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 Efficient reduction of Graphene oxide to Graphene Nanosheets by Silica based Ionic Liquid: Synthesis, Characterization and Catalytic properties of IMD-Si/FeCl4-@GNS

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Abstract

The aim of the present protocol is to develop a facile route for the synthesis of novel ionic liquid (IL) functionalized graphene nano sheets (IMD-Si/FeCl4⁻@GNS). An imidazolium IL with iron chloride as an anion (IMD-Si/FeCl4⁻) was used to reduce graphene oxide. IMD-Si/FeCl4⁻@GNS was well characterized by various techniques such as Fourier Transform Infrared (FTIR), Raman, Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-VIS DRS), Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX), Elemental mapping, Transmission Electron Microscope (TEM), Powder X-ray diffraction (XRD), Thermal Gravimetric (TG), Electron Paramagnetic Resonance (EPR), and X-Ray Photoelectron Spectroscopy (XPS) analyses. The IL functionalized material was investigated for its catalytic property and found to be an efficient catalyst for the synthesis of (*E*)-selective substituted thiosemicarbazone derivatives. The (*E*)-selectivity was confirmed by the DFT calculations which showed that the (*E*)-isomer was stabilized by 4.90 kcal/mol more than the (*Z*)-isomer. The catalyst maintained its catalytic activity for six successive runs.

Keywords: Ionic liquid, IMD-Si/FeCl4, heterogeneous catalyst, thiosemicarbazone

Introduction

In recent years, ionic liquids (ILs) have gained significant attention of the researchers because of their unique properties such as low surface energy, non-volatility, greater selectivity and environmental compatibility, high chemical and thermal stability, tunable miscibility with water and organic solvents, etc.¹ These valuable properties of ILs assisted most of the chemical and industrial field of research such as organic synthesis (as catalyst and green solvent)^{2,3}, liquid-liquid extraction⁴ and electrochemistry⁵. Due to the above-mentioned attributes, ILs have been successfully employed as a sustainable substitute of traditional mineral acids (such as sulfuric acid and hydrochloric acid) in chemical synthesis and catalysis⁶. Among the ILs, imidazolium-based ILs have been proved to be a remarkable ionic system due to their air and moisture stability⁷. Hence, these ILs have been extensively applied in many fields of research, especially in catalysis. Several organic transformations have been catalyzed by these ILs e.g. synthesis of benzoxanthene⁸, hydroxyketones⁹, phenylpropanethioate¹⁰, amidoalkyl naphthols¹¹, etc. Immobilization of ILs on the surface of carbonaceous materials has recently been introduced as a strategy to prepare supported heterogeneous IL catalysts for application in different growing fields¹².

Among the carbonaceous materials, graphene and functionalized graphene have opened up a new exciting field in science and technology on account of their unique properties such as ultrahigh carrier mobility at room temperature, high surface area, exceptional thermal conductivity, excellent mechanical properties, remarkable optical properties etc.¹³. Graphene nanosheet (GNS) is a 2D system with very strong sp² bonds, resulting in a layered structure with a high aspect ratio and a large π -electronic surface that requires no helicity control¹⁴. Different graphene functionalized materials have been prepared and applied as a catalyst in various organic reactions such as Pechmann condensation¹⁵, Aza-Michael addition reaction¹⁶, Knoevenagel condensation¹⁷, and Friedel-Crafts addition¹⁸ etc.

Thiosemicarbazone derivatives represent an important class of organic compounds that have received considerable interest because of appreciated anti-microbial activity against *Plasmodium falciparum* and *Plasmodium berghei*¹⁹, *Trypanosoma brucei rhodesiense*²⁰, *Trypanosoma cruzi*²¹ and *Toxoplasma gondii* etc.²²

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59 60 In continuation of our previous research work on supported heterogeneous catalysts ²³⁻²⁹, the present study has described an easy route for the synthesis of IL functionalized GNS (IMD-Si/FeCl₄⁻@GNS) as a recyclable catalyst. The catalytic activity of IMD-Si/FeCl₄⁻@GNS was explored by synthesizing a series of (*E*)-selective substituted thiosemicarbazone derivatives and proved to be an efficient catalyst by affording excellent yield of the products in very short time period.

Experimental section

Synthesis of silica modified imidazolium chloride (IMD-Si/Cl)

Silica modified ionic liquid (IMD-Si/Cl) was synthesized by reported procedure with some modifications.³⁰ For this, a mixture of 3-chloromethoxypropylsilane (30 mmol, 5.5 mL) and imidazole (30 mmol, 2.46 g) was placed in a three-necked round-bottom (RB) flask and heated with magnetic stirring at 110°C for 24 h under N₂ atmosphere. After 24 h, the reaction mixture was kept at room temperature for 1h. The obtained bright yellow product (liquid) was washed with ethyl acetate (3x15 mL) and dried over anhydrous Na₂SO₄ to get pure IL (IMD-Si/Cl). Yield: IMD-Si/Cl = 3.20g

Synthesis of silica modified imidazolium iron chloride (IMD-Si/FeCl4-)

A mixture of IMD-Si/Cl (0.01 mol, 2.8 g) and anhydrous FeCl₃ (0.01 mol, 1.62 g) was prepared in a RB flask containing acetone (35 mL). The reaction mixture was stirred at reflux temperature (80°C) for 12 h. After keeping the reaction mixture at room temperature for 1h, a dark yellow product (IMD-Si/FeCl₄⁻) obtained which was filtered, washed several times with acetone until the colorless filtrate was obtained and dried at room temperature (30°C) for 24 h for further use. Yield: IMD-Si/FeCl₄⁻ = 4.08g.

Synthesis of graphene oxide (GO)

GO was prepared by modified Hummer's method³¹. In a typical run, a mixture of graphite flakes (1.5 g) and NaNO₃ (0.5 g) was placed in an RB flask (250 mL) containing concentrated H₂SO₄ (25 mL) and stirred for 30 min at 0-5°C in an ice bath. KMnO₄ (3 g) was then added very slowly in portions (at the rate of 1g in 10 min to avoid explosion) with vigorous stirring. After the addition of KMnO₄, the ice bath was removed and the reaction mixture was kept at 35°C for 2 h.

After that, deionized water (50 mL) was added dropwise to the RB flask containing reaction mixture. The addition of water produces a huge amount of heat and the temperature rises to 100 °C resulting in a brown colored solution. After 20 min, 30% H_2O_2 (10 mL) and warm water (100 mL) were added to the brown solution in the RB flask and the mixture was stirred for 5 min producing a yellowish-brown solution. The resulting mixture was filtered through using Whatman filter paper and subsequently washed with 5% HCl and double distilled water (3x50 mL) until pH reached ~7. The resulting brown solid, was dried in an oven at 50°C for 12h to get brown graphite oxide powder (1.85g). To obtain GO, graphite oxide (1.67g) was dispersed in double-distilled water (500 mL) by ultrasonication for 3 h. The graphite oxide was exfoliated and turns into a stable brown colored GO dispersion. The suspension was centrifuged at 4000 for 50 min and then dried at 60°C for 4 h to get GO as brown free flowing powder. Yield: GO = 1.43g

Synthesis of IMD-Si/FeCl₄-@GNS

IL functionalized GO was obtained under N₂ atmosphere. GO (1g) was dispersed into absolute ethanol (250 mL) by sonication (30 min) and IL (IMD-Si/FeCl₄⁻) (0.5 g) added to it under N₂ atmosphere. After stirring the resultant mixture for 2 h, it turned black indicating the reduction of GO and formation of IMD-Si/FeCl₄⁻@GNS. The IMD-Si/FeCl₄⁻@GNS was isolated by centrifugation, washed with anhydrous ethanol (3x20 mL) and dried in a vacuum oven at 50°C for 24 h. Yield: IMD-Si/FeCl₄⁻@GNS = 1.27g.

General procedure for the synthesis of substituted (E)-thiosemicarbazone derivatives

Equimolar mixture of carbonyl compounds **1a-l**, thiosemicarbazide **2** and IMD-Si/FeCl₄⁻@GNS (80 mg) was taken in a 50 mL RB flask and the reaction mixture was stirred for 3-5 min at room temperature (30° C). The reaction progress was monitored by TLC. After the completion of the reaction, precipitated product was added to a separating funnel containing ethyl acetate and water. The organic product was extracted with ethyl acetate, and dried over anhydrous sodium sulphate. The excess solvent was evaporated under reduced pressure to get crude product which was then recrystallized with ethanol to get pure products **3a-l**. The catalyst (in aqueous phase) was filtered, washed with ethanol and oven dried for further catalytic runs. Yield: 90-96%

Results and Discussion

Characterization of IMD-Si/FeCl₄-@GNS

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 The synthesis of IMD-Si/FeCl₄⁻@GNS was outlined in **Figure 1**. The IMD-Si/FeCl₄⁻@GNS was well characterized by various techniques such as Fourier Transform Infrared (FTIR), Raman, Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-VIS DRS), Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX), Elemental mapping, Transmission Electron Microscope (TEM), Powder X-ray diffraction (XRD), Thermal Gravimetric (TG), Electron paramagnetic resonance (EPR), and X-Ray photoelectron spectroscopy (XPS) analyses. The detailed characterization of the catalyst was discussed below.



Figure 1: (a) Synthesis of IMD-Si/FeCl₄⁻ (b) Synthesis of IMD-Si/FeCl₄⁻@GNS

FTIR analysis

In the FTIR spectrum of GO (**Figure 2a**), a broad peak centered at 3437 cm⁻¹ was attributed to the vibration and deformation of –OH group. The stretching vibrations of C=O groups appeared at 1728, 1625 cm⁻¹, O-H deformation at 1408 cm⁻¹ and C-O epoxy stretching at 1225 cm⁻¹ respectively ³².



Figure 2. FTIR spectrum of (a) GO (b) IMD-Si/FeCl₄⁻ (c) IMD-Si/FeCl₄⁻@GNS and (d) Recycled catalyst

The FTIR spectrum of IMD-Si/FeCl₄⁻ (**Figure 2b**) displayed characteristic bands of imidazole ring and alkyl chain containing silicon functional group. In imidazole ring, the bands at 3382 cm⁻¹ and 3134 cm⁻¹ were due to the stretching vibrations of N–H and C–H respectively whereas two

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 sharp bands at 1578 cm⁻¹ and 1454 cm⁻¹ were assigned to ring in-plane symmetric/antisymmetricstretch $CH_2(N)^{33}$ and symmetric stretching of C–N respectively^{34a}. In alkyl chain, C–H stretching vibration appeared at 2837 cm^{-1 34b} while other bands at 1224 cm⁻¹, 1091 cm⁻¹ and 819 cm⁻¹ were ascribed to Si-O-C stretching, asymmetric Si-O-Si stretching and symmetric Si-O-Si stretching mode of vibrations respectively³⁵. The FTIR spectrum of GO supported IL, IMD-Si/FeCl₄⁻@GNS, (**Figure 2c**) showed a broad peak at 3406 cm⁻¹ due to O–H stretching of GNS and N–H stretching of imidazole ring. The intensity of C=O band (1726 cm⁻¹) was reduced in catalyst showing the formation of GNS. The characteristic peaks at 1726 cm⁻¹ (C=O), 1629 cm⁻¹ (C=C), 1580 cm⁻¹ CH₂(N), 1452 cm⁻¹ (C–N), 1220 cm⁻¹ (Si-O-C), 1090 cm⁻¹ (Si-O-Si) indicated the formation of IMD-Si/FeCl₄⁻@GNS.

UV-VIS DRS analysis

The UV-visible DRS spectrum of GO showed absorption peak at 230 nm and a shoulder at 305 nm ascribing a characteristic feature of π - π * transition of C–C bond and n– π * transition of C–O bond respectively (**Figure S1a**) ³⁶. A red shift was observed in the UV-visible spectrum of IMD-Si/FeCl₄⁻@GNS from 230 nm to 268 nm confirming the change in electronic configuration of honeycomb lattice of GO to highly reduced GNS (**Figure S1b**). In addition, an absorption band at 476 nm appeared due to d-d transition of FeCl₄⁻³⁷.

SEM and EDX/elemental mapping analyses

The surface morphologies of GO and IMD-Si/FeCl₄⁻@GNS were examined by SEM analysis (**Figure 3**). The SEM images of GO indicated the layered structure (**Figure 3a**) and IMD-Si/FeCl₄⁻@GNS showed presence of IL on the surface of GNS (**Figure 3b**). The EDX analysis of GO displayed the presence of C and O (**Figure 4a**) whereas that of IMD-Si/FeCl₄⁻@GNS confirmed the presence of C, O, Si, Cl and Fe (**Figure 4b**). The percentage of O in the GO and IMD-Si/FeCl₄⁻@GNS was found to be 23.73% and 21.96 % respectively. The decrease in percentage of O in the catalyst was due to removal of oxygen functionalities during reduction of GO. The elemental mapping images of GNS and IMD-Si/FeCl₄⁻@GNS were depicted in **Figure 5**. The presence of C and O was observed in mapping image of GNS (**Figure 5a-c**) whereas IMD-Si/FeCl₄⁻@GNS was constructed with C, O, Si, Cl and Fe elements as confirmed from

Figure 5d-i. These results revealed that each element in synthesized catalyst (IMD-Si/FeCl₄⁻@GNS) was uniformly distributed.



Figure 3: SEM images of (a) GO and (b) IMD-Si/FeCl₄-@GNS



Figure 4: EDX analysis of (a) GO and (b) IMD-Si/FeCl4-@GNS





Figure 5: Mapping images of (a) mixed elements in graphene nannosheets (b) carbon and (c) oxygen; (d) mixed elements in IMD-Si/FeCl₄@GNS (e) carbon (f) oxygen (g) silicon (h) chlorine and (i) iron

TEM analysis

 TEM images of GO, GNS and IMD-Si/FeCl4⁻@GNS were shown in **Figure 6**. The morphology of both GO and graphene showed folded sheets (**Figure 6a, 6b**). In the TEM image of IMD-Si/FeCl4⁻@GNS (**Figure 6c**), folded graphene sheets along with silica IL on its surface was clearly discernible. The electron diffraction pattern of IMD-Si/FeCl4⁻@GNS displayed well-defined hexagonal array indicating that the synthesized IMD-Si/FeCl4⁻@GNS had insignificant number of superimposed sheets (**Figure 6d**).



Figure 6. TEM images of (a) GO (b) GNS (c) IMD-Si/FeCl₄⁻@GNS (d) electron diffraction of IMD-Si/FeCl₄⁻@GNS

XPS analysis

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59 60 The surface information of the GO and IMD-Si/FeCl₄-@GNS was further investigated by XPS analysis (Figure 7). The XPS spectrum of GO showed two major peaks at 287.2 eV and 532.4 eV corresponding to binding energy of C 1s and O 1s respectively (Figure 7a). The IMD-Si/FeCl₄@GNS was composed of six peaks ascribing to C 1s, O 1s, Si 2s, N 1s, Fe 2p and Cl 2p (Figure 7b). The high resolution XPS spectrum for each elements of IMD-Si/FeCl₄-@GNS were also observed to confirm the oxidation state and nature of bonding in the catalyst (Figure 8). The C 1s peak of IMD-Si/FeCl₄ @GNS was deconvoluted into three major peaks, at 284.6 eV, 286.5 eV and 288.7 eV, attributing to the binding energies of C=C, C-O and C=O respectively (Figure 8a)³⁴. The binding energies of O 1s, N 1s and Si 2p were found to be 532.4 eV, 401.7 eV and 102.6 eV respectively as shown in Figure 8b-d. Two peaks were obtained in the XPS spectrum of Fe2p, at 712.1 eV and 725.2 eV, ascribing to the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ respectively (Figure 8e). The presence of Fe³⁺ was shown by the peak located at 712.1 eV ³⁸. The binding energies of Cl $2p_{3/2}$ and Cl $2p_{1/2}$ were appeared at 197.9 eV and 199.8 eV respectively (**Figure 8f**)³⁴. These results revealed the successful incorporation of imidazolium IL on the surface of GNS. The Fe content was found to be 5.76% (w/w) which corresponded to loading amount of 1.04 mmol/g of catalyst.



Figure 7. XPS analysis of (a) GO and (b) IMD-Si/FeCl₄-@GNS

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Figure 8: High resolution XPS spectra of IMD-Si/FeCl₄⁻@GNS showing the presence of individual elements (a) C 1s (b) O 1s (c) N 1s (d) Si 2p (e) Fe 2p (f) Cl 2p

Raman analysis

The Raman spectra of GO and IMD-Si/FeCl₄⁻@GNS was obtained in the range of 500 cm⁻¹ to 2500 cm⁻¹. The presence of carbon skeleton in GO (**Figure 9a**) and IMD-Si/FeCl₄⁻@GNS (**Figure 9b**) was confirmed by the appearance of two characteristic bands at 1364 cm⁻¹ and 1596 cm⁻¹ corresponding to D and G bands respectively. These two bands (D and G) confirmed the

defects, edges and structural disorders of solid carbon (graphite) and in-plane vibration of carbon atoms arising from the first-order scattering of E_{2g} mode of sp² hybridized carbon ³⁹.



Figure 9. Raman analyses of (a) GO and (b) IMD-Si/FeCl₄-@GNS

XRD analysis

 XRD patterns of natural graphite, GO, IMD-Si/FeCl₄⁻@GNS and recycled catalyst were shown in **Figure 10**. XRD pattern of graphite showed sharp peak at $2\theta = 26.7^{\circ}$ corresponding to (002) reflection plane (**Figure 10a**). The peak for exfoliated GO sample appeared at $2\theta = 13.1^{\circ}$ (002) (**Figure 10b**) suggesting the intercalation of water molecule in graphite galleries and generation of other oxygen functional groups in between the graphite layers upon oxidation³⁵. After the reduction of GO with IL, the peak at $2\theta = 13.1^{\circ}$ disappeared due to removal of most of the oxygen functionalities (C-OH, C-O and C=O)⁴⁰. Further, appearance of a broad peak at $2\theta =$ 23.4° (**Figure 10c**) corresponding to (222) reflection plane could be due to the presence of silica in the synthesized catalyst.

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Figure 10. XRD pattern of (a) Graphite (b) GO (c) IMD-Si/FeCl₄-@GNS and (d) Recycled catalyst

TG analysis

TGA curves of GO, IMD-Si/FeCl₄⁻@GNS and recycled catalyst were shown in **Figure S2**. All samples showed weight loss (9.67-11.23%) below 100°C due to evaporation of absorbed water molecules in between the galleries of carbon materials. However, IMD-Si/FeCl₄⁻@GNS showed less weight loss as compared to GO showing that less moisture was trapped in IMD-Si/FeCl₄⁻@GNS (**Figure S2b**). The total weight loss in GO was found to be 38.45% starting from 190°C (12.11%) due to the decomposition of oxygen-containing functional groups (CO, CO₂ and steam etc.) introduced during the oxidation of graphite (**Figure S2a**) ⁴¹. The total weight loss (32.76%) in IMD-Si/FeCl₄⁻@GNS at 600°C was due to decomposition of oxygen-containing functional groups and surface attached IL confirming that IMD-Si/FeCl₄⁻@GNS was thermally more stable than GO. This may be due to formation of large amount of Si-O-Si bond introduced by imidazolium IL which prevented the thermal decomposition of catalyst even at higher temperature.³⁴

EPR analysis

The X-band EPR spectrum of IMD-Si/FeCl₄⁻@GNS showed sharp singlet at g = 2.03264 which was due to the presence of Fe³⁺ ion of IMD-Si/FeCl₄⁻ incorporated in IMD-Si/FeCl₄⁻@GNS (**Figure S3**).

Evaluation of catalytic activity of IMD-Si/FeCl₄⁻@GNS for synthesizing substituted thiosemicarbazone derivatives

To identify the optimum reaction conditions, a representative model reaction of acetyl 1,3dimethylbarbituric acid 1c (2 mmol) and thiosemicarbazide 2 (2 mmol) affording (*E*)-2-(1-(1,3dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)ethylidene)hydrazinecarbothioamide 3c was investigated (Scheme 1) with several parameters such as different catalysts and solvents, catalyst loading on different supports, catalyst amount and temperature.



Scheme 1. Synthesis of (E)-2-(1-(1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)ethylidene)hydrazinecarbothioamide

In order to examine the effect of catalysts on model reaction, various catalysts had been used. We started the reaction with different imidazolium ILs and observed that reaction went well with these ILs and among them, IMD-FeCl₄⁻ afforded moderate yield in relatively lesser reaction time (**Table 1, Entries 1-7**). When silica modified imidazolium ILs were used, product yield was improved in lesser time period (**Table 1, Entries 8-11**). After finding out these results and considering the effect of surface area on reaction rate, we used IMD-Si/FeCl₄⁻ with different support materials (**Table 1, Entries 12-15**). Among the support materials used, GNS was found to be the most appropriate support affording 96% product yield in 3 min. Thus, IMD-Si/FeCl₄⁻@GNS was chosen as best catalyst for the desired reaction(**Table 1, Entry-15**). The high catalytic activity of prepared sample; IMD-Si/FeCl₄⁻@GNS, might be due to some factors

 such as presence of imidazolium IL which provide sufficient acidity to activate the carbonyl carbon of aldehyde and ketones which in turn facilitate the nucleophilic attack of NH₂ group of thiosemicarbazide.⁴² Moreover, the presence of graphene as support provides enough surface area to the catalyst to enhance the catalytic activity.⁴³ These factors could be responsible for high catalytic activity of IMD-Si/GeCl₄⁻@GNS.

After selecting the suitable catalyst, we, then inspected the model reaction with different solvents such as methanol, ethanol, isopropanol, PEG (200,400,600), acetone, hexane, acetonitrile, THF and in solvent-free condition. It was observed that with all solvents, the reaction afforded moderate to good yields in practically same reaction time (**Figure 11**, **Entries 1-10**). The solvent-free reaction condition managed to afford excellent yield in minimum reaction time (**Figure 11**, **Entry 11**).

To obtain the suitable loading amount of IMD-Si/FeCl₄⁻ on support, varying amount of IMD-Si/FeCl₄⁻ (5% w/w to 30 % w/w) was used and corresponding data collected (**Figure 12, Entries 1-4**). A linear relationship between IMD-Si/FeCl₄⁻ loading and product yield was

Entry	Catalyst	Time ^b	Yield ^c (%)
1	IMD-Cl ⁻	18 h	30
2	IMD-HSO ₄	12.5 h	33
3	IMD-CH ₃ COO ⁻	14 h	39
4	IMD-AlCl ₄	13 h	42
5	IMD-FeCl4 ⁻	8 h	57
6	IMD-NiCl ₄	10 h	45
7	IMD-ZnCl ₄	10 h	48
8	IMD-Si/AlCl4	9 h	54
9	IMD-Si/ NiCl ₄	8 h	59
10	IMD-Si/ZnCl4	6 h	64
11	IMD-Si/ FeCl ₄ ⁻	4.5 h	72
12	IMD-Si/FeCl ₄ -@SiO ₂	54 min	80
13	IMD-Si/FeCl ₄ ⁻ @ZrO ₂	48 min	85
14	IMD-Si/FeCl ₄ ⁻ @Al ₂ O ₃	39 min	90

 Table 1: Effect of different catalysts on model reaction^a

	15	IMD-Si/FeCl4 ⁻ @GNS	3 min	96
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^{*a*}*Reaction conditions*: acetyl 1,3-dimethylbarbituric acid **1c** (2 mmol), thiosemicarbazide **2** (2 mmol), catalysts (80 mg), $T = 30^{\circ}$ C. ^bReaction progress monitored by TLC. ^cIsolated yield.



Figure 11: Effect of solvents on model reaction^a

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 aReaction conditions: acetyl 1,3-dimethylbarbituric acid **1c** (2 mmol), thiosemicarbazide **2** (2 mmol) IMD-Si/FeCl₄ @GNS (80 mg), solvents, $T = 30^{\circ}$ C. *b*Reaction progress monitored by TLC. *c*Isolated yield.

observed i.e. on increasing the IMD-Si/FeCl₄⁻ loading from 5% w/w to 25 % w/w, yield of the product also increased. Further increase in loading amount did not affect the product yield. Thus, the optimum loading amount of IMD-Si/FeCl₄⁻ on support material that efficiently catalyzed the model reaction was found to be 25% (w/w).

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Figure 12: Effect of IMD-Si/FeCl₄⁻ loading on support for model reaction^a (*aReaction conditions*: acetyl 1,3-dimethylbarbituric acid **1c** (2 mmol), thiosemicarbazide **2** (2 mmol), IMD-Si/FeCl₄⁻@GNS (80 mg), $T = 30^{\circ}$ C. ^bReaction progress monitored by TLC. ^cIsolated yield)

The effect of catalyst amount on model reaction was obtained by carrying out the experiment with different amount of catalyst (20-100 mg) and corresponding results were shown in **Figure S4**. It was observed that 80 mg of catalyst was sufficient to catalyze the model reaction affording 96% of product yield in just 3 mins.

Catalytic property

In order to check the catalytic property of IMD-Si/FeCl4⁻@GNS, a series of biologically relevant thiosemicarbazone derivatives were synthesized (**Scheme 2**). Thiosemicarbazones (**3a-l**) were prepared by treating alicyclic/aromatic/heteroaromatic carbonyl compounds (**1a-l**), thiosemicarbazide **2** and 80 mg of IMD-Si/FeCl4⁻@GNS (25% w/w of IMD-Si/FeCl4⁻ and GNS) at 30°C under solvent-free condition for specified time period. In all cases, reaction proceeded smoothly affording high yield in short reaction time. Besides aldehydes, some heteroaromatic acetyls were also tested for the same reaction. It was found that yield was slightly decreased which might be due to less reactivity of acetyls than aldehydes.

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 Scheme 2: General procedure for the synthesis of substituted thiosemicarbazone derivatives (*^aReaction conditions*: Carbonyl compounds **1a-l** (2 mmol), thiosemicarbazide **2** (2 mmol), IMD-Si/FeCl₄⁻@GNS (80 mg), T = 30°C. ^bReaction progress monitored by TLC. ^cIsolated yield), TOF was calculated in h⁻¹.

The high turnover frequency (TOF) in the range of 114 h^{-1} to 230 h^{-1} of catalyst confirmed that catalyst was very efficient for the conversion of thiosemicarbazide to corresponding *E*-selective thiosemicarbazone derivatives.

2.4 Reaction mechanism

The plausible mechanism for the synthesis of substituted thiosemicarbazone derivatives using IMD-Si/FeCl₄⁻@GNS as a catalyst was shown in **Scheme 3**. The carbonyl carbon **1a-1** was activated by the catalyst (IMD-Si/FeCl₄⁻@GNS) to generate **A**. The intermediate **A** is then attacked by the nucleophilic reagent **2** (thiosemicarbazide) to form **B**. Dehydration of **B** yielded final products **3a-1**.^{42,52a} The geometry of compounds was found to (*E*) as confirmed from the DFT calculation. (ref) Matsa et. al. Also reported similar type of study for the synthesis of (E)-thiosemicarbazone derivatives.^{52b}



Scheme 3. Plausible mechanism for synthesis of compound 3a-l

Density functional theory (DFT) of thiosemicarbazone (3e)

In order to prove the formation of preferred *E*-isomer over *Z*-isomer, DFT calculations were performed on two isomers (Z and E) of the compound **3e** using Gaussian 09 software ⁵³. Optimized geometry of these two isomers were obtained at Becke's three parameter hybrid functional for the exchange part and the Lee– Yang–Parr (LYP) correlation function along with 6-311G (d,p) basis set (B3LYP) /6-311G (d,p) level of theory⁵⁴. The geometry of the compound (*E* or *Z*) in Cartesian representation was completely optimized in ground electronic state with tight convergence criterion. Optimized geometry of *Z*- and *E*-isomer was shown in **Figure 13**. In that state, the harmonic vibrational frequencies calculations were carried out at same level of theory without any imaginary frequency. Hence, on potential energy surface, a true and significant minima was located. Vibrational assignments were made with great accuracy using animated modes by visualization program GaussView 5⁵⁵. The minimum molecular energies of *Z*- and *E*-isomer were found to be -582587.4390 and -582592.3436 kcal/mol respectively. It was found that the (*E*)-isomer was stabilized by 4.9046 kcal/mol more than the (*Z*)-isomer. Therefore,

 some theoretical results were presented only for (E)-isomer. Dipole moment value for (E)-isomer was estimated to be 6.76 D with dipole moment vector pointed along the geometry. Spatial plot of HOMO and LUMO along with corresponding energy values and HOMO-LUMO gap was illustrated in **Figure 14**. In this Figure, HOMO and LUMO were localized mainly over the chain but also partially over the ring of the molecule. HOMO-LUMO transition showed the charge delocalization within the molecule.



Figure 13. Ground electronic state optimized structures of the (E)-isomer and (Z)-isomer



Figure 14. Spatial plots of HOMO and LUMO with their energy values and HOMO-LUMO gap for the *(E)*-isomer.

Recycling study of catalyst

The recycling experiment of catalyst was done using a representative reaction of acetyl 1,3dimethylbarbituric acid 1c, thiosemicarbazide 2 and 80 mg of catalyst at 30°C. After completion of the reaction (monitored by TLC) the reaction mixture was added to a separating funnel containing ethyl acetate (10 mL) and water (10 mL). The organic product (3a-l) was extracted with ethyl acetate, and the remaining catalyst in aqueous layer, was filtered and washed with ethanol for further catalytic purpose. The activity of catalyst was examined by successive runs and found that the catalyst retained good activity for minimum of six cycles (Figure 15). To investigate the structural change and thermal stability of the catalytic system after six successive runs, FTIR, SEM, TEM, XRD and TG analyses were performed. The FTIR spectrum of recycled catalyst after six runs was found similar to that of fresh catalyst retaining all characteristic vibrational frequencies in the same region as compared to fresh catalyst (Figure 2d). The SEM and TEM images of recycled catalyst also showed no morphological change in the catalytic system during reaction course after six runs (Figure S5). The XRD of reused catalyst was also same showing peak at $2\theta = 23.6^{\circ}$ which was approximately same as in fresh catalyst ($2\theta = 23.4^{\circ}$) (Figure 10d). The TG curve of recycled catalyst showed total weight loss of 34.12% at 593°C confirming that the recycled catalyst was thermally stable after six runs (Figure S2c).

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Figure 15: Recycling data of catalyst

Conclusion

In summary, a facile route to reduce GO by incorporation of IL to GO has been developed. IL modified GNS, IMD-Si/FeCl₄⁻@GNS, has been investigated for catalytic potential by synthesizing a library of (*E*)-thiosemicarbazone derivatives. The synthesized catalyst showed excellent catalytic activity affording 93-96% product yield in 3-6 min. Moreover, recyclability of catalyst up to six cycles was one of the main attracting features of this study. The present energy sustainable methodology can help green developments by avoiding hazardous chemicals. This study revealed that IL modified catalyst could be most promising catalyst for various organic transformations.

Conflict of Interest

There are no conflicts of interest to declare.

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Table of contents entry

An Ionic liquid modified graphene nanosheets (IMD-Si/FeCl₄-@GNS) has been synthesized as an efficient catalyst for the synthesis of *(E)*-selective thiosemicarbazones.

