



Lewis Acid Ionic Liquid Immobilized on Chitosan for Synthesis of Dichlorophenylphosphine

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Lewis acid ionic liquid immobilized on chitosan as a new catalyst was prepared *via* the synthesis of 1-trimethoxy-silylpropyl-3-methylindazoliumchloride- AlCl_3 , 1-trimethoxy-silylpropyl-3-methylindazolium-chloride- InCl_3 and 1-trimethoxy-silylpropyl-3-methylindazolium-chloride- FeCl_3 and then grafting them to chitosan respectively. Their catalytic activities were investigated in the synthesis of dichlorophenylphosphine. The results showed when the three catalysts' amounts were 0.0225, 0.0195 and 0.015 g respectively, the substrate of benzene could be completely transformed into dichlorophenylphosphine on the conditions of the phosphorus trichloride 0.22 g, the molar ratio of phosphorus trichloride to benzene 1.8 : 1, the reaction temperature 75 °C and the reaction time 120 min. Moreover, the molar ratios of ionic liquid moiety to benzene were merely 0.285, 0.187 and 0.172 % respectively, which were much lower than that of the corresponding pure ionic liquids to benzene. The catalyst can be reused for many times with fine catalytic efficiency. In addition, the new catalyst using chitosan with the higher deacetylation degree as carrier could improve catalytic activity and reusability.

Key Words: Chitosan, Lewis acid ionic liquids, Dichlorophenylphosphine, Immobilization, Catalyst.

INTRODUCTION

Dichlorophenylphosphine, also named as phenylphosphonic dichloride, is one of the most important monomers in the synthesis of aromatic organic phosphine compounds, as well as preparation of flame retardants, plasticizers, pesticides, nylon stabilizers and dyes¹. The study on dichlorophenylphosphine has been very active in the field of intermediates synthesis^{2,3}. It has been reported that the synthetic route of dichlorophenylphosphine can be listed such as phosphorus trichloride and hydrargyrum diphenyl in a sealed and heated reaction, phosphorus trichloride and benzene through gas phase reaction, the thermal decomposition of trichloro diphenyl phosphine, ultrasonic irradiation synthesis of dichlorophenylphosphine, phosphorus trichloride and benzene catalyzed by anhydrous aluminum chloride. The last method had been widely used owing to being simple and mild. However, the aluminum trichloride consumption as catalyst is very large and it can not be recovered.

Currently, Friedel-Crafts reaction catalyzed by Lewis acid ionic liquid has become a fascinating and useful field because ionic liquids showed potential application prospects in the

green synthesis⁴⁻⁷. Ionic liquids possess many unprecedented properties, including infinitesimally low vapour pressure, high thermal stability, low toxicity and easy handling. All these properties make them alternative green reaction media for replacing volatile solvents in various catalytic processes in spite of the existence of some controversies⁸.

At present, several reports described the use of immobilized ionic liquids in various acid-catalyzed reactions⁹⁻¹², which can be fixed in the inorganic ionic liquid or organic polymer porous materials. Wang *et al.*¹³ reported the ratio of ionic liquid moiety in catalyst to the substrate of benzyl chloride was 1.0 mol. % using the catalyst of $\text{PmimCl-FeCl}_3(1.5)\text{-MCM-41}$, which was much lower than that of pure BmimCl-FeCl_3 (58.9 mol. %). Compared to pure Lewis acidic ionic liquids, heterogeneous catalyst showed additional advantages which can facilitate catalyst separation from the reaction system and decrease the ionic liquid consumption.

Chitosan (CS) derives from a very rich natural resource of chitin. It is the product of deacetylation of chitin, which is widely distributed in the nature world and is extremely abundant. In addition, it is a green renewable resource¹⁴. Herein, 1-trimethoxy-silylpropyl-3-methylimidazolium chloride- MCl_3

(M = Al, Fe, In) was synthesized¹¹ and then grafted onto chitosan. Using chitosan as the ionic liquid immobilization material has not been reported in the literature and the catalysts of Lewis acid ionic liquid immobilized on chitosan were firstly prepared and then were applied to catalytic synthesis of important intermediates dichlorophenylphosphine. With respect to the reports on other immobilized ionic liquids¹⁵⁻¹⁷, the present study aimed to further minimize the consumption of ionic liquid, facilitate the separation of catalyst from reaction system and improve reusability of catalyst.

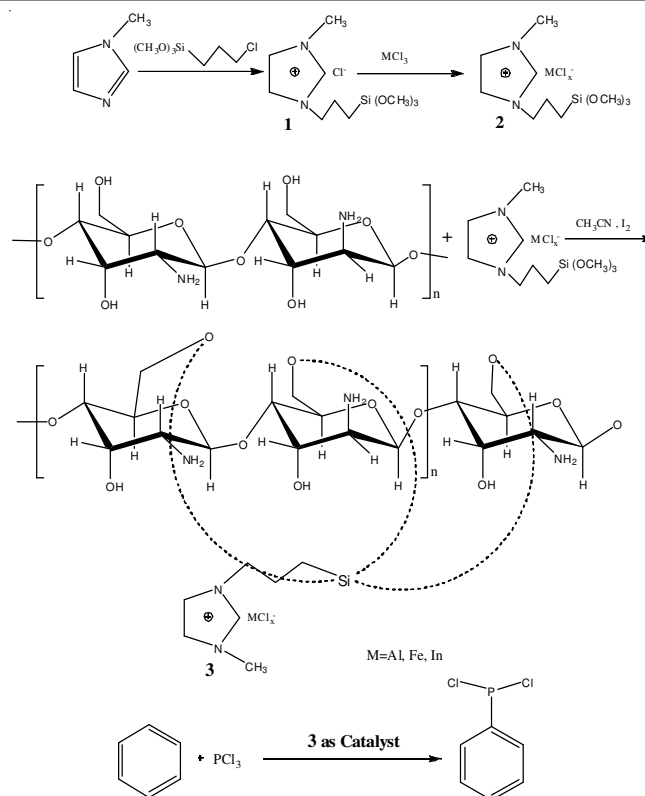
EXPERIMENTAL

Chitosans (CS) were obtained from Qingdao Haisheng Bioengineering Co. Ltd. They originated from crab shell and their deacetylation degrees were 80, 85, 90 and 95 % respectively. 1-Methylimidazole, 3-trimethoxysilylpropyl chloride, aluminium trichloride, indium trichloride, ferric trichloride, iodine, acetonitrile and dichloromethane were all analytical reagent grade and used as received. Other reagents were also analytical grade.

Catalyst preparation: 1-Trimethoxysilylpropyl-3-methylimidazolium chloride (compound **1**) was synthesized by refluxing 6.5 mL of 1-methylimidazole with 15 mL of 3-trimethoxysilylpropyl chloride at 65 °C for 72 h. Various amount of anhydrous MCl₃ (M for Al, In, Fe) according to different molar ratio of MCl₃ to the compound **1** (n, n = 1.0, 1.5, 2.0, or 3.0) were added to 0.46 g of the compound **1**, followed by stirring at 80 °C for 24 h. 1-Trimethoxysilylpropyl-3-methylimidazolium chloride-MCl₃ (compound **2**) was obtained^{10,11,18-20}. Then 0.6 g of chitosan, 0.3 g the compound **2** and 0.05 g iodine were dispersed in 35 mL dry acetonitrile solution, refluxing for 3 h under nitrogen atmosphere and afterward removing a part of solvent at 42 °C with reduced pressure distillation. Repeat refluxing and distilling for 8 times and then evaporate solvent. The obtained mixture was Soxhlet extracted with boiling dichloromethane for 36 h. Lewis acid ionic liquids had been immobilized on chitosan written Pmim Cl-MCl₃(n)-CS (compound **3**). The catalyst were prepared according to the proceeding as shown in **Scheme-I**.

X-ray diffraction (XRD-600-type, Shimadzu Corporation) was to determine the sample XRD spectra with CuK_α radiation ($\lambda = 1.542 \text{ \AA}$), tube voltage 40 kV, tube current 50 mA, DS/SS 0.5°, scan rate 4°/min (2 θ), scan range 8°-40°, test temperature 20 °C. Nicolet 5700 Fourier transform infrared spectroscopy was to analyze the infrared spectra of samples with a resolution of 4 cm⁻¹, KBr pellet. Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA 449 instrument with a heating rate of 10 °C min⁻¹ from room temperature to 700 °C under nitrogen atmosphere.

Synthesis of dichlorophenylphosphine: Add a certain amount of benzene, phosphorus trichloride and the catalyst (**Scheme-I**) in a three-neck flask, then experience a definite time for reaction at a certain temperature. Centrifuge it and wash the residue with petroleum ether. Dry and then reuse it. The reaction products were identified by a HP 5973 GC-MS. The concentration of reactants and products was determined by an Agilent Technologies 6890 gas chromatograph equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μ m) and a flame ionization detector (FID).



Scheme-I: Procedures for synthesis of novel catalyst to prepare dichlorophenylphosphine

RESULTS AND DISCUSSION

FT-IR spectra: As shown in Fig. 1(a-c), curve-b denoted the forming compounds **2** with reaction of FeCl₃, InCl₃, AlCl₃ and compound **1** respectively, while curve-a were their corresponding compound **3**. From the graphs, we found that the PmimCl-FeCl₃ (2.0)-CS displayed a similar FT-IR spectrum to that of the PmimCl-FeCl₃(2.0). Specially, stretching vibration bands at 3150; 2953, 2885; 1556, 1456, 1170 and 1242, 742 cm⁻¹; respectively to the aromatic C-H stretching; the aliphatic C-H stretching; the ring stretching of imidazolium molecule; and the C-Si stretching vibrations were observed for the both samples. Such observations suggested that the grafting process presented here did not change the structure of the chloroferrate ionic liquid.

Moreover, in the three FTIR spectra (a), (b) and (c), the clear characteristic absorption peak at 3450 cm⁻¹ while curve-a not assigned to the O-H stretching vibration peak of chitosan, but the peak obviously shrank compared to the absorption peaks of chitosan here. These can be explained *via* the decrease of the number of hydroxyl groups of the synthesized compounds **3**. The strong absorption peaks at near 1076 cm⁻¹ and 1257 cm⁻¹ were belonged to C-O stretching vibration peak and C-N stretching vibration peak of chitosan.

X-ray diffraction patterns: Take chitosan and three kinds of chitosan-based Lewis acid ionic liquid catalysts in characterization of X-ray diffraction. XRD patterns of three kinds of catalysts were very similar. They were very smooth and significantly different from that of Chitosan. The X-ray diffraction patterns of Chitosan and PmimCl-MCl₃ (2.0)-CS were shown in Fig. 2. Chitosan appeared strong diffraction peaks in 12°, 22° and 27°, while these peaks in PmimCl-MCl₃(2.0)-CS, XRD

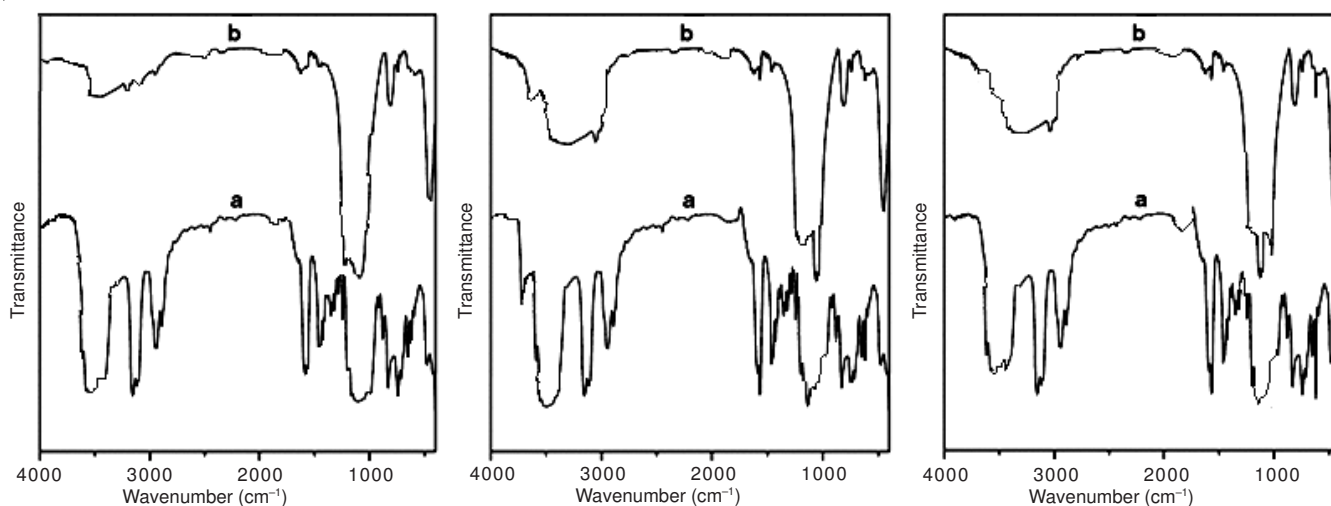


Fig. 1. FTIR spectra of Lewis acid ionic liquid immobilized on chitosan catalysts; (a) 1-Trimethoxysilylpropyl-3-methylimidazolium chloride- FeCl_3 (curve b) and PmimCl- $\text{FeCl}_3(2.0)$ -CS (curve a); (b) 1-Trimethoxysilylpropyl-3-methylimidazolium chloride- InCl_3 (curve b) and PmimCl- $\text{InCl}_3(2.0)$ -CS (curve a); (c) 1-Trimethoxysilylpropyl-3-methylimidazolium chloride- AlCl_3 (curve b) and PmimCl- $\text{AlCl}_3(2.0)$ -CS (curve a)

did not exist with only a smooth and decreased significantly peak in 22° . The reason was that the immobilization of PmimCl- $\text{MCl}_3(2.0)$ on chitosan led to the significant reduction of hydrogen bonds in the chitosan molecules with a lower crystallinity and an increase of no fixed pattern. These illustrated that the PmimCl- $\text{MCl}_3(2.0)$ had been immobilized on chitosan, reflecting that the synthesized compounds had been significantly undermined the originally strong hydrogen bonds within the chitosan molecules and increased clutter once again. This reveals the formation of new chemical bonds.

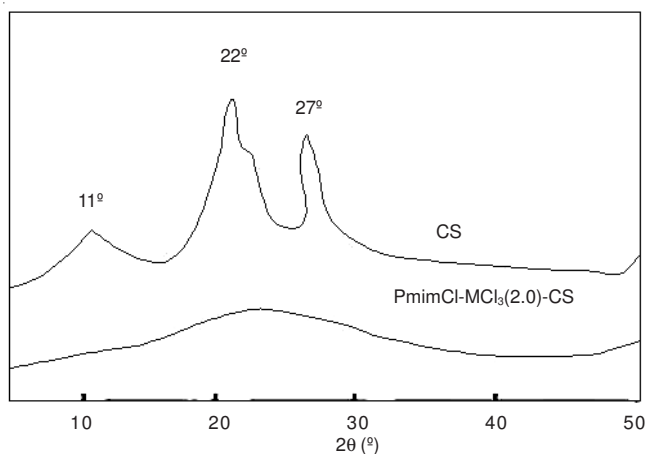


Fig. 2. X-ray diffraction patterns of CS and PmimCl- $\text{MCl}_3(2.0)$ -CS

TGA-DTG analysis: Fig. 3 (1) presents the TGA-DTG curves of PmimCl- $\text{InCl}_3(2.0)$ -CS, where two major weight losses in $35\text{--}120^\circ\text{C}$ and $425\text{--}560^\circ\text{C}$ were observed. The PmimCl- $\text{InCl}_3(2.0)$ -CS catalyst was the most stable in the three catalysts. The difference of TG-DTG between PmimCl- $\text{InCl}_3(2.0)$ -CS and PmimCl- $\text{InCl}_3(2.0)$ could be the most clearly reflected. The first weight loss centered at 65°C was apparently caused by desorption of physisorbed and chemisorbed water. For the second weight loss between 425°C and 560°C , this was attributed to the decomposition of the organic part of the PmimCl- $\text{InCl}_3(2.0)$ -CS. 1-trimethoxysilyl-propyl-3-

methylimidazolium chloride- $\text{InCl}_3(2.0)$ showed similar major weight loss in temperature range of from 450°C to 535°C [Fig.3(2)]. Moreover, the remaining weight of Lewis acid ionic liquid immobilized on chitosan at 700°C was 70 %, while that of single PmimCl- $\text{InCl}_3(2.0)$ was only 25 %. Lewis acid ionic liquid, which was immobilized on chitosan got more stable.

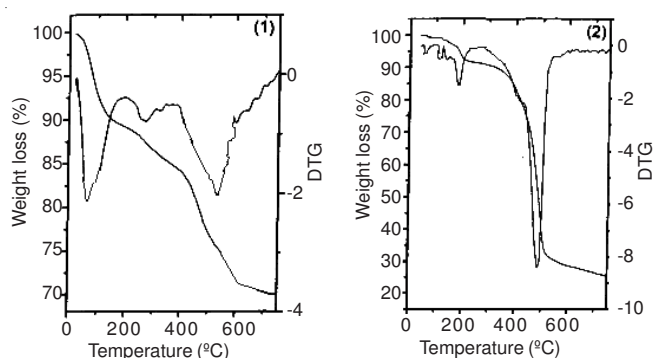


Fig. 3. TG-DTG curves of PmimCl- $\text{InCl}_3(2.0)$ -CS(DD = 90 %) (1) and PmimCl- $\text{InCl}_3(2.0)$ (2)

Catalytic properties

Effect of the molar ratio of $\text{MCl}_3/\text{PmimCl}$ on synthesis of dichlorophenylphosphine: The molar ratio of MCl_3 to compounds **1** had a notable effect (Table-1) on catalytic synthesis of dichlorophenylphosphine. The catalyst of PmimCl- $\text{MCl}_3(1.0)$ -CS showed a low catalytic activity (entry 2,6,10), while the catalyst following molar ratio of MCl_3 to compounds **1** from 1.0 to 1.5 (entry 3,7,11) displayed a high catalytic activity. The conversion of phosphorus trichloride and the selectivity of dichlorophenylphosphine reached 100 % after 180 min. Furthermore, when the molar ratio increased from 1.5 to 3.0, the conversion rate and the selectivity had not changed (entries 4, 8,12). It had been reported that FeCl_3 added to [Bmim]Cl was a complex chemical equilibrium, containing FeCl_3 , Fe_2Cl_6 , $[\text{Bmim}]^+ [\text{FeCl}_4]^-$ and $[\text{Bmim}]^+ [\text{Fe}_2\text{Cl}_7]^-$ mixture²¹⁻²⁶ according to the molar ratio of FeCl_3 to [Bmim]Cl.

When the molar ratio of FeCl_3 to $[\text{Bmim}]\text{Cl}$ was 1.0, FeCl_4^- was the major anion. When it reached or exceeded 1.5, Fe_2Cl_7^- was the main anion^{24,25}. As a fact, InCl_3 and AlCl_3 were very similar to FeCl_3 , therefore it was generally believed that Fe_2Cl_7^- , Al_2Cl_7^- , In_2Cl_7^- had catalytic activity in the Friedel-Crafts reaction, rather than FeCl_4^- , AlCl_4^- , InCl_4^- ²⁶. So it was easier to explain the reaction result of $\text{PmimCl-MCl}_3(1.0)\text{-CS}$ appearing obvious difference for catalytic synthesis of dichlorophenylphosphine. Thus, the best molar ratio of MCl_3 to compounds **1** was 2.0.

TABLE-1
RESULTS OF THE SYNTHESIS OF DCPD BETWEEN
BENZENE AND PHOSPHORUS TRICHLORIDE
OVER VARIOUS CATALYSTS

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	CS	0	0
2	$\text{PmimClAlCl}_3(1.0)\text{CS}$	8	100
3	$\text{PmimClAlCl}_3(1.5)\text{CS}$	76	100
4	$\text{PmimClAlCl}_3(2.0)\text{CS}$	100	100
5	$\text{PmimClAlCl}_3(3.0)\text{CS}$	100	100
6	$\text{PmimClFeCl}_3(1.0)\text{CS}$	7	100
7	$\text{PmimClFeCl}_3(1.5)\text{CS}$	73	100
8	$\text{PmimClFeCl}_3(2.0)\text{CS}$	100	100
9	$\text{PmimClFeCl}_3(3.0)\text{CS}$	100	100
10	$\text{PmimClInCl}_3(1.0)\text{CS}$	5	100
11	$\text{PmimClInCl}_3(1.5)\text{CS}$	70	100
12	$\text{PmimClInCl}_3(2.0)\text{CS}$	100	100
13	$\text{PmimClInCl}_3(3.0)\text{CS}$	100	100

Entries 1-13 were the reaction of benzene with phosphorus trichloride. The condition: CS (DD = 90 %). Phosphorus trichloride/benzene = 1.5/1 (mol), phosphorus trichloride 0.22 g, catalyst 0.02 g, $t = 180$ min, $T = 75$ °C

Effect of the amount of catalyst on synthesis of dichlorophenylphosphine: As shown in Fig. 4, with the increasing amount of catalyst $\text{PmimCl-MCl}_3(2.0)\text{-CS}$, the reaction conversion rate increased significantly, while the selectivity of dichlorophenylphosphine remained at 100 %. When the amount of the $\text{PmimCl-AlCl}_3(2.0)\text{-CS}$ was up to 0.0225 g, the reaction conversion reached 100 %. At the meantime, the molar ratio of the catalyst to substrated benzene was only 0.285 %, which was far lower than the amount of pure Lewis acid to ionic liquid used in catalytic synthesis²⁷. Similarly, $\text{PmimCl-FeCl}_3(2.0)\text{-CS}$ with 0.015 g and $\text{PmimCl-InCl}_3(2.0)\text{-CS}$ with 0.0195 g can make the reaction convert completely with no by-product and the corresponding molar ratio to substrated benzene was 0.172 % and 0.187 % respectively, which were far lower than the molar ratio of pure ionic liquid BimCl-FeCl_3 (58.9 mol %) used in catalytic synthesis²⁸. As the acidity order of Lewis acid was $\text{AlCl}_3 > \text{FeCl}_3 > \text{InCl}_3$, $\text{PmimCl-AlCl}_3(2.0)\text{-CS}$ should have the best catalytic activity in theory. But the experimental curve suggested its catalytic effect was not so good as $\text{PmimCl-FeCl}_3(2.0)\text{-CS}$ and $\text{PmimCl-InCl}_3(2.0)\text{-CS}$. The phenomenon was more and more obvious, especially when increasing the amount of catalyst. The results were mainly because $\text{PmimCl-AlCl}_3(2.0)\text{-CS}$ ionic liquid was more sensitive to moisture and thus easier to partial decomposition than the other two types of ionic liquids. The contact square to air increased with the increasing amount, so that the greater part was decomposed, making the difference

more obvious. In summary, the catalytic properties were determined not only by the strength of Lewis acid, but also by the characteristics of the metal itself²⁸.

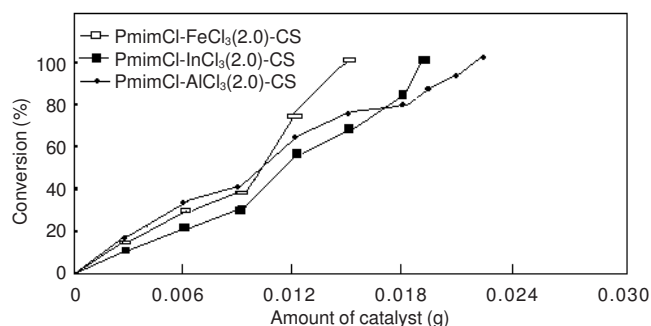
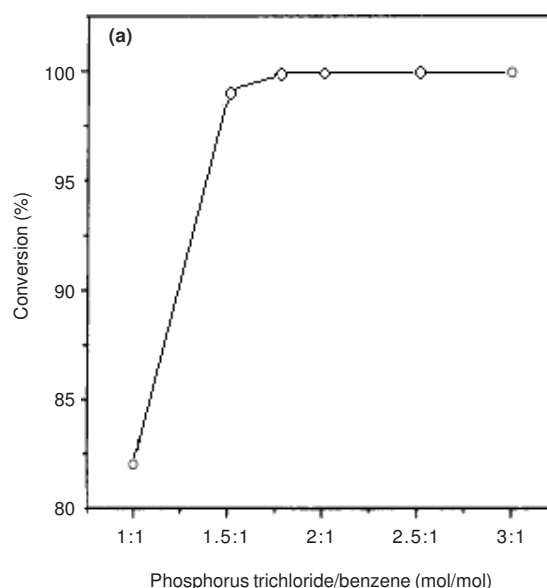


Fig. 4. Effect of the catalyst amount on the synthesis of dichlorophenylphosphine; condition: CS (DD = 90 %), phosphorus trichloride/benzene = 1.5/1 (mol), phosphorus trichloride 0.22 g, catalyst 0.02 g, $t = 180$ min, $T = 75$ °C

Effect of reaction condition on synthesis of dichlorophenylphosphine: At a certain condition, the $\text{PmimCl-InCl}_3(2.0)\text{-CS}$ (DD = 90 %) catalyst was chosen because it was more conducive to determine the effect of reaction condition and it was greatly stable in moist air. The results of Fig. 5 (a) showed that when the molar ratio of phosphorus trichloride to benzene was 1.5 : 1, the reaction conversion rate reached 97.5 % and when the molar ratio was up to 1.8 : 1, the reaction took the conversion as 100 %. Therefore, the most appropriate mole ratio of phosphorus trichloride to benzene was 1.8 : 1. Subsequently, the results from Fig. 5 (b) and (c) indicated that the reaction optimal conditions were the reaction temperature under 75 °C and the reaction time of 120 min.

Effect of reusability on the reaction yield: As shown in Table-2, its catalytic activity can reach over 90 % conversion rate in the optimum conditions when $\text{PmimCl-AlCl}_3(2.0)\text{-CS}$ was reused for 3 times. When it turned to the 4th use, the conversion rate was at 82 %. Obviously, the repetitive effects of $\text{PmimCl-AlCl}_3(2.0)$ and $\text{AlCl}_3(2.0)\text{-CS}$ for the catalytic reaction were lower on synthesis of dichlorophenylphosphine



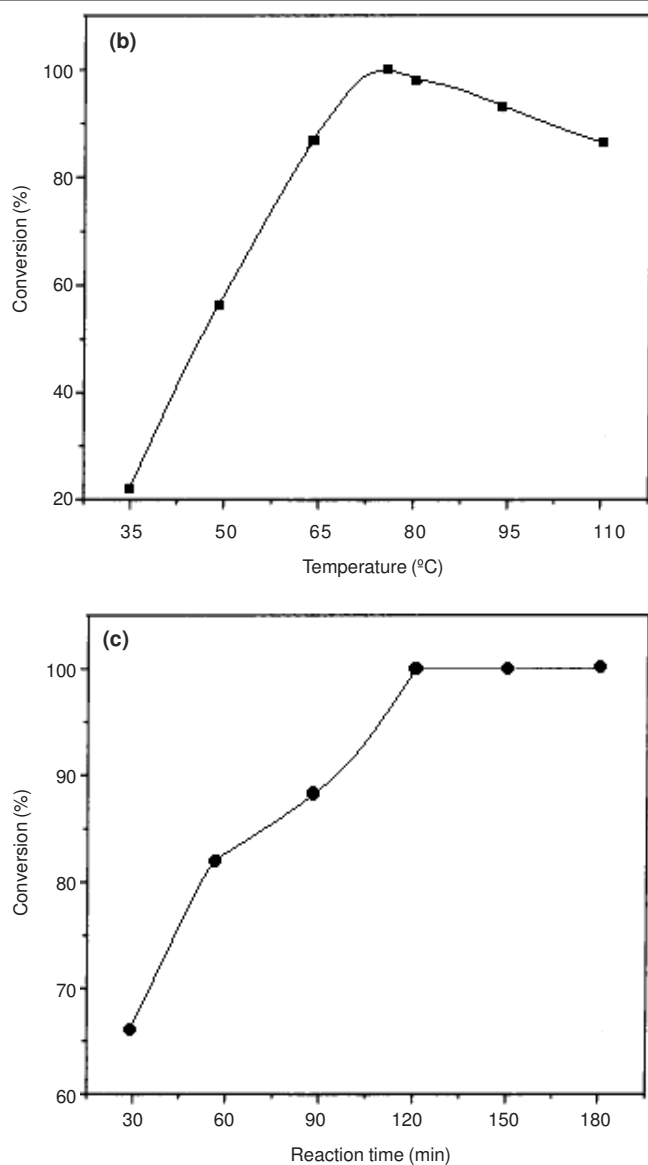


Fig. 5. Effect of phosphorus trichloride/benzene(a), Temperature(b) and Reaction time(c) on dichlorophenylphosphine synthesis; Condition (a): Phosphorus trichloride 0.22 g, catalyst 0.02 g, $t = 180$ min, $T = 70$ °C; Condition (b): Phosphorus trichloride/ benzene=1.8/1(mol), phosphorus trichloride 0.22g, catalyst 0.02 g, $t = 180$ min; Condition (c): phosphorus trichloride/benzene = 1.8/1(mol), phosphorus trichloride 0.22 g, catalyst 0.02 g, $T = 75$ °C

(entries 4-7). The repetitive utilization rate of PmimCl-AlCl₃(2.0)-CS catalyst was improved when increasing the catalyst to the amount of 0.05 g, its repetitive times reached entry 9 and the conversion rate of reaction remained at 90 % (entries 20-21). The stability of the catalyst was PmimCl-InCl₃(2.0)-CS > PmimCl-FeCl₃(2.0)-CS > PmimCl-AlCl₃(2.0)-CS, which can be reflected in the table(entries 8-19). The results showed that PmimCl-InCl₃(2.0)-CS was more stable to moisture and thus had a strong catalytic activity after being reused many times. These also demonstrated that the Lewis acid ionic liquid immobilized on chitosan catalyst significantly improved the reusability performance.

Effect of deacetylation degree on catalytic properties:

In order to effectively examine the effect of chitosan deacetylation degree on the catalytic efficiency and the repeated

performance, the PmimCl-InCl₃(2.0)-CS catalyst was selected to determine the influence, because it was the most stable in moist air. The experimental results were plotted into Figs. 6 and 7. The figures suggested that the higher deacetylation degree of chitosan represented the higher catalytic activity to synthesis of dichlorophenylphosphine. It was because the higher deacetylation degree had more positive character and stronger force with ionic liquid, thus it led to strong interaction with ionic liquids containing the larger reaction surface area. In a sum, chitosan with the higher deacetylation degree denoted the more catalytic activity and the more repetitive times on a certain conditions.

TABLE-2
REUSABILITY OF VARIOUS CATALYSTS FOR THE
SYNTHESIS OF DCPD BETWEEN BENZENE AND
PHOSPHORUS TRICHLORIDE

Entry	Catalyst	Run time	Conversion (%)	Selectivity (%)
1	PmimClAlCl ₃ (2.0)CS	1 st	100	100
2	PmimClAlCl ₃ (2.0)CS	3 rd	90	100
3	PmimClAlCl ₃ (2.0)CS	4 th	82	100
4	PmimClAlCl ₃ (2.0)	1 st	100	100
5	PmimClAlCl ₃ (2.0)	3 rd	27	100
6	AlCl ₃ (2.0)CS	1 st	100	100
7	AlCl ₃ (2.0)CS	4 th	13	78
8	PmimClFeCl ₃ (2.0)CS	1 st	100	100
9	PmimClFeCl ₃ (2.0)CS	5 th	91	100
10 ^a	PmimClFeCl ₃ (2.0)	1 st	100	100
11 ^a	PmimClFeCl ₃ (2.0)	3 rd	36	100
12	FeCl ₃ (2.0)CS	1 st	100	100
13	FeCl ₃ (2.0)CS	4 th	27	81
14	PmimClInCl ₃ (2.0)CS	1 st	100	100
15	PmimClInCl ₃ (2.0)CS	8 th	89	100
16	PmimClInCl ₃ (2.0)	1 st	100	100
17	PmimClInCl ₃ (2.0)	8 th	58	100
18	InCl ₃ (2.0)CS	1 st	100	100
19	InCl ₃ (2.0)CS	4 th	39	88
20	PmimClAlCl ₃ (2.0)CS	1 st	100	100
21	PmimClAlCl ₃ (2.0)CS	9 th	92	100

Entries 1-19 were the reaction of benzene with phosphorus trichloride. Phosphorus trichloride/benzene = 1.8/1(mol); phosphorus trichloride 0.22 g; catalyst respectively 0.0225 g (contained AlCl₃), 0.0195 g (contained AlCl₃), 0.015 g (contained AlCl₃); $t = 1200$ min; $T = 75$ °C, CS (DD = 90 %). Entries 20-21 are the reaction of benzene with Phosphorus trichloride. Phosphorus trichloride/benzene = 1.8/1 (mol), Phosphorus trichloride 0.22 g, catalyst 0.05g, $t = 120$ min, $T = 75$ °C. aRef. [27]

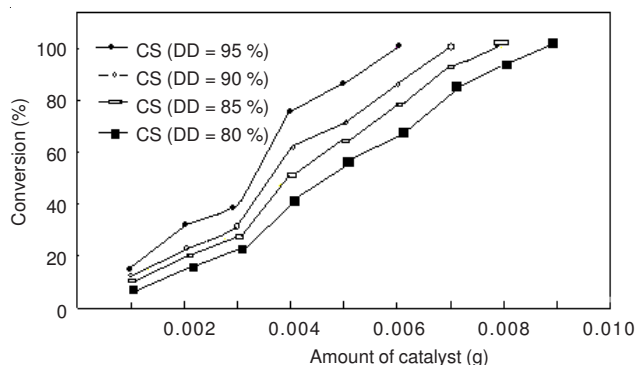


Fig. 6. Effect of deacetylation degree on catalytic activity; Condition: CS(DD = 90 %), phosphorus trichloride/benzene = 1.5/1 (mol), Phosphorus trichloride 0.22 g, catalyst 0.02 g, $t = 120$ min, $T = 75$ °C

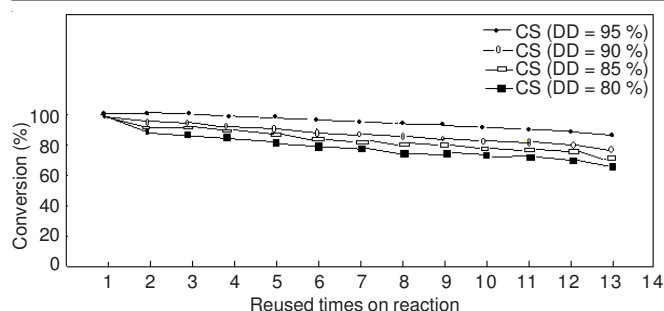


Fig. 7. Effect of deacetylation degree on reusability; Condition: CS (DD = 90 %), phosphorus trichloride/benzene = 1.5/1 (mol), phosphorus trichloride 0.22 g, catalyst 0.02 g, t = 120 min, T = 75 °C

Conclusion

Through synthesizing the catalysts of PmimCl-AlCl₃(1.0)-CS, PmimCl-AlCl₃(1.5)-CS, PmimCl-AlCl₃(2.0)-CS and PmimCl-AlCl₃(3.0)-CS, we found that PmimCl-AlCl₃(2.0)-CS and PmimCl-AlCl₃(3.0)-CS had a significant catalytic effect and had the same catalytic activity. Both PmimCl-FeCl₃(2.0)-CS and PmimCl-InCl₃(2.0)-CS had a similar character. The catalytic activity order of PmimCl-FeCl₃(2.0)-CS > PmimCl-InCl₃(2.0)-CS > PmimCl-AlCl₃(2.0)-CS demonstrated that the catalytic properties were not only determined by the strength of Lewis acid, but also by the characteristics of the metal ionic itself. The catalyst containing AlCl₃ was the most unstable catalyst, while the catalyst using InCl₃ can prevent from destroying the moisture in the air and is the most stable and convenient catalyst. The result suggested that the optimum conditions of the dichlorophenylphosphine synthesis were that phosphorus trichloride/benzene = 1.8/1 (mol), phosphorus trichloride 0.22 g, reaction time 120 min, reaction temperature 75 °C, the minimum amount of catalysts 0.0225 g (contained AlCl₃), 0.0195 g (contained InCl₃) and 0.015 g (contained FeCl₃) respectively. Under the optimum condition, the molar ratio of catalyst to benzene were only 0.285 %, 0.187 %, 0.172 %, which were far lower than the traditional reporting amount of catalyst. The new catalysts can be recycled and reused, keeping the high catalytic activity after using for many times. With the higher deacetylation degree of chitosan, the new type of synthesized catalyst had a larger contribution on catalytic activity and reusability. So it could offer a catalytic way as a new type of carrier for further study.

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