

Preparation of hierarchical zeolites for fine chemical synthesis

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Abstract (in english):

The thesis is focused on synthesis of hierarchical (micro-mesoporous) zeolites by several different methods and their application in catalytic reactions. Performance of hierarchical materials prepared by different approaches has been investigated, as well as the effect of framework topology and type of acidity on the outcome of the reactions. The work was elaborated in the Department of Physical and Macromolecular Chemistry of Charles University under the supervision of Mgr. Pavla Eliášová, Ph. D.

The work is divided into three parts. In the first part several methods of preparation of hierarchical zeolites have been investigated and compared in catalytic reactions. Desilication, selective removal of silicon from the framework, is a post-synthetic method that can be used to introduce additional mesoporosity into a zeolite. The process leads to formation of mesopores by introducing defects into the zeolite structure. The resulting mesopore size is very broad. To partially control the pore size, alkylammonium cations may be added to the solution to protect the crystal surface. The desilication was performed on **MTW** zeolite which contains one-dimensional parallel-oriented micropores (0.56 to 0.60 nm wide). It was discovered that although the desilication leads to an increase of the external surface area, it also causes a blockage of the micropores by the framework debris when the tetraalkylammonium ions are used. This blockage was possible to remove by subsequent washing with acidic solution.

Hierarchical zeolites can also be synthesized directly by addition of specially designed amphiphilic structure directing agents into the synthesis gel. The hydrophobic chains in the water based synthesis mixture agglomerate together and prevent crystal growth in a given direction. The resulting zeolite is recovered as an aggregation of thin crystallites. The **MTW** zeolite was prepared in the nanosponge form and compared with the samples prepared by desilication. Nanosponge shows superior properties in the means of external surface area and total pore volume.

The catalytic performance of the desilicated samples and nanosponge sample of the zeolite **MTW** was compared in the tetrahydropyranlation of alcohols, an acid catalysed reaction useful for protecting hydroxyl groups of organic molecules in multistep synthesis. In each reaction the

nanosponge sample gave superior conversion of reactants. Slight differences were observed between individual alcohols depending on their chain length and architecture. However, the desilicated samples with blocked micropores showed unexpectedly high conversions and activity in the means of turn over frequencies even comparable to the nanosponge. It has been concluded that despite the creation of mesopores by desilication of **MTW** zeolite, the diffusion path of the reactant/product molecules through the accessible micropore system is too long and the increase in the reaction rate is not very pronounced. Conversely, when the micropores are inaccessible, the reaction proceeds over the active centres located on the external surface of the catalyst, where the reaction rate is not limited by diffusion through micropores.

The role of different types of the acid sites (Brønsted and Lewis) in the catalysis of tetrahydropyranlation has not been investigated so far. Direct preparation of purely Brønsted or Lewis acidic zeolites is problematic. Hence, a commercial zeolite **MFI** in the H^+ form was partially ion exchanged with alkali metal ions to poison a portion of its Brønsted acid sites and thus produce a set of materials with varying acidity. The **MFI** samples were investigated in tetrahydropyranlation of 1-propanol at different temperatures. From the catalytic tests it is clear that sample with the largest concentration of Brønsted acid sites (H^+MFI) is the most active catalyst and therefore more suitable for the catalysis. Zeolites with predominant Lewis acidity provide lower conversions of 1-propanol and their performance highly depends on the reaction temperature.

In the next part of the work the Pechmann condensation of resorcinol (1,3-dihydroxybenzene) and ethyl acetoacetate to hymecromone (7-hydroxy-4-methylcoumarine) over a set of zeolite samples was investigated to assess the effect of framework topology, morphology and acidity of zeolite on the reaction. Aluminosilicate and gallosilicate form of zeolites **MFI** (with three-dimensional system of 10-ring channels), **MTW** (with one-dimensional system of 12-ring channels) and ***BEA** (with three-dimensional system of 12-ring channels) were prepared each in bulk and nanosponge form. Conversions of resorcinol over the samples increase in the following order: **MFI** < **MTW** < ***BEA**. On the other hand, formation of secondary side-product can be observed over the ***BEA** sample and slightly less over the **MTW**. The obtained activities in the means of turn over frequencies show that the hierarchical pore system enhances the performance of the narrow-pore **MFI** and one-dimensional **MTW**, whereas the impact on ***BEA** catalyst is negligible. The conversions as well as turn over frequencies show comparable performance of the aluminosilicates and gallosilicates.