Zeolites (crystalline porous aluminosilicates) are very important catalysts in chemical industry, especially in oil refinery industry and also in "fine chemistry".
The advantage of zeolites in comparison to other catalysts is the presence of strong acid sites, situated inside zeolitic channels. On these acid sites carbocations may be formed and stabilized by the negative charge of framework oxygens. Moreover, shape selectivity of reactions catalyzed by zeolites might be observed. On the other hand, the channels (micropores) where active sites are situated are relatively narrow which is the disadvantage of zeolites since the diffusion of reactant molecules to these sites is restricted. In consequence, some sites inside zeolite crystals are non active which may be remedied by the synthesis of hierarchical zeolites where both micropores and mesopores are present. Up to now, desilication in alkali solutions (mostly in NaOH) is the most effective and economic method of the formation of mesopores in zeolites.
Our laboratories have an experience in preparation of hierarchical zeolites by desilication of zeolites ZSM-5, ZSM-12, beta and mordenites. We published over 10 papers and the chapter in the monograph on this subject. We have found that the addition of tetraalkylammonium hydroxide to NaOH results in the obtaining of materials of better acidity and porosity than desilicated with NaOH only. We plan to use this experience in preparing new hierarchical zeolites based on zeolite Y and zeolite omega.
The "ultrastable" zeolites Y (that is zeolite Y treated with water vapor at high temperature, a procedure commonly known as "steaming") are the most important cracking catalysts in oil refineries. Their high activity is due to the presence of very strong acid sites (Si-OH-Al interacting with extraframework Al) and the presence of some mesopores of small volume. One of the goals of this project will be preparation of hierarchical zeolite Y by controlled desilication of "ultrastable" zeolite Y. Another target of our studies will be the more exotic zeolite omega, until now a rare object of scientific studies, containing acid sites of the highest strength. Unfortunately, the zeolitic channels in zeolite omega are very narrow, hence the application of zeolite omega as a catalyst is very limited. We plan to study desilication of zeolite omega in order to produce mesopores which will facilitate diffusion of reactants and products. We do hope to obtain catalysts revealing high acidity and good accessibility of acid sites, useful in reactions catalyzed by them.
The first attempts of desilication of zeolites Y were made in TOTAL refinery company. However, our preliminary experiments evidenced, that zeolites of better acidity and porosity can be obtained using the addition of tetraalkylammonium hydroxide to the regular desilication agent (NaOH). Zeolites Y synthesized with the addition of tetraalkylammonium hydroxide showed better crystallinity, porosity and acidity than those obtained in TOTAL company. To the best of our knowledge, the present project constitutes the first proposal to produce hierarchical zeolites of this type with respect to zeolite omega.
The first step of preparation of hierarchical zeolites of relatively low Si/Al (such as Y and omega) is the treatment with water vapor at high temperature ("steaming") in order to obtain zeolites of higher Si/Al optimal for desilication. The "steaming" produces also acid sites of high strength. Therefore the first step of our work will be a detailed study of the process of dealumination of zeolites by "steaming" ("ultrastabilization"). Nowadays, ultrastable Y zeolites are the most important catalysts in oil refineries, thus apart from the preparation of new hierarchical zeolites, our project will also be helpful in the optimization of zeolite catalysts used in practice in refineries.
We plan to realize our goals with the use of three main research methods: NMR spectroscopy (which will probe the status and properties of Si and Al atoms in zeolite framework), IR spectroscopy (which will probe properties of acid sites) and quantum chemical modeling (which will be helpful to understand the mechanisms of Si and Al extraction from zeolite framework and to rationalize the overall experiments). Physicochemical studies of hierarchical zeolites will be completed with catalytic tests, which will show how hierarchization of zeolites improves their catalytic activity. Auxiliary techniques like XRD, TEM, SEM, XPS, porosimetry and others, will be also used for complementary studies of properties of hierarchical zeolites.
Our laboratories have good experience in NMR and IR studies and in theoretical modeling. Prof. B. Sulikowski has significant experience in NMR studies (originating from the laboratory of Prof. J. Klinowski in Cambridge), Prof. J. Datka is a respected expert in IR studies of zeolites, mainly their acidity (he published ca. 200 papers on this subject). Prof. E. Brocławik (project leader) offers expertise in the subject of modeling of zeolitic systems. The synthesis of zeolite omega will be done by Dr W. Roth (retired from MOBIL company) who is a world-renown expert in the synthesis of zeolites.
Three research groups (represented by Professors Sulikowski, Datka and Brocławik) already have collaborated for many years, with ca. 50 papers published together. Our laboratories are equipped with high class instruments (NMR and IR spectrometers as well as advanced computational systems) necessary for the proposed studies of zeolites. The funds from the project will help us both to upgrade the research level by improving mutual cooperation between theoreticians and experimentalists and to enrich further the equipment available in our laboratories.
In summary, we expect to recognize and rationalize the processes of Al and Si extraction from zeolites on a molecular level and to propose the routes of obtaining new hierarchical zeolites with improved acidity and porosity and therefore exhibiting improved catalytic properties.