

CATALYTIC DECOMPOSITION OF NITROGEN-CONTAINING POLYMERS MIXED WITH ZEOLITE CATALYSTS

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Abstract

Thermal degradation of nitrogen-containing polymers may produce broad product range and environmentally hazardous compounds; therefore catalytic pyrolysis was investigated as an alternative process solving these problems.

In this work nitrogen-containing polymers (polyamides and polyurethane) and acidic zeolite catalysts were mixed and than pyrolysed at 500°C in a micro-pyrolyser on-line coupled with GC/MS.

The analysis of pyrolysis products revealed the nature of chemical reactions taking place in the presence of zeolites. The experimental results show that most polymer segments cracked to gases and to compounds of gasoline volatility, moreover aromatization takes place. However, there are distinctive differences in the decomposition paths of polymers depending on the cation of zeolite.

Keywords: Polyamide-6,6, Polyamide-6, PUR, catalytic conversion, Pyrolysis–GC/MS

1. Introduction

Pyrolysis proved to be a suitable method for recycling plastic waste at temperature range of 400–800°C [1]. Nevertheless, under thermal degradation of polymers often a broad range of products are evolved, a high operating temperature is required, and environmentally hazardous compounds may be produced. Catalytic pyrolysis proved to be an alternative process for avoiding the above disadvantages. A suitable catalyst can both control the nature of the products and reduce the reaction temperature. Among various commercial or laboratory prepared catalysts zeolite has been applied often [2–4].

Waste electronic and electric equipments (WEEE), and automotive plastic shredder contain nitrogen-containing polymers and various additives, therefore catalytic pyrolysis may be an adequate way of recycling this kind of waste. There are two methods of catalytic conversion, namely the catalytic upgrading of pyrolysis oils and the pyrolysis in the presence of catalyst.

The effect of zeolites on the thermal catalytic conversion of pyrolysis gases and oils of nitrogen-containing polymers has been studied in our laboratory earlier [5,6].

The purpose of this work was to examine the pyrolysis products derived from zeolite-polymer mixtures prepared in different ways and compositions in order to elucidate the chemical reactions taking place under pyrolysis of polyamides and polyurethanes in the presence of acidic zeolites.

2. Materials and Methods

2.1 Materials

2.1.1. Polymers

Polyamide-6,6 (PA-6,6), polyamide-6 (PA-6), polyamide-12 (PA-12), polyester based polyurethane (PUR_{est})

2.1.2. Catalysts

Zeolites used in this study were Y zeolites with average pore diameter 0.74 nm, namely ultra stable hydrogen form of Si/Al = 2.49 (HUSY) and NH₄NaY, Si/Al = 2.44 (Grace Davison).

2.2 Pyrolysis-GC/MS

Pyrolysis–GC/MS experiments were performed at 500°C for 20 s in a Pyroprobe 2000 pyrolyser (Chemical Data System, USA) equipped with a platinum coil and quartz sample tube interfaced to a gas chromatograph (Agilent 6890) coupled with a mass selective detector (Agilent 5973). The polymers were mixed with the catalysts in the ratios of 1:1, 1:3 and 1:5 and were placed into the sample holder quartz tube. Approximately 0.2 mg polymer sample was pyrolysed. Helium carrier gas at a flow rate of 20 mLmin⁻¹ purged the pyrolysis chamber held at 250°C that was split prior to be introduced into the GC column. The GC separation was carried out on a HP-5MS capillary column (30m×0.25mm×0.25µm, Agilent Technologies, USA). After 1 min of isotherm period at 50°C the oven temperature was programmed to 300°C at 10°Cmin⁻¹ heating rate and held at 300°C for 4 min. The temperature of the transfer line of GC/MS and the source of the mass spectrometer were 280 and 230°C, respectively. The mass spectrometer was

operating in electron-impact mode (EI) at 70 eV. The spectra were obtained over a mass range of 14–500 Da.

3. Results and Discussion

The acidic Y type zeolites (NH₄NaY and HUSY) have significant effect on the degradation of polyamides (PA-6,6, PA-6, PA-12) and polyurethane. Both have strong catalytic cracking activity, however some characteristic compounds of pyrolysis oils are different in the cases of HUSY and NH₄NaY.

3.1. Pyrolysis products of polyamides

Thermal decomposition of PA-6,6 and PA-12 leads to a wide range of N-containing compounds. Amines, amides and nitriles are found in these pyrolysates beside CO₂, unsaturated and cyclic hydrocarbons.

The structure and composition of these components are matching with the known thermal decomposition mechanisms of *cis*-elimination and intramolecular rearrangements producing cyclic diamide and other oligomeric cycles.

The most important thermal decomposition product of PA-6 is ϵ -caprolactam, however other N-containing and unsaturated hydrocarbons are also present.

Pyrolysis products of pure polyamides and polyamide-zeolite mixtures are considerably different. Most of the pyrolysis products of polyamides either disappear or notably diminish in the mixtures' pyrolysates, while the amount of some originally negligible or undetectable compounds increases significantly.

The cracking activity of zeolites is obvious. Heavy oil components no longer present in the polymer-zeolite pyrolysates, but the amount of gases and compounds of gasoline volatility became dominant. The intensity of light unsaturated and cyclic hydrocarbons are prominent, however several aromatic hydrocarbons (benzene, naphthalene, alkylbenzene and alkylnaphthalene compounds) are present as well. No peaks occur after 15 minutes retention time.

The presence of NH₄NaY has further consequences on the decomposition mechanisms of polyamides and on the oil composition. Not only the rearrangement of amide linkages along the macromolecular chains is inhibited, but this zeolite promotes the N-C_{alkyl} bond cleavage suppressing the homolytic cleavage of N-C_{carbonyl} bonds. Therefore hexanedinitrile, hex-5-enitrile are still determinant components in the pyrolysis oils of PA-6,6 and PA-6 respectively.

This specific effect of NH₄NaY may due to the ammonolysis by means of the evolved NH₃.

3.2. Pyrolysis products of aromatic polyester based polyurethane

At 500°C the decomposition of polyester segmented polyurethane leads to the formation of CO₂, 1,3-butadiene, tetrahydrofuran (THF), cyclopentanone, bis(4-isocyanatophenyl)methane (MDI), and a number of ester compounds.

Mixing the polyurethane sample with protonic Y zeolites results the alteration of MDI and the ester compounds of

high molecular mass into aromatic compounds while most of the gases and high volatility oil components are unchanged.

The pyrolysis oil composition of polyurethane mixed with NH₄NaY or HUSY is quite similar; however tetrahydrofuran is completely eliminated from the pyrolysis oil of polyurethane-HUSY, while in the oil of polyurethane-NH₄NaY it is still present.

Comparison of these present results with those of pyrolysis oils were transformed over zeolite catalysts [5,6] has also been carried out.

It can be concluded that in both cases strong cracking and aromatization were observed, but as for the mixtures the zeolite influences the thermal decomposition mechanisms as well. Therefore the product distribution differs and instead of extensive denitrogenation the formation of some nitrogen-containing pyrolysis products is enhanced.

4. Conclusions

Pyrolysis studies of polyamide-protonic Y and polyurethane-protonic Y zeolite mixtures revealed that these catalysts are directing the pyrolysis reactions producing dominantly olefins and aromatics of low molecular mass. Although both zeolites crack the polymer chains there are characteristic differences in the composition of the pyrolysis oils.

Since the zeolites affect the decomposition reactions of polymers the pyrolysis oil compositions are differ from those of the pyrolysis oil products of polymers were transformed over zeolite catalysts.

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