

SUMMARY

The seek for a catalyst characterized by acidic and textural properties ensuring optimal activity, selectivity and accessibility is an extremely important aspect of many catalytic studies. This dissertation presents the results concerning zeolites and their modification methods aimed to optimize an aluminosilicate materials for the catalytic plastics cracking, precisely low-density polyethylene (LDPE) and polypropylene (PP). The structural, textural and acid-redox characterization of aluminosilicates catalysts was carried out with the use of several first-choice techniques: ICP OES, low-temperature nitrogen sorption, TEM microscopy, and *in situ* FTIR spectroscopy. A novelty in the presented research was the implementation of *operando* FTIR spectroscopy simultaneously by coupling spectroscopy measurements with gas chromatography (GC) and mass spectrometry (MS). *Operando* spectroscopic studies provided insight into the catalyst under working conditions. During the catalytic decomposition of LDPE or PP the catalyst surface was monitored by time-resolved FTIR spectroscopy. The coupling of the gas chromatography and the mass spectrometry with the FTIR spectroscopy allowed for the quantitative assessment of reaction products, catalysts activity and selectivity over reaction path. The research was supported by thermogravimetric analysis (TGA) providing data on the activity of the catalyst and coke amount in the spent catalyst, as well. The coupling of a several different methods, i.e. FTIR, GC, MS, and TGA, allowed for an in-depth analysis, not only qualitative but above all quantitative, of the catalyst under the *operando* conditions. In addition to pioneering *operando* IR research, the two-dimensional correlation spectroscopy was used for the first time to analyze the process of LDPE and PP cracking.

The first part of the research was focused on the evaluation of the changes in the texture and acidic properties, resulting from the introduction of secondary mesoporosity, on low-density polyethylene cracking. The influence of the development of the external surface, the number of Lewis sites, as well as the accessibility and strength of acid sites was studied on the example of catalysts with MFI and BEA structures. It has been proven that the increase in the accessibility of proton sites as a result of the introduction of secondary mesoporosity in MFI structures, benefits their higher activity in catalytic cracking of polymers. The influence of the acid sites strength on the catalytic decomposition of low-density polyethylene catalysts was also studied. It has been evidenced that in the presence of BEA structures, the strength of the acid sites is the key determinant of the catalytic transformation of plastics. The redox function introduced into the aluminosilicate catalyst doped with palladium was also discussed as an important aspect of the catalytic property. It was shown that the use of a bifunctional catalyst

ensured high selectivity to the C₂-C₅ fraction along with a high content of isoparaffins formed without the addition of hydrogen from an external source, as well as a slower build-up of carbon deposit resulting from the high efficiency of hydrogenation of the reactants. The cracking of polypropylene over Y catalysts revealed the key role of the strength of the acid sites, while in the case of amorphous material, the presence of moderate-strength Brønsted sites, but highly dispersed in the three-dimensional mesopore system, was found an important parameter influencing the PP cracking.

The referring data obtained from the catalytic reaction to the properties of the aluminosilicate materials allowed to define the correlation between the catalyst properties and the efficiency and selectivity of catalytic cracking of plastics. Additionally, the correlation between zeolite properties and the nature of coke precursors, their location, further transformation, and finally, susceptibility to burning-off was also established.

Summing up, the doctoral dissertation were aimed to provide a comprehensive description of the textural and acidic properties of aluminosilicates dedicated as a highly effective and selective catalyst. The presented research allowed proposing an optimal catalyst for the transformation of plastics.