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Homogeneous and heterogeneous catalysts of organopalladium functionalized-polyhedral oligomeric silsesquioxanes for Suzuki–Miyaura reaction

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ABSTRACT

The mononuclear T_8-Pd and multinuclear T_{10}-Pd catalysts (**3** and **6**) were prepared from a reaction between Pd(COD)Cl_2 (COD = 1,5-cyclooctadiene) and the corresponding octameric T_8 and decameric T_{10} silsesquioxane cages, functionalized with pyridine–triazole ligands. The T_8-Pd complex **3** featuring one Pd(II) center was employed as a homogeneous catalyst for Suzuki–Miyaura cross coupling in a 1:1 EtOH:H_2O solvent. On the other hand, the multinuclear T_{10}-Pd catalyst **6** (*ca.* 4.6 Pd for each T_{10} cage) was obtained as amorphous insoluble materials with exceptionally high molecular Pd loading (1.61 mmol Pd g^{-1}). Under the same catalytic conditions, the homogeneous catalysts **3** exhibited slightly higher activity than the heterogeneous catalyst **6** (initial TOFs = 870 and 690 h^{-1}, respectively). Furthermore, for **6**, 4-(MeO)C_6H_4Br and $PhB(OH)_2$ substrates were catalyzed in the presence of a low catalyst loading of 3.6×10^{-3} mol% Pd under aerobic conditions to afford the coupled product in 91% yield (*i.e.*, turnover number (TON) = 2.5×10^4). The silsesquioxane-supported Pd catalyst **6** was recovered by simple centrifugation and reused for at least five catalytic cycles without a loss in activities.

1. Introduction

Polyhedral oligomeric silsesquioxanes prepared *via* a hydrolytic-condensation reaction of either alkoxy- or halosilane monomers have been considered as a promising organic–inorganic hybrid precursor. General features of silsesquioxanes include inorganic cage-like silica covalently attached with organic substituents (*e.g.* aryl, vinyl, allyl, and aliphatic-substituted groups) [1–3], which can be designed for subsequent modifications. For example, azido-functionalized polyhedral oligomeric silsesquioxanes are considered reactive materials, which can be further functionalized through "click" reactions [4,5]. These materials containing click linkers have already been used in various applications including electronics [6], polymer nanocomposites [7], bioconjugations [8], and self-assembling dendrimers [9]. However, examples of self-assembled catalytic units on those materials are still rare [10–12]. Recent studies have used polyhedral oligomeric silsesquioxanes as catalyst supports for alkene epoxidation and, in some cases, the resulting catalysts were superior to the homogeneous counterparts in terms of selectivity, efficiency, and reusability [13,14]. In addition, Tang et al. reported that a chiral rhodium catalyst supported on bifunctionalized silsesquioxane-based materials exhibited high performance for asymmetric transfer hydrogenation of aromatic ketones both in enantioselectivity and catalytic activity [15].

Catalytic applications involving 1,2,3-triazole-based ligands have recently been of much interest due to ligand's facile synthesis and convenient substituent modification [16–18]. For example, our group has recently reported the use of Pd(II) complexes featuring the bidentate pyridine–triazole ligands as efficient catalysts for Suzuki–Miyaura cross-coupling reactions [19]. To explore the role of silsesquioxanes as catalyst supports, this work for the first time introduces pyridine–triazole moieties onto the T_n silsesquioxanes. The pyridine–triazole group serves as a bidentate ligand for Pd(II) ions. In particular, the Pd(II) complex supported on the mono pyridine–triazole substituted octameric silsesquioxane was

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synthesized and investigated as a homogeneous catalyst for Suzuki–Miyaura cross coupling. Similarly, a fully decorated decameric silsesquioxane containing multiple Pd(II) complexes was explored as a heterogeneous catalyst. For Suzuki–Miyaura cross-coupling reactions, the multifunctionalized heterogeneous catalyst promotes not only high catalytic efficiency, but also excellent catalyst recovery while retaining its catalytic activity.

2. Experimental

2.1. Materials

(3-azidopropyl)hepta(*i*-butyl)octasilsesquioxane (**1**) and deca (3-azidopropyl) decasilsesquioxane (**4**) were prepared according to our previous report [4], while Pd(COD)Cl_2 (COD = 1,5-cyclooctadiene) was prepared according to the literature [19]. $CuSO_4$, sodium ascorbate, and 2-ethynylpyridine (purity; 98%), K_2CO_3, and $K_3PO_4{\cdot}H_2O$ were purchased from Sigma Aldrich. Ethyl acetate, dichloromethane and hexane were of commercial grade and distilled prior to use. The pre-coated silica gel 60 F_{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck&Co., Inc.

2.2. Physical measurements and instrumentations

Fourier transform nuclear magnetic resonance spectra of sample solutions were obtained by using Bruker's Ascend 400 high-resolution magnetic resonance spectrometer for ^{1}H (400 MHz), ^{13}C{^{1}H} (100 MHz) and ^{29}Si{^{1}H} (79 MHz) nuclei. The ^{29}Si{^{1}H} CP/MAS NMR spectrum was acquired at 60 MHz frequency with AVANCE 300 MHz Digital NMR Spectrometer (Bruker Biospin; DPX-300). Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane and residual solvent peaks were used as a reference. High-resolution mass spectra (HRMS) were recorded using a Bruker micro TOF spectrometer in the ESI mode and elemental analyses were performed on a Perkin Elmer 2400 CHN. The ICP-OES and MP-AES spectra were recorded by the inductively coupled plasma optical emission spectrometer, Spectro CIROS^{CCD} and the microwave plasma-atomic emission spectrometer (MP-AES) Systems 4200 MP-AES, respectively. The samples for ICP-OES and MP-AES were prepared as solutions in 2% nitric acid. Powder X-ray diffraction was performed by Bruker D8 Advance with a monochromatic Cu Kα (40 kV, 40 mA) source, step size of 0.010°, and a step time of 3 s/step. Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) measurements were carried out using Bruker Alpha instrument (Bruker Optics GmbH, Ettlingen, Germany) (4000 and 400 cm^{-1}). ATR-FTIR data analysis using OPUS software (Bruker Optic) was applied to pre-process the spectral data. Single-crystal X-ray diffraction of the catalyst **3** ($C_{39}H_{76}Cl_4N_4O_{12}PdSi_8$) was measured on a Bruker D8-Quest PHOTON-100 CMOS detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the APEX2 program [20]. Raw data frame integration was performed with SAINT [20]. An empirical absorption correction was applied to the data by the SADABS program [20]. The structure was solved using the direct methods and refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL2014 software package [21]. All hydrogen atoms were placed in calculated positions and refined isotropically with a riding model.

2.3. Synthesis of (3-(1H-1,2,3-triazol-4-yl-2-pyridine)propyl)hepta(i-butyl)octasilsesquioxane (2)

A mixture of 2-ethynylpyridine (0.10 mL, 1.02 mmol) and (3-azidopropyl)hepta(*i*-butyl)octasilsesquioxane (**1**) (0.12 g, 0.13 mmol) was dissolved in 5 mL of THF. To this solution mixture were added sodium ascorbate (0.13 g, 0.66 mmol) and $CuSO_4{\cdot}5H_2O$ (8.0 mg, 0.032 mmol) dissolved in deionized water. The solution was then stirred at room temperature for 3 d, after which it was poured into water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water and dried with anhydrous Na_2SO_4. Solvent evaporation afforded the crude product, which was further purified by column chromatography with a gradient eluent (10%, 15%, and 20% EtOAc in hexane) to produce the compound **2** as a white solid in 85% yield (0.11 g, 0.11 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.58 (d *J* = 4.4 Hz, 1H, Py*H*), 8.21 (s, 1H, N=C*H*), 8.18 (d *J* = 10 Hz, 1H, Py*H*), 7.80 (t *J* = 5.2 Hz, 1H, Py*H*), 7.24 (m, 1H, Py*H*), 4.40 (t *J* = 7.2 Hz, 2H, N—CH_2), 2.05 (quin *J* = 7.7 Hz, 2H, $CH_2CH_2CH_2$), 1.84 (sext *J* = 6.7 Hz, 7H, C*H*(CH_3)$_2$), 0.94 (m, 42H, CH(CH_3)$_2$), 0.65 (overlapped, 2H, CH_2Si), 0.60 (m, 14H, CH_2CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.2, 149.0, 147.9, 137.1, 122.8, 121.9, 120.3, 52.7, 25.7, 25.6, 24.1, 23.9, 23.8, 22.4, 22.3, 9.2. ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ −67.51, −67.87, −68.65 (relative intensity ratio = 3:4:1). HRMS (ESI-TOF) calcd. for $C_{38}H_{74}N_4O_{12}Si_8Na$ [M + Na]$^+$: 1025.3355, found 1025.3353. Anal. Calcd. for $C_{38}H_{74}N_4O_{12}Si_8$: C, 45.47; H, 7.43; N, 5.58. Found: C, 45.25; H, 7.82; N, 5.18.

2.4. Synthesis of dichloro-(3-(1H-1,2,3-triazol-4-yl-2-pyridine)propyl) hepta(i-butyl)octa-silsesquioxane palladium(II) complex (3)

A mixture of **2** (0.20 g, 0.20 mmol) and an equimolar of Pd(COD)Cl_2 (0.056 g, 0.20 mmol) in CH_2Cl_2 (8 mL) was stirred at room temperature. After 24 h, glass fiber filtration followed by solvent evaporation gave the crude product as a brown yellow solid. Further recrystallization in CH_2Cl_2 and diethyl ether afforded the catalyst **3** as a dark yellow solid in 55% yield (0.13 g, 0.11 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.79 (d *J* = 5.6 Hz, 1H, Py*H*), 8.54 (d *J* = 3.6 Hz, 1H, N=C*H*), 8.04 (s, 1H, Py*H*), 8.03 (s, 1H, Py*H*), 7.29 (t *J* = 4.7 Hz, 1H, Py*H*), 4.59 (t *J* = 7.2 Hz, 2H, N—CH_2), 2.05 (sext *J* = 6.2 Hz, 2H, $CH_2CH_2CH_2$), 1.93 (sext *J* = 6.5 Hz, 7H, C*H*(CH_3)$_2$), 0.94 (d *J* = 6.6 Hz, 42H, CH(CH_3)$_2$), 0.63 (overlapped, 2H, CH_2Si), 0.60 (m, 14H, CH_2CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 149.9, 148.3, 147.6, 140.3, 124.9, 124.6, 122.6, 55.5, 25.7, 23.9, 23.8, 22.4, 22.3, 9.3. ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ −67.45, −67.83, −68.35 (relative intensity ratio 3:4:1). HRMS (ESI-TOF) calcd. for $C_{38}H_{74}N_4O_{12}Si_8PdCl_2Na$ [M + Na]$^+$: 1203.1771, found 1203.1775. Anal. Calcd. for $C_{38}H_{74}N_4O_{12}Si_8PdCl_2$: C, 38.64; H, 6.32; N, 4.74. Found: C, 38.64; H, 6.58; N, 4.84.

2.5. Synthesis of deca(3-(1H-1,2,3-triazol-4-yl-2-pyridine)propyl) decasilsesquioxane (5)

A mixture of 2-ethynylpyridine (0.20 mL, 2.0 mmol) and deca(3-azidopropyl)decasilsesquioxane (**4**) (0.20 g, 0.15 mmol) was dissolved in 5 mL of THF. To this solution mixture was added a catalytic amount of sodium ascorbate (7.4 mg, 0.040 mmol) and $CuSO_4{\cdot}5H_2O$ (4.7 mg, 0.019 mmol) and the solution was stirred at room temperature for 3 d. Then, the reaction mixture was poured into water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water and dried with anhydrous Na_2SO_4. Filtration followed by solvent evaporation afforded the crude product, which was purified by column chromatography using 4:1 CH_2Cl_2/MeOH as an eluent. A yellow solid of **5** was obtained in 56% yield (0.20 g, 0.084 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.49 (d *J* = 4.0 Hz, 10H, Py*H*), 8.24 (s, 10H, N=C*H*), 8.09 (d *J* = 7.8 Hz, 10H, Py*H*), 7.68 (t *J* = 7.4 Hz, 10H, Py*H*), 7.15 (t *J* = 6.0 Hz, 10H, Py*H*), 4.36 (t *J* = 6.5 Hz, 20H, NCH_2), 1.96 (m, 20H, $CH_2CH_2CH_2$), 0.55 (m, 20H, CH_2Si). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.2, 149.2, 148.0, 137.0, 122.8, 122.6, 120.2, 52.4, 24.0, 9.2. ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25 °C, TMS): δ