

Pyrolysis of Polystyrene: The Influence of Commercially Available Oxides as Catalysts

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Summary: In this study four catalysts (γ -Alumina, α - Alumina, silica gel and silica ppt) with different physicochemical characteristics were tested for the pyrolysis of polystyrene (PS) under inert atmosphere in the temperature range 200-650 °C at heating rate 5 °C/min. The silica gel a mesoporous catalyst, with a greater pore size and surface area was found to be the most active materials in terms of reduction in maximum temperature. The γ -Alumina catalyst also shows good result because of the acidic sites, surface area, and pores size, however, its degradation effect is less than silica gel. The effect of α - Alumina catalyst on the pyrolysis of PS is less pronounced due to its small surface area, pore size and lack of acidic sites on its surface. The effects of these catalysts show that surface area, number of acidic sites and pore size were observed as the key factors for effective degradation of polymers.

Keywords: Polystyrene; Catalytic thermal degradation; Reduction in maximum degradation temperature; Thermogravimetry.

Introduction

Polystyrene is one of the most extensively used plastics. Products based on polystyrene are produced all over the world and is a source of serious environmental contamination. Thermal decomposition of waste plastic has an efficient role in transforming it into cost-effectively valuable hydrocarbons, which can be used as fuel for domestic and industrial use [1]. In thermal decomposition, the polymer is heated at sufficiently high temperature and as a result the macromolecular structure is broken into smaller fragments resulting into the formation of numerous valuable hydrocarbons [2]. Liu *et al.*, [3] obtained styrene monomer and gasoline fraction from the pyrolysis of polystyrene waste in a fluidized-bed reactor. Styrene monomer with a maximum yield was obtained at 600 °C. Using vacuum distillation the purity of styrene monomers increased to 99.6 wt%. Some monoaromatics with boiling point less than 200 °C were also obtained. Lai and Locke [4] used stepwise pyrolysis-liquid and gas chromatography for quantitative and qualitative determination of products from degradation of polystyrene. Othani *et al.*, [5] studied the pyrolysis of polystyrene using pyrolysis-gas chromatography in combination with pyrolysis-field ionization mass spectrometry. In another similar study Othani *et al.*, [6] using stepwise pyrolysis combined with on-line methylation, investigated end group analysis of polystyrene macromonomers. Lehrle *et al.*,

[7] used pyrolysis-gas-liquid-chromatography for kinetic study of thermal degradation of polystyrene. Dolezal *et al.*, [8] studied the effects of controlled aging and blending on thermal degradation of polystyrene with other polymers using pyrolysis gas chromatography. Fabbri *et al.*, [9] used pyrolysis gas chromatography mass spectrometry for determination of polystyrene in polluted sediments. The dried sediment was pyrolyzed in a pyrolyzer and the styrene evolved was determined. It was observed that the presence of clay minerals strongly affected the pyrolytic behavior of polystyrene; however, calcite and quartz influence was not appreciable. Most recently, Miandad *et al.*, [10] studied the influence of reaction time and temperature on the quality and yield of liquid oil produced from the decomposition of polystyrene. The optimum temperature and reaction time was observed to be 450 °C and 75 min. The fuel properties of the obtained oil showed similarity to commercial diesel. The GC-MS analysis of oil at optimum conditions detected styrene, toluene and ethyl-benzene in abundance.

In order to get valuable products from plastic waste several pyrolysis technologies were adopted. The most important among them are fluidized beds, spouted beds, microwave reactors and fixed beds reactors. However, every reactor has some advantages and disadvantages associated with it. For example, fluidized bed reactor is very efficient as far as control of

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operating conditions, gas solid contact, solid mixing, efficient contact with catalyst in situ, narrow product distribution and good catalyst circulation are concerned, however, it has some disadvantages *i.e.*, defluidization problems, attrition of bed material, limitations on bed material particle size and high investment [11-13]. On other hand, the spouted bed reactor has high heat transfer rates and also avoids defluidization problems; however, it has the problem of catalyst circulation [14-16, 17]. Similarly, a fixed bed reactor is very simple in construction and design. Moreover, it is low cost with no limitation on particle size, however, it has the disadvantages of difficulty in control of operating conditions, poor gas-solid contact and low heat transfer rate [18, 19]. In order to avoid problems associated with the established designs some non-conventional reactors such as molten baths [20, 21], microwave ovens [22-24] and plasma reactors [25-27] have also been proposed.

Wong *et al.*, [28] reviewed the current status and future scenario of plastic waste as source of energy and tried to tackle the dilemma of plastic waste disposal as a partial alternate of the diminishing fossil fuel with anticipation of advancing a sustainable environment. In another attempt Sharuddin *et al.*, [29] reviewed the pyrolysis of plastic wastes and the key process parameters that affected the end product. Moreover, several perspectives to optimize the oil production for individual plastic stuff were also discussed in detail. Lopez *et al.*, [30] reviewed the thermo-chemical routes for conversion of polyolefin plastic waste to valuable products. They focused on relating the features of various conversion technologies and processing conditions with the enhancement in the yield of products *i.e.*, light olefins, fuel and aromatics.

In most studies, pyrolysis gas chromatography equipment was used for the measurements. In this study our focus is on the pyrolysis of polystyrene using the technique of thermogravimetry. The procedure involves the thermal decomposition of polymer over the temperature range 200-650 °C and heating rate 5 °C/min using thermogravimetric analyzer. Effects of temperature, catalysts and time of pyrolysis on reduction in maximum degradation temperature were explored. This study will extend the existing database on thermal decomposition of polystyrene.

Experimental

Materials and Methods

The polystyrene sample used in present study was in powder form and purchased from Sigma Aldrich. All four different types of mixed oxides as catalysts used in present study were in powder form and commercially available. These catalysts were purchased from Sigma Aldrich and BDH Chemical Companies.

The physicochemical properties of all the four commercially available mixed oxides catalysts are presented in our previous communication [31].

Thermogravimetric Analysis

In the present work, thermogravimetric measurements were carried out to study the effects of different types of selective catalysts for polymer pyrolysis and to study complete information regarding PS degradation.

The non-isothermal analysis was carried out on Diamond TG/DTA Perkin Elmer, USA. The experiments were performed in nitrogen atmosphere at flow rate of 20 mL/min. A quantity of 6 ± 0.3 mg of sample in powder form was taken and equilibrated to 200 °C before being heated to 650 °C at heating rate of 5 °C /min. A complete description of the experimental procedure has been described in detail in our previous communication [32].

In this work, our main emphasis was to optimize the conditions and temperature for the degradation of polystyrene over temperatures range 200-650 °C and to find out T_{max} (temperature at maximum rate conversion). Moreover, the influence of different catalysts on degradation of polystyrene under specific experimental conditions was also assessed.

In order to study the pyrolysis of PS in the presence of γ -Alumina, silica ppt, α - Alumina, and silica gel as catalysts, homogeneous mixtures of pure PS and γ -Alumina, silica ppt, α - Alumina, and silica gel were 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 ranging from 200 to 650 °C at 5 °C/min.

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 [33, 34].

Results and Discussions

Thermogravimetric analysis of pure Polystyrene (PS)

Thermogravimetric analysis of polystyrene (PS) was carried out using Diamond TG/DTA. A precisely weighed 6 ± 0.3 mg of pure PS in powder form was heated in inert atmosphere as per following temperature profile; Heating started at 5 °C with a rate of 5 °C/min and stabilized at 250 °C for one minute. Then with a rate of 5 °C/min the temperature was increased up to 650 °C.

The TG/DTG curves for pure polystyrene are shown in Fig. 1. As evident from figure, the degradation curve of PS shows single step weight loss, with a steady degradation behavior at the available temperature progression. This type of single degradation of the PS was due to the polycyclic macromolecular structure. As shown in Fig the maximum temperature weight loss is about at 406 °C and at this temperature almost all the PS polymer can be converted into styrene monomers and other hydrocarbons.

Jiao and Sun [35] studied thermal degradation of polystyrene under air and nitrogen. They observed that 330- 470 °C is the main stage with a significantly weight loss ratio of 87%. In another study Kannan *et al.*, [36] carried out the degradation of polystyrene in nitrogen environment at 5°C/min and observed a peak volatilization decomposition temperature of 400 °C. Moreover, the values determined in this study are also in conformity with Liu *et al.*, empirical relationship [37].

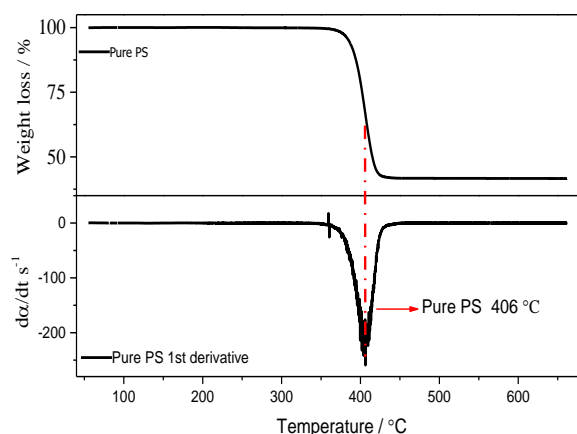


Fig. 1: TG degradation curve and 1st derivative curve for pure polystyrene.

Degradation of PS mixed with γ -Alumina

The TG/DTG curves for the mixtures of PS and various % concentrations (w/w) ratio of γ -Alumina as catalyst is illustrated in Fig. 2. The reduction in maximum degradation temperature of PS with γ -Alumina catalyst at 5%, 10%, 15% and 20 % (w/w) ratio (T_{max} and corresponding ΔT_{max}) is given in Table 1. As evident from figure, PS degradation is greatly influenced by acidic sites, pores size and surface area and amount of γ -Alumina catalyst added to the polymer in different ratio.

From the Fig and table it is evident that the weight loss reduction temperature is maximum at 20 % (w/w) as compared to 5, 10, 15 % (w/w) ratio of γ -

Alumina to PS. In the presence of 5 % (w/w) ratio of γ -Alumina, the reduction in maximum degradation temperature is 9 °C as compared to the pure PS. This minute difference in maximum degradation temperature is due to smaller number of active sites and less surface area available for the degradation of PS at 5% (w/w) ratio of γ -Alumina catalyst mixed with original compound, while at 10 % (w/w) ratio γ -Alumina mixed with the PS, the maximum reduction in degradation temperature is 55 °C as compared to thermally decomposed pure PS. This change is much pronounced as compared to at 5% (w/w). At 15 % (w/w) ratio of γ -Alumina the reduction in maximum degradation temperature is 59°C as compared to thermal degradation of pure PS. At 20 % (w/w) ratio of γ -Alumina catalyst, the effect is more prominent as the reduction in maximum degradation temperature is 98 °C as compared to pure PS. This is due to the fact that γ -Alumina at this high ratio contains acidic sites and the mesoporous structure provides maximum surface area for the reaction to occur. γ -Alumina catalyst has mesopores, so the styrene monomers of PS can easily enter inside the mesopores during the degradation process. As a result of this unique structure a high yield of styrene monomers are produced. That is why the reaction at 20% (w/w) ratio is more as compared to other fraction of the same catalyst [38].

Another factor for high yield of styrene monomers is the presence of competitive cross-linking reactions supported by γ -Alumina catalyst at the surface of the polymer. In this connection the most possible reaction path way would be the attack of a proton linked to Bronsted acid site of the aromatic ring. The resultants carbocations may go through a β -scission followed by inter/intermolecular hydrogen transfer. This signifies that acid catalysts favour cross linking reactions over cracking reactions at low temperature. As a result the PS is degraded into styrene monomers. While raising the temperature further the γ -Alumina catalyst deactivates due to the formation of black coke and residue in PS and henceforth, the γ -Alumina catalyst is unable to degrade the PS molecule into styrene monomers and other heavy hydrocarbons [39, 40].

From all the above investigations it is concluded that γ -Alumina catalyst reduced the maximum degradation temperature to a maximum extent, and similar trend was also observed in case of other polymers [31, 41]. Moreover, this is also attributed to the PS chain structure and degradation mechanism promoted by acid catalyst [36].

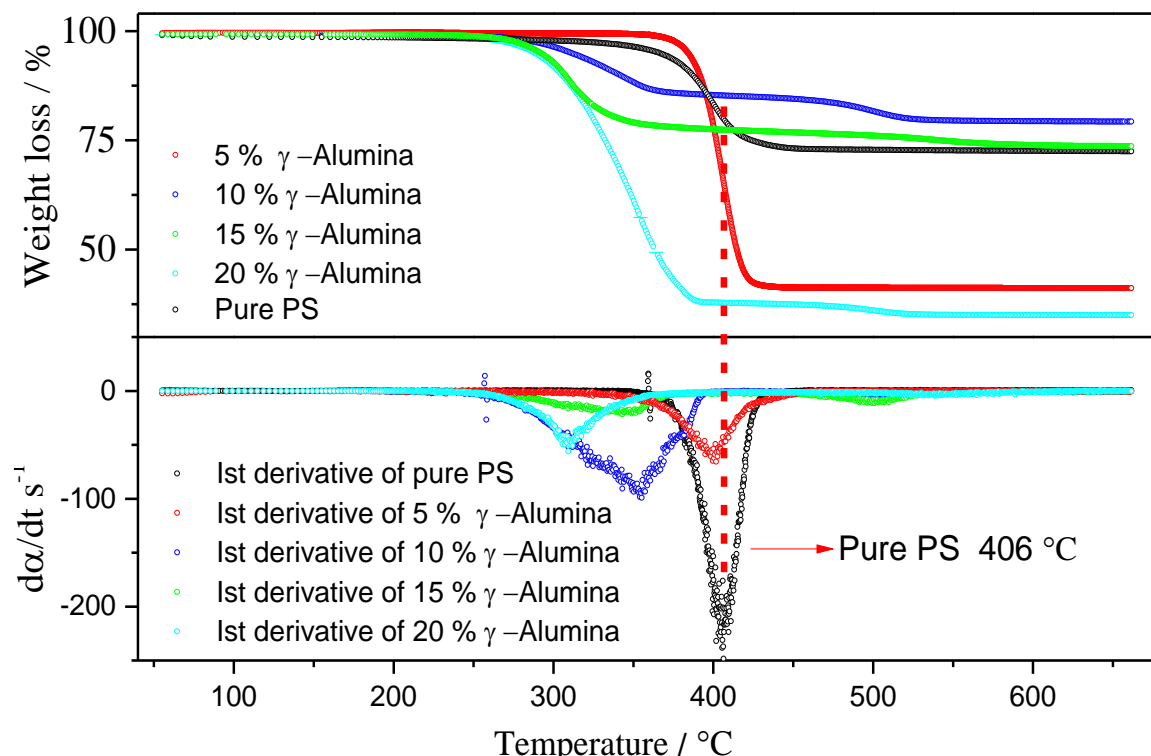


Fig. 2: TG degradation curves and 1st derivative curves for pure PS and PS containing 5, 10, 15 and 20 % (w/w) ratio of γ -Alumina catalyst.

Table-1: Reduction in maximum degradation temperature of PS with γ -Alumina catalyst at 5%, 10%, 15% and 20 % (w/w) ratio (T_{max} and corresponding ΔT_{max}).

Name	T_{max} (°C)	ΔT_{max} (°C)
Pure PS	406	----
5 % (w/w) γ -Alumina	397	9
10 % (w/w) γ -Alumina	351	55
15 % (w/w) γ -Alumina	347	59
20 % (w/w) γ -Alumina	308	98

Degradation of PS mixed with silica ppt

Catalytic thermal degradation of PS mixed with 5, 10, 15 and 20 % (w/w) ratio of silica ppt is shown in Fig. 3. The silica ppt catalyst different % (w/w) ratio performance over PS is given in Table 2. From the Fig and table it is clear that the reduction in maximum degradation temperature is high at 20 % (w/w) as compared to 5, 10, 15 % (w/w) ratio of silica ppt to PS.

The Fig shows that silica ppt shows good reactivity towards thermal decomposition of PS. The decomposition is much high as compared to the pure PS. The maximum degradation temperature is 406 °C

for pure polymer. While in the presence of 5 % (w/w) ratio of silica ppt catalyst the maximum degradation temperature reduces by 3 °C. At 10 % (w/w) ratio of silica ppt the reduction in T_{max} is 112 °C. At 15 % (w/w) silica ppt the reduction in T_{max} is 134 °C as compared to the pure polymer. At 20 % (w/w) ratio the reduction in T_{max} is 136 °C because at this fraction maximum pores and more surface area are available for the reaction to proceed.

Basically silica ppt has mesoporous structure with average pores size of 1.952 nm and surface area of 114.565 m²/g. This provides a favorable condition for the reaction to proceed on the surface at reduced temperature. Hence more is the amount of catalyst added to the polymer, more is the number of pores and surface area available for the reaction to occur. That is why the decomposition is more at 20% as compared to other fractions. Due to these characteristics, silica ppt catalyst shows good reactivity towards the degradation of PS molecule, because the styrene molecule can easily enter inside the mesopores. These results are in agreement with reported literature [39].

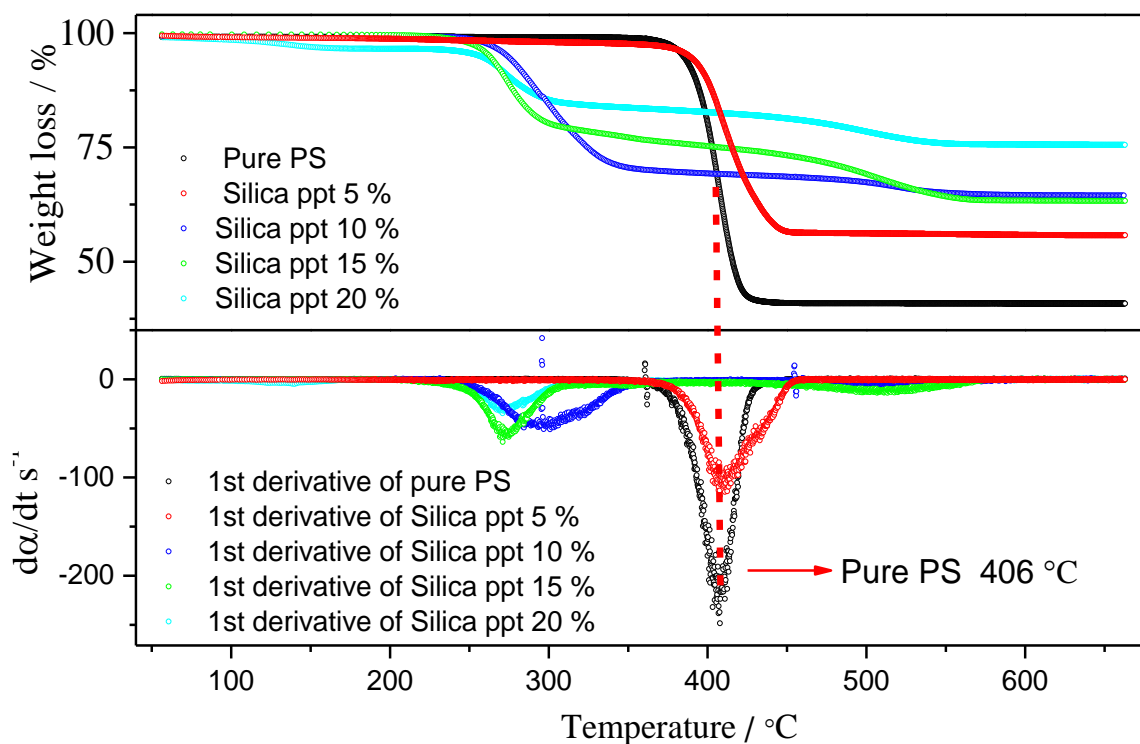


Fig. 3: TG degradation curves and 1st derivative curves for pure PS and PS containing 5, 10, 15 and 20 % (w/w) ratio silica ppt catalyst.

Table-2: Reduction in maximum degradation temperature of PS with silica ppt catalyst at 5%, 10%, 15% and 20% (w/w) ratio (T_{\max} and corresponding ΔT_{\max}).

Name	T_{\max} (°C)	ΔT_{\max} (°C)
Pure PS	406	-----
5 % (w/w) Silica ppt	403	3
10 % (w/w) Silica ppt	294	112
15 % (w/w) Silica ppt	272	134
20 % (w/w) Silica ppt	269	136

Degradation of PS mixed with α -Alumina

Fig. 4 illustrates the effect of α -Alumina catalyst mixed with PS at various fractions of α -Alumina. The reduction in maximum degradation temperature of PS with α -Alumina catalyst at 5%, 10%, 15% and 20% (w/w) ratio (T_{\max} and corresponding ΔT_{\max}) is shown in Table-3. From the Fig and table it is clear that the weight loss reduction temperature is maximum at 20 % (w/w) ratio as compared to 5, 10, 15 % (w/w) ratio of α -Alumina to PS.

It is evident from the Fig that the degradation of PS mixed with 5 % (w/w) ratio of α -

Alumina is less pronounced. The reduction in T_{\max} is only 2 °C. At 10 % (w/w) ratio, the reduction in T_{\max} is 10 °C. Further at 15 % (w/w) ratio the reduction in T_{\max} is 15 °C. Increasing it to 20 % (w/w) ratio the reduction in T_{\max} is 17 °C.

Comparing these results with γ -Alumina the reduction in T_{\max} is very small. This is due to the fact that α -Alumina though has the same surface area and average pore size with a mesoporous structure; however, it lacks acidic sites on its surface which is a key factor for the energy efficient degradation of polymers. Therefore, lack of acidic sites on its surface is a big hurdle in the way of decomposition to progress further. Whatever, the degradation is favoured by mesoporous nature is hindered by neutral behavior of the catalyst.

From the above observations it is evident that reduction in maximum degradation temperature is not good as observed in case of other catalysts. Moreover, at high temperature the reactivity of α -Alumina is reduced due to the formation of the residue and other solid fractions mainly char [38, 39].

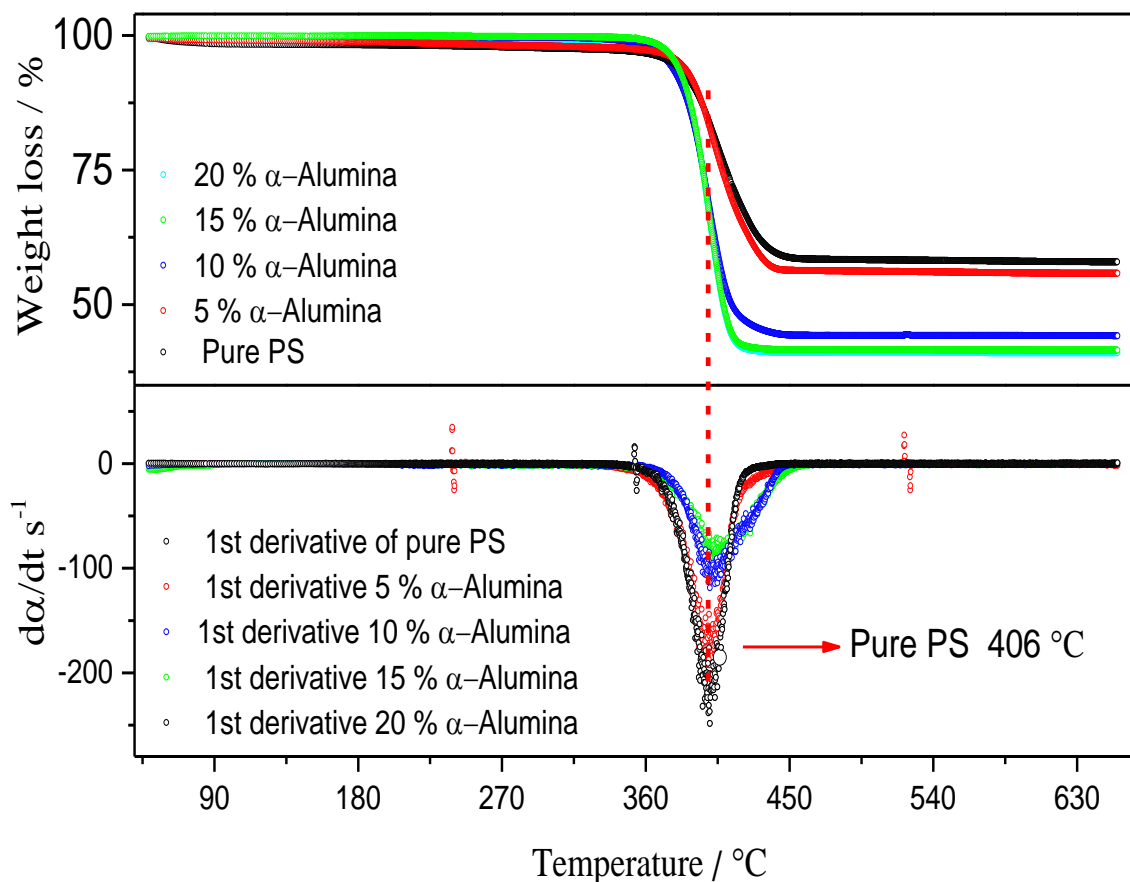


Fig. 4: TG degradation and 1st derivative curves for pure PS and PS containing 5, 10, 15 and 20 % (w/w) ratio of α - Alumina catalyst.

Table-3: Reduction in maximum degradation temperature of PS with α - Alumina catalyst at 5%, 10%, 15% and 20% (w/w) ratio (T_{\max} and corresponding ΔT_{\max}).

Name	T_{\max} (°C)	ΔT_{\max} (°C)
Pure PS	406	----
5 % (w/w) α - Alumina	404	2
10 % (w/w) α - Alumina	396	10
15 % (w/w) α - Alumina	391	15
20 % (w/w) α - Alumina	389	17

Degradation of PS mixed with silica gel

Fig. 5 shows the maximum reduction in degradation temperature of PS mixed with silica gel at different % (w/w) ratio. The silica gel catalyst different % (w/w) performance over PS is given in Table 4. From the Fig and table it is observed that the maximum reduction in degradation temperature at 20 % (w/w) is greater as compared to 5, 10, 15 % (w/w) ratio of silica gel to PS.

The Fig indicates that the reduction in maximum degradation temperature at 5 % (w/w) ratio

of silica gel mixed with PS is 2 °C as compared to the pure PS thermal degradation. At 10 % (w/w) ratio of the silica gel, the reduction in maximum degradation temperature is 97 °C. Further increasing the amount of silica gel *i.e.* at 15 % (w/w) more reduction in maximum degradation temperature is observed *i.e.* 135 °C. At 20 % (w/w) ratio of the catalyst and polymer the reduction in maximum degradation temperature is 137 °C. These results show that silica gel is highly reactive as compared to other catalysts. This tremendously high reactive nature of the silica gel is due to its greater pore size (\approx 6nm) and high surface area (550 m²/g).

Moreover, silica gel has a mesoporous structure with huge number of pores, the polymer when is mixed with the catalyst is settled in these pores and therefore provides enough surface area for the reaction to proceed swiftly and gently consuming less amount of heat. This leads to larger conversion of polystyrene to styrene monomers.

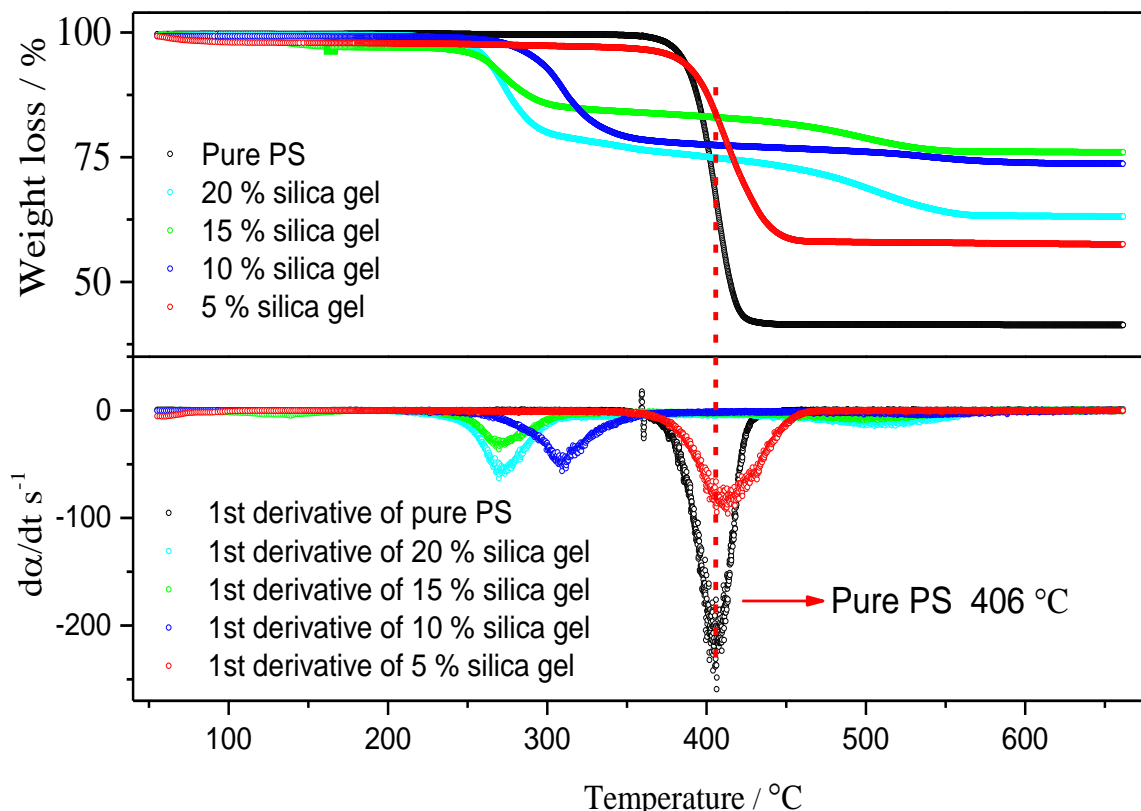


Fig. 5: TG degradation and 1st derivative curves for pure PS and PS containing 5, 10, 15 and 20 % (w/w) ratio silica gel catalyst.

Table-4: Reduction in maximum degradation temperature of PS with silica gel catalyst at 5%, 10%, 15% and 20% (w/w) ratio (T_{max} and corresponding ΔT_{max}).

Name	T_{max} (°C)	ΔT_{max} (°C)
Pure PS	406	----
5 % (w/w) Silica gel	404	2
10 % (w/w) Silica gel	309	97
15 % (w/w) Silica gel	271	135
20 % (w/w) Silica gel	269	137

Conclusions

The results of four commercially mixed oxides catalysts were investigated by thermogravimetric analysis for the reduction in maximum degradation temperature of PS. The best results were obtained with silica gel at 20% (w/w) in reducing the maximum degradation temperature. It was noticed that more reduction in maximum degradation temperature of PS is observed when the % (w/w) ratio of catalyst to PS is increased from 5 to 20 %. Among the catalyst used, α - Alumina catalyst shows less reactivity towards the polymer in reducing the maximum degradation temperature. It is concluded that mesoporous structure, pore size, surface area and acidic sites either Lewis or Bronsted

are the key factors for determining the reactivity of the catalyst towards the polystyrene.

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