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Graphical Abstract

Gold nanoparticles supported on supramolecular ionic liquid grafted graphene: a bifunctional catalyst for the selective aerobic oxidation of alcohols



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ARTICLE TYPE

Gold nanoparticles supported on supramolecular ionic liquid grafted graphene: a bifunctional catalyst for the selective aerobic oxidation of alcohols

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Gold nanoparticles supported on supramolecular ionic liquid grafted graphene have been synthesized and used as an bifunctional, efficient and recyclable heterogeneous catalyst

¹⁰ for the aerobic oxidation of various primary and secondary aliphatic and aromatic alcohols to the corresponding aldehyde and ketone derivatives in water as a green solvent at room temperature.

15 Introduction

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Selective oxidation of alcohols has major importance in both organic synthesis and industrial applications.¹⁻⁸ The world annual production of carbonyl compounds is more than 1×10^7 tones which most of them were produced from the oxidation of ²⁰ alcohols using traditional stoichiometric amounts of oxidants and aerobic oxidation under heterogeneous and homogeneous

- aerobic oxidation under heterogeneous and homogeneous catalytic strategy.^{9,10} One of the most important aspects of green chemistry is the aerobic oxidation of alcohols into the corresponding carbonyl derivatives. Another three important ²⁵ aspects are the development the aerobic oxidation transformative in a greener solvent such as water, avoiding the addition
- activators such as inorganic bases and carrying the reaction without any activation at ambient temperature. The combination of these four aspects is highly challenging and will provide the ³⁰ more benefits for chemical transformations in industry.¹¹⁻¹⁴
- Graphene as the high specific heterogeneous support has gained more attention in recent years and due to extraordinary thermal and mechanical properties, and high stability in different conditions are ideal support for noble metals.¹⁵⁻²⁴ However, the
- 35 stabilization of nanoparticles, and achievement of uniform distributions are two barriers to overcome which affect the metal-graphene interaction due to the chemical inertness of graphene. There are different methods to deal with these issues. One of the most important methods consists of functionalizing
- ⁴⁰ graphene, which also allows one to obtain chemically processable graphene.²⁵⁻²⁹ Recently, due to the importance of poly ionic liquids, several pioneer groups published reviews about this hot topic.³⁰⁻³⁴ Graphene nano-composite functionalized with poly ionic liquid has several advantages such as high dispersity,
- ⁴⁵ functionality, and high surface charge density.^{35,36}.Therefore, this system can cause highly dispersive and long term stable graphene sheets in reaction media.³⁶⁻³⁸ Poly ionic liquid functionalized on particle surface due to liquid-like appearance called supramolecular ionic liquids (SILs).^{39,40}

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The heterogeneous oxidation of alcohols with noble metals has been exponentially improved since their first report in 150 years ago. Gold was thought to be an ineffective noble metal for the ⁵⁵ oxidation reaction due to its chemical inertness.⁴¹⁻⁴⁴ Interactions of gold and support affect on the size of the encapsulated gold nanoparticles (Au NPs), and dispersity of catalyst in the reaction media which is very important in the performance of the catalyst to achieve the best results in the selective oxidation.^{41,45-53} In ⁶⁰ aerobic oxidation of alcohols with Au NPs, in order to activate the reactant inorganic bases such as NaOH and K₂CO₃ was usually employed which produced by-products.⁵¹⁻⁵⁵

In continuation of our efforts to introduce new and efficient catalysts for various organic transformations,⁵⁶⁻⁶⁴ herein we wish ⁶⁵ to report the synthesis of Au NPs in supramolecular ionic liquids grafted on graphene (Au NPs@SIL-g-G), which upon dispersion into water allows the aqueous aerobic oxidation of various primary and secondary aliphatic and aromatic alcohols to the corresponding aldehyde and ketone derivatives in the absence of ⁷⁰ inorganic base at room temperature. To the best of our knowledge, this is the first report that Au nanoparticles supported by graphene covalently functionlized with SILs was synthesized and used as a powerful catalyst for the aerobic selective oxidation of alcohols in water as a green solvent without using bases as ⁷⁵ activator. The synthesized catalyst exhibited excellent high

$$R^{1} R^{2} \xrightarrow{Au \text{ NPs@SIL-g-G (0.20 mol%, 0.005 g)}} R^{1} R^{2}$$

$$H_{2}O, 25 \text{ °C}$$
air, O₂ (1atm)

dispersion and hydrophilicity properties.

Scheme 1 Oxidation of alcohols by Au NPs@SIL-g-G hybrid materials

Experimental

Materials and instruments

80 All chemicals were purchased from Aldrich and used without further purification. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Transmission electron microscopy (TEM) analyzes were performed by LEO 912AB electron microscope. Identification and quantification were

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carried out on a Varian model 3600 gas chromatograph (Varian Iberica, Madrid, Spain) equipped with a split/splitless capillary injection port and flame ionization detector (FID). A CP-Sil-8 fused silica capillary column (25 m _ 0.32 mm i.d. and 0.52 mm s film thickness) from Chrompack was employed. Ultrasonic bath (EUROSONIC® 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W) was used to disperse materials in solvent. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractmeter using Cu Kα radiation. ¹⁰ Hitachi FE-SEM model S-4160 was used for surface imaging.

Preparation of 1-methyl-3-(oxiran-2-ylmethyl)-1H-imidazol-3ium chloride (3)

2-(Chloromethyl)oxirane (1) (3.9 mL or 50 mmol) and 1methylimidazole (2) (4.0 mL or 50 mmol) were added to a 100 ¹⁵ mL round-bottomed flask equipped with a reflux condenser and reacted for 24–72 h at 70 °C with stirring to the formation of a two-phase mixture under nitrogen atmosphere. The upper layer, which contained mostly the unreacted precursors, was decanted and washed with ethyl acetate for three times and product as a ²⁰ brown liquid was finally obtained. ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) 3.84 (3H, s, NCH₃), 4.05- 4.31 (3H, m, NCH₂CHCH₂O), 4.40-4.46 (2H, m, NCH₂CHCH₂O), 7.38-7.40 (1H, m, CH₃NCHCHN), 7.42-7.43 (1H, m, CH₃NCHCHN), 8.70 (1H, s, NCHN), (Scheme 2).

25 Preparation of graphene oxide

Graphene oxide (GO) was synthesized by Hummer method.⁶⁵ Graphite powder (1.00 g, 325 mesh) and concentrated H₂SO₄ (23 mL) were added to a 250 mL conical flask and the mixture was stirred. Sodium nitrate (0.50 g) was added and the resulting ³⁰ mixture was cooled to 0 °C. Under vigorous agitation, KMnO₄ (3.00 g) was added slowly and the mixture was stirred for 1h while the temperature was kept below 35 °C. Then, H₂O (45 mL) was added slowly to the reaction mixture and the solution was stirred for 30 min at 90 °C. Next, H₂O₂ (10 mL of a 30% so solution) and deionized water (140 mL) were added to the mixture. Then resulting precipitate was centrifuged and washed repeatedly with HCl (5%, 3×15 mL) and EtOH and dried under the vacuum at 60 °C. The GO was obtained as a brown powder.

Preparation of functionalized graphene oxide by 40 tris(hydroxymethyl)aminomethane

GO-tris(hydroxymethyl)aminomethane (GO-Tris) was synthesized by an epoxide ring-opening reaction between graphene oxide (GO) and tris(hydroxymethyl)aminomethane (Tris or THAM). Firstly, 10 mL GO dispersion in water

⁴⁵ (0.5mg/mL), Tris (20 mg), and KOH were added into a 100 mL flask, and then the mixture was subjected to ultrsonication for 30 minutes. After the ultrsonication, the solution was vigorously stirred at 80 °C for 24 h. Finally, the functionalized GO was centrifuged, washed with ethanol and water, and air-dried to ⁵⁰ obtain a black powder (Scheme 2).⁶⁶

Synthesis of SIL-g-GO

GO-Tris (0.5 g) and cesium hydroxide monohydrate (3.0 g) were placed in a 250 mL Schlenk flask, and 20 mL toluene was added. The mixture was stirred at 60 °C under an argon atmosphere for 1 55 h and evacuated at 60 °C for 12 h to remove toluene and water to generate the corresponding cesium alkoxide. Subsequently, 20 mL dry THF was transferred into the Schlenk flask. Compound 3 was transferred to a graduated ampoule and then transferred into the reaction flask containing the above mixture. The mixture was 60 heated to 60 °C and stirred for at least 12-24 h. The polymer solution was dried under the vacuum and dialyzed against deionized water. Finally a highly viscous black liquid-like product was obtained.⁶⁷ Solid potassium hydroxide was used for replacing chloride ion with hydroxide ion on SIL-g-GO that both 65 were added to water (50 mL), and the mixture was stirred vigorously at room temperature for 24 h. Then the mixture was centrifuged and washed with water and was dried under reduced pressure to give the supported basic SIL-g-GO (Scheme 2).



Scheme 2. Synthesis route of SIL-g-GO

Preparation of Au NPs@SIL-g-G hybrid materials

General procedure for the catalytic aerobic oxidation of alcohols

Aqueous solution of HAuCl₄ (0.2 g in 3.0 mL) and SIL-g-GO (0.2 g in 10.0 mL) were mixed and placed in an ultrasonic bath 5 (50 KHz) for 30 min to well disperse metal ions in the functionalized graphene oxide sheets. Then 10.5 mL of a 1.0 M NaBH₄ solution in 0.3 M aqueous NaOH was added to mixture to reduced and form gold nanoparticles. In the second step, another 10.5 mL of 1M NaBH₄ solution was added into the solution under ¹⁰ constant stirring for converting functionalized GO to functionalized reduced graphene oxide. After stirring for 4 h, it

was filtered under vacuum, washed well with ethanol and water

¹⁵ A mixture of an alcohol (1.0 mmol) and Au NPs@SIL-g-G (0.2 mmol% Au, 0.005 g) was added in portions to a two-necked vial containing H₂O (4.0 mL) as solvent under bubbling of air or O₂ at atmospheric pressure at room temperature. The progress of the reaction was followed by gas chromatography (GC). After the ²⁰ reaction, the catalyst was removed *via* centrifuge and washed twice with CH₂Cl₂ (6.0 mL) to separate the absorbed organic compounds. Then the organic phase was combined, extracted twice. Finally the solvent was removed under vacuum to give the pure product.



Scheme 3. Synthesis route of Au NPs@SIL-g-G

Results and discussion

25

Our approach was guided by four imperatives: (i) the synthesized system should have gold nanoparticles and basic centers to act as ³⁰ bifunctional catalyst for organic reaction (ii) the support should encapsulate metal nanoparticles to control the size and uniform distributions of nanoparticles; (iii) the catalyst should be hydrophilic to have good dispersity in water as reaction solvent and iv) developing an efficient, environmental-friendly and ³⁵ benign synthetic process for the facile conversion of selective

aerobic oxidation reaction.

GO was synthesized by Hummer method.⁴⁴ Typical scanning electron microscopy 5 image of the suspended GO sheets are shown in Fig. 1. The exfoliated graphene sheets with lateral ⁴⁰ dimensions of several micrometers were observed by SEM image.



Fig. 1 SEM image of GO

Basic supramolecular ionic liquid grafted graphene and 45 subsequent loading of gold have been outlined in Schemes 2 and 3. Briefly, based on nucleophilic substitution of epoxides groups on graphene oxide sheets with amino-groups of Tris, GO was covalently functionalized by Tris. Supramolecular ionic liquid, polyether polyol, was synthesized by a tri-branch initiator on graphene oxide and then the chloride ions exchanged with hydroxide ions and finally, gold nanoparticles were encapsulated ⁵ on SIL-g-GO.

As expected due to the hydrophilic properties of catalyst, Au NPs@SIL-g-G shows high despersity and stability in aqueous solution (Fig. 2). In short, covalently functionalization of graphene with SIL can be improved its despersity in a wide range of solvents. The super dispersion of Au NPs@SIL-g-G in water makes it ideal candidate for environmentally-friendly oxidation reaction.



Fig. 2 Dispersity of GO (A), graphene (B), Au NPs@SIL-g-G (C) in H₂O

¹⁵ TGA is a powerful technique for identification of polymer attached on support. Also, the percent of polymer connected to support can be reasonably calculated. The result showed that graphite is highly stable up to 700 °C. For GO, there are two weight loss from ~25 to ~130 °C and~150 to ~205 °C that are
²⁰ related to weight loss of water and pyrolysis of the oxygencontaining functional groups, generating CO and CO₂, respectively. Reduced graphene (rGO) is stable up to 700 °C. SIL-graphene shows the weight loss from ~380 to ~480 °C, which is in accordance with decomposition of the surface-bound
²⁵ SIL. So it can be concluded that the weight % of SIL supported on graphene is about ~30% (Fig. 3).



Fig. 3 TGA graph of pristine graphite (A), rGO (B), GO (C), and SIL-g-GO (D) obtained under nitrogen

³⁰ FT-IR has been used to analyze the presence of functional groups in the synthesized catalyst. In Fig. 4, spectra of GO, GO-Tris and SIL-graphene have been shown after background subtraction for each spectrum. The spectrum of GO shows bands around 1060 cm⁻¹ (v _{C-O}), 1220 cm⁻¹ (v _{phenolic}), and 1720 cm⁻¹ (v _{C=O}). ³⁵ Functionalized GO with Tris indicates a peak around 2900 cm⁻¹, which corresponds to C–H stretching of CH₂ group of Tris that there is not in GO spectrum. After the synthesis of SIL on the GO-Tris, due to the introduction of imidazolium groups, the peaks in 1430–1640 cm⁻¹ region were appeared that shows ⁴⁰ formation of the poly ionic liquid on graphene.



Fig. 4 FT-IR spectrum of GO (A), GO-Tris (B), and SIL-g-GO (C)

As shown in Fig. 5, the XRD pattern of Au NPs@SIL-g-G indicated a peak for rGO with a 2θ value of about 20.17° and ⁴⁵ well-defined peaks of the Au NPs with 2θ values of 38.21°, 44.38°, 64.61, 77.62° related to (111), (200), (220) and (311) Bragg's reflection based on the fcc structure of gold nanoparticles. The broadening of Bragg's peaks confirms the formation of nanoparticle. The Debye–Scherrer's equation was used to ⁵⁰ calculate the mean size of gold nanoparticles by determining the width of the (111) Bragg reflection.⁶⁸ The size of the nanoparticles was thus obtained to be about 3 nm for gold nanoparticles.



Fig. 5 X-ray diffraction (XRD) pattern of Au NPs@SIL-g-G hybrid material

TEM is one of the most powerful techniques used to investigate single layers and the level of the dispersion of graphene sheets in aqueous solution. Fig. 6A shows that thin graphene oxide sheets which can be well dispersed in aqueous solution. It is important to note, in addition to the above mention advantages, functionalization graphene with SIL causes well stabilizing, uniformly dispersing, and controlling size of gold nanoparticles 65 which is clearly shown in Fig. 6B. TEM analysis, indicated that the range of nanoparticles sizes is 2-3 nm.

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Fig. 6 HR-TEM images of graphene oxide (A), and Au NPs SIL-g-graphene (B)

To investigate the effect of catalyst loading on the catalytic activity, different weight ratios of HAuCl₄:SIL-g-GO, 1:1, 1:2 5 and 2:1, were employed to synthesis of catalyst. The weight percents of metal to supported catalyst was obtained by AAS data and it was tabulated in Table 1. The supported catalysts with different amounts of metal loading but with the same amounts of catalyst in the reaction (0.2 mmol%), to have a correct 10 comparison, were tested for oxidation reaction of benzyl alcohol as a model reaction. The results were shown in Table 1, that indicated increasing the catalyst reactivity for HAuCl₄:SIL-g-GO 1:1 compared to 1:2, but decreasing the catalytic activity with changing the ratio to 2:1, maybe due to the aggregation of metal 15 nanoparticles because of high metal loading. To evaluate the catalytic properties of this catalyst, oxidation reaction of benzyl alcohol was performed as a model reaction. The reaction was carried out in the presence of various amounts of catalyst (Table 2, entries 1-4). The optimized catalyst amount was 0.2 mol% 20 (with respect to benzyl alcohol). In order to obtain the best solvent, various solvents, such as THF, DMF, DMSO, H₂O, CH₃CN, toluene and solvent-free conditions were tested. As indicated in Table 2 (Entries 4 -10), the H_2O is the most suitable solvent for this reaction in terms of yield, easy work-up and 25 coincidence to green chemistry principle. The reaction was studied under O₂ instead of air atmosphere, too, so that the reaction time and yields for O2 are relatively better under the same conditions. But the air due to its lower cost and availability is preferred than O2. The optimization of aerobic oxidation of 30 benzyl alcohol is 0.2 mol% of catalyst in water in the absence of additive inorganic bases such as NaOH, K₂CO₃, and KOH under the atmosphere of oxygen at room temperature (Table 2, entry 4).

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To show the efficiency of the prepared catalyst for the oxidation reaction, a large variety of primary and secondary cyclic and ³⁵ aromatic alcohols to the corresponding carbonyl compounds were subjected to the optimized conditions. All products were obtained in high yields and excellent selectivities (Table 3). Almost no carboxylic acids or esters were observed for all substrates investigated. Allyl alcohols such as cinnamyl alcohols were also ⁴⁰ oxidized to the corresponding cinnamic aldehydes with high selectivity (Table 3, entry 10-12). No epoxy, carboxylic acid or ester as side products were observed. When a mixture of benzyl alcohol and 1-phenylethanol was employed as the reaction substrates, primary alcohol was selectively oxidized even in the

⁴⁵ presence of secondary one. Actually, this aerobic oxidation gave a mixture of benzaldehyde and acetophenone in 91% and 19% yields, respectively. These faster oxidations of primary alcohols show that Au–alcoholate I (see scheme 4) is formed as an

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intermediate, since the formation of metal-alcoholate species is ⁵⁰ recognized for such selective oxidation of primary hydroxy groups.^{69,70}

Table 1. Effect of catalyst loading on the catalytic activity.

Entry	HAuCl ₄ :SIL-g-GO weight ratio	Au (g)/Au NPs@SIL-g-G (g) (%) ^a	Conversion Yield ^b (%)
1	1:2	4.5	79
2	1:1	7.9	>99
3	2:1	11.4	81

^a Obtained with AAS

^b Reaction conditions: benzyl alcohol (1mmol), solvent (5mL), at 25 °C,
 ss air (1 atm), Au NPs@SIL-g-G (0.20 mmol% Au, x g), 1 h. Yield determined by GC analysis.

 Table 2 Optimization of the reaction conditions on oxidation reaction of benzyl alcohol^a

Entry	Amount of catalyst (Au content /mol %)	Solvent	Conversion Yield ^b (%)
1	None	H ₂ O	11
2	0.05	H_2O	30
3	0.10	H_2O	75
4	0.20	H_2O	>99
5	0.20	DMF	>99
6	0.20	DMSO	>99
7	0.20	THF	82
8	0.20	None	70
9	0.20	CH ₃ CN	40
10	0.20	toluene	55

^a Reaction conditions: benzyl alcohol (1mmol), solvent (5mL), at 25 °C, air (1 atm), 1 h. ^b Yield determined by GC analysis.

To evaluate the efficiency of catalyst in the presence of air, some 60 of the derivatives were examined and the results showed that

good yields were obtained which are comparable with the yields of those reactions in the presence of oxygen but in longer reaction times.

Gold NPs have attracted much interest in aerobic oxidation of ⁵ alcohols; however the mechanism of oxidation reaction with gold NPs is still not fully understood. According to our experimental results as well as the literature reports, we propose possible mechanism for the catalytic oxidation of alcohols over bifunctional catalytic system (Au nanoparticles and OH⁻ as base) which has been illustrated in Scheme 4. Deprotonation of alcohol was promoted at the basic sites of OH⁻ to from alkoxide on the Au surfaces. Gold catalyzes the β-hydride elimination to produce

- Au surfaces. Gold catalyzes the β -hydride elimination to produce corresponding aldehyde along with the formation of O₂ and H₂O.
- To understand the unique promotional effect of Au NPs@SIL-g-Is G, its catalytic activity was compared with that of other supported Au catalysts used in oxidation reaction of benzyl alcohol with respect to their yields, solvents, additive base, temperature, and time required for the reaction (Table 4). It is evident from Table 4 (Entries 3 and 4) that the high reaction temperatures are needed.
- 20 Long reaction time is another drawback of these reports. Using toxic solvents such as DCM and toluene make these reports unfavorable from green chemistry point of view. In addition, most of these examples required an equivalent of bases (Table 4, entries 2-4). Recently, Liu and co-workers⁴⁸ reported a 25 bifunctional catalysts containing Au NP and a solid base support, Au/MgCr-HT, for the oxidation of alcohols (Table 4, entry 5); however, the catalytic performance is limited by the use of toxic solvent (toluene) and high temperature (100 °C). To overcome the mentioned deficiencies, a new bifunctional catalytic system was 30 introduced based on functionalized graphene sheets with basic supramolecular ionic liquid. In the presented catalyst, a task specific ionic liquid containing Au NPs, and hydroxyl ions were immobilized on the graphene. This structure omits any external use of basic activators. The catalyst is usable on water as reaction 35 medium at room temperature. These properties and also high
- reaction yields are the most important advantages of the synthesized catalyst.

Table 3 Aerobic oxidation of alcohols using Au NPs@SIL-g-Graphene^a

	он ↓	Au NPs@	SIL-g-G (0.2	20 mol%, 0.00	5g) O		
	$R^{1} R^{2}$	l air	H₂O, 25 ℃ `or O₂ (1at	; m)	R ¹ R ²	2	
Entry	R ¹	R ²	Tir	ne (h)	Convers	sion/Isolated	Selectivity ^{,b} (%)
			Air	O_2	Air	O ₂	
1	Ph	Н	2.5	1	98/97	>99/99	>99
2	$4-ClC_6H_4$	Н	3	1.2	98/98	>99/98	>99
3	$4-MeC_6H_4$	Н	2.2	1	95/94	>99/98	>99
4	$2-MeC_6H_4$	Н	3.4	1.5	93/92	>99/99	>99
5	$4-MeOC_6H_4$	Н	3	1.3	94/92	98/96	>99
6	$4-NO_2C_6H_4$	Н	3.5	1.7	97/96	>99/99	>99
7	$CH_3(CH_2)_4$	Н	4	2	91/88	96/92	98
8	CH ₃ (CH ₂) ₆	Н	4.5	2	92/90	98/98	>99
9	Ph-CH ₂	Н	4.2	1.5	92/92	98/98	>99
10	PhCH=CH-	Н	2.5	1.4	95/90	95/90	97
11	4-MeC ₆ H ₄ CH=CH-	Н	3	1.5	92/89	96/94	98
12	4-MeOC ₆ H ₄ CH=CH-	Н	3	1.8	91/86	98/95	96
13	Ph	Me	2	1	95/94	97/95	99
14	Ph-CO	Ph	2.5	1	97/97	98/98	99
15	PhCH=CH-	Me	3	1.5	95/93	97/96	99
16	Cyclohexanol		2.8	1.2	96/94	99/99	99
17	4-tert-butylcyclohexanol		2.5	1.5	93/93	97/95	99

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16	2.3 dihydro 1 <i>H</i> inden 1 ol		r	1	08/06	>00/06	90
10	2,5-amyaro-111-mach-1-or		2	1	98/90	~ 99/90	30
17	Cyclooctanol		3.5	2	98/94	>99/97	98
18	Ph	Ph	6.3	4.2	92/90	95/91	97

^a Reaction conditions: alcohol (1.0 mmol), Au NPs@SIL-g-G (0.20 mmol% Au, 0.005 g), H₂O (4.0 mL), O₂ or Air (1 atm), 25 °C. ^b Se air.



Au NPs@SIL-g-G Scheme 4. Plausible pathways for the oxidation of alcohols over Au NPs@SIL-g-G

Table 1 Comparison of the regults of	ain ad from Au NDa@SIL a C with at	har commonted Appartalizate for	the avidation of honory alachal
Table 4 Comparison of the results obt	amed from Au NPS(<i>a</i> /SIL-g-G with ot	her supported Au catalysis for	the oxidation of benzyl alconol.

Entry	Cat.	Solvent	Temp.	Time	Base	Yield (%)	Selectivity	Ref.
			(°C)	(h)			(%)	
1	AuNPs-SIL-g-graphene	H ₂ O	25	1	-	>99	>99	-
2	PS–PAMAM–Au NPs ^a	DCM/H ₂ O	25	16	K ₂ CO ₃	99	-	71
3	Fe ₃ O ₄ /Au	toluene	100	6	K ₂ CO ₃	100	100	35
4	Fe ₃ O ₄ :PVP ^b /Au	H_2O	25	6	K ₂ CO ₃	94	5	72
5	Au/MgCr-HT ^c	toluene	100	1	-	96	99	73

^a Polystyrene-polyamidoamine-supported gold nanoparticles

^b Poly(N-vinyl-2-pyrrolidone)

10 ^c Layered double hydroxide hydrotalcite

The organic product phase was monitored for the presence of ppm amount of gold. The atomic absorption spectroscopy of the filtrate showed that the Au content in the solution was below the ¹⁵ detection limit (0.1 ppm).

Many reports of stable and recyclable supported homogeneous catalysts are based on a single data point in each run, often a reaction yield at a long time, to prove catalyst stability and

recyclability. But catalysis is a totally kinetic phenomenon, so ²⁰ one can argue that only kinetic data should be considered to prove recyclability, stability and deactivation. Measurement of initial rates obtained from kinetic plots is a good approach to investigate recyclability and deactivation. Since if a single data point was taken in each run after long reaction time, one might ²⁵ incorrectly conclude that the catalyst is completely stable and recyclable.⁷⁴ So, we investigated conversion yields for every run

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after 1h (The reaction proceed was monitored by GC) for oxidation reaction of benzyl alcohol in air atmosphere as a model reaction. After carrying out the reaction, the reaction mixture was filtered off and Au NPs@SIL-g-G separated as a black solid, s washed with EtOH (2×5 mL) and reused. The results showed in Fig. 7 Au NPs@SIL-g-G showed good stability and recyclability as the conversion yields after 1h for five runs didn't decrease significantly.



¹⁰ Fig. 7 The reusability of the catalyst in the oxidation of benzyl alcohol.

In this work, we have found several important achievements; (i) providing a suitable support for stabilizing and encapsulating gold nanoparticles to control their size and uniform distributions by grafting supramolecular ionic liquid to graphene (ii) having a 15 heterogeneous graphene based catalyst with good dispersity in water as reaction solvent and (iii) removing the need for an additive base by synthesis of a new efficient bifunctional heterogeneous catalyst, gold nanoparticles and basic centers (iv) developing an efficient, environmental-friendly and benign 20 synthetic process for the facile conversion of selective aerobic oxidation reaction of various primary, secondary and allyl alcohols into their corresponding aldehydes and ketones in water at room temperature with excellent yield and selectivity. Also the catalyst has good chemical stability in the reaction media proved

25 by investigating the recyclability of the catalyst.

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