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Palladium bipyridyl complex anchored on nanosized MCM-41 as a highly efficient and recyclable catalyst for Heck reaction

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Abstract—Palladium bipyridyl complex anchored inside the channels of nanosized MCM-41 silicas was found to be a highly efficient and recyclable catalyst for the Heck reaction with a turnover number up to 10^6 for each cycle.

Palladium catalyzed coupling of aryl halides and olefins, known as Heck reaction, is an important reaction for carbon–carbon bond formation.[1,2] Although the homogeneous condition for this catalysis is well documented, the search of new heterogeneous catalysts for both efficient and recyclable purposes has received much attention recently.[2c,d] Among various strategies, incorporation of active metals or their complexes into porous silica matrix is one of the promising approaches.[3] Ying and co-workers have reported the preparation of a highly dispersed Pd species throughout the entire MCM-41 for Heck reaction.[4] Other studies involving the palladium-amine[5] and -imine/pyridine[6] complexes anchored onto MCM-41 for this purpose have appeared. Although most of the known heterogeneous catalysts have demonstrated the purpose of recycle use, the catalytic turnover number (TON) for a single run appeared to be a challenge as compared to the homogeneous system. To our knowledge, the TON of the heterogeneous catalysis is usually lower by a factor between 10^1 and 10^2 than the corresponding homogeneous one.[3g,7,8] For the catalysis carried out within a confined space, saturation of the product and salt inside pore generally decreases the activity of catalysts.[6a] In this context, we found that a bipyridine–palladium complex grafted onto the surface of nanosized MCM-41 performs as a high efficient and recyclable catalyst for the Heck reaction, offering an opportunity to meet the goal of green chemistry.

According to the procedure reported by Lin et al.,[9] the nanosized (70–120 nm) mesoporous material MCM-41 possessing worm-hole type pore structure with a narrow average pore diameter of ca. 2.9 nm and surface area of $888\,\mathrm{m^2\,g^{-1}}$ was used for loading the palladium catalyst. The size of the MCM-41 materials is much less than the normal micro-sized ones, facilitating easy transport of the reactants and products. For the ligand part, 4,4′-bis(bromomethyl)-2,2′-bipyridine **1** was prepared according to the reported method.[10] Treating **1** with 3-aminopropyltriethoxysilane in the presence of Et_3N at 50 °C for 6 h resulted in the formation of functionalized bipyridine **2**.[13] Because of the sensitivity of triethoxysilyl groups toward moisture, **2** was subsequently reacted with $PdCl_2(PhCN)_2$ in dried toluene to give the desired species **3**. The resulting palladium complex **3** was modified onto the freshly calcined nano-sized MCM-41 material in toluene by refluxing for 48 h, and the unreacted silanol groups on the silica surface was silylated by the treatment with chlorotrimethylsilane (Scheme 1). The amount of Pd complex anchored on the wall of MCM-41 was quantified to be 0.14 mmol/g by ICP mass spectrometer.

From the N_2 adsorption–desorption isotherm study, the palladium-loaded MCM-41 possesses a BET (Brunner–Emmett–Teller) surface area of $660\,\mathrm{m^2\,g^{-1}}$ with a narrow pore size distribution centered at 2.5 nm. The grafting of

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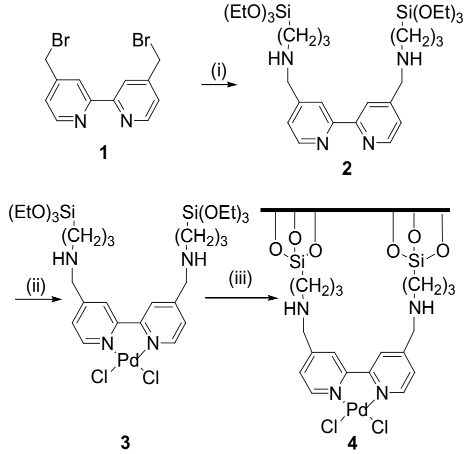

Scheme 1. Preparation of Pd grafting nano-sized MCM-41: (i) $H_2N(CH_2)_3Si(OEt)_3$, Et_3N, THF; (ii) $(CH_3CN)_2PdCl_2$; (iii) (a) MCM-41, toluene, Δ; (b) Me_3SiCl.

metal complex decreases the pore size and surface area somewhat, but with enough space left for the reactant molecules. One notices that there is a very large jump of adsorption volume near saturation pressure. This reflects the large contribution to adsorption by the interparticle texture porosity, which shows these MCM-41 particles are indeed in nanosized dimension. The TEM images of as calcined and grafted material are shown in Figure 1 for comparison, indicating the preservation of nanoparticle morphology upon grafting of complexes.

For the catalytic activity test, coupling reactions of various aryl iodides and bromides with acrylates and styrene were investigated. In a typical experiment, freshly distilled *N*-methylpyrrolidinone (NMP) solvent was added to a degassed flask containing a mixture of aryl halide, olefin, and triethylamine in a ratio of 1:1.5:1, followed by the addition of the catalyst. The resulting mixture was heated in an oil bath at the specified temperature for a certain period of time. The catalyst was recovered by centrifugation and washed subsequently with THF and water twice for each washing. The liquid portion was added to water, extracted with ethyl acetate, and concentrated to yield the desired product, which was either characterized by ^{1}H NMR spectroscopy or separated by column chromatography. All of the results are summarized in Table 1.

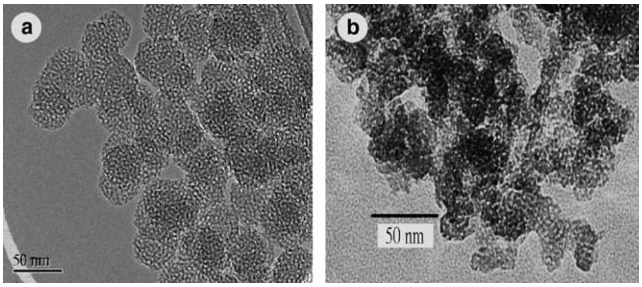

Figure 1. TEM images of (a) as calcined; (b) Pd complex grafted MCM-41 silicas.

Reaction of aryl iodides with methyl acrylate in the presence of Et_3N yielded the corresponding cinnamate in ~80% yields (entries 1, 4). Replacing Et_3N with Bu_3N, the products could be isolated almost quantitatively (entries 2–3, 5–6), presumably due to the higher boiling point of such base. However, the reaction of aryl bromides with butyl acrylate or styrene did not proceed at 100 °C. It took place smoothly at an elevated temperature with excellent turnover numbers for activated aryl bromide (entries 7–11). In the case of *p*-bromoacetophenone, the turnover frequency (TOF) can reach upto 6.6×10^4 (entry 7). As for bases, trialkylamine appeared to be a better choice. The use of sodium acetate or potassium carbonate provided only trace of product (entries 12–13) presumably due to the poor solubility of these salts in the organic solvents. Reaction of bromobenzene with butyl acrylate afforded the coupling product in good yield, but poor result with styrene (entries 14, 15). Unfortunately, this catalyst performance appeared to be poor with the deactivated aryl bromides (entry 16).

To demonstrate the good transport of molecules inside the nanosized MCM-41, the identical palladium complex was modified onto the wall of fibrous MCM-41 silicas (pore size ~2.7 nm) for comparison.[12] For the fibrous silica consisted of long channels (in 10^3 nm dimension), one would expect the difficulty in material transporting inside the channels. In addition, the same palladium complex catalyzed the coupling reaction under homogeneous conditions was studied for comparison. Figure 2 shows the difference of yield versus time in the coupling reaction of phenyl iodide with acrylate among these systems. It appears that nanosized catalyst **4** behaves in the same order of activity as the homogeneous one, but much better than the catalyst prepared via the support of the fibrous MCM-41 silica. This result clearly demonstrates very little diffusion interference along the nanosized MCM-41 channels for transporting molecules (i.e., the reactant molecules are easily accessing to the catalytic sites). On the other hand, the reaction proceeded slowly in the fibrous MCM-41 system, reflecting the difficult transport of substrates.

For the recycling study, reaction was conducted by using 100 mg (4.76×10^{-2} mol% Pd) of catalyst in the coupling of phenyl iodide with methyl acrylate ([substrate]/[Pd] = 2100). After the first run of the reaction, the catalyst was recovered by simple centrifugation and then dried under vacuum overnight. Under the same conditions, a complete conversion of the substrate into the desired product by using the recovered catalyst was observed within 5 h. Furthermore, the catalyst remained the same activity after four reuse runs, for example, close to 100% conversion for each use, without any saturation phenomenon during the reaction. As for the metal leaching, we checked the solution of the reaction mixture after the catalysis and found less than ppb level of palladium in the liquid portion of the reaction mixture. This observation also explains that the recycled catalysts remain the high activity after several uses.[11]

In summary, we have prepared an extremely efficient and recyclable palladium anchored nano-sized MCM-

Table 1. Results of the Heck reaction catalyzed by nanosized MCM-41-Pd[a]

Entry	Aryl halide	Olefin	Pd (mol%)	Base	*T* (°C)	*t* (h)	Yield (%)[b]	TON[d]
1	C_6H_5I	Methyl acrylate	9.33×10^{-5}	Et_3N	100	96	83	8.90×10^5
2	C_6H_5I	*n*-Butyl acrylate	9.33×10^{-5}	Bu_3N	100	96	98	1.05×10^6
3	C_6H_5I	Styrene	1.17×10^{-3}	Bu_3N	100	72	95[c]	8.12×10^4
4	*p*-MeC_6H_4I	Methyl acrylate	1.33×10^{-4}	Et_3N	100	96	81	6.09×10^5
5	*p*-MeC_6H_4I	*n*-Butyl acrylate	9.33×10^{-5}	Bu_3N	100	96	97	1.04×10^6
6	*p*-MeC_6H_4I	Styrene	9.35×10^{-4}	Bu_3N	100	72	97[c]	1.04×10^5
7	*p*-$CH_3COC_6H_4Br$	*n*-Butyl acrylate	9.33×10^{-5}	Bu_3N	170	16	98	1.05×10^6
8	*p*-$CH_3COC_6H_4Br$	Styrene	4.67×10^{-3}	Bu_3N	170	72	75[c]	1.61×10^4
9	*p*-BrC_6H_4CHO	*n*-Butyl acrylate	1.04×10^{-4}	Bu_3N	170	24	85	8.17×10^5
10	*p*-$BrC_6H_4NO_2$	*n*-Butyl acrylate	1.87×10^{-4}	Bu_3N	170	16	93	4.97×10^5
11	*p*-$BrC_6H_4NO_2$	Styrene	4.67×10^{-3}	Bu_3N	170	72	70[c]	1.54×10^4
12	*p*-$BrC_6H_4NO_2$	*n*-Butyl acrylate	9.33×10^{-3}	NaOAc	170	48	Trace	—
13	*p*-$BrC_6H_4NO_2$	*n*-Butyl acrylate	9.33×10^{-3}	K_2CO_3	170	48	Trace	—
14	C_6H_5Br	*n*-Butyl acrylate	4.70×10^{-4}	Bu_3N	170	48	72	1.53×10^5
15	C_6H_5Br	Styrene	1.87×10^{-2}	Bu_3N	170	72	20[c]	1.07×10^3
16	*p*-BrC_6H_4OMe	*n*-Butyl acrylate	4.67×10^{-3}	Bu_3N	170	96	12	2.57×10^3

[a] $[RX]/[Pd] = 10^6$; in *N*-methylpyrrolidinone.

[b] Isolated yields.

[c] *trans:cis* ~ 90:10.

[d] mol mol of Pd^{-1}.

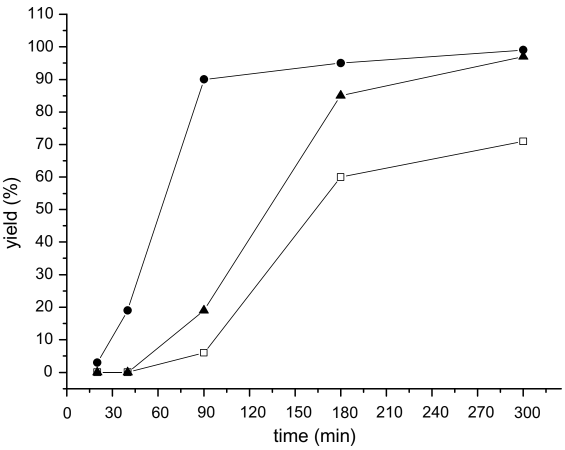

Figure 2. Plot of yields versus time for the Heck reaction of iodobenzene with methyl acrylate catalyzed by fibrous (□), nanosized (●) Pd anchored MCM-41 (0.14 mmol Pd/g), and homogeneous catalysis by the substituted bipyridyl palladium(II) complex (▲) at 100 °C. [substrate]/[Pd] = 2100:1.

41 for the Heck reaction, which might be useful for commercial purposes. The structure of silica support appears to be the key for this excellent activity presumably due to the good exchange of reactants, salts, and products inside the channels.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.08.065. Figure of the N_2 adsorption–desorption isotherm for the unloaded MCM-41 and the MCM-41 sample after loaded with palladium catalyst.

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13. Bipyridinyl ligand **2**: ^{1}H NMR (C_6D_6) δ: 0.67–0.73 (m, 4H), 1.14 (t, $J = 7.0$ Hz, 18H), 1.63–1.68 (m, 4H), 2.42 (t, $J = 7.0$ Hz, 4H), 3.50 (s, 4H), 3.75 (q, $J = 7.0$ Hz, 12H), 7.07 (d, $J = 4.2$ Hz, 2H), 8.57 (d, $J = 4.2$ Hz, 2H), 8.78 (s, 2H); ^{13}C NMR δ: 8.4 (2C), 18.6 (6C), 23.8 (2C), 52.4 (2C), 53.0 (2C), 58.4 (6C), 120.7 (2C), 123.1 (2C), 149.3 (2C), 151.2 (2C), 156.8 (2C). HRMS: *m*/*z* calcd for $C_{30}H_{54}N_4O_6Si_2$, 622.3582; found, 622.3539.