

Preparation and properties of novel phosphonium-type ionic liquids/silica gel nanocomposites

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Introduction

There has hitherto been an increasing amount of interest in ionic liquids (ILqds), because ILqds are non-flammable and thermally stable solvents and as such as very promising replacements for the traditional volatile organic solvents [1]. In fact, most ILqds have a high thermal stability, often beginning to decompose around 400 °C with minimal vapor pressure below their decomposition temperature [2]. ILqds have also been shown to be suitable reaction media for numerous catalytic reactions, and the immobilization of ILqds on a silica surface gave rise to the concept of supported ionic liquid catalyst, and this supported ionic catalyst has been used widely in a variety of reaction systems such as Fridel–Crafts acylations [3]. On the other hand, considerable interest has been devoted to the controlled fabrication of nanostructured materials with a variety of unique properties, which results from a function of nanoscale materials' size and structural order [4]. Therefore, the hybridization of ILqds and silica nanoparticles is in particular interest from a developmental viewpoint of novel functional materials imparted by both ILqds and the nanoscale materials.

Now, we have found that tetraethoxysilane reacted with silica nanoparticles in the presence of phosphonium-type ionic liquids under alkaline conditions to afford the corresponding ionic liquids/silica nanocomposites with a good dispersibility into a variety of solvents. Interestingly, these ionic liquids/silica nanocomposites thus obtained exhibited no weight loss even at 800 °C equal to the original silica gel, although the corresponding parent ionic liquids were completely degraded at 400–700 °C. These results will be described herein.

Experimental

To a methanol solution (20 ml) of tri-*n*-butyl-*n*-dodecylphosphonium 3,5-di(methoxycarbonyl)benzenesulfonate (0.5 ml), were added tetraethoxysilane (TEOS: 2.3 mmol), silica nanoparticle methanol solution [30% (wt.): 3.33 g; average particle size: 11 nm (Methanol Silica-sol (TR): Nissan Chemical Industrials Ltd., Tokyo, Japan)], and 25% aqueous ammonia solution (0.50 ml). The mixture was stirred with a magnetic stirring bar at room temperature for 5 h. After the solvent was evaporated off, to the obtained crude products was added methanol (25 ml). The methanol solution was stirred with magnetic stirring bar at room temperature for 1 day, and then was centrifuged for 30 min. The expected ionic liquid containing nanocomposite was easily separated from the methanol solution. The nanocomposite powders thus obtained were dried in vacuo at 50 °C for 2 day to afford purified particle powders (0.46 g). Other ionic liquids—encapsulated silica nanocomposites were also prepared under similar conditions.

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Results and discussion

Tetraethoxysilane (TEOS) reacted with silica nanoparticles in the presence of phosphonium-type ionic liquid: tri-*n*-butyl-*n*-dodecylphosphonium 3,5-di(methoxycarbonyl) benzenesulfonate [TBDP-DMBS] under alkaline conditions to afford TBDP-DMBS-encapsulated silica nanocomposites in 29% isolated yield. Similarly, TEOS reacted with silica nanoparticles in the presence of other phosphonium-type ionic liquids listed in Chart 1 under alkaline conditions to afford the corresponding ionic liquids-encapsulated silica-nanocomposites in 28–63% isolated yields. These results were shown in Scheme 1.

The contents of P-ILqds in the nanocomposites thus obtained were studied by the use of inductively coupled plasma (ICP) analyses, and the results were

demonstrated in Scheme 1. ICP analyses of phosphorus atoms in nanocomposites show that the contents of introduced phosphonium-type ionic liquids into the nanocomposites were estimated to be 2.2–15.1%, respectively. Thus, it was demonstrated that a variety of P-ILqds in Chart 1 were tightly encapsulated into the nanocomposites.

We have measured the size of these P-ILqds/silica nanocomposites in methanol by dynamic light-scattering (DLS) measurements at 25 °C. P-ILqds/silica composites were nanometer size-controlled particles (69.3–248.0 nm; see Table 1) with good dispersibility and stability in not only methanol but also ethanol and water. The transmission electron microscopy (TEM) of TBDP-DMBS/SiO₂ composites also showed the formation of P-ILqds/SiO₂ nanocomposites with a mean diameter of 100 nm (see Fig. 1).

Chart 1

Phosphonium-type ionic liquids	abbreviation
Tri- <i>n</i> -butyl- <i>n</i> -octylphosphonium bis(trifluoromethylsulfonyl)imide	$\text{Bu}_3^+ \text{P C}_8\text{H}_{17} \text{N}^-(\text{SO}_2\text{CF}_3)_2$ [TBOP-TFSI]
Tri- <i>n</i> -butyl- <i>n</i> -octylphosphonium tetrafluoroborate	$\text{Bu}_3^+ \text{P C}_8\text{H}_{17} \text{BF}_4^-$ [TBOP-BF ₄]
Tri- <i>n</i> -butyl-methylphosphonium dimethylphosphate	$\text{Bu}_3^+ \text{P Me O}^-\text{P}(=\text{O})(\text{OMe})_2$ [TBMP-DMP]
Tri- <i>n</i> -butyl- <i>n</i> -octylphosphonium hexafluorophosphate	$\text{Bu}_3^+ \text{P C}_8\text{H}_{17} \text{PF}_6^-$ [TBOP-PF ₆]
Tri- <i>n</i> -butyl- <i>n</i> -dodecylphosphonium 3,5-di(methoxycarbonyl)benzenesulfonate	$\text{Bu}_3^+ \text{P C}_{12}\text{H}_{25} \text{O}^-\text{SO}_2\text{-C}_6\text{H}_3(\text{CO}_2\text{Me})_2$ [TBDP-DMBS]
Tri- <i>n</i> -hexyl-[3-(trimethoxysilyl)propyl]phosphonium chloride	$(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{P}^+(\text{C}_6\text{H}_{13})_3 \text{Cl}^-$ [THSP-Cl]
Tri- <i>n</i> -butylhydroxyethylphosphonium chloride	$\text{Bu}_3^+ \text{P CH}_2\text{CH}_2\text{OH Cl}^-$ [TBHEP-Cl]
Tetra- <i>n</i> -butylphosphonium <i>o,o</i> -diethylphosphorodithioate	$\text{Bu}_4^+ \text{P}^-\text{S-P}(=\text{S})(\text{OEt})_2$ [TBP-DEPT]
Tri- <i>n</i> -butyl- <i>n</i> -octylphosphonium trifluoroacetate	$\text{Bu}_3^+ \text{PC}_8\text{H}_{17} \text{OC}(=\text{O})\text{CF}_3^-$ [TBOP-TFAc]

Scheme 1

P-ILqds	Yield of P-ILqds/SiO ₂ nanocomposite (%) ^{a)}	The content of introduced P-ILqds into nanocomposite (%) ^{b), c)}
TBOP-TFSI	28	4.0
TBOP-BF ₄	57	3.5
TBMP-DMP	63	4.2
TBOP-PF ₆	42	7.3
TBDP-DMBS	29	10.1
THSP-Cl	39	15.1
TBHEP-Cl	56	8.2
TBP-DEPT	31	2.2
TBOP-TFAc	38	8.8

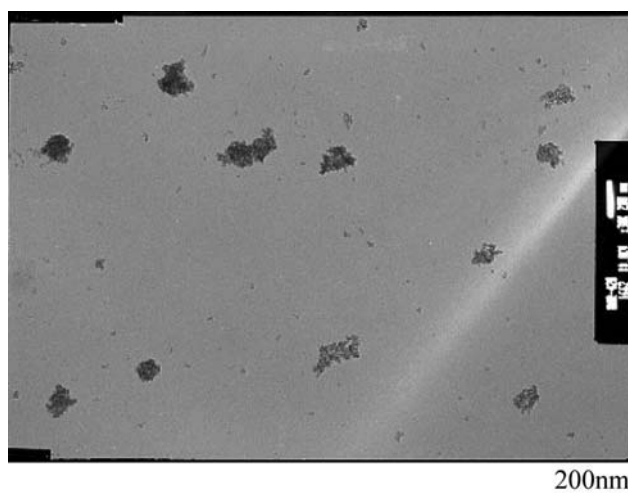
a) isolated yield based on P-ILqds, TEOS and silica-nanoparticles

b) determined by ICP analyses

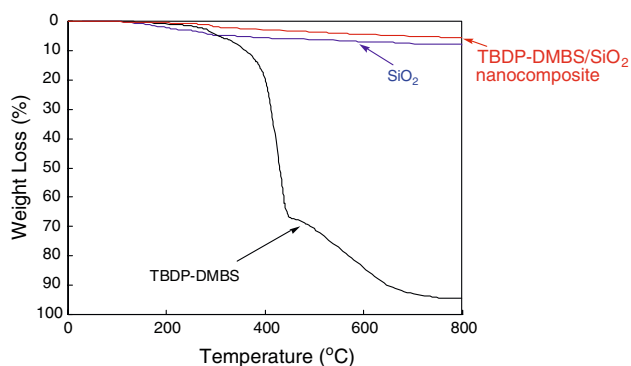
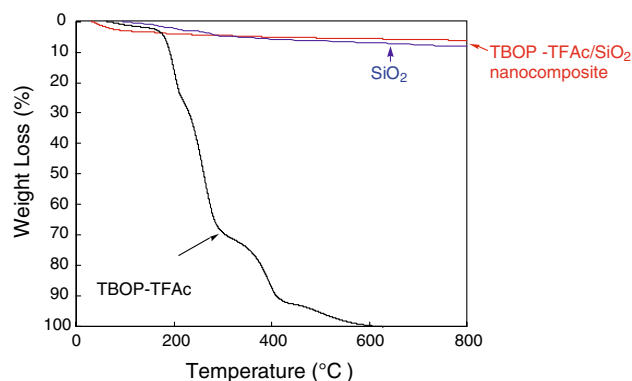
c) based on the used P-ILqds

Table 1 Size of P-ILqds/silica nanoparticles in methanol solutions determined by dynamic light scattering measurements

P-ILqds in nanocomposites	Size of nanocomposites (nm)
TBOP-TFSI	69.3 ± 10.6
TBOP-BF ₄	193.2 ± 46.9
TBMP-DMP	109.6 ± 25.9
TBOP-PF ₆	248.0 ± 55.0
TBDP-DMBS	142.7 ± 36.1
THSP-Cl	143.0 ± 25.6
TBHEP-Cl	124.4 ± 23.5
TBP-DEPT	114.2 ± 29.0
TBOP-TFAC	106.8 ± 17.3

**Fig. 1** TEM image of TBDP-DMBS/SiO₂ nanocomposites in MeOH

Thermal stability of P-ILqds/silica gel nanocomposites was studied by the use of thermogravimetric analyses (TG), in which the weight loss of these nanocomposites was measured by raising the temperature around 800 °C in air atmosphere, and the results were shown in Figs. 2, 3.

**Fig. 2** Thermogravimetric analyses of TBDP-DMBS/SiO₂ nanocomposites**Fig. 3** Thermogravimetric analyses of TBOP-TFAC/SiO₂ nanocomposites

As shown in Figs. 2, 3, the weights of parent P-ILqds (TBDP-DMBS and TBOP-TFAC) markedly dropped around 200–300 °C and decomposed completely around 600–700 °C. On the other hand, unexpectedly, we could not observe the weight loss of TBDP-DMBS/silica and TBOP-TFAC/silica nanocomposites at all from room temperature to 800 °C equal to the original silica gel, which was prepared by the reaction of TEOS and silica-nanoparticles under the similar alkaline conditions as shown in Scheme 1, although the parent TBDP-DMBS and TBOP-TFAC decomposed completely around 600–700 °C (see Figs. 2, 3). In particular interest, the weight loss ratios of these nanocomposites were found to become lower compared to the original silica gel. Especially, the average particle size [130.9 ± 37.0 nm (determined by DLS)] of TBDP-DMBS/silica nanocomposites after the calcination was almost the same as that (142.7 ± 36.1 nm) before the calcination. In addition, we observed no change of the dispersibility and the shape including the color of the nanocomposites after the calcination.

A similar tendency for the no weight loss of the nanocomposites was observed in other P-ILqds/silica nanocomposites in Scheme 1, and these results were shown in Table 2.

As shown in Table 2, the weight loss (4.8–7.7%) of a variety of phosphonium salt-type ionic liquids/silica nanocomposites at 800 °C was found to be lower compared to that (8.2%) of the original silica gel. The weight loss (83–97%) of the original P-ILqds except for TBOP-TFAC at 800 °C shows that the pyrolytic fragmentation of P-ILqds during the calcination process should afford in part the noninflammable inorganic phosphorus derivatives.

On the other hand, micrometer size-controlled TBOP-TFSI/silica composites (particle size: 4.3 ± 0.3 μm), which was prepared by the reactions of TEOS

Table 2 The weight loss of P-ILqds/SiO₂ nanocomposites and the original P-ILqds at 800 °C (C determined by thermogravimetric analyses)

P-ILqds in nanocomposites	Weight loss of P-ILqds/SiO ₂ nanocomposites (%)	Weight loss of original P-ILqds (%)
TBOP-TFSI	5.4 [8.2] ^a	97
TBOP-BF ₄	5.8	94
TBMP-DMP	5.2	88
TBOP-PF ₆	6.0	94
TBDP-DMBS	5.7	95
THSP-Cl	7.7	83
TBHEP-Cl	6.3	97
TBP-DEPT	4.8	86
TBOP-TFAC	6.3	100

^a NOriginal SiO₂

and TBOP-TFSI in the absence of silica-nanoparticles under the similar alkaline conditions as that of Scheme 1, have a lower thermal stability compared to that of the original silica gel. The weight loss (20.1%) of the composites at 800 °C became higher compared to that (16.5%) of the parent silica gel, which was prepared by the hydrolysis of TEOS under alkaline conditions. Furthermore, this white-colored composite changed to the gray after the calcination. This would be due to their poor molecular-level combination under the architectures of these micrometer size-controlled composites.

A similar tendency was observed in the traditional phosphonium salts/silica nanocomposites such as bis[tetra(hydroxymethyl)phosphonium] sulfate [(CH₂OH)₄P⁺]₂ SO₄²⁻/silica nanocomposites (particles size: 103.7 ± 35.6 nm), which were prepared by the reactions of TEOS and silica nanoparticles in the presence of the corresponding phosphonium salt under alkaline conditions, and this phosphonium salt-type nanocomposite was found to decompose easily compared to that of the original silica gel [the weight loss of this nanocomposite at 800 °C: 18.7%; the weight loss of the original silica gel at 800 °C: 8.2%].

These findings suggest that pyrolytic products derived from P-ILqds in the nanocomposite should be encapsulated quite effectively into the nanometer-size controlled silica matrices through the calcination process, because molecular-level combination, which is due to the strong interaction between the pyrolytic

products and residual silanol groups, should be essential for the architecture of the novel host moieties for the encapsulation of the pyrolytic products into the silica matrices during the calcination process. On the other hand, such molecular-level interaction could not be participated into the silica matrices in the cases of micrometer-size controlled P-ILqds/silica composites and phosphonium salt/silica nanocomposites.

In conclusion, it was demonstrated that TEOS could react with silica nanoparticles in the presence of a variety of P-ILqds under alkaline conditions to afford PILqds/silica nanoparticles with a good dispersibility and stability in methanol, ethanol and water. In particular interest, we find a unique PILqd/silica nanocomposite with no weight loss even at 800 °C equal to the original silica gel, although the corresponding micrometer-size controlled PILqd/silica composite and traditional phosphonium salt/silica nanocomposites decomposed more effectively at 800 °C compared to the original silica gel. Thus, our present phosphonium salt-type ionic liquid/silica gel nanocomposite has high potential for new organic–inorganic polymer hybrid materials. Further studies including the preparation of other ionic liquids such as imidazolium- and pyrazolium-type ionic liquids/silica nanocomposites are actively in progress.

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