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Anchored Pd Complex in MCM-41 and MCM-48: Novel Heterogeneous Catalysts for Hydrocarboxylation of Aryl Olefins and Alcohols

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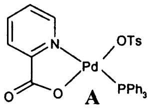
Carbonylation of aryl olefins and alcohols provide highly promising and eco-friendly routes for the synthesis of aryl propanoic acids having applications as nonsteroidal, antiinflammatory drugs.[1] This is considered as one of the best examples of the role of catalysis in developing cleaner, environmentally benign routes replacing stoichiometric organic synthesis[2] as evidenced by the commercial success of the Hoechst-Celanese process for the synthesis of ibuprofen,[3] which involves mainly a Pd catalyst with 10% HCl as a promoter.[4] High regioselectivity for ibuprofen (>95%) is achieved at high pressures (16−35 MPa) while, the selectivity reduces to 67% with a TOF of 50−70 h^{-1} at lower pressures (6−7 MPa). In recent reports,[5] a significant enhancement in the catalytic activity (TOF = 800−2600 h^{-1}) and regioselectivity (99%) for ibuprofen at lower pressures has been demonstrated with modified promoters, different phosphorus ligands, and Pd complexes.[5c,d]

These homogeneous catalysts often pose a serious threat on the practical utility due to difficulties in catalyst-product separation and reuse. Using supported Pd catalysts[6] for carbonylation of aryl halides[6a] and *p*-isobutylphenylethanol (IBPE),[6b] high activity (TOF = 1675−3375 h^{-1}) and selectivity (99%) for branched carboxylic acid derivatives was achieved for IBPE; however, in both cases it was concluded that the catalytic activity was due to Pd leaching into the solution under reaction conditions. Pd-impregnated catalysts (Pd on SiO_2, Al_2O_3, and clay) have also been used for hydrocarboxylation of olefins[7a] and IBPE[7b] wherein leaching of Pd metal after repeated reuse and use of HCl as a corrosive acidic promoter are the major drawbacks. Therefore, the problem of developing a true heterogeneous Pd catalyst for such carbonylation reactions still remains an open challenge.



A: Pd(pyca)(PPh$_3$)(OTs)

We report here for the first time, novel heterogeneous catalysts containing a Pd complex anchored in mesoporous supports[8] such as MCM-41 and MCM-48 for hydrocarboxylation of aryl olefins and alcohols with high regioselectivity, activity, and recyclability without the leaching of Pd complex from the supports. Unlike silica gel supports, Si-MCM-41 and Si-MCM-48 are highly ordered mesoporous silica having high surface areas, high porosity, well-defined porous structures, and controllable narrow pore-size distribution.[9] The stoichiometric reactions involved in hydrocarboxylation of aryl olefins and alcohols are presented in Scheme 1.

Scheme 1. Hydrocarboxylation of Alkenes or Alcohols to Acids with Pd-pyca−MCM-41 and Pd-pyca−MCM-48 Catalysts

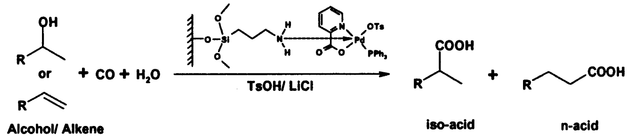


Table 1. Comparison of Activity and Selectivity of Various Catalyst Systems for Hydrocarboxylation

catalysts	substrate	conversion (%)	selectivity (%) iso	selectivity (%) n	TOF (h^{-1})	time (h)
A	S[a]	97.00	99.01	0.98	2600	0.18
B	S	98.12	99.31	0.68	463	12.0
C	S	98.37	99.03	0.96	417	12.0
A	4-Me-S	95.06	99.12	0.81	1173	0.83
B	4-Me-S	97.80	98.60	1.38	406	12.0
C	4-Me-S	98.11	99.10	0.88	367	12.0
A	4-^{t}Bu-S	95.00	99.00	0.98	1313	0.35
B	4-^{t}Bu-S	93.40	99.31	0.67	286	12.0
C	4-^{t}Bu-S	95.10	99.23	0.75	262	12.0
A	IBPE	99.00	99.00	0.99	804	0.60
B	IBPE	95.60	97.50	2.45	450	12.0
C	IBPE	95.00	97.90	1.98	439	11.0

[a] S = styrene; catalyst: 50 mg (10 mg for **A**); substrate: 4.8 mmol; LiCl: 0.5 mmol; TsOH: 0.5 mmol; PPh_3: 0.095 mmol; H_2O: 0.01 mmol; solvent: MEK; P_{CO}: 3.06 MPa; agitation speed: 18.34 Hz; temperature: 388 K; total liquid volume: 2.5×10^{-5} m^3; Pd content: 0.18 wt % in **B** (Pd-pyca−MCM-41); 0.20 wt % in **C** (Pd-pyca−MCM-48); TOF = turn over frequency.

For preparation of the anchored Pd complex catalysts, 3-aminopropyltrimethoxysilane (APTS) was used to functionalize MCM-41 and MCM-48 by a procedure described elsewhere.[10] On treatment of these functionalized supports with Pd(pyca)(PPh$_3$)(OTs) (**A**),[5c,d] stable heterogeneous catalysts were obtained. Following this approach, Pd-pyca−MCM-41 (catalyst **B**) and Pd-pyca−MCM-48 (catalyst **C**) were prepared (see Supporting Information, for syntheses of catalysts **B** and **C**).

These catalysts were characterized by FT-IR, powder-XRD (for details see Supporting Information, Table 1), TEM, XPS, and solid-state ^{31}P CP-MAS NMR. Powder-XRD patterns and TEM images of the parent materials and anchored catalysts showed the typical hexagonal phase (*p*6*mm*) of MCM-41 with the main (100) Bragg reflection and cubic phase (*Ia*3*d*) of MCM-48 with distinct (211) and (220) reflections indicating a high degree of ordered mesoporosity (see Supporting Information, Figures 1 and 2). Catalysts **B** and **C** showed no changes in the porous structures after functionalization and incorporation of complex **A** inside the mesopores. We imaged parent MCM-41 and MCM-48 materials and Pd-anchored materials by TEM to direct the location of the grafted complex **A** inside the mesopores. We could observe a striking difference in the images of the materials, where the exterior surface retains strong image contrast[10] probably due to complex **A** inside the mesopores (treated with Ph_2SiCl_2), in comparison to the complex anchored (without Ph_2SiCl_2 treatment) both on the interior as well

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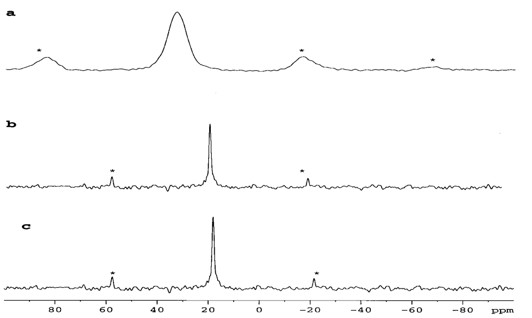

Figure 1. ^{31}P CP MAS NMR chemical shifts of (a) Pd-pyca complex, (b) Pd-pyca−MCM-41 before reaction, (c) Pd-pyca−MCM-41 after 3rd recycle, at 500 MHz (* in NMR patterns denote sidebands at 8 kHz).

as exterior walls of MCM-41 (see Supporting Information, Figure 2 **B** and **C**). Catalyst **C**, as an example, was chosen for X-ray photoelectron spectra (XPS), which showed typical Pd(II) oxidation state (Pd $3d_{5/2} = 337.0$ eV, Pd $3d_{3/2} = 343.0$ eV) and no cluster formation of Pd metal in the catalyst (see Supporting Information, Figure 3 and Table 2). FT-IR of the catalysts **B** and **C** showed both the stretching vibrations at 1329 cm^{-1} ($\nu_{O=C-O}$) and 1669 cm^{-1} ($\nu_{C=O}$), similar to those of complex **A** (1330 and 1668 cm^{-1} respectively).[5d] The Pd−N stretching frequencies of catalysts **B** and **C** at 564 cm^{-1} (ν_{Pd-N}) varied from that of complex **A** ($\nu_{Pd-N} =$ 568 cm^{-1}),[5d] which reflects a possible coordination between N_{APTS} and Pd-atom. ^{31}P CP MAS NMR of catalysts **A** and **B** (Figure 1 a and b) showed only one major ^{31}P signal ($\delta_{iso} = 33.13$ ppm) for complex **A**, as envisaged from the structure, while that of catalyst **B** has a shifted ^{31}P signal ($\delta_{iso} = 17.968$ ppm). We presume APTS (tethered inside the mesopore walls) when anchored with Pd-pyca complex donates an electron pair from N_{APTS} to the Pd atom (Scheme 1). This in turn increases the electron density on the P atom of PPh_3 by dπ (P) ↔ dπ (Pd) bonding. This is consistent with the results of FT-IR analysis.

The hydrocarboxylation experiments were carried out using catalysts **A**, **B**, and **C** in a stirred high-pressure reactor. (Carbonylation reactions are very hazardous because of handling with CO gas at high pressures and temperatures; hence, we suggest extreme precautions and proper guidance while performing reactions.) The details of the procedure followed were similar to those described in our previous report.[5d] The reaction mixtures and products were analyzed by gas chromatography (GC) to determine conversion, selectivity, and turnover frequency (TOF). The results on hydrocarboxylation of styrene, substituted styrenes as well as *p*-isobutylphenylethanol (IBPE), using these catalysts are presented in Table 1. The results showed almost complete conversion (>95%) of all the substrates with a regioselectivity >98% for the desired 2-arylpropanoic acids. The TOF values for the anchored catalysts were in the range of 415−465 h^{-1} for styrene and 435−450 h^{-1} for IBPE as substrates, respectively. Catalysts **B** and **C** show almost similar TOFs, which may be due to similar rates of interaction of the substrate molecules and the Pd atom residing inside the mesoporous matrices. Although the TOF values are lower for anchored catalysts compared to that for the homogeneous complex catalyst **A** (TOF = 800−2600 h^{-1}), these heterogeneous catalysts are easier to separate and reuse in practice.

To prove the stability of these catalysts, hot reaction-mixture filtrates were analyzed for Pd content (0.7 ppm, $\sim 3.5 \times 10^{-4}$ % of total Pd content in the system) by ICP-AES, which showed almost no leaching of Pd metal from catalysts **B** and **C** in the liquid phase during reactions. The filtrates also showed no hydrocarboxylation activity, when tested without any addition of fresh catalysts. The catalysts were found to be very stable, restoring high activity and selectivity even after three recycles, as has been presented for hydrocarboxylation of styrene with catalysts **B** and **C** (see Supporting Information, Figures 4 and 5). Comparison of catalysts **B** and **B-3** (recycle 3 with catalyst **B**) analyzed by ^{31}P CP MAS NMR (Figure 1−c), showed no change in δ_{iso} values. Thus, the geometry of the Pd-pyca anchored inside the MCM-41 remains intact even after the third recycle. This observation provides evidence that complex **A** is encapsulated inside the mesopores and does not leach out under reaction conditions. In contrast to this, the catalyst prepared by anchoring the complex **A** on silica gel as a support showed a considerable amount of leaching of Pd metal (∼15%) during reaction (similar to that observed by Fraile et al. for epoxidation reactions[9a]). The anchored Pd catalysts in MCM-41 and MCM-48 reported here represent the first case of true heterogeneous Pd catalysts for hydrocarboxylation of aryl olefins and alcohols.

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Supporting Information Available: Syntheses, powder-XRD, TEM, FT-IR, XPS data, and recycle-runs of Pd-pyca−MCM-41 (**B**) and Pd-pyca−MCM-48 (**C**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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