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Recyclable ligand-free mesoporous heterogeneous Pd catalysts for Heck coupling

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Abstract—Ligand-free Pd–MCM41 catalysts are highly active in the Heck coupling of bromoarenes including deactivated bromo derivatives to give coupled products in high yields with high selectivities without the need to exclude air or moisture. The catalyst samples exhibit unprecedented stability among heterogeneous catalysts and can be reused at least 20 times to achieve complete conversion without any additional activation treatment.

The Heck reaction[1] is an established, useful protocol for carbon–carbon bond formation and has found widespread applications in the stereoselective synthesis of various alkenes. Usually aryl halides are reacted with alkenes in the presence of palladium and a suitable base in a single step under mild conditions.[2] Efforts have recently been made to develop new catalysts to replace air- and moisture-sensitive phosphine ligands, which also allow the use other aryl derivatives. These new catalysts include palladacycles,[3] *N*-heterocyclic carbene–palladium catalysts,[4] a macrocyclic recoverable triolefin complex,[5] and thiourea–Pd(0) complexes.[6] Attention has also been paid to the search for new, efficient, and recyclable heterogeneous catalysts. Among various strategies, incorporation/grafting of metal complexes into suitable solids such as polymers[7] or porous siliceous materials[8] have been demonstrated to be promising approaches. Equally useful catalysts can be prepared by entrapping[9] or immobilizing[10] metal nanoparticles, and generating and depositing active metal particles onto solid supports.[11] In this context, the recent observation that $Pd(OAc)_2$ is a highly active catalyst in the Heck reaction in low concentrations (catalyst amount below 0.1 mol %) is a significant new development,[12] but further improvement is needed. Decomposition of the catalytically active component, metal leaching, insufficient catalyst activity, and difficulties with respect to recovery and recycling properties are the major problems requiring significant effort.

Heterogeneous systems may offer solutions for some of these problems. Ordered mesoporous silica materials prepared by micelle-templated synthesis[13] have recently found wide application as catalyst materials. Among various possibilities, surface modification has been used quite extensively to produce active catalytic materials. The functional groups of such hybrid organic–inorganic materials[14] may serve as anchoring sites for metal complexes (heterogenization of homogeneous catalysts)[13b,f] or, having suitable catalytic properties, they may act as surface active sites.[13f,15] Mesoporous silicas may also serve as supports for metal particles.[13a,b,f,15c]

Metallic palladium has been incorporated into various silica materials including amorphous silica[11e,f,16] and ordered mesoporous silicas such as MCM-41,[11a,16,17] HMS,[11c] SAB-15,[11c] and ETS-10.[11e] These heterogeneous systems have been used as catalysts in hydrogenation[11e,16,17] and in various coupling reactions.[11e,f] In fact, Pd–MCM-41 prepared by vacuum deposition has already been applied in the Heck coupling.[11a]

We have found that a new, heterogeneous ligand-free Pd–MCM-41 system is an efficient and recyclable catalyst in the Heck coupling. For our catalyst synthesis we used a literature method[18] described for the synthesis

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Keywords: C–C Coupling; Heck reaction; Palladium; MCM-41; Heterogeneous Catalysis; Recycling.

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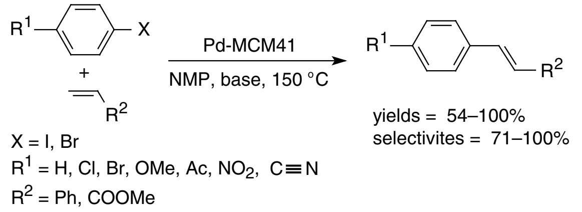
of MCM-41 and modified it for palladium incorporation.[19] Catalysts were generated via simultaneous self assembling of mesoporous MCM-41 silica and particle generation. Three catalysts with palladium loadings of 1.39%, 3.0%, and 5.85% based on inductively coupled plasma atomic emission spectroscopy (ICP-AES) were made and characterized by various physical methods. BET surface areas of the samples calculated by the BJH method were found to decrease (1099, 979, and 806 m^2/g, respectively), with increasing palladium loading, whereas pore diameters and d_{100} indexed unit-cell sizes determined by low-angle XRD increase slightly. The 1.39% Pd–MCM-41 sample exhibited three reflections characteristic of the MCM-41 structure (d_{100}—2.35°, d_{110}—4.07°, d_{200}—4.6°) but increasing Pd loading resulted in the formation of less ordered structures. Pd dispersion values measured by hydrogen chemisorption were 8.2%, 5.7%, and 13.6%, respectively. Further characterization data can be found in a recent publication.[20]



Scheme 1. The Heck reaction.

All three catalysts showed high activity and selectivity in the Heck coupling of iodobenzene with styrene (conversions: 76–84%, selectivities: 84–87%) and methyl acrylate (89–100% conversions and 100% selectivities) (Table 1).[21] Moreover, activities in the transformation of activated bromoarenes were also satisfactory. In all reactions complete *E* selectivity was observed, whereas in the transformations of styrene, products of α coupling were found (Table 1 and Scheme 1). It was also seen that activities depend on palladium loadings and parallel metal dispersion: in most cases catalytic performance of 3.0% Pd–MCM-41 with the lowest Pd dispersion (5.7%) showed lower activity.

Table 2. Pd-catalyzed Heck reaction of bromoarenes over 1.39% Pd–MCM-41 catalyst[a]

Aryl halide	Alkene	Time (h)	Conv. (%)	Sel.[b] (%)
Bromobenzene	Me acrylate	3	86	96
	Styrene	6	93	93
4-Bromobenzonitrile	Me acrylate	3	97	93
	Styrene	6	90	95
4-Bromoanisole	Me acrylate	3	82	94
	Styrene	6	91	89
1,4-Dibromobenzene	Me acrylate	3	100	93
	Styrene	6	85	92
1-Bromo-4-chlorobenzene	Me acrylate	3	64	100
	Styrene	6	54	91
1-Bromonaphthalene[c]	Me acrylate	3	100	100
	Styrene	6	100	92
3-Bromopyridine[d]	Me acrylate	22	94	100
	Styrene	22	57	93

[a] Reaction conditions: 1 equiv of aryl halide, 1.2 equiv of alkene, and Na_2CO_3, 0.2 equiv of Bu_4NCl, 0.3 mol % Pd.

[b] In all reactions complete *E* selectivity was observed. Side products: transformation of styrene—the product of α coupling, transformation of methyl acrylate–butyl cinnamate.

[c] Without Bu_4NCl.

[d] Without Bu_4NCl, with NaOAc as the base.

In further studies a wide range of other aryl halides were reacted with styrene and methyl acrylate and appropriately selected reaction conditions, namely the use of various bases and additives and the ratio of the reacting components, were tested. Aromatic chloro compounds were found not to react but high reactivities could be achieved with deactivated bromoarenes (4-bromoanisole, 1-bromo-4-chlorobenzene, 1,4-dibromobenzene) (Table 2). Under these conditions (the use of a small excess of alkene and Na_2CO_3 with Bu_4NCl as additive), bromobenzene also showed increased reactivity. The use of Bu_4NCl as additive was particularly beneficial in harmony with earlier observations.[2b,22] Interestingly, however, both 1-bromo-naphthalene and 3-bromopyridine gave much better results without the additive.

Table 1. Pd-catalyzed Heck reaction over Pd–MCM-41 catalysts with various Pd loadings[a]

Aryl halide	Alkene	1.39%		3.0%		5.85%	
		Conversion[b] (%)	Selectivity[c] (%)	Conversion[b] (%)	Selectivity[c] (%)	Conversion[b] (%)	Selectivity[c] (%)
Iodobenzene	Styrene	84	84	76	86	82	87
	Me acrylate	100	100	98	100	89	100
4-Iodoanisole	Styrene	93	80	83	80	88	80
	Me acrylate	100	100	100	100	100	100
4-Bromonitrobenzene	Styrene	97	95	100	95	95	95
	Me acrylate	100	100	99	100	100	100
4-Bromoacetophenone	Styrene	97	93	77	93	89	100
	Me acrylate	90	100	91	100	84	92

[a] Reaction conditions: equimolar amounts of aryl halide, alkene, and Na_2CO_3, NMP solvent; time: 1 h for iodobenzene, 2 h for all other aryl halides.

[b] Determined by GC.

[c] In all reactions complete *E* selectivity was observed. In the transformation of styrene, the product of α coupling was also formed.

Table 3. Recycling of Pd–MCM-41 catalysts and 10% Pd-on-carbon in the Heck coupling of iodobenzene with methyl acrylate[a]

Entry	Catalyst	Run 1	Run 3	Run 5	Run 7	Run 8	Run 10	Run 12
1	1.39% Pd–MCM-41	85	75	83	53	19	0	0
2	1.39% Pd–MCM-41[b]	85	97	98	86	34	0	0
3	1.39% Pd–MCM-41[c]	93	93	93	80	65	44	28
4	3.0% Pd–MCM-41	76	77	77	77	54	1	0
5	5.85% Pd–MCM-41	80	75	82	79	82	60	20
6	10% Pd-on-carbon	87	72	35	0			

[a] Reaction conditions: equimolar amounts of aryl halide, alkene, and NEt_3, 150 °C, 60 min.

[b] After the first use 10 μL of 4×10^{-2} M iodine solution in NMP was added.

[c] 170 °C, 45 min.

Recovery and catalyst reuse are important issues in the Heck coupling. Easy catalyst separation and recycling in successive batch operations can greatly increase the efficiency of the reaction. Reports exist, which show some success in this respect using immobilized complexes[7f,8a–d,g,23] and heterogeneous catalysts with metallic Pd[9,10,11b,f] in a limited number of reuses. We showed in an earlier study[11h] that new heterogeneous Pd catalysts with organic–inorganic hybrid supports exhibit promising characteristics in recycling studies. Therefore, detailed studies were performed with these new Pd–MCM-41 catalysts to explore their performance in reuse experiments.

First, all three catalysts were tested and their performance was compared to a commercial sample. Commercial 10% Pd-on-carbon rapidly loses activity (Table 3, entry 6) whereas all Pd–MCM-41 samples maintain activities for much longer (entries 1, 4, and 5). Treatment of 1.39% Pd–MCM-41 after the first run with iodine as described in an earlier study[24] proved to be useful to increase catalyst activity but was not suitable to prolong the lifetime of the catalyst (entry 2). Increased reaction temperature, however, did result in improvements in both activities and the number of reuses (entry 3).

In further studies changes in the reactant ratio and a combination of various bases were tested with 1.39% and 5.85% Pd–MCM-41 catalysts, which led to better performance. We observed further significant improvements at increased reaction temperature upon increasing the amount of both methyl acrylate and base by 50% (Table 4, entry 1): complete conversion was achieved and the catalyst could be reused 20 times without any loss of activity. Similar excellent results were observed for both catalyst samples using a mixture of organic and inorganic bases (entries 2 and 3). Furthermore, both the activity and the number of reuses could be maintained at lower temperature with the mixed bases (entry 4).

Table 4. Recycling of 1.39% and 5.85% Pd–MCM-41 catalysts in the Heck coupling of iodobenzene with methyl acrylate[a]

Entry	Catalyst	Run 1	Run 2–5	Run 10	Run 15	Run 20
1	1.39% Pd–MCM-41[a]	98	100	100	100	100
2	1.39% Pd–MCM-41[b]	100	100	100	100	100
3	5.85% Pd–MCM-41[b]	100	100	100	100	100
4	1.39% Pd–MCM-41[c]	100	100	100	100	100

[a] 170 °C, 45 min; methyl acrylate and NEt_3: 1.5 equiv each.

[b] 170 °C, 45 min; 1.5 equiv of methyl acrylate, 1 equiv of NEt_3, 0.5 equiv of Na_2CO_3.

[c] 150 °C, 60 min; 1.5 equiv of methyl acrylate, 1 equiv of NEt_3, 0.5 equiv of Na_2CO_3.

In conclusion, we have prepared new heterogeneous palladium catalysts supported on mesoporous MCM-41 and successfully used them in the Heck coupling of iodo- and bromoarenes. More importantly, the catalysts are stable under the reaction conditions and retain high activity and selectivity for at least to 20 successive runs without the need to exclude air or moisture. This excellent catalyst performance and the easy preparation and separation of the catalysts make these new Pd-on-MCM-41 systems a useful alternative to other heterogeneous Pd catalysts.

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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.2005.09.048.

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