

Abstract

Germanosilicate zeolites attracted a lot of attention during the last decade. The reason for such interest is related to the unique structural properties of germanosilicates, which include zeolites of **UTL**, **UOV**, **ITH**, **IWR**, **IWW**, and **CIT-13** types. The frameworks of these materials can be described as Si-rich layers connected by double four ring (D4R) units preferentially occupied by Ge atoms. Hydrolytic instability of Ge–O bonds in mentioned frameworks compared with Si–O bonds in conventional zeolites gives the opportunity for controllable chemically selective transformation of the germanosilicate frameworks towards novel types of zeolites including their 2D analogues.

This PhD thesis focuses on modification of the structure and textural properties of germanosilicates using different ways of post-synthesis treatment: the ADOR (**A**ssembly – **D**isasassembly – **O**rganization – **R**eassembly) transformation and post-synthesis degermanation and alumination. Presented work was carried out in the Department of Synthesis and Catalysis at J. Heyrovský Institute of Physical Chemistry in Prague under the supervision of Dr. Maksym Opanasenko and advising of Prof. Jiří Čejka.

First way of post-synthesis treatment applied in this work was the recently developed method of zeolite synthesis – the ADOR transformation. Investigation of germanosilicates **UOV**, **CIT-13** and **IWR** possessing Ge-rich D4R units in the frameworks allowed us to expand the “IPC-family” by 3 novel zeolites (IPC-12, IPC-13, and IPC-17, respectively) and confirm versatility of this technique.

It was found that the framework of novel IPC-12 zeolite consists of the same layers as parent **UOV** zeolite, but they are connected by O-bridges in contrast to **UOV** possessing connectivity through the D4R units. The possibility of IPC-12 formation by 2 different ways was demonstrated. The first one is based on a controllable Disassembly under moderately acidic conditions ($\text{pH} = 1$) followed by calcination (Reassembly); the other one consists of direct **UOV**-to-IPC-12 rearrangement at highly concentrated acid ($\text{pH} < -1$).

The frameworks of new zeolites IPC-13 and IPC-17 obtained by the ADOR protocol were shown to have structure similarities. The layers in these materials were connected by the single four ring (S4R) units, in contrast to D4R connectivity for parent **CIT-13** and **IWR** germanosilicates (respectively). Thus, the ADOR approach can be applied to control zeolite

structure properties, as transformation of D4R units into O-bridges or S4R change the pore system in final materials.

Moreover, modification of the ADOR approach as a method was performed. For the first time, it was demonstrated that the ADOR can be realized under solvent-free conditions. It was achieved by the treatment of zeolite with H₂O/HCl vapours, i.e. without direct contact of material with the respective solution. Application of germanosilicate **IWW** led to the formation of a new zeolite IPC-18. In the zeolite IPC-18 the layers have the same structure as in the parent **IWW** but connected by S4R units in contrast to D4R units in the parent material.

Second part of this work was devoted to post-synthesis modification of germanosilicate zeolites not leading to the frameworks transformation. Germanosilicates **UOV**, **ITH**, and **IWW** possessing the D4R units enriched with Si atoms were applied for tuning of textural properties and design of hierarchical materials. Their acidic degermanation resulted in formation of additional micro- and mesopores, which amount was demonstrated to be controlled by appropriate choice of chemical composition of the starting material and conditions of the treatment (pH, temperature and duration).

Post-synthesis alumination was studied for germanosilicates **UOV**, **ITH**, CIT-13, **UTL**, and **IWW**. Incorporation of Al atoms in zeolite framework resulted in formation of both Brønsted and Lewis acid centres. The process was accompanied with formation of additional mesopores and increase of the surface area, which makes obtained materials perspective for investigation in catalysis.

Comparison of post-synthesis alumination with direct synthesis of aluminium containing zeolites showed that the post-synthesis treatment is more suitable method for Al incorporation, as it resulted in introduction of a higher amount of Al atoms into the framework and generation of a higher number of both Brønsted and Lewis acid centres.

For the first time the mechanism of post-synthesis alumination in germanosilicates was studied using XRD, ²⁴Al and ²⁹Si MAS NMR and ICP-OES techniques. Kinetic investigation of post-synthesis substitution of Ge by Al atoms for germanosilicate **UOV** showed that this process proceeds through multi-stage mechanism. The first step consists of degermanation and partial disassembly of the **UOV** framework followed by Al incorporation and healing the silanol defects in the framework in the second step.