Catalytic Thermal Decomposition of Polyethylene Determined by Thermogravimetric Treatment

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Summary: In this study low density polyethylene (LDPE) has been studied by thermogravimetric analysis (TGA) using commercially available oxides as catalysts. TGA experiments were used to evaluate the activity of different catalysts on low density polyethylene (LDPE) degradation and to study the effect in terms of type and amount of catalyst used. All the catalysts used improved the pyrolysis of LDPE. The reaction rates were found to increase with increase in amount of catalyst. Among the catalysts used, alumina acidic active catalyst performed better at all four fractions. Moreover, alumina acidic active reduced weight loss temperature better than others tested catalysts. The effect of alumina neutral catalyst on the pyrolysis of LDPE is less pronounced due to its small surface area and pore size. The effect of these catalysts showed that surface area, number of acidic sites and pore size were found as the key factors for the energy efficient degradation of polymers.

Introduction

Polymer is a complex, homogeneous material having a high molecular weight. They are usually made of small structural units bonded by covalent bonds. Plastics based on polyethylene are present in large amount in domestic and industrial waste and can cause serious pollution problems. The huge consumption of plastics created pollution which has negative impact on environment [1]. Almost 15 million tons plastic waste is produced in Europe per year. While in USA, 20 million tons of wastes are produced. In these countries the plastic waste is mainly discarded by landfill or ignition [2]. Feed stock recycling of LDPE cracking over different acidic catalysts is in practice throughout the world and is popular and unique method [1, 3]. The discarded products of the polymers such as LDPE are valuable source of energy and large number of hydrocarbons. Suitable catalysts during pyrolysis are those which can easily crack the polymer chain into monomers at low temperature [4].

Over the last 20 years most of the work reported in the literature using catalyst has been tested for the degradation of plastic waste products such as acid mesoporous material, non-acidic mesoporous solids FCC catalyst, zeolites and metallic oxides [5]. Use of catalysts is the best way for the pyrolysis of plastic polymers because the catalytic pyrolysis method has two major advantages. Firstly, it controls the isolation of compounds during the pyrolysis. Secondly, this method lowers the operating temperature for degradation of the plastic polymers [6].

Thermogravimetric Analysis (TGA) measures the mass change of a material as a function of temperature and time, in a controlled atmosphere. It is ideally used to assess volatile content, thermal stability, degradation characteristics, aging/lifetime breakdown, sintering behavior and reaction kinetics. TGA is widely used method to study solids breakdown and also its performance kinetics. The way of thermal decomposition is very complex step and involved chain fission, radical recombination, carbon hydrogen bond breaking, mild chain beta-scission and radical addition reactions [7-9].

There have been numerous pyrolysis studies of polyethylene, over wide range of experimental conditions using variety of pyrolysis procedures and these have been reviewed. Decomposition products of LDPE have been determined by many investigators in order to explain the mechanism of decomposition.

Marcilla. *et al*. [10] studied thermal degradation of polyethylene in the presence of different catalysts. Thermobalance, was used for the study of polyethylene pyrolysis. Polyethylene was mixed with various catalysts in different ratios. They studied the various effects of the catalyst, such as amount of the catalyst addition and the nature of the catalyst etc.

Nisar *et al*. [11] carried out an experimental study of the thermal decomposition of polyethylene in an inert atmosphere in the temperature range 300-800°C using Shimadzu PYR-2A pyrolyzer for

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heating the sample. The method allows the accurate control and measurement of the pyrolysis temperature. The production of hydrocarbons and the corresponding monomers of these polymeric systems were monitored. The effects of variation of temperature, sample size, pyrolysis atmosphere, residence time and catalyst on the distribution of these products were studied. As the carrier gas rapidly swept the primary products from the hot zone into the chromatographic column, so the secondary decomposition is largely eliminated and the pyrolysis products give accurate information about the nature, composition and structure of the pyrolysis material.

Ali *et al.* [12] studied the effect of different catalysts on the thermal degradation of polymers using TGA. The reaction rate was found to increase with increasing catalyst and decreasing particle size. The number of acid sites and catalysts pore size along with impregnation with transition metals were found as the key factors for energy efficient degradation of polymers.

The catalyst used so far for the degradation of polymers has less active site which is required for the degradation of the polyethylene polymer. In the present work it is intended to minimize the degradation temperature up to its minimum level by thermo gravimetric analysis, using suitable catalysts, such as alumina acidic active, alumina neutral, silica gel and silica precipitate and its comparison for reduction of degradation temperature of the LDPE.

Results and Discussion

Thermogravimetric Analysis of Pure Low Density Polyethylene (LDPE)

The thermogravimetric analysis of low density polyethylene (LDPE) was carried out using TGA (Model Diamond TG/DTA). A precisely weighed 6 ± 0.3 mg of pure LDPE in powder form was heated in inert atmosphere as per following temperature profile: Heating started at 5 ^{o}C with a rate of 5 ^{o}C/min and stabilized at 250 ^{o}C for one minute. Then with a rate of 5 ^{o}C/min the temperature was increased up to 650 ^{o}C.

The TGA curve for pure low density polyethylene is shown with filled diamonds in Fig. 1. From the Fig it is evident that the degradation of LDPE takes place in a single step. However, going into the details profile of the temperature versus %weight loss it can be concluded that this weight loss is initially as a result of water evaporation and subsequently due to lighter hydrocarbon in the

temperature range 209-281 ^{o}C. At high temperature 509-525 ^{o}C no residue is left. These observations are in agreement with the results reported in the literature [13].

Degradation of LDPE Mixed with Alumina Acidic

In order to study the pyrolysis of LDPE in the presence of catalyst, a homogeneous mixture of pure LDPE and alumina acidic active as catalyst was prepared in the ratio of 5, 10, 15 and 20% (w/w). A precisely weighed 6 ± 0.3 mg of each mixture sample was pyrolyzed in the temperature range of 200-650 ^{o}C and heating rate of 5 ^{o}C/min.

The TGA curves for the mixtures of LDPE and various % concentrations (w/w) ratio of alumina acidic active as catalyst and their comparison with pure low density polyethylene can also be observed in Fig. 1. As evident from Fig, LDPE degradation is greatly influenced by amount of alumina acidic active added to the polymer in different ratio.
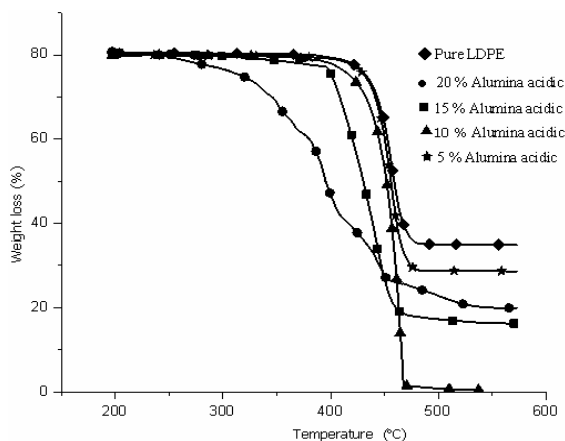

Fig. 1: TG degradation curves for pure LDPE and LDPE containing 5, 10, 15 and 20 % (w/w) ratio alumina acidic catalyst.

The Fig shows the maximum temperature weight loss rate of conversion of LDPE and mixed with alumina acidic at different % (w/w) ratio. The alumina acidic catalyst different % (w/w) performance over LDPE is also given in Table-1. From the Fig and Table it is clear that the weight loss reduction temperature is maximum at 20 % (w/w) as compared to 5, 10, 15 % (w/w) ratio of alumina acidic to LDPE.

Table-1: Temperature and maximum reduction rate in degradation of LDPE and its mixtures with alumina acidic catalyst at 5%, 10%, 15% and 20 % (w/w) ratio T_{max} and corresponding $\Delta T_{max.}$

Name	T_{max} (°C)	ΔT_{max} (°C)
Pure LDPE	525	-
5 % (w/w) Alumina acidic	499	26
10 % (w/w) Alumina acidic	495	30
15 % (w/w) Alumina acidic	470	55
20 % (w/w) Alumina acidic	460	65

As the alumina acidic catalyst contains high pore size and acidic sites which is the tool for breaking of the LDPE polymer chain. Therefore, when the amount of the catalyst is increased the rate of the weight loss is also increased as a result of increase in number of pores which are incorporated into the long chain of the polymer, resulting into the breakage of the LDPE into numerous low molecular weight compounds.

It was observed that the catalytic thermal decomposition of LDPE increased with increasing reaction time. The trend for pure and LDPE mixed with alumina acidic 20% (w/w) ratio as a function of reaction time is shown in Fig. 2.

Furthermore, it is evident from the Table that at 5 % (w/w) ratio of alumina acidic to LDPE weight loss maximum temperature is 499 °C as compared to the non catalytic thermal degradation which is 525 °C and as such the catalyst reduces the degradation temperature by 26 °C. At 10 % (w/w) ratio alumina acidic weight loss temperature decreases to 495 °C from 525 °C, and thus reduces the degradation temperature by 30 °C. Similarly at 15 % (w/w) alumina acidic mixed with LDPE the maximum degradation temperature is 470 °C which is less by 55 °C. And last at 20 % (w/w) of the alumina acidic catalyst, the maximum weight loss occurred at the expenditure of maximum temperature of 460 °C and this reduces the maximum degradation temperature by 65 °C.

This shows that the production of volatiles products such as light hydrocarbons, liquid, and some solids hydrocarbons is more at 20 % (w/w) of alumina acidic catalyst. These observations are indicative of the fact that alumina acidic active catalyst enhances the degradation rate of LDPE to a greater extent and converted LDPE into light hydrocarbons as well as liquid and other heavy hydrocarbons. Increasing the temperature above 460 °C, ash formation takes place and the catalyst becomes deactivated and hence forth no more conversion of LDPE is possible [14]. This higher reactivity of alumina acidic active catalyst is due to the presence of strong acidic active centers on this catalyst [15-17].

Similarly, alumina acidic active catalyst also contains higher pores size of 58Å which is more helpful in rapidly degrading the long chain molecules of LDPE and henceforth reduces the maximum degradation temprature to a larger extent.
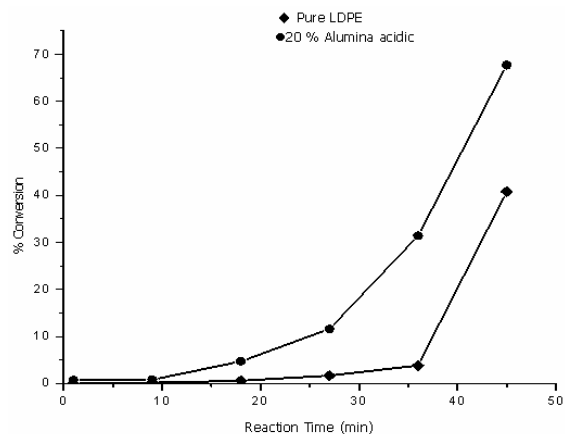

Fig. 2: Conversion of pure LDPE and mixed with alumina acidic 20% (w/w) ratio as a function of reaction time.

From the above discussion it can be concluded that alumina acidic active catalyst is more active and suitable catalyst for the pyrolysis and craking of long chain polymers. These observations are in agreement with the results reported in the literature [18].

Degradation of LDPE Mixed with Silica Precipitate

A homogeneous mixture of pure LDPE and silica precipitate as catalyst was prepared in the ratio of 5, 10, 15 and 20% (w/w) ratio. A precisely weighed 6 ± 0.3 mg of each mixture sample was pyrolyzed in the temperature range of 200-650 °C and heating rate of 5 °C/min.

The TGA curve for mixture of LDPE and silica precipitate at various concentrations as a catalyst is given in Fig. 3 and Table-2. As shown in Fig, increase in the concentration load of the silica precipitate catalyst on LDPE, the weight loss % is increased at low temperature. This shows that increasing the amount of silica precipitate more surfaces are available for the degradation of the LDPE polymer chain. When the amount of the catalyst is increased then a decrease in maximum degradation temperature is observed. As shown in

Table-2, at 5 % (w/w) ratio of silica precipitate to polymer, the maximum degradation temperature is 499 ^{o}C, thus reducing the degradation temperature by 26 ^{o}C. When the ratio of catalyst to LDPE is 10 % (w/w) the highest decomposition temperature goes down to 495 ^{o}C thus reducing the maximum weight loss temperature by 30 ^{o}C. Furthermore, at 15% (w/w) silica precipitate to LDPE, the maximum decomposition temperature is 490 ^{o}C, thus, reducing the maximum weight loss temperature by 35 ^{o}C. At 20 % (w/w) ratio the degradation is maximum at 488 ^{o}C and this reduces the maximum degradation temperature by 37 ^{o}C.

Table-2: Temperature and maximum reduction rate in degradation temperature of pure LDPE and its mixtures with silica ppt catalyst at 5%, 10%, 15% and 20% (w/w) ratio T_{max} and corresponding $\Delta T_{max.}$

Name	T_{max} (^{o}C)	ΔT_{max} (^{o}C)
Pure LDPE	525	-
5 % (w/w) Silica ppt	499	26
10 % (w/w) Silica ppt	495	30
15 % (w/w) Silica ppt	490	35
20 % (w/w) Silica ppt	488	37

The reduction in maximum degradation temperature is due to high pore size and high surface area imparted to the mixture by silica ppt. Although, silica ppt has no Lewis acidic sites which are mainly responsible for the degradation of the polymers, however, the breaking of long chain of LDPE is due to mesoporous structure of silica ppt catalyst which provides high pore size, large surface area and active Bronsted acidic sites i.e Si-OH which leads to conversion of the LDPE into other valuable hydrocarbons. The maximum conversion temperature at 20 % (w/w) ratio is 488°C and further increase in pyrolysis temperature of the LDPE in the presence of silica ppt as catalyst is not proceeding because of the deactivation of the catalyst [19, 20].
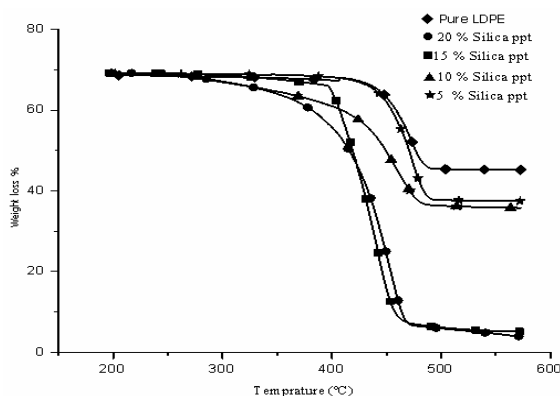
Fig. 3:   TG degradation curves for pure LDPE and LDPE containing 5, 10, 15 and 20 % (w/w) ratio silica ppt catalyst.

Hence it can be concluded that increase in the % (w/w) ratio of silica precipitate catalyst to LDPE, the rate of the degradation is increased and almost all the LDPE molecule is converted into other hydrocarbons at minimum degradation temperature as compared to the non-catalytic thermal decomposition of pure LDPE. These observations are in coincidence reported in literature [15].

It has also been observed that the catalytic thermal decomposition of LDPE increased with increasing reaction time (Fig. 4).
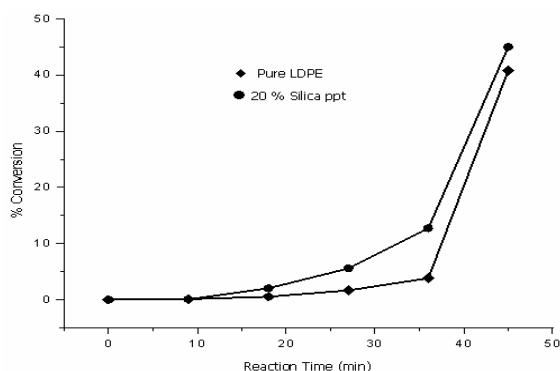
Fig. 4:   Conversion of LDPE mixed with silica ppt % (w/w) ratio as a function of reaction time.

Degradation of LDPE Mixed with Alumina Neutral

To investigate the pyrolysis of LDPE in the presence of alumina neutral catalyst, a homogeneous mixture of pure LDPE and alumina neutral as catalyst was prepared in the ratio of 5, 10, 15 and 20 % (w/w). A precisely weighed 6 ± 0.3 mg of each sample mixture was pyrolyzed in the temperature range of 200-650 ^{o}C and heating rate of 5°C/min. The results are given in Fig. 5 and Table-3. The results show that LDPE degradation is not significantly influenced by % (w/w) ratio. As alumina neutral has smaller surface area and small pore size hence it is of little help in degrading the LDPE to a larger extent. Though the degradation is more as compared to pure LDPE, however it is not appreciable. In the presence of 5% (w/w) ratio of alumina neutral catalyst the LDPE is degraded at 512 ^{o}C which reduces weight loss maximum temperature to about 13 ^{o}C as compared to the thermal degradation of pure LDPE which is 525°C. The results show that at 5 % (w/w), though the conversion is high but reduction in maximum degradation temperature is less as shown in Table-3. This is due to the fact that alumina neutral having low surface area and neutral in nature, having no acidic sites, is providing little space for the reaction to occur and the decomposition reaction is almost similar to the non-catalytic reaction of LDPE.

Table-3: Temperature and maximum reduction rate in degradation temperature of LDPE and mixed alumina neutral catalyst at 5%, 10%, 15% and 20 % (w/w) T_{max} and corresponding ΔT_{max}.

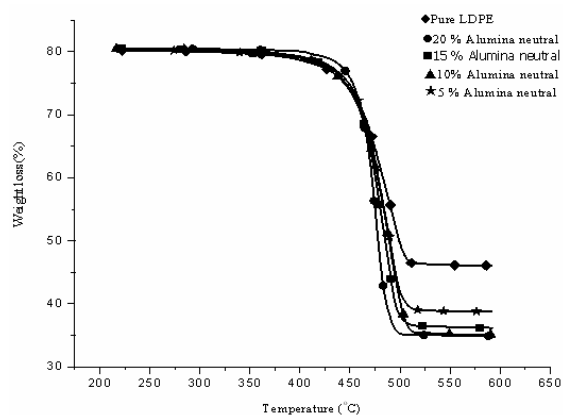| Name	T_{max} (°C)	ΔT_{max} (°C)
Pure LDPE	**525**	**-**
5 % (w/w) Alumina neutral	**512**	**13**
10 % (w/w) Alumina neutral	**498**	**27**
15 % (w/w) Alumina neutral	**496**	**29**
20 % (w/w) Alumina neutral	**490**	**35**

Fig. 5: TG degradation curves for pure LDPE and LDPE containing 5, 10, 15 and 20 % (w/w) ratio alumina neutral catalyst.

At 10 % (w/w) ratio of alumina neutral catalyst to LDPE the maximum degradation temperature observed is 498 °C, thus reducing the degradation temperature by 27 °C. Similarly at 15 % (w/w) of alumina neutral to LDPE the weight loss maximum temperature is reduced by 29 °C. At 20 % (w/w) of alumina neutral to LDPE the maximum decomposition temperature is 490 °C and this reduces the degradation temperature by 35 °C as compared to non-catalytic thermal degradation of LDPE. This shows that in the presence of 20 % (w/w) of the alumina neutral to LDPE the conversion is more as compared to other fractions because at this ratio more surface area is available for the decomposition reaction to progress. Another factor which also helps in decreasing the maximum degradation temperature of LDPE from 525°C to 490°C is the hexagonal structure of alumina neutral catalyst which provides maximum sites for the reaction to occur [21, 22].

From the above discussion we may conclude that when the amount of alumina neutral is less in the reaction mixture i.e 5% (w/w) of alumina to LDPE, the maximum degradation temperature is high because of lesser availability of surface area for the reaction to occur. Though the weight loss is greater

as compared to pure LDPE, however, it is negligible as compared to 20% (w/w) of alumina to LDPE. Another important factor which was noticed is the production of large amount of gaseous hydrocarbons at 5% (w/w) of alumina to LDPE, where the amount of liquid hydrocarbons was observed to be more at 20% (w/w) of alumina to LDPE. This is due to the fact that at 5% (w/w) of alumina to LDPE the maximum degradation temperature is high which leads to depolymerization of LDPE into monomers with the production of light gaseous hydrocarbons where as at 20% (w/w) of alumina to LDPE, the maximum degradation temperature is less, and the formation of free radicals is large as a result of sufficiently large amount of surface area provided by the catalyst. This provides sufficient time for the free radicals formation. These free radicals then stabilize together to form heavy liquid hydrocarbons. That is why the amount of gaseous hydrocarbons is reduced at 20% (w/w) of alumina to LDPE as compared to 5 % (w/w) of alumina to LDPE [23].

It was also observed that maximum degradation temperature of the LDPE in the presence of neutral alumina is relatively high as compared to other catalysts used in this study. The main reason for this is coke formation when the small particulates of alumina neutral abundantly fill up the crevices on the surface of the LDPE, and this leads to deactivation of the catalyst [22]. This trend is also evident in Fig. 6. The Fig shows that the % conversion is not appreciable when the reaction time is increased.
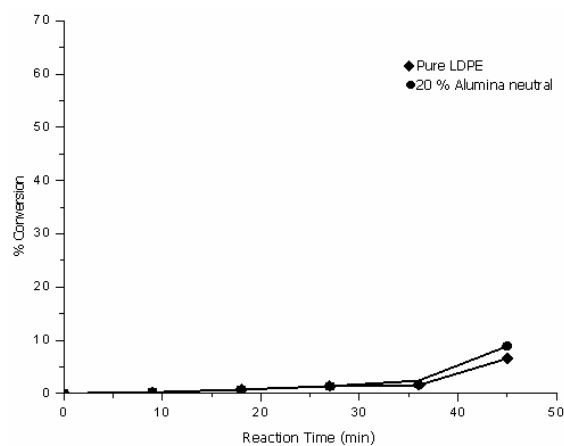

Fig. 6: Conversion of LDPE mixed with alumina neutral % (w/w) ratio as a function of reaction time.

Degradation of LDPE mixed with Silica gel

To study the pyrolysis of LDPE in the presence of catalyst, a uniform mixture of pure LDPE and silica gel as catalyst was prepared in the ratio of 5, 10, 15 and 20 % (w/w). A precisely weighed 6 ± 0.3 mg of each mixture was pyrolyzed in the temperature range of 200-650 °C and heating rate of 5 °C/min.

The observations obtained from the TGA curves for different mixtures of LDPE and silica gel at 5, 10, 15 and 20 % (w/w) ratio is given in Fig. 7 and Table-4. As clear from the Fig, the results are deeply affected by silica gel catalyst at different % (w/w). The Table shows that in the presence of 5 % (w/w) ratio of silica gel catalyst to LDPE, the maximum degradation temperature observed is 493ºC. This shows that the maximum degradation temperature is reduced by 32 ºC as compared to pure polymer. At 10 % (w/w) of silica gel to LDPE the weight loss maximum degradation temperature is 489 ºC and this reduces the maximum weight loss temperature by 36 ºC. Further increasing ratio to 15 % (w/w) of silica gel to LDPE more reduction in maximum weight loss degradation temperature is observed i.e. 39 ºC. At 20 % (w/w) of silica gel to LDPE the maximum weight loss occurred at 470 ºC and this reduces the maximum weight loss degradation temperature by 55 ºC as compared to the non-catalytic thermal decomposition of LDPE.

Table-4: Temperature and maximum reduction rate in degradation temperature of LDPE and mixed Silica gel catalyst at 5%, 10%, 15% and 20 % (w/w) T_{max} and corresponding ΔT_{max} .

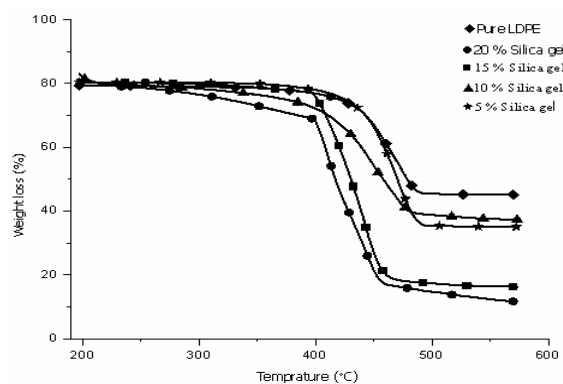| Name	T_{max} (ºC)	ΔT_{max} (ºC)
Pure LDPE	**525**	**-**
5 % (w/w) Silica gel	**493**	**32**
10 % (w/w) Silica gel	**489**	**36**
15 % (w/w) Silica gel	**486**	**39**
20 % (w/w) Silica gel	**470**	**55**

Fig. 7: TG degradation curves for pure LDPE and LDPE containing 5, 10, 15 and 20 % (w/w) ratio silica gel catalyst.

From the above observations it can be concluded that the weight loss maximum degradation temperature is decreased with increasing the % (w/w) of silica gel catalyst to LDPE from 5-20 %. As at 5 % (w/w) ratio of silica gel to LDPE the reduction in maximum weight loss degradation temperature is low because less amount of the catalyst is available and this provides little surface for the reaction to occur while at 20 % (w/w) maximum reduction in weight loss temperature is observed because maximum numbers of pores and surface area are available for the reaction to proceed. As the pore size and surface area of silica gel is more as compared to silica precipitate and alumina neutral catalysts used in this study, therefore it is more helpful in breaking down the long chain of LDPE into other organic compounds including light hydrocarbons, liquid fraction etc at lower temperature. It has been observed that the catalytic thermal decomposition of the LDPE increased with increasing reaction time as shown in Fig. 8.
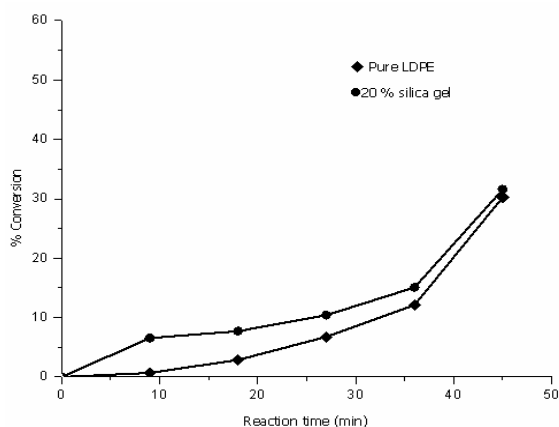

Fig. 8: Conversion of LDPE mixed with silica gel % (w/w) ratio as a function of reaction time.

It was also noted that at 20 % (w/w) of silica gel to LDPE the maximum weight loss temperatures is 470 ºC, however, raising the temperature further leads to formation of residue and this reduces the reactivity of silica gel to a great extent, resulting into reduction of gaseous hydrocarbons. If the residue is heated at 560 ºC, almost 90 % of it is converted into liquid and higher hydrocarbons. This is due to the fact that the high pore size, surface area and hexagonal structure of silica gel play an efficient role in incorporating the catalyst into the small crevices available on the surface of polymer chain and this results in cementing the surface of the polymer from the outside, leaving no space for the reaction to occur, hence no catalytic decomposition is possible at

this stage and the gaseous hydrocarbons stop to evolve. As far as production of liquid fraction and higher hydrocarbons after deactivation of catalyst above 470ºC is concerned, this occurs as a result of thermal degradation of the residual mass and catalyst has no role to play in the reaction to occur at this stage. As a consequence of this a very small amount of char is left. These results are in agreement with those reported in literature [21-23].

Experimental

The low density polyethylene (LDPE) sample used in present study was in powder form and was commercially available. The polymer was purchased from Sigma-Aldrich Chemical Company. The Physiochemical properties of the LDPE polymer are described in Table-5.

Table-5: Physiochemical properties of LDPE.

Properties	Units	Values
Density	g cm^{-3}	0.915
Molecular weight	Daltons	28, 000 to 280, 000
Melting temperature	ºC	115
Particle size	mm	less than 1.5
Pores size	μm	100

All four different types of catalysts used in present study were in powder form and commercially available. These catalysts were purchased from Merck Chemical and Sigma Aldrich Chemical Companies. The physiochemical properties of all the four catalysts are given in Tables 6 - 9.

Table-6: Physiochemical properties of alumina active catalyst.

Properties	Units	Values
Surface area	m^2/g	About 155
O_2 in H_2O	-	4.5 ± 0.5
Average pore size	Å	70-270
Particle size	mm	0.063-0.200

Table-7: Physiochemical properties of alumina neutral catalyst.

Properties	Units	Values
Surface area	m^2/g	About 155
O_2 in H_2O	-	7.0 ± 0.5
Average pore size	Å	58
Particle size	mesh	70

Table-8: Physiochemical properties of catalyst silica gel.

Properties	Units	Values
Surface area	m^2/g	550
O_2 in H_2O	-	7.0 ± 0.5
Average pore size	cm^3/g or Å	approx. 0.8 or 60
Particle size	mesh or μm	70-230, or 63-200

Table-9: Physiochemical properties of catalyst silica ppt.

Properties	Units	Values
Surface area	m^2/g	200 ± 25
Pore size	μm	0.014
Density	g/ml	1.46

Themogravimetric Analysis

Thermogravimetric analysis (TGA) is an analytical instrumental technique that is used to measure mass as a function of change in temperature and the resulting weight loss curve can be used to show the point at which maximum weight loss is occurred. In the present work, the TGA measurements were carried out to study the effect of different types of selective catalysts for polymer pyrolysis and to study complete information regarding LDPE degradation [12].

The thermogravimetric analysis was carried out by a TGA instrument of Model Diamond TG/DTA Perkin Elmer, USA. The experiments were conducted under flowing atmosphere of nitrogen at a purge rate of 20 ml/min. All the samples were studied in fine powder form. A quantity of 6 ± 0.3 mg was placed in an open ceramic pan. The sample was first equilibrated to 200 ºC before being heated to 650 ºC at heating rate of 5 ºC /min.

In this work, our main emphasis was to find out the optimum temperature and conditions for the degradation of polyethylene over temperatures range 200- 650 ºC and to evaluate temperature at maximum rate conversion (T_{max}). Moreover, the effect of various catalysts on degradation of products obtained from each sample under specific experimental condition was also assessed. The results obtained will extend the existing data on the thermal degradation of polymers.

Sample Preparation for TGA

All experiments were performed with 5, 10, 15 and 20 % (w/w) ratio of polymers and the catalysts. The samples were prepared by mechanically mixing dried proportion of polymers and catalysts in a 5, 10, 15 and 20 % (w/w) for the catalytic pyrolysis study by TGA [2, 3]

Conclusion

The results of four commercially available catalysts were investigated by TGA analysis for the reduction in maximum degradation of LDPE. The best results were obtained with the more acidic catalyst (alumina acidic active at 20% (w/w) in reduction in maximum degradation temperature. The

maximum degradation temperature reduces when the % (w/w) ratio of catalyst to LDPE increases from 5 to 20 %. Among the catalysts used, alumina neutral catalyst shows less reactivity towards the polymer in reducing the maximum degradation temperature. This is due to small pore size, surface area and no acidic sites either Lewis or Bronsted associated with this particular catalyst.

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