



Short communication

Sulfonated reduced graphene oxide as a highly efficient catalyst for direct amidation of carboxylic acids with amines using ultrasonic irradiation



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ABSTRACT

Sulfonated reduced graphene oxide nanosheets (rGO-SO₃H) were prepared by grafting sulfonic acid-containing aryl radicals onto chemically reduced graphene oxide (rGO) under sonochemical conditions. rGO-SO₃H catalyst was characterized by Fourier-transform infrared (FT-IR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray photoelectron spectroscopy (XPS). rGO-SO₃H catalyst was successfully applied as a reusable solid acid catalyst for the direct amidation of carboxylic acids with amines into the corresponding amides under ultrasonic irradiation. The direct sonochemical amidation of carboxylic acid takes place under mild conditions affording in good to high yields (56–95%) the corresponding amides in short reaction times.

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1. Introduction

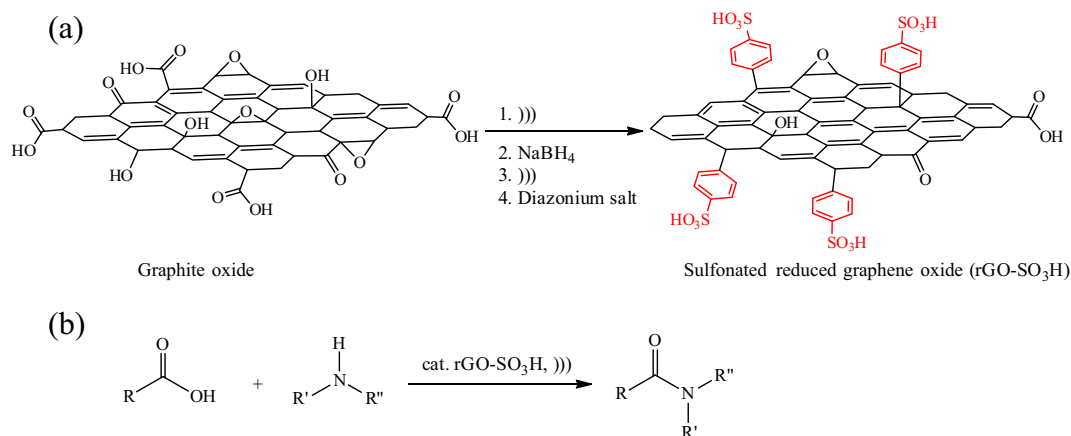
Amide is one of the most important functional groups in organic chemistry; amides are present in many natural products, peptides, synthetic polymers, pharmaceuticals, and biological systems [1]. Several amide derivatives have biological properties such as anti-tumor, antifungal, antihistamine, anthelmintic, and antibacterial activity [2,3]. They are also useful and valuable intermediates for the synthesis of various important compounds [4]. Usually amides can be synthesized by the reaction of carboxylic acids [5] or their derivatives such as halides [6], esters [7], and carboxylic salts [8] with amines. A number of methods have been developed for the synthesis of amide compounds, including rearrangement of aldoximes [9], transamidation of amides with amines [10,11], cross coupling of amides with aryl halides [12], aminocarbonylation of aryl halides [13] or terminal alkynes [14], hydration of nitriles [15] and Ugi reaction [16]. The catalytic procedures developed for oxidative amidation of aldehydes [17], alcohols [18–21] and alkylarenes [22] with amines or amine salts are quite attractive from atom economy and green chemistry view points. Recently, *N*-heterocyclic carbene (NHC)-catalyzed oxidative amidation of aromatic aldehydes with amines in the presence of *N*-bromosuccinimide as an

oxidant has been proposed for the synthesis of amides [17]. Bantreil et al. established a domino reaction for the formation of benzamides in one step from various benzyl alcohols in the presence of copper salt [18]. Recently, Wang et al. investigated direct oxidative amidation between methylarenes and free amines in water by employing *tert*-butyl hydroperoxide as the environmental benign oxidant with the co-catalysis of tetrabutyl-ammonium iodide and FeCl₃ in the presence of 4 Å molecular sieves [22]. Nevertheless, some of the reported methods require stoichiometric amounts of coupling reagents and suffer from poor atom efficiency or the use of highly hazardous reagents. Despite the low reactivity of acids, direct amidation is still the most preferred industrial process from both atom economy and environmental points of view. Thus, it is desirable to use a cheap and environmentally benign catalyst for direct amidation in order to overcome these problems.

Solid acids have the great potential to replace liquid acids as environmentally benign acid catalysts [23,24]. Acidic carbons, based on the concept of green chemistry, were investigated as stable and highly active protonic acid catalysts for several acid-catalyzed reactions [25,26]. Graphene oxide and graphite oxide have been effectively applied as useful heterogeneous catalysts for certain organic transformations [27–32]. Recently, we have demonstrated the efficiency of graphite oxide as a solid acid catalyst for esterification of organic acids with alcohols [33] and ring-opening of epoxides with various alcohols [34].

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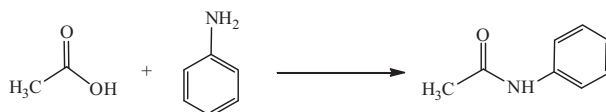
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Scheme 1. (a) Synthesis of rGO-SO₃H; (b) direct sonochemical amidation of carboxylic acids with amine derivatives using rGO-SO₃H catalyst.

Table 1

Different conditions for the direct amidation of acetic acid with aniline^a.



Entry	Catalyst	Conditions	Time	Yield (%)
1	–	Solvent-free, room temperature	72 h	20
2	–	Acetonitrile, reflux	48 h	32
3	Graphite oxide (5 mg)	Solvent-free, room temperature	48 h	29
4	rGO-SO ₃ H (5 mg)	Solvent-free, room temperature	8 h	45
5	rGO-SO ₃ H (5 mg)	Solvent-free, 70 °C	2 h	86
6	rGO-SO ₃ H (5 mg)	Bath ultrasonic, solvent-free, 70 °C	20 min	92
7	rGO-SO ₃ H (5 mg)	Bath ultrasonic, solvent-free, room temperature	20 min	94
8	–	Bath ultrasonic, solvent-free, room temperature	100 min	–
9	Graphite oxide (5 mg)	Bath ultrasonic, solvent-free, room temperature	20 min	8
10	rGO-SO ₃ H (2.5 mg)	Bath ultrasonic, solvent-free, room temperature	20 min	27

^a Reaction conditions: acetic acid (1 mmol) and aniline (1 mmol).

Sonochemical waves were employed to exfoliate graphite oxide and functionalized graphene oxide. An original approach was recently proposed by Maktedar et al. for the direct functionalization of graphene oxide with 6-aminoindazole through sonochemical nucleophilic substitution reaction [35]. Wang et al. applied sulfonated graphene as a solid catalyst for the ester-exchange reaction [36]. Sulfonated graphene catalyst prepared by grafting sulfonic acid-containing aryl radicals onto the two-dimensional surface of graphene was successfully used for the etherification of glycerol with isobutene [37].

In continuation of our efforts on the use of graphite oxide, we investigate in this work a simple procedure for the preparation of sulfonated reduced graphene oxide (rGO-SO₃H) (Scheme 1a). The catalytic activity of rGO-SO₃H as a reusable solid acid catalyst was further investigated for the direct amidation of carboxylic acids with amines into the corresponding amides under ultrasonic irradiation (Scheme 1b). Although the effect of ultrasound in chemical reactions is known [38], to the best of our knowledge, there are only a few examples on the amidation reaction [39–41].

2. Experimental section

2.1. Analysis and characterization of materials used in this study

Ultrasonic irradiation was accomplished with an Elmasonic P ultrasonic cleaning unit (bath ultrasonic) with a frequency of 37 kHz and 100% output power. IR spectra were recorded from

KBr disks with a Bruker Vector 22 FT-IR spectrometer. Raman spectra were recorded using a dispersive Raman spectrophotometer Bruker model SENTERRA. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) data were obtained using a VEGA3 LMU TESCAN SEM. X-ray diffraction (XRD) data were performed using a Bruker D8 Advance Theta-2theta diffractometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 F1. Differential scanning calorimetry (DSC) was carried out on a NETZSCH DSC 204 F1 Phoenix. X-ray photoelectron spectroscopy (XPS) were collected on a VG ESCALAB MK-II spectrometer with Al K α as the excitation source ($h\nu = 1486.6$ eV) operated at 10.5 kV and 20 mA at a pressure better than 10^{-8} Pa. GC–MS analysis was performed on a FISON GC 8000 series TRIO 1000 gas chromatograph equipped with a capillary column CP Sil.5 CB, 60 m \times 0.25 mm i.d. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 and 75 MHz spectrometer using tetramethylsilane as internal standard. Elemental analyses were performed on a ThermoFinnigan Flash EA 1112 series elemental analyzer.

2.2. Synthesis of sulfonated reduced graphene oxide nanosheets (rGO-SO₃H)

Typically, 150 mg of graphite oxide [30] powder in 150 mL water were mixed in a reaction container using bath ultrasonic with a frequency of 37 kHz for 30 min. A solution of 1.2 g NaBH₄ in 30 mL water was added dropwise into the graphite oxide

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