Plastic Pyrolysis Using Montmorillonite-Based Catalysts

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Abstract

Waste plastic disposal and excessive use of fossil fuels have caused environment concerns in the world. Both plastics, which are themselves derived from oil, and petroleum-derived fuels are hydrocarbons that contain the elements of carbon and hydrogen. The difference between them is that plastic molecules have longer carbon chains than those in LPG, petrol, and diesel fuels. Therefore, it is possible to convert waste plastic into fuels.

The main objectives of this study were to check the effectiveness, in the processes of plastic pyrolysis, of montmorillonite-based catalysts with different modifications. The investigated catalysts were divided into three groups depending on their preparation pathway. The work is presented in two parts. The first part contains results for all catalysts tested. The catalytic degradation of polyethylene, which is the most common plastic found in waste and presents the simplest structure of all plastic materials, was analyzed using thermogravimetry (TG) and differential scanning calorimetry (DSC) methods under a nitrogen atmosphere. In the second part of this work three catalysts showing best results were tested with four different types of waste plastics.

The main results that were obtained are that montmorillonites, in particular the ones that have been acid-treated and intercalated with metallic cations, are effective catalysts for the degradation of pure HDPE but further studies are required to ensure their effectiveness in the processing of actual plastic waste that contains contaminants that hinder the catalytic activity.

KEYWORDS: Polyethylene, montmorillonite, catalytic degradation, differential scanning calorimetry (DSC), thermogravimetry (TG), plastics, pyrolysis.

1. Introduction

Waste plastic disposal and excessive use of fossil fuels have caused environment and economical concerns in the world. USA, Europe and Japan generate about 50 million tons of post-consumer plastic waste material per year [1]. Due to the convenience to manufacturing and use, the world plastic production has been increasing since it was first commercially manufactured. One of the major concerns for the extensive use of the plastics is the disposal of the waste plastic. In addition, the plastics are mostly produced from non-sustainable oil or coal, and thus they are non-sustainable products.

Europe consumes about 25% of the global plastic production, which is equivalent to 60 million tons per year and, to account for the growing production and consumption, tertiary recycling needs to be developed. Tertiary recycling includes all these methods of processing which attempt to convert the plastic wastes to basic chemicals by the use of chemical reactions. This returns plastics to their constituent monomers, which can be reused, or to high-value hydrocarbon feed stock materials and fuel oils that can be used in the petrochemical industry or as fuels.

Pyrolysis and catalytic conversion of plastic is a superior method of reusing the waste when compared to incineration, which is the main route used today for non-recyclable plastics. Additionally, the distillate product is a fuel which makes the process economically feasible and environmentally friendly due to the overall lower consumption of fossil fuels. Furthermore, significantly lower net costs of waste disposal can be obtained with simultaneous increase of reused wastes [2]. Pyrolysis of waste plastic seems to be one of the most promising emerging technologies that may prove to be an economical method to solve non-recyclable waste plastic problem.

In this study there are two major objectives. The first objective is to study the catalytic pyrolysis process of polyethylene, as a potential representative material of waste plastics, and as its major component. The second objective is to assess the influence of different types of montmorillonite–based catalysts on actual waste plastic degradation.

2. Experimental

2.1 Materials

The base mineral was montmorillonite extracted from bentonite from Milowice (Mt) and commercial montmorillonite (K30) from Sigma Aldrich. The following materials (after base materials modification) were used as a catalysts: Mt, K30H15, K30H60, K30H90, K30H120, MtH60Al, MtH90AlCu, K30Al, K30H15Al, K30H60Al, K30H90Al, K30H120A, creating a group of 12 catalyst investigated in this study.

Because of big number of catalysts tested, they were divided into three groups depending on their modification path, as presented on the Table 1.

Modification	acid treated	pillared
I group		
K30 H15	■	
K30 H60	■	
K30 H90	■	
K30 H120	■	
II group		
K30 H15Al	■	■
K30 H60Al	■	■
K30 H90Al	■	■
K30 H120Al	■	■
III group		
Mt		
K30Al		■
Mt H60Al	■	■
Mt H90AlCu	■	■

Table 1. Catalysts preparation table.

2.2 Characterization methods

To determine acid strength distribution of catalysts the temperature-programed desorption (TPD) of ammonia was conducted.

The catalyst samples were saturated with ammonia by placing them in a closed test-tube together with an ammonium solution; this solution saturated the atmosphere within the vessel with gaseous ammonia and was kept at 40 °C for 4 hours in the thermostat. After saturation, desorption experiments were carried out in a DSC/TG apparatus, using a quartz pan. The samples were heated up to 500 °C with a heating rate equal to 10°C/min.

The acid strength distribution was obtained for all three groups of catalysts from the NH_3-TPD by a numerical deconvolution method [3].

2.3 TG/DSC analysis

Most of the TG/DSC experiments (calcination, pyrolysis, activation testing) were carried-out in a PerkinElmer Simultaneous Thermal Analyzer STA6000. Before the runs, nitrogen flow was maintained through the system for 5 min with the flow rate of 19.8 ml/min to purge all the air out of the oven. The same flow rate was maintained during the experiments. The investigated polyethylene samples and samples with previously calcined in 500°C catalysts were placed on an alumina TG pan and the thermal degradation was analyzed. The PE/catalyst mixture was prepared at room temperature in order to obtain a mixture of 10 - 11 mg. The quantity of catalyst used was approximately 1 mg, depending on the experiment. The runs were performed under nitrogen with continuous flow and with constant heating rate of 10°C/min. For each experiment in the temperature program there were four stages carried out, as schematically sown in Fig. 1 The first one was isothermal stabilization at 30ºC for 10 minutes. At the second stage, temperature was increased from 30 to 700ºC with a heating rate of 10°C per minute and at the third stage the final temperature (700°C) was maintained for 10 minutes, followed by the last stage - the sample cooling to 30ºC with the rate of 100ºC per minute.
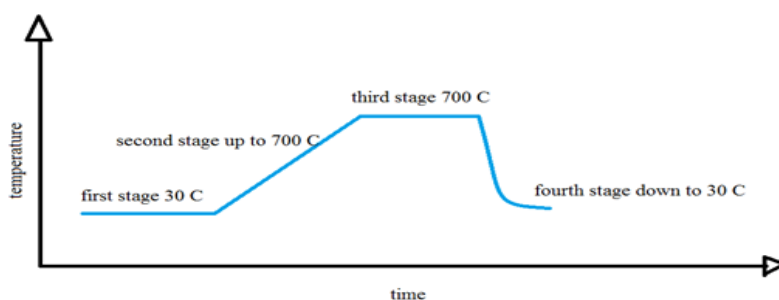

Figure 1. Temperature profile for the polyethylene degradation

The data collected during the experiments were stored in the computer connected with the equipment. The evaluation of the data received from the analyzer was conducted by the specialized software Pyris Series STA6000. This tool was used for converting the obtained data points into plots used for the further interpretation of the results.

The influence of the temperature was analyzed. All experiments were carried-out with a constant heating rate. During the heating, measurement of changes in weight and heat flow were performed in order to investigate the behavior of the sample as a function of temperature.

3. Results and discussion

3.1 Acid strength distribution:

Acid sites in montmorillonites have different strengths and number of acid sites, depending on their position in the framework and their environment. In the first group of catalysts K30H60 presents the highest number in the widest range of acid strengths, with desorption energy levels from 45 to 140 kJ mol-1. However, all catalysts present significant heterogeneity of acid strength. In the case of the second group, it presents higher overall number of acid sites of high desorption energy level than catalysts from the first group. All catalysts show the highest amount of acid sites at energy level of 80 kJ/mol. The third group investigated shows an almost uniform distribution of different strength acid sites. As shown in Table 2 all catalysts present significant heterogeneity in number of acid sites. An interesting fact is that the overall number of acid sites obtained for the second group of catalysts (after cation intercalation) is around 3000[10^{-6}mol/mg].

catalyst	number of acid sites [10^-6*mol/mg]
K30H15	1281
K30H60	4823
K30H90	1561
K30H120	2931
K30H15Al	3339
K30H60Al	3254
K30H90Al	2927
K30H120Al	2703
Mt	1665
K30Al	2795
MtH60Al	1438
MtH90AlCu	2159

Table 2 Numbers of acid sites for all catalysts investigated

3.2 Catalytic degradation of PE

The results obtained from the DSC/TG analysis of the polyethylene (PE) degradation using all three groups of catalysts investigated are shown in Figure 2.

The first graphic shows the curve corresponding to the DSC signal with two endothermic peaks. The first peak with no accompanying weight loss corresponds to the melting of the PE sample. It can be observed that the melting point remains constant for all experiments, which for the tested polyethylene, is obtained at 127 °C. Additionally the shapes of peaks are very similar. It can be concluded that the melting temperature is not influenced by the catalysts.

The second endothermic peak at the higher temperature is related to the degradation process. This peak is accompanied with a considerable weight loss. The formation of gas phase products involves two steps. The first one corresponds to the breakage of the bonds and the formation of smaller molecules and the second one corresponds to the evaporation of these smaller products. Each of the steps is associated with different energy consumption. The beginning of the second DSC signal is due to the energy which is given to the sample when the bonds in the polymer begin to break. This breakage of the bonds in the polyethylene produces lighter products that eventually become

sufficiently small to be volatile at the temperature of reaction and evaporate from the pan, leading to the observed mass losses. Additional consumption of energy will also occur due to the evaporation process and the potential further degradation of released, newly created compounds.
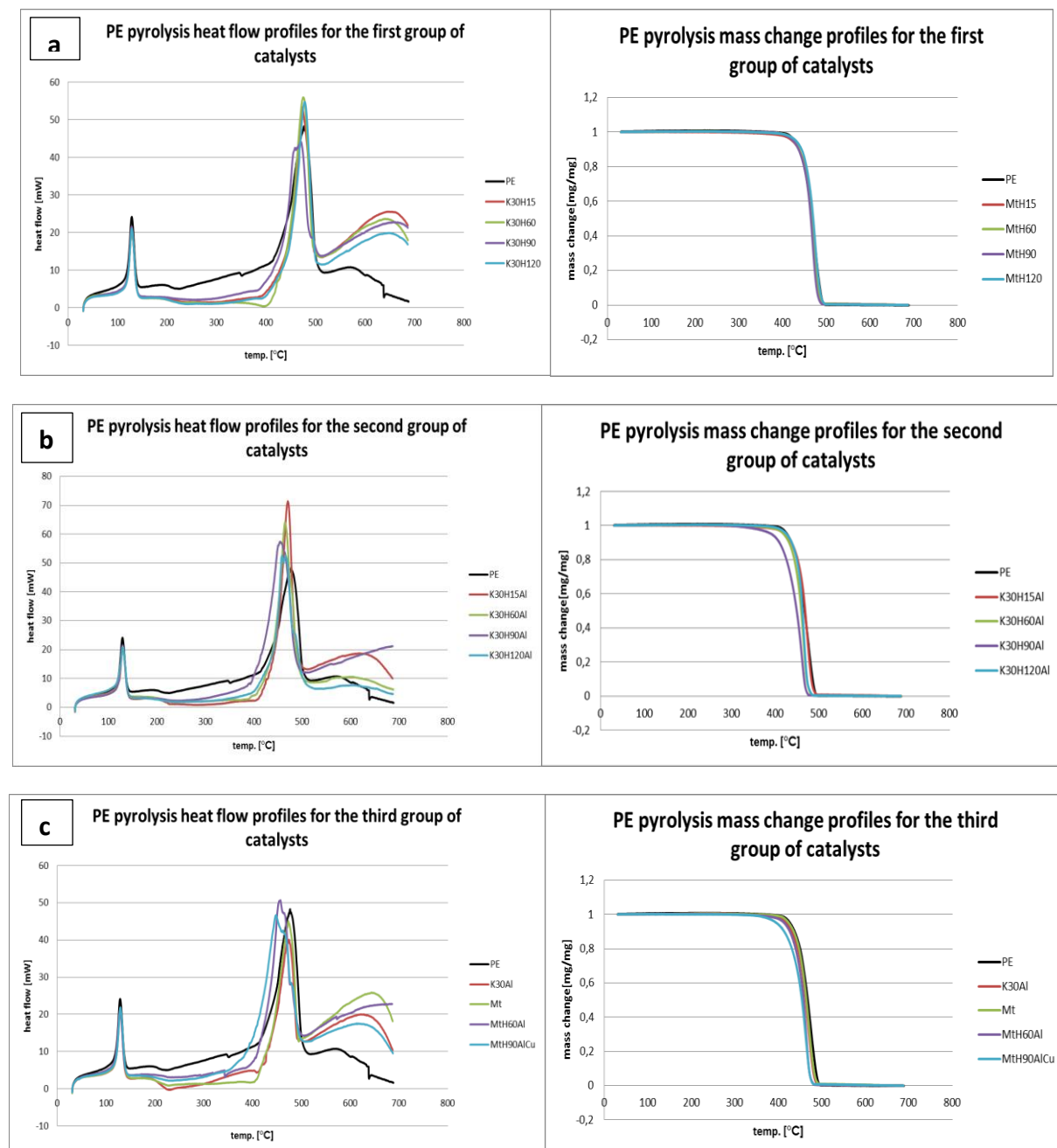

Figure 2 TG/DSC analysis results of a) first group, b) second group and c) third group of catalysts

It is clear that all montmorillonites treated only with acid for different lengths of time show little activity, leading to the negligible decrease in the degradation temperature. In the two other groups of catalysts only two catalysts (one in each group) can be found interesting in terms of improving degradation temperature noticeably, which are K30H90Al and MtH90AlCu.

3.3 Activity-acidity relationship

The conversion of hydrocarbons over montmorillonites is catalyzed by their Brönsted acid sites whose acidity was evaluated by temperature-programmed desorption (TPD) of ammonia in the 3.1 chapter. As studied by others [4, 5] Brönsted-type relationships relate the rate constant of reactions catalyzed by acids with dissociation constant of bases. In other words, ammonia desorption energies, which depends on the strength of the acid sites, can be related with the polyethylene degradation reaction constant rate. This statement leads to the conclusion that activity-acidity relationships derived from acid-catalyzed reactions could be obtained for the whole family of montmorillonite catalysts. Using the Arrhenius equation (1) for a first order reaction model, the rate data as a function of temperature could be present.

$$k = A \exp(-E_a/RT) \tag{1}$$

In this work, the stated above dependence was calculated for the best four catalysts tested in the polyethylene degradation process, resulting in obtaining four plots for each catalyst with two curves representing experimental data of behavior of the PE mass and a fitted model curve of the same process. Due to the presence of the model curve calculated with a solver, two fitting parameters could be estimated: energy of activation of the reactions [Ea] and their rate constants [k], shown in Table 3.

catalyst	k(T)	Ea [kJ/mol]	number of active sites
MtH90AlCu	0,0989	55850	2159,13
K30H90Al	0,1312	53222	2926,55
MtH60Al	0,0615	73081	1437,62
K30H60Al	0,0454	80963	3253,91

Table 3 Energy values, rate constants and number of acid sites obtained for polyethylene decomposition reaction and from the adsorption of ammonia over various catalysts.

The results obtained show no clear relation between calculated number of acid sites and energy received from a model. However we can see that, if we exclude for the moment K30H60Al, the catalysts with the larger amount of acid sites do present the higher frequency (pre-exponential) factors and the lower activation energies, when compared with MtH60Al. The case of K30H60Al is peculiar since it has a large number of acid sites but has the lowest frequency factor and the highest activation energy; this may be related to the fact that this catalyst has many acid sites but mostly in the low acidity range. Analyzing the model fitted to the experimental data, it seems clear that a more detailed look into the mass degradation processes occurring in the sample during the pyrolysis, is required, probably by taking the actual acid-strength distribution of the different catalysts.

3.4 Deactivation study

The study of deactivation was carried out for three catalysts which showed the strongest influence on the polyethylene pyrolysis process: MtH90AlCu, K30H90Al and MtH60Al. The experiments were carried out for the 10 mg of polyethylene with 1 mg of the catalyst under the heating rate of 10°C/min. Each experiment consisted of 3 cycles. After the first cycle a new, more or less equal, amount of polyethylene was added to the catalyst used in the previous cycle and then the action was repeated for the third cycle. This procedure allowed to check if the catalysts still retained the activity in the following cycles.

In this study the loss in performance caused by deactivation is investigated with the focus on the surface blocking phenomena, due to the fact that only pure polyethylene is pyrolysed.

All degradation temperatures for tested catalysts: MtH60Al, MtH90AlCu and K30H90Al are shown in Table 4, Table 5 and Table 6, respectively.

MtH60Al	first cycle	second cycle	third cycle
first activation test	472	472	470
second activation test	473	468	472
third activation test	471	471	464

Table 4 Degradation temperature for PE with MtH60Al obtained from DSC/TG analysis.

MtH90AlCu	first cycle	second cycle	third cycle
first activation test	466	466	462
second activation test	459	460	463
third activation test	460	458	463

Table 5 Degradation temperature for PE with MtH90AlCu obtained from DSC/TG analysis.

K30H90Al	first cycle	second cycle	third cycle
first activation test	464	468	468
second activation test	467	457	471
third activation test	469	469	462

Table 6 Degradation temperature for PE with K30H90Al obtained from DSC/TG analysis.

Presented results indicate that, although some slight deactivation took place, a part of the activity was still retained for all catalysts tested. Unfortunately, the temperatures obtained for the reference first cycle are higher when compared to results obtained from the first pyrolysis test conducted. At the very first polyethylene degradation test with the MtH60Al catalyst the degradation temperature equal to 457 °C, in the case of MtH90AlCu 448°C and for the K30H90Al the first obtained temperature was at the level of 454°C. This is probably due to the loss of original properties of catalysts, caused by the most probable adsorption of molecules from the external environment. These results indicate that these catalysts are extremely sensitive to the environment in which they are stored and careful control of these conditions is required, for instance by storing them under constant humidity conditions to protect the surface, for this kind of difficulties to be reduced.

3.5 Pyrolysis of waste plastics.

This chapter contain the results and summation of the pyrolysis of four different types of waste plastics in the presence of three different catalysts showing the best results in PE pyrolysis process. Namely, they are: MtH60Al, MtH90AlCu and K30H90Al.

Investigated waste plastics are sampled form a group of four plastic materials described as follows:

- A3 as an electric cables containing aluminum cations and flame retardants sample

- A6 as an electric cables containing copper cations and flame retardants sample

- A5 as an electric cables containing aluminum cations and flame retardants, but obtained from another source than material 1 sample

- A2 as a three times washed mixture of different plastics (mostly PP and PE materials) containing fibers and water sample.

The methods and techniques used to study the degradation of waste plastic materials are the same as described in polyethylene pyrolysis process investigation, resulting in obtaining TG/DSC plots and tables containing degradation temperatures presented below.

sample	Tdegradation [°C]	sample	Tdegradation [°C]		sample	Tdegradation [°C]		sample	Tdegradation [°C]
A3	468	A6	296	464	A5	294	472	A2	467
A3+MtH90AlCu	472	A6+MtH90AlCu	287	470	A5+MtH90AlCu	283	473	A2+MtH90AlCu	470
A3+K30H90Al	481	A6+K30H90Al	304	460	A5+K30H90Al	286	480	A2+K30H90Al	464
A3+MtH60Al	482	A6+MtH60Al	325	471	A5+MtH60Al	290	460	A2+MtH60Al	461

Table 7 Degradation temperatures obtained in pyrolysis of the A3, A6, A5, A2 material with different catalysts.

Obtained results for the first catalyst MtH90AlCu indicate that its presence in all of tests caused an apparent rise in degradation temperature. For the catalysts K30H90Al and MtH60Al the degradation temperature was improved only in the process where A6, A2 and A5, A2 were pyrolysed respectively. The very small influence of the catalyst introduction, causing negligible temperature changes, makes their use unfounded, in what the efficiency of plastics degradation is concerned. However, the observed mass changes indicate the may be differences in the products, which might be of advantage, in case a certain range of hydrocarbons is sought or obtained.

4. Conclusions

Acid strength distribution investigation proved, that the three modification methods used: acid activation, cation intercalation and cation impregnation, influences the acidity of montmorillonites, resulting in similar distributions of acid strengths but different number of acid sites. The optimal time of hydrochloric acid treatment of pure montmorillonite is 60 minutes. However, the modification with Al hydroxycations that was performed after the acid activation indicates a 90 minutes of acid treatment as the most efficient to obtain the highest amount of active sites.

The catalytic pyrolysis of polyethylene for the group of montmorillonites with different time of exposure to hydrochloric acid was investigated using DSC/TGA analysis. From first group catalysts, K30H90 (montmorillonite activated for 90 minutes), has shown the best results in reduction of degradation temperature. Unfortunately, the discussed group did not contribute to decrease the degradation temperature sufficiently. It is highly probable that the acid modification, which may have destroyed part of the structure, led to reduction of the porosity.

The second group studied using DSC/TGA analysis presented montmorillonites activated with acid at different times and treated with aluminum hydroxycations. All catalysts show considerable improvement in temperature decrease in comparison to the first group, and the best results were obtained for K30H90Al. Still, the overly delaminated structures of montmorillonites, observed during X-ray analysis, could not be pillared with alumina hydroxycations, so the cations could only create aggregates on the surface. This might explain low efficiency of the second group.

In the last tested group consisting of

- unmodified montmorillonite,

- industrially acid activated montmorillonite treated with aluminum hydroxycations,

- montmorillonite acid activated for 60 minutes and pillared with alumina hydroxide cations,

- montmorillonite acid activated for 90 minutes, pillared with alumina hydroxide cations and promoted with copper cations,

the lowest degradation temperature was obtain for the last listed: MtH90AlCu. Moreover, this catalyst showed the best results from all catalysts investigated in this work. The high efficiency of the MtH90AlCu may be explained by the fact that , as a result of the used preparation procedure, both delamination and pillaring took place, and additionally Lewis sites arising from copper cations were introduced.

Several catalyst were effective in reducing the degradation temperature of pure HDPE and the deactivation studies have also shown that, when using pure HDPE, several catalysts are capable of maintaining the activity after use. However, when the same catalysts were used to degrade actual plastic waste, the results were, unfortunately, not very encouraging and only a limited activity was observed for some of the catalysts and some of the waste materials tested.

Further work is required to understand what components of the plastic wastes are deleterious to the catalyst activity and how to improve the process so that the effectiveness of the catalysts in pyrolysing PE can be used in actual plastic waste.

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