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FULL PAPERS

Modified Graphene Oxide based Zinc composite: an efficient catalyst for Nformylation and carbamate formation reactions through CO₂ fixation

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Abstract: Catalytic fixation of CO_2 through chemical reactions is always a challenging task of synthetic chemistry. This paper represents the design and synthesis of an eco-friendly low cost zinc metal containing heterogeneous catalyst of aminically modified Graphene Oxide. Characterization of the catalyst has been carried out by Raman and FTIR spectra, AAS, XRD, TEM, SEM, EDX and N₂ adsorption desorption studies. It was found that the catalyst was very proficient for the CO_2 fixation through N-formylation and carbamate formation reactions of amines. Catalytic N-formylation reaction of both

1. Introduction

CO2 fixation reaction for the formation of value-added products is the most demanding approach in recent years in order to control the green house $gas^{[1]}$. CO_2 is anabundant renewable low-cost, and nontoxic C1 resource which has attracted a great attention in the field of synthetic chemistry as well as green chemistry^[2]. Till date, different methodologies of CO2 fixation reaction like cyclo addition of CO2 into aziridines or epoxides^[3], formylation and carboxylation of aliphatic/aromatic halides^[4,5], N-formylation^[6], Nmethylation^[7], carbamates production^[8] and oxazolidinones formation^[9] have been developed. Among them N-formylation is an important class of reaction as through this reaction formamides are produced which are widely used in the synthesis of valuable heterocycles and pharmaceutical products as well as biological intermediates^[10-14]. Moreover the formylated products are also very useful as Lewis base organocatalysts in hydrosilylation reactions and other organic transformations. In peptide chemistry formyl group is used for protecting the amine functional group ^[15].

Generally two routes are involved in the synthesis of Nformamides, one is CO_2 fixation route and another is non CO_2 fixation route where chloral, formaldehyde, paraformaldehyde, formate, formic acid, methanol etc. are used as CHO sources^[16] and generates copious wastes resulting in poor atom-economy^[17]. Carbon dioxide fixation pathway is the cleanest and most attractive atom-economical green route for the production of Nformamides. In addition, capturing and utilization of the green house gas CO_2 for manufacturing of fine chemicals is highly pleasing. Due to the stability of CO_2 , catalytic N-formylation of amines using CO_2 is a challenging task^[18], again, selectivity is a crucial factor in this protocol as methylated amines may also get generated as a consequence of over reduction of the formed formamides^[19].

Recently, formamides are synthesized from amines through CO_2 fixation reaction using hydrosilanes or molecular hydrogen as the hydrogen sources.

aromatic and aliphatic amines gave high yield of corresponding formylated products in presence of Polymethylhyrosiloxane as reducing agent under 1 bar CO_2 pressure and mild temperature. Formation of carbamates from aniline or its derivatives and alkyl/aryl bromide with good product selectivity was also achieved under same CO_2 pressure in presence of our synthesized catalyst at room temperature with solvent-free condition. The catalyst is reusable and efficient even after six cycles.

In the last few years, use of hydrosilanes as a reducing agent of CO₂ has been increased extensively^[22]. Cantat and co-workers have utilized hydrosilane for the formylation of amines through CO₂ fixation^[23]. After that couple of other catalysts such as imidazolium-based ionic liquids^[24] and thiazolium carbene^[25] were reported. Although few catalytic systems showed good recyclability but most of metal based catalysts worked under homogeneous condition which makes the separation process difficult and cost-effective. To overcome those difficulties and make the protocol less costly, we have synthesized a diethylenetriamine functionalized Graphene Oxide based zinc metal catalyst, Zn(II)DETA@GO. GO is easily producible, inexpensive material and synthesized Zn(II)DETA@GO is an efficient and recylable catalyst for N-formylation reaction under 1 atm CO₂ pressure in presence of PMHS reducing agent at ambident temperature (80°C).

Organic carbamates are highly important in the field of pharmaceuticals (as pro-drugs and drugs)^[26] and agriculture^[27]. They grasp a pivotal role as anti-HIV, anti-diabetic, anti-inflammatory, anti-progestational, anti-Alzheimer, anti-fungal, anti-estrogenic, anti-convulsant, anti-bacterial, anti-osteoporosis, anti-cancer, anti-filarial, anti-helminths, anti-tubercular, anti-obesity, anti-viral, anti-malarial, drugs and CNS, CVS active agents^[28]. The compounds are very popular for the protection of amino group in the peptide chemistry^[29], as linker in the combinatorial chemistry^[30] and as intermediate in the organic synthesis^[31].

The traditional methods for the synthesis of organic carbamates required either cumbersome or toxic reagents, such as carbon monoxide, phosgene or its derivatives^[32]. Replacement of these reagents by CO₂ will be highly appropriate and straightforward. A numbers of homogeneous and heterogeneous metal catalysts based on Al, Sn, Ru, and Au etc. have already been developed for the conversion of amines to carbamates using CO₂ as the carbon source^[33]. To improve the reaction conditions potassium superoxide and macrocyclic polyether were further used for the preparation of carbamates^[34]. Except those catalysts, various inorganic and organic base-catalyzed or mediated transition metal-free systems have been introduced recently^[35]. But all of these protocols are involved in either harsh reaction conditions, such as high pressure and temperature or require additional reagents and exhibit poor functional group tolerance. Therefore, it is highly preferable to build up a new cost effective, chemoselective and green methodology which would work under atmospheric CO₂ pressure and at room temperature (RT). For these reasons, we have synthesized a cheap material,

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Zn(II)DETA@GO composite, which can act as an efficient heterogeneous catalyst in the formation of organic carbamates through CO_2 fixation reaction under 1 bar pressure and at room temperature.

Herein, we published the synthesis, characterization of an aminically modified Graphene Oxide based zinc catalyst (Zn(II)DETA@GO) and its competent catalytic activity towards CO₂ fixation reactions for the preparation of N-formamides and organic carbamates under mild conditions.

2. Experimental

Preparation of Graphene Oxide (GO):

Synthesis of Graphene oxide was carried out by oxidation of graphite flakes (Aldrich) using the following reported method^[36]. In this method, a 200 mL mixture of concentrated H₃PO₄ and H₂SO₄ (20:180 v/v) was taken in a 500 mL round bottom flaks. Then graphite flakes (1.5 g) were added slowly to the mixture. Next KMnO₄ (9.0 g) was added in portions to the above mixture. After that, the above solution was continued to stir for 16h at 50°C. The mixture was then cooled followed by the addition of 3 ml 30% H₂O₂. Then it was cooled in ice bath for several hours until the appearance of brown coloration. The mixture was centrifuged, decanted and washed properly with hydochloric acid solution (10%), deionized H₂O, EtOH one by one. Finally, the obtained brown graphene oxide (GO) was dried under vacuum at room temperature.

Synthesis of Zn(II) metal assisted Diethylenetriamine functionalized Graphene Oxide (Zn(II)DETA@GO):

GO (1g) was suspended in 50 ml toluene in a 100 ml conical flask and it was sonicated for about 2 hours. Then 0.18 mL (1.68 mmol) of Diethylenetriamine (DETA) was mixed to the solution which was further sonicated for 1 hour. After that, 27.26 mg (0.2 mmol) of zinc (II) chloride salt was added dropwise and the whole mixture was continued to stir for 4 hours. In the last step, the mixture was centrifuged, washed throughly with toluene and finally dried under vacuum oven at 100°C to get Zn(II)DETA@GO catalyst.



Scheme 1. Schematic presentation of Zn(II)DETA@GO composite preparation.

Typical procedure for the formation of N-formamide derivatives using CO_2 and PMHS

The general synthesis procedure is described here for the conversion of amine to corresponding N-formamide using Zn(II)DETA@GO as catalyst and PMHS as reducing agent (Scheme 2). In a 25 mL round bottom flask, equipped with a

magnetic stir bar and fitted with condenser was charged with amine (5 mmol), Polymethylhyrosiloxane (Si-H: 15 mmol), catalyst (40 mg) and *n*-Bu₂O (10 mL). Then the flask along with condenser was degassed and sealed with carbon dioxide of atmospheric pressure using a balloon set up. Then the mixture was continued to stir for 10 h at 80°C. After that the mixture was cooled and diluted with ethyl acetate. The conversion and selectivity of the product were checked by Gas Chromatography. Through column chromatography pure product was separated for ¹H NMR.



Scheme 2. Catalytic N-formylation reaction through CO₂ fixation.

General method of the catalytic formation of carbamates from aniline or its derivatives

Synthesis of carbamates was performed in a 25 mL round bottom flask, equipped with a magnetic stir bar. Then the flask was charged with amine (5 mmol), *n*-butyl or benzyl bromide (5 mmol) and 40 mg of Zn(II)DETA@GO catalyst and the mixture was stirred for 3h at room temperature under CO_2 atmosphere using balloon set up. The progress of the reaction was checked by TLC. After completion of the reaction, mixture was diluted with EtOAc and worked up with brine solution. Then ethyl acetate part was collected and dried through sodium sulphate. The conversion of the product was analyzed by GC. The product was purified by column chromatography and characterized by ¹H NMR.

3. Results and Discussion

3.1. Characterizations

FTIR specta

FTIR spectra of GO and Zn(II)DETA@GO composite is shown in Figure 1. A broad band in the range 3000-3650 cm⁻¹ centered at 3381 cm⁻¹ in IR spectra of GO is due to the O-H stretching of adsorbed water molecules, alcohol and carboxylic acid functional groups. The peak at 1720 cm⁻¹ is attributed to the C=O stretching associated to carboxyl, ketone and aldehyde groups; 1621 cm⁻¹ to the sp² C=C; 1223 cm⁻¹ and 1055 cm⁻¹ to C-O stretching of phenolic and epoxy groups respectively^[37]. In the spectra of Zn(II)DETA@GO composite the broad bands at 3401 and 3220 cm⁻¹ are due to O-H stretching frequency and -N-H stretching vibration of amine, respectively. The peak at 1720 cm⁻¹ is dramatically disappeared in Zn(II)DETA@GO and two new bands appeared at 1572 cm⁻¹ (-NH bending)^[38], 1340 cm⁻¹ (-CN stretching vibration)^[39]. These results clearly indicate the effective grafting of diethylenetriamine on GO surface. The bands at lower region 616 cm⁻¹ (Zn-O vibration), 578 cm⁻¹ (Zn-N vibration), 472 cm⁻¹ (Zn-O vibration) confirm the complexation of zinc metal to the amine grafted GO surface^[40].

Powder XRD analysis

Figure 2 shows the XRD patterns of GO and Zn(II)DETA@GO. The diffraction patterns of graphene oxide showed two characteristic diffraction peaks at $2\theta \approx 9.9195^{\circ}$ and 42.4166° due to the (002) plane of GO and (100) plane of hexagonal structure of carbon^[41]. After reaction with both diethylenetriamine and Zn metal on GO surface, the (002) plane of GO slightly moved to a higher angle of $2\theta \approx 11.3688^{\circ}$. This shifting of the plane is because of molecular intercalation and sonication^[42]. Not only that after modification with amine and metal a broad peak of centered nearly at $2\theta \approx 24^{\circ}$ appeared which is similar to reduced graphene confirming the major oxygen containing groups of GO have been successfully functionalized^[43].



Figure 1. FTIR spectra of GO and Zn(II)DETA@GO.



Figure 2. XRD plots of GO and Zn(II)DETA@GO.

Raman spectra

Raman spectra of GO and Zn(II)DETA@GO composite have also been studied to understand the structural changes that occured during the chemical reaction from GO to Zn(II)DETA@GO. Pure graphene oxide displays two characteristic peaks in the Raman spectrum, one at 1342 cm⁻¹ which is assigned as the D band and other at 1602 cm⁻¹ which corresponds to the G band (Figure 3). The D band is associated with the disorders and structural defects, while G band is usually due to the E_{2g} phonon of sp^2 carbon atoms due to the stretching vibrations in graphene sheets^[44]. In the Raman spectrum of Zn(II)DETA@GO, appearance of both D and G bands indicate the existence of graphitic carbon^[45]. Based on prevoluosly reported literatures it was found that when metal/metal nanoparticles are deposited on the surface of GO, the intensity ratio of D and G band (I_D/I_G) generally increases due to electronic interaction between metal/metal nanoparticles and GO^[46].

Here, the intensity ratio (I_D/I_G) of composite is 0.95 where as that of graphene oxide is 0.85. Moreover, the peak position of D band was shifted from 1342 cm⁻¹ to 1351 cm⁻¹ and G band was shifted from 1602 cm⁻¹ to 1598 cm⁻¹ in Zn(II)DETA@GO. All these results confirm the electronic interaction between amine-Zn and GO in Zn(II)DETA@GO, thus indicating the successful incorporation of Zn metal on DETA@GO.



Figure 3. Raman spectra of GO and Zn(II)DETA@GO.

FESEM and **HRTEM** analysis

Structure and morphology of the catalyst have been predicted from FESEM and HRTEM analysis. The FESEM images (Figure 4a and 4b) reveal well defined and inter linked 3D graphene sheets, forming a porous network having appearances of a sponge like structure. The HRTEM images (Figure 5a and 5b) expose transparent layers of functionalized graphene oxide.



Figure 4. FESEM images of Zn(II)DETA@GO.



Figure 5. HRTEM images and elemental mapping of Zn(II)DETA@GO.

In the HRTEM images, absence of any particles indicates that active site, Zn is stabilzed through -NH and -NH₂ or –OH moieties of the functionalized graphene oxide. The presence of carbon, oxygen, nitrogen functionalities and well uniform distribution of zinc ion in the functionalized graphene oxide have been further confirmed from elemental mapping (Figure 5c).

N2 adsorption-desorption study

In order to investigte the surface area and pore size of the synthesized catalyst, we have done N₂ adsorption–desorption study for Zn(II)DETA@GO. N₂ adsorption-desorption isotherm of catalyst exihibits a typical type IV sorption isotherms with a hysteresis loop at a relative pressure range of $0.44 < p/p_0 < 1.0$ (Figure 6)^[43]. The pore size distribution curve calculated through BJH method displayed pores with a typical size of 3.8 nm, indicating Zn(II)DETA@GO is a kind of mesoporus material. Also, BET surface area of the catalyst was found 20.697 m²/g.



Figure 6. Nitrogen adsorption–desorption ishotherm of *Zn(II)DETA*@GO

3.2. Catalysis

Catalytic N-formylation reaction

We examined different reaction paramaters like temperature, solvent, catalyst amount, reducing agent, etc. taking Nmethylaniline as substrate under 1 atm CO₂ pressure. At first variation of reaction temperature of N-formylation reaction of Nmethylaniline in n-Bu₂O medium under 1 bar CO₂ pressure in presence of 40 mg catalyst and PMHS was observed. We got maximum product yield (92%) at 80°C after 10h (Table 1, entry 3). With increasing temperature at 100°C the yield of product decreased to 80% due to the formation of methylated product and polymerization of PMHS (Table 1, entry 4). At room temperature (RT) and 60°C product yield also decreased to 69% and 74% respectively may be due to slow reaction rate (Table 1, entry1-2). Then the above reaction was monitored without solvent under same reaction condition at 80°C but we got only trace amount of product for the reaction (Table 1, entry 5). Different solvents were used for this formylation reaction (Table 1, entry 6-9) but the maximum yield was obtained using n-Bu₂O as solvent. Amount of catalyst was also monitored for the reaction (Table 1, entry 10-14), in absence of catalyst no reaction was observed. For further optimization of the reaction, effect of reducing agent was also tested (Table 1, entry 15-18).

In presence of our synthesized catalyst, we performed Nformylation reaction with some other amines like substituted aniline, benzyl amine, cyclohexyl amine, butyl amine etc. under optimized reaction conditions. Anilines containing both electrondonating and electron-withdrawing substutients derivatives produced their corresponding formamide with high selectivity and yield (Table 2). Besides, other amines (benzyl amine, cyclohexyl amine, butyl amine) were also very tolerated for producing formamide with excellent yield (Table 2).

Table1.Conditions for	optimization	of	N-formylation	reactions	of
N-methylaniline using	1 bar CO ₂ pre	ss	ure ^a		

Entry	Solvent	Silane	Cat. Amt. (mg)	Temp. (°C)	T (h)	GC Yield (%)
1	<i>n</i> -Bu₂O	PMHS	40	RT	24	69
2	<i>n</i> -Bu₂O	PMHS	40	60	24	74
3	<i>n</i> -Bu₂O	PMHS	40	80	10	92
4	<i>n</i> -Bu₂O	PMHS	40	100	10	80
5	No solvent	PMHS	40	80	10	Trace
6	MeCN	PMHS	40	80	10	14
7	dioxane	PMHS	40	80	10	12
8	THF	PMHS	40	80	10	30
9	Toluene	PMHS	40	80	10	35
10	<i>n</i> -Bu₂O	PMHS	00	80	10	No reaction
11	<i>n</i> -Bu₂O	PMHS	10	80	10	75
12	n-Bu ₂ O	PMHS	20	80	10	88
13	n-Bu ₂ O	PMHS	30	80	10	90
14	n-Bu ₂ O	PMHS	50	80	10	92
15	n-Bu ₂ O	PhSiH₃	40	80	10	85
16	n-Bu ₂ O	Ph ₂ SiH ₂	40	80	10	89
17	n-Bu ₂ O	Et₃SiH	40	80	10	82
18	n-Bu ₂ O	Ph ₂ MeSiH	40	80	10	89

^aReaction conditions: N-methylaniline (5 mmol), silane (15 mmol), solvent (5 ml).

Table 2.	Catalytic	N-formylation	reaction of	famines	through	CO_2
fivationa						

fixatio	nª					
Entry	Amine	Product	Conv. ^b (%)	% of GC Yield (isolated yield)	Time (h)	TOF ^c (b ⁻ ,
1		Сно 2а	100	92 (88)	10	13 16
2	1b	2b	100	93 (90)	10	13.10
3	MeO Ic	мео 2с	100	90 (87)	8	16.45
4	CI 1d	ст 2d	100	88 (84)	12	10 ^ J
5	Br 1e	Br 2e	100	85 (80)	12	10.>
6	CI If	LI L	100	82 (80)	12	10 96
7	1g NH2	2g	100	91 (88)	8	16.45
8	Ih	2h	100	80 (77)	7	18.79
9		NH 2i	100	92 (87)	5	26.32

^aReaction conditions: amine (5 mmol), PMHS (15 mmol based on Si-H), catalyst (40 mg, 0.038 mmol based on Zn metal), *n*-Bu₂O (10 mL), CO₂ (1 atm, balloon), 80°C, ^bGC conversion, ^cTOF (turn over frequency) = no. of moles of the substrate being converted per mole of active site of the catalyst /time (in h).

The comparison between previously reported protocols for the catalytic N-formylation reaction of N-methylaniline (using silane as reducing agent) and that of our developed protocol is summerized in Table 3. Most of the catalytic systems^[47a-f] worked under relatively high CO₂ pressure (0.5 MPa-3 MPa) with high yield (88-96%) of formylated product. There are only few catalytic protocols^[47g-i] reported where the catalysis was performed under atmospheric CO₂ pressure with good product yield (87-94%). But

among them only one catalytic system^[47] was heterogeneous in nature and the rest were homogeneous in nature where reusability and recyaclability of the catalyst remained big problem. Our synthesized catalyst gave high yield (92%) of formyl product under 1 atm of CO₂ pressure after 10h. Moreover, the catalyst can be recycled and reused; even after six consecutive catalytic cycles the catalyst conserves its good catalytic efficiency.

Table 3. Comparison table for the catalytic N-formylation reaction of N-methylaniline with other reported systems where silane is used
as reducing agent

SI. No.	Catalyst	Reaction conditions	Catalytic nature	Time (h)	Product Yield (%)	Ref.
1	γ-valerolactone (GVL)	amine (1 mmol), PhSiH ₃ (2 mmol), catalyst (1 g), CO ₂ (3 MPa), 80°C	Homogeneous	3	96	47a
2	[BMIm]Cl	amine (1 mmol), PhSiH ₃ (2 mmol), catalyst (1 mmol), CO ₂ (1.0 Mpa), 30°C.	Heterogeneous	5	95	47b
3	Pd@HMP-1	amine (1 mmol), Ph_2MeSiH (2.5 mmol), catalyst (50 mg), dioxane (5 mL), water (0.3 mL), CO_2 (1 Mpa), 60°C	Heterogeneous	20	93	47c
4	DVB@ISZ ^a	amine (1 mmol), PhSiH ₃ (1 mmol), catalyst (0.25 mol %), CO ₂ (1.0 Mpa), 40°C	Heterogeneous	20	96	47d
5	Glycine Betaine	amine (0.5 mmol), catalyst (3 mol%), PhSiH ₃ (1 mmol), CH ₃ CN (1 mL),CO ₂ (0.5 Mpa), RT	Homogeneous	4	95	47e
6	ILSZ1	amine (1 mmol), PhSiH ₃ (1 mmol), Catalyst (1 mol%), CO ₂ (0.5 Mpa), 40°C	Heterogeneous	6	88	47f
7	Cu(OAc) ₂ .H ₂ O	amine (1.4 mmol), PMHS (3.2 mmol based on Si–H), catalyst (0.001mmol), Phosphine ligand (P: 0.003 mmol), dioxane (5 mL), CO_2 (1 atm, balloon), $80^{\circ}C$	Homogeneous	30	87	47g
8	Cs ₂ CO ₃	amine (0.5 mmol), PhSiH ₃ (1 equiv), catalyst (1 mol %), CO ₂ (1 atm), CH ₃ CN (1 mL), RT	Homogeneous	12	90	47h
9	[Et₄NBr] _{50%} -Py-COF	amine (1 mmol), catalyst (5 mol%) PhSiH ₃ (2 mmol), CO ₂ (1 atm), dry DMF (1 mL), 30°C	Heterogeneous	24	94	47i
10	Zn(II)DETA@GO	amine (5 mmol), PMHS (Si–H: 15 mmol), catalyst (40 mg, 0.038 mmol based on Zn metal), <i>n</i> -Bu ₂ O (10 mL), CO ₂ (1 atm, balloon), 80°C	Heterogeneous	10	92	This work

^aDVB= poly divinylbenzene, SA= ionic liquid-fundtionalized Al(salen)

Catalytic formation of carbamates throuh CO_2 fixation reaction

Carbamates grasp an inimitable position in the field of agriculture as well as in medicinal chemistry. These compounds can be synthesized in a variety of methodologies. Conventionally, the compounds are produced through the reaction of amines and alcohols in presence of phosgene (COCl₂) which is highly toxic in nature. To replace the phosgene related pathways and make it eco-friendly, researchers have developed various protocols afterward. Use of dialkyl carbonate (such as dimethyl carbonate, diethyl carbonate etc.) is more eco-friendly and promising reagent to produce carbamates from respective amines.^[48]

Nowadays utilization of CO₂ as a C1 feedstock for the synthesis of carbamates from amines and alcohols or alkyl/aryl halides or metal alkoxide/alkoxy silanes in presence of catalyst is the most suitable and desirable route^[49]. Previously He et. al. reported the synthesis of organic carbamates from amines, CO₂, and alkyl halides in presence of K₂CO₃/PEG₄₀₀ under homogeneous catalytic condition^[49a]. Recently Das and his group have

published^[49d] a base (Cs₂CO₃) catalysed route for the production of carbamates from amines and alkyl bromide where CO₂ is used as a carbon source (Scheme 3).



Scheme 3. Catalytic synthesis of carbamates from amines, organohalide and $\mbox{CO}_2.$

To improve that protocol we have designed and developed an eco-friendly cheap amine functionalized GO based Zn catalyst

(Zn(II)DETA@GO) which can efficiently produce carbamates from amines and alky/aryl halide under atmospheric CO₂ pressure in solvent free conditions. Moreover, our catalyst can be recycled and even after six catalytic cycle, the catalyst maintain its good catalytic efficacy.

Initially we varied the catalyst amount and reaction time in order to optimize the reaction conditions through the formation of butyl phenylcarbamate from aniline and *n*-butyl bromide as model reaction and the results are summerised in Table 4. In absence of catalyst no reaction was occurred between aniline and *n*-butyl bromide under 1 atm of CO_2 pressure at room temperature in 24 h (Table 4, entry 1). While the reaction was performed under same reaction conditions in presence of catalyst (20 mg) we got 58% conversion of the substrates after 5 h (Table 4, entry 2). The best result was obtained (i.e. 100% conversion of substrates) in presence of 40 mg of catalyst under same CO_2 pressure and temperature in 3 h (Table 4, entry 4). Different aniline derivatives and *n*-butyl bromide or benzyl bromide were used for the synthesis of carbamates in presence of the catalyst under optimized reaction conditions. Both electron-donating and electron-withdrawing substituent of aniline gave very good conversion as well as selectivity of the desired product (Table 5).

Table 4. Variation of catalyst amount and	reaction time for the formation of butyl phenylcarbamate	e from aniline and <i>n</i> -butyl bromide ^a
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Entry	Catalyst amount (mg)	Time (h)	CO ₂ pressure (atm)	GC conversion (%)
1	0	24	1	No reaction
2	20	5	1	58
3	30	5	1	70
4	40	3	1	100
5	40	2	1	81

^aaniline (5 mmol), *n*-butyl bromide (5 mmol), room temperature.

Table 5.	Substrates scope	e for the catalytic	carbamates	formation rea	ction under 1	atm CO ₂ pressure ^a
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Entry	Amine	Halide	Product	Conversion ^b	Time	% of GC
Lindy	7 411110	Tando	i loddot	(%)	(h)	vield
				(/)	()	(isolated
						yield)
		$\wedge \wedge$		100	3	98 (95)
1	$\langle \rangle \rightarrow NH_2$	Br				
	× 2-	4a				
	3a		5a			/
•				100	3	95 (91)
2		4b	MeO-HN 0			
	3b		5b			
		$\wedge \wedge$	0	100	3	92 (88)
3	$Br \longrightarrow NH_2$			100	5	52 (00)
-		4c	Br - HN 0			
	3c		5c			
		$\land \land$		100	3	90 (87)
4		Br				
		4d				
	30		5d			
		$\wedge \wedge$		100	3	96 (93)
5		Br				
		40				
			5 e			
	3e					
		$\land \land$		100	3	95 (90)
6	NHCH ₃	Br				
	26	4f				
	31		5f			
		\sim	0	100	3	94 (90)
7	$\langle \rangle \rightarrow NH_2$	Br				
	3g	4g	50			
		\wedge	0 0	100	3	93 (80)
8	MeO	Br		100	5	55 (65)
Ũ			MeOHN O			
	3h	4h				
			n			
		\land	0	100	3	88 (85)
9	Br — ()—NH2	Br			Ŭ	00 (00)
-						
	3i	4i				
1			5i			



^aReaction conditions: amine (5 mmol), halide (5 mmol), catalyst (40 mg), room temperature, CO₂ pressure (1 atm), ^bGC conversion.

Heterogeneity test of catalyst Zn(II)DETA@GO

To check the heterogeneous nature of our catalyst, we performed hot filtration test for N-formylation reaction of N-methylaniline. The N-formylation reaction was carried out under optomized reaction conditions in presence of the catalyst for 4h. We got 32% yield of desired product after 4h. Then the catalyst was isolated by filtration and the filtrate was continued to stir under same reaction conditions for another 4h. It was observed that the percentage yield of the desired product remained same after that time. Therefore no reaction was performed without catalyst. For furthur confirmation we have done ICP-AES analysis of the filtrate and the recovered catalyst. We did not get any metal trace in the filtrate and in the catalyst got same metal loading as that of fresh catalyst (6.26%). No leaching of Zn metal from the support was also confirmed by IR and AAS analysis of fresh and used catalyst. We got similar IR spectrum of both fresh and used catalyst (Figure S2) which signified that Zn metal was intact with the catalyst surface even after the catalytic reaction. Zinc loading in fresh catalyst and the used catalyst after first cycle was also found same (6.26 %). AAS analysis was also performed for the product mixture of N-formvlation reaction of N-methylaniline after isolating the catalyst through filtration but no presence of Zn metal was found in result. All these experimental data clearly confirmed the heterogeneous nature of Zn(II)DETA@GO catalyst.

Recyclabity test of the catalyst

The prime characteristics of a heterogeneous catalyst is its easy separation, recoverability and recyclability. The catalytic recyclability of our catalyst was checked in both N-formylation reaction of N-methylaniline and carbamates formation reaction between aniline and *n*-butylbromide in use of CO₂. The catalyst was isolated by simple filtration and thoroughly washed with distilled H₂O followed by hot MeOH and Et₂O after each catalytic cycle. Then the catalyst was dried under a vacuum desicator. Figure 6 established that the catalyst is very efficient even after use of six cycles.





Conclusion

An eco-friendly low cost zinc metal containing heterogeneous catalyst, (Zn(II)DETA@GO) has been designed and synthesized and thoroughly characterized with Raman and IR spectroscopy, XRD, AAS, ICP-AES, SEM, TEM, EDX and N₂ adsorption desorption studies. The catalyst has been found much efficient for the fixation of CO_2 in N-formylation reaction and carbamates formation reaction of amines. Here, our reported protocol of N-formylation reaction is cost-effective and environment-friendly which works at mild temperature under 1 atm of CO_2 pressure in presence of PMHS reducing agent. The production of carbamates from aniline or its derivatives and organo-halides also executes under same CO_2 pressure at room temperature and solvent-free condition. Not only that, the catalyst is enough stable and it preserved its catalytic effectiveness even after six catalytic cycles.

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Keywords: Graphene oxide; Amine functionalized Zn metal; carbon dioxide fixation; N-Formylation; Organic carbamates.

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Table of Contents

FULL PAPER



CO₂ fixation via Formylation and carbamates formation of amines: Zinc metal ions are attached to theaminically modified Graphene Oxideandthe resulting material is well characterized. The material is very efficient for the fixation of CO_2 through N-formylation and carbamate formation reactions over a wide range of amines under very mild condition.

Resmin Khatun,Surajit Biswas, Md. Sarikul Islam, Imdadul Haque Biswas, Sk Riyajuddin, Kaushik Ghosh, Sk. Manirul Islam*

Modified Graphene Oxide based Zinc composite: an efficient catalyst for N-formylation and carbamate formation reactions through CO₂fixation