

Understanding the synergistic effects of Si/Al and structure of zeolites for isobutane alkylation based on experiments and MD simulations.

Bihong Li¹, Weizhong Zheng^{1*}, Weizhen Sun^{1*}, and Ling Zhao¹

1 State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

**Corresponding author: wzzheng@ecust.edu.cn; sunwz@ecust.edu.cn*

Highlights

- Effect of different Si/Al of BEA zeolite on alkylation were explored.
- The diffusion behaviors of C4 reactants and products were studied.
- Rich distribution of Al promotes the relative diffusion of isobutane in the BEA zeolite.
- Low Si/Al benefits the diffusion of weight hydrocarbons to inhibit the deactivation of zeolite.

1. Introduction

Isobutane alkylation with low molecular weight olefins (C3-C5) under strongly acidic conditions is an important industrial process for producing high-quality and clean gasoline. However, traditional commercial H₂SO₄ and HF catalysts have several fatal drawbacks, including high corrosiveness and high volatility. Solid acid, such as zeolite, is considered a potential substitute due to its structural designability of structure and acid adjustability¹. Nevertheless, zeolite catalysts often suffer from rapid deactivation which limits their industrial application². The occurrence of alkylation reactions and deactivation is determined by the acidity and pore structure of the zeolite. It is understood that three-dimensional straight pores and strong acidity are conducive to isobutane alkylation reactions. It is extremely desirable to clarify the synergistic effects of acidity and structure of zeolite on the alkylation. However, to the best of our knowledge, few researchers have revealed the effects of acidity and pores on the alkylation reaction process at the microscopic level because of the complex and variable reactions during isobutane alkylation. Molecular simulations, especially molecular dynamics (MD) simulations, can provide information on the diffusion behavior of reactants and products. In addition, the diffusion behaviors of reactants/products during the reaction generally affects quality of alkylate. Thus, in this work, three BEA zeolites with Si/Al from 4.8 to 20 were applied to investigate the influence of acidity and structure by combining alkylation evaluation experiments and MD simulations.

2. Methods

NaB-1 was synthesized hydrothermally from an aluminosilicate mixture with a molar ratio of 38.7-40.9 SiO₂/1.0 Al₂O₃/ 10.0-14.7 Na₂O/570-1653 H₂O without organic template³. After ion exchange with 1 M NH₄Cl, it was calcined at 550 °C for 6 h to get protonic B-1 (HB-1). The Si/Al of HB-1 is 4.8. HB-2 (Si/Al ≈ 15) and HB-3 (Si/Al ≈ 20) were purchased from Nankai University Catalyst Co. Ltd. The alkylation reactions were conducted in a fixed bed reactor with 2 g catalyst. The final alkylate products were analyzed using gas chromatography with Agilent GC7890A. The diffusion behaviors of hydrocarbons in the BEA zeolite with different Si/Al were calculated using MD simulations. OPLS-AA and CLAYFF force fields were applied to treat the interaction between C4 reactants or products and BEA zeolites. The C4 reactants and BEA zeolite simulated boxes were presented after 26 ns MD simulation using nose-hoover thermostat under the canonical (NVT) ensemble at 353 K. The simulation boxes for the products and BEA zeolite were provided by Monte Carlo simulations with 500,000 product cycles. Subsequently, diffusion behaviors for the hydrocarbon and BEA zeolite simulation boxes were obtained by running the nose-hoover thermostat at 353 K over 100 ns.

3. Results and discussion

For the alkylation reactions, the three zeolites (HB-1, HB-2, HB-3) have similar product distributions and similar RON (~ 93) within 100 min. With the time of stream, the C8 products of HB-

1 continue to increase, while the C8 products of HB-2 and HB-3 both decrease. The RON of products presents the same trend. Interestingly, the time for the presence of the drop of RON in HB-2 is approximately twice as long as in HB-3. Heavy products show the opposite trend to C8 products. Thus, Al-rich HB-1 has the highest alkylation lifetime and the slowest C9+ generation rate. According to the MD simulation results, it can be seen that as the increase of Si/Al, the diffusion rate of reactants speeds up, while the diffusion rate of the products slows down. The relatively dispersed Al distribution of HB-1 zeolite makes a strong adsorption interaction for 1-butene, inhibiting the diffusion of 1-butene, which limits the diffusion of the isobutane. Therefore, both diffusion rates are smaller than that of HB-2 and HB-3. Nevertheless, the diffusion rate of isobutane is greater than that of 1-butene, which prolongs the alkylation catalytic lifetime. Moreover, the increase of zeolite Si/Al enhances its hydrophobicity, increases product adsorption capacity, and inhibits product expansion, thereby promoting the generation of alkylation-heavy components and accelerating catalyst deactivation. By analyzing the diffusion coefficient in each direction, it is found that straight channels are conducive to the diffusion of reactants and products, further verifying the role of straight channels.

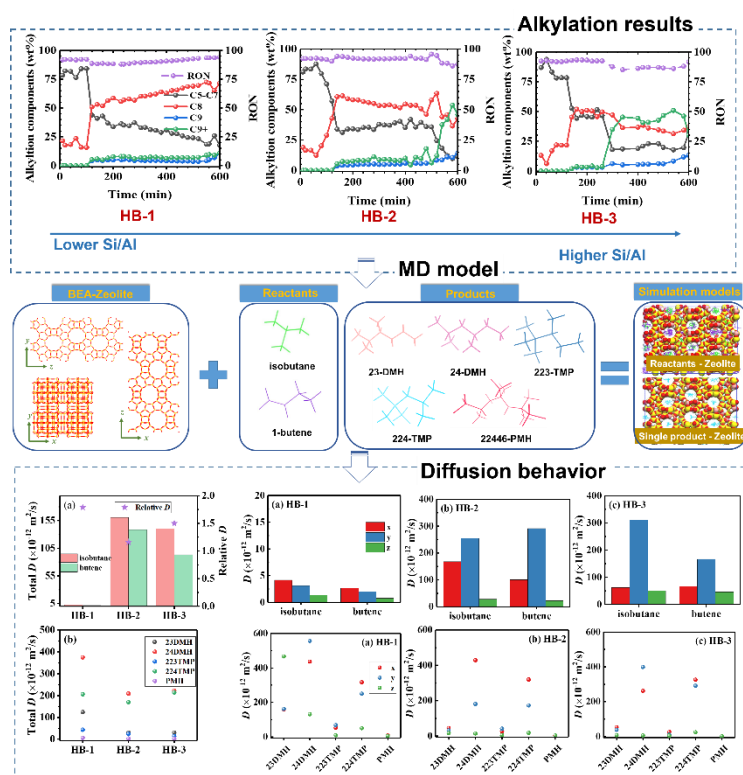


Figure 1. Effect of BEA zeolite with different Si/Al for isobutane alkylation by experiment and MD methods.

4. Conclusions

Al-rich BEA catalysts are beneficial to increasing the ratio of isobutane to butene in the microenvironment and inhibiting self-polymerization of butene. The straight 12-membered ring large pore channel promotes the relative diffusion of isobutane and product diffusion, which delays pore channel clogging.

References

- [1] A. Primo, H. Garcia, Chem. Soc. Rev. 43 (2014) 7548-7561
- [2] A. Feller, J. O. Barth, A. Guzman, I. Zuazo, J. A. Lercher, J. Catal. 220 (2003) 192-206
- [3] H.Y. Zhang, B. Xie, X.J. Meng, U. Müller, B. Yilmaz, M. Feyen, S. Maurer, H. Gies, T. Tatsumi, X.H. Bao, W.P. Zhang, D.D. Vos, F.S. Xiao, Micro. Meso. Mater. 180 (2013) 123-129

Keywords

Isobutane alkylation; BEA zeolite; Si/Al; Molecular dynamic simulation.