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ORIGINAL PAPER

Synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates from *O*-isobutyl xanthate and amines using a nano-platinum multi-walled carbon nanotube catalyst

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Abstract Twelve *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates, eight of which are novel, were synthesized from *O*-isobutyl xanthate and 3- and 4-substituted anilines in the presence of a nano-platinum aminophenyl modified multi-walled carbon nanotube catalyst. The nano-Pt catalyst was prepared on a carbon nanotube support modified by diazotization, nitro group reduction, and subsequent microwave-assisted nano-Pt precipitation. The catalyst was characterized by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, thermogravimetric analysis, and transmission electron microscopy. The nano-platinum/modified carbon nanotube catalyst was compared with a commercial Pt/active carbon catalyst in terms of product purity and yield. The results obtained by the use of the catalysts were additionally compared with those obtained by reaction of sodium isobutyl xanthogenacetate and 3- and 4-substituted anilines. Full structure characterization of the synthesized *N*-(substituted phenyl)-*O*-isobutyl thionocarbamates was achieved using FT-IR, ^{1}H and ^{13}C NMR, and mass spectrometric methods, and their purity was proved by elemental analysis and gas chromatography. The new catalytic method offers advantages over the commercial method, such as higher yields and no product purification is required, thus conforming to the principles of ecologically friendly syntheses.

Keywords Amines · Nanostructure · Nucleophilic substitutions · Heterogeneous catalysis · Thionocarbamates · Nano-Pt/NH_2Ph-MWCNT

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Introduction

Thio- and thionocarbamates are derivatives of thiocarbamic acid, either thiol or thiono esters, respectively [1, 2]. Their structural characteristics, direct bonding of the carbonyl and thiocarbonyl group and nitrogen, contribute to their broad range of biological activities, such as fungicidal [3, 4], bactericidal [3, 5], herbicidal [6–8], germicidal and pesticidal [9–11], and insecticidal [12, 13]. In addition, *O*-alkylthionocarbamates were used as polymerization accelerators and selective flotoreagents [14].

There are many procedures for the synthesis of alkyl thionocarbamates, such as aminolysis of alkaline salts of xanthogenacetic acid with or without a catalyst. As an example, an alkyl thionocarbamate was synthesized from diethyl dixanthogenate and xanthate and amines in the presence of manganese(II) acetate and nickel zeolite catalysts [15]. Thionocarbamates can also be prepared by the reaction of xanthogenates and amines in the presence of nickel and palladium salt catalysts [16]. The oxidation of an amine salt of xanthogenic acid, by hydrogen peroxide and sodium hypochlorite, led to a high yield of isopropyl thionocarbamate [14].

N-Phenyl thionocarbamate was synthesized from phenyl chlorothionoformate and corresponding amines in dioxane [17]. Raney nickel and platinum or palladium on a carbon support were used in the reaction of sodium alkyl

xanthogenate and amine in order to obtain thionocarbamates [18].

The synthesis of *N*,*O*-diphenyl thionocarbamates was achieved from aniline and aryl chlorothioformate in acetonitrile [19], and aromatic isothiocyanates reacted with equimolar quantities of primary and secondary alcohols or diols to give good yields of *O*-alkyl thiocarbamate [20]. *S*-aryl (alkyl) thiocarbamates were synthesized from isocyanate and disulfide in the presence of $Zn/AlCl_3$ as catalyst [21], as well as starting from thiol and isocyanate under catalyst- and solvent-free conditions [22]. Moreover, thermal rearrangement of thionocarbamates to thiocarbamates, or the process at ambient temperature in the presence of a catalyst, is a useful method for such interconversions [23, 24].

Organic reactions in aqueous media have attracted considerable attention in recent years, because they offer a powerful tool for minimizing waste production and harmful organic solvent disposal. Some particular properties of water make this solvent very attractive (i.e., non-toxicity, non-inflammability, high heat capacity, possibility of controlling pH, isolation of insoluble solid products by filtration, and the recycling of inorganic catalysts and the water itself), allowing organic processes in aqueous medium to be safer, very efficient, and highly selective [25].

The main goal of the present study was to develop a new catalyst, compare it with a commercial Pt/active carbon catalyst as well as with the results of a commercial synthesis of thionocarbamates [15].

Amino-functionalized multi-walled carbon nanotubes (MWCNT) were prepared by two protocols. The first procedure was based on the chemical transformation of carboxylic acid residues, introduced onto the MWCNT surface by chemical oxidation, by direct coupling of 1,4-phenylenediamine (PDA) with the carboxylic groups to introduce amino terminal groups (PDA-MWCNT). Preactivation of the carboxylic groups with *N*,*N*-diisopropylethylamine (DIEA) and subsequent formation of an active ester using *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (N-HATU) enabled amide bond formation [26].

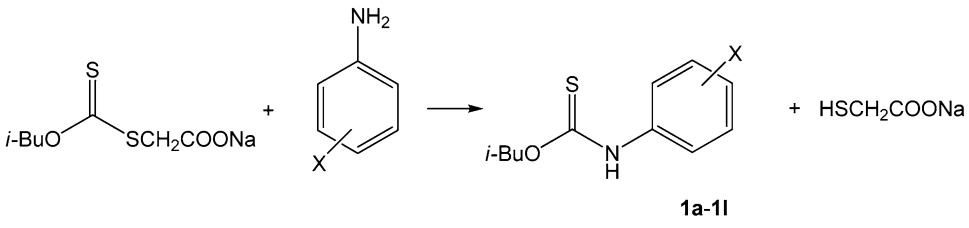
The second protocol involved in situ diazotization with 4-nitroaniline, affording direct coupling on the graphitic surface, and subsequent reduction of the nitro group with lithium aluminum hydride to produce terminal amino functionality (NH_2Ph-MWCNT). Modification of the MWCNT by these two pathways should influence catalyst synthesis and their activity in the synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates. Nanoplatinum precipitation on NH_2Ph-MWCNT and PDA-MWCNT surfaces was performed by microwave-assisted chloroplatinic acid reduction in the presence of ethylene glycol to afford Pt/NH_2Ph-MWCNT and Pt/PDA-MWCNT catalysts. The results of the thionocarbamate synthesis in the presence of catalyst were compared with those obtained from isobutyl xanthogenacetic acid sodium salt and 3- and 4-substituted anilines (Scheme 1). An additional benefit of this method, which gives moderate yields of the products, is the isolation of sodium thioglycolate as a by-product, which is used as a component in cosmetic products.

Results and discussion

In the presented work, a new synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates **1a–1l** was performed, starting from sodium isobutyl xanthate and 3- and 4-substituted anilines in the presence of Pt/NH_2Ph-MWCNT and Pt/PDA-MWCNT catalyst. The optimal reaction conditions were defined with respect to the reaction time, temperature, and catalyst concentration achieving optimal catalyst activity and product purity (data not presented). Two modifications of the MWCNT were performed in order to study their catalytic efficiency, as well as the effect of such modified graphitic supports on their catalytic ability. The success of the catalyst-promoted synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates was compared with the results obtained using Pt/active carbon and a well-known commercial method [15].

The catalysts were prepared by two protocols: the first method included MWCNT oxidation/amidation and the

Scheme 1



X = H, 4-OCH_3, 4-OH, 4-CH_3, 4-I, 4-F, 4-Br, 4-Cl, 3-Cl, 3-Br, 3-OCH_3, 4-$N(CH_3)_2$

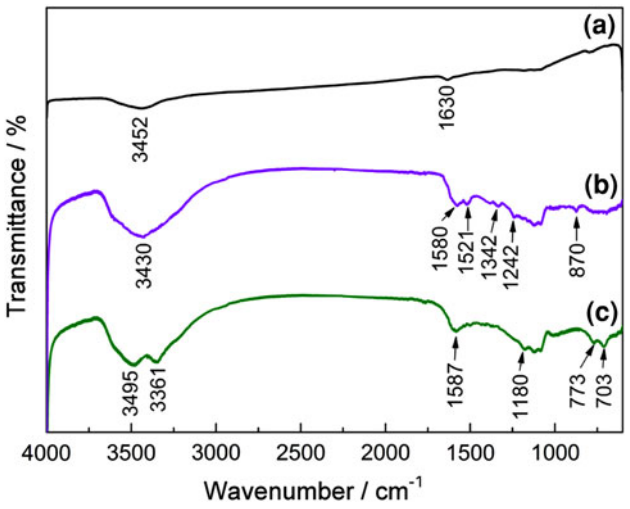


Fig. 1 FT-IR transmission spectra of *a* raw-MWCNT, *b* NO_2Ph-MWCNT, and *c* NH_2Ph-MWCNT

second diazotization/reduction; both methods introduced terminal amino groups. Diazotization/reduction is the method of choice as it gave a catalyst with better performance. The selected catalyst was used in thionocarbamate synthesis and its performance was compared with that of a commercial Pt/active carbon catalyst to estimate its feasibility for commercial implementation. The synthesized Pt/NH_2Ph-MWCNT catalyst and intermediary products were characterized by FT-IR spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and elemental analysis.

FT-IR spectroscopy

The FT-IR spectra of the raw MWCNT (raw-MWCNT) and the nitrophenyl (NO_2Ph-MWCNT) and aminophenyl (NH_2Ph-MWCNT) modified MWCNT (Fig. 1) confirm that nitrophenyl groups were introduced by diazotization (Fig. 1b), and subsequent reduction produced amino terminal groups (Fig. 1c). A broad band at ca. 3,452 cm^{-1} is attributed to the hydroxyl stretching vibration (ν_{OH}) and the peak at ca. 1,630 cm^{-1} is assigned to the C=C skeletal graphitic stretching vibration (Fig. 1a) [27]. The FT-IR transmission spectrum of NO_2Ph-MWCNT (Fig. 1b) shows the appearance of a band at ca. 1,580 cm^{-1} (broad band overlapped with the C=C stretching vibration), which is ascribed to the asymmetric nitro group stretch vibration, as well as the symmetric nitro group vibration at 1,342 cm^{-1}. Amino groups, obtained by reduction of nitro groups, are evidenced by the peaks at ca. 3,495 and 3,361 cm^{-1}, which are due to the asymmetric and symmetric NH_2 stretch vibrations, respectively, overlapped with the ν_{OH} vibration (Fig. 1c). In addition, the band at ca. 1,587 cm^{-1} and a new one at ca. 1,180 cm^{-1} correspond to N–H in-plane and C–N bond stretching, respectively. Oxidation, the N-HATU-promoted amidation of MWCNT by the phenylenediamine method, and characterization of the obtained material (PDA-MWCNT) were presented elsewhere [26].

TEM study

The morphology of the NH_2Ph-MWCNT and Pt/NH_2Ph-MWCNT materials was analyzed by high resolution TEM (HRTEM) and high angle annular dark field (HAADF) images are shown in Fig. 2. The sidewalls of raw-MWCNT are integrated and smooth with a trace of impurities and metallic nanoparticles of various shapes and dimensions found inside the nanotubes [26]. Most of the catalyst residue was removed by purification, as was determined by inductively coupled plasma mass spectrometry (ICP-MS) of a nitric acid extract [28]. Compared with those of the raw-MWCNT, the sidewalls of NO_2Ph-MWCNT and NH_2Ph-MWCNT (Fig. 2a) are more corrugated and there are detectable amorphous prominences on the outer graphite sheets and inside the nanotubes. Obvious morphological differences between these two samples were not observed. The modified MWCNT still had a similar cylinder wall structure like that of the raw-MWCNT, and the interplanar spacing was similar [26]. Representative HRTEM and HAADF images of the Pt/NH_2Ph-MWCNT show a satisfactory homogenous distribution of Pt nanoparticles over the NH_2Ph-MWCNT surface (Fig. 2b, d). The mean Pt particle diameter was less then 3 nm. The electron diffraction pattern of the Pt nanoparticles, shown in Fig. 2c, indicates the presence of mainly twinned platinum particles.

Thermogravimetric analysis

TGA not only gives useful information about the thermal stability of the groups present on the MWCNT surface, but also enables the determination of Pt content in the Pt/NH_2Ph-MWCNT catalyst. TGA weight loss curves obtained by heating the raw-MWCNT, NO_2Ph-MWCNT, and NH_2Ph-MWCNT in nitrogen and the Pt/NH_2Ph-MWCNT in air are presented in Fig. 3. As shown in Fig. 3, the weight loss curves of modified samples overlap below 200 °C. Absorbed water and traces of the reactants used in the purification and modification processes were desorbed below 200 °C [29, 30]. These processes are followed by defragmentation of the nitro- and aminophenyl groups present on the MWCNT walls; these processes occur between 200 and 500 °C [31]. At temperatures over 500 °C, the graphitic structure shows considerable stability with no significant weight loss. On the other hand, the TG curves for Pt/NH_2Ph-MWCNT in air showed that oxidative thermal degradation completely removes the organic material leaving 6.15% residue of PtO_2. According to this

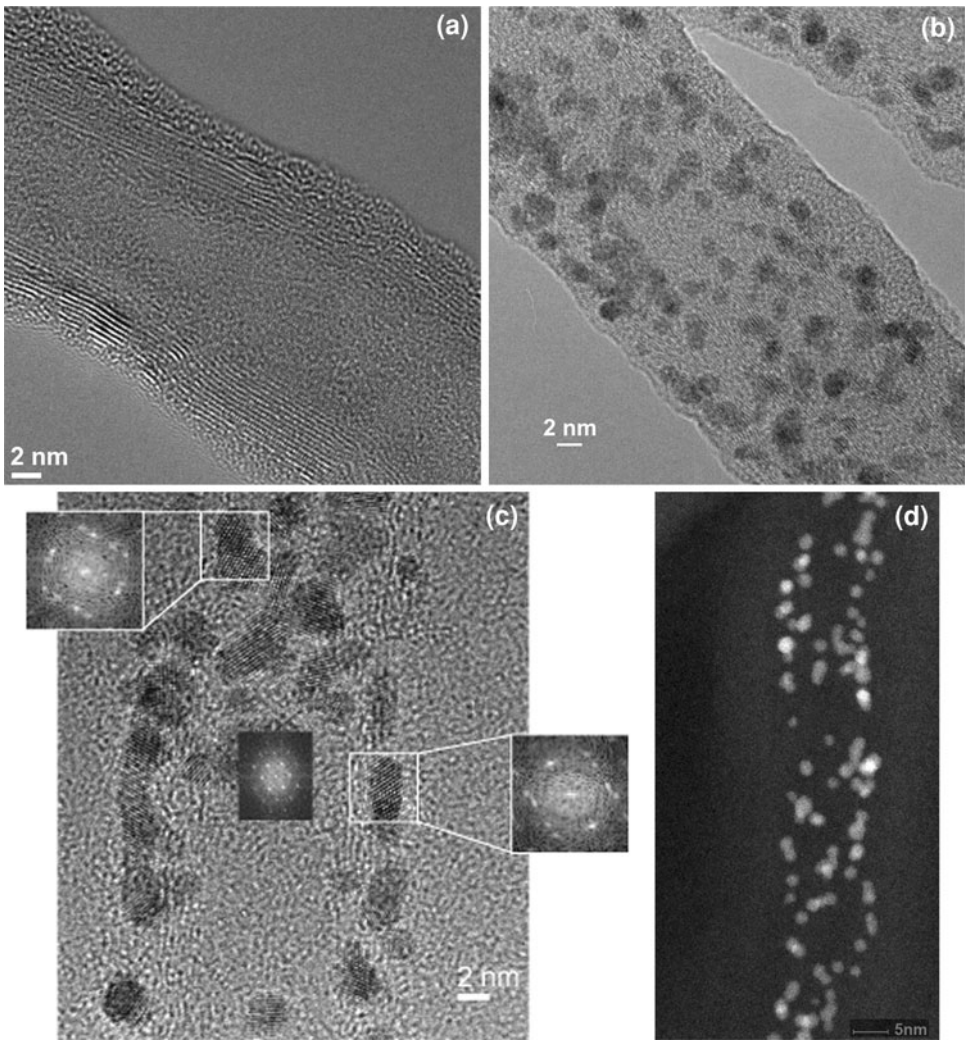


Fig. 2 HRTEM images of **a** NH_2Ph-MWCNT and **b** Pt/NH_2Ph-MWCNT; **c** electron diffraction pattern of Pt nanoparticles; **d** HAADF image of Pt/NH_2Ph-MWCNT

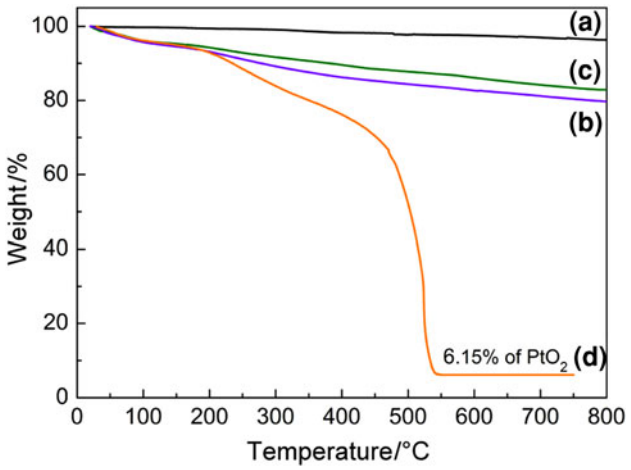


Fig. 3 TGA curves of *a* raw-MWCNT, *b* NO_2Ph-MWCNT, *c* NH_2Ph-MWCNT under nitrogen; and *d* Pt/NH_2Ph-MWCNT under air

result, it could be calculated that 5.28% of Pt nanoparticles were deposited on the NH_2Ph-MWCNT support. Also, TGA analysis showed a 4.95% Pt nanoparticle loading on PDA-MWCNT (not presented).

Elemental analysis

The attachment of surface functional groups on the sidewall of the MWCNT was further confirmed by elemental analysis (Table 1). No nitrogen was detected in the analysis of the raw-MWCNT but a significant amount of nitrogen (1.61%) was observed for NO_2Ph-MWCNT which is due to diazotization, and an even higher nitrogen content of 2.16% after reduction of the nitro group. Based on the results presented in Table 1, the nitrogen content (2.16%) of NH_2Ph-MWCNT provides an estimation of the amount of attached aminophenyl groups (around 14 wt%), which is in good accordance with the TGA results. Furthermore, the increased oxygen content for NO_2Ph-MWCNT (6.98%) and the subsequently

Table 1 Elemental analysis of raw-MWCNT, NO_2Ph-MWCNT, and NH_2Ph-MWCNT

Sample	C/%	H/%	N/%	O/%[a]
raw-MWCNT	97.46	0.32	0	2.22[b]
NO_2Ph-MWCNT	90.23	1.18	1.61	6.98
NH_2Ph-MWCNT	93.89	1.76	2.16	2.19

[a] Calculated as difference (catalyst percent was found to be negligible [32])

[b] Oxygen present due to oxidative purification performed by supplier

decreased content for NH_2Ph-MWCNT (2.19%) also provide direct evidence for the reduction of the nitro groups.

According to the established optimal synthesis methods A–D, described in the "Experimental", a series of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates **1a**–**1l** were obtained and the results are given in Table 2.

Somewhat lower yields of the *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates were obtained when method A was employed (Table 2). The results indicate that method A, the reaction of thioacyl nucleophilic substitution of NaEtXAc by 3- and 4-substituted anilines, does not offer the possibility for scale-up, as was found for *N*-alkyl and *N*,*N*-dialkyl-*O*-ethyl thionocarbamate [15]. These results strongly indicate that the significantly lower basicity of 3- and 4-substituted anilines is a factor of primary significance, which limits the achievement of acceptable conversion to the desired product. The data from MS, FT-IR, ^{1}H, and ^{13}C NMR spectroscopy of the *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates **1a**–**1l**, presented in the "Experimental", undoubtedly corroborate the structure of the synthesized compounds.

The satisfactory reaction yields obtained by method B and the simple work-up offer the possibility for the implementation of optimized laboratory technology on a semi-industrial scale. In addition, it was found that no dangerous by-products were found in the wastewater effluent, and the simple wastewater treatment for the removal of organic residues indicates this method to be an alternative option to existing processes. Somewhat lower yields were obtained by the use of Pt/PDA-MWCNT catalyst which indicates low suppressing influence of the amide bridging group in Pt/PDA-MWCNT on catalyst activity, comparing to direct bonding in Pt/NH_2Ph-MWCNT. From this point of view, the goals of future studies will be focused on new syntheses of MWCNT supports and a method for catalyst precipitation or, alternatively, the synthesis of catalysts based on other active metals with the intention of producing catalysts with higher activities.

In conclusion, the presented work describes the optimal synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates from *O*-ethyl isobutyl xanthate and 3- and 4-substituted anilines in the presence of nano-platinum multi-walled carbon nanotube catalysts. Satisfactory conversions of the starting materials into products using Pt/NH_2Ph-MWCNT (34.0–80.9%) and somewhat lower yields in the presence of a Pt/PDA-MWCNT and Pt/active carbon catalysts (20.9–78.5% and 20.8–70.1%, respectively) were achieved. The techno-economic aspect of the new method B is satisfactory, especially regarding catalyst recyclability and simple product purification to achieve acceptable commercial purity. Considering possible applications of the nano-Pt/NH_2Ph-MWCNT catalyst, it provides an acceptable and versatile method for the preparation of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates. This method has several unique merits, namely, simple operation, mild reaction conditions, avoidance of hazardous

Table 2 Yields and purities of *N*-(3- and 4-substituted phenyl) *O*-isobutyl thionocarbamates obtained by methods A–D

Comp.	Substituent	Method A		Method B		Method C		Method D	
		Yield/%	Purity[a]/%	Yield/%	Purity[a]/%	Yield/%	Purity[a]/%	Yield/%	Purity[a]/%
1a	H	32.1	99.2	40.1	99.3	39.4	99.0	38.2	99.4
1b	4-OCH_3	45.9	99.0	63.1	99.2	52.2	99.1	50.1	98.9
1c	4-OH	44.5	99.0	61.0	99.5	49.8	99.4	48.2	98.8
1d	4-CH_3	30.3	98.7	48.9	99.6	45.6	99.0	36.1	99.1
1e	4-I	52.1	98.7	72.3	99.4	66.4	98.4	59.3	99.4
1f	4-F	18.3	98.7	34.0	99.3	30.4	99.0	20.8	99.5
1g	4-Br	51.4	98.7	74.5	99.7	70.8	99.1	61.8	98.7
1h	4-Cl	40.6	98.7	56.2	99.7	55.6	99.1	43.3	99.6
1i	3-Cl	18.8	98.8	34.1	99.8	20.9	99.2	21.3	99.3
1j	3-Br	44.2	98.8	69.1	99.2	68.2	99.0	48.6	98.8
1k	3-OCH_3	41.3	99.2	60.2	98.9	54.6	98.8	44.8	99.7
1l	4-$N(CH_3)_2$	67.6	99.0	80.9	99.3	78.5	99.4	70.1	99.6

[a] Determined by GC method

organic solvents, employment of moderately toxic and inexpensive reagents, short reaction times, and high product yields. This new environmentally benign process represents a suitable alternative to existing methods, and contributes to the protection of the environment.

Experimental

FT-IR spectra were recorded in the transmission mode using a BOMEM (Hartmann & Braun) spectrometer. TEM measurements were performed using FEI-CM200 super-twin and CM300 ultra-twin microscopes (Philips Electronic Instruments) operating at 200 and 300 kV and equipped with Gatan 1 k × 1 k and 2 k × 2 k CCD cameras, respectively. The particle shapes were determined by real space crystallography using high-resolution images taken from particles near or at the edge of the carbon black substrate, and/or by numerical Fourier filtering of the digitized image intensity spectrum of particles on the top of the carbon. TGA was performed using a TA Instruments SDT Q600 at a heating rate of 20 °C min^{-1} and a nitrogen or air flow of 100 cm^3 min^{-1}. Elemental analyses were performed using a VARIO EL III elemental analyzer. The ^1H and ^{13}C NMR spectral measurements were recorded on a Bruker AC 250 spectrometer, at 250 MHz for the ^1H NMR and 62.89 MHz for the ^{13}C NMR spectra. The spectra were recorded at room temperature in dimethyl sulfoxide-d_6 (DMSO-d_6) in 5-mm tubes. The chemical shifts are expressed as δ values in parts per million referenced to the tetramethylsilane reference standard signal. The mass spectra were recorded on a ThermoFinnigan Polaris Q ion trap mass spectrometer, including TraceGC 2000 (ThermoFinnigan, Austin, TX, USA), integrated GC–MS/MS system.

Materials

Commercially available MWCNT (raw-MWCNT, Sigma Aldrich), prepared by a chemical vapor deposition method, was used as received without further purification. *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were purified and dried to remove any trace of moisture [33]. All other reagents, such as 3- and 4-substituted anilines (Sigma Aldrich), 1,4-phenylenediamine (PDA, Sigma Aldrich), isopentyl nitrite (Sigma Aldrich), lithium aluminum hydride ($LiAlH_4$, Sigma Aldrich), ethylene glycol (EG, Alfa Aesar), solutions of H_2PtCl_6 (Alfa Aesar) and KOH (Sigma Aldrich), were used as received. The commercial Pt on active carbon catalyst was supplied by Acros Organics. Millipore deionized water (DI, 18 MΩ cm) was used for sample washing and solution preparation.

Diazotization of MWCNT (Fig. 4)

The initial solvent-free functionalizations were performed on purified MWCNT [31] under an inert atmosphere [34, 35]. Raw-MWCNT (110 mg) and 400 mg 4-nitroaniline were added to a flask equipped with a reflux condenser and a magnetic stirrer. Then, 6 cm^3 isoamyl nitrite was slowly added via a syringe. Heating (60 °C) under vigorous stirring resulted in the commencement of paste formation. After 3 h, the paste was diluted with DMF and filtered through a polytetrafluoroethylene (PTFE) (0.05 μm) membrane filter. The collected solid was washed with DMF until the filtrate became colorless. DMF was removed by washing with diethyl ether, and the product NO_2Ph-MWCNT was dried in a vacuum oven at 60 °C for 6 h.

Reduction of NO_2Ph-MWCNT (Fig. 4)

NO_2Ph-MWCNT (100 mg) was dispersed in anhydrous THF by sonication for 30 min. After the sonication, 10 mg of $LiAlH_4$ was added to the dispersion and the sonication continued for 1 h. The reaction mixture was then slowly added to 200 cm^3 of methanol and vacuum-filtered through a 0.05-μm-pore-size PTFE membrane filter. The product NH_2Ph-MWCNT was dried in a vacuum oven at 60 °C for 6 h [36].

Catalyst synthesis—nano-Pt/NH_2Ph-MWCNT from NH_2Ph-MWCNT (Fig. 4)

The preparation of Pt/NH_2Ph-MWCNT was carried out from 2.2 cm^3 of a 0.01 mol dm^{-3} aqueous solution of

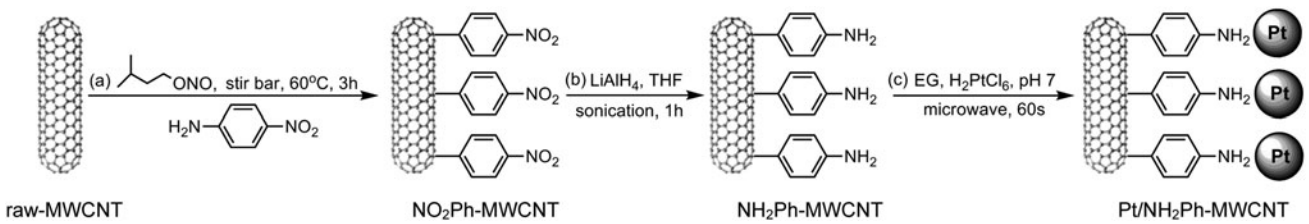


Fig. 4 Pt/NH_2Ph-MWCNT catalyst preparation: **a** diazotization of purified MWCNT; **b** reduction of NO_2Ph-MWCNT; **c** microwave-assisted precipitation of nano-Pt on NH_2Ph-MWCNT

H_2PtCl_6 and 80 mg of NH_2Ph-MWCNT in 50 cm^3 of EG using microwave heating by a method described elsewhere [37, 38].

Catalyst synthesis—nano-Pt/PDA-MWCNT from PDA-MWCNT

Nano-Pt/PDA-MWCNT was synthesized from PDA-MWCNT analogously to the preparation of nano-Pt/NH_2Ph-MWCNT.

Synthesis of N-(3- and 4-substituted phenyl)-O-isobutyl thionocarbamates [15] (method A)

The synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates was performed analogously to the published method, except that 50 cm^3 of an ethanolic solution of 4-substituted aniline (0.34 mol) was added to an aqueous solution of isobutyl xanthogenacetic acid sodium salt (0.34 mol). After heating at 80 °C for 5 h, the ethanol was evaporated and the precipitate was dissolved in dichloromethane. The organic layer was washed with 5% hydrochloric acid, then with water until neutral, and dried over sodium sulfate. After removal of the solvent, the crude product was crystallized from ethanol. The results of the synthesis are given in Table 2. The pure *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates had satisfactory elemental analysis and MS, ^{1}H, and ^{13}C NMR spectral data.

Synthesis of N-(3- and 4-substituted phenyl)-O-isobutyl thionocarbamates in the presence of the nano-Pt/NH_2Ph-MWCNT catalyst (method B)

To a 50 cm^3 three-necked flask containing 25 cm^3 DI water and equipped with a magnetic mixer, dropping funnel, condenser, and thermometer was added 8.41 g of 75% active commercial sodium isobutyl xanthate (0.038 mol). After the xanthate had completely dissolved, 20 mg Pt/NH_2Ph-MWCNT catalyst was added followed by 3.95 cm^3 70% ethylamine. The reaction mixture was heated to 80 °C and maintained at that temperature for 6 h. After cooling to room temperature, the reaction mixture was filtered to remove catalyst and the reaction product was purified by two successive washings with DI water and then dried. The results of the synthesis are given in Table 2.

Synthesis of N-(3- and 4-substituted phenyl)-O-isobutyl thionocarbamates in the presence of the nano-Pt/PDA-MWCNT catalyst (method C)

The synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamates was performed analogously to method B in the presence of Pt/PDA-MWCNT. The results of the synthesis are given in Table 2.

Synthesis of N-(3- and 4-substituted phenyl)-O-isobutyl thionocarbamates in the presence of Pt/active carbon (method D)

The synthesis of *N*-(3- and 4-substituted phenyl)-*O*-isobutyl thionocarbamateswas performed analogously to method B in the presence of a Pt/active carbon catalyst. The results of the synthesis are given in Table 2.

Catalyst regeneration

The Pt/NH_2Ph-MWCNT, Pt/PDA-MWCNT, and Pt/active carbon catalysts were regenerated by refluxing in a short-chain aliphatic alcohol, because the substances adsorbed onto the catalyst surface are readily soluble in the alcohol. The regenerated catalyst was used in ten cycles without significant activity loss. Characterization of regenerated catalyst showed that the applied experimental method has no influence on the properties of the catalyst [39].

N-Phenyl-O-isobutyl thionocarbamate (**1a**)
M.p.: 74 °C (Ref. [40] 75 °C).

N-(4-Methoxyphenyl)-O-isobutyl thionocarbamates (**1b**, $C_{12}H_{17}NO_2S$)
M.p.: 72 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.95$ (6H, d, $J = 6.8$ Hz, $(CH_3)_2CH$), 2.07 (1H, m, $CHCH_2O$), 3.79 (3H, s, $PhOCH_3$), 4.33 (2H, d, $J = 6.2$ Hz, CH_2O), 6.86 and 7.18 (4H, AA′XX′, $J = 8.6$ Hz, Ph), 8.74 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1$, 27.7, 55.4, 78.7, 114.0, 126.0, 130.0, 157.3, 188.7 ppm; FT-IR (KBr): $\bar{\nu} = 3{,}471$, 3,214, 3,122, 3,050, 2,996, 2,955, 2,830, 2,061, 2,010, 1,870, 1,600, 1,550, 1,509, 1,459, 1,413, 1,358, 1,302, 1,251, 1,206, 1,173, 1,041, 961, 828 cm^{-1}; MS (70 eV): $m/z = 239.3$ (M^+).

N-(4-Hydroxyphenyl)-O-isobutyl thionocarbamate (**1c**, $C_{11}H_{15}NO_2S$)
M.p.: 92 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.93$ (6H, d, $J = 6.6$ Hz, $(CH_3)_2CH$), 2.05 (1H, m, $CHCH_2O$), 4.32 (2H, d, $J = 6.2$ Hz, CH_2O), 6.82 and 7.08 (4H, $J = 9$ Hz, Ph), 7.93 (1H, s, NH), 8.67 (1H, bs, OH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.0$, 27.7, 78.8, 115.7, 124.6, 129.8, 153.6, 188.7 ppm; FT-IR (KBr): $\bar{\nu} = 3{,}346$, 3,230, 3,056, 2,959, 1,878, 1,603, 1,556, 1,510, 1,470, 1,437, 1,386, 1,302, 1,271, 1,193,1,044, 831, 736 cm^{-1}; MS (70 eV): $m/z = 225.3$ (M^+).

N-(4-Methylyphenyl)-O-isobutyl thionocarbamates (**1d**, $C_{12}H_{17}NOS$)
M.p.: 70 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.97$ (6H, d, $J = 6.8$ Hz, $(CH_3)_2CH$), 2.09 (1H, m, $CHCH_2O$),

2.31 (3H, s, PhCH_3), 4.34 (2H, d, $J = 6.2$ Hz, CH_2O), 7.14 (4H, s, Ph), 8.96 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1, 20.8, 27.6, 78.3, 121.8, 129.4, 134.5, 188.6$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}436, 3{,}222, 3{,}040, 2{,}971, 1{,}889, 1{,}597, 1{,}542, 1{,}509, 1{,}463, 1{,}405, 1{,}355, 1{,}315, 1{,}288, 1{,}201, 1{,}036, 964, 801$ cm^{-1}; MS (70 eV): $m/z = 223.3$ (M^+).

N-(4-Iodophenyl)-O-isobutyl thionocarbamate (**1e**, $C_{11}H_{14}INOS$)
M.p.: 115 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.96$ (6H, d, $J = 6.8$ Hz, (CH_3)$_2$CH), 2.10 (1H, m, CHCH$_2$O), 4.34 (2H, d, $J = 6.2$ Hz, CH_2O), 7.11 (2H, bs, Ph), 7.64 (2H, d, $J = 9.0$ Hz, Ph), 8.86 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1, 27.5, 78.9, 89.2, 126.8, 136.8, 137.9, 188.8$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}454, 3{,}220, 3{,}095, 3{,}040, 2{,}969, 2{,}869, 1{,}890, 1{,}591, 1{,}538, 1{,}485, 1{,}393, 1{,}355, 1{,}278, 1{,}204, 1{,}033, 822$ cm^{-1}; MS (70 eV): $m/z = 335.2$ (M^+).

N-(4-Fluorophenyl)-O-isobutyl thionocarbamate (**1f**, $C_{11}H_{14}FNOS$)
M.p.: 49 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.96$ (6H, d, $J = 6.6$ Hz, (CH_3)$_2$CH), 2.08 (1H, m, CHCH$_2$O), 4.33 (2H, d, $J = 6.2$ Hz, CH_2O), 7.03 (2H, m, Ph), 7.27 (2H, s, Ph), 9.18 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.0, 27.6, 78.8, 115.8, 127.8, 133.4, 163.6, 188.7$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}181, 3{,}017, 2{,}964, 2{,}875, 1{,}871, 1{,}610, 1{,}550, 1{,}509, 1{,}469, 1{,}409, 1{,}384, 1{,}353, 1{,}288, 1{,}214, 1{,}156, 1{,}034, 1{,}089, 828$ cm^{-1}; MS (70 eV): $m/z = 227.2$ (M^+).

N-(4-Bromophenyl)-O-isobutyl thionocarbamate (**1g**, $C_{11}H_{14}BrNOS$)
M.p.: 59 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.95$ (6H, d, $J = 6.8$ Hz, (CH_3)$_2$CH), 2.10 (1H, m, CHCH$_2$O), 4.34 (2H, d, $J = 6.8$ Hz, CH_2O), 7.26 (2H, bs, Ph), 7.45 (2H, d, $J = 9.0$ Hz, Ph), 8.88 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1, 27.6, 78.9, 123.8, 126.8, 132.7, 136.1, 188.7$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}218, 3{,}102, 3{,}043, 2{,}967, 2{,}871, 1{,}889, 1{,}592, 1{,}541, 1{,}489, 1{,}417, 1{,}397, 1{,}353, 1{,}204, 1{,}075, 1{,}035, 824$ cm^{-1}; MS (70 eV): $m/z = 287.1$ (M^+).

N-(4-Chlorophenyl)-O-isobutyl thionocarbamate (**1h**)
M.p.: 58 °C (Ref. [41] 68–69 °C).

N-(3-Chlorophenyl)-O-isobutyl thionocarbamate (**1i**)
M.p.: 75 °C (Ref. [42] 78 °C).

N-(3-Bromophenyl)-O-isobutyl thionocarbamate (**1j**, $C_{11}H_{14}BrNOS$)
M.p.: 62 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 1.00$ (6H, d, $J = 6.6$ Hz, (CH_3)$_2$CH), 2.12 (1H, m, CHCH$_2$O), 4.36 (2H, d, $J = 6.0$ Hz, CH_2O), 7.22 (3H, m, Ph), 7.60 (1H, s, Ph), 8.96 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1, 27.6, 79.0, 122.4, 124.9, 128.2, 130.2, 138.2, 188.7$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}217, 3{,}038, 2{,}967, 1{,}919, 1{,}588, 1{,}536, 1{,}470, 1{,}400, 1{,}358, 1{,}329, 1{,}279, 1{,}071, 1{,}023, 918, 859, 761, 669, 603$ cm^{-1}; MS (70 eV): $m/z = 287.1$ (M^+).

N-(3-Methoxyphenyl)-O-isobutyl thionocarbamates (**1k**, $C_{12}H_{17}NO_2S$)
M.p.: 60 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.99$ (6H, d, $J = 6.6$ Hz, (CH_3)$_2$CH), 2.12 (1H, m, CHCH$_2$O), 3.78 (3H, s, Ph-OCH_3), 4.34 (2H, d, $J = 6.2$ Hz, CH_2O), 6.70 (1H, dd, $J = 2.4, 6.0$ Hz, Ph), 6.90 (2H, bs, Ph), 7.22 (1H, t, $J = 8.2$ Hz, Ph), 9.06 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1, 27.6, 55.2, 77.0, 107.6, 110.9, 113.9, 129.6, 138.1, 159.9, 188.6$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}217, 2{,}963, 2{,}871, 2{,}835, 1{,}901, 1{,}596, 1{,}539, 1{,}464, 1{,}407, 1{,}327, 1{,}254, 1{,}056, 933, 766, 682$ cm^{-1}; MS (70 eV): $m/z = 239.3$ (M^+).

N-[4-(N,N-Dimethylamino)phenyl]-O-isobutyl-thionocarbamate (**1l**, $C_{13}H_{20}N_2OS$)
M.p.: 61 °C; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 0.95$ (6H, d, $J = 6.8$ Hz, (CH_3)$_2$CH), 2.07 (1H, m, CHCH$_2$O), 2.94 (6H, m, N(CH_3)$_2$), 4.32 (2H, d, $J = 6.8$ Hz, CH_2O), 6.68 (2H, t, $J = 8.2$ Hz, Ph), 7.13 (2H, m, Ph), 8.53 (1H, bs, NH) ppm; ^{13}C NMR (62.89 MHz, DMSO-d_6): $\delta = 19.1, 27.7, 40.5, 77.0, 112.3, 123.5, 126.4, 127.3, 148.5, 188.5$ ppm; FT-IR (KBr): $\bar{\nu} = 3{,}428, 3{,}184, 3{,}019, 2{,}961, 2{,}800, 1{,}615, 1{,}523, 1{,}445, 1{,}412, 1{,}347, 1{,}215, 1{,}169, 1{,}046, 948, 821, 724$ cm^{-1}; MS (70 eV): $m/z = 252.3$ (M^+).

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