

Cross-section of interlayer space, as one of the factors that determine the selectivity of intercalated montmorillonites in oligomerization reactions

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Abstract

The intercalation process of layered silicates, for example, such as montmorillonite, by introducing into the interlayer space the polyoxycations produced by the cation hydrolysis reaction, is one of the promising ways to increase the catalytic activity of layered silicates. Indeed, montmorillonite (MON), characterized in its natural state by the expanding structural cell and thickness of the silicate layer 0.94 nm, is not sufficiently active. However, during intercalation, the interlayer space increases due to the substitution of interlayer cations for large oligomeric cations, and the activity of montmorillonite increases. It is important to note that the intercalation process does not lead to a violation of the primary structure of layered silicates.

Previously, the authors synthesized Fischer-Tropsch synthesis catalysts based on heteropolyacids applied to nanocomposite acid-activated montmorillonite. In this paper we present the results of modeling the processes of formation of the target products by the molecular dynamics method implemented in the Adsorption Locator module of Accelrys Material Studio 6.0. The effect of the cavity dimensions on the selectivity of the formation of C₆-C₁₂ isoalkanes was estimated from the dependence of the adsorption energy on the pore sizes. Calculation of oligomer structures was carried out by the method of quantum-chemical modeling in the RM1 approximation.

The optimum structural characteristic (pore diameter) for heterogeneous porous materials was determined based on the results of the study with the aim of intensifying the oligomerization process of butane-butene and propane-propene fractions with the maximum yield of C₆-C₁₂ isoolefins.

References

- [1] Zh.F. Galimov, M.N. Rakhimov. Silicophosphate catalysts for the oligomerization of refinery gases. Synthesis, properties and application. *Ufa: Reagent*. **1999**. 164p. (russian)
- [2] A. Clearfield. Preparation of pillared clays and their catalytic properties in *Advanced Catalysts and Nanostructured Materials*. Academic Press. **1996**. P.345-394.
- [3] T.J. Pinnavaia, M.-S. Tzou, S.D. Landau and R.H. Raythatha. On the pillaring and delamination of smectite clay catalysts by polyoxocations of aluminum. *J. of Molecular Catalysis*. **1984**. Vol.27. No.1-2. P.195-212.
- [4] I. Benito, A. del Riego, M. Martnez, C. Blanco, C. Pesquera, F. Gonzalez. Toluene methylation on Al₁₃- and GaAl₁₂-pillared clay catalysts. *Applied Catalysis A: Gen*. **1999**. Vol.180. No.1-2. P.175-182.
- [5] H. Auer, H. Hofmann. Pillared clays: characterization of acidity and catalytic properties and comparison with some zeolites. *Applied Catalysis A*. **1993**. Vol.97. No.1. P.23-38.
- [6] R.R. Shiriyazdanov, A.R. Davletshin, F.S. Vildanov, E.G. Telyashev, M.N. Rakhimov, E.A. Ipatova, R.R. Abdushev, Yu.A. Khamzin. Processing of gas streams of oil refineries in ecologically safe motor fuels on new generation catalysts. *Chemistry and technology of fuels and oils*. **2014**. No.6. P.12-16. (russian)
- [7] Carlos Henriques. Catalysis by zeolites. *EUCHEME*. **2012**.

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- [8] A. Poursaeidesfahani, M.F. de Lange, F. Khodadadian, D. Dubbeldam, M. Rigutto, N. Nair, Thijs J.H. Vlugt, Product shape selectivity of MFI-type, MEL-type, and BEA-type zeolites in the catalytic hydroconversion of heptane. *J. Catal.* **2017**. Vol.353. P.54-62.
- [9] B. Smit, T.L. Maesen, Towards a molecular understanding of shape selectivity. *Nature*. **2008**. Vol.451. P.671-678.
- [10] Thomas Demuth, Pascal Raybaud, Sylvie Lacombe, Hervé Toulhoat. Effects of zeolite pore sizes on the mechanism and selectivity of xylene disproportionation – a DFT study. *Journal of Catalysis*. **2004**. Vol.222. P.323-337.
- [11] I.V. Vakulin, R.F. Talipov, P.A. Pasko, G.R. Talipova, O.Yu Kupova Features of formation transition states of 1,3-dioxanes by Prins reaction in the pores of synthetic zeolites A and carbon nanotubes. *Microporous and Mesoporous Materials*. **2018**. Vol.270. P.30-33.
- [12] J. Jae, G.A. Tompsett, A.J. Foster, K.D. Hammond, S.M. Auerbach, R.F. Lobo, G.W. Huber, Investigation into the shape selectivity of zeolite catalysts for biomass conversion. *J. Catal.* **2011**. Vol.279. P.257-268.
- [13] (a) B.J. Delley. *Chem. Phys.* **1990**. Vol.92. P.508-517; (b) B.J. Delley. *Chem. Phys.* **2000**. Vol.113. P.7756-7764; (c) Materials Studio Version 6.0. *Accelrys Inc., San Diego*. **2011**.
- [14] J.J. Pluth, J.V. Smith. Crystal structure of boggsite, a new high-silica zeolite with the first three-dimensional channel system bounded by both 12- and 10-rings. *Am. Mineral.* **1990**. Vol.75. P.501-507.
- [15] X. Bu, P. Feng and G.D. Stucky. Large-cage zeolite structures with multidimensional 12-ring channels. *Science*. **1997**. No.278. P.2080-2085.