

Abstract

Zeolite materials experienced their greatest success in the second half of the last century when their unique properties on fields of adsorption, separation and catalysis were discovered. Above mentioned properties are caused by their repeated microporous structure which enables them to operate as molecular sieves. The development of many advanced microporous and mesoporous materials in recent years has brought only a few industrial applications of these novel materials since they are often expensive, unstable, and from an ecological point of their production unaccepted materials. At the same time zeolite materials have become victims of its own success, due to their microporous structure, which leads to accessibility limitations for substrate molecules to the active sites inside the microporous structure. In this doctoral dissertation, I wanted to combine the preparation of zeolite ZSM-5 on ecologically and economically acceptable way and creation of mesopores in a microporous structure with the aim of improving the accessibility to the active adsorption and catalytic sites in ZSM-5 on a semi-industrial scale.

Firstly, I prepared the ZSM-5 zeolite on a laboratory scale using the most affordable sources of silicon and aluminum produced on an industrial scale in the company that produces zeolite. I wanted to investigate the crystallization process of ZSM-5 zeolite without the use of organic structure directing agents using conventional procedures for syntheses of zeolites. Based on the laboratory results I transferred the synthesis of ZSM-5 zeolite to semi-industrial scale taking in the account all desired morphological characteristics of synthesized zeolites, which are necessary for their successful application in industrial processes. The transfer to a semi-industrial scale consisted of the raw materials preparation, preparation of aluminosilicate gel, crystallization, filtration, ion exchange and drying of the crystalline ZSM-5 zeolite which was then used in further dissertation research. At the same time the process for the preparation of fully crystalline zeolite granules of ZSM-5 zeolite was developed. The new procedure comprises the hydrothermal transformation of amorphous aluminosilicate granules into completely crystalline granules of ZSM-5 zeolite without the use of organic structure directing agents. It is a unique process of hydrothermal conversion of amorphous aluminosilicate gel (shaped by sodium silicate) into crystalline granules of ZSM-5 zeolite with the synthesis yield increased by twice, compared to the synthesis of the powdered ZSM-5 zeolite.

Later on I focused on the post-synthesis modifications of powdered ZSM-5 zeolite synthesized on a semi-industrial scale, with the aim of zeolite preparation with hierarchical pore structure by desilication of ZSM-5 zeolite using sodium hydroxide solution. I studied the most influential parameters on the desilication process such as sodium hydroxide concentration, time and temperature of desilication process for a ZSM-5 zeolite having a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between 20 and 40. I defined a connection between the desilication degree and adsorption capacity of water and toluene. Further, I studied the influence of dilution on the desilication process and determined optimal conditions for the transfer of desilication process on semi-industrial scale. In the last part of the thesis, I prepared granulated forms of synthesized and desilicated zeolites and examined their effectiveness in the rapid catalytic pyrolysis of lignin. I studied the relationship between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of zeolites and the composition of the resulting bio-oil. I monitored the changes in the quality of bio-oil using desilicated ZSM-5 zeolite. I found out that improved accessibility to the active sites in desilicated ZSM-5 zeolite, which is the result of a hierarchical pore structure, is of great importance for improving the efficiency of ZSM-5 zeolite as a catalyst in the process of lignin pyrolysis. The results showed that the relationship between the added zeolite catalysts and lignin is proportional regarding the efficiency of the catalytic pyrolysis process, which gives the additional advantage to desilicated ZSM-5 zeolite prepared in the economically and ecologically acceptable preparation way.

Keywords: zeolite ZSM-5, synthesis, semi-industrial scale, hierarchical zeolites, granulation.