

Design of Recyclable PS Films and Foams for Better Environment

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Degradation of polystyrene into styrene, including monomer and dimer, was studied using various kinds of solid acids and bases as catalysts. Among the solid catalysts used BaO was found to be the most effective, and about 90 wt % of polystyrene was converted into styrene when thermally degraded polystyrene was conducted on to BaO powder at 623 K. Then, polystyrene films with dispersed BaO powder were produced 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 were well converted into styrene by a simple thermal degradation at 623 K without assistance of other catalytic compounds. Films were expanded into polystyrene foams with dispersed BaO using a gas absorption/evolution technique.

Introduction

Waste PS was reported to be converted into styrene by a simple thermal degradation at 873 K [1], and the degradation temperature (873 K) have been desired to be lowered in the presence of suitable catalysts. The conversion of waste PS into styrene is a kind of chemical recycling, which has been considered the most attractive method for the recycling of waste plastics [2]. We have tried to find out the effective catalysts for chemical recycling of waste PS into styrene at the lower temperatures in the present work. Among the various solid acid and base catalysts employed, BaO was concluded the most effective catalyst to recover styrene from waste PS [3]. Furthermore, we have made a design of recyclable PS films and foams, where a small amount of BaO powder was dispersed inside. The PS films and foams with dispersed BaO were well converted into styrene when simply heated at 623~673 K without addition of any other catalytic compounds [4].

Experimental

Catalytic degradation of PS

The apparatus employed in the present work is given in Fig.1, where a thermal and catalytic degradation of PS was carried out at 873 (for thermal) and 623 K (for catalytic) for 3 h. In every experimental run, 15 g of polystyrene pieces was placed at the bottom of the reactor (300 x 200φ), made of stainless steel. Polystyrene pieces were obtained from Idemitsu Co.Ltd.(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, when catalytic degradation was carried out. Accordingly, the thermally degraded products pass through the catalyst bed together with nitrogen gases supplied at the bottom of the reactor. The flow rate of nitrogen gases was settled to be 50 ml/min throughout the present work.

Catalytically degraded products were collected by a reservoir through a cooling tube, where gases (C_1 to C_4) were separated from oils (C_5 to C_{20}) to be 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. The weight difference of catalysts before and after the degradation was ascribed to the amounts of coke deposited on catalyst surfaces. Carbonaceous compounds adhered to the reactor wall were eliminated by n-hexane and were measured as degradation residues.

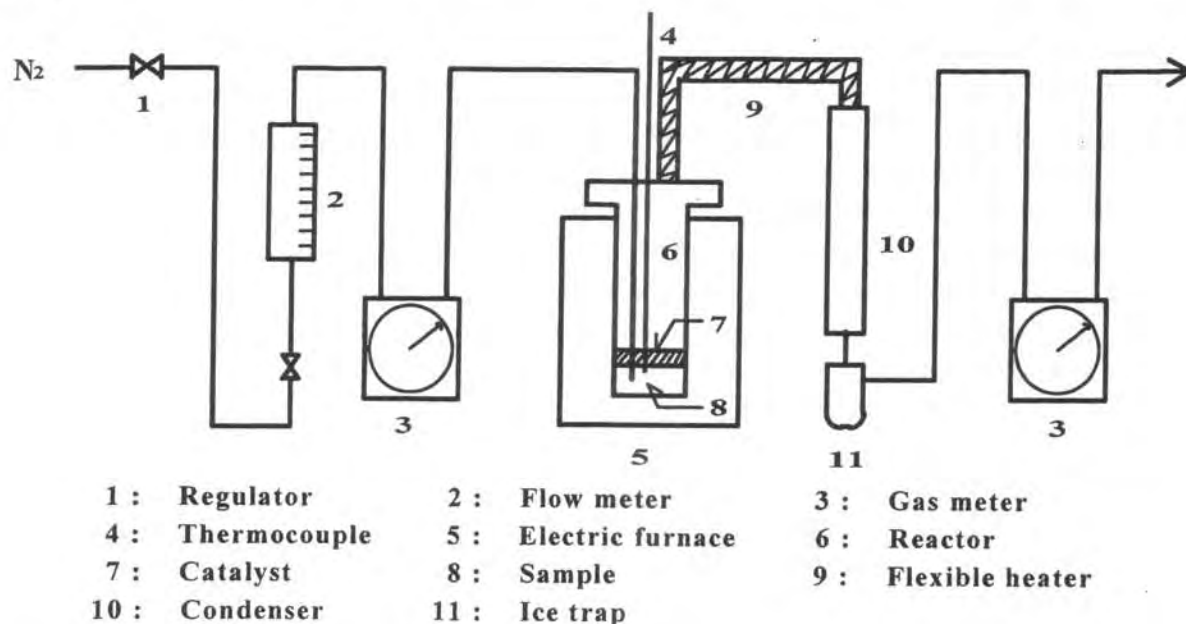


Fig. 1 Apparatus employed for thermal and catalytic degradation of polystyrene

Preparation of catalysts

Solid acids such as alumina, silica, and silica/alumina, with Si/Al ratio of 4, were prepared by sol/gel techniques using aluminium triisopropoxide, silicon tetraethoxide and their mixture, respectively. Precipitates obtained were dried and calcined at 773 K for 4 h [5]. ZSM5 zeolite with Si/Al ratio of 4 was prepared from aerosil silica, sodium aluminate and tetrapropylammonium hydroxide according to a patent [6], and was cation-exchanged to HZSM5 using ammonium hydroxide. Solid bases were prepared from aqueous solution of corresponding metal nitrates and ammonium hydroxide as a precipitant. Precipitates were dried and calcined at 723 K for 4 h. Active carbon was supplied from Sumitomo Kagaku Co. and was used without further purification.

Preparation of PS films and foams with dispersed BaO powder

PS films with dispersed BaO (BaO/PS films below) were prepared using a heating-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 iteratively poured into the gap in order to achieve the homogeneous dispersion of BaO powder inside the films. The BaO/PS films (1 mm thick) prepared were crushed into small pieces sized about 5x5 mm, and conducted to a simple thermal degradation 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, filled with 30 atm of either CO₂ or N₂, at room temperature for 24 h. Then, the films were picked out and placed in an oven heated at 393 K, and the gases absorbed inside the films were rapidly evolved into the atmosphere, which was associated with the expansion of the films to BaO/PS foams. The foams were crushed and submitted to a simple thermal degradation at 673 K.

Results and Discussion

Catalytic degradation of PS into styrene

Results obtained for the catalytic degradation of PS pieces at 623 K for 3 h on 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 the degradation for 3 h are expressed in terms of wt % of PS pieces used. The contents of oils are expressed in terms of wt % of the oils produced, and considerable amounts of benzene and ethylbenzene were produced by catalytic degradation on solid acids. This is partially because of further cracking and hydrogenation of styrene yielded, resulted in a decrease of the fraction of styrene in the oils produced. Production of benzene and indan derivatives is also one of the features of the oils produced by solid acids, since they were not detected in the oils obtained by solid bases.

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

catalyst	MgO	CaO	BaO	K ₂ O	SiO ₂ /Al ₂ O ₃	HZSM5	thermal degradation*	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	80.1	76.5
cokes	8.2	4.2	0.3	3.1	6.0	5.9	-	10.1
gases	-	-	-	-	tr	tr	-	-
residues	3.8	6.5	3.2	4.1	4.2	8.5	16.1	3.8
balance**	91.6	93.5	96.9	93.7	89.8	91.6	96.1	90.4
<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	11.2	8.5
α-methylstyrene	6.2	6.6	1.4	2.5	4.5	5.2	8.6	6.8
toluene	3.9	3.9	1.6	2.2	2.3	3.1	5.1	4.4
benzene	-	-	-	-	4.5	6.4	-	-
ethylbenzene	0.7	0.9	0.2	0.3	9.0	2.0	2.4	4.3
indan	-	-	-	-	2.2	1.8	-	-

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

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

Design of recyclable PS films and foams

It was found that the solid bases were found to be more effective than the transition metal oxides and the solid acids for the recovery of styrene from polystyrene. Among the solid bases employed BaO was the most effective, and more than 90 wt % of polystyrene was converted into styrene, including monomer and dimer, at 623 K. Consequently, the catalytic degradation of polystyrene into styrene is promising on BaO as a degradation catalyst. However, we need at least two reactors in this processing; one is for the thermal and catalytic degradation of polystyrene, and the other is for regeneration of deactivated catalysts, caused

by deposition of coke and carbonaceous compounds over the surfaces after a long time use. If the polystyrene products have already involved a small amount of catalyst, one reactor will be enough to operate the processing because we do not need to worry about the catalyst deactivation and regeneration. Then, we have tried to make a design of the recyclable PS films by dispersing a small amount of BaO powder on to 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 2 shows the results obtained for a simple thermal degradation of BaO/PS films at 623 K. For comparison, the results obtained for a simple thermal degradation of pure PS pieces and for catalytic degradation on BaO are also given. Accordingly, one possible design for recyclable plastic films is to disperse a small amount of catalyst powder on to the plastic pieces when they are molded into thin films, although changes in the mechanical properties of the films have to be measured.

Table 2 Degradation of polystyrene films with dispersed BaO powder 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
monmer + dimer	65.0	88.4	88.9

BaO/PS films were expanded into BaO/PS foams by a gas absorption/evolution method using either N₂ or CO₂ in an autoclave. BaO/PS foams were conducted to a simple thermal degradation at 673 K. There was a significant difference in the yields of styrene for the thermal degradation of BaO/PS foams expanded with N₂ (84.3 %) and with CO₂ (68.0 %). This was explained in terms of the formation of BaCO₃ when CO₂ was absorbed into BaO/PS films at 393 K. It was evidenced by XRD measurements that BaO easily reacted with CO₂ to form BaCO₃ at 393 K. Styrene was not well recovered on BaCO₃, since it is not a kind of solid base but rather solid acid.

References

- 1) Nishizaki, H.; Sakakibara, M.; Yoshida, K.; Endoh, K. *Nippon Kagaku Kaishi*, 1977, 1899.
- 2) Williams, V. Preprint of "Symposium of Waste Plastic Recycle", Tokyo, 1993, p.21.
- 3) Zhang, Z.; Hirose, T.; Nishio, S.; Morioka, Y.; Azuma, N.; Ueno, A.; Okada, M. *Ind. Eng. Chem. Res.*, 34, 4514 (1995).
- 4) Hirose, T.; Takai, Y.; Azuma, N.; Morioka, Y.; Ueno, A. *J. Mater. Res.*, 13, 77 (1998).