

## Dissertation abstract

### Two-dimensional zeolites as catalysts for liquid-phase alkylation of mesitylene

Zeolite catalysts are characterized by high activity and selectivity, as well as high thermal stability. They are referred to as "green catalysts" because they can be used in processes that pose environmental problems, replacing toxic inorganic, water-soluble catalysts. Bearing in mind both their environmental advantages and the wide variety of zeolite structures causing limited applications, the synthesis and subsequent modifications of zeolite MCM-56, a member of the MWW family was selected.

For this study, a series of hydrothermal syntheses of MCM-56 zeolite were performed using hexamethyleneimine (HMI) as the structure-building agent, with or without addition of aniline, acting as a structure-promoting agent. The method using aniline reduces the cost of synthesis and the toxicity of the post-synthesis mixture, providing a more environmentally friendly way to obtain MCM-56 zeolite. In addition to the syntheses, various paths for conducting post-synthetic modifications were investigated, and the results were described in 5 parts.

An important aim of the conducted research was to check the catalytic activity of the prepared materials in the Friedel-Crafts alkylation reaction of 1,3,5-trimethylbenzene (mesitylene) with benzyl alcohol, which occurs only on acid centers located on the external surfaces of MWW layers. This is due to the large molecular size of mesitylene, which cannot diffuse through pores smaller than 0.8 nm. The test reaction allowed a comparison of the catalysts, which showed structural differences and different accessibility to the active centers.

The main part of the thesis collects the results of the authors' research on MCM-56 zeolite and its derivatives, produced by various methods. To begin with, two MCM-56 zeolites were compared. One was synthesized by a method using hexamethyleneimine (HMI/Si = 0.3) as a structuring agent, while the other was synthesized using a mixture of hexamethyleneimine and aniline (HMI/Si = 0.1, AN/Si = 0.2). The problem raised at the beginning of the study was related to the correct choice of the starting material for further work. It has been found that the synthesis using aniline in combination with HMI, results in materials with interesting properties, and additionally reduces the use of harmful reagent HMI.

In the second part of the study, the zeolite precursor MCM-56-HMI/An was subjected to modifications involving layer separation (swelling), followed by a study on the effect of sonication time on the course of the pillaring process, which was carried out in two ways. The first was based on a standard method using an excess amount of tetraethyl orthosilicate (TEOS). The second was based on a new synthetic approach, in which TEOS was added to the precursor in an isopropyl alcohol environment. The final materials obtained in this study showed an increase in surface area and changes in structure, demonstrating an increase in the mesopore volume. Despite the reduced acidity, the modified zeolites retained high catalytic activity. They showed a significant increase in the individual activity of the acid centers, especially in the case of materials pillared in the presence of isopropyl alcohol.

The third part of the study demonstrated the possibility of forming a colloidal system from MCM-56 zeolite synthesized in the presence of aniline, producing a system of dispersed monolayers in the liquid phase. In the process of transferring zeolite powder to the form of a colloidal dispersion, solutions of a mild surfactant (tetrabutylammonium hydroxide) of various concentrations were used. Subsequently, a possibility of separating the layers by introducing silica supports has been studied. Higher alkalinity of the starting solutions resulted in higher porosity of the obtained derivatives. The modified materials with high catalytic activity were separated, which additionally did not exhibit decreased acidic properties. It has been found that for similar concentrations of acid centers, the activity was mainly controlled by their availability due to increased porosity.

In the fourth part of the work, the possibility of forming hybrid systems consisting of MWW zeolite monolayers derived from a colloidal system of MCM-56-HMI and MFI-structured zeolite domains was explored. Syntheses of such systems were conducted by an in-situ method, involving recrystallization of colloid-derived MWW layers into MFI-structured domains, and by an ex-situ method, in which colloid-derived MWW layers were deposited on microcrystals of previously obtained MFI-type zeolite. The existence of domains derived from the two studied structures in close contact was demonstrated using various physicochemical techniques (XRD, IR, TEM). It was found that despite dilution of the active MWW phase with the inactive MFI zeolite, the catalytic activity of the obtained hybrid systems was very high. It was proved that the resulting catalytic activity of such hybrid systems can be higher than the sum of the activities of the components. This observation provides a basis for creating and studying other hybrid systems in which the inactive material can be combined with MCM-56 monolayers.

In the fifth part of the study, supported zeolite catalysts were synthesized. For this purpose, various silicas differing in water content, surface area, and origin (Aerosil, Ludox, Ultrasil) were used as supports or support precursors for deposition on MWW layers from the colloidal systems. It has been observed that mixed MWW-silica systems obtained from the liquid silica precursor (Ludox), showed higher catalytic activity, despite the high content of inactive support in the form of amorphous silica. On the other hand, low catalytic activity found for materials synthesized using solid silica supports (Aerosil, Ultrasil) should be attributed to the negligible content of the zeolitic active phase.

All performed studies demonstrated that the MCM-56 zeolite is a good starting material for synthesis of materials exhibiting increased accessibility of the active centers, developed external and mesopore surfaces, and reduced diffusion limitations. Appropriate selection of the modification pathways resulted in obtaining materials exhibiting unique properties that potentially can be used as catalysts in reactions involving large organic molecules.