

Catalytic degradation of polystyrene into styrene and a design of recyclable polystyrene with dispersed catalysts

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Abstract

Degradation of polystyrene into styrene, including monomer and dimer, was studied using various kinds of solid acids and bases as catalysts. It was found that solid bases were more effective catalysts than solid acids for the degradation of polystyrene into styrene. This was attributed to differences in the degradation mechanisms of polystyrene over solid acids and bases. Among the solid bases employed, BaO was found to be the most effective catalyst, and about 90 wt.% of polystyrene was converted into styrene when thermally degraded polystyrene was admitted to BaO powder at 623 K.

Polystyrene films with dispersed BaO powder were then prepared as a model of a recyclable plastic using a twin-roller heated at 393 K; the amount of BaO dispersed was only 1 wt.% of the polystyrene films. More than 85 wt.% of the polystyrene films with dispersed BaO were converted into styrene by simple thermal degradation at 623 K without assistance of other catalytic compounds. The films were expanded into polystyrene foams with dispersed BaO using a gas absorption/evolution technique. Styrene could be recovered from these foams by heating them at 673 K. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic degradation; Polystyrene; Styrene; Dispersed catalysts

1. Introduction

Various kinds of techniques to convert plastic wastes into either solid or liquid fuels have been proposed. In the middle of the 1970s, thermal degradation of plastic wastes into fuel oils was studied extensively, but the oils obtained showed a wide distribution of carbon atom numbers and contained a significant fraction of olefins [1–3]. Since olefins are easily polymerized into unusable compounds during storage and transportation, the oils obtained by a thermal degradation were not fit for fuel oils [4]. In the middle of the 1980s until the early 1990s, catalytic degradation of plastic

wastes was studied using solid acids and bases as catalysts [5–7]. It was found that the oils obtained by catalytic degradation over those solid acids contained lower amounts of olefins and were rich in aromatics compared to the oils obtained by a thermal degradation. To date, more than 30 processes have been commercially operated using solid acid catalysts such as silica/alumina and ZSM5 zeolite [8]. Plastic wastes treated by catalytic degradation processes are mainly limited to waste polyolefins and polystyrene (PS). Waste polyvinyl chloride (PVC) has been excluded because of the emission of hazardous gases [9].

However, waste PS has been reported to be converted into styrene by simple thermal degradation at 873 K [10] but the degradation temperature needs to be lowered by using suitable catalysts. The conversion of

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waste PS into styrene is a kind of chemical recycling, and has been considered the most attractive method for the recycling of waste plastics [11]. We have therefore tried in the present work to find effective catalysts for the chemical recycling of waste PS into styrene at the lower temperatures. Among the various solid acid and base catalysts employed, BaO was found to be the most effective catalyst to recover styrene from waste PS [12]. Furthermore, we have tried to design recyclable PS films and foams in which a small amount of BaO powder is dispersed. The PS films and foams with dispersed BaO were found to be well converted into styrene when simply heated at 623–673 K without addition of other catalytic compounds [13]. Part of these results have already been published elsewhere, but all the results are combined and reviewed in this paper.

2. Experimental

2.1. Catalytic degradation of PS

The apparatus employed in the present work is shown in Fig. 1, where a thermal and catalytic degradation of PS was carried out for 3 h at 873 K

(for thermal degradation) and 623 K (for catalytic degradation). In every experimental run, 15 g of PS pieces was placed at the bottom of a reactor ($300 \times 200\phi$) made of stainless steel. PS pieces were obtained from Idemitsu (HH-30, $M_w = 24.9 \times 10^4$ and $M_w/M_n = 2.73$). The catalyst powders (1.5 g) packed with a stainless steel gauge were held on the catalyst bed, located just above the PS pieces. Accordingly, the thermally degraded products pass through the catalyst bed together with nitrogen supplied at the bottom of the reactor. The flow rate of nitrogen was kept constant at 50 ml/min throughout the present work.

Catalytically degraded products were collected in a cooled reservoir where the product gases (C_1 – C_4) were separated from the oils (C_5 – C_{20}) and measured by a gas meter. The analyses of the oils collected were made by gas chromatography (HP-5890), using a 10 m DB-2887 capillary column, and if necessary, by SCF (supercritical fluid chromatography) [14]. The weight differences of the catalysts before and after the degradation were ascribed to amounts of coke deposition on the catalyst surfaces. Carbonaceous compounds adhering to the reactor wall were dissolved in *n*-hexane and were measured as degradation residues.

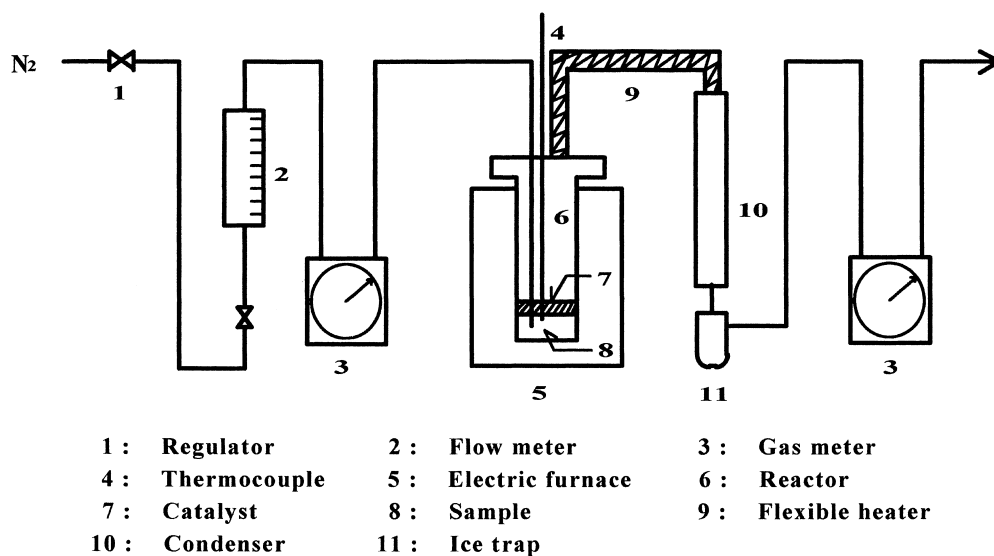


Fig. 1. Apparatus employed for the catalytic degradation of PS.

2.2. Preparation of catalysts

Various kinds of solid acids and bases were prepared as catalysts for the degradation of PS into styrene. Solid acids such as alumina, silica and silica/alumina (with a Si/Al ratio of 4) were prepared by sol/gel techniques using aluminum triisopropoxide, silicon tetraethoxide or a mixture of those as appropriate. The precipitates obtained were dried and calcined at 773 K for 4 h [15,16]. ZSM5 zeolite, with a Si/Al ratio of 4, was prepared from aerosil silica, sodium aluminate and tetra-*n*-propylammonium hydroxide according to a US patent [17] and was cation-exchanged to HZSM5 using ammonium hydroxide before use. Solid bases and some transition metal oxides, with the exception of titanium oxide, were also prepared from aqueous solution of the corresponding metal nitrates and ammonium hydroxide as a precipitant. The precipitates obtained were dried and calcined at 723 K for 4 h. Titanium oxide was prepared by hydrolysis of titanium tetraisopropoxide dissolved in isopropyl alcohol [18]. Active carbon was supplied from Sumitomo Kagaku and was used as a catalyst without further purification.

2.3. Preparation of PS films and foams with dispersed BaO powder

PS films with dispersed BaO (BaO/PS films below) were prepared using a heated twin-roller, made of chrome stainless steel. BaO powder (1 g) was mixed with 99 g of PS pieces and the mixture was poured into a narrow gap between the rollers. The films prepared were repeatedly poured into the gap in order to achieve a homogeneous dispersion of BaO powder inside the films. The BaO/PS films (1 mm thick) prepared were crushed into small pieces sized about $5 \times 5 \text{ mm}^2$, and conducted to a simple thermal degradation system at 623 K.

BaO/PS foams were prepared from BaO/PS films using a gas absorption/evolution technique. BaO/PS films were held in an autoclave at room temperature and filled with 30 atm of either CO₂ or N₂ for 24 h. The films were then picked out and placed in an oven heated at 393 K when the gases absorbed inside the films rapidly evolved into the atmosphere and this was associated with an expansion of the films to give

BaO/PS foams. The foams were crushed and submitted to simple thermal degradation at 673 K.

3. Results and discussion

3.1. Catalytic degradation of PS into styrene

Results obtained for the catalytic degradation of PS pieces at 623 K for 3 h over various kinds of solid acids and bases are given in Table 1, where the results obtained for a simple thermal degradation of PS at 873 K are also given. The fraction of oils, cokes, gases and the residues measured after degradation for 3 h are expressed in terms of wt.% of PS pieces employed. The contents of oils are expressed in terms of wt.% of the oils produced and the results indicated that considerable amounts of benzene and ethylbenzene were produced by catalytic degradation over the solid acids. This is partially because of the further cracking and hydrogenation of the styrene produced, which resulted in a decrease of the fraction of styrene in the oils produced. Production of benzene and indan derivatives was also one of the features of the oils produced by the solid acids but they were not detected in the oils obtained by solid bases. The formation of benzene and indan derivatives on solid acids starts with an attack of a proton on the branched phenyl group to produce a π -complex cation; this is then converted into a σ -complex cation which is released as benzene as follows:

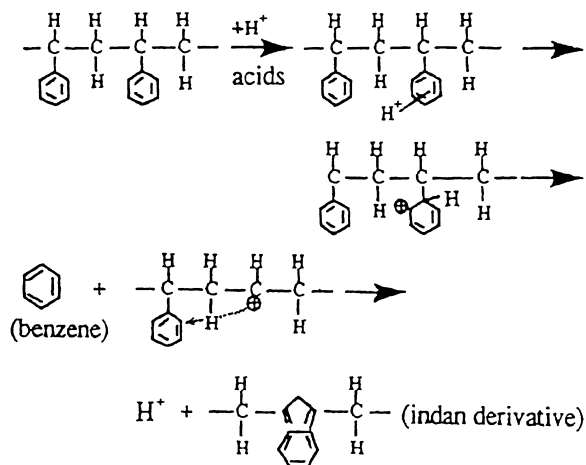


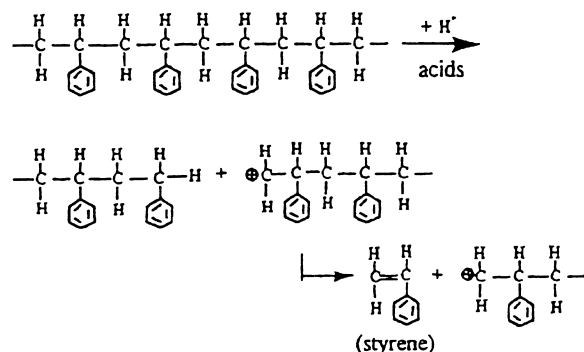
Table 1
Catalytic degradation of PS on solid acids and bases at 623 K for 3 h

	Catalyst							Thermal degradation ^a
	MgO	CaO	BaO	K ₂ O	SiO ₂ /Al ₂ O ₃	HZSM5	Active C	
BET surface area (m ² g ⁻¹)	47.4	1.2	0.8	–	533.9	426.0	–	–
<i>Contents of products (wt.%)</i>								
Oils	79.6	82.8	93.4	86.5	79.6	78.2	76.5	80.1
Cokes	8.2	4.2	0.3	3.1	6.0	5.9	10.1	–
Gases	–	–	–	–	Trace	Trace	–	–
Residues	3.8	6.5	3.2	4.1	4.2	8.5	3.8	16.1
Balance ^b	91.6	93.5	96.9	93.7	89.8	91.6	90.4	96.1
<i>Contents of oils (wt.%)</i>								
Styrene	79.1	75.5	76.4	77.8	59.9	64.4	70.0	70.0
Dimer	8.2	11.1	18.3	15.6	10.3	7.0	8.5	11.2
α-Methylstyrene	6.2	6.6	1.4	2.5	4.5	5.2	6.8	8.6
Toluene	3.9	3.9	1.6	2.2	2.3	3.1	4.4	5.1
Benzene	–	–	–	–	4.5	6.4	–	–
Ethylbenzene	0.7	0.9	0.2	0.3	9.0	2.0	4.3	2.4
Indan	–	–	–	–	2.2	1.8	–	–

^a Thermal degradation was carried out at 873 K for 3 h.

^b Balance means the material balance of C before and after the reaction.

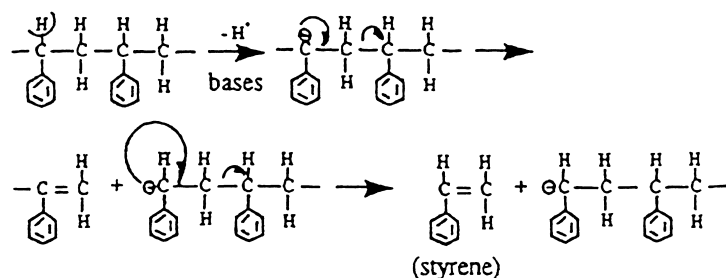
The main components in the oils obtained by solid acids were styrene monomer and dimer. Since cracking of hydrocarbons on solid acids has been explained in terms of β-scission of C–C bonds [19,20], these were probably produced by β-scission of C–C bonds in the PS main chains as follows:



In the present work, the catalytic degradation of PS involved the degradation of vaporized fragments of PS produced by thermal degradation. Accordingly, the lower yields of styrene obtained on solid acids

than those obtained by simple thermal degradation are partially due to further cracking of styrene into toluene and benzene and further hydrogenation into ethylbenzene. Coke formation caused by the strong interaction between acid sites and styrene or its precursors is also responsible for the lower yields of styrene on solid acids (see Table 1).

On the solid bases, the fraction of styrene monomer found in the product oils increased to about 75 wt.%, and the fraction of styrene including both monomer and dimer increased to about 90 wt.%, as given in Table 1. Partially because there was no formation of benzene and indan derivatives in the oils obtained using solid bases or by simple thermal degradation, and partially because of the considerable proportions of styrene dimer in those oils, it can be concluded that the degradation on solid bases probably proceeds by a route similar to that for the simple thermal degradation reaction, i.e., by depolymerization. Thermal degradation of PS starts with a random initiation to form polymer radicals [21,22], but the catalytic degradation on solid bases may start with the formation of carboanions by the elimination of a hydrogen atom of PS adsorbed on base sites as follows:



The difference in the fraction of residues formed by thermal degradation and by catalytic degradation on solid bases is due to the fast degradation of the vaporized fragments of PS on base sites. Studies on the relationship between base strengths and their catalytic activities for HCl elimination of 1,1,2-trichloroethane revealed the important role of base sites for hydrogen atom elimination from 1,1,2-trichloroethane [23]. Although the base strengths of solid bases employed in this work have not yet been measured, the higher yields of styrene from PS may be ascribed to the stronger base sites on the surface of the solid bases.

It has been reported that some transition metal oxides have many base sites on their surfaces [24] and that the compositions of the oils produced by transition metal oxides are therefore similar to those obtained by solid bases; they contain no benzene, no indan derivatives, and a small amount of ethyl benzene, as shown in Table 2. The titanium oxides are however sometimes acidic, depending upon the preparation conditions [25], and the oils produced by titanium oxide prepared in the present work contained small amounts of benzene and considerable amounts of ethylbenzene.

The apparent rates of PS degradation on the solid acids and bases at 623 K are given in Fig. 2. On the solid bases such as BaO and K₂O, the degradation was almost complete within 20 min, while on the solid acids, the degradation was not yet complete even after 90 min of the reaction. The slow rates on solid acids are due to the catalyst deactivation caused by coke deposition and by the formation of carbonaceous compounds over the catalyst surfaces. The degradation rate on solid bases seems to be enhanced by carboanions generated by the elimination of hydrogen atoms of PS adsorbed on the base sites. The rates depended upon the solid base employed, and this suggests that the rate determining step of PS degradation is in the elimination of hydrogen atoms to generate carbo-

anions; depolymerization proceeds with a constant rate regardless of the catalyst employed. Accordingly, the role of base sites is to generate carboanions at the initial stage in order to accelerate the depolymerization of PS, as illustrated above. Note that the depolymerization reaction proceeds automatically with the transformation of electrons through the carbon atoms of the polymer chain.

3.2. Design of recyclable PS films and foams

The yields of styrene monomer and dimer given in Table 1 are more clearly illustrated in Fig. 3, in which the catalysts employed are classified into three groups: solid bases, transition metal oxides, and solid acids.

Table 2
Catalytic degradation of PS on various metal oxides at 623 K for 3 h

	Catalyst					
	TiO ₂	Cr ₂ O ₃	Fe ₂ O ₃	Co ₃ O ₄	CuO	ZnO
BET surface area (m ² g ⁻¹)	150.9	—	6.7	5.9	1.6	0.7
<i>Contents of products (wt.%)</i>						
Oils	76.3	82.4	83.6	82.4	83.9	82.5
Cokes	9.8	5.4	4.2	3.1	2.6	2.4
Gases	—	—	—	—	—	—
Residues	5.7	4.7	4.8	6.7	4.8	6.5
Balance ^a	91.8	92.5	92.6	92.2	91.3	91.4
<i>Contents of oils (wt.%)</i>						
Styrene	70.0	75.5	74.3	75.9	73.5	76.1
Dimer	8.3	12.5	12.7	12.7	14.4	9.9
α-Methylstyrene	8.5	5.6	5.0	5.2	5.1	6.2
Toluene	4.1	3.3	3.6	3.3	3.1	4.0
Benzene	0.1	—	—	—	—	—
Ethylbenzene	5.5	0.8	0.7	0.6	0.7	0.7
Indan	—	—	—	—	—	—

^a Balance means the material balance of C before and after the reaction.

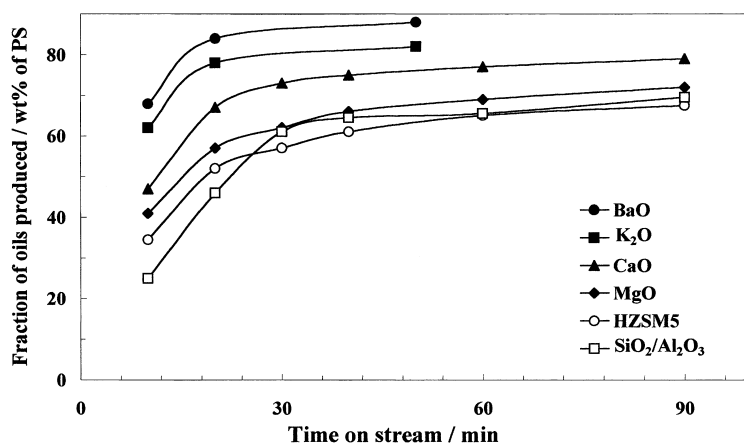


Fig. 2. Apparent rates of PS degradation on solid acids and bases at 623 K.

The solid bases were found to be more effective than the transition metal oxides and the solid acids for the recovery of styrene from PS. Among the solid bases employed, BaO was the most effective, and more than 90 wt.% of PS was converted into styrene, including monomer and dimer at 623 K.

Consequently, the catalytic degradation of the vaporized fragments of PS into styrene using BaO as degradation catalysts is promising. However, we need at least two reactors for this process, one for the thermal and catalytic degradation of the PS wastes and the other for regeneration of deactivated catalysts; this degradation is caused by deposition of coke and

carbonaceous compounds over the surfaces after a long period of use. If the PS products already include a small amount of catalyst, one reactor will be enough to operate the process because we do not need to worry about catalyst deactivation and regeneration. We have thus tried to make recyclable PS films by dispersing a small amount of BaO powder onto PS pieces when they are molded into thin PS films. The amount of BaO dispersed in the BaO/PS films was only 1 wt.% of the films.

Table 3 shows the results obtained for simple thermal degradation of BaO/PS films at 623 K. For comparison, the results obtained for simple thermal

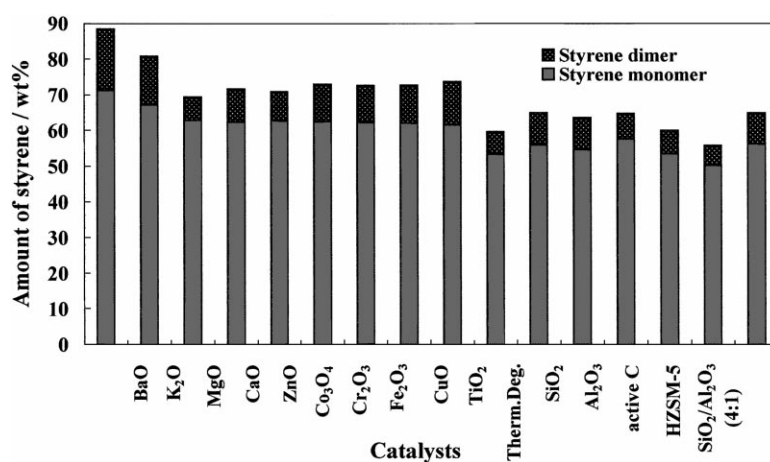


Fig. 3. Recovery of styrene monomer and dimer by catalytic degradation of PS at 623 K.

Table 3

Comparison of the BaO/PS films degradation with the thermal and catalytic degradation of PS at 623 K

	Thermal degradation	Catalytic degradation on BaO	Degradation of BaO/PS films
Oil formed (wt.%)	80.1	93.4	92.6
<i>Contents of oils (wt.%)</i>			
Styrene	70.0	76.4	77.4
Dimer	11.2	18.3	18.9
α -Methylstyrene	8.6	1.4	0.9
Toluene	5.1	1.6	1.4
Ethylbenzene	2.4	0.2	0.1
<i>Styrene yields (wt.%)</i>			
Monomer	56.1	71.4	71.6
Monomer + dimer	65.0	88.4	88.9

Table 4

Degradation of BaO/PS foams, prepared with CO₂ and N₂, at 673 K for 3 h

	BaO/PS foams		Catalytic degradation ^a	
	In CO ₂	In N ₂	BaO	BaCO ₃
Yield of oils (wt.%)	76.4	89.0	91.7	78.5
<i>Contents of oils (wt.%)</i>				
Styrene	93.1	94.7	93.2	80.8
Toluene	1.7	1.1	1.3	5.4
Ethylbenzene	0.3	Trace	0.1	1.2
α -Methylstyrene	2.8	0.5	1.0	7.8
1,3-Diphenylpropane	1.9	0.7	1.4	3.1
Recovery of styrene (wt.%)	68.0	84.3	85.5	63.4

^a Catalytic degradation was carried out at 623 K for 3 h.

degradation of pure PS pieces and for catalytic degradation on BaO are also given in Table 3. As can be seen, the results obtained for the thermal degradation of BaO/PS films are almost the same as those obtained for the catalytic degradation on BaO, although the surroundings of the BaO in the working state are significantly different in both cases. BaO in the latter case works in the gas phase, but the BaO in the former case works in the melted PS. This means that the BaO catalyst works in a similar way regardless of the circumstances, i.e., elimination of hydrogen atoms from PS or its vaporized fragments to generate carboanions. However, a small difference was observed in the apparent degradation rates of the BaO/PS films and of

the catalytic degradation on BaO, as shown in Fig. 4. The catalytic degradation on BaO proceeded faster than the thermal degradation of the BaO/PS films. This is probably due to the difference in the migration rates of the PS fragments in the gas phase and in the liquid phase. Accordingly, one possible design for recyclable plastic films is to disperse a small amount of catalyst powder on the plastic pieces when they are molded into thin films. However, any changes in the mechanical properties of the films have to be measured.

The BaO/PS films were expanded into BaO/PS foams by gas absorption/evolution techniques using either N₂ or CO₂ in an autoclave. Homogeneously expanded BaO/PS foams were prepared by rapid and

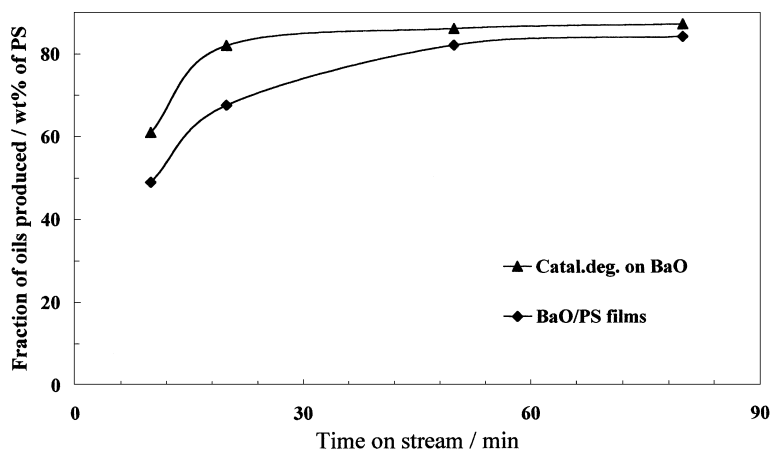


Fig. 4. Apparent rates of catalytic degradation on BaO and thermal degradation of BaO/PS films at 623 K.

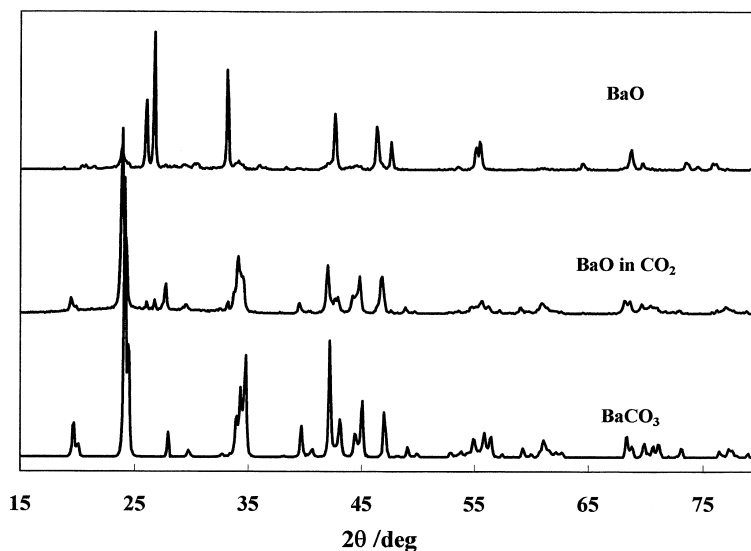


Fig. 5. XRD spectra of BaO, BaCO₃ and BaO reacted with CO₂ in an autoclave at 393 K for 24 h.

homogeneous evolution of N₂ or CO₂ absorbed in the films when they were heated at 393 K. In commercial processing, a small amount of CaCO₃ powder is dispersed in PS films in order to achieve homogeneous evolution of the absorbed gases. Thus in the present BaO/PS films, a small amount of dispersed BaO powder was found to work well as an additive for homogeneous expansion of the films.

Both BaO/PS foams expanded with N₂ and CO₂ were conducted to a simple thermal degradation vessel at 673 K and the results obtained are shown in Table 4. For comparison, results obtained by the catalytic degradation of PS on BaO and BaCO₃ at 623 K are also given in Table 4. Note that the BaO used here was prepared from BaCO₃ by calcination at 1273 K for 5 h, so that the results given in Table 4 for the catalytic degradation on BaO are slightly different from the results given in Table 1, for which the BaO was prepared from Ba(NO₃)₂. Nevertheless, the yields of styrene on BaO were found to be much higher than those on BaCO₃ because BaCO₃ shows acidic properties rather than basic properties. There was a significant difference between the yields of styrene for the thermal degradation of BaO/PS foams prepared with N₂ and those prepared with CO₂. This could be explained in terms of the formation of BaCO₃ when CO₂ was absorbed into the BaO/PS films at 393 K. Fig. 5

shows the XRD patterns of pure BaO and BaCO₃ powders and of a BaO powder reacted with CO₂ at 30 atm and 393 K in an autoclave for 24 h; the results show that the BaO reacted with CO₂ to form BaCO₃ at this temperature.

4. Conclusions

The conclusions obtained in the present work are as follows:

1. Solid bases are effective catalysts for the chemical recycling of PS wastes into styrene, and of the solid bases employed, BaO is the most effective catalyst.
2. Around 90 wt.% of PS was converted into styrene when a BaO catalyst was employed for the degradation of PS at 623 K.
3. The role of solid bases is to eliminate hydrogen atoms from vaporized PS fragments to generate carboanions, intermediates in the depolymerization of PS.
4. The rate determining step is the elimination of hydrogen atoms from the vaporized PS fragments adsorbed on base sites.
5. Solid acids are not good catalysts for chemical recycling of PS wastes to give styrene since they bring about further cracking and hydrogenation

of the product styrene into benzene and ethylbenzene.

6. Considerable amounts of benzene and indan derivatives are formed on solid acids.
7. Recyclable PS films and foams can be made by dispersing a small amount of BaO powder in the PS films and foams.
8. Around 85% of these PS films and foams may be converted into styrene by heating the BaO dispersed PS films and foams at 623 and 673 K, respectively.

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