

## DEGRADATION OF WASTE POLYOLEFINS IN THE PRESENCE OF MODIFIED ZEOLITE AND MESOPOROUS CATALYSTS

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### ABSTRACT

*The total amount of plastic wastes generated by our society is growing rapidly. The main source of plastic is the municipal solid waste. Plastics contained in the municipal solid wastes can be estimated about 10% of total waste by weight and the amount goes up to 20% when consider in volume.*

*The low biodegradability of different plastics creates a serious environmental problem that is directing the governments and environmental organizations and enterprises to propose a hierarchy to solve the problem of plastic wastes based on source reduction re-use and recycling.*

*Up to now and considering the case of European Union only ~10 wt.% of plastic wastes have been recycled, while ~73 wt.% have gone to landfills and ~17 wt% have been incinerated. While incineration can be used to recover the waste as energy, the loss of a potential chemical source and negative public acceptance limit the extend of this solution.*

*If we accept that landfill storage is not a rational solution and can only be considered as provisional, then one is left with the most desired primary and secondary waste recycling.*

*The primary recycling however, are limited to pure thermoplastics, therefore secondary technologies used for treatment of mixed plastic wastes is growing in importance. In this way plastic wastes are converted into monomers, fuels or valuable chemicals for petrochemistry.*

### 1. INTRODUCTION

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While incineration can be used to recover the waste as energy, the loss of a potential chemical source and negative public acceptance limit the extend of this solution. If we accept that landfill storage is not a rational solution and can only be considered as provisional, then one is left with the most desired primary and secondary waste recycling.

The primary recycling however, are limited to pure thermoplastics, therefore secondary technologies used for treatment of mixed plastic wastes is growing in importance. In this way plastic wastes are converted into monomers, fuels or valuable chemicals for petrochemistry.

Traditional thermal cracking, i.e. pyrolysis can be applied to transform both thermoplastics and thermosets into gases, liquid hydrocarbons and solid residue. Thermal cracking and hydrocracking have been studied at laboratory and pilot plant level, and some commercial installation have been built for treatment of mixed plastic wastes, even those containing chlorine. However, thermal cracking yields low value unstable hydrocarbons within a very broad range of molecular weight. Catalytic degradation can operate at lower temperatures and can produce products with better quality (much narrower boiling point distribution and much higher stability).

A large number of laboratory studies have been conducted for direct catalytic degradation of polymers, especially for pyrolysis of polyolefines. A high variety of catalysts have been used that even if performing well, they can be uneconomical due to the price of catalyst and to the high-energy demand.

Among the catalysts studied acidic zeolites and mesoporous materials performed special activity in the temperature range of 300-500 °C.

The objective of this work is to study the potential of modified ZSM5 zeolite and MCM41 mesoporous silica as catalysts for degradation of polypropylene and polystyrene using thermal analytical measurements and laboratory reactor experiments.

## 2. EXPERIMENTAL

Commercial polypropylene (PP) and polystyrene (PS) in granule form have been used as model feed. The synthesized Na-ZSM-5 zeolite was modified by solid-state ion exchange with  $\text{FeCl}_3$  to prepare the Fe-ZSM-5 sample, while Ti-ZSM-5 catalyst was synthesized by isomorphism substitution, as well as the Fe- and Ti-MCM-41 materials. The catalysts were characterized by XRD method, IR-spectroscopy, and the surface areas were determined by BET procedure. The reactions were carried out in a semi batch Pyrex reactor with GC analysis.

### 3. RESULTS AND DISCUSSIONS

The product yields for thermal and catalytic degradation of polypropylene performed at 400°C are shown in Fig. 1. The H-ZSM-5 catalyst possessing strong acid sites produced less liquid products and more gaseous components than the other, transition metal containing catalysts. These results are in agreement with the fact that strong acid sites catalyze the degradation/cracking of heavier hydrocarbons. For PP degradation, the non-acidic Na-ZSM-5 and the Fe-ZSM-5 samples produced liquid hydrocarbons with yields about 90%, which is higher than that of non-catalytic thermal degradation.

Similar results have been obtained for PS degradation; however, the activity of the catalyst with small pore sizes (ZSM-5) has had lower activity (no reaction observed below 350 °C).

From the results obtained it can be concluded that not only the zeolite structure but also the polymer structure determines the activity of a micro- or mesoporous material in the catalytic degradation of polyolefines. The polymer chain ends are able to penetrate into the pore system of the catalysts, reaching the active sites located inside the channel.

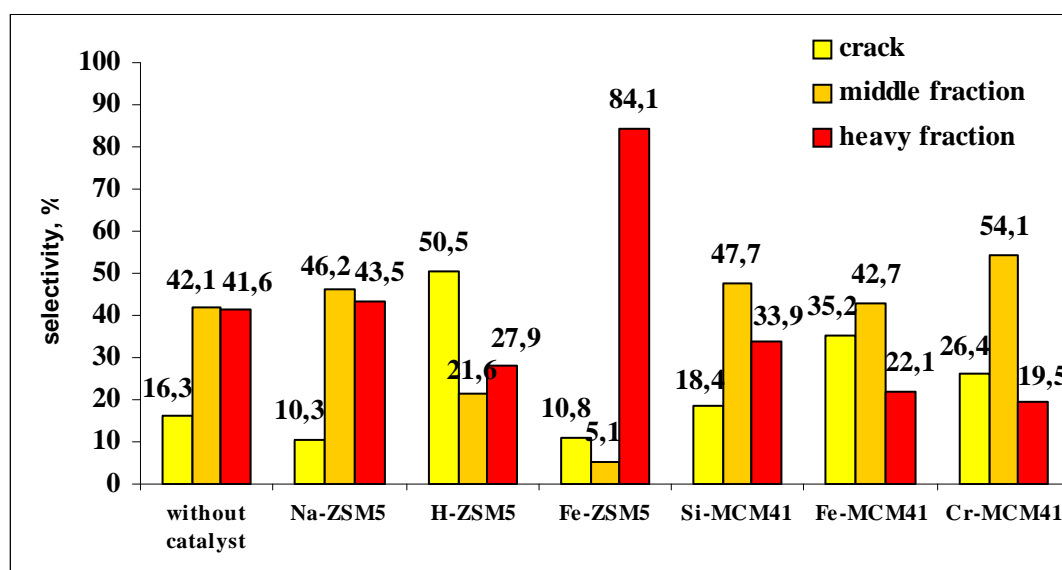


Fig. 1: Product selectivity in the degradation of polypropylene over different catalysts at 400 °C reaction temperature

Polymer with aromatic ring, i.e. polystyrene show lower relative activity in the case of catalyst with small pore size (ZSM-5). While there are no differences in the relative activity observed if the catalyst pores are large enough for the main chain to penetrate. By other hand the higher pore size resulted in higher initial reactivity, but the coke deposition is improved in the catalyst of large pores, can lead to a fast deactivation.

#### 4. REFERENCES

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