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POLYMER-SUPPORTED LEWIS ACID CATALYSTS. V. COMPLEXES OF TITANIUM CHLORIDE OR STANNIC CHLORIDE WITH POLY(β -DIKETONE) CARRIER

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ABSTRACT

A polymer carrier containing β -diketone groups was synthesized by a free radical polymerization of methacrylacetone monomer and combined with titanium tetrachloride or stannic chloride in chloroform to form two very stable complexes containing 19.5 and 18.3% Cl which are equivalent to 1.40 mmol TiCl_4/g complex beads and 1.28 mmol SnCl_4/g complex beads, respectively. The two complexes showed good catalytic activity in many organic reactions such as acetalation, ketal formation, and esterification. The catalysts can be reused at least 8 times without losing their activity in organic reactions.

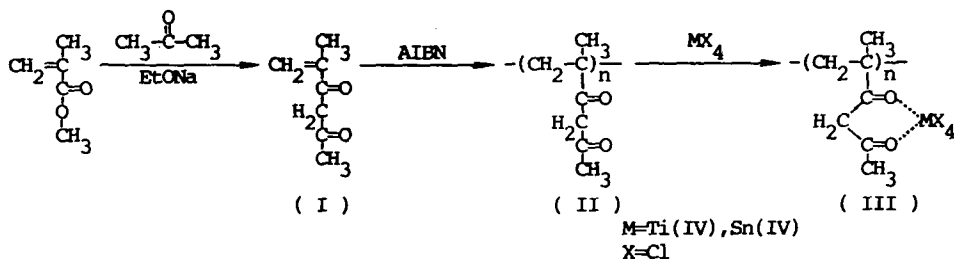
INTRODUCTION

It is well known that stable complexes can be easily formed between a transition metal ion and a β -diketone. The structures and properties of many of these complexes have been studied extensively. Some of these have been looked upon as organometallic compounds [1, 2].

In recent years we have reported a series of polymer-supported Lewis acid catalysts for organic reactions and cationic polymerizations [3–6]. In order to improve the stability of these catalysts, we synthesized a new polymer support containing β -diketone groups which combined with titanium tetrachloride or stannic chloride to form two very stable complexes. These complexes not only

showed very good stability but also good catalytic activity in many organic reactions.

Synthesis of Polymer Carrier (Scheme 1)



SCHEME 1. The synthesis method for the monomer, polymer carrier, and polymeric catalysts containing β -diketone groups.

(1). Synthesis of the Monomer Containing β -Diketone Groups

Place 11.5 g fresh cut sodium metal in 40 mL absolute ethanol in a 500-mL three-necked flask with a motor stirrer, a condenser equipped with a drying tube, and an addition funnel at 0°C. After 10 min, 200 mL methyl methacrylate (MMA) was added dropwise over 15 min. This was followed by the dropwise addition of 20 g acetone over 1 h. The reaction was stirred continuously for 1 h. The reaction solution was placed in a freezer overnight. A yellow viscous solution was obtained. The solution was dropped into 200 mL ice-water and the layers were separated in a funnel. The bottom layer was drawn off, and the top layer was washed 2 times with 10% NaOH. The washing solution and the bottom layer were put into ice-water together and acidified with 30% hydrochloric acid to pH 1. The solution was separated and the bottom layer was drawn off. The top layer was extracted twice with ethyl ether. The ether extract and the bottom layer were dried together by CaCl_2 . The ether was removed by distillation, and a red viscous product was obtained by vacuum distillation at 120°C/40 mmHg. The yield was 60% (based on acetone).

(2). Preparation of Polymer Carrier Beads

Polymer carrier beads were prepared by copolymerization of a monomer containing β -diketone groups (25%, wt), styrene (73.5%, wt), and divinylbenzene (DVB, 1.5%, wt) in the presence of azodiisobutyronitrile (AIBN) in water. Beads of 20–100 mesh were used as functional polymer carriers.

Preparation of Complexes of Poly(β -diketone) with Titanium Tetrachloride or Stannic Chloride

20 g of the polymer carrier beads containing β -diketone groups was swollen in 200 mL chloroform. A 10-mL solution of titanium tetrachloride or stannic chloride in chloroform (2:1, v/v) was added to the swollen polymer carrier and reacted for 24 h at room temperature. The reaction mixture was filtered and washed 5 times with chloroform. The polymeric catalyst beads were dried under vacuum for 72 h, giving dark brown (for SnCl_4) and light brown (for TiCl_4) catalyst beads, respectively.

Determination of the Quantity of TiCl_4 and SnCl_4 Complexed in the Catalysts

The complex samples were decomposed by burning them in an oxygen bottle. The chlorine content was determined volumetrically. The amounts of TiCl_4 and SnCl_4 complexed in the polymer catalysts were calculated from the chlorine content.

Determination of the Acidity of the Complex Catalysts

The pH values of the acetone–water solution obtained by hydrolyzing the complex samples in acetone–water (60%) were determined at 25°C with a pH meter (digital pH/temperature meter).

Ultraviolet and Infrared Spectral Analysis

UV spectra of the uncrosslinked complex of poly(β -diketone) with TiCl_4 and SnCl_4 in DMSO were obtained with a ultraviolet/visible spectrophotometer (Shimadzu UV-250). The infrared spectra of these solutions were determined with an IR spectrophotometer (Shimadzu IR-408).

Test of Catalytic Activity in Organic Reactions

Esterification, acetalation, and ketal formation were carried out in the presence of the polymeric complex catalysts of poly(β -diketone) with TiCl_4 or SnCl_4 in benzene. The reaction solutions were refluxed by using a Dean-Stark trap for 1–2 h at 85–95°C. The yields of these reactions were determined by GC using butyl acetate (for esterification reactions) and chlorobenzene (for other reactions) as internal standards.

RESULTS AND DISCUSSION

Preparation of Polymer Carriers and Catalysts

The functional monomer containing β -diketone groups was synthesized by a crossed Claisen condensation reaction between methyl methacrylate (MMA) and acetone in the presence of sodium ethoxide. In order to prevent an Aldol condensation reaction between the two acetones, excessive methyl methacrylate was added in the reaction.

The functional polymer carrier containing β -diketone groups was synthesized by suspension copolymerization of styrene, methacrylacetone (MAAC), and divinylbenzene (DVB) in the presence of AIBN. The polymer carrier beads of 20–100 mesh contain 19% (mol) of MAAC and 1.2% (mol) of DVB.

The polymer-supported Lewis acid catalysts of complexes of polymethacrylacetone (PMAAC) and stannic chloride or titanium tetrachloride were prepared by the reaction of the polymer carrier PMAAC with SnCl_4 or TiCl_4 in chloroform. The

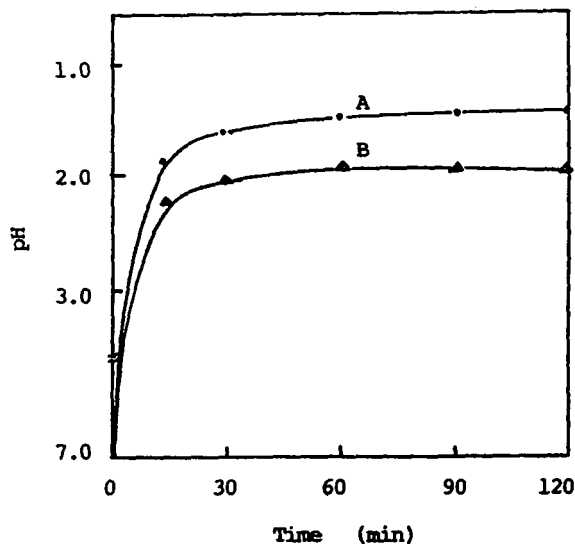


FIG. 1. Dependence of the pH of 50 mL acetone–water solution (60%) containing 2 g polymeric catalyst beads. (A) PMAAC– SnCl_4 , (B) PMAAC– TiCl_4 .

chlorine content of the polymer catalysts is 18.3% for the polymethacrylaceton- SnCl_4 complex (PMAAC-SnCl_4) and 19.5% for the polymethacrylaceton- TiCl_4 complex (PMAAC-TiCl_4). This is equivalent to 1.28 mmol SnCl_4/g complex beads and 1.40 mmol TiCl_4/g complex beads.

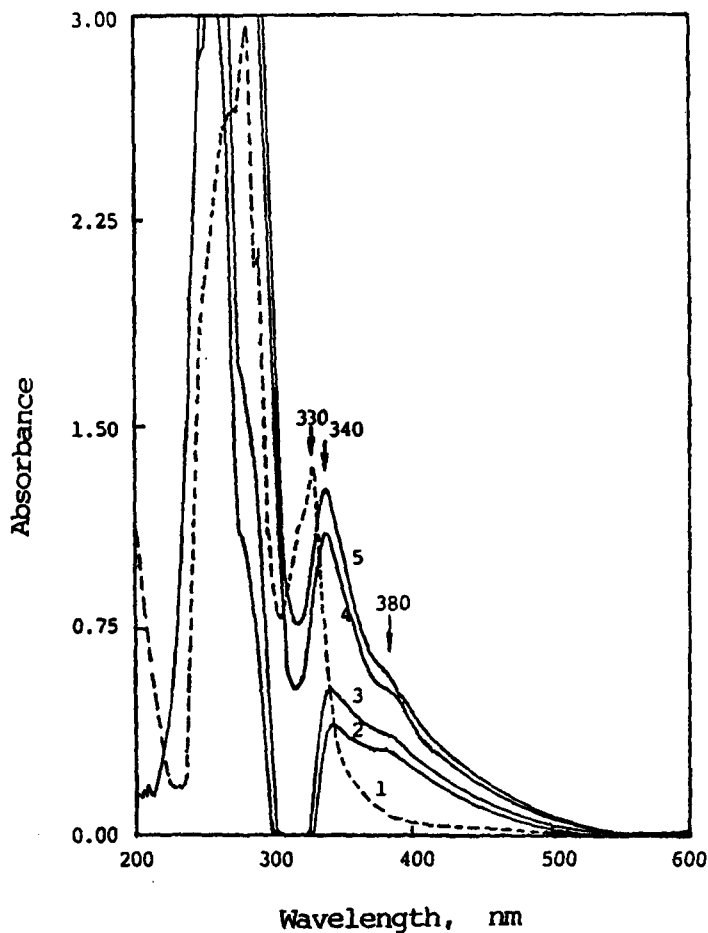


FIG. 2. UV spectra of PMAAC-SnCl_4 and PMAAC in DMSO. (1) PMAAC ; (2, 3, 4, 5) are 1, 1.5, 2.5, and 5% of uncrosslinked PMAAC-SnCl_4 in DMSO, respectively.

Acidity of the Solution Containing Polymer Catalysts

The acidity of an acetone–water solution (60%) containing polymer catalyst beads reaches equilibrium in approximately 15 min (Fig. 1) due to hydrolysis of the complexed SnCl_4 and TiCl_4 .

UV and IR Spectral Analysis

The UV spectra of the solutions of uncrosslinked polymethacrylate (PMAAC) and its complexes with SnCl_4 (PMAAC-SnCl_4) in DMSO are shown in Fig. 2. New absorption bands appear at 340 and 380 nm in the PMAAC-SnCl_4 complex as a function of PMAAC-SnCl_4 concentration (see Fig. 2). Two new absorption bands at 360 and 375 nm also appeared for the polymeric complex PMAAC-TiCl_4 . It is evident that formation of the complexes of polymer carrier PMAAC with SnCl_4 and TiCl_4 led to the appearance of the two new absorption bands.

A very obvious difference between the IR spectrum of polymer carrier PMAAC and the complex of the polymer carrier with stannic chloride (PMAAC-SnCl_4) is at 1705 cm^{-1} , which is a characteristic absorption band of the C=O group of the

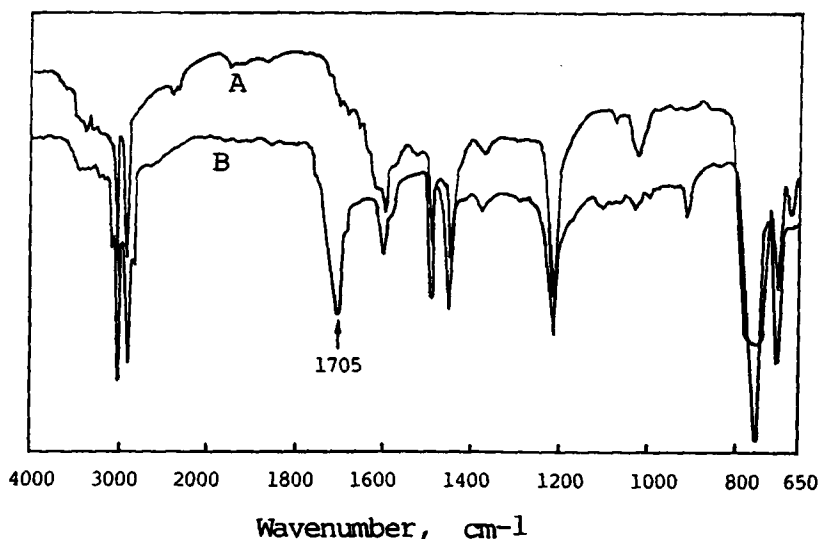
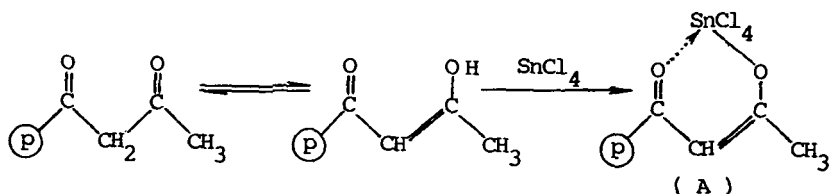
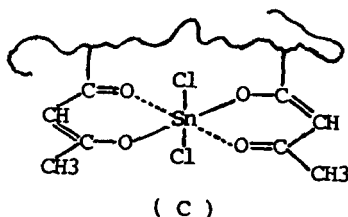
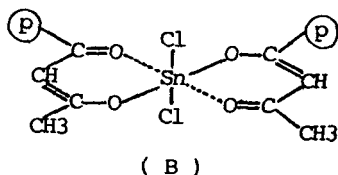


FIG. 3. IR spectra of PMAAC-SnCl_4 complex and PMAAC polymer carrier. (A) PMAAC-SnCl_4 , (B) PMAAC.

uncomplexed polymer (see Fig. 3). In the IR spectrum of the polymeric complex, the characteristic band disappears, indicating that a complex of β -diketone in the polymer carrier with SnCl_4 is formed. The proposed structure, shown below (A), would be very stable:



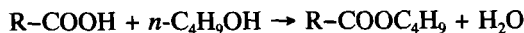
Because the β -diketone group is a very strong electron donor ligand, complexes like (B) and (C) might also be formed between Sn(IV) or Ti(IV) and the polymer carrier. The formation of all of these complexes would result in stabilization of the polymer-supported Lewis acid catalysts.



Results of Catalytic Activity on Organic Reactions

(1). Results of Catalytic Esterification


Results of the esterification of carboxylic acids with *n*-butanol catalyzed by the polymer catalysts PMAAC-SnCl_4 and PMAAC-TiCl_4 (Table 1) indicates that the catalytic activity of the two polymer-supported catalysts is similar to that of the polystyrene- SnCl_4 complex catalyst (PS-SnCl_4) [3] and polystyrene- TiCl_4 complex catalyst (PS-TiCl_4) [4] in the reactions.



(2). Results of Catalytic Acetalation

The results in Table 2 clearly verify that the polymer-supported catalysts PMAAC-SnCl_4 and PMAAC-TiCl_4 show good catalytic activity in the acetalation of substituted benzaldehydes with *n*-butanol and ethylene glycol, and that the

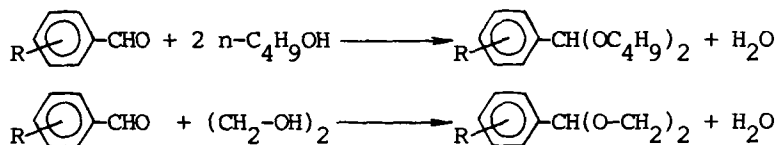
TABLE 1. The Results of Catalytic Esterification of Acids with *n*-Butyl Alcohol^a

R in acids	Catalyst ^b	Time, h	Yields, %
-CH ₃	A	2	50
	B	2	36
	C	4	74
	D	2	53
-CH ₂ CH ₃	A	2	44
	B	2	38
	C	4	100
	D	2	80
	A	2	13
	B	2	20
	C	4	22
	D	2	26

^aCatalysts: A = PMAAC-SnCl₄, B = PMAAC-TiCl₄, C = PS-SnCl₄ [3], and D = PS-TiCl₄ [4].

^bReaction condition: mole ratio of acid/alcohol = 1:2; the yield was determined by GC.

yields are in accord with the Hammett substituent constants. That is, the reaction is aided by electron-withdrawing groups. In addition, the stronger affinity between aldehyde or alcohol and the β-diketone groups in the polymer catalysts resulted in higher catalytic activity compared to that of PS-SnCl₄ and PS-TiCl₄ [3, 4].



(3). Results of Catalytic Ketal Formation

The results in Table 3 indicate that the polymer catalysts PMAAC-SnCl₄ and PMAAC-TiCl₄ show better catalytic activity in ketal formation than do the polymer catalysts PS-SnCl₄ [3] and PS-TiCl₄ [4]. This result might also be related to the stronger affinity between ketone, alcohol, and the β-diketone groups in the former.

TABLE 2. The Results of Catalytic Acetalation of Substituted Benzaldehydes with *n*-Butanol and Ethylene Glycol^a

R in aldehyde	Catalyst ^b	Time, h	Yields, %	
			<i>n</i> -BuOH	(CH ₂ OH) ₂
H	A	0.5	58	100
	B	0.5	54	100
	C	4	67	
	D	2	62	
<i>o</i> -OH	A	1	33	69
	B	1	26	67
	C	4	31	
	D	2	24	
<i>p</i> -Cl	A	1	73	100
	B	1	76	100
	C	4	81	
	D	2	73	
<i>p</i> -NO ₂	A	1	100	100
	B	1	98	100
	C	4	100	
	D	2	87	
<i>m</i> -NO ₂	A	0.7	99	100
	B	0.7	100	100
<i>o</i> -OCH ₃	A	0.7	87	89
	B	0.7	76	84
	D	2	19	

^aReaction condition: mole ratio of aldehyde/alcohol = 1:2 in the reaction of *n*-BuOH; aldehyde/alcohol = 1:1 in the reaction of ethylene glycol. The yields were determined by GC.

^bCatalysts: A = PMAAC-SnCl₄, B = PMAAC-TiCl₄, C = PS-SnCl₄[3], and D = PS-TiCl₄ [4].

TABLE 3. Results of Catalytic Ketal Formation^a

Catalyst	R in alcohol	n in ketone	Time, h	Yields, %
PMAAC-SnCl ₄	-H	1	2	92
		2	2	100
		3	2	100
	-CH ₃	1	2	85
		2	2	100
		3	2	100
PMAAC-TiCl ₄	-H	1	2	93
		2	2	100
		3	2	100
	-CH ₃	1	2	87
		2	2	100
		3	2	100
PS-SnCl ₄ [3]	-H	1	4	72
		2	4	96
		3	4	65
PS-TiCl ₄ [4]	-H	1	2	87
		2	2	99
		3	2	86
	-CH ₃	1	2	28
		2	2	44
		3	2	24

^aReaction condition: mole ratio of ketone/alcohol = 1:1 in all reactions; the yields were determined by GC.

TABLE 4. Yields of Reuse in Catalytic Ketal Formation^a

	Reuse times							
	1	2	3	4	5	6	7	8
PMAAC-SnCl ₄	100	100	100	100	100	100	100	98
PMAAC-TiCl ₄	100	100	100	100	100	100	100	100
PS-SnCl ₄ [3]	100	55	20	10				

^aReaction condition: 1 g of the catalysts was reused in the ketal formation reaction of cyclohexanone with ethylene glycol, the reaction time was 1 h for each reaction, and the yields were determined by GC.



Reuse Property of the Polymer Catalysts

The results of ketal formation for cyclohexanone with ethylene glycol catalyzed by PMAAC-SnCl₄ and PMAAC-TiCl₄, respectively (Table 4), show that the reuse capability of these catalysts is much better than that of PS-SnCl₄ [3] and PS-TiCl₄ [4]. In the ketal formation of cyclohexanone with ethylene glycol, the catalytic activity of the PMAAC-SnCl₄ and PMAAC-TiCl₄ catalysts remains completely unchanged even after being reused 8 times. It is fully evident that the PMAAC-SnCl₄ and PMAAC-TiCl₄ catalysts are very stable and exhibit high catalytic activity due to the β-diketone groups which had been introduced into the polymer backbone.

CONCLUSIONS

A new polymer carrier containing β-diketone groups, polymethacrylacetone (PMAAC), was synthesized and combined with stannic chloride or titanium tetrachloride to form two very stable polymeric Lewis acid complexes comprising a six-membered ring structure. Both polymer-supported Lewis acid catalysts, PMAAC-SnCl₄ and PMAAC-TiCl₄, not only showed good catalytic activity in many organic reactions such as esterification, acetalation, and ketal formation, but also excellent stability as evidenced by their ability to be reused. Therefore, complex catalysts of stannic chloride or titanium tetrachloride with a polymer carrier containing β-diketone groups will be useful as polymer-supported Lewis acid catalysts in industrial applications.

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