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Phosphazenium chloride catalysts immobilized on SBA-15 mesoporous material and silica gel: new exceptionally active catalysts for the chlorination of organic acids

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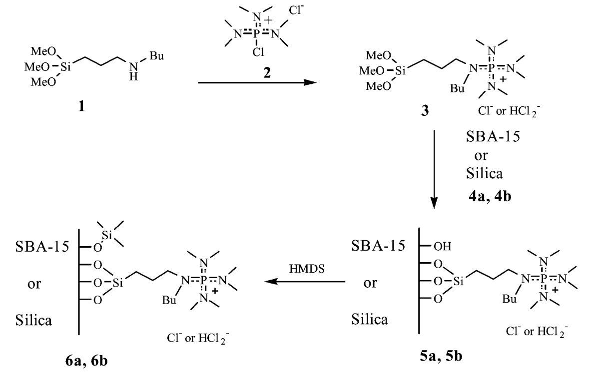
Novel reusable phosphazenium chloride catalysts immobilized on SBA-15 mesoporous material and silica gel show exceptional activities and selectivities even in the continuous chlorination reaction of organic acids with thionyl chloride or phosgene.

Organic acid chlorides have been used as raw materials in producing fine chemicals such as polymerization initiators, surfactants, agrochemicals, and pharmaceuticals because of their high reactivity. Product yields in the chlorination of organic acids with thionyl chloride and phosgene, however, are low without using active catalysts due to high preference for the formation of acid anhydride. Homogeneous base catalysts, such as imidazole, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) and N,N-dimethyl formamide show high activity even at low temperature,[1] but the difficulty in the separation of used catalysts from products reduces the advantages of catalyst application.

Quaternary ammonium chloride and phosphonium chloride catalysts immobilized on polystyrene resin are active in the chlorination reactions.[2] Benzyl groups of polystyrene resin combining catalysts, however, are fragile at elevated temperature of 80–90 °C, bringing about an irreversible catalyst deactivation. On the other hand, guanidinium chloride catalysts immobilized on silica, not polystyrene resin, show a high stability compared to quaternary ammonium chloride catalysts.[3] Even though these immobilized catalysts provide a convenient separation, they require a high reaction temperature of 80–160 °C to obtain a feasible yield of chlorination products.

Phosphazenes composed of nitrogen and phosphorous atoms are known to be very strong bases with high pK_a of 24–47 due to the number of combining phosphazene units.[4] Since the large flat nuclei of phosphazene molecules are very suitable for the delocalization of positive charges, phosphazenium chloride can work as a catalyst supplying activated chloride ions to organic acids.

We prepared phosphazenium chloride catalysts immobilized on SBA-15 mesoporous material and silica gel, following the procedure described in Scheme 1. These catalysts show exceptional activity and selectivity in the chlorination of 2-ethylhexanoic acid, achieving more than a 95% yield at ambient temperature only for 30 min reaction.



Scheme 1 Immobilization of phosphazenium chloride on SBA-15 mesoporous material (a) and silica (b).

SBA-15 mesoporous material was prepared by using poly-(alkylene oxide) block copolymer detergent (average M_n = 5,800, Aldrich, P-123) as a template.[5] Tetraethoxysilane (Aldrich, 98%, TEOS), P-123, hydrochloric acid (Daejung, 35%), and deionized water were mixed to make a reaction mixture with a composition of 1 SiO_2 : 0.017 P-123 : 2.9 HCl : 203 H_2O. SBA-15 mesoporous material was obtained by heating the reaction mixture at 90 °C for 24 h. Pore diameter and surface area of calcined mesoporous material were determined from its adsorption isotherm of nitrogen to be 100 Å and 590 $m^2 g^{-1}$, respectively. Silica gel (Aldrich, Davisil grade 646, 35–60 mesh) was also used as a support for phosphazenium chloride. Its surface area and average pore diameter provided by the manufacturer were 300 $m^2 g^{-1}$ and 150 Å, respectively.

Silane containing a secondary amine **1** was synthesized by reacting 3-chloropropyltrimethoxysilane (Aldrich, 97%) with *n*-butylamine (Junsei, 95%) in a nitrogen atmosphere at 115–120 °C for 20 h. Separately, a precursor of phosphazenium chloride **2** was synthesized by the reaction of hexamethylenephosphoramide (Aldrich, 99%, HMPA) with phosgene gas (Korea Fine Chemicals, 99%) in methylene chloride. A part of the dissolved precursor (1.05 equiv.) **2** in anhydrous methylene chloride was added to a solution of secondary amine (1.0 equiv.) **1** and triethylamine (1.2 equiv.) diluted in the same solvent at 10 °C under a nitrogen stream. Then the coupling between **1** and **2** was carried out at room temperature for 10 h. After evaporating the solvent and triethylamine, homogeneous phosphazenium chloride **3** was obtained as a very hygroscopic solid. Dissolved phosphazenium chloride **3** in anhydrous chloroform reacted with hydroxyl groups of dried SBA-15 mesoporous material **4a** and silica gel **4b** under reflux conditions for 24 h. Immobilized phosphazenium chlorides **5a** and **5b** were obtained by washing with chloroform, toluene and ether followed by filtering and drying in a vacuum oven at 110 °C. Finally, unreacted hydroxyl groups of supports were masked by reacting them with 1,1,1,3,3,3-hexamethylene disilazene (Aldrich, 97%, HMDS). Phosphazenium chloride-immobilized catalysts were denoted as PZ/SBA **6a** and PZ/SIL **6b** catalyst according to their supports.

^1H and ^{13}C NMR spectra of phosphazenium chloride **3** show the formation of phosphazenium chloride and the disappearance of residual secondary amine in ^{13}C NMR.[6]

Mesopores of SBA-15 mesoporous material remained even after immobilizing phosphazenium chloride, while its pore volume and surface area were considerably decreased by immobilizing large phosphazenium chloride molecules. IR absorption bands at 2800–3000 cm^{-1} of the PZ/SBA catalyst exhibited the immobilization of organic molecules on the SBA-15 mesoporous material. These bands were retained even at 300 °C under evacuation, indicating stable immobilization of phosphazenium salt on the mesoporous material. The ^{31}P MAS NMR spectrum of the phosphazenium chloride-immobilized catalyst **6a** also showed a phosphorus peak at a chemical shift of

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37.6 ppm as shown in Fig. 1, otherwise the phosphorus peak of homogeneous phosphazenium chloride showed a chemical shift of 47.7 ppm. The lower chemical shift of phosphorus of the PZ/SBA **6a** catalyst suggests that phosphazenium ion was immobilized on the support as a salt.[7]

Phosphazenium chloride catalysts immobilized on the supports were also prepared by a stepwise reaction: the immobilization of secondary amine **1** on the support, masking of non-reacted hydroxyl groups with HMDS, and the coupling of the precursor **2** to immobilized secondary amine. These catalysts, denoted as PZ/SBA **7a** and PZ/SIL **7b** catalysts according to their supports as for **6a** and **6b**, showed identical IR and NMR spectra to those of PAZ/SBA **6a** and PZ/SIL **6b** catalysts, indicating that the immobilization procedure did not bring about any change in the immobilized state of phosphazenium chloride.

Hydrogen chloride is additionally coordinated on phosphazenium chloride, similar to its additional coordination on guanidinum chloride.[8] The immobilizing amounts of phosphazenium chloride were 0.33, 0.29, 0.36 and 0.22 mmol g^{-1} on PZ/SBA **6a**, PZ/SIL **6b** PZ/SBA **7a**, and PZ/SIL **7b** catalysts, respectively.

Phosphazenium chloride catalysts immobilized on SBA-15 mesoporous material and silica gel, regardless of their immobilization procedures, were highly active and selective in the chlorination of benzoic acid at 40 °C. Table 1 shows 97.0% yield of the chlorinated product over the PZ/SBA **7b** catalyst after only 1 h. Exceptional activity and selectivity for the chlorinated products were also obtained over immobilized phosphazenium catalysts in the chlorination of aromatic and aliphatic organic acids. Although the reaction was carried out at elevated temperature for the reaction of terephthalic acid, steric acid and lauric acid because of their high melting points, these catalysts provided high yield of above 95%.

Uncatalyzed chlorination of 2-ethylhexanoic acid with thionyl chloride was slow at ambient temperature, achieving only 10% yield of chlorinated product for 1 h reaction. On the other hand, the PZ/SBA **7a** and PZ/SIL **7b** catalysts require only 30 min for quantitative completion of the chlorination reaction. The immobilized phosphazenium chloride catalysts can be repeatedly used in the chlorination reaction of organic acids. No meaningful lowering of catalytic activity was observed during 6 repeated runs, adding new reactant after decanting reacted materials. A continuous flow chlorination of 2-ethylhexanoic acid with thionyl chloride exhibited high conversion of about 95% following a single pass of the reactant through the catalyst bed with LHSV = 31.3 h^{-1} at ambient temperature.†

Since positive charges are highly delocalized on phosphazenium nuclei, chloride anions coordinated on them show strongly nucleophilic properties. The high feasibility of the reaction of chloride anions with organic acid molecules on phosphazenium nuclei results in a high activity. In other words, the chlorination can proceed through the attack of chloride anions coordinated on phosphazenium nuclei to electrophilic carbonyl groups of organic acids, forming a complex with it.

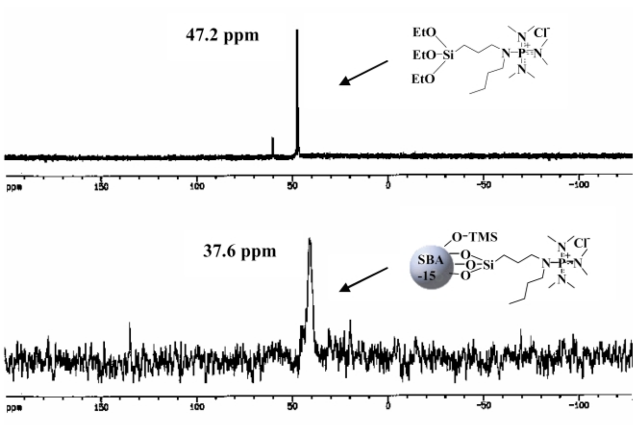

Fig. 1 ^{31}P solid MAS NMR spectra of the immobilized phosphazenium chloride PZ/SBA **6a** and homogeneous phosphazenium chloride.

Table 1 Chlorination of aromatic and aliphatic acids with thionyl chloride and phosgene as chlorinating regents over phosphazenium chloride-immobilized catalysts[a]

Acid	Catalyst	Temp./ °C	Time/h	Conversion (%)	Selectivity (%)
Benzoic[bc]	None	40	10	94	45
″	**6a**	″	2.5	100	99
″	**6b**	″	3	100	98
″	**7a**	″	1	100	97
″	**7b**		4	98	97
Terephthalic[bd]	**7a**	120	3	100	99
″	**7b**	″	4.5	100	99
2-Ethyl-hexanoic[b]	None	40	18	95	60
″	**7a**	25–30	0.5	100	99
″	**7b**	″	0.5	100	100
Stearic[b]	None	80	6	87	90
″	**7a**	80	2	99	99
Lauric[b]	None	80	6	80	70
″	**7a**	80	2	99	99
Lauric[e]	None	110	4	47	4
″	**7b**	125	3	100	95
″	Reuse[f]	125	3	100	95

[a] Reaction conditions: acid/chlorinating reagent 10/15 (as mmol), catalyst loading amounts = 0.1 g. [b] Thionyl chloride used as chlorinating reagent. [c] Methylene chloride used as solvent. [d] Monochlorobenzene used as solvent. [e] Phosgene used as chlorinating reagent. [f] **7b** was reused 5 times.

In conclusion, we can prepare immobilized phosphazenium chlorides, which show exceptional activity and selectivity in the chlorination of organic acids. These catalysts also show high stability. Easy formation and stabilization of active chloride anions on phosphazenium nuclei due to their high basicity and large nuclei suitable for delocalization of anion may be responsible for their promising catalytic activity and selectivity for the chlorination of organic acids.

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Notes and references

† A glass column with 15 mm diameter and 20 mm length was packed with 9.2 g of the PZ/SIL catalyst **7b**. A mixture of 2-ethylhexanoic acid (100 mmol) and thionyl chloride (200 mmol) was passed through the top of the column at room temperature. The retention time for a single pass was 15 min. At the bottom of the column, products were sampled and analysed by a gas chromatograph with CP-Sil 5CB capillary column (25 m × 0.25 mm). This test was repeated 6 times under the same conditions.

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