A Solid-phase Self-organized Catalyst of Nanopalladium with Main-chain Viologen Polymers: α -Alkylation of Ketones with Primary Alcohols

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Preparation of 2: To a solution of **1** (1.68 g; 4.0 mmol) in water (100 mL) was added a solution¹ of PdCl₂ (709 mg; 4.0 mmol) and NaCl (4.68 g) in water (100 mL) at 25 °C, giving orange precipitates. The mixture was stirred at the same temperature for 1 h. Purification by filtration (pore size: 1 μ m), washing with water and drying at 5 Pa for 12 h afforded the insoluble product **2** (1.77 g) as an orange powder.

CP-MAS ¹³C NMR (232MHz; solid) δ 148.9, 146.8, 135.0, 131.1, 128.0, 64.4; IR (ATR) ν 3471, 3117, 3055, 2920, 2851, 1636, 1611, 1436, 1421, 809, 768 cm⁻¹; Anal. calcd. for (C₁₈H₁₆Br₂Cl₂N₂Pd·3H₂O)_n: C 33.18%, H 3.40%, N 4.30%, found: C 31.91%, H 2.66%, N 4.33%

¹ The solution was prepared by mixing PdCl₂ and NaCl in water at 80 °C.

Preparation of nano-Pd-V 3: A solution of NaBH₄ (450 mg) in EtOH (75 mL) was slowly added dropwise over 10 min to a suspension of **2** (900 mg) in EtOH (75 mL) at 25 °C, and the suspension was stirred for 6 h. Purification by filtration (pore size: 1 μ m), washing with water and drying at 5 Pa for 12 h gave nano-Pd-V **3** (630 mg) as a dark brown powder.

CP-MAS ¹³C NMR (232MHz; solid) δ 130.9, 128.8, 63.9, 56.8, 52.8, 42.1, 31.5, 15.5; IR (ATR) ν 3471, 3117, 3054, 2920, 2851, 1636, 1436, 1236, 1090, 891 cm⁻¹; Anal. calcd. for (C₁₈H₁₆Br₂N₂Pd·3H₂O)_n: C 37.24%, H 3.82%, N 4.82%, found: C 37.51%, H 3.72%, N 5.08%

General Procedure for α -alkylation of the ketones **4 with the primary alcohols **5** in the presence of nano-Pd-V **3** and Ba(OH)₂·H₂O:** To a suspension of nano-Pd-V **3** (10 mg) and Ba(OH)₂·H₂O (63 mg) was added water (42 μ L), and the suspension was mixed by a vortex mixer for 1 min at 25 °C. Compound **4** (0.334 mmol) and **5** (0.668 mmol) were added to the reaction mixture, which was stirred at 100 °C for 24 h. For the reactions shown in Table 2, entries 4-12, the mixture was purified by column chromatography (eluent: EtOAc/hexane) to give **6**. For the reactions shown in Table 2, entries 1-3, EtOAc (8 mL) was added to the reaction mixture, which was then centrifuged at 4000 rpm for 5 min. EtOAc layer was decanted and analyzed by GC to determine the GC yield of **6a**. To the residue was added water (8mL), followed by centrifugation at 4000 rpm for 5 min and decantation of the aqueous layer to give a black powder that was dried at 5Pa for 12 h and used for the next reaction as areusable catalyst.

1-cyclohexyl-3-(4-methoxyphenyl)propan-1-one (6g)

¹H NMR(500 MHz, CDCl₃) δ 7.09 (d, J =8.5 Hz, 2H), 6.81 (d, J =8.5 Hz, 2H), 3.78 (s, 3H), 2.82 (t, J =7.6 Hz, 2H), 2.71 (t, J =7.6 Hz, 2H), 2.27-2.33 (m, 1H), 1.58-1.81 (m, 5H), 1.16-1.34 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ 213.3, 157.9, 133.5, 129.2, 113.8, 55.2, 51.0, 42.8, 28.8, 28.4, 25.8, 25.6; IR (ATR) 2926, 2853, 1704, 1611, 1512, 1466, 1448, 1230, 1239, 1177, 1090, 1035, 890, 827, 630 cm⁻¹; MS(EI(+)) 246 (M⁺), 163 (M⁺), 121 (bp); HRMS (ESI(+)) calc for C₁₆H₂₂O₂Na (M+Na⁺) 269.1518, found 269.1526

Registry Numbers; **1**: 32168-10-8; **4a**: 111-13-7; **4b**: 821-55-6; **4c**: 2550-26-7; **4d**: 823-76-7; **4e**: 98-86-2; **4f**: 100-06-1; **5a**: 111-87-5; **5b**: 112-30-1; **5c**: 100-51-6; **5d**: 105-13-5; **6a**: 45206-91-5; **6b**: 18277-00-4; **6c**: 56741-23-2; **6d**: 56705-47-6; **6e**: 5396-91-8; **6f**: 43125-06-0; **6h**: 1669-49-4; **6i**: 1083-30-3; **6j**: 5739-38-8

Figure S-1. SEM imaged of **3**

NONE SEI 3.0kV X7,000 1 μ m WD 4.2mm

NONE SEI 3.0kV X50,000 100nm WD 4.2mm

Figure S-2. TEM and STEM/EDS imaged of **3**

The STEM/EDS analysis was performed onto a carbon sheet having a Cu mesh.

¹H NMR of 6g

¹³C NMR of **6g**