

Thermal and Catalytic Decomposition of Mixed Plastics

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The decomposition of a mixture of polymers with composition close to that frequently met in municipal plastic waste, but without PVC, over HZSM-5 and orthophosphoric acid modified (PZSM-5) zeolite were comparatively studied. The reaction products were analysed by chromatographic, IR and ¹H-NMR as well as by standard testing methods.

Catalytic decomposition increased the amount of gaseous products, lowered the condensate fraction, and changed their composition with respect to the non-catalytic method at the same pyrolysis temperature. The gaseous products contained a large C₃ fraction, while the liquid products contained mainly aromatic hydrocarbons. PZSM-5 catalyst promoted the formation of α -alkyl condensed aromatic rings. The global yield of the reaction products from the catalytic decomposition at 400 – 450 °C over both catalysts were close to that obtained by non-catalytic decomposition at 600 – 700 °C temperature range. The composition of all products depend on the catalyst activity and acidity. Zeolite catalyzed the transformation of a portion of the degradation products into liquid aromatic hydrocarbons. The decomposition over ZSM-5 led to high number of isomers, while the decomposition over PZSM-5 increased the aromatic content.

Introduction

The thermal recycling of polymer waste produces a liquid which is an important source of hydrocarbons for the petrochemical industry, and the method is convenient for the purpose of environmental protection. Pyrolysis is a method for the recycling of plastic wastes at temperature range of 500 – 800 °C in the absence of oxygen. Due to a poor thermal conductivity of plastic materials and to the endothermicity of polymer decomposition, this process has high-energy consumption. In order to decrease the temperature of process, catalysts have been used. Number of reports has been published on the catalytic decomposition of polymers over amorphous or crystalline catalysts [1-5]. Thermal and catalytic decomposition of polymers can take place simultaneously or separately [1,2]. There are only few studies on non-catalytic and catalytic decomposition of mixed plastics [6]. This paper reports a comparative study of the catalytic decomposition of a mixture of polymers over two zeolite catalysts

Experimental

Materials

A mixture of commercial polymer samples consisting 24 % high density polyethylene (HDPE), 39 % low density polyethylene (LDPE), 21 % polypropylene (PP), 10 % polystyrene, 4 % acrylonitrile-butadiene-styrene copolymer (ABS) and 1.5 % polyethyleneterphthalate (PET) were prepared by mechanical mixing.

The NaZSM-5 catalyst was first synthesized and then was transformed into NH₄-form by ion exchange with 0.2 M ammonium nitrate (5, 7). Further calcination to change the NH₄-form into H-form was carried out at 500^oC. Finally HZSM-5 was chemically modified with orthophosphoric acid to PZSM-5 [8-10]. In the next stage, PZSM-5 was mixed with 20% bentonite and turned into pellets of 1.5 mm cross-section similar to that obtained from ZSM-5. The PZSM-5 structure was established by X-ray diffraction analysis using a Cu K_α beam. PZSM-5 catalyst is stable in an acidic medium with a high crystallinity with a X-ray diffraction pattern identical to that of NaZSM-5 and HZSM-5 catalysts [11,12].

Pyrolysis

The polymer decomposition was carried out in two-step process, using the equipment previously described [12]. The first step was a continuous thermal process at 450-460 °C and the second step was a catalytic one in a fixed bed at 420-440 and 450-490^oC. The gaseous products from the first step were brought immediately into contact with PZSM-5 or HZSM-5 catalysts. Both steps were carried out in metallic equipment under atmospheric pressure with a small depression for the extraction of pyrolysis products from the reactor. After every test, the catalyst was regenerated at 550^oC under a flow of air for at least 8h. Both catalysts regained more than 95% of their activity after regeneration.

Analysis and characterization

Details of gas and liquid oil analysis conditions by gas chromatography and mass spectrometry could be find elsewhere (19). The pyrolysis liquid products were distilled at 100, 125, 150, 175, 200, 225 and 250^oC and the global products and cuts were characterised. Average molecular weights of the pyrolysis products were determined by ebulliometry in benzene solutions.

Results and Discussion

The mass balance of the pyrolysis experiments are given in the following table.

Catalyst type and pyrolysis temperature (°C)	Wt. %		
	Gas + loss	Liquid	Coke + residue ^a
ZSM-5 T<450	23.28	52	23.66
ZSM-5 T>450	32.68	48.33	17.99
PZSM-5 T<450	28.67	45.33	24
PZSM-5 T>450	36.00	47.33	15.67
Non-catalytic	11.67	87.33 ^b	-

^a residue obtained from the second pyrolysis step. The residue from the first pyrolysis step was less than 1 % on mass. b: wax

The first step of pyrolysis was a non-catalytic process which lead to a high yield of waxy product with 87.33 wt % on the initial material basis. By the catalytic decomposition over both catalysts, the wax was turned into a light yellow liquid with a high gas yield. A low coke formation on the catalysis is one of the advantages of using PZSM-5 catalyst. At T<450^oC, a part of the heavy product remained undecomposed and inhibited the catalyst activity. The gas evolution started earlier in catalytic than non-catalytic decomposition. A sharp increase in gas production volume was observed within 20 to 50 min of the experiment which was then leveled off. The gaseous products contain essentially the same type of hydrocarbons, but with different distribution. Polymer mixture produces 38-39 wt. % C₃ and C₄, with a low quantity of ethane, ethylene and methane by decomposition over ZSM-5, while decomposition over PZSM-5 produced 86.48 wt % C₃ and 6.86 wt % C₄. Liquid products

The distillation curves of liquid products obtained by thermocatalytic decomposition over PZSM-5 and HZSM-5 catalysts were found similar. The cuts with boiling point below 100°C were present only in the catalytic decomposition products. The quantity of the cuts with average boiling points below 175°C was at least 4 times higher than that obtained from non-catalytic decomposition and represented as the major fraction.

The products resulted from the non-catalytic decomposition have higher number average molecular weights than those of catalytic decomposition. Decomposition products contain numerous compounds differing in their concentration depending on the catalyst nature and decomposition temperature. High molecular weight compounds were significantly reduced during the thermocatalytic decomposition and new low molecular weight compounds such as aromatics, naphthenes, isoalkanes and isoalkenes were produced. Pyrolysis liquids had a high proportion of aromatic hydrocarbons due to polystyrene decomposition. However, high concentration of aromatics was produced by decomposition over PZSM-5 at both decomposition temperatures. No preference for a certain class of products was recorded for non-catalytic decomposition. With respect to the relative amount of paraffins, all the liquids resulted from the catalytic decomposition were similar in the range of C₁ to C₂₅. Non-catalytic decomposition produced high amount of paraffins with carbon number higher than 18. The decomposition at T > 450°C over both catalysts produced high yield of olefins with carbon number lower than 10. But, olefins with carbon number higher than 12 were produced in non-catalytic decomposition and catalytic decomposition at T < 450°C.

Considerable quantities of naphthalene, methyl and dimethylnaphthalene were produced along with benzene, toluene, xylenes, styrene, trimethylbenzenes, ethyl-benzene, methylethylbenzene, and propylbenzene over PZSM-5. C₁₀ – C₁₂ isoparaffins were the main compounds produced by decomposition over PZSM-5 at T > 450°C, while C₆ – C₉ naphthenes were the main class of compounds produced by the decomposition over ZSM-5 and PZSM-5 at T < 450°C. The IR spectra of various cuts at different decomposition temperatures were recorded. The spectra were found similar in 2000 – 4000 cm⁻¹ region with some differences in the intensity of certain bands at 1200 – 2000 cm⁻¹ region. The most important change was found in the bands around 1600 cm⁻¹ assigned to alkenes and monosubstituted benzene. The differences were also found in 400 – 1200 cm⁻¹ region, assigned to the aromatic hydrocarbons especially for those cuts were obtained from the catalytic decomposition at T < 450°C. The spectra of the cuts from the decomposition over ZSM-5 exhibited many sharp and strong bands at 830 and 870 cm⁻¹ assigned to di- and trisubstituted benzene. The spectra of the cuts from the decomposition over PZSM-5 were simpler than those of decomposition over ZSM-5. The disubstituted benzene were abundant. The spectra analysis of the oil distillate at 200-250 °C and the distillation residue indicated a significant difference between the catalytic and non-catalytic decomposition particularly at those regions which are assigned to the vicinal di and trisubstituted aromatic and alkenes. The spectral analysis indicated intensity differences between the decomposition products rather than the appearance of new compounds.

¹H-NMR spectra were recorded for 125-150 °C and 200-250 °C distillation cuts. The catalytic decomposition produced more alkyl aromatic compounds but less alkenes than non-catalytic decomposition. Interestingly, a significant difference was observed in between the distribution of compounds produced over the two catalysts used in this study. PZSM-5 produced more aromatics at temperature below 450 °C than that of ZSM-5. But, ZSM-5 produced more aromatic at temperature higher than 450 °C. Reduction in olefinic compounds is due to the hydrogenation of alkenes produced under the catalytic decomposition.

The steric effect of the catalysts influenced the composition of the aromatic hydrocarbons. HZSM-5 effectively decomposed polymer mixtures to light aromatic

hydrocarbons. PZSM-5 catalyst with a low acidity and a great steric effect, catalyzed the formation of condensable products with high amount of naphthalene, isoparaffins and naphthenes with low carbon numbers.

Change in the composition of liquid products can be explained by the catalyst structures and their acidity. For PZSM-5 catalyst, the channels' diameter is somehow modified by treatment with orthophosphoric acid. This caused a removal of aluminum ion from lattice position and reduction in acidity. A portion of the orthophosphoric acid is remained in the combined state inside of the channels [13].

Conclusion

The HZSM-5 zeolite and orthophosphoric acid modified zeolite (PZSM-5) are suitable for the catalytic decomposition of polymer mixtures without PVC. Decomposition over these catalysts increased the gas yield and aromatic content of the liquid products

The channel diameter of PZSM-5 catalyst is somehow modified due to the treatment with orthophosphoric acid. This caused a removal of aluminum ion from lattice position. Impregnation of HZSM-5 with acid also decreased the number of silanol groups and Brønsted acid sites. All of the reactions that took place inside the channels during the treatment with orthophosphoric acid increased the selectivity and decreased the acidity of PZSM-5 catalyst.

The condensable products contained large quantities of aromatic hydrocarbons but less alkane, olefin and naphthene products. PZSM-5 catalyzed the transformation of a portion of the degradation products into liquid hydrocarbons with a high amount of substituted benzene and substituted naphthalene. The results are similar with those obtained for polyolefins' decomposition over the same catalysts [14].

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