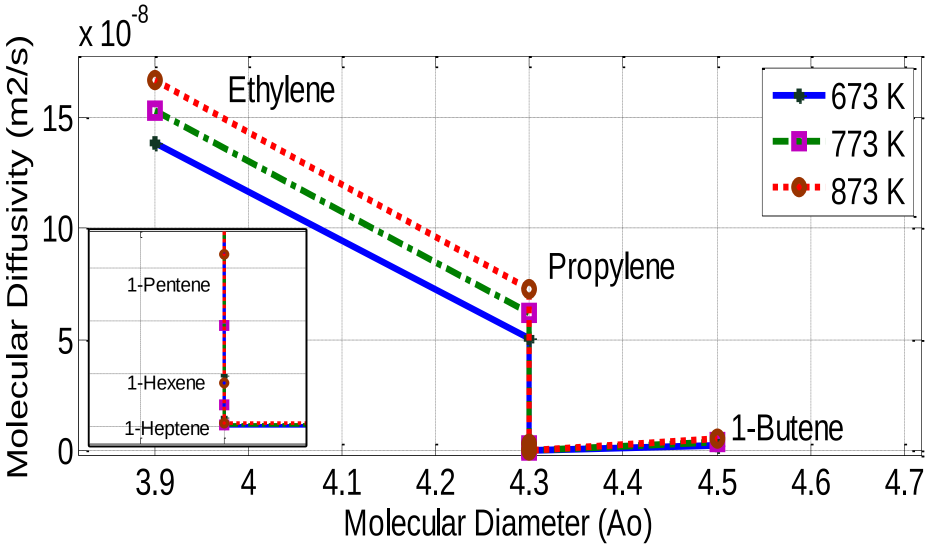

Figure 1. Olefin ($C_{2=}$ - $C_{7=}$) Diffusivities at Various Temperatures

4. Conclusions

Intracrystalline diffusivities of light olefins were calculated by GT model in highly siliceous HZSM-5. It is analyzed that these diffusivities are very high as compared to self-diffusivity which shows that electrostatic forces also have pronounced effect on olefins movements. Selectivity of propylene in ZSM-5 also enhances highly with temperature as ethylene to propylene diffusivity ratio decreases.

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Keywords

Intracrystalline Diffusivity; GT model; LJ potential; HZSM-5; Olefin.