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POLYMER-SUPPORTED LEWIS ACID CATALYSTS.
I. POLYSTYRENE–GALLIUM TRICHLORIDE COMPLEX

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ABSTRACT

Polystyrene-divinylbenzene (5-7%) copolymer beads are combined with anhydrous gallium trichloride in CS_2 to form a stable complex containing 3.06% Cl (equivalent to 0.287 mmol $GaCl_3$/g complex beads). The complex showed good catalytic activity in organic synthetic reactions such as acetalation, esterification, ketal formation, etherification, and Friedel-Crafts alkylation. The catalyst can be reused several times without losing its activity and can be easily separated from the reaction mixtures.

INTRODUCTION

Polymers with various functions and specific characters can be made by changing their composition and structure. Recently, uses of functional polymers in chemical reactions became increasingly widespread, and this has been one of the important and rapidly developing fields of polymer science [1-8].

Polymer catalysts are functionalized polymers and have received much attention. Polymer catalysts consisting of polystyrene with $AlCl_3$ and BF_3 have been made by Neckers and Sket and used in organic synthetic reactions [3-7].

We have reported a number of polymer-supported Lewis acid catalysts with good catalytic activity in organic reactions during the last several years [8-10]. In this paper we will report another polymer-supported Lewis acid catalyst. A stable polymer-supported Lewis acid catalyst was first formed by reaction of polystyrene with anhydrous $GaCl_3$. This can be easily hydrolyzed in air, and the product does not lose its activity for at least two years. It shows good catalytic activity in organic synthetic reactions such as esterification, acetalation, ketal formation, etherification, and Friedel-Crafts alkylation. It is not only easy to produce at low cost, but it is also easily usable as a catalyst and can be easily separated from reaction mixtures without pollution. Furthermore, it can be reused and regenerated.

EXPERIMENTAL

Preparation of Polymer-Supported Catalyst

Pearl polystyrene (20 g) (containing 5-7% divinylbenzene of 16-50 mesh size and 0.3-1.25 nm pore diameter), swelled by 60 mL of CS_2, was stirred with 2 g of anhydrous $GaCl_3$ at room temperature for 4 h, and the pearls became bright red. Cold water (200 mL) was then added to the reaction mixtures to decompose the uncomplexed $GaCl_3$. It was filtered and washed four times with chloroform and twice with ethyl ether. The pearls became yellow and were vacuum dried 3 days before use.

Determination of the Quantity of $GaCl_3$ Complexed

The complex samples were decomposed by burning in an oxygen bottle. The chlorine content was determined volumetrically and by ion-selective electrode. The amount of $GaCl_3$ complexed with polystyrene was calculated from the chlorine content.

Determination of Acidity of the Complex

The pH's of the acetone-water solutions obtained by hydrolyzing the pearl samples in acetone-water were determined at 20°C by a pH meter (digital pH/temperature meter 3055).

Ultraviolet and Infrared Spectral Analysis

UV spectra of uncrosslinked polystyrene ($\overline{M}_w = 2.3 \times 10^5$) complexed with $GaCl_3$ in CS_2 (containing 5% of $GaCl_3$) were obtained with a ultraviolet-visible spectrophotometer (Shimadzu UV-300). The infrared spectra of the same solutions were determined with an IR spectrophotometer (Nicolet FT-IR 7199 B). The structure of the complex was derived from these spectra.

Test of Catalytic Activity in Organic Reactions

Acetal and ketal formation, esterification, and etherification were carried out in benzene, using the polymer-supported catalyst of polystyrene-gallium trichloride complex (PS-$GaCl_3$). It was refluxed using a Dean-Stark trap for 2 h at 82-95°C. Yields of these reactions were determined by gas chromatography (SP 2307 type) against an internal standard. For example, propionic acid (7.4 g, 0.1 mol), *n*-butyl alcohol (14.8 g, 0.2 mol), benzene (60 mL), and PS-$GaCl_3$ complex catalyst beads (1.0 g) were allowed to react in a 100-mL flask with a Dean-Stark trap and a condenser. The mixture was heated under reflux for 2 h. The reaction solution was analyzed by GLC against chlorobenzene as an internal standard. The amount of *n*-butyl propionate and the residual *n*-butanol were determined relative to the peak area of the internal standard.

RESULTS AND DISCUSSION

Amount of $GaCl_3$ Complexed with Polystyrene

The content of chlorine in the PS-$GaCl_3$ complex was 3.06%, equivalent to 0.287 mmol $GaCl_3$/g of complex beads.

Acidity of the Solution Obtained on Hydrolysis of PS-$GaCl_3$

The relationship between the pH of 50 mL acetone-water solution (3:2, v/v) containing 2 g PS-$GaCl_3$ complex beads and time is shown in Fig. 1. The acidity due to the hydrolysis of the complexed $GaCl_3$ reached equilibrium in 1 h.

UV and IR Spectral Analysis

The UV spectra of the solution of uncrosslinked polystyrene-gallium trichloride complex are shown in Fig. 2. The absorption of PS-$GaCl_3$ complex

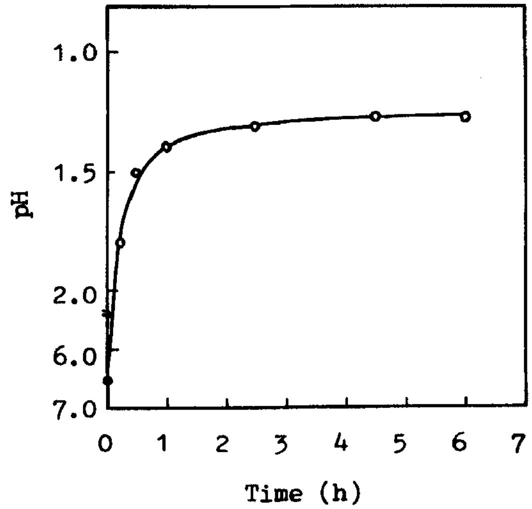


FIG. 1. Change of the pH of the acetone-water solution containing PS-$GaCl_3$ with time.

in CS_2 at low concentration was the same as that of $GaCl_3$ in CS_2 (a band at 380 nm), but when the concentration of the PS-$GaCl_3$ complex was increased, a new absorption band at 400-500 nm was formed. At 5.0% PS-$GaCl_3$ a new, strong band appeared at 470 nm which was also given by the complex of $GaCl_3$ with benzene (see Fig. 2).

The main differences between the IR spectra of PS-$GaCl_3$ complex and polystyrene (PS) were at 1500-1600 and 400-800 cm^{-1} (Fig. 3). These regions of the IR spectra represent the C—C stretching vibration and the C—H bending vibration of the benzene ring. It is evident that the structure of the PS-$GaCl_3$ complex is similar to that of the $GaCl_3$-benzene complex because the Lewis acid $GaCl_3$ is complexed with the benzene rings of the polystyrene and the $GaCl_3$ is stabilized due to the decreased mobility of the benzene rings hindered by the long polystyrene chain. The PS-$GaCl_3$ complex is especially stable; even after over 2 years of storage the complex did not lose its catalytic activity.

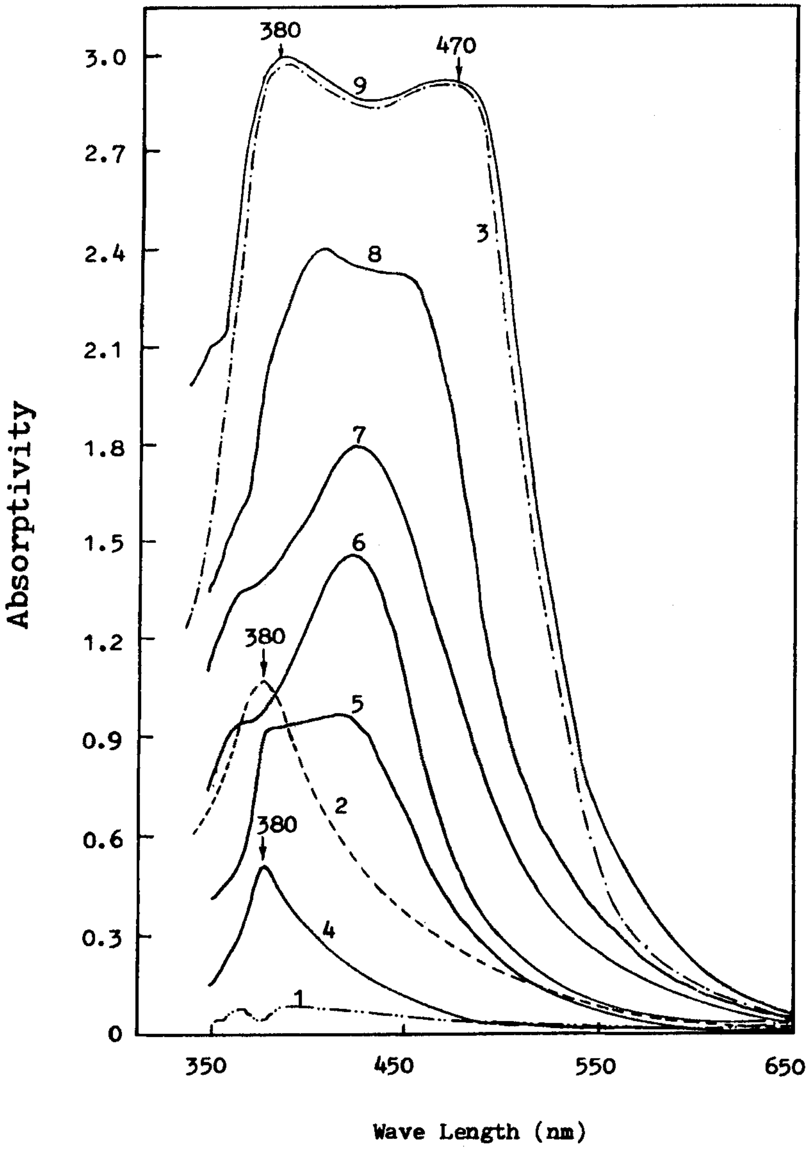


FIG. 2. UV spectra of PS-$GaCl_3$ and reference compounds in CS_2. 1, PS; 2, $GaCl_3$; 3, PS•benzene; PS-$GaCl_3$ concentration: 4, 0.13%; 5, 0.25%; 6, 0.5%; 7, 1.0%; 8, 2.5%; 9, 5.0%.

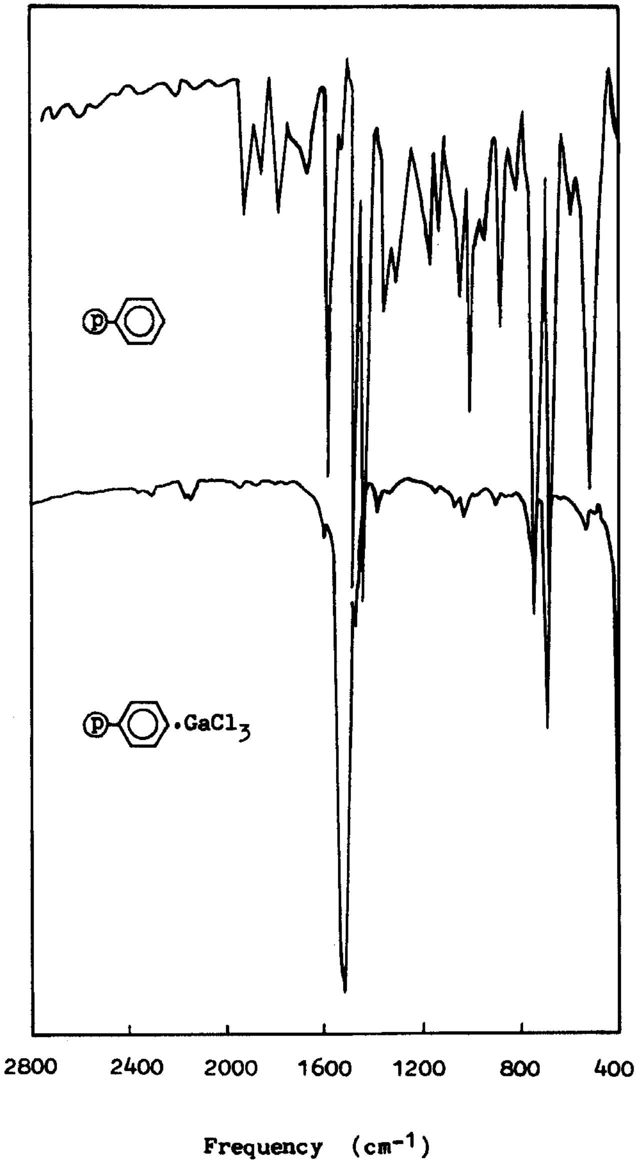


FIG. 3. IR spectra of PS-$GaCl_3$ and polystyrene.

TABLE 1. Catalytic Esterification[a]

R in R–COOH	Catalyst	Mole ratio, acid/alcohol	Reaction time, h	Yield, %
$-CH_3$	A	1:2	2	47
	B	"	24	30
	C	"	2	7
$-CH_2CH_3$	A	1:2	2	60
	B	"	2	70
	C	"	2	11
	A	1:5	2	12
	B	1:20	5	22.9
	C	1:5	4	0

[a] Catalyst: A, PS-$GaCl_3$; B, PS-$AlCl_3$ [6]; C, PS (white beads). Yields were determined by gas chromatography with chlorobenzene as internal standard.

Results of Catalytic Activity in Organic Reactions

(1). Results of Catalytic Esterification

Yields of esterifications of carboxylic acids with *n*-butyl alcohol catalyzed by the polymer-supported Lewis acid catalyst are shown in Table 1.

$$\text{R–COOH} + n\text{-}C_4H_9OH \xrightarrow[\text{benzene}]{\text{catalyst}} \text{R–COOC}_4H_9 + H_2O$$

(2). Results of Catalytic Acetalation

Yields of acetalations of substituted benzaldehyde with *n*-butanol are shown in Table 2.

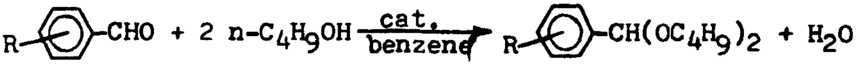


TABLE 2. Catalytic Acetal Formation[a]

R in RC_6H_4CHO	Catalyst	Reaction time, h	Yield, %
H	A	4	52
	B	2.5	21
	C	2	8
o-NO_2	A	4	98
	B	18	62
m-NO_2	A	4	75
	B	4	96
p-NO_2	A	4	91
	B	24	48
	C	2	9
o-Cl	A	4	71
m-Cl	A	4	63
p-Cl	A	4	89
p-Br	A	4	100
p-F	A	4	74
o-OH	A	4	27
m-OH	A	4	27
p-OH	A	4	16
p-$N(CH_3)_2$	A	4	0

[a] Catalysts: A, PS-$GaCl_3$; B, PS-$AlCl_3$ [7]; C, PS (white beads). Mole ratios (aldehyde/alcohol) are 1:5 in all reactions. Yields were determined by gas chromatography with butyl acetate as internal standard.

TABLE 3. Catalytic Ketal Formation of Cycloketones with Ethylene Glycol

Catalyst	*n* in Ketone	Reaction time, h	Yield, %
PS-$GaCl_3$ [a]	1	2	67
	2	2	91
	4	2	53
PS-BF_3 [3]	1	2	61
	2	2	94
	4	2	50

[a] Yields were determined by gas chromatography with *n*-butanol as internal standard. Mole ratio (ketone/alcohol) 1:1 in all reactions.

TABLE 4. Catalytic Ketal Formation of Cycloketones with *n*-Butanol[a]

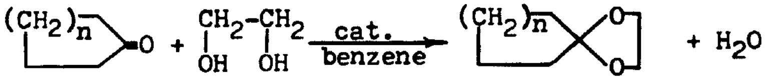
Catalyst	*n* in Ketone	Mole ratio (ketone/alcohol)	Time, h	Yield, %
PS-$GaCl_3$	1	1:3	2	26
	2	1:3	2	33
	4	1:3	2	21

[a] Yields were determined by gas chromatography with chlorobenzene as internal standard.

It is evident that the polymer-supported Lewis acid catalyst PS-$GaCl_3$ complex exhibited very high catalytic activity on the acetalation of substituted benzaldehydes and the yields were in accord with the Hammett substituent constants.

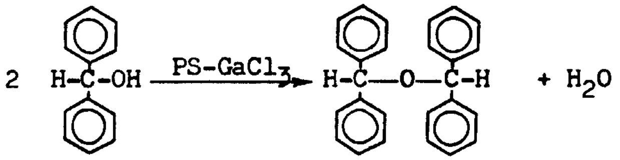
(3). Result of Catalytic Ketal Formation

Yields of ketal formations of cycloketones with ethylene glycol and *n*-butanol are shown in Tables 3 and 4.



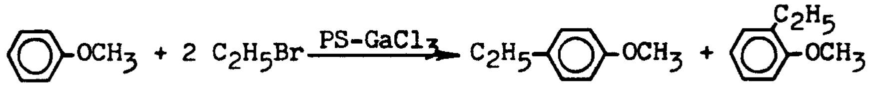
From Tables 3 and 4 it is evident that the polymer-supported Lewis acid catalyst PS-GaCl$_3$ complex exhibits good catalytic activity in ketal formations. The yields of ketal formation of cyclohexanone with ethylene glycol and *n*-butanol were the highest among that of cycloaliphatic ketones with 5-8 membered rings. The yields of ketal formations of cycloketones with ethylene glycol were higher than those with *n*-butanol.

(4). Catalytic Etherification

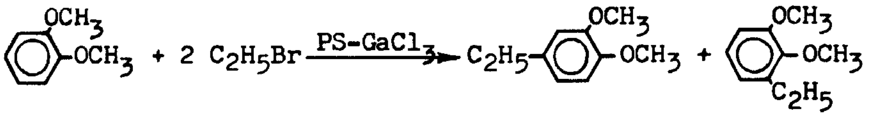


yield: 20%

(5). Catalytic Friedel-Crafts Alkylations



total yield: 31%



total yield: 56%

(6). Reuse of the Catalyst

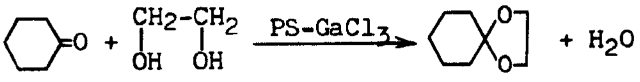


TABLE 5. Reuse of the Same Catalyst[a]

No. of reuses:	1	2	3	4	5	6
Yield (%):	90	90	88	87	81	70

[a]Reaction conditions: 0.1 mol cyclohexanone, 0.1 mol ethylene glycol, 1.5 g PS-$GaCl_3$ complex beads, 50 mL benzene, reaction time 1 h. Yields were determined by GLC.

Results for ketal formation of cyclohexanone with ethylene glycol catalyzed by previously used polymer-supported Lewis acid catalyst PS-$GaCl_3$ complex are shown in Table 5.

The yields of the reactions were a little lower when the catalyst PS-$GaCl_3$ complex had been reused six times. The polymer support can be regenerated with fresh $GaCl_3$ when the catalyst loses its activity.

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