Mechanism Studies on the Catalytic Degradation of Waste Polystyrene into Styrene in the Presence of Metal Powders

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ABSTRACT: In the present article, the effects of Al, Zn, Fe, Ni, and Cu powders on the thermal degradation of waste polystyrene were studied. The results show that the catalytic effects of metal powders have a relationship with their activities. The catalytic effects increase with the increasing activities of metals. It is suggested that polystyrene degrades through a transient intermediate in the presence of metal powders, and the degradation of the transient intermediate is the rate-determining step. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1139–1143, 1999

Key words: waste polystyrene; degradation; metal powders; mechanism; transient intermediate

INTRODUCTION

Recycling of waste plastics has been an interesting subject in the field of environmental science and technology for a long time. Although several methods have been proposed for recycling waste plastics, it is suggested[1] that material recovery will not be a long-term solution to the present problem and that the most attractive method is chemical recycling into the corresponding monomers or raw chemicals that could be reused for the production of plastics or other advanced materials.

It is reported[2] that about half of waste polystyrene (WPS) could be converted into styrene monomer by a simple thermal degradation at 723 K, so it was expected that a much higher recovery of styrene monomer from WPS could be obtained by catalytic degradation. Solid acids, such as silica-aluminas[3] and zeolites,[3,4] and solid bases, such as BaO and CaO,[5] have been preferably employed as catalysts for the degradation of WPS. The reaction mechanism of the degradation of polystyrene (PS) into styrene monomer on solid acids and bases was briefly discussed in one article,[5] in which it was said that the degradation may start with the formation of carbon ions.

In the present article, the catalytic, as the simple thermal, degradation of WPS in the presence of Al, Zn, Fe, Ni, and Cu powders was studied in detail. On the basis of these experiments, the relationship between the strength of the catalyst and the activity of metal was summarized. The mechanism was also discussed in this article; it is thought that PS degrades through the formation of the transient intermediate.

EXPERIMENTAL

1. Preparation of the Sample

To obtain an intimate mixture of WPS and metal powders, WPS + metal powder samples needed in thermogravimetric analysis were prepared by dissolving appropriate amounts of WPS in benzene at about 30°C. After the addition of metal powders, the mixtures were retroevaporated until solvents were removed. The remaining polymer-

coated metal powders were dried for 8 h at 100°C. The film obtained was cut into small pieces 2 mm in diameter.

2. Apparatus and Measurements

Thermogravimetric analysis was carried out on a WRT-1-type microbalance (Shanghai Balancing Instruments Factory). The analytical parameters were as follows: sample mass: about 5 mg; chart speed: 4 mm min^{-1}; atmosphere: dynamic dried nitrogen, 80×10^{-6} m^3 min^{-1}; heating rate: 10°C min^{-1}; sample holder: 5×5-mm ceramic crucible without cover.

The distillates of catalytic degradation were analyzed on GC-9A (Japan Shimadzu Co.).

3. The Condition and Procedure of Catalytic Degradation of PS

The condition of catalytic degradation of WPS was as follows: temperature: 420°C; time: 10 min; type of reactor: Pyrex vessel; heater: electric furnace; amount of catalyst: 1% (wt %) of the PS pieces employed.

4. Data Processing

All the thermogravimetric data was analyzed on a computer using self-compiling BASIC programs.

The kinetics can be represented by the general equation:

$$d\alpha/dt = kf(\alpha) \quad \text{or} \quad g(\alpha) = kt$$

where α is the fraction of weight loss at the reaction time t, k is the rate constant, and $f(\alpha)$ and $g(\alpha)$ are the functions describing the reaction mechanisms. According to the Arrhenius equation, where A is the frequency factor, E is the activation energy, and T (K) is the temperature,

$$k = A \times e^{-E/RT}$$

at a constant heating rate

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \times e^{-E/RT} f(\alpha)$$

According to Coats and Redfern method,[6] the integral form is

$$g(\alpha) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E} \right] e^{-E/RT}$$

Table I E, T_i, and T_f for the Degradation of WPS + Metal

WPS + Metal	E (KJ/mol)	T_i (°C)	T_f (°C)
WPS	250.36	290	440
WPS + Al	196.53	270	427
WPS + Zn	208.68	275	427
WPS + Fe	211.37	277	430
WPS + Ni	212.53	280	428
WPS + Cu	279.80	299	445

Taking logarithms of both sides,

$$\log \frac{g(\alpha)}{T^2} = \log \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - \frac{E}{2.303RT}$$

Usually $U/RT \gg 1$, so the plot of $\log[g(\alpha)/T^2]$ versus $(1/T)$ will give a straight line of slope $(E/2.303R)$, then the activation energy E can be obtained.

RESULTS AND DISCUSSION

1. The Effects of Metal Powders on the Apparent Activation Energy and Reaction Temperature

Thermogravimetric analysis was performed with samples with a weight ratio of WPS to metal powder of 10 : 1. In Table I are given the E, T_i, T_f obtained according to the thermogravimetric (TG) curves of catalytic degradation of PS in the presence of metal powders, together with those of the simple thermal degradation, where E is the apparent activation energy, T_i, T_f are the temperature corresponding to the initial weight loss and the final constant weight loss, respectively.

From Table I, note that the order of the apparent activation energies for the simple thermal degradation and catalytic degradation of WPS in the presence of metal powders is: WPS + Al < WPS + Zn < WPS + Fe < WPS + Ni < WPS < WPS + Cu. It is known that the activity of the four metals Al, Zn, Fe, and Ni decreases gradually; however, the apparent activation energies of the catalytic degradation in the presence of them increase gradually. Furthermore, T_i and T_f, which characterize the reaction on the TG curve, also increase with the decreasing activity of the metals. The presence of Cu powder, different from the other metals, increases the E of the degradation of PS by about 30 kJ/mol in comparison with
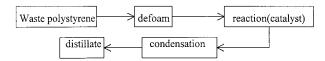
Figure 1 The procedure of catalytic degradation of waste polystyrene.

Scheme 1

the simple thermal degradation. The two characteristic temperatures T_i and T_f are also higher than those of simple thermal degradation; therefore, the presence of Cu powder hinders the degradation of PS. From the analysis above, it can be concluded that the catalytic effects of metals on the degradation of WPS have a relationship with their activities. The higher the activity of the metal, the stronger its catalytic effect is.

2. The Effects of Metal Powders on the Product of the Degradation of WPS

The yield of styrene monomer recovered is an important factor for the recycling of the waste polymer. There is a large amount of styrene monomer in the distillate of the degradation of WPS. The more styrene in the distillate of catalytic degradation, the higher the catalyst's selectivity into the styrene is. The catalytic degradation of WPS as well as the simple thermal degradation was performed according to Figure 1. All the figures are expressed in terms of weight percent of the WPS pieces employed.

A trace amount of gases was produced in all courses of reaction. The material balances after the degradation are also shown in Table II, which suggests 5–10 wt % loss during the degradation, probably because of the strong adhesion of carbonaceous compounds onto the reactor wall.

As can be seen in the third column of Table II, the order of the selectivity of the five metals into styrene monomer as well as that of simple thermal degradation is WPS + Al > WPS + Zn

> WPS + Fe > WPS + Ni > WPS + Cu > WPS. This order is in agreement with that of the activity of the metals. From Table I, it can be seen that the presence of Cu powder hinders the degradation of PS; however, in Table II, the yield of styrene monomer in the presence of Cu powder is higher than that of simple thermal degradation. From Table II, the addition of metal powders increases the yields of distillates and decreases the amounts of residues in comparison with simple thermal degradation.

3. The Mechanism of Catalytic Degradation

It was suggested[7–9] that the simple thermal degradation of PS starts with the formation of radicals. When PS is heated, polymer chains undergo scission initially at random, producing radicals (**A**) and (**B**), as shown in Scheme 1.

In a recent detailed study,[8] it was reported that the radical (**A**) is involved in depropagation (producing monomer), intermolecular transfer (leading to chain scission), and intramolecular transfer (producing dimer and other short-chain fragments), and radical (**B**) is likely to react mainly by intermolecular transfer or scission given to radical (**A**) and α-methylstyrene.

The catalytic degradation of PS on the catalysts of solid acids and bases[5] was that of the vaporized fragments of PS formed by a thermal degradation, but in the present work, the catalysts were added

Table II The Results of Catalytic Degradation of Polystyrene in the Presence of Metal Powders

WPS + Metal	Distillate	Styrene	Gas	Residue	Balance
—	76.5	58.5	—	15.7	92.2
Al	85	68.5	—	7.4	92.4
Zn	86	67.1	—	7.8	93.8
Fe	83	64.7	—	9.8	92.8
Ni	83	64.1	—	10.1	93.1
Cu	77.6	61	—	13.6	91.2

Scheme 2

directly into the melted PS. When metal powders were added into the reaction vessel, the degradation could be divided into two steps. First, the radicals form transient intermediates with the metals (Scheme 2, M means metal); second, the transient intermediates degrade (in Scheme 3 the process of producing styrene monomer is given), which is similar to the degradation of radicals. Supposedly the first step is very rapid, and the second step (i.e., the degradation of transient intermediates) is the rate-determining step. That is to say, the stability of the transient intermediates determines the whole process of the degradation.

From Table II, note that the addition of metal powders increases the yield of styrene monomer. Probably this is because that after the formation of the transient intermediate between metal and radical, the weak effect between metal and radical refrains (not prohibits) the radical from the intermolecular and intramolecular transfer. It was reported[10] that the transfers were the primary reason for the variety of products of degradation. Therefore, the presence of metal catalysts made the degradation move toward depropagation (producing monomer), and as a result, increased the yield of styrene monomer and decreased the yield of other products.

From Table III, it can be noted that the electronegativity of the metals Al, Zn, Fe, and Ni increase gradually; therefore, the forces between the metals and radicals in transient intermediates also increase gradually. That is to say, the stability of the transient intermediate increases as the electronegativity of the metal increases. The more stable the transient intermediate, the more energy needed when it degrades. So the

order of the apparent activity energy of the degradation of WPS in the presence of Al, Zn, Fe, and Ni is WPS + Al < WPS + Zn < WPA + Fe < WPS + Ni. This order agrees with the results of the present experiment.

As can been seen in Table III, the electronegativity of Cu is less than that of Ni. According to the above paragraph, the order of the apparent activation energies of the catalytic degradation of WPS should be WPS + Cu < WPS + Ni. However, this order is contrary to the experimental result. Perhaps this is because the outer-shell electron configuration of Cu is $3d^9 4s^2$. When Cu forms a transient intermediate with the radical, the electron configuration of Cu is similar to $3d^{10} 4s^2$, which is rather stable. The degradation of the transient intermediate of this configuration needs more energy than that of the others.

CONCLUSIONS

As a result of our experiments, we found that the catalytic effects of the metals Al, Zn, Fe, Ni, and Cu on the degradation of WPS have a relationship with their activities. Within a certain range, the higher the activity of the metal, the lower the apparent activation energy of the degradation is and the greater the amount of styrene monomer in the distillate. We also found that PS degrades in the presence of metal powders through transient intermediate. The degradation of the transient intermediate is the rate-determining step of the whole process.

Scheme 3

Table III   The Electronegativity and Outer-Shell Electron Configuration of Metals

Metal	Al	Zn	Fe	Ni	Cu
Electronegativity	1.61	1.65	1.83	1.91	1.90
Outer-shell electron configuration	$3s^2 3p^1$	$4s^2 4p^0$	$3d^6 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$

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