

## Palladium(II) containing hydrotalcite as an efficient heterogeneous catalyst for Heck reaction

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### Abstract

Palladium(II) containing hydrotalcite (Pd-HT) has been found to be an efficient and reusable catalyst in Heck reaction between aryl halides (X = Br, I) and olefins to give carbon–carbon coupled products in good to moderate yields. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Palladium catalyst; Mg–Al hydrotalcite; Heterogeneous catalyst; Heck reaction; Coupling reactions

Palladium catalyzed carbon–carbon coupling (Heck reaction) between aryl halides and olefins is an important reaction in modern organic synthesis [1–3]. The reaction is generally catalyzed by either Pd(0) or Pd(II) complexes in solution [4–7]. In order to circumvent the problems like catalyst recovery and air sensitivity associated with reactions under homogeneous conditions, heterogeneous catalyst systems are under development. These include polymer/dendrimer supported palladium catalysts [8,9], palladium on carbon [10,11] and palladium supported on metal oxides [12], clays [13], and molecular sieves [14,15]. Recently novel Ni, Co, Cu and Mn heterogeneous catalysts have also been reported to catalyze the reaction of aryl iodides with olefins [16]. Many advances in

homogeneous [17–19] and heterogeneous [20–22] Heck catalysis have recently been reported.

Hydrotalcite (HT) like anionic clays [23–29] have the general formula,  $[M^{(II)}(1-x), M^{(III)}_x(OH)_2]^{x+} [(A^{n-})_x/n \cdot yH_2O]^{x-}$  where  $x = 0.1-0.33$ ,  $M^{(II)} = Mg, Cu, Ni, Co$ , and  $Mn$ ,  $M^{(III)} = Al, Fe, Cr$ , and  $Ga$ ,  $A^{n-}$  is an interlayer anion such as  $CO_3^{2-}$ ,  $NO_3^-$  and  $SO_4^{2-}$ . Preparation of Palladium(II) supported hydrotalcites has been reported in the literature [23,24]. Palladium(II) supported hydrotalcite [27] and related Ni–Al hydrotalcite [28] have been used in the oxidation of alcohols using molecular oxygen. To our knowledge, Pd-hydrotalcite (Pd-HT) has not been used as a heterogeneous catalyst for the Heck reaction. Herein, we report the synthesis and characterisation of palladium hydrotalcite and its use as a heterogeneous catalyst for the Heck reaction.

Various Pd containing Mg–Al hydrotalcites were synthesized from soluble salts of the metals in the required atomic ratios by co-precipitation in a

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solution containing a slight excess of  $\text{Na}_2\text{CO}_3$  at pH 10 [30]. The ratios of Mg:Al chosen were 2 and 3 and the Pd loadings were 1–6 mol% with respect to Mg. The catalyst, Pd-HT(25) (Table 1) was prepared as follows. A solution of 20 mmol of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 10 mmol of  $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 15 ml of demineralised water was added dropwise to a solution of 285 mmol of NaOH and 38 mmol of  $\text{Na}_2\text{CO}_3$  in 60 ml of water over a period of 0.5 h with vigorous stirring. When the addition was half done, 1 mmol of  $\text{Pd}(\text{OAc})_2$  was added in one lot and the addition was continued. The solution was then heated at 80 °C for 18 h with stirring and the contents were cooled and filtered. The precipitate obtained was washed repeatedly with water till the filtrate was neutral to litmus and dried at 110 °C for at least 24 h. Other samples were prepared by varying the amount of  $\text{Pd}(\text{OAc})_2$ .

The catalysts thus prepared were characterized by XRD, TGA/DTA, and  $\text{N}_2$  adsorption and found to be truly HT like materials. X-ray powder diffraction patterns (Fig. 1) showed in all cases the presence of a well-crystallized HT phase, which suggested that palladium was probably present inside the brucite sheets of the hydrotalcite. However, the presence of small amounts of extra framework Pd cannot also be ruled out. The surface areas of the dried samples (measured by  $\text{N}_2$  adsorption (BET method) after activation at

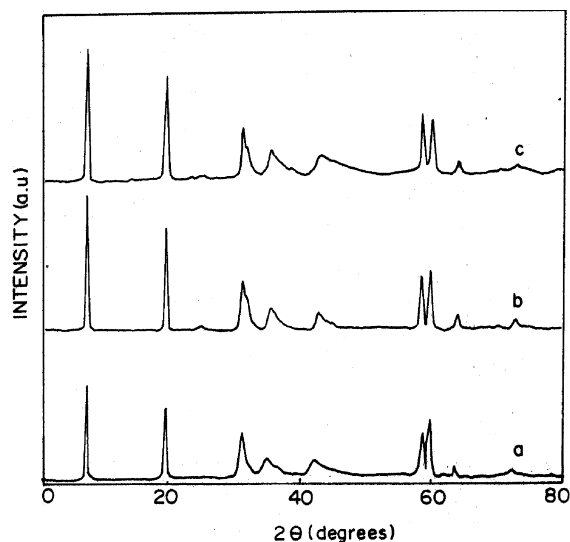


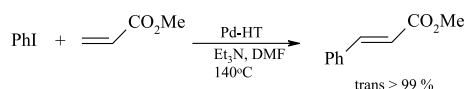
Fig. 1. XRD patterns of hydrotalcite samples: (a) hydrotalcite (HT); (b) Pd-hydrotalcite (Pd-HT(25)); (c) Pd-HT(25) after one reaction cycle.

200 °C) did not change with Pd loading and were  $\sim 20 \text{ m}^2/\text{g}$  for all the samples. TGA analysis showed that the catalysts were stable up to 200 °C (the structure began to collapse at about 230 °C). Atomic Absorption Spectroscopy (AAS) (Table 1) and elemental analysis were used to obtain the chemical compositions of the samples. For e.g., based on AAS and microanalysis (Pd: 3.7%;

Table 1

Heck reaction of iodobenzene with methyl acrylate over Pd-HT

Catalyst designation/ [mol% of Pd loaded] <sup>a</sup>	Composition (molar) <sup>b</sup> Pd:Mg:Al	Time (h)	Conv. <sup>c</sup> (%)	% Yield of methyl cinnamate (isolated)
Pd-HT (21)/[1]	0.68:100.00:40.85	36	23	10
Pd-HT (22)/[2]	1.52:100.00:40.67	36	19	10
Pd-HT (23)/[3]	2.76:100.00:39.31	24	34	16
Pd-HT (24)/[4]	3.35:100.00:41.02	8	98	71
Pd-HT (25)/[5]	4.13:100.00:39.80	4	100	82
Pd-HT (26)/[6]	4.20:100.00:41.33	4	100	84
Pd-HT (35)/[7]	4.37:100.00:27.72	24	29	20



<sup>a</sup> Pd used in the preparation is given inside square brackets as mol% with respect to Mg.

<sup>b</sup> As estimated by AAS; Mg/Al for all the samples  $\cong 2.5$  except for the last sample, Mg/Al  $\cong 3.6$ .

<sup>c</sup> Conversion of Iodobenzene.

Mg: 21.48%; Al: 9.53%; C: 2.59%; H: 3.67%) the molar composition for Pd-HT(25) was derived as:  $\text{Pd}_{0.025}\text{Mg}_{0.6}\text{Al}_{0.24}(\text{OH})_{18}(\text{CO}_3)_{1.5} \cdot 0.4\text{H}_2\text{O}$ . The compositions of the different Pd-HT samples are presented in Table 1. It is seen that the Pd content of the catalyst does not increase significantly beyond ~4% even when larger amounts of Pd are used in the catalyst preparation.

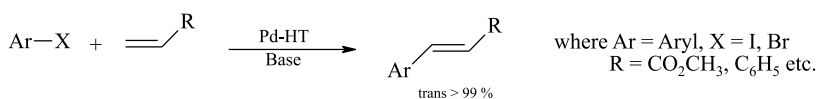
Heck reaction of iodobenzene with methyl acrylate was carried out using these catalysts after activation at 120 °C for 6 h (Scheme in Table 1). A typical reaction was carried out by combining under argon atmosphere, 3 mmol of iodobenzene, 3.9 mmol of methyl acrylate, 3.6 mmol of triethyl amine and Pd/HT 20% w/w (with respect to iodobenzene) in dry DMF solvent. The stirred mixture was heated at 140 °C. The reaction was monitored by GC/TLC. After the desired run duration, the reaction was quenched with 5 ml of water and the catalyst was filtered. Next, 50 ml of water was added to the filtrate and the product was extracted with ethyl acetate (50 ml × 2). The organic layer was given dil. HCl, water and brine wash and dried over  $\text{Na}_2\text{SO}_4$ . The product obtained after evaporation of the solvent was purified

by column chromatography. The results of the screening of the catalysts are presented in Table 1.

It is found that the yield of methyl cinnamate increases with Pd loading. Catalysts with a Pd loading of ~4% with Mg/Al  $\cong$  2.5 appear to be the most active (Table 1). Pure HT without Pd loading did not produce methyl cinnamate even after 36 h. When the reaction was carried out with 0.1 mol% of  $\text{Pd}(\text{OAc})_2$  as the catalyst, the product yield was 14%. Surprisingly, the Pd-HT sample prepared with Mg/Al  $\cong$  3.6 was not as active as the other Pd-HT samples (with Mg/Al  $\cong$  2.5 and Pd  $\cong$  3–4%; compare Pd-HT(35) with Pd-HT(24–25)). In toluene and acetonitrile solvents no reaction was observed under reflux conditions. The catalyst was not active at temperatures below 140 °C. The heterogeneous nature of the reaction over Pd-HT was tested as follows. The catalyst (Pd-HT(25)), iodobenzene and triethyl amine (except the olefin) were mixed in dry DMF and heated at 140 °C under argon atmosphere with constant stirring for 4–5 h. The catalyst was filtered out quickly under argon and methyl acrylate was added to the reaction mixture followed by

Table 2  
Heck reaction over heterogeneous catalyst: Pd-HT(25)

Ar	X	R	Amount of catalyst (% w/w)	Time (h)	% Yield <sup>b</sup> (isolated)	TON <sup>c</sup>
C <sub>6</sub> H <sub>5</sub>	I	CO <sub>2</sub> CH <sub>3</sub>	10	8	82	928
C <sub>6</sub> H <sub>5</sub>	I	CO <sub>2</sub> CH <sub>3</sub>	10 <sup>a</sup>	5	69	781
C <sub>6</sub> H <sub>5</sub>	I	C <sub>6</sub> H <sub>5</sub>	10	8	87	985
C <sub>6</sub> H <sub>5</sub>	I	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	10	20	59	668
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	I	CO <sub>2</sub> CH <sub>3</sub>	10	7	87	863
<i>p</i> -ClC <sub>6</sub> H <sub>5</sub>	I	CO <sub>2</sub> CH <sub>3</sub>	10	7	88	852
C <sub>6</sub> H <sub>5</sub>	Br	CO <sub>2</sub> CH <sub>3</sub>	20	20	35 <sup>d</sup>	257
C <sub>6</sub> H <sub>5</sub>	Br	C <sub>6</sub> H <sub>5</sub>	20	12	67 <sup>d</sup>	492
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	Br	C <sub>6</sub> H <sub>5</sub>	20	12	67 <sup>d</sup>	492
<i>p</i> -CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	Br	C <sub>6</sub> H <sub>5</sub>	20	12	48 <sup>d</sup>	277
C <sub>8</sub> H <sub>7</sub>	Br	CO <sub>2</sub> CH <sub>3</sub>	20	12	45 <sup>d</sup>	259



<sup>a</sup> With the recovered catalyst (first recycle); surface area 65 m<sup>2</sup>/gm.

<sup>b</sup> All products gave satisfactory IR and NMR spectra.

<sup>c</sup> Turn over numbers were calculated on the basis of amount of Pd estimated by AAS (TON = mol of product × mol<sup>-1</sup> of catalyst–Pd).

<sup>d</sup> *N*-Methyl pyrrolidinone solvent; K<sub>2</sub>CO<sub>3</sub> base; 150 °C.

10% more of the triethyl amine base and the reaction was continued for another 4 h at 140 °C. Analysis by GC did not reveal any product formation. This showed that the reaction did not proceed on the removal of the solid catalyst suggesting its heterogeneous nature. Results of the reactions with various substrates are presented in Table 2. It is obvious from the results that good yields of the products can be obtained with all aryl iodides with even 10% w/w of the catalyst. The highest turn over number (TON) achieved was around 1000. Under similar experimental conditions, aryl bromides did not appear to be much reactive. Hence, the reaction conditions were modified; NMP (*N*-methyl pyrrolidinone) was used as the solvent, K<sub>2</sub>CO<sub>3</sub> as the base, and the temperature was raised to 150 °C. Stilbene was isolated in good yield, under these conditions, from the reaction of bromobenzene and styrene (TON = 492). The reaction of 1-bromonaphthalene with methyl acrylate gave 45% yield of the product. In all the cases, selectivity was observed to be >90% (Table 2). The catalyst, however, was not effective with the less reactive aryl chlorides. Chlorobenzene failed to react with methyl acrylate. The activated aryl chlorides like *p*-nitrochlorobenzene also gave low yields. Addition of NaI/CuI did not bring about any improvement.

The catalyst could be recycled without any treatment, though some loss was noticed in the yield of methyl cinnamate from the reaction between iodobenzene and methyl acrylate (Table 2). Interestingly, the reaction was faster over the recycled catalyst than over the fresh one, which could be attributed to the increase in surface area of the catalyst.

In conclusion, Pd-hydrotalcite is active as a catalyst for Heck reaction. The recoverability of the catalyst with recyclability coupled with reasonably large turn over numbers makes it a suitable candidate for possible exploitation in C–C bond formation reactions.

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