ORIGINAL PAPER

Preparation and characterization of multi-walled carbon nanotubes (MWCNTs), functionalized with phosphonic acid (MWCNTs-C-PO₃H₂) and its application as a novel, efficient, heterogeneous, highly selective and reusable catalyst for acetylation of alcohols, phenols, aromatic amines, and thiols

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Abstract A novel, efficient, heterogeneous, and reusable multi-walled carbon nanotubes (MWCNTs), functionalized with phosphonic acid (MWCNTs-C-PO₃H₂) has been synthesized. The synthesized CNTs were characterized using some electron microscopic techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), Energy dispersive X-ray spectroscopy (EDAX), and also some thermal and spectroscopic methods such as thermogravimetry (TG). The nitrogen adsorption behavior of the MWCNTs-C-PO₃H₂ catalyst was evaluated using the TG instrumentation system at 25 °C. The catalyst was applied successfully for highly efficient and selective acetylation of alcohols, phenols, thiols and aromatic amines with acetic anhydride at room temperature under solvent-free conditions. The reusability of the catalyst was checked and the recovered catalyst was reused for five runs without significant loss in activity.

Introduction

Functionalization of carbon nanotubes (CNTs) is an effective way to improve the physical properties and develop the solubility of CNTs. Some of the functionalization approaches, reported before, have involved the formation of covalent bonds and non-covalent interactions [1–9]. Some functionalized CNTs have been applied as a catalyst in organic synthesis, for example, ([Ni ((OH)₂-salen)] MWCNTs) was used as a catalyst in oxidation of phenol with H_2O_2 [10], oxidation of cyclohexene was catalyzed by ([Mn ((OH)₂-salen)]MWCNTs) [11], and synthesis of 1,4-Disubstituted 1,2,3-Triazoles via copper(II) complex of 4'-phenyl-2,2':6',2''-terpyridine on activated multiwall carbon nanotubes [AMWCNTs–O–Cu^{II}–PhTPY] as a catalyst [12].

Phosphoric acid and phosphonic acid have recently attracted much attention because of their high charge carrier concentration, thermal stability, and oxidation resistance. More importantly, amphoteric phosphoric/phosphonic acids, which are advantageous over sulfonic acid, can make possible proton conduction in the dry state by forming dynamic hydrogen bond networks [13, 14]. So far, the functionalization with phosphoric acid has been widely studied [15–17], but acid leaching by water is problematic for their applications due to the hydrolytically unstable linkage O-P of phosphoric acid with silicate or polymer backbones. To avoid the problem, the use of phosphonic acid derivatives has been reported [18, 19]. Phosphonic acids are considered to be a promising proton carrier at intermediate temperatures (100-150 °C) because of their good proton donor and acceptor properties. Furthermore, phosphonic acids have a better thermal stability than sulfonic acid [20, 21]. In this regard, the phosphonic acid functionalization via hydrolytically stable C-P bond is more attractive.

Recently, a few number of phosphonic functionalized CNTs have been prepared via covalent bond formation, for example, by reacting fluorinated carbon nanotubes (F-CNTs) with 3-aminopropylphosphonic acid [22] or π - π stacking interactions [23, 24]. But there is not any report about functionalization of CNTs with phosphonic acid functional group via formation of C–P covalent bond

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between carbon atoms of CNTs with phosphor atom of phosphonic acid group. Therefore, because of the interesting features of phosphonic acid functional group [20, 21], we decided to synthesize multi-walled carbon nanotubes (MWCNTs) functionalized with phosphonic acid via direct C–P covalent bond (MWCNTs–PO₃H₂) and then study its efficiency as a novel heterogeneous Brønsted acid catalyst in acetylation of hydroxyl groups of alcohols, phenols, aromatic amines, and thiols, which is the most commonly transformations used in organic synthesis as an efficient and inexpensive way for protection of thiol, amino, alcoholic, and phenolic hydroxyl groups in a multistep synthetic process [25].

Experimental

All products were known and their physical and spectroscopic data were compared to those of authentic samples. Chemicals were either prepared in our laboratories or were purchased from Fluka or Merck. The purity of the products was determined by TLC on silica gel polygram SIL G/UV 254 plates. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250 (1H-NMR 250 MHz and 13C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard.

The synthesized CNTs were characterized using some electron microscopic techniques such as scanning electron microscopy (SEM, XL-30 FEG SEM, Philips, 20 kV), atomic force microscopy (AFM, DME-SPM, version 2.0.0.9), and also using some thermal and spectroscopic methods such as thermogravimetry.

Preparation of MWCNTs-C-PO₃H₂

Acetylene gas with a flow rate of ~50 mL min⁻¹ was bubbled into a sloution containing ferrocene (0.30 g), triphenylphosphine (3.0 g), and thiophene (0.7 mL) in benzene (25 mL). This was mixed with hydrogen and argon with flow rates to 0.5 and 800 mL min⁻¹, respectively, followed by introduction into a quartiz tube passed through a 80-cm tubing furnace set at 1,300 °C. The produced phosphore-doped carbon nanostructures were then directly purified from any amorphous carbon via purging oxygen and aerosols of hydrogen peroxide into the production line, followed by on-line activation using ultraviolet (UV) and microwave irradiators.

Preparation of MWCNTs-O-PO₃H₂

To synthesize MWCNT–O– PO_3H_2 , the CVD-synthesized MWCNTs were initially activated via O_3 treatment to form

MWCNT–OH [26–28], Then phosphoryl chloride (2.0 mL) was added to ~0.05 g of hydroxy-functionlized MWCNTs in 25 mL round-bottom flask under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 2 h. Water (10 mL) was poured to the resultant mixture and whole mixture was stirred at room temperature for 1 h to produce MWCNTs–O–PO₃H₂. After centrifuging the suspension solution and several washing of solid with acetone, the synthesized MWCNT–O–PO₃H₂ was dried in vacuum oven at 60 °C for 4 h.

General procedure for acetylation reactions

Alcohol, aniline, phenol or thiol (2.0 mmol) was added to a solution of acetic anhydride (2.0 mmol) and catalyst (MWCNTs–C–PO₃H₂) (0.1 mol %, 0.052 g) in a 5 mL round-bottom flask, which was equipped with a magnetic stirrer. The reaction mixture was stirred at room temperature. After completion of the reaction, which was determined by TLC monitoring (petroleum ether and ethyl acetate, 70:30), ethanol (5 mL) was added to the residue and the resultant mixture was stirred at room temperature for 10 min. Then, the catalyst was separated by centrifuge and ethanol was evaporated under reduced pressure. The crud product was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (70:30) to give the pure product.

Results and discussion

The CVD techniques were used for the synthesis of MWCNTs–C–PO₃H₂ (Fig. 1A). For this purpose, acetylene with 99 % purity and ferrocene were used as CNT precurser and catalyst. Iron nanoparticles were librated in situ from ferrocene and catalyzed MWCNTs formation in the presence of thiophene as as sulfur precursor for increasing the length of CNT [29].

Then phoshorous atom was doped on carbon nanostructures by the reaction of MWCNTs with triphenylphosphine at 1,300 °C under the atomsphere of hydrogen and argon in a quartiz tube. Then hydrogen peroxide oxidized the produced phoshore-doped carbon nanostructures to obtain MWCNs–C–PO₃H₂ and also simultaneously purified it from any amorphous carbon as graphically shown in Fig. 1B.

Normal distribution of CNTs was evaluated based on scanning electron microscopy (SEM) and atomic forced microscopy (AFM) as shown in Fig. 2A, B. Based on the SEM image (Fig. 2A), the external diameter of the CVD-synthesized MWCNTs was estimated to 3–8 nm. In addition, according to the AFM image (Fig. 2B); the width of the band at half-height of the voltage profile peak (Fig. 2C)



Fig. 1 Schematic of CVD-synthesized MWCNTs-C-PO₃H₂ catalyst (**A**), and schematic representing the CVD-synthesis of MWCNT-C-PO₃H₂ (**B**)



Fig. 2 Characterization of MWCNTs–C– PO_3H_2 including: SEM image (A), AFM image (B), and voltage profile image (C)

revealed the size of the MWCNTs. This value was in good agreement with the results obtained from SEM image.

The residual EDAX spectrum indicated that, large amounts of phosporesous atoms ($\sim 4.1 \%$ w/w) were positioned in the MWCNTs matrix (Fig. 3).

The thermogram of the MWCNTs–C– PO_3H_2 samples, taken using a home-made thermogravimetric (TG) analyzer, was also shown in Fig. 4A.

In accordance with the thermogram (Fig. 4A), the significant decrease observed in the weight percentage of the MWCNTs–C–PO₃H₂ sample (~11.65 %) at 270 °C, was related to the decomposition of –PO₃H₂ functional group.



Fig. 3 Residual EDAX spectrum of MWCNTs-C-PO₃H₂

This result revealed that there was an acceptable relation between the weight percentage of phosphor, which was functionalized on MWCNTs ($\sim 4 \%$), and the result obtained from the EDAX spectrum (Fig. 3). Also, as it was shown (Fig. 4A), MWCNTs were completely decomposed at ~ 750 °C.

The nitrogen adsorption behavior of the MWCNTs–C– PO₃H₂ catalyst was also evaluated using the TG instrumentation system at 25 °C. According to the nitrogen adsorption isotherms (Fig. 4B), significant increasing was observed ~830 m² g⁻¹ in the active surface area of the MWCNTs when functionalized with –PO₃H₂ group.

Back-titration method was also utilized as an effective technique for evaluation of the percentage of acidic functional group doped on MWCNTs and characterizing the structure of MWCNT functionalized by phosphonic acid. For this propose, initially MWCNTs–O–PO₃H₂ was synthesized by oxidation of MWCNT according to the known procedure [26–28], phosphorylation of MWCNTs–OH and hydrolysis of MWCNTs–O–POCl₂, respectively (Scheme 1).



Fig. 4 Thermogram of MWCNT-PO₃H₂ (A), and nitrogen adsorption isotherms of MWCNTs and MWCNTs-C-PO₃H₂ at 25 °C (B)



Scheme 1 Schematic representing the CVD-synthesis of MWCNT– O– PO_3H_2



Fig. 5 FT-IR spectra of MWCNTs-O-PO₃H₂ (A), and MWCNTs-C-PO₃H₂ (B)

Then 0.01 g of each pure carbon nanomaterial (MWCNT, MWCNTs– PO_3H_2 and MWCNTs– $O-PO_3H_2$) was suspended in excess amount of NaOH (0.01 M, 10 mL) and sonicated at a frequency of ~500 kHz for 30 min. The carbon nanomaterial was separated by centrifugation and the solution was titrated with HCl (0.05 M). According to the data obtained from this method, the weight percentage of the acidic group was evaluated to be



Scheme2 Acetylation of 1-phenylethanol with acetic anhydride

Table 1 Acetylation of 1-phenylethanol with acetic anhydride in the presence of MWCNTs–C– PO_3H_2 in different conditions at room temperature

Entry	Solvent	Catalyst (mol %)	Time (min)	Yield ^a (%)
1	Solvent-free	None	60	25
2	Solvent-free	0.05	20	75
3	Solvent-free	0.07	13	87
4	Solvent-free	0.1	10	95
5	Solvent-free	0.15	10	95
6	EtOH	0.1	60	50
7	EtOAc	0.1	60	53
8	CH_2Cl_2	0.1	20	96
9	CH ₃ CN	0.1	90	90
10	CHCl ₃	0.1	20	92
11	H ₂ O	0.1	60	_

^a Isolated yield

around 3.95 % and a significant change in pH to 5.8 and 6.02 was observed for MWCNTs–C–PO₃H₂ and MWCNTs–O–PO₃H₂ compared with the pure MWCNTs, respectively. Although the phosphorous oxidation number is five for both compounds, these results revealed stronger acidity of MWCNTs–C–PO₃H₂ compared with MWCNTs–O–PO₃H₂. Stronger acidic strength of MWCNTs–C–PO₃H₂ might be as a direct consequence of the inductive effect of carbon atom [30] and resonance effect of the oxygen atom attached to phosphorous atom in MWCNTs–O–PO₃H₂.

For more evidence about the C–P bond formation, the FT-IR spectra of both $MWCNTs-O-PO_3H_2$ and

Table 2 Acetylation of alcohols and phenols to the corresponding esters in the presence of MWCNTs-C-PO ₃ H ₂ under solvent-free condition	ons
at room temperature	

Entry	Substrate	Product ^a	Time [min]	Yield ^b [%]
1	ОН	OAc	5	97
2	O ₂ N OH	O ₂ N OAc	10	92
3	СІ	Cl	10	94
4	МеО	MeO	5	95
5	ОН	OAc	10	95
6	СН3 ОН	CH ₃ OAC	10	95
7	и ОН	UNIT OAc	10	95
8	CI OCHCH ₃ OCH ₂ CH ₃ OH	Cl P OCHCH ₃ OAc	60	80
9	H ₃ C H ₃ C H ₃ C	$H_{3}C$ $H_{3}C$ $H_{3}C$ $H_{3}C$	20	80

Entry	Substrate	Product ^a	Time [min]	Yield ^b [%]
10	O2N OH	O ₂ N OAc	90	85
11	ОН	OAc	60	90
12	OH	OAc	70	84
13 ^c	НО	Aco	55	87
14 ^c	OH OH	OAc	80	83
15	ОН	OAc	50	90
16	OH CH ₃	OAc CH ₃	65	87
17	H ₃ C OH	H ₃ C OAc	60	90
18	CH ₃	OAc CH ₃	80	85

Entry	Substrate	Product ^a	Time [min]	Yield ^b [%]
19	Br	Br	60	90
20	Cl	Cl	60	82
21	SH	SAc	40	93
22	SH	SAc	5	95
23	NH ₂	NHAc	15	95
24	HO COOH	HO NHAC COOH	20	90
25	NC NH ₂	NC NHAc	25	95
26	CN NH ₂	CN	30	93

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Table 2 continued

Table 2 continued

Entry	Substrate	Product ^a	Time [min]	Yield ^b [%]
27	Cl NH ₂	Cl	15	95
28	O ₂ N NH ₂	O ₂ N NHAc	35	95
29	Br	Br. NHAc	15	96
30		N Ac	70	75

^a All products were fully characterized by ¹H NMR, ¹³C NMR spectra and compared to those of authentic samples

^b Isolated yield

^c Two equivalent of Ac₂O were used

MWCNTs–C–PO₃H₂ was studied as shown in Fig. 5. Significant differences were observed in accordance with the spectra shown in Fig. 5. As clearly revealed in the FT-IR spectrum of MWCNTs–C–O–PO₃H₂ (Fig. 5A), the sharp and strong peak positioned at 1,061 cm⁻¹ is related to the formation of P–O–CH [31]. Also the shoulder situated at 1,233.9 cm⁻¹ is related to the P=O bond formation [32]. Whereas, in accordance with the FT-IR spectrum of MWCNT–C–PO₃H₂ (Fig. 5B), no absorbance peak is observed at absorption regions at around 1,061 cm⁻¹, however, the sharp absorbance peak representing the formation of P=O bond still existed.

After characterization of the catalyst, we decided to utilize it for acetylation of alcohols and phenols with acetic anhydride to their corresponding acetate esters.

For optimization of the reaction parameters, we investigated the ability of MWCNTs–C– PO_3H_2 for the acetylation of 1-phenylethanol with equimolar of acylating reagent, acetic anhydride, as a model reaction (Scheme 2).

Initially, the reaction was performed under solvent free condition at room temperature in the presence of different amount of the catalyst. According to the results, shown in Table 1 (entries 1–5), the model reaction gave only 25 % yield of the desired product in the absence of the catalyst after 1 h at room temperature and the highest yield of the corresponding acetate was produced after 10 min when 0.1 or 0.15 mol % of the catalyst was used (Table 1, entry 4 and 5). Examination of the model reaction in the presence of 0.1 mol % of the catalyst in different solvents at room temperature showed that 1-phenylethyl acetate was obtained more efficiently in dichloromethane compare with the other solvents (Table 1, entry 11). According to the represented results in Table 1, the best efficiency was observed under solvent-free condition in the presence of 0.1 mol % of the catalyst and at room temperature.

Therefore, with the optimized condition in hand, the scope of method and its versatility on the different type of alcohols was explored. According to the results, shown in Table 2, primary alcohols such as benzylic alcohols were easily acetylated and gave the corresponding acetates in excellent yields and the data obtained in this way revealed

Table 3	Selective acetylation of alcohols,	phenols, thiols and a	romatic amines by o	competitive method wi	th MWCNTs-C-PO ₃ H ₂	under solvent-
free conc	litions at room temperature					

Entry	Substrate	Product ^a	Time [min]	Yield [%] ^b
1	CH ₃ OH	CH ₃ OAc OAc	5	10 90
2	H ₃ C H ₃ C H ₃ C H ₃ C	H_3C H_3C H_3C H_3C H_3C	5	95 0
3	CH ₃ OH	OAc CH ₃ OAc	10	0 95
4	ОН С ОН	OAc OAc	5	0 95
5	OH H ₃ C H _H C OH	OAc H ₃ C H ₃ C H ₃ C	20	10 75

Entry	Substrate	Product ^a	Time [min]	Yield [%] ^b
6	Br NH ₂	Br NHAc	15	10 87
7	HO COOH	HO $COOH$ AcO CO_2H	25	100 0
8	OH SH	OAc SAc	40	20 78
9	OH SH NH ₂	OAc SAc NHAc	15	0 10 88
	-	-		

Table 3 continued

 $^{a}\,$ The substrates were treated with Ac_2O (1.0 eq)

^b Isolated yield

the substituents had no remarkable effect on the acetylation yield (Table 2, entries 1–4). Also secondary alcohols smoothly transformed to the desired acetate in excellent yields (Table 2, entries 6–8), in the presence of the catalyst under solvent-free conditions at room temperature, except the α -hydroxyphosphonate that was converted to the related product in longer reaction time and lower yield (Table 2, entry 8). As a tertiary alcohol, *t*-butanol was also carried out the acetylation reaction in excellent yield after 20 min (Table 2, entry 9). Then, the ability of this catalyst was investigated in acetylation of phenols. According to the summarized data in Table 2, the related phenyl acetates were obtained in excellent yields from phenols with both electron-donating and electron-withdrawing substituents (Table 2, entries 10–20). No competitive Fries rearrangement was observed for phenolic substrates and in general, acetylation of phenols proceeded in longer reaction times in comparison with alcohols.

The ability of this catalyst was also checked in acetylation of thiols and the related products were obtained in excellent yields (Table 2, entries 21and 22).

Entry	Catalyst (Mol %)	Reaction conditions	Time [min]	Yield [%]	Ref.
1	MWCNTs-C-PO ₃ H ₂ (0.1 mol %)	RT/Solvent-free, 1 eq Ac ₂ O	5	97	_
2	Mn (haacac) Cl)] (5 mol %)	30 °C/Solvent-free, 1.5 eq Ac ₂ O	300	97	[33]
3	TiCl ₃ (OTf) (1 mol %)	RT/Solvent-free, 1 eq Ac ₂ O	Im. ^a	96	[34]
4	Sn (IV) (tpp) (BF ₄) ₂ (1 mol %)	RT/CH ₃ CN, 2 eq Ac ₂ O	1	99	[35]
5	MoO ₃ /Al ₂ O ₃ (5 mol %)	RT/Solvent-free, 2 eq Ac ₂ O	20	99	[36]
6	Ce (OTf) (1.0 mol %)	RT/CH ₃ CN, 1.5 eq Ac ₂ O	15	98	[37]
7	Mg(ClO ₄) ₂ (1 mol %)	RT/Solvent-free, 1 eq Ac ₂ O	15	100	[38]
8	$H_{14}[NaP_5W_{30}O_{110}]$ (o.1 mol %)	RT/Solvent-free, 1.5 eq Ac ₂ O	75	98	[39]
9	tin ^(IV) porphyrin-hexamolybdate (1 mol %)	RT/CH ₃ CN, 2 eq Ac ₂ O	4	100	[40]
10	[V ^{IV} (TPP)(OTf) ₂] (0.5 mol %)	RT/CH ₃ CN, 3 eq Ac ₂ O	0.5	90	[41]

Table 4 Comparison between different acid catalysts with MWCNTs-C-PO₃H₂ for acetylation of benzyl alcohol with acetic anhydride

^a Immediately



Fig. 6 Reuse of MWCNTs–C– PO_3H_2 for acetylation of 1-phenyl-ethanol with acetic anhydride

Also we examined the ability of this catalyst in acetylation of aromatic amines such as aniline and substituted anilines with different electron-withdrawing groups such as CN, NO₂, Cl, Br, and COOH (Table 2, entries 23–30). According to the summarized data in Table 2, the related amides were obtained in excellent yields. Also diphenylamine, as a secondary amine, was transformed to the desired amide in good yield in the presence of the catalyst under solvent-free conditions at room temperature (Table 2, entry 30).

Selective acetylation of alcohols, phenols, thiols, and aromatic amines was also examined by competitive method (Table 3). Therefore, one equivalent of each substrate was mixed and then the acetylation reaction was run in the presence of 0.1 mol % of MWCNTs–C–PO₃H₂ and one equivalent of acetic anhydride at room temperature under solvent-free conditions. The data obtained in this way revealed primary alcohols can be highly selective acety-lated against secondary and tertiary alcohols (Table 3, entries 1 and 2). Also, it was possible to do selective acylation of all types of alcohols in the presence of phenols

(Table 3, entries 3–50. The results were shown –SH group in thiophenol can be highly selective acetylated in the presence of –OH group in phenols (Table 3, entry 8). Also primary amino group can be highly selective acetylated in the presence of –OH group in phenols and –SH group in thiophenol (Table 3, entries 7 and 9) and secondary amines (Table 3, entry 6).

Comparing efficiency of MWCNTs–C–PO₃H₂ with some of the reported catalysts in the literature showed superiority of this free metal and heterogeneous catalyst, at least concerning the amount of catalyst and acetic anhydride used in the acetylation of benzyl alcohol (Table 4).

For checking the reusability of the catalyst, the reaction of 1-phenylethanol with acetic anhydride was carried out using 0.1 mol % MWCNTs–C–PO₃H₂ in a 10 mmol scale. After completion of the reaction, the catalyst was recovered by centrifuge and dried under air. Then the dried catalyst was reused for five successive reactions without further purification and considerable loss in catalyst activity, Fig. 6.

Conclusions

In this study, efficient, free metal, heterogeneous, and reusable multi-walled carbon nanotubes (MWCNTs), functionalized with phosphonic acid (MWCNTs–C– PO_3H_2) have been synthesized and applied successfully for highly efficient and selective acetylation of phenolic hydroxyl groups, and different classes of alcohols, aromatic amines and thiols with acetic anhydride under solvent-free conditions and at room temperature with easy work up.

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