

Supplementary information

Synthesis and bifunctional catalysis of metal nanoparticle-loaded periodic mesoporous organosilicas modified with amino groups

Yu Horiuchi,^{a,} Dang Do Van,^a Yusuke Yonezawa,^a Masakazu Saito,^b Satoru Dohshi,^c
Tae-Ho Kim^d and Masaya Matsuoka^{a,*}*

^a *Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*

^b *Department of Chemistry and Materials Science, National Institute of Technology, Gunma College, 580 Toriba-machi, Maebashi, Gunma 371-8530, Japan.*

^c *Technology Research Institute of Osaka Prefecture, 1-18-13, Kishibe-naka, Suita, Japan*

^d *Division of Mechanics and ICT Convergence Engineering, Sun Moon University, Republic of Korea.*

E-mail: horiuchi@chem.osakafu-u.ac.jp; matsumac@chem.osakafu-u.ac.jp

¹H NMR spectral data

The products in Knoevenagel condensation reactions were also analysed by ¹H NMR spectroscopy. ¹H NMR spectral data were as follow:

α-Cyanocinnamate. ¹H NMR (400 MHz, CDCl₃): δ = 8.25 (1H, s); 7.99 (2H, d, 8.26 Hz); 7.56 (1H, t, 7.53 Hz); 7.5 (2H, t, 8.26 Hz); 4.38 (2H, q, 9.18 Hz); 1.40 (3H, q, 9.18 Hz)

Benzylidenemalononitrile. ¹H NMR (400 MHz, CDCl₃): δ = 7.87 (2H, d, 7.96 Hz); 7.73 (1H, s); 7.61 (1H, t, 7.04 Hz); 7.51 (2H, t, 7.96 Hz)

trans-β-Nitrostyrene. ¹H NMR (400 MHz, CDCl₃): δ = 7.99 (1H, d, 13.23 Hz); 7.57 (1H, d, 13.23 Hz); 7.53 (2H, d, 7.72 Hz); 7.48 (1H, t, 7.35 Hz); 7.44 (2H, t, 7.72 Hz)

Diethyl benzylidenemalonate. ¹H NMR (400 MHz, CDCl₃): δ = 7.72 (1H, s); 7.43 (2H, m); 7.36 (3H, m); 4.32 (2H, q, 7.35 Hz); 4.28 (2H, q, 7.35 Hz); 1.31 (3H, t, 7.35 Hz); 1.26 (3H, t, 7.35 Hz)

Experimental procedure

Synthesis of PME-DMED: PME modified with *N,N*-dimethylethylenediamine (PME-DMED) was synthesised by epoxidation of bridging ethylene moieties within PME and the following nucleophilic addition reaction with *N,N*-dimethylethylenediamine. Firstly, PME (500 mg) was loaded into a Schlenk flask and degassed at room temperature for 30 min under vacuum. After nitrogen purge, dehydrated acetonitrile (12 mL) and 2 M aqueous NaOH solution (50 mg) were added into the flask and cooled in an ice bath. Then, TBHP (3 mL) was added to the mixture, which was stirred at 273 K for 5 h. The resulting white solid was separated by filtration, washed with acetonitrile and ethanol and dried under vacuum, yielding an epoxide

product (PME-EP).

Subsequently, PME-EP (300 mg) was loaded into a Schlenk flask and degassed under vacuum at room temperature for 30 min and at 393 K for 12 h. After cooling to room temperature and nitrogen purge, dehydrated toluene (15 mL) and *N,N*-dimethylethylenediamine (5 mL) were added into the flask and stirred at 333 K for 12 h. The resulting white solid was separated by filtration, washed with toluene and methanol and dried under vacuum, yielding PME-DMED.

Synthesis of Pd/PME-DMED: Pd NPs-loaded PME-DMED was synthesised by a simple colloidal method. A mixture of 10 mM aqueous PdCl₂ solution (1.4 mL), ion-exchanged water (10 mL) and PVP (33 mg) was stirred in an ice bath. To the solution, 88 mM aqueous NaBH₄ solution (1 mL) was added dropwise, which was stirred at 273 K for 30 min. After that, PME-DMED (150 mg) was added into the solution and resulting mixture was stirred at 273 K for 4 h. The thus-obtained solid was separated by filtration, washed with ion-exchanged water and dried under vacuum, yielding Pd/PME-DMED.

Tsuji-Trost reaction: The catalyst (30 mg) was placed into a 35 mL Schlenk flask, which was then fully purged with Ar. A solution of ethanol (3 mL), allyl methyl carbonate (0.3 mmol) and ethyl acetoacetate (3.6 mmol) was introduced into the flask, deoxygenated by bubbling of Ar for 30 min and stirred at 353 K for 24 h. The progression of the reaction was monitored by gas chromatography (Shimadzu GC-14B with a flame ionization detector) equipped with an InertCap®1 capillary column.