Abstract

The conversion of methanol to olefins by catalysts has attracted the interest of the scientific community due to the vast reserves of natural gas. Methanol is produced from natural gas via synthesis gas and biomass via gasification, which represents an alternative to other fossil energy sources like oil and coal. In this work, we have studied new catalytic materials for the reaction of methanol to olefins optimizing the properties of these currently used commercially and proposing new alternative materials. The catalysts currently used are based on zeolites which are microporous materials of high specific area but present as drawbacks a short lifetime before deactivation by coking, or a low stability when water is present in the reaction medium. Increasing the specific area by decreasing the size of crystal or increasing mesoporosity will improve the diffusion properties of the catalyst.

The silicoaluminophosphate SAPO-34 is currently the material commercially used. In this thesis, the synthesis of this material has been drastically optimized by decreasing the crystal size and improving the stability against humidity. Decreasing the size of the crystal has increased catalyst life against coke deposition and has made possible to relate product selectivity to the distribution of silicon in the particle of the catalyst which varies upon contact with ambient moisture. The stability to humidity has been improved by post-synthesis treatment with steam. Thus, we have synthesized samples with longer lifetime in the reaction of methanol. The effect of crystal size reduction has also been studied for zeolite SSZ-13 that is isomorphous with SAPO-34, by addition of surfactant agents during the synthesis and it has also been tested how this size reduction produces an increased lifetime of the catalyst.

Finally, lifetime and hydrothermal stability of zeolite ZSM-5, current catalyst component of the methanol to propylene process, have been optimized. We have studied the effect of increased mesoporosity by base / acid treatments on the catalytic properties and it has been proved that mesoporosity increases lifetime while, conversely, hydrothermal stability is affected. In the final part, the hydrothermal stability of mesoporous ZSM-5 has been improved by addition of phosphorus. The study has
shown that the activity of the catalyst based on mesoporous ZSM-5 can be preserved by improving the hydrothermal stability including phosphorus into the catalyst composition.