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Thermal and chemical recycle of waste polymers

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Abstract

Catalytic degradations of polyethylene into fuel oils and of polystyrene into styrene monomer have been studied using solid acids and bases as catalysts. Solid acids such as silica–aluminas and ZSM-5 zeolite were found to be effective to degrade waste polyethylene into fuel oils, and solid bases such as BaO and K_2O were concluded to be effective to convert waste polystyrene into styrene monomer. A design of recyclable polystyrene films will be briefly mentioned.

Keywords: Polyethylene catalytic degradation of; Si–Al catalysts; ZSM-5

1. Introduction

It has been of current interests to develop techniques for recycling waste plastics into fuel oils and/or advanced chemicals [1]. Since more than 70% of the plastics currently produced have been composed of polyethylene, polypropylene, polystyrene and polyvinylchloride, most of the work has concerned with these four kinds of polymers. Among these polymers, polyethylene and polypropylene have been intended to be converted into fuel oils, while polystyrene has been expected to be recycled into styrene monomer [2]. In the case of polyvinylchloride, the main problem is how to eliminate chloride ions from polyvinylchloride [3].

In the present paper, the catalytic degradation of polyethylene into fuel oils and of polystyrene into styrene monomer will be discussed in terms of the solid acids and bases, which were used as catalysts for the polymer degradations. Finally, a design of recyclable polystyrene films will be discussed, where a small amount of catalyst powders are dispersed into polystyrene pieces when they are molded into polystyrene films.

2. Experimental

2.1. Catalyst preparation

Catalysts employed for the polyethylene degradation are given in Table 1 with their catalytic performances at 673 K. SiO_2, Al_2O_3 and TiO_2 were prepared from gels obtained by hydrolysis of the corresponding metal alkoxides such as tetraethoxysilane, aluminum triisopropoxide and titanium tetraisopropoxide, according to a previous paper [4]. MgO and ZnO were prepared from the aqueous solution of the

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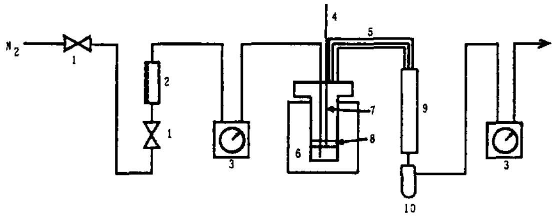

Fig. 1. Schematic diagram of the apparatus employed: 1: pressure regulator, 2: flow meter, 3: gas meter, 4: thermocouple, 5: flexible heater, 6: electric furnace, 7: reactor, 8: catalyst bed, 9: condenser, 10: reservoir of distillates.

corresponding metal nitrates using aqueous ammonia as a precipitant. The precipitates obtained were dried in an oven at 383 K for 12 h, followed by calcination at 773 K for 4 h. ZSM-5 zeolite, with a Si/Al ratio of 14, was prepared from aerosol silica, sodium aluminate and tetra-n-propylammonium hydroxide according to a US patent [5] and was cation-exchanged to H-ZSM-5 using ammonium hydroxide. Active carbon was kindly donated by Sumitomo Kagaku Co. and was used as a catalyst without further purification. Silica–alumina were prepared from gels obtained by hydrolysis of a mixed alkoxide solution of tetraethoxysilane and aluminum triisopropoxide so that the SiO_2/Al_2O_3 weight ratio is 4.

Catalysts employed for the polystyrene degradation are given in Table 3 with their catalytic performances. Most of the solid acids and bases in Table 3 were prepared in the same manner as mentioned above. BaO, K_2O and transition metal oxides were prepared from the aqueous solution of nitrates using ammonium hydroxide as a precipitant.

2.2. *Catalytic degradation of vaporized polymer fragments*

The catalytic and thermal degradation was carried out using 15 g of polyethylene powder ($Mn = 16.2 \times 10^3$, $MW = 63.5 \times 10^3$) and/or polystyrene pieces ($Mn = 24.9 \times 10^4$, $MW = 9.12 \times 10^4$) using a flow reactor made of stainless steel, as given in Fig. 1. At the bottom of the reactor, polymer samples were placed, and just above the sample 1.5 g of the catalyst powders packed with a stainless steel gauge were located. Accordingly, the vapor of thermally degraded products may pass through the catalyst bed with nitrogen gases, supplied at the

Table 1
Polyethylene degradation on solid acids

	H-ZSM-5	$SiO_2(4)$–$Al_2O_3(1)$	SiO_2	Al_2O_3
Oils (wt.-%)	45	52	69	67
Straight (wt.-%)	19	34	54	75
Gases (wt.-%)	50	37	16	13
Waxes (wt.-%)	1	4	6	10
Residues (wt.-%)	trace	trace	trace	trace
Reaction time (h)	< 3	4	5	5
Material balance (%)	96	93	91	90

Polyethylene degradation on solid bases

	ZnO	MgO	TiO_2	Carbon	Thermal
Oils (wt.-%)	70	61	68	60	44
Straight (wt.-%)	85	68	70	78	68
Gases (wt.-%)	12	14	14	12	20
Waxes (wt.-%)	5	9	7	7	13
Residues (wt.-%)	3	trace	3	5	17
Reaction time (h)	7	7	7	7	> 7
Material balance (%)	90	84	92	84	94

bottom of the reactor with a flow rate of 50 ml/min. Catalytically degraded products were introduced into a cooling glass tube, and gases (C_1 to C_4) were separated from oils (C_5 to C_{20}) to be measured by a gas meter.

Catalytic degradation of polyethylene was carried out at 673 K, while that of polystyrene was performed at 623 K in flowing nitrogen. Gases were analyzed by GC (Shimadzu GC-8A) using a column packed with VZ-10, and the oils were by GC (HP-5890) using a 10 m DB-2887 capillary column. Some of the carbonaceous compounds adhered on the cooling glass tube were eliminated by n-hexane and were measured as waxes. Weight difference of catalyst before and after the degradation was measured as cokes deposited on the catalyst surface.

2.3. A design of recyclable polystyrene films

Since, among various solid acids and bases, barium oxide was the most effective to convert polystyrene into styrene monomer and dimer, a small amount of barium oxide (1 wt.-% of polystyrene used) was dispersed into polystyrene pieces when they were molded into thin films using a heating twin-roller made of stainless steel. The polystyrene thin films thus prepared were divided into small pieces sized around 2 × 2 mm, and then thermally degraded at 623 K without any catalytic compounds in the catalyst bed.

3. Results

In Table 1 are given the catalytic performances of solid acids and bases for the polyethylene degradation at 673 K. The term 'straight' in Table 1 means n-paraffins and 1-olefins and the reaction time represents the time required to complete the degradation of 15 g of polyethylene at 673 K. The degradation was assumed to be completed, when no more oils were formed in the cooling tube.

Table 2
Fractions of oils from polyethylene on solid acids and bases

Components	Catalytic degradation (wt.-%)			Thermal degradation (wt.-%)
	H-ZSM-5	$SiO_2(4)$–$Al_2O_3(1)$	ZnO	
1-Olefins	7	4	34	24
n-Paraffins	12	30	51	44
Aromatics	35	13	0	3
Others	46	53	15	30

The fractions of oils yielded from polyethylene on solid acids and bases are summarized in Table 2. The results obtained on ZnO are given as a representative solid base, since the results obtained on other solid bases were almost the same. Others at the bottom column in Table 2 are mainly the amounts of branched-isomers of n-paraffins and 1-olefins.

Catalytic performances of solid acids and bases for the degradation of polystyrene at 623 K are given in Table 3, where the amount of gases produced were negligibly small for all the catalysts employed. In Table 4, the compositions of oils from polystyrene degraded on solid acids and bases are shown. Since the chemical recycling of waste polystyrene into styrene is the main purpose of this work, recovery of styrene monomer and dimer on the catalysts employed is depicted in Fig. 2.

Table 3
Catalytic degradation of polystyrene on solid acids and bases

Catalyst	MgO	CaO	BaO	K_2O	ZnO	TiO_2	SiO_2–Al_2O_3	H-ZSM-5	Thermal
Oils	79.6	82.8	93.4	86.5	82.5	76.3	79.6	78.2	80.1
Cokes	8.2	4.2	0.3	3.1	2.4	9.8	6.0	5.9	–
Gases	–	–	–	–	–	–	trace	trace	–
Residue	3.8	6.5	3.2	4.1	6.5	5.7	4.2	8.5	16.1
Balance	91.6	93.5	96.9	93.7	91.4	91.8	89.8	91.6	96.1

Table 4
Comparison of oils obtained from polystyrene by thermal and catalytic degradation on BaO, and from polystyrene films dispersing 1 wt.-% BaO at 623 K

	Thermal degradation	Catalytic degradation on BaO	Degradation of PS films
Oils (wt.-%)	80.1	93.4	92.6
Contents of oils			
Styrene	70.0	76.4	77.4
Dimer	11.2	18.3	18.9
α-Methyl styrene	8.6	1.4	0.9
Toluene	5.1	1.6	1.4
Ethylbenzene	2.4	0.2	0.1
Styrene yields			
Styrene monomer	56.1	71.4	77.1
Monomer + dimer	65.0	88.4	88.9

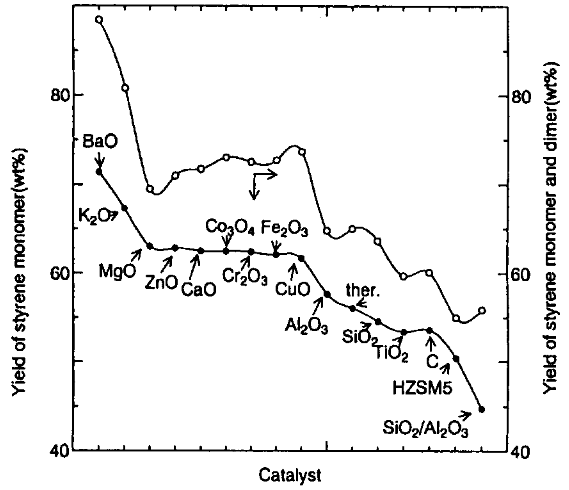

Fig. 2. Recovery of styrene monomer from polystyrene on various catalysts.

Results obtained for the degradation of polystyrene films dispersing barium oxide powders are given in Table 5, where the results obtained for the simple thermal degradation of polystyrene and for the catalytic degradation on barium oxide are also given for comparison.

4. Discussion

4.1. Catalytic degradation of vaporized polyethylene fragments

As can be seen in Table 1, amounts of residues after the catalytic degradation were extremely reduced compared with those after a simple thermal degradation, suggesting that low-volatile compounds produced by the thermal degradation were readily cracked into light hydrocarbons on the catalysts employed. It is also found in Table 1 that more oils were produced on solid bases than on solid acids, though the time required to complete the degradation on solid bases was much longer than on solid acids. The composition of oils on solid bases was, however, rich in 1-olefins, and were poor in aromatics and branched isomers. It has been reported that oils mainly consisting of olefins are not expected for fuel oils because of their polymerization during preservation and/or transportation [6]. Moreover, a low octane number is expected for the oils produced on solid bases, since the oils mainly consisted of straight chain hydrocarbons; n-paraffins and 1-olefins. Although the degradation on solid acids resulted in a large amount gas, the oils yielded were much different from the oils obtained on solid bases. The oils produced on solid acids were

Table 5
Compositions of oils from polystyrene on solid acids and bases

Catalyst	MgO	CaO	BaO	K_2O	ZnO	TiO_2	SiO_2–Al_2O_3	H-ZSM-5	Thermal
Styrene	79.1	75.5	76.4	77.8	76.1	70.0	59.9	64.4	70.0
Styrene dimer	8.2	11.1	18.3	15.6	9.9	8.3	10.3	7.0	11.2
α-Methyl styrene	6.2	6.6	1.4	2.5	6.2	8.5	4.5	5.2	8.6
Toluene	3.9	3.9	1.6	2.2	4.0	4.1	2.3	3.1	5.1
Benzene	–	–	–	–	–	0.1	4.5	6.4	–
Ethylbenzene	0.7	0.9	0.2	0.3	0.7	5.5	9.0	2.0	2.4
Indan	–	–	–	–	–	–	2.2	1.8	–

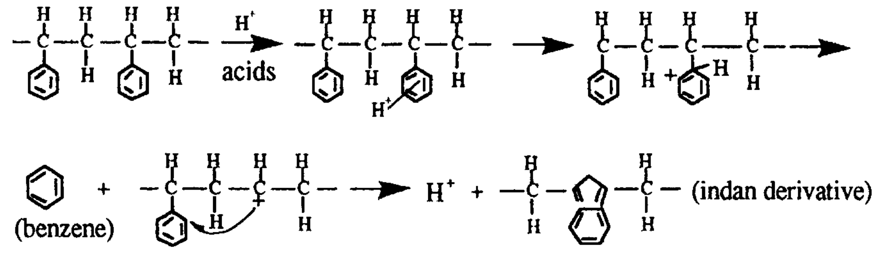

Fig. 3. Mechanism to produce benzene and indan during polystyrene degradation.

rich in aromatics and branched isomers, indicating a high octane number. Olefins were hydrogenated into paraffins and/or cracked into light hydrocarbons, associated with isomerization and aromatization on the solid acids, resulting in less amounts of olefins in the oils produced on solid acids. The role of solid acids is considered to eliminate hydrogen in the polyethylene fragments adsorbed on acid sites, and to form carbonium ions on the hydro-carbon chains, followed by C–C bond fission into light hydrocarbons.

Consequently, solid acids such as H-ZSM-5 and silica–alumina are effective as catalysts for the production of high quality fuel oils from waste polystyrene.

4.2. Catalytic degradation of vaporized polystyrene fragments

Waste polystyrene is a model for chemical recycling into monomer, which will be reused for the production of polymer. As is seen in Table 3 and 4, more amount of styrene was yielded from polystyrene degraded on solid bases rather than on solid acids. Productions of benzene and indan are one of the features of the polystyrene degradation on solid acids, and the mechanisms assumed are given in Figs. 3 and 4.

Hydrogenation of styrene into ethylbenzene and cracking of styrene into benzene proceeded on the solid acids, resulting in the decrease in the yields of styrene, as shown in Table 4.

While on the solid bases such as BaO and K_2O, more than 80 wt.-% of polystyrene employed was converted into both styrene monomer and dimer, as depicted in Fig. 2. The formation of styrene from polystyrene on solid bases might start with an elimination of hydrogen atom to form carbanions, followed by the consecutive depolymerization through the carbanions. Thus, the role of solid bases is merely to eliminate hydrogen from polystyrene fragments.

4.3. Degradation of polystyrene films dispersing BaO powders

As can be seen in Table 5, around 90 wt.-% of polystyrene was converted into both styrene

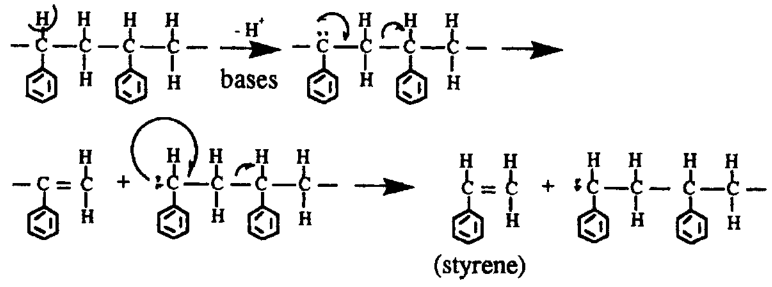

Fig. 4. Depolymerization mechanism of polystyrene on solid bases.

monomer and dimer by thermal degradation of polystyrene films dispersing a small amount of BaO powders at 623 K. These styrene monomer and dimer could be reused for the production of polystyrene. In this sense, the polystyrene films dispersing BaO catalyst can be considered as one of the models of the recyclable polymer, which has been extensively studied from the view point of the technology for saving carbon resources as well as for environmental issues.

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