Magnetically separable phase-transfer catalysts[†]

Masato Kawamura and Kazuhiko Sato*

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Magnetic nanoparticles-supported quaternary ammonium and phosphonium salts were prepared and evaluated as phasetransfer catalysts. Some of them exhibited good activities that were comparable to that of tetra-*n*-butylammonium iodide. The catalysts were readily separated using an external magnet and reusable without significant loss of their catalytic efficiency.

Recently, much attention has been focused on phase-transfer reactions since they have been recognized as environmentally benign alternatives to many homogeneous reactions.¹ A practical problem associated with phase-transfer catalysis technology is the difficulty of separating conventional phase-transfer catalysts (PTCs) such as quaternary ammonium salts. The immobilization of a PTC on a solid support has afforded a solution to overcome this problem.^{2,3} So far, cross-linked polystyrene resin (PS resin) is the most common catalyst support and has been utilized for many phase-transfer reactions.⁴ However, PS resin-supported PTCs have several drawbacks including swelling in organic solvents, which usually requires a long conditioning time prior to use, and their activities being highly dependent on the solvent used.⁵ Moreover, the activities of PS resin-supported PTCs are often lower than those of their non-supported counterparts, and the deactivation often occurs in the reuse process.⁶

Magnetic nanoparticles (MNPs) have emerged as new catalyst supports.⁷ A striking feature of the MNPs-supported catalysts is that they can be readily separated using an external magnet, which achieves simple separation of the catalysts without filtration. Additionally, the MNPs-supported catalysts showed not only high catalytic activity but also a high degree of chemical stability, and they do not swell in organic solvents. Although the use of MNPs has been promising, the application of MNPs to catalyst support is still limited as compared with that of PS resin.

Herein, we report the first example of magnetic nanoparticlessupported PTCs through the immobilization of a quaternary ammonium and phosphonium salt on magnetite and the preliminary evaluation of their catalytic activity in phase-transfer reactions.

Magnetite nanoparticles were chosen for use as magnetic supports since they could be readily prepared by the conventional coprecipitation method.⁸ As described in Scheme 1, the silane coupling agents 1-2 were initially prepared by reaction of the corresponding amines or phosphines with (3-iodopropyl) trimethoxysilane. The immobilization of 1-2 was performed



Scheme 1 Preparation of magnetite nanoparticles-supported ammonium and phosphonium salts 3-4.

according to a previously described method,⁹ and magnetite nanoparticles were treated by excess 1–2 to give magnetitesupported ammonium salts 3 and phosphonium salts 4. The catalyst loadings of 3–4 were determined by iodide-ion analysis to range from 0.10 to 0.25 mmol g⁻¹. A SEM image of 3c is shown in Fig. 1. It was confirmed that the catalyst was made up of nanometer-sized particles. The PS resin-supported counterpart 5c was also synthesized from commercially available chloromethylated polystyrene (Argonaut PS-Cl, 1% cross-linked).¹⁰

To evaluate the catalytic activity of 3-4 as PTCs, the reaction of PhONa with n-BuBr was examined as a model reaction. As control experiments, tetra-n-butylammonium iodide (TBAI) and 5c were employed for the same reaction.¹¹ The results are summarized in Table 1. As can be seen from entries 3-8, the catalytic activity was strongly affected by the alkyl group of ammonium moiety.¹² Although 3a did not catalyze the reaction (entry 3), the catalytic activities of **3b-d** were comparable to that of TBAI (entries 4-6 vs 2). It seemed that lipophilicity of the ammonium moiety initially increased the catalytic activities. However, the reactions with 3e and 3f produced the ether in moderate yields, which were inferior to that using 3c. We thus concluded that the long alkyl groups (n-C₇H₁₅- and n-C₈H₁₇-) were hydrophobic to the extent that the diffusion of the catalyst was restrained. Phosphonium salt 4b was less effective than the corresponding ammonium salt 3b (entry 4 vs 9), and the activity



Fig. 1 SEM image of 3c.

National Institute of Advanced Industrial Science and Technology (AIST), Central 5 Higashi 1-1-1, Tsukuba, Ibaraki, Japan. E-mail: k.sato@aist.go.jp; Fax: +81-29-861-4852; Tel: +81-29-861-4852 Electronic compensation: information (ESD) available. Emperimental

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 Table 1
 O-Alkylation reaction of PhONa with n-BuBr under phasetransfer conditions

ONa +	<i>n</i> -BuBr ——	3 mol% catalyst
Entry ^a	Catalyst	%Yield ^b
1	None	28
2	TBAI	86
3	3a	36
4	3b	86
5	3c	93
6	3d	84
7	3e	69
8	3f	70
9	4b	80
10	4g	79
11	5c	50

^{*a*} All reactions were performed at 100 °C for 12 h in toluene/H₂O (1/1) with 0.75 mmol of PhONa·3H₂O and *n*-BuBr (1.5 equiv.). ^{*b*} Determined by GC analysis using *n*-tetradecane as an internal standard.

Table 2Recycling of 3c for the alkylation reaction of PhONa with*n*-BuBr

Entry ^a	Recycle	%Yield ^{<i>k</i>}	
1	lst	94	
2	2nd	90	
3	3rd	90	
4	4th	89	

^{*a*} All reactions were performed at 100 °C for 12 h in toluene/H₂O (1/1) with 0.75 mmol of PhONa·3H₂O and *n*-BuBr (1.5 equiv.). ^{*b*} Determined by GC analysis using *n*-tetradecane as an internal standard.

of **4g** was identical to that of **4b**. It should be noted that the immobilization on magnetite-nanoparticles did not decrease the catalytic activity whereas the reaction with PS resin-supported catalyst **5c** was much less effective under the same conditions (entry 11).

Easy and rapid separation of the catalyst by magnetism is the most advantageous feature of these catalysts. After the reaction, the catalysts were concentrated on the sidewall of the reaction vessel using an external magnet, the aqueous and the organic phases were separated by decantation, and the residual catalyst in the reaction vessel was washed and dried and then subjected to the next run directly. We examined the recycling of **3c** for the reaction of PhONa with *n*-BuBr. As shown in Table 2, **3c** was reusable without any significant loss of activity for the 4th recycling.

The halogen exchange reaction of 1-bromooctane was also examined as another model reaction (Scheme 2). This reaction proceeded negligibly without PTC (12 h, 6%), whereas the reaction with 3 mol% TBAI gave 1-iodooctane in good yield (6 h, 92%). The activity of **3c** was comparable to that of TBAI, although the yield was slightly reduced under the same reaction conditions (6 h, 85%; 9 h, 92%). On the other hand, **5c** showed low activity, and the yield of 1-iodooctane was drastically decreased (40%, 6 h).

In summary, we have developed magnetically separable PTCs through the immobilization of ammonium and phosphonium salts on magnetic nanoparticles. The catalysts are readily reusable

$$n-C_8H_{17}Br$$
 + Nal $\xrightarrow{3 \text{ mol}\% \text{ catalyst}}{\text{ toluene/H}_2O, 100 °C} n-C_8H_{17}I$

catalyst = TBAI (6 h, 92%), **3c** (6 h, 85%; 9 h, 92%), **5c** (6 h, 40%)

Scheme 2 Halogen exchange reaction of 1-bromooctane under phase-transfer conditions.

without loss of catalytic activity. To the best of our knowledge, this is the first example of magnetically separable PTCs. We believe that these results expand the scope of phase-transfer catalysis technology. Further investigation of magnetically collectable PTCs is currently in progress.

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