Efficient Heterogeneous Palladium–Montmorillonite Catalysts for Heck Coupling of Aryl Bromides and Chlorides

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Abstract: New palladium catalysts were prepared using ion exchange or intercalation of Pd species into montmorillonite. The catalysts promote Heck reaction of various aromatic halides including aryl chlorides to give coupling products in high yields at low catalyst ratios down to 0.001 mol%.

Key words: C–C coupling, Heck reaction, palladium, montmorillonite, heterogeneous catalysts

The Pd-catalyzed reactions of substituted aromatics, characteristically aryl halides, with unsaturated compounds (activated alkenes and terminal alkynes) or aryl boronates are referred to as Heck-type arylation processes. These cross-coupling reactions have become invaluable synthetic methodologies to produce aromatics with vinyl or ethynyl substituents, and biaryls. The original processes known today as Heck coupling,¹ Suzuki–Miyaura reaction,² and Sonogashira coupling³ have broadened significantly because the scope of the reactants widened tremendously.

In recent years new Pd complexes of high activities have been developed in ever-increasing numbers, which are able to promote the reaction of aryl chlorides.⁴ Palladacycles also proved to be useful and effective.⁵ In addition, efforts have been made to search for new, efficient, and recyclable heterogeneous or heterogenized Pd catalysts⁶ and Pd nanoparticles.⁷ In this respect, recent observations by Köhler et al. are of particular interest.⁸ High dispersion of Pd species in the +2 oxidation state was shown to be a crucial requirement allowing Pd leaching and re-deposition and resulting in catalytic activities comparable to those of the best homogeneous systems.

We argued that montmorillonite, a smectite clay mineral with a layered lattice silicate structure, could be a suitable support fulfilling the above requirement. Good catalyst performance of reduced Pd–montmorillonite catalysts in selective hydrogenations was recently disclosed.⁹ More importantly, studies for the application in the Heck coupling of montmorillonite-based Pd catalysts prepared by ion exchange¹⁰ or using immobilized complexes¹¹ are also known. In addition, Pd–Cu–montmorillonite was shown to be active in cross-coupling of aryl amines with methyl

SYNLETT 2006, No. 18, pp 3130–3134 Advanced online publication: 25.10.2006 DOI: 10.1055/s-2006-951493; Art ID: S07906ST © Georg Thieme Verlag Stuttgart · New York acrylate.¹² In all these latter studies^{10–14} K-10 montmorillonite, an acid-treated clay, was applied.

On the basis of this information and our recent successful efforts to develop new, highly stable and active heterogeneous Pd catalysts for the Heck coupling¹³ and the Suzuki reaction,¹⁴ which also exhibit unprecedented stability in recycling studies¹⁵ we have decided to prepare and use montmorillonite-based Pd catalysts in the Heck reaction.

Two catalysts were prepared using a high-sodium-content montmorillonite. Treatment with a slightly acidic solution of $Pd(NO_3)_2$ resulted in the exchange of Pd^{2+} ions for Na⁺ ions (Pd content = 2.16%).¹⁶ The intercalation of $[Pd(OH_2)_4]^{2+}$ ions can be achieved by treating montmorillonite with an aqueous solution of $Pd(NO_3)_2$ (Pd content = 1.29%).^{16,17} The two catalyst samples thus prepared will be referred to as Pd–montm1 and Pd–montm2, respectively. The metal loadings correspond to 25% (Pd–montm1) and 38% (Pd–montm2) of the ion-exchange capacity of the montmorillonite sample used here (1.05 mmol g⁻¹). As shown earlier¹⁷ the ions are homogeneously dispersed throughout the support and found between the silicate sheets.

First, the catalysts were tested in Heck coupling of bromobenzene and other, activated and deactivated aryl halides (Scheme 1) under reaction conditions applied in our previous studies using 0.1 mol% of Pd [150 °C, NMP (Nmethyl-2-pyrrolidinone) as solvent, no special precaution to exclude air and moisture].^{13,15,18} As seen in Table 1 both catalysts showed good catalyst performance under appropriately selected reaction conditions. Deactivated compounds (4-iodoanisole, 4-bromoanisole) and 3bromopyridine, however, required the use of an increased amount of the catalysts (0.3 mol%) to have satisfactory results. Tetrabutylammonium bromide (TBAB), which acts as supporting ligand and phase-transfer agent also assisting in the decomposition of HPdX species,¹⁹ was also necessary to be used in two cases. In all reactions complete E selectivity is observed, whereas products of α coupling (6–11%) are also formed in the transformation of styrene.

Next, studies were performed by running reactions with decreased molar ratios of catalysts in the transformation of methyl acrylate and styrene with bromobenzene. Results summarized in Tables 2 and 3 show unequivocally that these new Pd–montmorillonite catalysts are efficient in catalyzing Heck couplings. TON and TOF data acquired at the lowest substrate to catalyst ratios (Table 3, entries 3, 4, 7, 8, and 9) are in the range of 50,000–70,000

Aryl halide	Alkene (Scheme 1)	Time (h)	Pd–montm1		Pd-montm2	
			Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
4-Iodoanisole ^{a,b}	$R^2 = COOMe$	2	97	92	87	80
	$\mathbf{R}^2 = \mathbf{P}\mathbf{h}$	2	96	92	90	82
4-Bromobenzene ^c	$R^2 = COOMe^d$	3	85	81	87	82
	$\mathbf{R}^2 = \mathbf{P}\mathbf{h}$	3	80	77	85	80
4-Bromoanisole ^{a,c}	$R^2 = COOMe^d$	3	83	80	76	71
	$\mathbf{R}^2 = \mathbf{P}\mathbf{h}$	6	84	91	79	77
4-Bromacetophenone ^c	$R^2 = COOMe$	2	100	97	99	94
-	$\mathbf{R}^2 = \mathbf{P}\mathbf{h}$	2	90	95	91	95
1-Bromo-4-chlorobenzene ^c	$R^2 = COOMe$	2	100	99	100	99
	$\mathbf{R}^2 = \mathbf{P}\mathbf{h}$	2	100	99	100	99
4-Bromopyridine ^e	$R^2 = COOMe$	2	73	68	78	74
	$\mathbf{R}^2 = \mathbf{P}\mathbf{h}$	2	95	90	88	84

Table 1 Transformation of Aromatic Iodo and Bromo Derivatives in the Presence of 0.1 mol% of Pd–Montmorillonite Catalysts (Scheme 1)^a

^a Catalyst ratio in the transformation of 4-iodoanisole, 4-bromoanisole, and 3-bromopyridine: 0.3 mol%. Reaction temperature: 150 °C.

^b Reactant ratios: aryl halide–alkene–NaOAc = 1:1:1.

^c Reactant ratios: aryl halide–alkene–Na₂CO₃ = 1:1.2:1.2.

^d TBAB (0.2 equiv).

^e Reactant ratios: aryl halide–alkene–NaOAc = 1:1.2:1.2.



Scheme 1

and above 17,000 h^{-1} , respectively. These values are close to those observed with homogeneous Pd complexes and are similar to those found by Köhler et al.^{8b}

Since aryl chlorides are, in general, unreactive in the presence of heterogeneous Pd catalysts,^{4a} it is an important issue to test the activity of new catalysts in the transformation of aryl chlorides. In fact, only a handful of successful attempts are known.^{6c,d,h,8,20} The best recent results were achieved by the use of a layered double hydroxide supported nanopalladium catalyst,^{6c} Pd-exchanged NaY zeolite,^{20b} and Pd on carbon applied in poly(ethylene gylcol) as phase-transfer catalyst.^{20c} One of the most successful examples is the recent result by Köhler's group using solid supported catalysts with soluble Pd species.⁸ Because of the importance of this issue, we have also attempted to transform aryl chlorides over our newly developed catalysts.

Our first tests reacting 4-chloroacetophenone with methyl acrylate and styrene under the usual reaction conditions gave encouraging results: both catalysts showed satisfactory activities (Table 4). Moreover, our catalysts worked at lower temperature than the catalyst samples developed and applied in Köhler's study (150 °C vs. 160 °C).^{8b} In contrast, the reactivity of the neutral chlorobenzene was much inferior. In fact, conversion values were lower even under the reaction conditions used by Köhler [catalysts (0.1 mol%), TBAB (60 mol%), Ca(OH)₂ as base, 160 °C].

Table 2 Transformation of Bromobenzene with Methyl Acrylate^a

Catalyst	Catalyst concentration (mol%)	Conversion (%)	Yield (%)	TON ^b	$TOF^{c}(h^{-1})$
Pd-montm1	0.012	97	92	8,083	2,694
	0.005	94	87	18,800	6,267
Pd-montm2	0.01	93	90	9,300	3,100
	0.005	85	79	17,000	5,667

^a Reaction conditions: bromobenzene (10 mmol), methyl acrylate (15 mmol), Na₂CO₃ (12 mmol), NMP (10 mol), 150 °C, 3 h.

^b Moles of aryl halide converted/moles of Pd.

^c TON/h.

Entry	Catalyst	Catalyst concentra- tion (mol%)	Time (h)/Temp (°C)	Conversion (%)	Yield (%)	TON	$TOF(h^{-1})$
1	Pd-montm1	0.005	3/150	93	91	18,600	11,042
2		0.001	3/150	45	42	45,000	
3			6/150	68	64	68,000	
4		0.0008	6/160	53	50	66,250	
5	Pd-montm1	0.005	3/150	97	90	19,400	6,467
6		0.0014	3/150	72	68	51,429	17,142
7		0.001	6/150	53	50	53,000	8,833
8		0.001	3/160	53	51	53,000	17,667
9			6/160	73	71	73,000	12,167

^a Reaction conditions: bromobenzene (10 mmol), styrene (15 mmol), Na₂CO₃ (12 mmol), NMP (10 mL).

 Table 4
 Transformation of Aromatic Chloro Derivatives^a

Aryl halide	Alkene (Scheme 1)	Pd-montm1	°d–montm1		Pd-montm2	
		Conversion (%)	Yield (%)	Conversion (%)	Yield (%)	
4-Chloro acetophenone ^b	$R^{2} = COOMe$ $R^{2} = Ph$	73 73	69 70	90 87	85 83	
Chlorobenzene ^c	$R^2 = Ph$	17	16	19	17	

^a Reactant ratios: aryl halide–alkene–base–TBAB = 1:1.2:1.2:0.6.

^b Catalyst (0.1 mol%), Na₂CO₃ as base, 150 °C, 3 h.

^c Catalyst (0.1 mol%), Ca(OH)₂ as base, 160 °C, 6 h.

The transformation of styrene and 4-chloroacetophenone in the presence of lower amounts of catalysts down to about 0.005 mol% gave still reasonable results (Table 5, entries 1, 2 and 5–8). Reactions with even lower catalyst quantities but performed at higher temperature and longer reaction time resulted in reasonably high TON values. Data also show that the use of Ca(OH)₂ as the base gave only marginal improvements as compared with sodium carbonate (Table 5, entries 4 and 11).

The results disclosed here strongly support the suggestion that heterogeneous palladium catalysts, in fact, are pseu-

Table 5 Transformation of 4-Chloroacetophenone with Styrene^a

do-homogeneous systems.²¹ Leaching of soluble Pd species from heterogeneous Pd catalysts into solution is welldocumented.^{13b,20d,22} A related interesting observation was made by Arai et al. who showed that the active palladium species could be deposited onto a suitable support and reused in repeated reactions.^{22b,23} Furthermore, it was found that very small amounts of Pd species in solution can promote the coupling reaction. For homogeneous systems high activities were observed with Pd(OAc)₂ called 'homeopathic ligand-free palladium'.²⁴ In this respect, observations by Leadbeater about performing related Suzuki

Entry	Catalyst	Catalyst concentra- tion (mol%)	Time (h)/Temp (° C)	Conversion (%)	Yield (%)	TON	TOF (h^{-1})
1	Pd-montm1	0.0045	3/150	79	70	17,555	5,852
2		0.0045	6/160	86	81	19,111	3,185
3		0.0027	6/160	71	65	26,296	4,383
4		0.005	3/160	93ª	88	18,600	6,200
5	Pd-montm1	0.0048	3/150	88	83	18,300	6,111
6			6/150	95	90	19,792	3,299
7		0.0045	3/160	91	88	20,222	6,741
8			6/160	93	88	20,667	3,444
9		0.0025	6/160	81	77	32,400	5,400
10		0.0016	6/150	52	49	32,500	5,417
11		0.005	3/160	91 ^b	85	18,200	6,067

^a Reaction conditions: 4-chloroacetophenone (10 mmol), styrene (12 mmol), Na₂CO₃ (12 mmol), TBAB (0.6 mmol), NMP (10 mL). ^b Ca(OH)₂ as base.

coupling in water promoted by microwave irradiation using Pd in ultra-low concentrations are of particular interest.²⁵

For heterogeneous catalysts, clear evidence of the involvement of soluble palladium species in the catalytic cycle was provided by showing a correlation between the concentration of leached Pd and the reaction rate.^{8a,22b,26} It is also clear that an appropriate selection of support materials and preparation techniques allow the synthesis of highly active heterogeneous catalysts, which are able to promote the coupling reaction of all types of aryl chlorides with satisfactory activities.

On the basis of the highly successful application of Pd-MCM-41 catalysts in recycling experiments disclosed in a previous study,¹⁵ these new Pd-montmorillonite catalysts were also reused after recovery in the reaction of bromobenzene with styrene.²⁷ Data in Table 5 show that under the usual reaction conditions on using 0.3 mol% of catalysts steadily decreasing conversions were observed (entries 1 and 2). Changing the base from sodium carbonate to a mixed organic-inorganic base $(Et_3N + Na_2CO_3)$ and an increase in reaction temperature did not result in any improvements (Table 5, entries 3 and 4). This, however, is not surprising considering the fact that Pd ions in ion-exchanged montmorillonites are mobile and, therefore, sensitive species. Pd complexes, for example, tend to decompose above 120 °C to form palladium metal.¹⁷ This process certainly occurring under reaction conditions applied here (150-160 °C) combined with the leaching/redeposition process, obviously results in restructuring of the original catalysts yielding a material significantly different from the original one concerning, in particular, dispersion of both ionic and metallic active sites.

Leaching phenomena are known to depend on the oxidation state of palladium.^{21,22b} Pd(0) metal particles in zeolites, for example, were shown to function as truly heterogeneous catalysts.^{22d} In contrast, reduced Pd species were found to leach out more easily when deposited on silica, active carbon, and Mg-smectite.^{22b} Therefore, we attempted to use reduced catalysts in recycling experiments assuming that the adverse effects of leaching/redeposition are less significant, even though that catalyst restructuring (changes in particle size) are known to occur.^{21,23a} Samples were reduced with hydrogen and the reduction temperature (200 °C) was selected to avoid the formation of Pd β -hydride phase,²⁸ which can be detrimental to catalytic activity. Under such conditions, complete reduction of Pd ions takes place to form metal crystallites located at the external surface of the support.

Indeed, catalyst sample Pd–montm1 reduced with hydrogen exhibited much better stability in repeated runs (Table 6, entry 6). However, both reduced catalysts showed an overall lower activity.

 Table 6
 Catalyst Recycling Experiments with Coupling of Bromobenzene and Styrene

Entry	Catalyst	Run 1	Run 2	Run 3
1	Pd-montm1 ^a	77	65	55
2	Pd-montm2 ^a	89	77	64
3	Pd-montm1 ^b	71	51	16
4	Pd-montm2 ^b	78	55	15
5	Pd-montm1 ^a	55	46	22
6	Pd-montm2 ^a	59	61	55

^a Reaction conditions: alkene (1.5 equiv), Na₂CO₃ (1.2 equiv), catalyst (0.3 mol%), 150 °C, 3 h.

^b Reaction conditions: alkene (1.5 equiv), Et_3N (1 equiv), Na_2CO_3 (0.5 equiv), catalyst (0.3 mol%), 160 °C, 3 h.

In conclusion, we have synthesized two new palladiummontmorillonite catalysts. The catalysts are easy to prepare and insensitive to air and moisture. Both catalysts exhibit high activity in Heck coupling of aromatic bromo and activated chloro derivatives with turnover numbers close to those found in a recent study for a range of supported Pd catalysts.⁸ Further studies including the use of appropriate catalyst characterization techniques, however, are certainly needed to improve the performance of these new montmorillonite-supported palladium catalysts. The main focus is to increase stabilities and enhance activities to achieve the more challenging task of the coupling of deactivated aryl chlorides.

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- centrifugation and washed thoroughly with water. Finally, the wet products were oven-dried (95 °C, 1 Torr, 6 h). The palladium content was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES). Catalysts used in recycling experiments were reduced in flowing hydrogen (200 °C, 2 h).
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