

## Preparation of polystyrene foams dispersing catalysts for recycling into styrene

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Chemical recycling of waste polystyrene into styrene using catalysts during thermal decomposition showed that solid base catalysts were effective for the chemical recycling of waste polystyrene, because of high yield of distillates from polystyrene and high selectivity into styrene monomer in the distillates. The degradation rates of polystyrene on solid bases were significantly higher than those on solid acids. In order to make a design for disassembly of waste polystyrene into styrene monomer, barium oxide powders, the most effective catalyst for the chemical recycling of waste polystyrene, were dispersed by several techniques into polystyrene to form resins. Thermal degradation of these resins into monomer was carried out as successfully as on the powders of barium oxide catalyst.

### 1. Introduction

It has been of current interests to develop techniques for recycling waste plastics into fuel oils and/or advanced chemicals<sup>1)</sup>. Nowadays, more than 70 % of the plastics produced in Japan have been composed of polyethylene, polypropylene, polystyrene and polyvinylchloride, so that, most of the investigation has concerned with these four kinds of polymers. Among these polymers, polystyrene has been expected to be recycled into styrene monomer.

In the present paper, the catalytic degradation of polystyrene into monomer will be discussed in terms of the solid acids and bases. In Addition, a design of recyclable polystyrene resins, where a small amount of catalyst is dispersed with several types of form, will be discussed<sup>2)</sup>.

### 2. Experimental

#### 2.1. Catalyst preparation.

Catalysts used for the polystyrene degradation were solid acids, solid bases, and some transition metal oxides. Solid acids were prepared by sol-gel techniques<sup>3)</sup>. ZSM-5 zeolite was prepared according to a US patent (1972), and was cation-exchanged to H-ZSM-5 before use. Solid bases and transition metal oxides, except titanium oxide, were prepared by calcination (723 K) of precipitates obtained from aqueous solutions of corresponding metal nitrates. Titanium oxide was prepared by hydrolysis of

titanium tetraisopropoxide dissolved in isopropyl alcohol. Active carbon (Sumitomo Kagaku Co.) used without further purification.

#### 2.2. Degradation of vaporized polystyrene.

The thermal and catalytic decomposition of polystyrene were carried out at 623 K for 3 h using a flow reactor (300 x 250) made of stainless steel, as shown in Fig.1. At the bottom of the reactor was placed 10 g of polystyrene pieces, and 1.0 g of catalyst powders packed with a stainless steel gauge were held on the catalyst bed, located just above the polystyrene pieces. Therefore, the vapor of thermally degraded products may pass through the catalyst bed together with nitrogen gases supplied at the bottom of the reactor.

Catalytically degraded products were introduced into a cooling glass tube, where gases (C<sub>1</sub> to C<sub>4</sub>) were separated from oils (C<sub>5</sub> to C<sub>20</sub>). The gases and oils were respectively analyzed by GC (gas chromatography equipped with packing or capillary column) or by SFC (supercritical fluid chromatography). Carbonaceous compounds adhered to the reactor wall were eliminated by *n*-hexane after the reaction and were measured as degradation residues (waxes). The weight difference of the catalyst before and after the degradation was ascribed to coke deposition on the catalyst surface.

#### 2.3. Designs of recyclable polystyrene.

In order to design a new type of polystyrene resin, which is suitable for chemical recycling, several

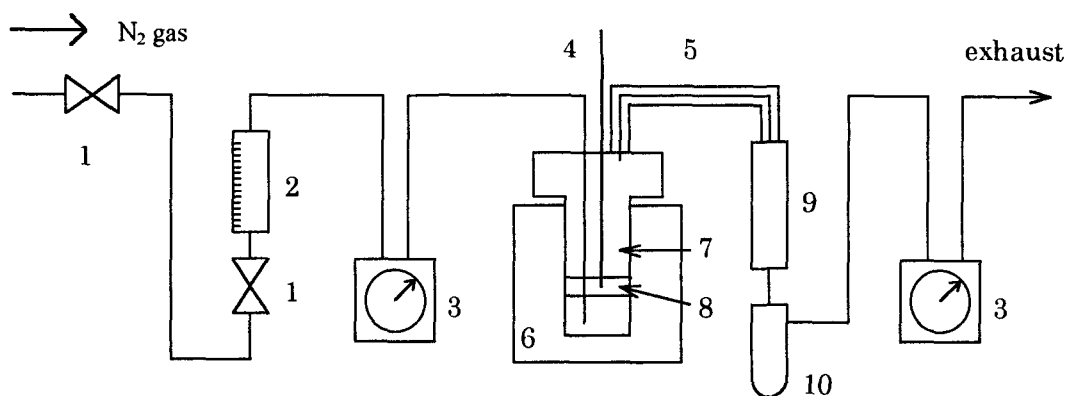


Fig.1 Apparatus employed for the catalytic degradation of polystyrene; 1: regulator, 2: flow meter, 3: gas meter, 4: thermocouple, 5: flexible heater, 6: electric furnace, 7: reactor, 8: catalyst bed, 9: condenser, 10: oil reservoir.

forms of complex were prepared from polystyrene and catalyst powders as follows;

a) A small amount of barium oxide was dispersed into polystyrene pieces using a heating twin-roller as shown in Fig.2, when they were molded into thin films. In these films barium oxide is expected to act as catalyst when they are thermally degraded.

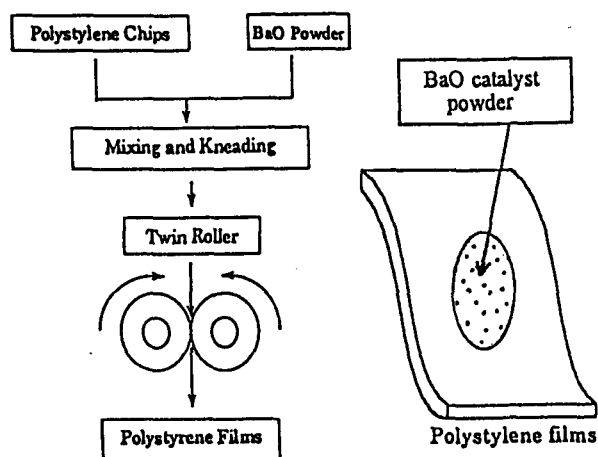


Fig. 2 Molding into thin films dispersing catalyst

b) The films prepared above, were converted into foams with carbon dioxide in a autoclave. In ordinary foaming process of plastics, calcium carbonate is used as foaming nuclei. In the present case, barium oxide may act as catalysts on the degradation as well as the nuclei on the foaming.

c) In order to mold mechanically strong resins, fibers made of glass or carbon (so-called fillers) are sometimes dispersed into polymer pieces. In the present work, glass fibers, on which surface barium oxide was deposited, were employed as fillers. These

fillers are expected to act as also 'catalyst' when the resins are degraded.

The recyclable polystyrene resins thus prepared were divided into small pieces, and then thermally degraded at 623 K without any catalyst on the bed in the reactor.

### 3. Results and Discussion

In Fig.3 are given the results obtained for catalytic degradation of polystyrene on solid acid and base catalysts, together with the results obtained by a simple thermal degradation. A trace or negligibly small amount of gases was produced in all runs of the present work. In the figure the yields of styrenes, both monomer and dimer, are plotted against the catalysts used. These were roughly classified into three groups: solid bases, transition metals and solid acids from left to right on the figure.

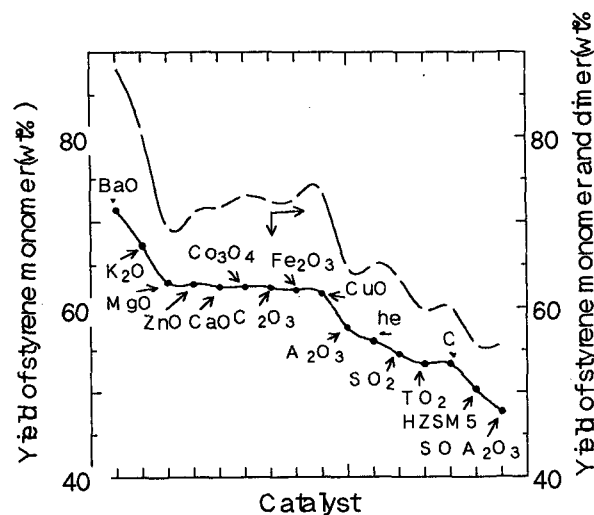


Fig. 3 Yields of styrene monomer and dimer from polystyrene degraded over various catalysts.

Accumulated amounts of oils yielded at every 10 min of the catalytic degradation of polystyrene (10 g) at 623 K are drawn in Fig. 4 and 5, as well as those yielded by a simple thermal degradation. These figures may represent the apparent rates of oil formation on solid acids and bases, although a strong dependence upon the flow rate of nitrogen gases, which carried the vaporized fragments of polystyrene on to the catalyst powder, was observed.

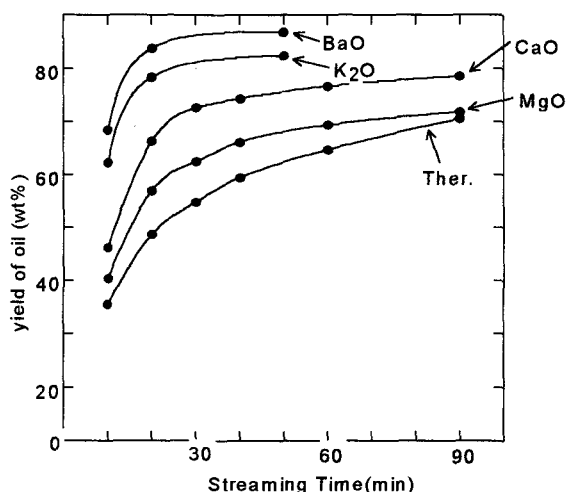


Fig.4 Degradation rates of polystyrene over solid base catalysts at 623 K

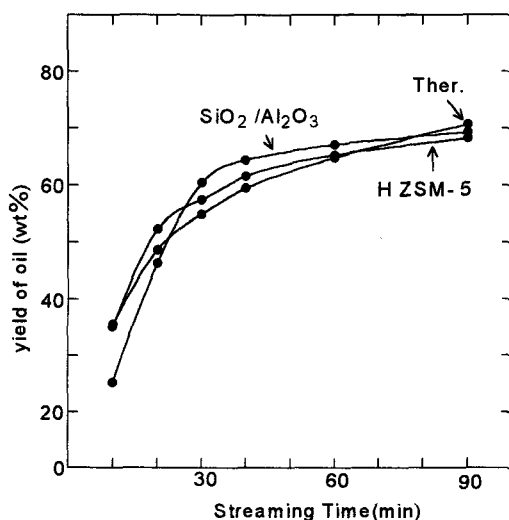


Fig.5 Degradation rates of polystyrene over solid acid catalysts at 623 K.

In a commercial plant for the catalytic degradation of waste plastics into fuel oils, solid acids such as

silica-alumina or H-ZSM-5 zeolite have been successfully employed as catalysts. This is due to the presence of strong acid sites on the catalyst surfaces, which have the potential to disrupt C-C bonds in the waste plastics and to hydrogenate olefins, yielded by the degradation, into paraffins. Since olefins are easily oxidized or polymerized into unusable compounds during storage and transportation, these tendencies of solid acids are unfavorable toward the chemical recycling of waste polystyrene into styrene.

On catalytic degradation by solid acids, considerable amounts of benzene, ethylbenzene and indan were formed. These products were partially attributed to the further cracking and hydrogenation of styrene yielded, which 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 obtained by solid acids, since they were not detected in those produced by solid base catalysts.

The mechanism of the formation of benzene and indan derivatives on solid acid catalysts starts with an attack of proton to branched phenyl group to produce  $\pi$ -complex cation, which is converted into  $\sigma$ -complex cation to be released as benzene, as shown in Fig.6.

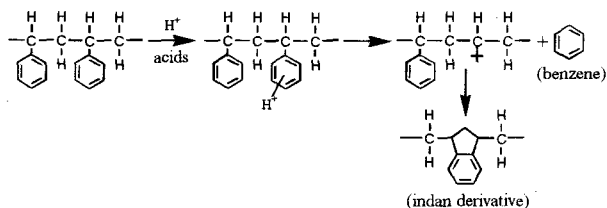


Fig.6 Degradation mechanism of polystyrene on solid acids.

On base catalysts the fraction of styrene in the oils obtained increased to around 75 wt %, and the fraction of styrenes containing both monomer and dimer to about 90 wt %, as shown in Figure 2. Since benzene and indan derivatives were detected neither in the oils yielded by solid bases nor in those produced by the simple thermal degradation of polystyrene, and since a considerable amount of styrene dimer was observed in those oils, the degradation on solid bases may proceed in a way similar to that in the simple thermal degradation, i.e., depolymerization. The catalytic degradation on solid bases may start with the formation of carboanions by the elimination of a hydrogen atom of polystyrene

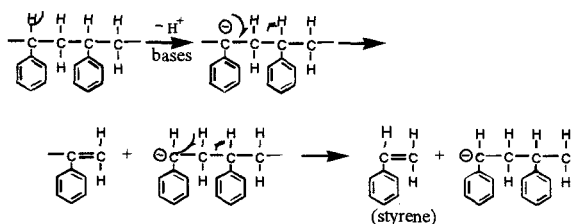


Fig.7 Degradation mechanism of polystyrene on solid bases.

adsorbed on base sites as shown in Fig.7.

The degradation rate, as well as the yields of styrene recovered, is also an important factor for the chemical recycling of waste plastics, since large amounts of waste plastics can be supplied to the still containing active catalysts. Apparent degradation rates on solid acids and bases are depicted in Fig.4 and 5, respectively. The degradation of polystyrene was almost complete within 20 min on the solid bases such as barium and potassium oxides, while on the solid acids it took longer than 90 min to thoroughly degrade the polystyrene pieces.

The slow rates on the solid acid catalysts were explained in terms of catalysts deactivation caused by coke deposition and by the formation of carbonaceous compounds over the catalyst surfaces.

Since barium oxide powder was found to be the most active catalyst for the degradation of polystyrene and to exhibit the highest yield of styrenes, it was dispersed into polystyrene by several techniques to make recyclable resins. Three types of testing polymer were prepared as stated in the experimental section. Results obtained for the thermal degradation of these resins are shown in Table 1, together with the result obtained for the simple catalytic degradation by barium oxide.

Results for the films are almost the same as those obtained for the simple catalysis, although the circumstances of BaO in the working state are significantly different in both cases.

Low activity and selectivity for the polymer loading fillers are due to that the amount of BaO deposited on glass fibers is too small.

Table 1. Comparison of degradation for polystyrenes made by each technique at 623 K (mol %).

	oils formed (wt %)	styrene monomer	styrene dimer	yields of monomer + dimer
Thermal degradation	80.1	70.0	11.2	65.0
Catalytic degradation	93.4	76.4	18.3	88.4
Films (BaO powder)	92.6	71.6	17.3	82.3
Foams (from the above films)	76.4	76.7	16.5	71.2
Fillers (BaO on glass fibers)	84.0	76.8	11.5	74.2

<sup>1)</sup> V. Williams, Preprint, "Symposium of Waste Plastic Recycle", Tokyo (1993), p 21.

<sup>2)</sup> Z. Zhang, T. Hirose, S. Nishio, Y. Morioka, N. Azuma, A. Ueno, H. Ohkita, and M. Okada, *I&EC RESEARCH*, **1995**, 34, 4514.

<sup>3)</sup> A. Ueno, H. Suzuki, and Y. Kotera, *J. Chem. Soc., Faraday Trans. 1* **1983**, 79, 127.