

## Palladium Catalysts Supported onto the Ionic Liquid-Functionalized Carbon Nanotubes for Carbon-Carbon Coupling<sup>†</sup>

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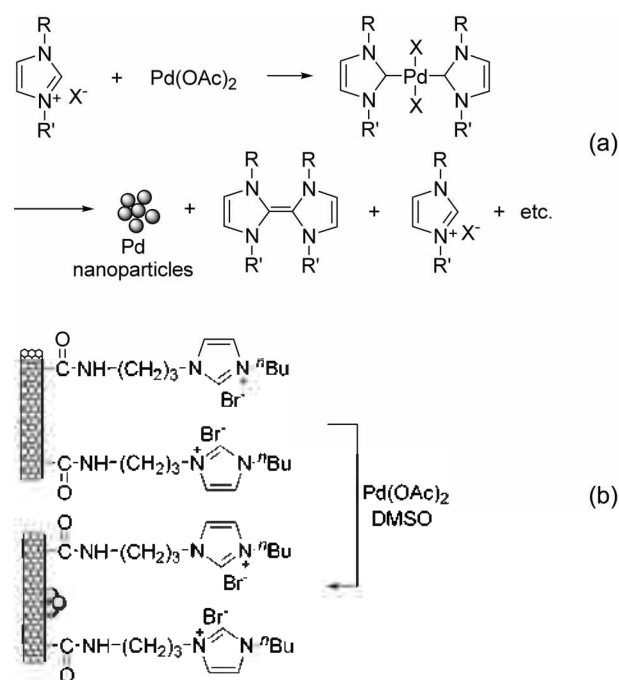
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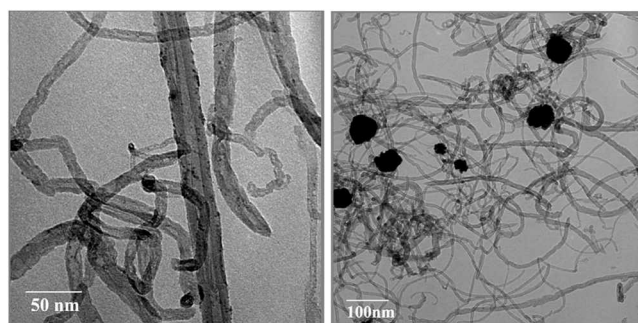
Due to their characteristic and tunable properties, ionic liquids (ILs), particularly consisting of imidazolium cations and counter anions, have attracted increasing interest as an alternative to conventional organic solvents for a wide range of synthesis, catalysis as well as formation of self-assembled monolayers etc.<sup>1</sup> Quite recently, we have demonstrated for the first time that the solubility of the multi-walled carbon nanotubes (IL-MWCNTs), which functionalized covalently with imidazolium salts, could also be varied through the anion-exchange.<sup>2</sup> Since the IL-CNT hybrid materials retain the original properties of each component, it could provide more opportunities for the applications of both ILs and CNTs. One of the possible potential applications of the IL-CNT hybrid material is catalyst supports because both ILs and CNTs are known to be very promising materials for catalysts immobilization.<sup>3</sup> Here we now report the preliminary results on the application of the IL-MWCNT hybrid materials as supports for effective recyclable palladium catalyst in carbon-carbon coupling reactions.

It has been known that Pd-carbene complexes could be formed by reaction of imidazolium salt with Pd(OAc)<sub>2</sub>, and they are decomposed to generate Pd nanoparticles (equation a in Scheme 1).<sup>4</sup> To immobilize the Pd catalyst, a mixture of IL-MWCNT and Pd(OAc)<sub>2</sub> with 1:1 ratio (wt/wt) in DMSO was heated to 120 °C for 12 hr under nitrogen atmosphere (equation b in Scheme 1). Transmission electron microscopy (TEM) analysis showed Pd nanoparticles with very small (2–5 nm) size were deposited onto the CNT surfaces (left in Figure 1). However, due to the poor solubility of the IL-MWCNT-Pd, formation of Pd-carbene complexes could not be elucidated at the present time. After reaction with Pd(OAc)<sub>2</sub>, the water soluble IL-MWCNT having imidazolium bromide became insoluble not only in water but also in organic solvents such as dichloromethane, DMSO, and DMF etc. ICP analysis showed that 2.5 mmol/g of Pd was immobilized onto the IL-MWCNT.

To test the catalytic activity and re-usability of the Pd nanoparticles supported onto the IL-MWCNT hybrid, Suzuki couplings of *p*-bromo acetophenone with phenyl boronic acid have been carried out first in the presence of IL-MWCNT-Pd (5 mol% of Pd) catalyst. The IL-MWCNT-Pd catalyst showed excellent catalytic efficiency, and provided



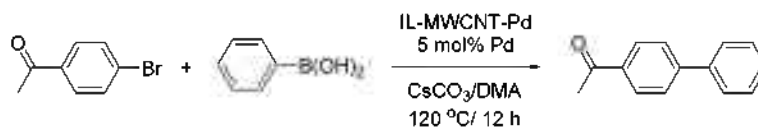
Scheme 1



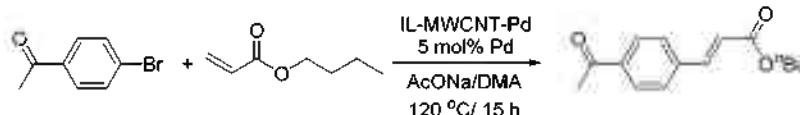
**Figure 1.** TEM images of the IL-MWCNTs (left), IL-MWCNT-Pd (middle), and recovered IL-MWCNT-Pd after 10<sup>th</sup> run of Sonogashira coupling (right)

the coupling product with 89% isolated yield. The recovered catalyst was reused ten times without any significant loss of catalytic activity. All recovery procedures have been done in air without any special precautions. Surprisingly, the catalytic activity of the catalysts recovered from 10<sup>th</sup> cycle in Suzuki coupling reactions still retained, and thus, used again in Heck and Sonogashira coupling reactions allowing 30

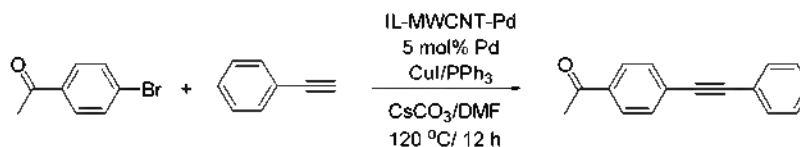
<sup>†</sup>This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement

**Table 1.** Carbon-Carbon coupling of *p*-bromoacetophenone using IL-MWCNT-Pd as catalysts<sup>d</sup>(a) Suzuki coupling<sup>b</sup>

run	1	2	3	4	5	6	7	8	9	10
Yield (%) <sup>c</sup>	89	90	92	89	88	90	89	91	91	92

(b) Heck coupling<sup>c</sup>

run	1	2	3	4	5	6	7	8	9	10
Yield (%) <sup>c</sup>	89	89	85	87	84	85	85	84	85	83

(c) Sonogashira coupling<sup>f</sup>

run	1	2	3	4	5	6	7	8	9	10
Yield (%) <sup>c</sup>	95	91	88	87	80	73	59	55	53	51

<sup>a</sup>All reaction was carried out in under nitrogen atmosphere and the catalysts were recovered by filtration using 0.2  $\mu\text{m}$  nylon membrane filters and then, washed successively with DMT, water, ethanol and distilled dichloromethane, and dried under vacuum for next run. <sup>b</sup>4-Bromoacetophenone (300 mg, 1.5 mmol), phenylboronic acid (220 mg, 1.8 mmol), cesium carbonate (978 mg, 3.0 mmol), and IL-MWCNT-Pd (600 mg, 5 mol% Pd) in dimethylformamide (3.5 mL). <sup>c</sup>4-Bromoacetophenone (200 mg, 0.98 mmol), *n*-butyl acrylate (141 mg, 1.1 mmol), anhydrous sodium acetate (91 mg, 1.1 mmol) and the recovered IL-MWCNT-Pd (400 mg, 5 mol% Pd) from 10<sup>th</sup> run of Suzuki coupling in *N,N*-dimethylacetamide (2 mL). <sup>d</sup>4-Bromoacetophenone (200 mg, 0.98 mmol), phenylacetylene (123 mg, 1.2 mmol), CsCO<sub>3</sub> (391 mg, 1.2 mmol), CuI (10 mg, 0.05 mmol), PPh<sub>3</sub> (13 mg, 0.05 mmol), and the recovered IL-MWCNT-Pd (400 mg, 5 mol% Pd) from 10<sup>th</sup> run of Heck coupling in *N,N*-dimethylacetamide (2 mL). <sup>e</sup>Isolated yield.

times re-using in three different C-C coupling reactions consecutively (Table 1a-c). However, the catalytic activity of the recovered catalyst was slowly decreased upon reuse. TEM analysis of the recovered catalysts after 30 times reusing showed severe aggregation of the Pd nanoparticles (right in Figure 1) suggesting that the decreased catalytic activity may largely due to the aggregation of Pd nanoparticles. Hence, it is clear that the ionic liquid-functionalized CNTs could be a good support material for Pd catalysts.

In summary, we have developed palladium catalyst supported onto imidazolium-functionalized MWCNTs. These CNT-supported palladium catalysts exhibited high catalytic activity in Suzuki, Heck and Sonogashira coupling reactions with high turnover numbers (*ca* 500). These results clearly demonstrated the potential utility of the ionic liquid-functionalized multiwalled carbon nanotubes as support materials for transition metal catalysts.

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