Laboratoire Catalyse Spectrochimie (LCS)
ENSICAEN - Université de Caen - CNRS

Report on PhD thesis entitled:

SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF NOVEL ZEOLITES

Prepared by

Pavla Eliášová

at Charles University in Prague, Faculty of Science, Prague

The PhD thesis presented by Pavla Eliášová is dedicated on the synthesis of *original* zeolitic materials by top-down approach. The thesis is perfectly structured and the main achievements are properly summarized.
The objectives of this work were:

-Synthesis of *original* zeolitic materials combined with comprehensive characterization.
-Development of new synthesis methods toward new zeolite structures.
-Testing of the novel zeolitic materials in catalytic reactions (toluene alkylation with isopropyl alcohol and hydroarylation of styrene) in comparison with commercial zeolites (MFI- and BEA- type structures).

The thesis is organized in 6 chapters, starting with introduction of molecular sieves (zeolites) having framework type structures. Then the main emphasis is on materials where the third dimension is limited to 2-3 nm thus resulting in two-dimensional layered/lamellar type molecular sieves. Even from the first chapter, one can see that

Directrice de Recherche, CNRS
Laboratoire Catalyse et Spectrochimie
ENSICAEN
6 boulevard Maréchal Juin,
14050 Caen Cedex 4, France

Tel +33/02 31 45 27 37
Fax +33/02 31 45 28 22
svetlana.mintova@ensicaen.fr

P. Eliášová is very familiar with the state of the art representing the synthesis of porous materials with well-distinguished properties resulting from their different structures. The schematic presentations of the methods apply for the preparation of 2D from 3D structures assist the complete understanding of the approaches known, and indicate the future modifications to be reflected. In the end of the first chapter, a detailed description of the two types of zeolites UTL and IWW is provided, thus clearly indicating the materials under consideration of her future work.

In chapter two, the synthesis and post synthesis modification of UTL zeolite, resulting in the preparation of novel IPC-1P structure is presented. Zeolite UTL is a germanium silicate, which has the unique ability to undergo structural changes in neutral or acid environment resulting in transformation into layered material. This is explained with the presence of almost pure silica solid layers connected with double-four-ring units specially occupied by germanium. These germanium-based units were considered as instable elements. Therefore very elegant post synthesis modification comprising hydrolysis, swelling, and pillaring were applied, which resulted in the preparation of new structures **(**IPC-1P, IPC-1SW, IPC-1PI). Moreover, it was found that the lamellar IPC-1P structure allows further modification. Via increasing the interlayer space by intercalation of surfactants and amorphous silica, new-pillared material is formed. However, this new material (IPC-1PI) does not retain any micropores, but it is stated that modified interlayer distance will increase the accessibility to important reactive sites situated on the layer surface. No shape-selectivity for the new structure in catalytic reactions is expected.

Based on the numerous syntheses and post synthesis approaches applied, a new preparation strategy named **ADoR** is proposed. The name **"ADoR"** is properly selected. The remarkable abbreviation means that first is necessary to synthesize the parent zeolite- **A**ssembly, then hydrolyse it into layered material– **D**isassembly, followed by **o**rganization of the layers and final calcination leaded to new material– **R**eassembly. P. Eliášová used numerous schemes with excellent design representing clearly the synthesis and post-synthesis modification steps in a form easy to be understand from the readers. This results point that imagination can be one of the main driving forces for preparation of new materials.

Based on the **ADoR** method, two novel zeolites, IPC-2 (OKO) and IPC-4 (PCR) from the UTL were prepared and described in the next chapter. In the first step, the UTL structure is unzipped/disassembled into layers, and then further manipulated. Via using different linkers, the synthesis of zeolites with predictable structure is demonstrated. The differences in the arrangement of the layers resulted in materials with various micropore volumes which has been found to decrease in the order UTL> IPC-2> IPC-4. Additionally, these materials have different pores based on 14-12-ring for UTL, 12-10-ring for IPC-2, and 10-8-ring for IPC-4.

Another part of the study reports on the synthesis of IWW type zeolite and the 3D-2D-3D transformation. IWW was prepared as pure germanosilicate with two different compositions as Ge-rich IWW and Ge-poor IWW. In the IWW zeolite, the location and the amount of Ge was found to influence significantly on the structure stability in acid environment. Ge-rich IWW was fully disassembled in two-dimensional material (IPC-5P), while hydrolysis of Ge-poor IWW led to a defective IWW structure preserving some interlayer connections. Moreover, the layered IPC-5P material was converted into three-dimensional IWW structure by incorporation of silylating agent.
Subsequent study was dedicated on healing structural defects caused by acid hydrolysis in the Ge-poor IWW zeolite via incorporation of Al. The accessibility to acid sites is increased in this sample in comparison to the one prepared by direct synthesis approach.

The next chapter of the thesis summarizes the catalytic experiments of the new materials (Al-IPC-1PI, Al-IPC-2 and Al-IPC-4) in comparison with conventional zeolites (Al-MFI and Al-BEA zeolite). The catalytic behavior of the novel zeolites was tested in toluene alkylation with isopropyl alcohol and hydroarylation of styrene.

The main results from this very comprehensive PhD thesis are summarized in the last chapter, and the main achievements are:
(1) Zeolite UTL is the first example for 3D-2D zeolite transformation with preservation of the original features of the layers.
(2) Two novel zeolites IPC-2 and IPC-4 are prepared. Moreover, the IPC-2 and IPC-4 materials with OKO- and PCR- type structures respectively are included in the International Zeolite Database.

(3) New zeolite containing Al is prepared in catalytic active forms; the Al-IPC-1PI shows higher toluene conversions in comparison to the sample where Al was introduced during the synthesis (Al-IPC-2) resulting in fast deactivation by coking.
(4) The ADoR concept is successfully applied on the IWW germanosilicate. The 3D-2D-3D transformation of zeolite framework is demonstrated.

The very important statements made in the thesis (see bellow) open the floor for essential discussion during the PhD defense: "*The ADoR strategy provides a unique method to design and prepare new zeolitic structures through so called top-down synthesis……..*"

In conclusion, the synthesis of *original* zeolitic materials combined with the various methods for characterization and their catalytic performance make the PhD thesis very comprehensive. In addition to the vast experimental work, P. Eliášová has carried out comprehensive study to understand the mechanism of formation of these materials. Significant progress was made in understanding the entire process of formation and transformation from 3D to 2D and 3D structures. The thesis is very well written and has to be accepted without modifications.

In view of the amount of experimental work, the quality of the work and the excellent way of summarizing the results, I do not hesitate to strongly recommend the acceptance of this thesis for public defence and to give ***the highest mark*** for the entire work.

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Dr. Svetlana Mintova