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Silicon Nanowires Supported Palladium Nanoparticles: An Efficient and Recyclable Heterogeneous Catalyst for Heck Reaction

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Silicon nanowires supported palladium catalysts were obtained by modifying Pd nanoparticles on the surface of silicon nanowires and employed as heterogeneous catalysts in Heck coupling reaction without the use of phosphorus ligands or the protection of an inert atmosphere. The catalysts demonstrated good catalytic activity and superior recyclability.

Key Words: Palladium nanoparticles, Silicon nanowires, Heck reaction, Heterogeneous catalyst, Recyclability.

INTRODUCTION

Palladium catalysts are comprehensively used in Heck coupling reaction, which is a versatile method for carbon-carbon bond formation between aryl halides and alkenes in organic synthesis[1-3]. Traditional homogeneous Pd catalysts have been proved very efficient for this reaction and received significant progress[4-7]. However, some problems have hampered their industrial application, such as the catalysts' high cost, toxicity, unrecyclability, sensitivity to oxygen and water[8,9]. To address these concerns, heterogeneous Pd catalysts have demonstrated some positive advance over the past decades[10-13].

Many polymer-supported[14,15] and inorganic solid-supported[16-20] heterogeneous catalysts have been reported till now. Compared to other supports, Si nanostructures (easily converted to Si-H surfaces by HF treatment)[21,22] have the advantages of easy surface modification with various metals, large specific surface areas and easy acquisition in bulk[23-25]. These unique features enable Si nanostructures a promising support for nanocatalysts.

Nanometal modified silicon nanowires (SiNWs) have been reported showing excellent photocatalytic properties[26-28] and high-selectivity in hydrocarbon oxidation[29]. Most importantly, SiNWs supported metal nanoparticles can keep from congregating and growing large as they are fixed by SiNWs, which make it possible for the catalysts to have stable high catalytic efficiency and excellent recyclability. In light of this superior characteristic and the respective merits of nanosized Pd and Si nanostructures, SiNWs supported Pd nanoparticles may be a promising catalyst for organic catalytic reaction.

Herein, we employed the SiNWs supported Pd heterogeneous catalysts in Heck coupling reaction. As expected, the catalysts shows stable and good catalytic activity and can be recycled for at least ten successive runs without appreciable loss of catalytic activity.

EXPERIMENTAL

All starting materials and reagents were commercially available and used without further purification. All products gave satisfactory analytical data corresponding to the reported literature values.

The powder X-ray diffraction (XRD) pattern was recorded by a Shimadzu XRD-6000 X-ray diffractometer equipped with CuK_α radiation (λ = 0.15406 nm); a scanning rate of 0.05 ° s^{-1} was applied to record the pattern. Scanning electron microscopy (SEM) images were obtained on an X-600 scanning electron microscope. The nanostructure of the catalyst was further observed by high-resolution transmission electron microscopy (HRTEM), which was taken on a JEOL-2010 transmission electron microscope, with an accelerating voltage of 200 kV. NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) on a Varian INOVA-400 NMR spectrometer in $CDCl_3$.

Preparation of the catalysts: In a typical preparation of the catalysts, 3 mg SiNWs prepared with the oxide-assisted

growth method *via* a simple thermal-evaporation of SiO powder[26,30] were etched with 5 mL 5 % HF aqueous solution for 10 min, then were rinsed with distilled water and immersed in 5 mL 5 × 10^{-3} M $PdCl_2$ aqueous solution for 10 min. The yellow SiNWs gradually turned black ones, which meant that the SiNWs were modified by Pd nanoparticles.

General procedure for the Heck reaction catalyzed by Pd/Si nanostructure: In a 25 mL glass flask were placed aryl iodide (1 mmol), alkene (1.2 mmol), triethylamine (Et_3N, 2 mmol), SiNWs supported Pd catalyst (0.1 mol %) and 10 mL of N,N-dimethyl formamide (DMF) as solvent. The reaction was initiated at a certain temperature controlled by silicon oil bath. After completion of the reaction, the mixture was extracted with ethyl acetate and washed with saturated NaCl. The organic phase was dried over anhydrous Na_2SO_4. After filtration and removal of solvent *in vacuo*, the residue was purified by column chromatography over silica gel with a mixture of ethyl acetate and petroleum ether as eluent. The desired products 1-6 were obtained.

Recycling procedure of the catalysts: In the recycling experiment, the precipitate was separated by centrifugation and washed sufficiently with ethyl acetate three times, then the catalysts were recovered and reused in the next run directly.

RESULTS AND DISCUSSION

Catalyst characterization: Fig. 1(a) shows the XRD pattern of the as prepared silicon nanowires (SiNWs). All diffraction peaks can be indexed as the cubic phase of Si and no other characteristic peaks were observed[31], which indicates that SiNWs have high purity. Fig. 1(b) reveals the XRD pattern of SiNWs supported Pd catalysts. Only the characteristic peaks of Pd were observed except Si. This indicates that the product has a high degree of crystallinity[32].

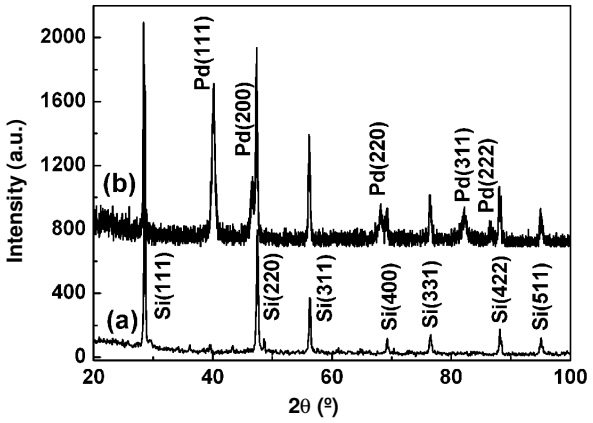


Fig. 1. XRD patterns of (a) SiNWs and (b) SiNWs supported palladium nanostructure.

Fig. 2(a) presents a SEM image of SiNWs, which are smooth and uniform with the average diameter of *ca.* 60 nm and the length larger than several micrometers. The EDX spectrum [Fig. 2(a), inset] shows the atomic ratio of Si:Pd in the SiNWs supported Pd nanoparticles catalyst is 23.05:5.70. Fig. 2(b) shows the HRTEM image of a single SiNW modified with Pd. The image confirms that Pd nanoparticles were grown

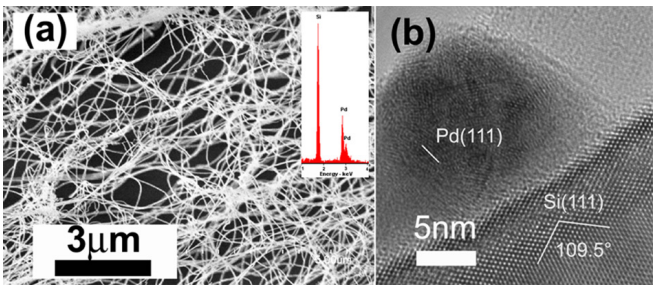


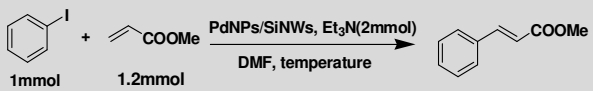
Fig. 2. (a) SEM image of SiNWs and EDX spectrum (inset) of SiNWs supported Pd catalyst; (b) HRTEM image of a single SiNW supported Pd nanostructure

on the surface of SiNW. The crystal lattices of the Si and Pd both showing (111) crystal planes are also observed, which indicates that they are both crystalline.

All of the above characterization results are consistent with each other and adequately prove the fact that the SiNWs have been modified with Pd nanoparticles.

Testing of the catalysts: To investigate their activity in organic catalytic reaction, the as-prepared SiNWs supported Pd nanoparticles catalysts were firstly employed to the Heck coupling reaction. During the course of optimization of the reaction conditions, the coupling of iodobenzene with methyl acrylate was initially studied as a model reaction using Pd/Si as catalysts. The effects of temperature and reaction time were investigated and the results are presented in Table-1. With the reaction temperature increased from 25 to 140 ºC, the yield increased significantly. Prolonging the reaction time may result in relatively higher yield. The experimental results showed that the optimum condition for this reaction was DMF in combination with triethylamine under 140 ºC for 1 h, which delivered a 94 % yield of the product 1 when 0.1 mol % of SiNWs supported Pd catalyst was used (Table-1, entry 12). And then this condition was chosen for the further study. All results were obtained without the protection of an inert atmosphere or the use of phosphorus ligands.

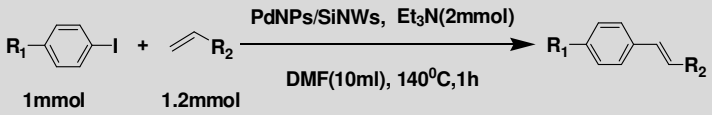
TABLE-1
EFFECTS OF SOLVENT, TEMPERATURE AND REACTION TIME ON THE HECK COUPLING OF IODOBENZENE AND METHYL ACRYLATE CATALYZED BY 0.1 mol % OF PdNPs/SiNWs



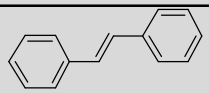
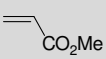
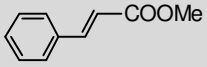
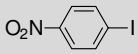
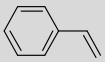
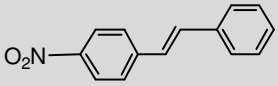
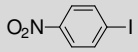
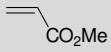
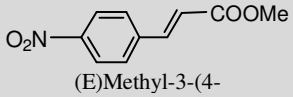
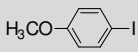
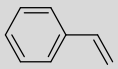
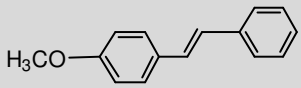
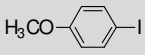
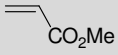
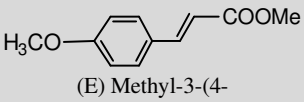
Entry	Temperature (ºC)	Time (h)	Yield (%)
1	25	24.0	0
2	60	4.0	Trace
3	80	4.0	20
4	100	2.0	60
5	100	4.0	74
6	120	2.0	69
7	120	4.0	80
8	140	0.5	79
9	140	1.0	94

We next tested several examples of SiNWs-supported palladium catalyzed Heck coupling of aryl iodides with olefins under the optimum reaction conditions and the results are summarized in Table-2. It was found that the yields were generally

TABLE-2
HECK REACTION OF ARYL IODIDES WITH ALKENES



R_1 = -H, -OCH_3, -NO_2; R_2 = -CO_2Me, -Ph

Entry	Aryl iodides	Alkene	Product	Yield (%)	NMR data
1			 (E)-1,2-Diphenylethene	88	^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.55 (d, *J* = 7.2 Hz, 4H), 7.39 (t, *J* = 7.6 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.13 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.6, 129.0, 128.0, 126.9.
2			 (E) Methyl cinnamate	94	^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.63 (d, *J* = 16.0 Hz, 1H), 7.44–7.41 (m, 2H), 7.29 (t, *J* = 6.0 Hz, 3H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.6, 145.1, 134.6, 130.5, 129.1, 128.3, 118.0, 51.9.
3			 (E)4-Nitrophenyl phenylethylene	81	^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 8.22-8.19 (m, 1H), 7.95-7.88 (m, 7H), 7.64-7.47 (m, 1H), 7.39-7.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 139.1, 133.7, 131.5, 129.3, 127.4, 127.3, 126.7, 125.3, 124.6, 103.2.
4			 (E)Methyl-3-(4-nitrophenyl)acrylate	87	^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 8.27 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 16.0Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.7, 148.7, 142.1, 140.7, 128.9, 128.6, 124.6, 124.4, 122.3, 52.3.
5			 (E)4-Methoxy phenyl phenylethylene	85	^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.50 (q, 4H), 7.37 (t, *J* = 15.2 Hz, 2H), 7.25 (t, *J* = 14.0 Hz, 1H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.5, 137.9, 130.4, 128.9, 128.4, 128.0, 127.5, 126.8, 126.5, 114.4, 55.6.
6			 (E) Methyl-3-(4-methoxyphenyl)acrylate	90	^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 7.68 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.0, 161.6, 144.8, 138.4, 130.0, 127.3, 116.6, 115.4, 114.5, 55.6, 51.8.

high for both electron-donating and electron-withdrawing aryl iodides. Besides, these conditions allow for both alkenes of acrylate and styrene. All coupling products were purified and characterized; only E-isomers were obtained which was confirmed by NMR ($^3J_{H\text{-}H}$ = 16 Hz).

Catalysts recycling: Since the Pd nanoparticles were supported on the layer deposited SiNWs, the catalysts were expected to be easily recycled. Then, experiments were carried out to examine the recyclability of SiNWs-supported palladium catalysts. The coupling reaction of iodobenzene with methyl acrylate under the optimum reaction conditions was selected as the typical reaction. As can be seen from Fig. 3, the catalysts were reused successfully and no obvious decrease in reaction yields was observed even after 10 recycling times. This high recyclability may be due to the Si/Pd catalysts' unique traits. During the process of reaction, the SiNWs supported Pd nanoparticles are kept from congregating and growing large because they are fixed by the SiNWs, which makes it possible for Pd catalysts to have high efficiency during the reaction and in recycling use. The results obviously indicate that the catalytic activity and stability of Pd/Si catalysts are promising, which may find wider application in the catalytic field.

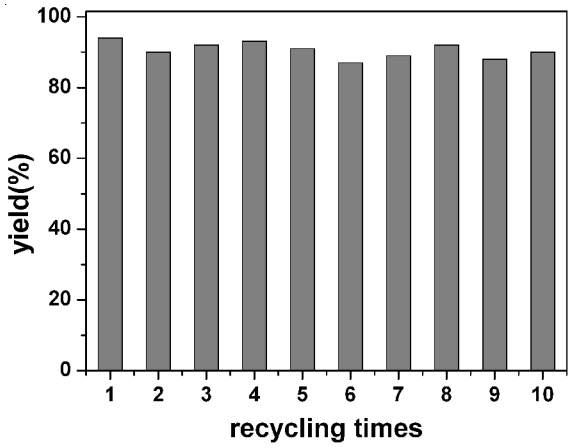


Fig. 3. Recycling of SiNWs supported Pd catalysts for the Heck reaction of iodobenzene with methyl acrylate

Conclusion

In summary, silicon nanowires are a powerful substrate support (enhance efficiency and selectivity) for nanocatalysts which preventing agglomeration of nanoparticles during the preparation and utilization of nanocatalysts. This unique

property enables the SiNWs supported Pd nanoparticles an efficient recyclable heterogeneous catalysts for Heck coupling reaction. The easy fabrication of SiNWs supported metal nanoparticles with excellent characters makes them possible to find many applications as multifunctional, high-performance catalysts.

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