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Hydrogenation of aryl ketones using palladium nanoparticles on single-walled carbon nanotubes in an ionic liquid

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) are used as supporting materials for palladium (Pd) nanoparticles generated in situ in ionic liquid (IL); Pd nanocatalysts on SWNTs exhibit superior reactivity for hydrogenation of aryl ketones in IL under mild conditions (1 atm of H_2 (g) and room temperature) and can be reused above 10 times without any loss of catalytic activity.

1. Introduction

The room temperature ionic liquids (RTILs) have been attracting growing interest as environmentally benign reaction solvents in the chemical synthesis and biotransformations.[1,2] Recently, the ionic liquids (ILs) have offered special opportunities due to their unique characteristics in new applications, such as electrochemical device[3] and dye-sensitized solar cell.[4] Nonetheless, a great effort has been devoted for developing new green solvents for chemical reactions up to now. The alternative use of ionic liquids as green solvent enhanced the activity, selectivity, and stability of catalysts. Moreover, the impressive progress for generation of transition-metal-nanoparticles in ionic liquid and their efficient catalysis have been reported in recent years.[5] Among them, palladium nanoparticles/ionic liquid (IL) system is very useful for various organic synthesis.[6] However, the palladium nanoparticles in IL were readily aggregated in hydrogenation using H_2, resulting in the decrease of their catalytic activity. To overcome this problem, Huang et al. used the phenanthroline ligand-stabilized Pd nanoparticles in hydrogenation of olefins.[7] Recently, Chun et al. reported the Pd nanoparticles deposited on imidazolium bromide-functionalized ionic multi-walled carbon nanotube (MWCNT) for hydrogenation of olefin.[8]

The carbon nanotubes (CNTs) are very attractive as supporting materials for immobilization of metal-nanoparticles and biomolecules because of their large surface area to volume ratio and unique properties.[9] However, their applications in chemical reactions have been a little explored, because they are essentially insoluble in any solvent and are present in bundles or ropes. Interestingly, we have found that SWNTs are well dispersed in ionic liquids. And Fukushima et al. reported that SWNTs formed gels when mixed with ionic liquid, and entangled nanotube bundles were found to untangle within the gel to form much finer bundles.[10] These observations led us to envisage that the SWNTs would be suitable as the supporting materials for immobilization of metal-nanoparticles in ionic liquid. We herein wish to report that Pd nanoparticles on SWNTs are useful for hydrogenation of aryl ketones in IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]).

2. Results and discussion

Figure 1a shows the scanning electron microscopy (SEM) image of SWNTs used in this study which were produced by a chemical vapor deposition (CVD) method.[11] And Pd nanoparticles were generated by hydrogen reduction of a palladium(II) acetate, followed by direct adsorption on SWNTs in [BMIM][PF_6] in situ.[12] Figure 1b shows the SEM image and the energy dispersive X-ray spectroscopy (EDS) spectrum of these palladium nanoparticles attached on SWNTs.[13]

In order to evaluate the catalytic reactivity of Pd nanoparticles on SWNTs synthesized in IL, the hydrogenation of various aryl ketones was investigated. In typical experiments, the hydrogenation of aryl ketone was performed with a solution containing substrate (0.3 mmol), palladium nanoparticles (6 mol %), H_2 (1 atm), and SWNTs (5 mg) in IL (1 ml) at room temperature. After the >99%

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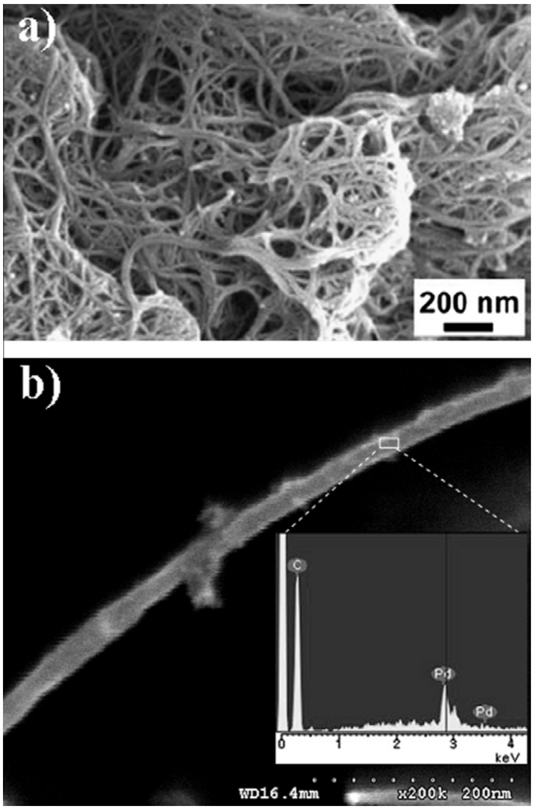
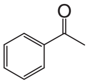
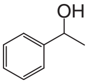
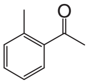
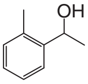
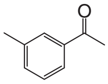
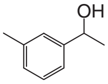
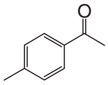
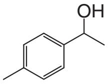
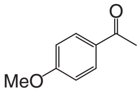
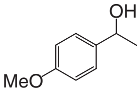
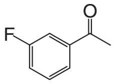
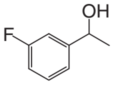
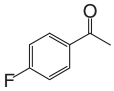
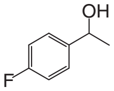
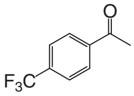
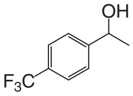
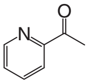
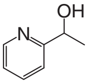
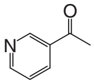
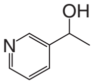
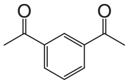
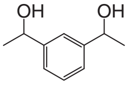
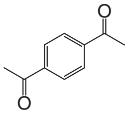
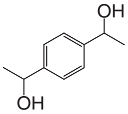
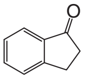
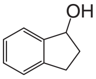
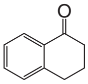
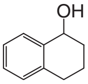


Figure 1. (a) SEM image of single-walled carbon nanotubes (SWNTs) and (b) SEM and EDAX image of palladium (Pd) nanoparticles on SWNTs.

Table 1

Hydrogenation of aryl ketones catalyzed by [Pd nanoparticles on SWNT] in [BMIM][PF_6][a]

Entry	Substrate	Product	Rxn. time (h)	Yield[b] (%)
1			24	99
2			72	94[c]
3			30	99
4			30	99
5			30	99
6			72	99
7			72	99
8			24	99
9			24	99
10			24	99
11			80	85[d]
12			80	86[d]
13			72	97[c]
14			72	94[c]

[a] The reaction conditions: 0.3 mmol substrate, 1 atm H_2, 5 mg SWNT, 1 ml [BMIM][PF_6], rt.

[b] The yields were determined by ^1H NMR.

[c] The reactions were not completed and no by-products were detected.

[d] The reactions were completed, but some partially reduced products were detected.

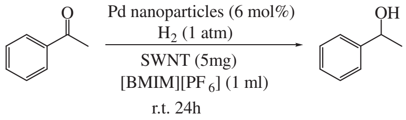
completion of the reaction was checked by TLC, the solution mixture was extracted with ethyl ether and the ethereal phase was concentrated. The yield was determined by ^1H NMR. The results were given at Table 1.

The hydrogenation of the nonsubstituted acetophenone was completed in 24 h at room temperature with a quantitative yield (entry 1). The acetophenones substituted by methyl group, which is electron-donating motif, on *meta*, *para* positions needed a little bit longer reaction time for the reaction completion but gave the quantitative yields, (entries 2 and 3) while the reaction of acetophenone *ortho*-substituted by a methyl group exhibited 94% yield in 72 h and was not completed with much longer reaction time without any by-product (entry 3). These may be caused by the steric effect of *ortho*-substituted methyl group near the carbonyl reaction center. The 4′-methoxy acetophenone containing stronger electron-donating strength gave similar reactivity to 4′-methyl acetophenone (entry 5). The substrates having electron withdrawing fluorine exhibited around 2.4 times lower reactivity than those having electron-donating substituents (entries 7 and 8). Interestingly, the substrate with a trifluoromethyl substituent showed better reactivity, resulting in faster reaction (entry 8). In case of heteroaromatic substrates, 2-acetyl- and 3-acetylpyrdine, similarly good reactivity was observed (entries 9 and 10). Also, the diketone substrate such as acetyl acetophenone can be efficiently hydrogenated by Pd nanoparticles on SWNTs in IL, but partially reduced products were detected (entries 11 and 12). The fused aryl ketone substrates exhibited similar reactivities to 2′-methly acetophenone (entries 13 and 14).

Moreover, these reactions reached completion without producing by-products which result from the C–O bond cleavage and over-reduction of aromatic ring. Also, the [Pd on SWNT]/IL system (99% yield) is more reactive than Pd/IL (39% yield) and [Pd on activated carbon]/IL (92% yield) systems[14] within the same reaction time, 24 h. These results suggest that the palladium nanoparticles were not aggregated under H_2, but remained stable and reactive on the large surface of SWNTs.

The stability of palladium nanoparticles on SWNTs was further examined by repeating its catalytic reaction, which is the hydrogenation of acetophenone (Table 2). Interestingly, the catalytic activity of the palladium nanoparticles on SWNTs was not reduced even after the tenth run. This clearly shows that the SWNTs in IL can stabilize the palladium nanoparticles by preventing their aggregation.

Table 2
Reuse of palladium nanoparticles on SWNTs in IL



Run[a]	1	2	3	4	5	6	7	8	9	10
Yield[b] (%)	99	99	99	99	99	99	99	99	99	99

[a] The first run was carried out with fresh Pd nanoparticles on SWNTs and the second to tenth runs were done with recovered Pd nanoparticles on SWNTs.

[b] The yields were determined by ^{1}H NMR.

3. Conclusion

In conclusion, this work has demonstrated that SWNTs could serve as supporting materials for immobilization of palladium nanoparticles in IL. The palladium nanoparticles on SWNT in IL were very reactive and stable for hydrogenation of aryl ketones. We believe that SWNTs are particularly promising as the supporters for immobilization of other metal nanoparticles or of biomolecules. Further studies on the immobilization on SWNTs in IL will expand the scope of the utilization of various catalysts for organic synthesis.

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12. The palladium nanoparticles on SWNTs were prepared in [BMIM][PF_6]. The SWNTs (5 mg) was grounded in IL (1 ml) for 30 min, and then Pd(II) acetate (0.018 mmol) was dissolved in the solution. The Pd(II) acetate was in situ reduced in IL with 1 atm of hydrogen for 5 min at room temperature. The aryl ketone (0.3 mmol) was added to this solution under 1 atm of hydrogen at room temperature. After the >99% completion of the reaction was checked by TLC, the products were extracted with ethyl ether. The ethereal phase was concentrated and analyzed by ^{1}H NMR.
13. Scanning Electron Microscopy and EDAX were recorded in a Hitachi S-4300 FEG. The palladium nanoparticles on SWNT samples were prepared by removing IL after hydrogenation.
14. [Pd on activated carbon]/IL system was prepared by above method with using activated carbon instead of SWNTs.