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# Preparation of microcapsule-supported palladium catalyst using SPG (Shirasu Porous Glass) emulsification technique

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**Abstract**

A new method for the preparation of microcapsule-supported palladium catalyst was described. The highly monodisperse crosslinked polystyrene microcapsules containing phosphine ligand were synthesized by the self-assembling of phase separated polymer (SaPSeP) method using diphenyl(4-vinylphenyl)phosphine and divinylbenzene as a monomer and crosslinking agent, respectively, and 2,2′-azobisisobutyronitrile (AIBN) as an initiator within the droplets of oil-in-water (O/W) emulsions, which were prepared by using the Shirasu Porous Glass (SPG) membrane emulsification technique. The prepared microcapsule-supported palladium catalyst exhibited high catalytic activity for Heck reaction and can be reused several times without loss of activity.


*Keywords:* Microcapsule-supported palladium catalyst; SPG emulsification technique; Heck reaction

The methods for the preparation of polymer-supported catalysts can broadly be separated into two groups [1,2]: in the first, a polymer is prepared by first using a monomer bearing ligand moiety, before the catalyst is anchored to the polymer through a complexation reaction between the transition metal atom and ligand moiety on the polymer. In the second, a polymer is modified by a ligand, and then the catalyst is attached to the polymer through the method mentioned above. The metal complexes of polymer-supported catalysts are usually linked to the polymer chain, and protrude into the reaction solvent. This leads to the loss of catalyst activity when they are recovered by filtration and recycled due to the leaching of active catalyst species from polymeric support.

To resolve the above-mentioned problem, we researched on the preparation of microcapsule-supported palladium catalyst using Shirasu Porous Glass (SPG) emulsification technique [3]. The principle of the preparation is schematically described in Scheme 1. At first, monodispersed size-controllable microcapsules containing phosphine ligands were prepared by the using diphenyl(4-vinylphenyl)phosphine and divinylbenzene as a monomer and crosslinking agent, respectively. Palladium was then attached onto microcapsules inside. These newly formed microcapsules acted as microreactors, in which the catalysis will occur. Even if palladium species breaks off from one phosphine ligand, it may attach to another phosphine ligand inside of the microcapsule. Therefore, the microcapsule-supported palladium catalyst should be very stable, and could be reused several times without loss of activity. As

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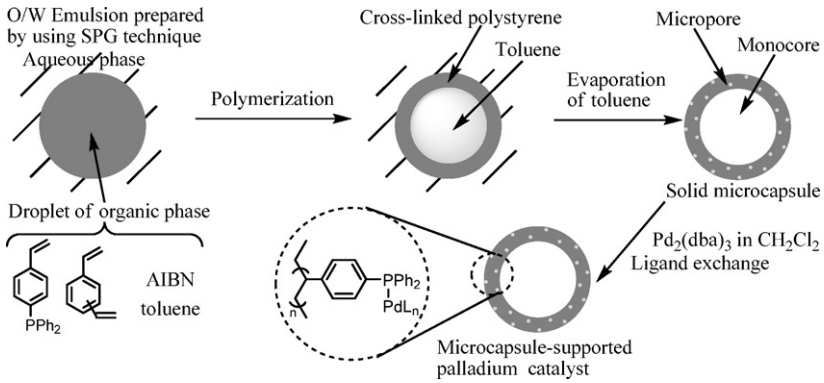



Scheme 1. Schematic illustration for the preparation of the microcapsule-supported palladium catalyst.

expected, the microcapsule-supported palladium catalyst exhibited high catalytic activity in Heck reaction of various aryl iodides with methyl acrylate in toluene/$H_2O$ (v/v = 4:1). Here we wish to report our primary results.

## 1. Experimental

The emulsification procedure was carried out by utilizing a hydrophilic SPG membrane emulsification kit with average pore size of 2.8 μm. Prior to emulsification, the membrane was soaked in deionized water containing a small amount of sodium dodecylsulfate (SDS) for over 30 min after ultrasonic treatments. Then, the SPG membrane was installed into the SPG membranes module as a filter media. The dispersed phase consisting of diphenyl(4-vinylphenyl)phosphine (10 mmol, 2.88 g), divinylbenzene (DVB, 2.5 mmol, 0.72 g), 2,2′-azobisisobutyronitrile (AIBN, 3 wt% of monomers), and toluene (2.4 mL) was poured into a pressure tight vessel, and allowed to permeate into the continuous phase containing polyvinyl alcohol (PVA, 1.0 wt%), SDS (0.3 wt%), and deionized water (60 mL) through the hydrophilic membrane under nitrogen gas pressure.

The obtained emulsion was transferred into a three-neck bottle glass that had a condenser, a magnetic stirrer and a nitrogen inlet nozzle. Emulsion polymerization was carried out for 24 h at 70 °C under $N_2$ atmosphere. After the polymerization had finished, the reaction mixture was cooled to room temperature and methanol was added for the precipitation of the polymer particles. The polymer particles were then washed with deionized water, methanol, acetone, dichloromethane, and methanol successively, and dried in a vacuum. The white powder of the microcapsule particles was obtained in 52% yield (1.87 g).

A mixture of $Pd_2(dba)_3$ (250 mg), microcapsules (1.0 g), and $CH_2Cl_2$ (20 mL) was stirred at room temperature under $N_2$ atmosphere for 3 h. The desired microcapsule-supported palladium catalyst was obtained by ligand-exchange reaction, and the content of Pd in the microcapsules was determined by ICP (Inductively Coupled Plasma) analysis after the microcapsules were filtrated, washed with $CH_2Cl_2$, and dried in a vacuum.

Aryl iodide (0.5 mmol), methyl acrylate (2.0 equiv.), *n*-$Bu_3N$ (3.0 equiv.), microcapsule-supported Pd(0) catalyst (1.0 mol% Pd), and solvent (toluene/$H_2O$, v/v = 4:1, 2 mL) were added to a Schlenk reactor. The resulting mixture was stirred at 90 °C for 24 h under $N_2$ atmosphere. After completion of the reaction, the mixture was allowed to cool to room temperature, and the catalyst was collected by filtration, washed with acetone, water, and ethanol, then dried under vacuum and reused. The organic filtrate was evaporated under vacuum to give a crude product. The crude product was purified by flash chromatography using silica gel column (eluent:EtOAc/Petroleum = 15:1) to give the desired product, which was characterized through $^1H$ NMR spectroscopy. The $^1H$ NMR data of methyl cinnamate are shown here (400 MHz, $CDCl_3$): $\delta$ 3.78 (s, 3H), 6.41 (d, 1H, $J$ = 16.0 Hz), 7.35–7.36 (m, 3H), 7.48–7.51 (m, 2H), 7.66 (d, 1H, $J$ = 16.0 Hz).

## 2. Results and discussion

The highly monodisperse cross-linked polystyrene microcapsules containing phosphine ligand were synthesized by the self-assembling of phase separated polymer (SaPSeP) method using diphenyl(4-vinylphenyl)phosphine and DVB

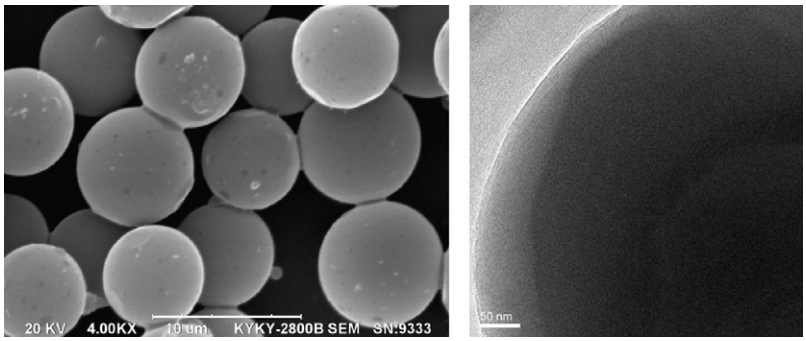


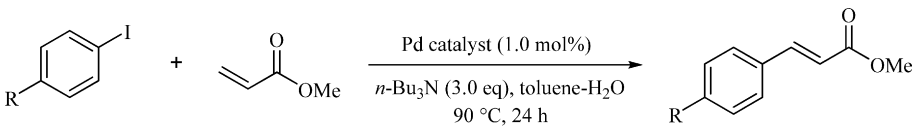

Fig. 1. The SEM image (left) and the TEM image (right) of the microcapsules prepared using SPG emulsification technique.

as a monomer and crosslinking agent, respectively, and AIBN as an initiator within the droplets of oil-in-water (O/W) emulsions [4], which were prepared by using the SPG membrane emulsification technique. When toluene was utilized as a solvent in the organic phase, lowest ratio of phosphorus to carbon on the surface of the microcapsule (0.89%) was observed by energy dispersive X-ray (EDX) spectrometry combined with scanning electron microscope [5], which indicated that 90% of phosphine ligands existed inside the microcapsule (ratio of phosphorus to carbon on the whole microcapsule was 8.90% determined by EDX combined with transmission electron microscope) [6]. The scanning electron microscope (SEM) image and the transmission electron microscope (TEM) image were shown in Fig. 1. As shown in Fig. 1 (left), the size of the prepared microcapsules was uniform. The TEM image (Fig. 1, right) clearly indicated that the microcapsules possess a hollow structure.

The microcapsule-supported palladium catalyst was obtained by treating the microcapsules with a solution of $Pd_2(dba)_3$ in dichloromethane. ICP analysis revealed that the ratio of Pd was 2.17 wt%, and the EDX determination shows that no Pd existed on the surface of microcapsule, which clearly indicated the Pd was completely immobilized inside the microcapsule.

The microcapsule-supported palladium catalyst was then employed in the Heck reaction to evaluate its catalytic activity and stability [7]. Heck reactions of various aryl iodides with methyl acrylate were tested under optimized conditions, the catalysis results of which are summarized in Scheme 2. The reaction of iodobenzene with methyl acrylate offered the corresponding product methyl cinnamate in excellent yield (98%). When the 4-methy-iodobenzene was examined a satisfactory reaction yield was obtained (82%). Reactions of 4-methoxy-iodobenzene, 4-cyano-iodobenzene, and 4-acetyl-iodobenzene provided corresponding products in moderate yields (71–74%). The content of the soluble palladium species in the reaction of iodobenzene with methyl acrylate was only 0.036 wt% determined by ICP, which indicated that the catalysis mainly occurred inside of the microcapsules. The microcapsule-supported palladium catalyst was also repeatedly used in the reaction of iodobenzene with methyl acrylate, and the yields were 98% in run 1, 96% in run 2, and 92% in run 3. Finally, it was found that this catalyst could not promote the reaction of bromobenzene with methyl acrylate.

In conclusion, we present a new method for the preparation of microcapsule-supported palladium catalyst. The Pd species were anchored inside of the microcapsules, and therefore the microcapsules acted as microreactors. It was considered that the substrates entered the microcapsule through its pores, and then which were transformed to products by the catalysis of palladium. The microcapsule-supported palladium catalyst obtained can be reused several times without loss of catalytic activity.




Yield: R = H, 98%; R = Me, 82%; R = OMe, 71%; R = CN, 71%; R = COMe, 74%.

Scheme 2. Heck reaction of aryl iodides with methyl acrylate catalyzed by microcapsule-supported palladium catalyst.

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## References

[1] For recent reviews, see: (a) J. Liu, P.H. Toy, Chem. Rev. 109 (2009) 815; (b) M.R. Buchmeiser, Chem. Rev. 109 (2009) 303; (c) C.A. McNamara, M.J. Dixon, M. Bradley, Chem. Rev. 102 (2002) 3275; (d) N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217; (e) B. Clapham, T.S. Reger, K.D. Janda, Tetrahedron 57 (2001) 4637.

[2] For selected recent references, see: (a) S. Schweizer, J.M. Becht, C.L. Drian, Adv. Synth. Catal. 349 (2007) 1150; (b) J.C. Hershberger, L. Zhang, G. Lu, et al. J. Org. Chem. 71 (2006) 231; (c) A. Köllhofer, H. Plenio, Chem. Eur. J. 9 (2003) 1416; (d) V. Chandrasekhar, A. Athimoolam, Org. Lett. 4 (2002) 2113; (e) A.B. Charette, A.A. Boezio, M.K. Janes, Org. Lett. 2 (2000) 3777.

[3] The Shirasu Porous Glass (SPG) emulsification technique was employed for the preparation of microcapsules containing phosphine ligands for the first time. E. Kamio, A. Kato, S. Yonemura, et al., Colloid Polym. Sci. 286 (2008) 787.

[4] (a) H. Minami, H. Kobayashi, M. Okubo, Langmuir 21 (2005) 5655;
(b) H. Minami, M. Okubo, Y. Oshima, Polymer 46 (2005) 1051.

[5] G.D. Fu, Z. Shang, L. Hong, et al. Macromolecules 38 (2005) 7867.

[6] H. Takadama, H.M. Kim, T. Kokubo, et al. Chem. Mater. 13 (2001) 1108.

[7] Because we have recently researched on the palladium-catalyzed Stille type C–C bond forming reaction, the Stille reaction was first examined to evaluate the catalytic activity and stability of the microcapsule-supported palladium catalyst. However, we found the desired Stille reaction did not occurred at all, and the starting materials were recovered. It may be due to the bulky structures of allyltributylstannane and phenyltributylstannane. (a) S.R. Lu, Z.W. Xu, M. Bao, et al. Angew. Chem. Int. Ed. 47 (2008) 4366; (b) M. Bao, H. Nakamura, Y. Yamamoto, J. Am. Chem. Soc. 123 (2001) 759; (c) H. Nakamura, M. Bao, Y. Yamamoto, Angew. Chem. Int. Ed. 40 (2001) 3208.