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DEGRADATION OF PURE AND WASTE PVC AND PET IN THE PRESENCE OF MODIFIED POROUS CATALYSTS

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ABSTRACT

The catalytic degradation of pure and mixed polymers such as poly-(vinylchloride) (PVC) and poly-(ethylenterephthalat) (PET) was followed by thermal analytical method (TA) and was performed in a laboratory batch system (LBS) using modified ZSM-5, MCM-41 and hydrotalcites based catalysts. In degradation of PET, the acidic H-ZSM-5 resulted in less liquid products and more gaseous components than the other, transition metal containing catalysts. The degradation of PVC takes place in two steps, the first is the departure of HCl at about 300 °C followed by formation of aromatic hydrocarbons. Minimal residue could be obtained over Fe,Mg,Al-hydrotalcites and mixed oxide catalyst. From the results obtained it can be concluded that not only the catalyst structure but also the polymer structure determines the activity of a micro- or mesoporous material in the catalytic degradation of plastics or plastic wastes. Therefore, different optimal conditions (catalyst and reaction temperature) can be applied for each plastics studied (pure, mixed and waste) in thermal treatment.

Keywords:
plastic pyrolysis, porous catalysts, degradation, polymer waste, PVC, PET

1. INTRODUCTION

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 [1].

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 of growing importance. In this way plastic wastes are converted into monomers, fuels or valuable chemicals for petrochemistry [2].

Traditional thermal cracking, i.e. pyrolysis can be applied to transform both thermoplastics and thermosets into gases, liquid hydrocarbons and solid residue [3]. 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 [4]. 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) [5].

A large number of laboratory studies have been conducted for direct catalytic degradation of polymers, especially for pyrolysis of polyolefins, however, there are a lot of study deal with the degradation of PET and PVC. 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 [6-10].

The objective of this work is to study the potential of modified ZSM-5 zeolite, MCM-41 mesoporous silica, hydrotalcites (HD) and HD originated mixed oxides as catalysts for degradation of PET and PVC using thermal analytical measurements and laboratory reactor experiments.

Table 1: Properties of catalysts

Prepared catalyst sample	Structure (XRD, IR, TEM)	BET surface area, m^2/g
$CaCO_3$*	-	3.3
CaO*	-	1.5
Na-ZSM-5	ZSM-5	360
H-ZSM-5	ZSM-5	385
Fe-ZSM5	ZSM-5	346
Cu-ZSM-5	ZSM-5	352
Ni-ZSM-5	ZSM-5	370
Fe-MCM-41	MCM-41	890
Ti-MCM-41	MCM-41	1010
Cr-MCM-41	MCM-41	960
Mg-Al-LDH	hydrotalcite	20
Fe-Mg-Al-LDH	hydrotalcite	25
Cr-Mg-Al-LDH	hydrotalcite	12
Cu-Mg-Al-LDH	hydrotalcite	32
Ca-Mg-Al-LDH	hydrotalcite	16
Mg-Al-MO	Mg- + Al-oxide	40
Fe-Mg-Al-MO	Mg- + Al- + Fe(III)-oxide	42
Cr-Mg-Al-MO	Mg- + Al- + Cr(III)-oxide	50
Cu-Mg-Al-MO	Mg- + Al- + Cu(II)-oxide	27
Ca-Mg-Al-MO	Mg- + Al- + Ca-oxide	21

*commercial product (MOLAR RT, Hungary)

2. EXPERIMENTAL SECTION

Catalysts

The catalyst samples were prepared in our laboratory except $CaCO_3$ or CaO (MOLAR RT, Hungary).

The synthesized Na-ZSM-5 zeolite was modified by conventional or solid state ion-exchange to form H-, Fe-, Cu-, Ni- and Ti-ZSM5 samples [11].

The Ti- or Fe-MCM-41 specimen was prepared from sodium silicate, CTMA-Br and $Ti(SO_4)_2$ or $Fe(NO_3)$ solution at pH 12 [12]. The crystallization was carried out at 373 K for 2 days followed by calcination at 823 K for six hours.

The Fe/Al/Mg-hydrotalcite (M^{II}/M^{III} = 2, and M^{III}: 0.9 Al and 0.1 Fe) was prepared by coprecipitation at constant pH = 10 ± 0.2 of an aqueous solution of $Mg(NO_3)_2$, $Al(NO_3)_3$ and $Fe(NO_3)_3$ with a solution of NaOH and Na_2CO_3 [13].

The structure of the catalysts was characterized by X-ray diffraction, IR-spectroscopy and transmission electron microscopy, their thermal stability was followed by thermal analytical method. The specific surface area and pore size distribution of the samples were determined by nitrogen adsorption isotherms.

The properties of the samples have corresponded to the data of literature. The physical characteristics of the catalysts used are shown in Table 1.

Methods

Commercial plastics: HDPE, PP, PET and PVC in granulate form have been used as model feed. The degradation of pure polymers was followed using either by utilizing of thermoanalytical method (*MOM Derivatograph Q, Hungary*) or in a laboratory batch reactor system with gaschromatographic product analysis (*Shimadzu GC2010, Japan*).

3. RESULTS AND DISCUSSIONS

TG experiments

The TG analysis for pure PET - as it is show non Fig. 1 - proves a relatively sharp, one steep weightloss with a maximum in the DTG curve placed at 480 °C. This behavior corresponds with the thermal degradation of this polyester of narrow molecular mass distribution. Figures 2 and 3 show TG analysis of PET/H-ZSM5 and PET/Ti-MCM41 catalyst mixture with 10 % catalyst content.

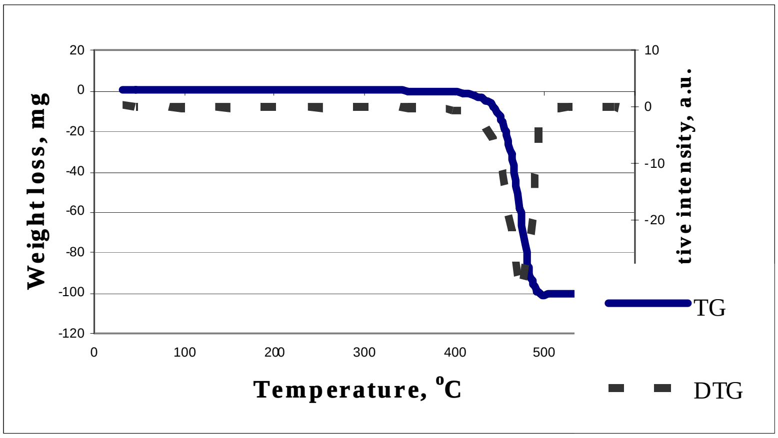

Figure 1: Thermal analytical study of PET degradation without catalyst

In the case of the PET/catalyst mixture it is clearly observed that the polymer degradation takes place at a quite lower temperature, due to the polymer catalytic cracking. In the presence of this catalyst, the weight loss starts at temperatures between 400 and 425 °C, indicating that a significant reduction occurs in the threshold temperature compared to the pure thermal degradation (with DTG maxima as characteristic temperature at 485 and 480 °C, respectively). Moreover, clear differences could be observed in regards to this temperature among the catalysts; the data can be seen in Table 2.

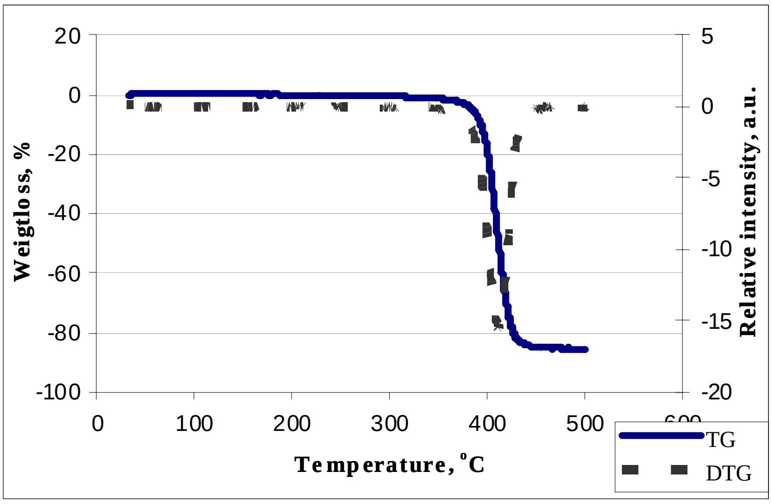

Figure 2: Thermal analytical study of PET degradation over H-ZSM-5 catalyst

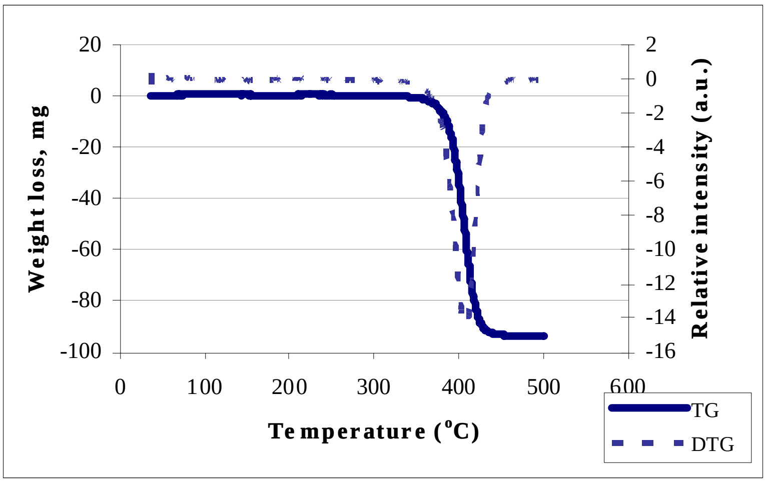

Figure 3: Thermal analytical study of PET degradation over Ti-MCM-41 catalyst

The difference of the PET and the PVC in the catalytic degradation can be seen in Figs. 4 and 5. The decomposition of PVC takes place at least in two steps, the first is due to the release of HCl with ~ 300 °C characteristic temperature, the second peak corresponds to the pyrolysis of the residual hydrocarbon framework (440 - 470 °C temperature range).

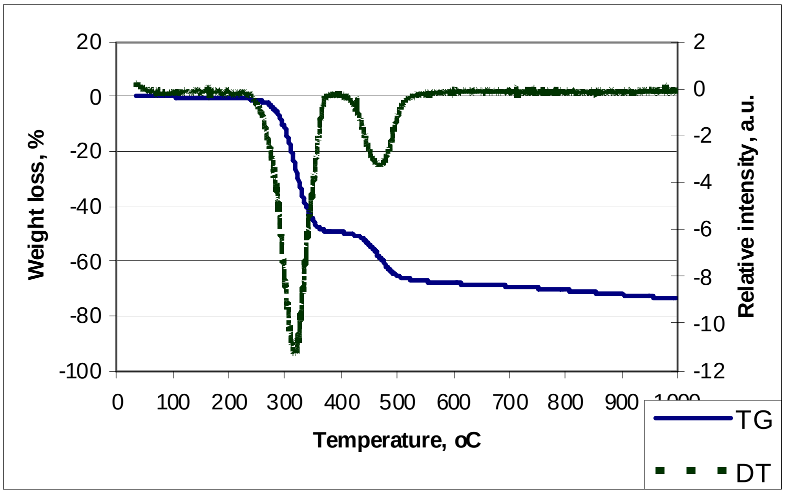

Figure 4: Thermal analytical study of PVC degradation over Fe-ZSM-5 catalyst

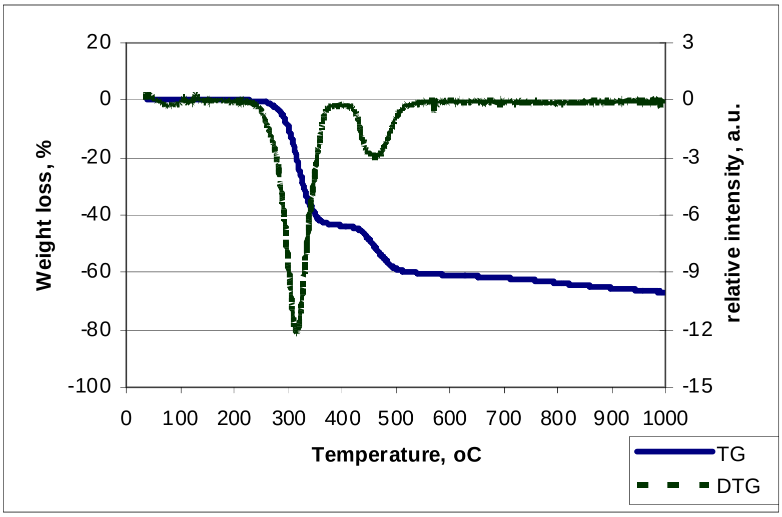

Figure 5: Thermal analytical study of PVC degradation over Ti-MCM-41 catalyst

Table 2: Characteristic temperature of plastic decomposition (DTG peak maxima)

Catalyst	DTG peak maximum, °C	
	PET	PVC*
none	473	320, 478
CaO	-	310, 459
$CaCO_3$	-	313, 460
Na-ZSM-5	465	316, 470
H-ZSM-5	412	313, 423
Fe-ZSM-5	423	310, 452
Cu-ZSM-5	-	312, 460
Ti-ZSM-5	-	305, 456
Fe-MCM-41	461	269, 443
Ti-MCM-41	458	275, 450
Mg,Al-oxide	452	281, 475
Fe,Mg,Al-oxide	447	292, 471
Cr,Mg,Al-oxide	445	310, 456
Cu,Mg-Al-,oxide	456	304, 442
Ca,Mg,Al-oxide	-	290, 445

**for PVC two peaks can be identified to characteristics*

4. CATALYTIC DECOMPOSITION OF PET AND PVC IN THE BATCH REACTOR

Considering the solid residual (in mass %) determined at 400 °C at the end of the reactions (after two hours) could be calculated the nominal conversion and the relative amounts of gaseous (crack), liquid (oil) and solid (residue) products. These data can serve for characterization of the process and there are collected in Table 3. In the case of PVC the amount of HCl collected in a trap with NaOH solution can be seen in this Table, as well.

Table 3: Conversion of plastic decomposition in the different catalysts at 400 °C

	PET				PVC				
	conv.	crack %	oil %	resi-due %	conv.	crack %	oil %	resi-due %	HCl %
none	0.853	23.1	36.7	40.2	0.726	3.0	28.5	58.5	72.9
CaO	-	-	-	-	0.894	4.5	52.8	42.7	36.6
$CaCO_3$	-	-	-	-	0.896	6.3	55.7	38.0	27.4
Na-ZSM-5	0.733	18.7	43.4	37.9	0.872	6.8	36.4	43.2	76.8
H-ZSM-5	0.882	55.5	22.7	21.8	0.875	43.7	33.8	22.5	53.5
Fe-ZSM-5	0.836	23.4	46.7	29.9	0.965	30.1	44.2	25.7	63.9
Ti-ZSM-5	0.874	34.6	43.2	22.2	0.909	24.2	46.1	29.7	52.9
Fe-MCM-41	0.756	32.6	46.6	20.8	0.889	11.4	56.9	32.7	62.9
Ti-MCM-41	0.873	28.5	44.4	27.1	0.842	16.8	44.9	38.3	65.8
Mg,Al-oxide	0.740	32.0	35.2	32.8	0.936	10.1	62.7	27.2	37.3
Fe,Mg,Al-oxide	0.943	20.3	47.5	32.2	0.843	16.6	54.7	28.7	65.6
Cr,Mg,Al-oxide	0.866	37.1	42.4	20.5	0.912	21.3	60.1	18.6	60.3
Cu,Mg,Al-oxide	0.857	26.2	56.4	17.4	0.886	-	-	-	-
Ca,Mg,Al-oxide	0.953	-	-	-	0.826	-	-	-	-

The H-ZSM-5 catalyst possessing strong acid sites resulted in less liquid products and more gaseous components than the other, transition metal containing catalysts. These results are in agreement with the fact that acidic sites catalyze the degradation/cracking of heavier hydrocarbons.

The Cl balance can be calculated from the relative amount of HCl, and it is clerly seen that the basic catalysts react with the HCl formed in the pyrolysis. This reaction could results the deactivation of the catalyst, however, its importance is the possible mineralization of chlorine.

The effect of the temperature for the reaction of PET in the presence of Al-Mg-oxide catalyst can be seen on Fig. 6. On higher temperatures the formation of gaseous products are preferential.

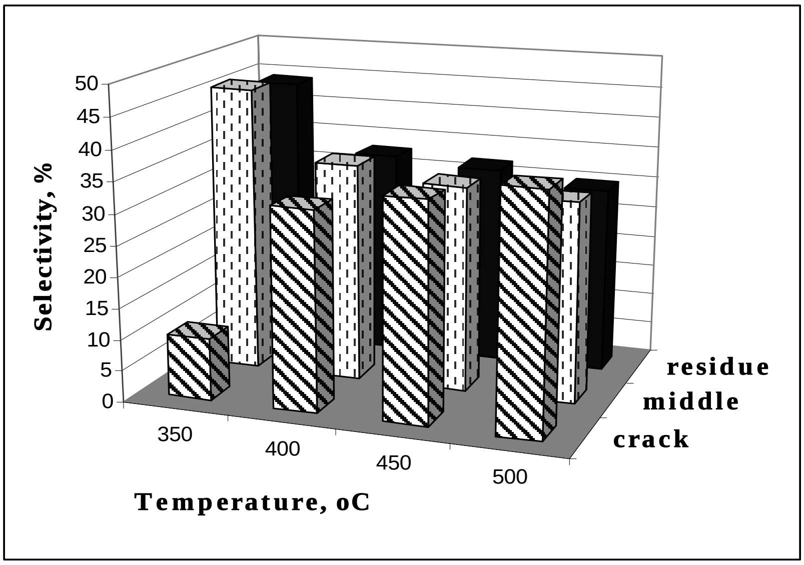

Figure 6: Product distribution in PET degradation at different temperatures in the present of Al-Mg-oxide catalyst

5. CONCLUSIONS

For PET degradation the non-acidic Na-ZSM-5 and the Fe-ZSM-5 samples product liquid hydrocarbons with yields about 90 % which is higher than that of non-catalytic thermal degradation. while the H-ZSM-5 sample enhances the formation of low molecular weight (gaseous) products.

The catalytic degradation of PVC takes place at least in two steps: the first one is the leaving of HCl. In this reaction. The catalysts with basic character (CaO, $CaCO_3$, hydrotalcites and Mg-Al-mixed oxides) have definite activity, principally due to the stabilization of the system by the reaction with the releasing HCl.

From the results obtained it can be concluded that not only the catalyst framework but also the polymer structure determinate the activity of porous materials in the catalytic degradation of plastic wastes. The polymer chain ends are able to penetrate into the pore system of the catalyst, reaching the active sites into the channel system.

Polymer with aromatic ring. i.e. PET show lower activity in the case of catalysts with smaller pore sizes (ZSM-5). By other hand, the higher pore size resulted in higher initial reactivity, but the coke deposition was improved in the catalysts of large pores, can lead to a fast deactivation.

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