

## Abstract

The presented PhD thesis is focused on the synthesis, characterization, and modifications of zeolites and zeolitic materials. The main interests are two-dimensional (2D) zeolites and modification of their interlamellar space. Presented work was performed at the Department of Synthesis and Catalysis at J. Heyrovský Institute of Physical Chemistry in Prague, Czech Republic under the supervision of Prof. Jiří Čejka.

Zeolites are inorganic crystalline solids with a microporous framework structure. They are widely used as catalysts, sorbents, and ion-exchangers. Conventional zeolites have been recognized as three-dimensional (3D) tetrahedrally-connected frameworks. However, some of them are also known to exist in various layered forms (2D zeolites). Recently, the transformation of 3D germanosilicate **UTL** into layers (IPC-1P) has started a new branch in 2D zeolites chemistry. This chemically selective degradation of **UTL** framework was performed via acid hydrolysis. In the structure of this germanosilicate, Ge atoms are preferentially located in specific building units, double-four-rings (D4R), which connect dense silica layers. Modifications of the layered precursor IPC-1P led to discovery of the two novel 3D zeolites: IPC-4 (**PCR**) and IPC-2 (**OKO**). This novel approach in the zeolite synthesis, called **ADOR** chemistry (**A**ssembly, **D**isasassembly, **O**rganization, **R**eassembly), is in principle applicable to other germanosilicates with D4R units.

The thesis was focused on the investigation of the interlamellar space of 2D zeolite precursor – IPC-1P. The interlayer space was expanded by intercalation of organic compounds like amines and quaternary ammonium cations. The organic molecules organize the layers in designable way, e.g. with controlled interlayer distance. Calcination of variously intercalated precursor produces materials with substantial differences in the structure. This confirms that the use of various intercalates affects the organization of layers.

Intercalated IPC-1P precursor was subsequently modified either with silanes, alkoxysilanes, silsesquioxanes or polyhedral oligomeric siloxanes. Stabilization of IPC-1P with various silanes or siloxanes produces mostly IPC-2 zeolite, but also more expanded structures. It shows that the interlayer inorganic connections can be relatively short (e.g. one additional Si atom).

Expanded layers were connected with permanent props, which create large spectrum of novel materials with controllable textural properties. The interlayer distance of them was

tuneable (expansion up to 35 Å). Amorphous silica props were introduced by pillaring procedure resulting in materials exhibiting BET areas and mesopores volumes up to 900 m<sup>2</sup>/g and 0.6 cm<sup>3</sup>/g, respectively. The incorporation of organic props (made of silsesquioxanes) resulted in hybrid organic-inorganic zeolitic materials. Final materials have relatively good thermal stability (up to 350 °C) and show BET areas and mesopores volumes larger than 1000 m<sup>2</sup>/g and 1.0 cm<sup>3</sup>/g, respectively.

The main aim of presented work was to produce new zeolites predicted by theoretical calculations. Theoretical studies suggested that there are millions of possible zeolite topologies. However, up-to-date only about two hundred were prepared by traditional solvothermal methods. The limitation of the synthesis of predicted zeolite frameworks is known as *zeolite conundrum*. Several criteria have been formulated to explain why most zeolites are unfeasible synthesis targets. Here, the procedure of the synthesis of two new zeolites is reported. Both of them were previously recognized as 'unfeasible'.

The novel materials were denoted as IPC-9 and IPC-10 and belong to the family of **ADOR** zeolites. These zeolites were obtained by reorganization of IPC-1P layers. Intercalation of proper organic molecules (choline, diethyldimethylammonium cation) at basic pH induces the shift of the layers to the preferable position. The layered precursor intercalated with choline or diethyldimethylammonium cation was denoted as IPC-9P. Direct condensation of IPC-9P creates new zeolite IPC-9 with higher framework energy than their unshifted analogue IPC-4. IPC-10 is formed by alkoxylation of IPC-9P. This new zeolite can be described as shifted analogue of IPC-2, with single-four-ring (S4R) units incorporated in between layers. New structures have exceptional channel systems exhibiting odd-member channels (10-7-rings and 12-9-rings for IPC-9 and IPC-10, respectively). Structures of IPC-9 and IPC-10 zeolites were confirmed using Rietveld refinement and Le Bail method by comparison of calculated XRD powder patterns with experimental ones. BET areas were 128 m<sup>2</sup>/g and 217 m<sup>2</sup>/g for IPC-9 and IPC-10, respectively. HRTEM images also proved the structure of new zeolites to be consistent with the predicted structural models.

The **ADOR** approach has been extended towards new synthetic pathway. The newly prepared zeolites have unprecedented energetics and rare structural features. The results presented in the thesis show great opportunity for further exploration of this area and the possibility of preparing a whole new class of structures that cannot be accessed by traditional methods of synthesis. This study suggests that the *zeolite conundrum* is solved.