

# Pd–Cu–Exchanged montmorillonite K10 clay: an efficient and reusable heterogeneous catalyst for vinylation of aryl halides

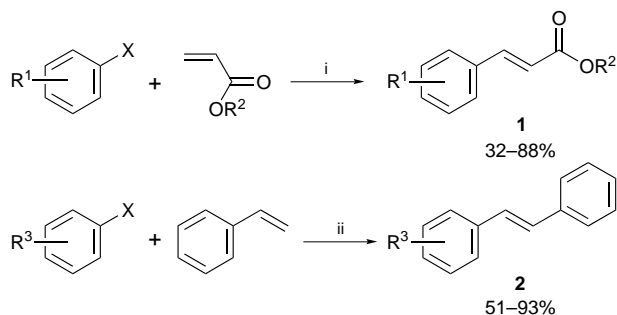
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Palladium and copper exchanged montmorillonite K10 clay has been found to catalyse very efficiently the reaction between aryl halides ( $X = \text{Br}, \text{I}$ ) and acrylates, and styrenes affording alkyl (*E*)-cinnamates and (*E*)-stilbenes respectively in high yields.

The palladium-catalysed vinylation of aryl halides ( $X = \text{Br}, \text{I}$ ) (Heck reaction) provides a very convenient and powerful method for forming carbon–carbon bonds at unsubstituted vinylic positions.<sup>1</sup> Major improvements in Heck-type reactions over the last decade have been brought about by the introduction of tetraalkylammonium salts, silver(I) or thallium(I) salts as promoting additives or by use of organotrifluoromethanesulfonates.<sup>2</sup> Two recent promising approaches involve reactions in aqueous (or water–organic solvent) media<sup>3</sup> and the use of vinyl iodonium salts.<sup>4</sup> For the Heck reaction, a  $\text{Pd}^{\text{II}}$  salt or complex is employed which is reduced *in situ* to an active zero valent palladium species under homogeneous conditions. The  $\text{Pd}^{\text{II}}$  species that is subsequently regenerated in the reaction<sup>2</sup> is very difficult to separate and reuse for the reaction directly without further processing. In view of the practical and industrial applications, improvements in catalyst efficiency and catalyst recycling are essential. To overcome these problems, heterogeneous catalysts such as polymer-supported palladium catalysts and  $\text{Pd}-\text{Ph}_2\text{P}-\text{Si}$  supported on clay have been reported for the arylation of alkenes.<sup>5</sup> However, these catalysts suffer from drawbacks such as (i) their preparation involves many steps and the use of expensive phosphorus and silicon compounds and (ii) deactivation of the catalyst on its reuse. We report here our preliminary results on the use of Pd and Cu exchanged montmorillonite K10 (Mont.K10) clay catalysts for the vinylation of aryl halides ( $X = \text{Br}, \text{I}$ ) (Scheme 1).

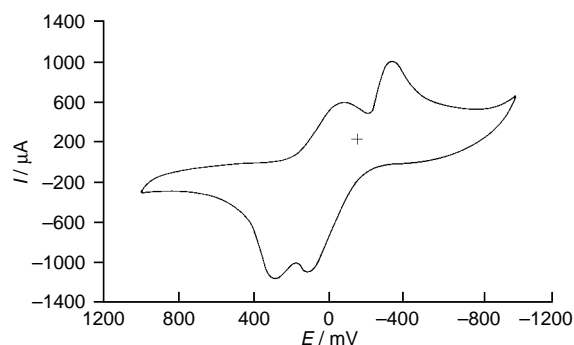
Pd, Cu and Pd–Cu exchanged clay catalysts were prepared by exchanging the clay with dilute aqueous  $\text{PdCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$  or a mixture of two respectively. For example, Pd (0.29 wt%)-Cu (0.36 wt%)-exchanged Mont.K10 clay catalyst was prepared by treating Mont.K10 clay (25 g) with 600 ml aqueous  $\text{PdCl}_2$  and  $\text{Cu}(\text{NO}_3)_2$  under vigorous stirring at room temperature for 24 h, centrifuging and washing the Pd–Cu exchanged clay with distilled deionised water repeatedly until the discarded filtrate was free from  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions, and drying the resulting mass



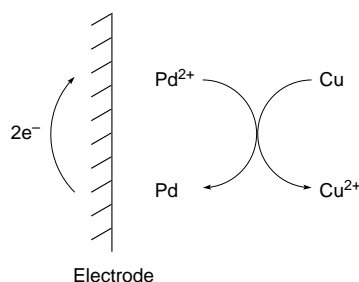
**Scheme 1** Reagents and conditions: i, Pd–Cu–Mont.K10 (10% m/m),  $\text{K}_2\text{CO}_3$ , DMF, reflux, 2 h; ii, Pd–Cu–Mont.K10 (15% m/m),  $\text{K}_2\text{CO}_3$ , DMF, reflux, 2–3 h

at 110 °C for 12 h. The metal content of the catalysts was determined using an electron dispersive X-ray microscope (EDX) (Kevex, US) connected to a JEOL (JSM-5200) scanning electron microscope (SEM). The surface area of Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.10 and Cu (0.39 wt%)-Mont.K10 being 262.9 and 238.9  $\text{m}^2 \text{g}^{-1}$  respectively (BET method). The XRD pattern and FT-IR spectra of these samples show that they are crystalline, however no significant differences were observed among their structures. Definite information about the nature of the metal species present in the catalyst could be obtained from cyclic voltammetry (CV). Fig. 1 shows the CV of Cu–Pd exchanged Mont.K10 clay at a scan rate of 50  $\text{mV s}^{-1}$ . It clearly indicates two reversible peaks with  $E_{1/2}$  (vs. saturated calomel electrode) at  $-0.119$  and  $+0.117$  V. We attribute, after comparing the potential values from literature,<sup>6</sup> the peak at  $+0.117$  to a  $\text{Pd}/\text{Pd}^{2+}$  process and the one at  $-0.119$  V to a  $\text{Cu}/\text{Cu}^{2+}$  process. Although two one-step electron processes (*i.e.*  $\text{Cu}^{2+}/\text{Cu}^+$  and  $\text{Cu}^+/\text{Cu}$ ) are possible, separate experiments with Cu and Pd exchanged Mont.K10 clay have shown that the CV behaviour corresponds to  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Pd}/\text{Pd}^{2+}$  redox processes. Hence the presence of Pd is mediating the Cu redox process (Fig. 2). This explains the high activity of the Pd–Cu exchanged catalyst compared to the Cu or Pd exchanged catalyst.

Results of the reaction of iodobenzene with acrylates, over different catalysts and over the best catalyst Pd (0.29 wt%)-Cu (0.36 wt%)-exchanged Mont.K10 clay catalyst are presented in Tables 1 and 2 respectively.<sup>†</sup> A comparison of the results in



**Fig. 1** Cyclic voltammogram of Pd–Cu exchanged Mont.K10 clay at a scan rate of 50  $\text{mV s}^{-1}$



**Fig. 2** Pd mediates the redox behaviour of Cu

**Table 1** Results of Heck reaction between methyl acrylates and iodobenzene or *p*-methoxyiodobenzene over different catalysts<sup>a</sup>

Entry	Catalyst	Yield (%) of methyl cinnamate <b>1</b>	
		R <sup>1</sup> = H	R <sup>1</sup> = OMe
1	Cu (0.07 wt%)-Mont.K10	0	0
2	Cu (0.39 wt%)-Mont.K10	30	51
3	Pd (0.33 wt%)-Mont.K10	41	56
4	Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.K10	83	88
5	Pd (1.73 wt%)-Cu (0.16 wt%)-Mont.K10	56	61
6	Cu (0.32 wt%)-kaolin	0	0

<sup>a</sup> Reaction conditions: iodobenzene (3 mmol), methyl acrylate (6 mmol), anhydr. K<sub>2</sub>CO<sub>3</sub> (8 mmol), catalyst (10% m/m), DMF (5 ml), reflux, 2 h.  
<sup>b</sup> Isolated yield obtained after chromatographic purification.

Table 1 shows that among the catalysts, the Pd (0.29 wt%)-Cu (0.36 wt%)-exchanged Mont.K10 clay catalyst gives the best results for the Heck reaction. The higher activity of this catalyst seems to be due to a synergistic effect produced by the presence of Pd and Cu in close vicinity. The results also indicate that for this catalyst to be more active, enough copper must be present along with the palladium. It is remarkable that Cu (0.39 wt%)-Mont.K10 clay also catalyses the Heck reaction leading to the formation of (*E*)-cinnamate esters. The choice of solvent for the arylation reaction catalysed by the Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.K10 clay catalyst is also critical as the reaction fails when carried out in MeCN under reflux. Among the different bases tried for this reaction, *viz.* NaHCO<sub>3</sub>, K or Na acetate, K<sub>2</sub>CO<sub>3</sub>, Et<sub>3</sub>N and Bu<sub>3</sub>N, K<sub>2</sub>CO<sub>3</sub> gave the best results (*i.e.* high yields with 100% selectivity).

Table 2 lists the results for different types of aryl halides (X = Br, I) that have been vinyllated with methyl or ethyl acrylate to afford the corresponding cinnamates in high yields using the Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.K10 clay catalyst. In all the substrates examined, exclusive formation of the (*E*)-cinnamate was observed (GC, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectroscopy). Table 3 shows the results of the reaction of various aryl halides (X = Cl, Br, I) with styrene producing (*E*)-stilbenes in high yields using Pd-Cu-Mont.K10 catalyst (15% m/m). A remarkable feature of these catalytic systems is that even less reactive substituted bromobenzenes react with styrene to give (*E*)-stilbenes in excellent yields. The reaction however did not proceed using aryl iodides with substituents such as nitro, amino, chloro *etc.* The reaction also failed when methyl vinyl ketone and cyclohexenone were used as alkenylating agents instead of acrylate. Mechanistically, it is proposed that aryl halides react with copper presumably to yield an organocopper species, which then transmetalates to Pd<sup>II</sup> followed by olefin insertion, β-hydride elimination and dissociation of palladium hydride species<sup>2</sup> (Scheme 2).

**Table 2** Results of the reaction of aryl halides with acrylates over Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.K10 clay catalyst

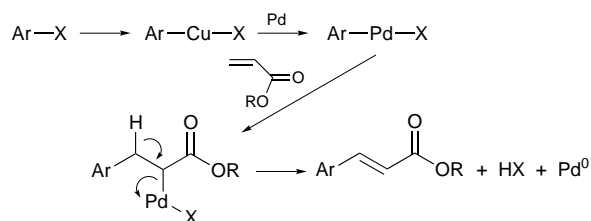
Entry	Aryl halide		Acrylate R <sup>2</sup>	Yield (%) of cinnamate <b>1</b> <sup>a,b</sup>
	R <sup>1</sup>	X		
1	H	I	Me	83
2	H	Br	Me	32
3	4-OMe	I	Me	88
4	4-Me	I	Me	76
5	2-OMe	I	Me	69
6	2-Me	I	Me	58
7	4-OMe	I	Et	86

<sup>a</sup> Characterised by IR, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectroscopy. <sup>b</sup> Isolated after chromatographic purification.

**Table 3** Results of the reaction of aryl halides with styrene over Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.K10 clay as catalyst

Entry	Aryl halide		<i>t</i> /h	Yield (%) of stilbene <sup>a,b</sup>
	R <sup>3</sup>	X		
1	H	I	2	93
2	H	Br	2	51
3	H	Cl	12	0
4	Cl	Br	3	81
5	Cl	I	3	88
6	OMe	I	3	72

<sup>a</sup> Characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectroscopy. <sup>b</sup> Isolated after chromatographic purification.

**Scheme 2**

The catalyst from the reaction mixture was recovered by simple filtration and was successfully reused three times without losing its activity in the alkenylation of 4-methoxyiodobenzene with methyl acrylate.

In conclusion, the Pd (0.29 wt%)-Cu (0.36 wt%)-Mont.K10 clay catalyst has high activity for the Heck reaction in which aryl halides (X = Br, I) are reacted with acrylates and styrenes to form the corresponding (*E*)-cinnamates and (*E*)-stilbenes respectively in high yields. The high activity of the catalyst is attributed to a synergistic effect produced by the presence of Pd and Cu species in the catalyst.

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## Footnotes and References

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† In a typical reaction procedure, iodobenzene [580 mg, 2.8 mmol (1:1 styrene)], methyl acrylate (500 mg, 5.8 mmol), anhydr. K<sub>2</sub>CO<sub>3</sub> (1 g, 7.2 mmol) and catalyst (58 mg, 10% by weight of PhI) in DMF (5 ml), were refluxed for 2 h. After completion of the reaction (TLC monitoring), the catalyst was separated by filtration and the reaction mixture was poured into water followed by its extraction with ethyl acetate to give the crude product which was subsequently purified by column chromatography to afford methyl (*E*)-cinnamate (380 mg, 83%), δ<sub>c</sub> (50.3 MHz, CDCl<sub>3</sub>) 51.6, 117.9, 127.9, 128.3, 128.9, 129.2, 130.3, 134.4, 144.8 and 167.3; *m/z* 162 (M<sup>+</sup>, 65%), 161 (45), 131 (100), 117 (5), 103 (82) and 73 (91).

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