The exceptional activity of a phosphazenium hydroxide catalyst incorporated onto silica in the transesterification of tributyrin with methanol

Mi-Young Kim,[a] Gon Seo,*[a] O Zoon Kwon[b] and Duk Rye Chang[c]

Received (in Cambridge, UK) 25th February 2009, Accepted 16th March 2009
First published as an Advance Article on the web 17th April 2009
DOI: 10.1039/b903969d

A phosphazenium hydroxide catalyst incorporated onto silica showed exceptional activity in the transesterification of tributyrin with methanol and could be used repeatedly without suffering any appreciable deactivation.

Biodiesel produced by the transesterification of triglyceride with a lower alcohol is a carbon-neutral fuel without the net emission of CO_2 and also a sustainable transportation fuel without using petroleum sources.[1–4] Homogeneous base catalysts, such as potassium and sodium hydroxides, are mainly employed in the transesterification of vegetable oil and animal fat with methanol because of their high activity and convenience. However, the post-treatment of biodiesel products to neutralize the remaining base and wash out salts are relatively expensive, thereby lowering the feasibility of biodiesel. Although several heterogeneous catalysts, such as zeolites, alkali earth oxides and hydrotalcites, have been applied as base catalysts for transesterification, their low activities and inconvenient pre-treatments limit their application.[2–5] Lipase incorporated onto mesoporous silica has also been extensively studied because of its high activity, despite its relatively high cost.[6] Heterogeneous catalysts have many advantages: their easy separation from biodiesel products simply by filtering, their capability for repeated use and their high handling safety without causing corrosion.

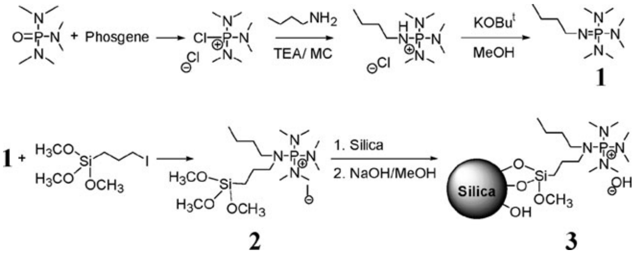
Phosphazenes are extremely strong bases that are effectively used in several organic reactions as catalysts. Phosphazene bases efficiently accelerate the aza-Henry reaction of ketimines compared to trimethyl guanidine.[7] Phosphazene bases also show the best performance among various organic bases in Suzuki–Miyaura coupling reactions for the synthesis of dictyomedins.[8] Moreover, the use of phosphazene catalysts has enabled the water-free alcoholysis of vegetable fatty esters in water-free conditions.[9]

We have already reported the preparation method for a phosphazenium chloride catalyst incorporated onto silica and its exceptional activity in the chlorination of organic acids.[10] The high electron density on the phosphazene moiety is responsible for its high catalytic activity. Phosphazenes and phosphazenium compounds incorporated onto divinylbenzene cross-linked polystyrene show a high activity in various organic reactions.[11] These phosphazene catalysts can be repeatedly used because of their high stability.

In this Communication, we have incorporated phosphazenium iodide onto silica by reacting silica with the adduct of phosphazene and (3-iodopropyl)trimethoxysilane. The further treatment of phosphazenium iodide with sodium hydroxide produces an effective phosphazenium hydroxide catalyst incorporated onto silica ($PzOH/SiO_2$). This catalyst shows a comparable activity with sodium hydroxide in terms of its turnover frequency (TOF) in the transesterification of tributyrin with methanol. Moreover, the catalyst retains its high activity in the transesterification reaction, even after repeated use, further enhancing its feasibility for application to biodiesel production as a commercial catalyst.

Scheme 1 shows the preparation process for the $PzOH/SiO_2$ catalyst. Firstly, phosphazene **1**, with one *n*-butyl substituent, was prepared from the reaction of hexamethylphosphoramide (99%, Aldrich) and phosgene, followed subsequently by a reaction with *n*-butylamine (∼98.5%, Yakury) and potassium *t*-butoxide (99%, TCI). The further reaction of **1** with (3-iodopropyl)trimethoxysilane (∼97%, Fluka) produced phosphazenium iodide **2**, with *n*-butyl and trimethoxysilyl substituents. **2** was easily incorporated onto silica (Merck, Silica 60, 0.040–0.063 mm, S_{BET} = 476 $m^2\ g^{-1}$) by refluxing in toluene. Phosphazenium hydroxide incorporated onto silica hydrated under ambient conditions, **3**, was obtained by treating **2** with 0.1 M NaOH dissolved in methanol (99.8%, Aldrich; MeOH).

A thermogravimetric (TG) curve of **3**, recorded in an ambient atmosphere, indicates the amount of phosphazenium hydroxide incorporated onto the silica, because the oxidative



Scheme 1 Preparation of the $PzOH/SiO_2$ catalyst incorporated onto silica.

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[a] *School of Applied Chemical Engineering and The Research Institute for Catalysis, Chonnam National University, 300 Yongbong-Dong, Buk-Gu, Gwangju 500-757, Korea. E-mail: gseo@chonnam.ac.kr; Fax: +82 62 530 1899; Tel: +82 62 530 1876*
[b] *Samchully Pharmaceutical Co., Ltd, Sihwa Industrial Complex 1Na-802, 1241-2, Jeongwang-Dong, Siheung-Si, Gyeonggi-Do 429-450, Korea. E-mail: ozkwon@scp.co.kr; Fax: +82 31 448 3001; Tel: +82 31 448 1403*
[c] *Korea Institute of Industrial Technology, 1110-9 Oryong-Dong, Buk-Gu, Gwangju 500-480, Korea. E-mail: drchang@kitech.re.kr; Fax: +82 62 600 6179; Tel: +82 600 6130*

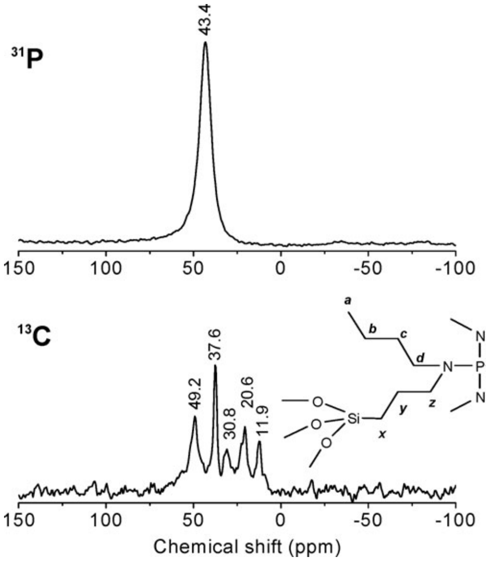

Fig. 1 ^{13}C and ^{31}P MAS NMR spectra of the $PzOH/SiO_2$ catalyst.

removal of carbon, hydrogen, oxygen and phosphorus reduces the weight of the $PzOH/SiO_2$. The weight loss at 200–600 °C of **3** obtained from the TG curve suggested that 3.0 wt% of the phosphazenium hydroxide was incorporated, equivalent to 0.10 mmol of phosphazenium hydroxide per gram of silica. This value is in a good agreement with the amount of phosphazenium hydroxide, 0.14 mmol g^{-1}, determined from the exchange capacity of hydroxide by a titration using 0.01 N HCl and thymol blue indicator.[12]

The ^{13}C and ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of the phosphazenium hydroxide catalyst indicate that the phosphazene moiety is perfectly preserved, even in its incorporated state, as shown in Fig. 1.[13]

The strong basicity of the $PzOH/SiO_2$ catalyst induced strong adsorption of CO_2 onto it, as shown in Fig. 2. The CO_2 adsorbed at 50 °C showed three absorption bands at 2310, 2343 and 2362 cm^{-1}, which were attributed to the asymmetric vibration mode of weakly bound CO_2, the asymmetric OCO stretching of gaseous CO_2 and the asymmetric stretching of CO_2 adsorbed onto the cationic species, respectively.[14,15] The band at 2362 cm^{-1} remained after evacuation, even at 200 °C, demonstrating the very strong basicity of the PzOH catalyst.

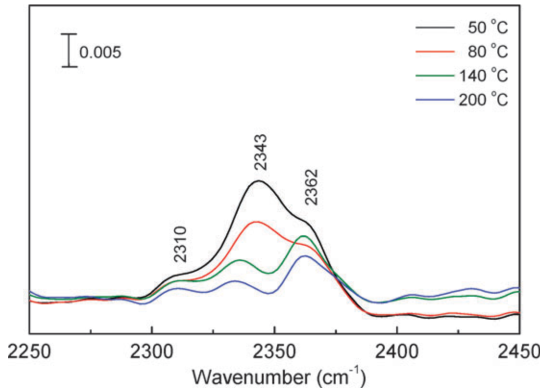

Fig. 2 The IR spectra of CO_2 adsorbed onto the $PzOH/SiO_2$ catalyst. The catalyst was evacuated at 200 °C before exposure to CO_2 at 30 Torr and 50 °C. The IR spectra were recorded under evacuation while increasing the temperature of the sample wafer.

The transesterification of tributyrin (99%, Aldrich; TriB) with methanol (99.8%, Aldrich; MeOH) was carried out in an autoclave.† The conversion denoted the percentage of TriB consumed with respect to that charged as a reactant. The selectivity for methyl butyrate was defined as the percentage of methyl butyrate among the produced esters.

The conversion of TriB gradually increased with increasing catalyst loading, as shown in Fig. 3. The proportional increase in conversion with increasing catalyst loading indicated that the transesterification over the $PzOH/SiO_2$ catalyst was controlled by the surface catalytic reaction at low catalyst loadings. The amount of catalyst required for complete transesterification also varied with the ratio of MeOH to TriB, as expected. A high MeOH concentration in the reactant induced a high TriB conversion.

The activity of the $PzOH/SiO_2$ catalyst was represented by its TOF in order to compare its activity to that of sodium hydroxide. Table 1 lists the conversion, TOF and selectivity obtained in the transesterification reaction over the $PzOH/SiO_2$ and NaOH catalysts. The loading levels of these catalysts were controlled to obtain similar levels of conversion and selectivity. The TOF of TriB was calculated based on the numbers of phosphazenium hydroxide and sodium hydroxide molecules. The conversion and TOF decreased with decreasing MeOH : TriB molar ratio over both catalysts. The strong coordination of TriB with hydroxide ions resulted in low conversions at low MeOH : TriB molar ratios. However, the TOF was 0.16, 0.036 and 0.018 over the $PzOH/SiO_2$ catalyst, compared to 0.23, 0.066 and 0.088 over the NaOH catalyst at MeOH : TriB ratios of 30 : 1, 12 : 1 and 6 : 1, respectively. The TOF over both catalysts decreased with decreasing MeOH : TriB ratio. The TOF over the $PzOH/SiO_2$ catalyst was as low as one-fifth that over the NaOH catalyst under severe conditions of MeOH : TriB = 6 : 1, but this value indicated that the $PzOH/SiO_2$ catalyst was very active and comparable to the homogeneous sodium hydroxide catalyst. At MeOH : TriB = 12 : 1, the activity of the $PzOH/SiO_2$ catalyst, as represented by its TOF, was about half that of the sodium hydroxide catalyst, even though it was heterogeneous and maintained the advantages of separation and repeated use.

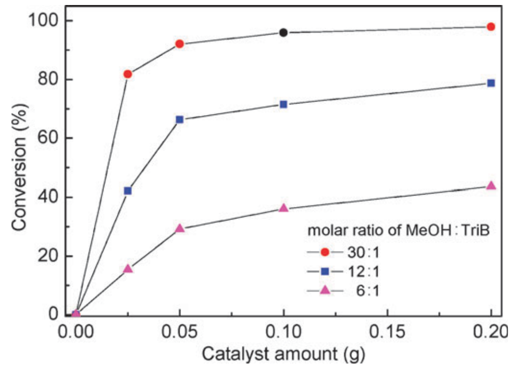

Fig. 3 Transesterification of TriB with methanol over the $PzOH/SiO_2$ catalyst at 60 °C for 2 h with different levels of catalyst loading.

Table 1 Transesterification of TriB with MeOH over the $PzOH/SiO_2$ and NaOH catalysts†

Catalyst	Loading/mg	MeOH : TriB ratio	Repeated use	Conversion (%)	TOF/s^{-1}	Selectivity (%)
$PzOH/SiO_2$	25	30 : 1	—	81	0.160	68
″	100	12 : 1	—	72	0.036	72
″	100	6 : 1	—	36	0.018	50
NaOH	0.1	30 : 1	—	83	0.230	59
″	0.3	12 : 1	—	71	0.066	70
″	0.1	6 : 1	—	32	0.088	35
$PzOH/SiO_2$	1000	30 : 1	—	99	—	97
″	″	″	1	100	—	99
″	″	″	2	94	—	92
″	″	″	3	98	—	94
″	″	″	4	87	—	85

[a] Reaction: TriB = 0.005 mol, reflux for 2 h.

The activity of the $PzOH/SiO_2$ catalyst in the transesterification was maintained over its repeated use, as shown in Table 1. The conversion also remained high with repeated use, without the requirement for further treating with hydroxide or rinsing with solvent. This result demonstrates the high stability of the catalyst under these reaction conditions. The selectivity for methyl butyrate was high over the catalyst, suggesting that further purification of products to remove partially converted TriBs is unnecessary.

The $PzOH/SiO_2$ catalyst exhibited an exceptional activity in the transesterification of TriB with methanol, even in its incorporated state on the silica. Although the TOF of the transesterification was affected by the MeOH : TriB molar ratio, the activity of the $PzOH/SiO_2$ catalyst was about one-fifth that of the homogeneous sodium hydroxide catalyst at the lowest MeOH : TriB molar ratio. The $PzOH/SiO_2$ catalyst continued to preserve its advantages as a heterogeneous catalyst in terms of its separation and the capability for its repeated use. The removal of methanol and methyl butyrate *via* distillation from the filtrates offers the promise of providing water-free glycerin without emitting any waste water. The exceptional activity and high convenience of the $PzOH/SiO_2$ catalyst raises hope for the wider application of incorporated phosphazenium hydroxide catalysts in the important field of biodiesel production.

This work was supported by a Korea Research Foundation Grant (MOEHRD) (KRF-2007-412-J02001).

Notes and references

† Four small vials charged with the reactants (8.36 ml) and catalyst were installed in the stirring shaft of an autoclave preheated at 60 °C. The transesterification was started by stirring the vials at 200 rpm for 2 h. Various molar ratios of MeOH : TriB (6 : 1, 12 : 1 and 30 : 1) were used. After the transesterification, the products were analyzed using a gas chromatograph (Donam, DS6200) equipped with a HP-5 capillary column and an FID detector. The response factors for TriB, dibutyrin, monobutyrin and methyl butyrate were determined through the multi-point calibration method using dibutylether (99.3%, Aldrich) as an internal standard. For the repeated use of the $PzOH/SiO_2$ catalyst, the vial containing the products and catalyst was centrifuged for 5 min. After decanting the products, new reactants were charged into the vial, and the transesterification was performed by following the same procedure described above.

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