Supporting Information

(18 Pages)

Immobilization of Pd(OAc)₂ in Ionic Liquid on Silica: Application to Sustainable Mizoroki-Heck Reaction

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Representative procedures for the catalyst immobilization and its use to Mizoroki-Heck reaction.

EPMA, SEM and AFM pictures of supported and un-supported silica before use.

EPMA and SEM pictures of supported silica after 6 cycles.

¹HNMR spectra of the products **3a ~ i**.

Representative procedure for catalyst preparation: To a stirred solution of Pd(OAc)₂ (690 mg) in [bmim]PF₆ (1 g) and THF (10 mL) was added silica powder (10 g, spherical for flash column chromatography, diameter; 40 ~ 50 mm, pore size; 5 ~ 7 nm, pore volume; 0.80 ~ 1.00 mL/g, surface area; 600 ~ 700 m²/g). After being stirred for 90 min, THF was evaporated to dryness *in vacuo* to give a light brown dry powder which was rinsed with diethyl ether until the diethyl ether layer became colorless, and was dried *in vacuo*. The amount of Pd(OAc)₂ supported was 560 mg (0.25 mmol/g) based on weight gain.

Representative procedure for Mizoroki-Heck reaction: To a suspension of the immobilized catalyst {400 mg, 0.1 mmol as Pd(OAc)₂} in *n*-dodecane (2 mL) was added iodobenzene **1** (112 mg, 1 mmol), cyclohexyl acrylate **2** (189 mL, 1.2 mmol) and tri(*n*-butyl)amine (279 mL, 2 mmol) under nitrogen atmosphere. The suspension was heated at 150 °C until disappearance of iodobenzene **1** by GLC monitoring. After being cooled to room temperature, the *n*-dodecane layer was passed through a silica column with the aid of *n*-hexane to remove *n*-dodecane. Subsequently, the product was eluted with *n*-hexane–ethyl acetate. The *n*-hexane–ethyl acetate eluent was evaporated to dryness to give a residue which was purified by medium-pressure LC (eluent: ethyl acetate : *n*-hexane = 1 : 20) to afford cyclohexyl cinnamate **3** (234 mg, 98%). The catalyst was re-used intact for the next reaction without any pre-treatment.

EPMA pictures of supported silica

Phosphorous

Fluorine

Palladium

SEM picture of supported silica (10 KV, x 1,700)

SEM picture of un-supported silica (5 KV, x 1,900)

SEM picture of supported silica (5 KV, x 70,000)

SEM picture of un-supported silica (5 KV, x 70,000)

AFM picture of supported silica (500 nm x 500 nm)

AFM picture of un-supported silica (500 nm x 500 nm)

EPMA pictures of supported silica after 6 cycles

Palladium

Fluorine

Phosphorous

SEM picture of supported silica after 6 cycles (5 KV, x 70,000)