

POLYMER-SUPPORTED LEWIS ACID CATALYSTS. VI. POLYSTYRENE-BONDED STANNIC CHLORIDE CATALYST

RAN Ruicheng (冉瑞成) and FU Diankui (付殿奎)

(Department of Chemistry, Peking University, Beijing 100871)

ABSTRACT

A polystyrene-bonded stannic chloride catalyst was synthesized by the method of lithium polystyryl combined with stannic chloride. This catalyst is a polymeric organometallic compound containing 0.25 mmol Sn (IV) /g catalyst. The catalyst showed sufficient stability and catalytic activity in organic reaction such as esterification, acetalation and ketal formation, and it could be reused many times without losing its catalytic activity.

INTRODUCTION

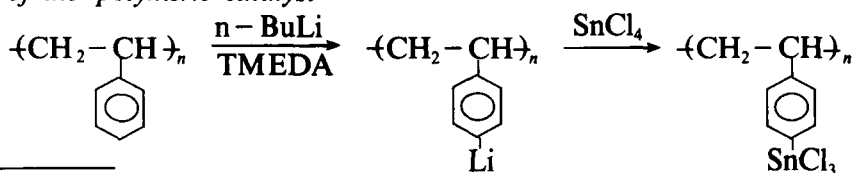
In 1970's, Neckers and his colleagues reported a polymer protected aluminum trichloride reagent which could be used as a catalyst of esterification and acetalation^[1-3]. In the past years, we had reported a series of polymer supported Lewis acid catalysts for organic reactions and cationic polymerizations^[4-9].

These catalysts showed sufficient stability and catalytic activity in many organic reactions, such as esterification, acetalation and ketal formation. Some of them also can catalyze cationic polymerization of α -methylstyrene^[10]. However, these catalysts are polymeric complexes of a Lewis acid with a polymer carrier, in which the Lewis acid can be washed out slowly by solvent during reaction. So their stability, e. g. property of reuse, are not perfect, and it would still lead to pollution of the Lewis acid.

In order to prevent from the pollution of the Lewis acid in polymer-supported Lewis acid catalysts, a polystyrene-bonded Lewis acid, stannic chloride, a new type of polymeric catalyst, was reported in this paper. Basically, this catalyst is an organometallic compound, so the metal atom of the Lewis acid in the catalyst cannot be washed out by solvents in reaction system. The new polymeric catalyst exhibited better stability and catalytic activity with the character of the Lewis acid in some organic reactions.

EXPERIMENTAL

Synthesis of the polymeric catalyst



Scheme 1 The method of synthesis of the catalyst

150 mL of cyclohexane, 20 g of beads of crosslinked polystyrene (3% DVB, 6–50 mesh) and 30 mL of N, N, N', N'-tetramethylethylenediamine (TMEDA) were added in proper order into a three-necked flask with a stirrer, a condenser with a dry tube and a rubber stopper. After heating for 10 minutes at 55 °C, 20 mL of n-BuLi (3 M) were added into the reaction system with syringe under nitrogen atmosphere. After 15 minutes, the polymer beads changed from white to red in color. The reaction was continued for 1 h, then cooled to room temperature and 10 mL solution of stannic chloride in cyclohexane (50%, V/V) were added into the reaction system. After stirring for 20 minutes, the solution of the reaction system was discarded. The polymer beads were washed 3 times with methanol, then dried in vacuum for 72 h at 50 °C.

Determination of the quantity of stannic chloride bonded on polymer

The chlorine content of the polymeric catalyst was determined volumetrically with a method described by Ran and Shen^[9]. The content of Sn(IV) metallic ion in the polymeric catalyst was measured by the weight method. The ratio of chlorine to Sn(IV) ion can be found.

Determination of the acidity of the polymeric catalyst

The pH of the acetone-water solution, obtained by hydrolyzing the polymeric catalyst samples in acetone-water, were determined at 25 °C with a pH meter.

Ultraviolet and infrared spectral analysis

UV spectra of the model compound, uncrosslinked polystyrene combined with stannic chloride by the same method described above, were obtained with an ultraviolet/visible spectrophotometer (Shimadzu UV-250). The infrared spectra of the same samples 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 polystyrene-bonded stannic chloride catalyst. It was refluxed in benzene with a Dean-Stark trap for 2 h at 85–95 °C. Yields of these reactions were determined by gas chromatography (SP-2307 type) against an internal standard.

RESULTS AND DISCUSSION

Preparation of the polymeric catalyst

The polymeric catalyst, polystyrene-bonded stannic chloride, was synthesized by the method as shown in scheme 1. The contents of metal ion Sn(IV) and chlorine in the polymeric catalyst were 3.0% Sn(IV) and 1.9% Cl which corresponded to 0.25 mmol Sn(IV)/g catalyst and 0.535 mmol Cl/g catalyst, respectively. So the ratio of Cl to Sn(IV) was 2.14:1, which means that on the average, a Sn(IV) atom linked with 2.14 atoms of Cl in the polymeric catalyst. In other words, there were about 70% of Sn(IV) linked with at least two

phenyls of polystyrene. It would increase by 4.1% of crosslinking degree (up to 7.1%) of the catalyst. This result was confirmed by swelling tests of the polymeric catalyst and the beads of crosslinked polystyrene carrier (see Fig. 1).

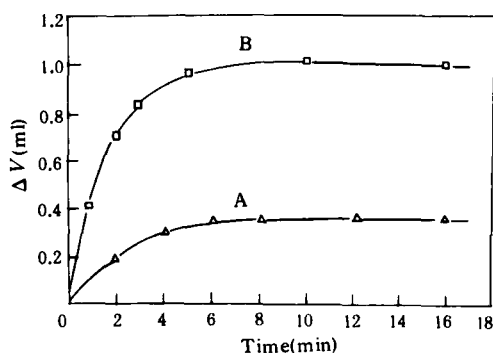


Fig.1 Dependence of increase in volume of the polystyrene-bonded stannic chloride and polystyrene carrier beads on time by swelling in chloroform
A, the polymer catalyst; B, polystyrene

Acidity of the solution containing the catalyst beads

The pH of an acetone-water solution (60%) containing polystyrene-bonded stannic chloride catalyst beads was shown in Figure 2, which shows that the acidity due to hydrolysis of the stannic chloride bonded on polystyrene reached equilibrium in 10 minutes. It is well known that the acidity of a Lewis acid substituted by an organic group depends on type and amount of the organic group. Generally, the acidity is stronger in the case of substituted by aromatic groups than by aliphatic groups and is weaker with increasing number of organic groups^[10]. So the polystyrene-bonded stannic chloride catalyst would be a good polymer-supported Lewis acid catalyst with stronger acidity.

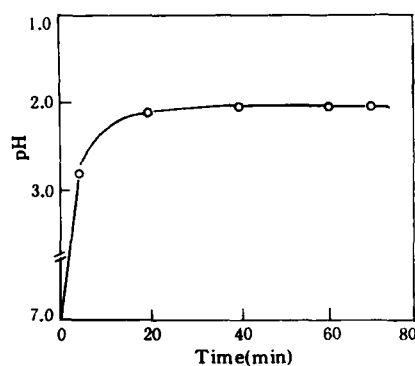


Fig.2 The pH dependence on time in 50 mL acetone-water solution containing 1 g polystyrene-bonded stannic chloride catalyst beads

UV and IR spectral analysis

The UV spectra of uncrosslinked polystyrene-bonded stannic chloride are shown in Figure 3. It was found that a new absorption band at 285 nm appeared which could be caused by the formation of polystyrene-bonded stannic chloride, for there was no absorption band at 285 nm for polystyrene^[11].

The IR spectrum of PS-SnCl_4 and PS were similar except that the new absorption bands appeared at 450 cm^{-1} and $1500\text{--}1650\text{ cm}^{-1}$ [11].

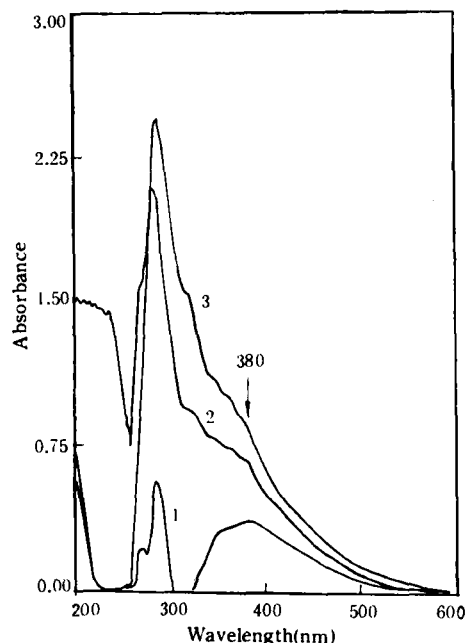


Fig. 3 UV spectra of uncrosslinked polystyrene bonded stannic chloride in DMSO
1) 1.25%; 2) 2.5%; 3) 5.0%; respectively.

Results of catalytic activity on organic reactions.

(1) Results of catalytic esterification

Yields of esterification of carboxylic acids with *n*-butanol in the presence of the polystyrene bonded stannic chloride catalyst were shown in Table 1.

It was evident that the catalytic activity of polystyrene-bonded stannic chloride catalysts was not better than that of the complex of polystyrene and stannic chloride (PS-SnCl_4)^[4] in esterification. This outcome could be explained by two reasons. First, the Lewis acidity would be weaker by decreasing chlorine of stannic chloride in the catalyst, which was substituted by one or more of the organic groups.

Table 1 Yields of catalytic esterification of carboxylic acid with *n*-butyl alcohol[‡]

R in the acids	Catalyst *	Time (h)	Yields (%)
-CH ₃	A	2	42
	B	4	74
	C	4	0
-CH ₂ CH ₃	A	3	39
	B	4	100
	C	4	5
- 	A	3	11
	B	4	22
	C	4	0

* Catalysts: A = $\text{P}-\langle\bigcirc\rangle-\text{SnCl}_3$; B = $\text{P}-\langle\bigcirc\rangle\cdot\text{SnCl}_4$ [4]; C = PSt.

‡ The mole ratio was acid /alcohol = 1:2; the yields were determined by GC.

as the phenyl of the polystyrene carrier^[10]. On the other hand, owing to the increase of crosslinking degree, the reaction which was carried out in the pores of the polymer carrier would be more difficult for the bulky organic reagent.

(2) Results of catalytic acetalation

The yields of acetalation of substituted benzaldehydes with *n*-butyl alcohol and ethylene glycol in the presence of the polystyrene-bonded stannic chloride catalyst were shown in Table 2. From the Table, it could be seen that the catalytic activity of the polystyrene bonded stannic chloride catalyst was not better than that of the polystyrene stannic chloride complex catalyst in the acetalation reactions of substituted benzaldehydes with *n*-butyl alcohol, but the catalytic activity was very good in the reaction with ethylene glycol. Evidence by the volume effect of the organic reagent on catalytic activity of the polymer catalyst was obvious. So the result clearly showed that the crosslinking degree of polymer carrier increased in the polymer catalyst.

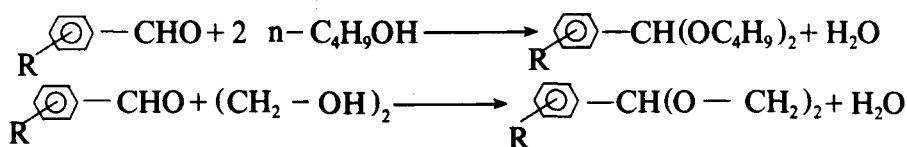


Table 2 Yields of catalytic acetalation of substituted benzaldehyde with *n*-butyl alcohol and ethylene glycol^{##}

R in the aldehyde	Catalyst*	Time (h)	Yield (%)	
			<i>n</i> -BuOH	(CH ₂ OH) ₂
H	A	1 / 3	14	100
	B	4	67	
O - OH	A	1 / 3	4	76
	B	4	31	
<i>p</i> - Cl	A	1 / 3	16	96
	B	4	81	
<i>p</i> - NO ₂	A	1 / 3	32	100
	B	4	100	
<i>m</i> - NO ₂	A	1 / 3	24	100
	B	4	86	

* Catalysts: A = $\text{P}-\text{C}_6\text{H}_4-\text{SnCl}_3$; B = $-\text{P}-\text{C}_6\text{H}_4 \cdot \text{SnCl}_4$ ^[4].

The mole ratio was alcohol / aldehyde = 1:1; Yields were determined by GC.

(3) Results of catalytic ketal formation

The results shown in Table 3 explained that the polystyrene-bonded stannic chloride catalyst exhibited very good catalytic activity in the ketal formation, in comparison with that of polystyrene-stannic chloride complex catalyst^[11].

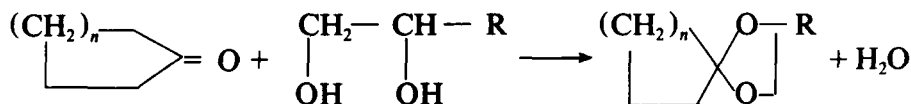


Table 3 Results of catalytic cyclic ketal formation [#]

Catalyst	R in the glycol	n in the cyclic ketone	Time (h)	Yield (%)
$\text{P}-\text{C}_6\text{H}_4-\text{SnCl}_3$	-H	1	2	81
		2	2	100
		3	2	100
	-CH ₃	1	2	73
		2	2	100
		3	2	100
$\text{P}-\text{C}_6\text{H}_4 \cdot \text{SnCl}_4^{[4]}$	-H	1	4	72
		2	4	96
		3	4	65

Reaction condition; alcohol /ketone=1:1 (mol/mol), reaction yields were determined by GC.

In the reaction the ketones were cyclopentanone (n=1), cyclohexanone (n=2), cycloheptanone (n=3), respectively.

(4) Results of reuse in catalytic ketal formation

The results of reuse in catalytic ketal formation of cyclohexanone with ethylene glycol were shown in Table 4. It was evident that the property of the polystyrene bonded stannic chloride catalyst was much better than that of polystyrene-stannic chloride complex catalyst in reusing catalytic ketal formation. This fact also fully proved that the stannic chloride bonded on polystyrene was far more stable than that of complex catalyst of polystyrene and stannic chloride^[4].

Table 4 Yields of reuse in ketal formation of cyclohexanone with ethylene glycol*

Reuse times	1	2	3	4	5	6	7	8	9
$\text{P}-\text{C}_6\text{H}_4-\text{SnCl}_3$	100	100	100	100	100	97	92	89	84
$\text{P}-\text{C}_6\text{H}_4 \cdot \text{SnCl}_4^{[4]}$	100	55	20	10					

*Reaction condition: 1 g of the catalyst reused in the reaction repeatedly, reaction time was 1 hour in each time reaction, yield was determined by GC.

CONCLUSION

The new polymer-supported Lewis acid catalyst, polystyrene-bonded stannic chloride catalyst, was synthesized by the method of lithium polystyryl combined with stannic chloride in cyclohexane. In the catalyst the ratio of Cl to Sn (IV) was 2.14: 1. This would increase by 4.1% of crosslinking degree (from 3% went up to 7.1%) in the polymer carrier. However, the new polymer-supported Lewis acid catalyst showed much better stability than that of complex catalyst of polymer and Lewis acid. Owing to the Cl of stannic chloride in the catalyst was substituted by one or more organic groups, the Lewis acidity of the catalyst would be weaker, but it exhibited good catalytic activity in many organic reactions. So the new type of polymer-supported Lewis acid catalyst would be a useful and

hopeful new polymeric catalyst.

Keywords :

Polymer-supported Lewis acid catalyst; Polystyrene-bonded stannic chloride catalyst; Catalytic activity in organic reactions

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