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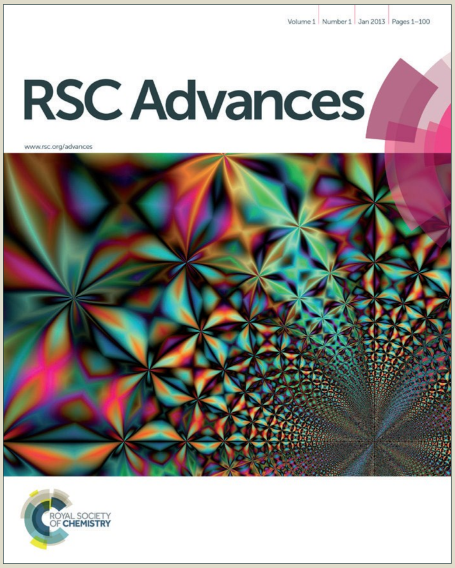

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A novel iron(III)-based heterogeneous catalyst for aqueous oxidation of alcohols using molecular oxygen

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A novel silica supported iron(III)-based heterogeneous catalyst ($FeCl_3$-imine@SiO_2) has been synthesized and characterized by several techniques, such as FTIR, Nitrogen adsorption analysis (BET), SEM-EDX, XRD, EPR, AAS and XPS analyses. The catalyst showed excellent activity for selective oxidation of alcohols to corresponding carbonyl compounds in water under atmospheric pressure of oxygen without using any additive. Notably, the heterogeneous catalyst showed remarkable improvement over its homogeneous counterpart, might be attributable to the synergic effect between the metal and the supported ligand. The catalyst could be easily recovered by simple filtration and reused several times without compromising with its activity. A wide range of primary and secondary alcohols including heterocyclic alcohols are tolerated as substrates.

Key words: heterogeneous catalyst; iron(III); alcohol oxidation; molecular oxygen; water

Introduction

Selective oxidation of alcohols to corresponding carbonyl compounds is one of the most industrially significant reactions in organic synthesis. The use of transition metal-based homogeneous[1] and heterogeneous[2] catalysts are well-precedented for this reaction mainly because of their ability to replace conventional oxidation methods of using stoichiometric oxidants such as chromate or permanganate with molecular oxygen. From both economic and green chemistry perspectives, molecular oxygen is an ideal oxidant as it is readily available and produces water as the only by-product.[1,3] Unfortunately, majority of the reported protocols for efficient oxidation of alcohols using molecular oxygen require noble metals such as palladium,[4]

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†Electronic Supplementary Information (ESI) available: Textural data of BET studies, FTIR spectra, XPS survey spectra, reusability diagram and GC-MS spectra of the carbonyl products.

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rhodium,[5] ruthenium,[6] gold,[7] platinum,[8] *etc*. Apart from their costs, these noble metals also have serious toxicity issues which make these catalytic systems impractical for industrial use.[1*d*] Hence, over the years, considerable efforts have been made towards replacement of these expensive precious metal catalysts with cheaper base metals like copper or iron.[1*a*-c] Although, copper-based systems already displayed tremendous potential to act as an alternate to platinum metal catalysts in oxidation of alcohols,[9] iron-based systems remain relatively underexplored. It is fair to say that from sustainability point of view iron is in much more advantageous position over copper due to its to its lower price, and high environmental acceptability.[10] It is surprising to note that the first iron-catalyzed oxidation of alcohols was reported only in 2002,[11] while copper-catalyzed alcohol oxidation was first reported in 1966.[12] Since the first report, iron-catalyzed systems have been increasingly investigated in alcohol oxidation studies.[13,14]. Typical examples are Wang's $FeCl_3$-TEMPO-$NaNO_2$ system,[13*a*] Repo's $FeCl_3$-thyamine system,[13*b*] Liu's $Fe(NO_3)$-TEMPO-NaCl system,[13*c*,13*d*] *etc*. However, majority of these successful systems are homogeneous in nature where separation and recovery of the catalyst is extremely difficult which pose significant limitations to their industrial scale applications. Thus, in recent years, strategies have been adopted to immobilize iron(III) salts/compounds into/onto different supports such as aluminosilicates,[14*b*] carbon,[14*c*] mesoporous silica,[14*i*] graphene-oxide[14*g*], polymer,[14*e*] *etc*. and applied in alcohol oxidation reaction. Although notable progress was achieved in some cases with respect to development of stable and reusable catalysts of high efficiency, such catalysts usually showed lower activities compared to their homogeneous counterparts. Moreover, except one report of iron-oxide nanoparticles as catalyst,[14*b*] in all the cases the reactions were performed in organic solvents that are not only expensive but also toxic in nature.

In recent years, because of economical and environmental issues, organic reactions in water have gained much attention. However, to the best of our knowledge, there is no report on the use of iron-based heterogeneous catalysts for alcohol oxidation reaction in water with molecular oxygen as terminal oxidant. In this work, we disclose a simple procedure for the preparation of a new iron(III)-based heterogeneous catalyst supported on silica and its application for alcohol oxidation reaction with molecular oxygen in neat water.

Experimental section

General information

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3-Aminopropyl-functionalized silica gel (APTES@SiO_2: 1 mmol/g of silica gel; 200–400 mesh) was purchased from Sigma-Aldrich. Acetamide and anhydrous $FeCl_3$ was purchased from Thermo Fisher scientific. The substrates used in the alcohol oxidation reactions were purchased from Sigma-Aldrich, Spectrochem and Rankem. All other chemicals and solvents were purchased from different Indian firms. The solvents were distilled and dried prior to use.

The Fourier transform infrared (FTIR) spectra (KBr; 1800-1400 cm^{-1}) of the materials were recorded on a Shimadzu IR spectrophotometer (prestige-21). X-ray powder diffraction (XRD) was performed with a Bruker diffractometer (model AXS D8) with Cu-Ka (1.541 °A) radiation. The scanning electron microscope (SEM) images were obtained from JEOL Model JSM - 6390LV and energy dispersive X-ray (EDX) peaks were recorded in JEOL Model JED – 2300. The iron content was determined by atomic absorption spectroscopy (AAS) using a Thermo Scientific spectro photometer (IEC 3000). Electron spin resonance (ESR) spectra was recorded on a JEOL instrument (JES-FA200) at liquid N_2 temperature. Nitrogen adsorption studies were carried out at 77 K using a Quantachrome, ASIQA 2010 analyzer. Prior to analysis the samples were degassed by heating at 200 ^{o}C for 4 h under vacuum. Specific surface area was calculated following the Brunauer–Emmett–Teller (BET) calculation and pore-size distribution was obtained by using the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed at ''*Centro de Materiais da Universidade do Porto*'' (Portugal), in a Kratos Axis Ultra HSA spectrometer using a non-monochromatized Mg Ka radiation (1253.6 eV). Gas chromatography–mass spectrometry (GC–MS) studies were done using Agilent 7820A GC system with Agilent 5975 Series MSD Mass detector equipped with a 30 m × 0.25 mm × 0.5 µm HP-5MS capillary column.

Synthesis of the silica based materials:

Synthesis of imine-functionalized silica gel: *imine@SiO_2*

In a suspension of 3 g of APTES@SiO_2 in 40 mL ethanol, 3 mmol of acetamide was added in small portions under continuous stirring. The solution was then stirred under refluxing condition for 6 hrs. The solids were separated from the solvent by filtration and washed repeatedly through Soxhlet extraction with ethanol and acetone. The resulting acetamide grafted silica was dried at 120 ^{o}C for 24 h and designated as imine@SiO_2.

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Immobilization of $FeCl_3$ onto imine@SiO_2: *$FeCl_3$-imine@SiO_2*

2.5 g of imine@SiO_2 was added to a solution of 2.5 mmol of anhydrous $FeCl_3$ in 40 mL of acetonitrile and the reaction mixture was stirred at 60 ^{o}C for 8 h. The resulting solution was filtered off and the brown solids were washed several times through Soxhlet extraction with acetonitrile (until the extracted solvent became colorless). The material was designated as $FeCl_3$-imine@SiO_2.

General procedure for the alcohol oxidation reactions

A 50 mL two necked round bottomed flask fitted with a condenser and gas bubbler was charged with alcohol (1 mmol), catalyst (46 mg, 2 mol% Fe) and water (6 mL). Then O_2 (1 atm.) was bubbled into the mixture for the required time and the reaction mixture was heated at 80 ^{o}C with continuous stirring. On completion of the reaction, the catalyst was separated from the reaction mixture by simple filtration. The filtrate was extracted with ether and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure the concentrated organic product is then extracted with ether and analyzed by GC-MS. The product was isolated by column chromatography technique using ethyl acetate/hexane (1:9) as eluent

Results and discussion

Synthesis and characterization of the catalyst

The catalyst, $FeCl_3$-imine@SiO_2, has been prepared in two steps (Scheme 1). Firstly, commercially available 3-aminopropyltriethoxysilane functionalized silica gel (APTES@SiO_2) underwent a condensation reaction with acetamide to get an imine-functionalized silica gel (imine@SiO_2) which subsequently treated with anhydrous $FeCl_3$ to get the iron-catalyst. The FTIR spectra (Fig. S1, ESI) of the silica-based material are in good agreement with the proposed coordination environment. In particular, the bidentate bonding mode of the supported ligand in $FeCl_3$-imine@SiO_2 was confirmed by the shift of $\upsilon_{CH=N}$ band from 1646 cm^{-1} to 1630 cm^{-1} and υ_{NH_2} band from 1531 cm^{-1} to 1511 cm^{-1}. The nitrogen adsorption-desorption isotherms of the silica-based materials displayed typical type IV patterns with a sharp hysteresis loop, which is characteristics of mesoporous materials (Fig. 1). The surface area and pore size distribution of the support (APTES@SiO_2) studies reveals a high specific surface area of about 416 m^2/g with specific pore volume of 0.65 cm^3/g (Table S1, ESI). These values upon metal immobilization

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($FeCl_3$-imine@SiO_2) decreases significantly to 283 m^2/g and 0.43 cm^3/g which is consistent with successful immobilization of iron onto silica matrix.

The XRD patterns (Fig. 2) of the imine@SiO_2 material exhibit a broad peak centered at $2\theta = 22.48^0$ for silica which upon immobilization of $FeCl_3$ does not show any prominent shift ($2\theta = 22.13^0$), except a slight decrease in intensity. No crystalline phases related to metallic iron or iron oxides were observed in the spectra of $FeCl_3$-imine@SiO_2. However, a prominent peak at $2\theta = 35.9^0$ was observed which matched well with the XRD patterns of $FeCl_3$ or $FeCl_3$ doped polymer,[15] suggesting the presence of $FeCl_3$ crystallites within silica matrix. The SEM image of the fresh catalyst material shows silica particles are of different dimensions (Fig. 3a). The existence of iron in the catalyst was further confirmed by SEM-EDX analysis. The ESR spectra of $FeCl_3$-imine@SiO_2 displays six lines (Fig. 4) with an average *g* value of 2.01, typical for a Fe^{+3} high spin (I = 5/2) system with hyperfine splitting. The iron content determined by AAS analysis was found to be 0.44 mmol g^{-1}.

The XPS survey spectrum (Fig. S2, ESI) of the iron-based material clearly shows the presence of iron, chloride and nitrogen, besides of carbon, silica and oxygen. In the N 1s region (Fig. 5a) the high resolution spectrum exhibits two peaks at 398.0 eV and 400.2 attributable to amine and imine group respectively.[16] The Fe(2p) band(Fig. 5b) splits into two peaks, $2p_{3/2}$ and $2p_{5/2,}$ with corresponding binding energies at 711.1 eV and 724.8 eV respectively and the values are very much close to the Fe2p binding energies of reported iron(III) compounds.[14*c*,16]

Catalytic activity

The catalytic activity of the material $FeCl_3$-imine@SiO_2 was investigated for alcohol oxidation reaction using water as solvent. Initial experiments for determining comparative efficacy and optimization study (*e.g.* temperature, catalyst quantity) was performed by considering oxidation of benzyl alcohol as model reaction (Table 1). Initially, oxidation reaction was performed under aerobic condition by bubbling air into the reaction mixture at room temperature. After 24 h only 42% benzaldehyde formation was detected by GC-MS (entry 1). However, when the same reaction was performed by bubbling molecular O_2 (1 atm.) for 8 h moderate improvement in benzaldehyde formation was noticed (entry 2). On increasing temperature to 80 ^oC, significant improvement in the product yield was observed (entry 4). Interestingly, under similar experimental condition, homogeneous $FeCl_3$ as catalyst gave only 36% benzaldehyde (entry 5).

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It may be worth to mention that usually immobilized catalysts show lesser activity compared to their homogeneous counterparts, however in our case a significant improvement in yield was observed by the catalyst $FeCl_3$-imine@SiO_2 compared to homogeneous $FeCl_3$ possibly suggesting a cooperative effect between the metal and supported ligand which plays a crucial role in promoting oxidation reaction.

Encouraged by our initial result, we extended the scope of our iron-based catalyst for a range of other representative primary and secondary alcohols including heterocyclic alcohol (Table 2). Under the optimized condition (80 ^{o}C, 2.0 mol% Fe), primary benzylic alcohols bearing electron-donating groups at *para* position were effectively converted to their corresponding aldehydes in excellent yields (entries 2 and 4). However, conversions of benzylic alcohol bearing electron-withdrawing substituents at *para* position were found to be moderate (entry 5). Our result also revealed that the positional isomers of the substituents have a significant influence on the catalytic performances. For instance, oxidation of *m*-methylbenzylalcohol gave 73% product while under similar experimental condition *p*-methylbenzylalcohol gave 92% aldehyde (entries 3 and 2). The secondary benzyl alcohols like benzhydrol (entry 10) or 1-phenyl ethanol (entry 9) also gave excellent yields of corresponding ketones. In fact, our protocol was also amenable to allylic alcohols such as cinnamyl alcohol (entry 7) or heterocyclic alcohol like furfuryl alcohol (entry 8) which are usually considered to be difficult substrates for alcohol oxidation reaction.[4e] In fact, our catalytic system was also found to be effective for oxidations of aliphatic alcohols like cyclohexanol (entry 12) or 1-octanol (entry 13), however only moderate yields were obtained.

Reusability and heterogeneity test

Our study (Fig. S3, ESI) reveals that the catalyst could be reused at least five cycles without significant loss in activity. The AAS analysis of the five times used catalyst shows a very negligible decrease in the Fe content (<2%). The SEM picture of the used catalyst (Fig. 4b) is very much similar to that of the fresh catalyst (Fig. 4a) except slight decrease in silica particle sizes, clearly indicating the surface morphology of the catalyst remained unaffected even after five consecutive uses. The SEM-EDX spectra of the used catalyst also shows the presence of Fe suggesting that the catalyst could be reused for further runs. In order to confirm the heterogeneity of our system we have performed hot filtration test by taking benzyl alcohol as a model

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substrate. For this purpose the oxidation reaction was stopped after 2 h and the solid catalyst was separated from the mixture by filtration under hot condition (conversion 46%) and the filtrate was then allowed to continue stirring under identical conditions. After 4 h of stirring no further change in the product concentration was noticed (Fig. 6), indicating that no leaching of catalyst was occurred.

Conclusion

In conclusion, an iron(III)-based heterogeneous catalyst has been developed for the first time that effectively oxidizes primary and secondary alcohols to corresponding carbonyl compounds in water with molecular oxygen without using any additive or base. The low costs coupled with environment friendly properties of the materials used in our protocol (*e.g.* iron, silica, O_2, water) will make this system a sustainable alternative to expensive platinum metal based catalysts**.**

Acknowledgement

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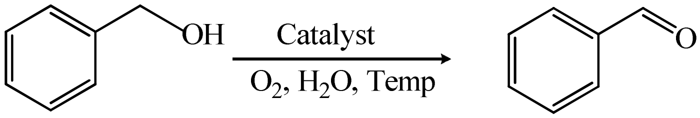
Table 1. Optimization of reaction conditions for the oxidation of benzyl alcohol[a]



Entry	Catalyst	Oxidant	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%)[b]
1	$FeCl_3$@imine-SiO_2	air	3	30	24	42
2	$FeCl_3$@imine-SiO_2	O_2	3	30	8	64
3	$FeCl_3$@imine-SiO_2	O_2	3	60	8	85
4	$FeCl_3$@imine-SiO_2	O_2	3	80	8	96
5	$FeCl_3$	O_2	3	80	8	36
6	$FeCl_3$@imine-SiO_2	O_2	2	80	8	96
7	$FeCl_3$@imine-SiO_2	O_2	1	80	8	84
8	$FeCl_3$@imine-SiO_2	O_2	2	80	6	96

[a] Reaction conditions: benzylalcohol (1 mmol), O_2 (1 atm., bubbling), iron-catalyst, water (6 mL); [b] GC yield

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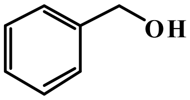
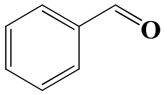
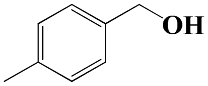
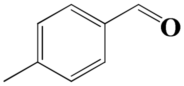
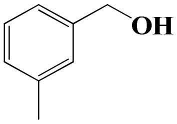
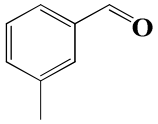
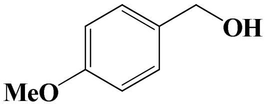
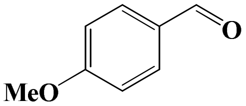
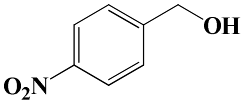
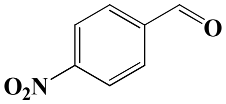
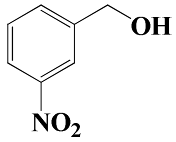
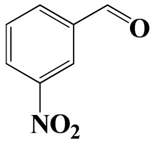
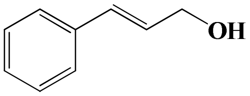
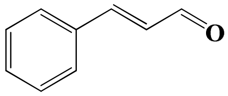
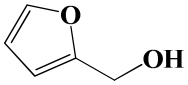
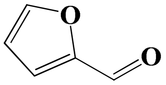
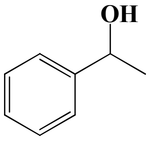
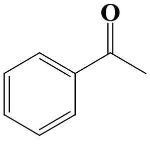
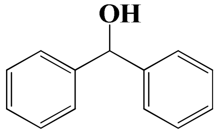
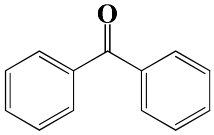
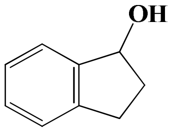
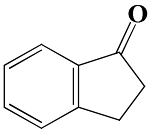
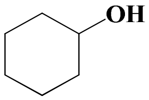
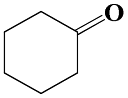
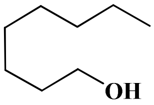
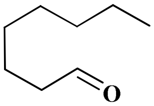
Table 2: Oxidation of various alcohols in aqueous media catalyzed by $FeCl_3$-imine@SiO_2 using molecular O_2

Entry	Substrate	Product	Time(h)	Yield(%)^{a,b}
1			6	96 (93)
2			6	92 (88)
3			6	73 (68)
4			6	89 (86)
5			7	65 (63)
6			7	46 (44)
7			6	89 (87)
8			6	78
9			6	90 (87)
10			6	91 (90)
11			7	73
12			7	51
13			8	62

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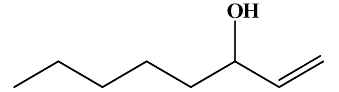
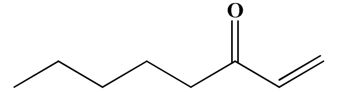
14			8	56

Reaction conditions: Alcohol (1 mmol), O_2 (1 atm.), H_2O (6 ml), catalyst (2 mol%), 80 ^{o}C, ^{a}GC yield; ^{b}Isolated yield in the parenthesis.

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Legends: Scheme, Tables and Figures

Scheme 1: Synthesis of the silica supported iron catalyst, $FeCl_3$-imine@SiO_2.

Fig. 1: N_2 adsorption-desorption isotherms of silica-based materials.

Fig. 2: Powder XRD patterns of (a) APTES@SiO_2 and (b) $FeCl_3$-imine@SiO_2.

Fig. 3a SEM-EDX spectra of $FeCl_3$-imine@SiO_2 (before catalysis).

Fig. 3b SEM-EDX spectra of $FeCl_3$-imine@SiO_2 (after 5th use).

Fig. 4: ESR spectra of $FeCl_3$-imine@SiO_2 recorded at liquid nitrogen temperature.

Fig. 5: XPS spectra of $FeCl_3$-imine@SiO_2

Fig. 6 Hot filtration test for the benzyl alcohol oxidation using $FeCl_3$-imine@SiO_2

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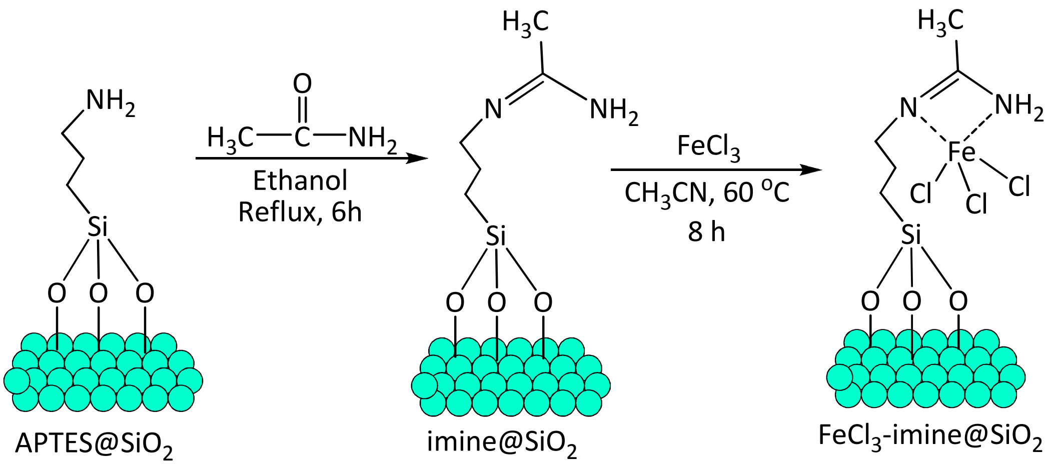

Scheme 1

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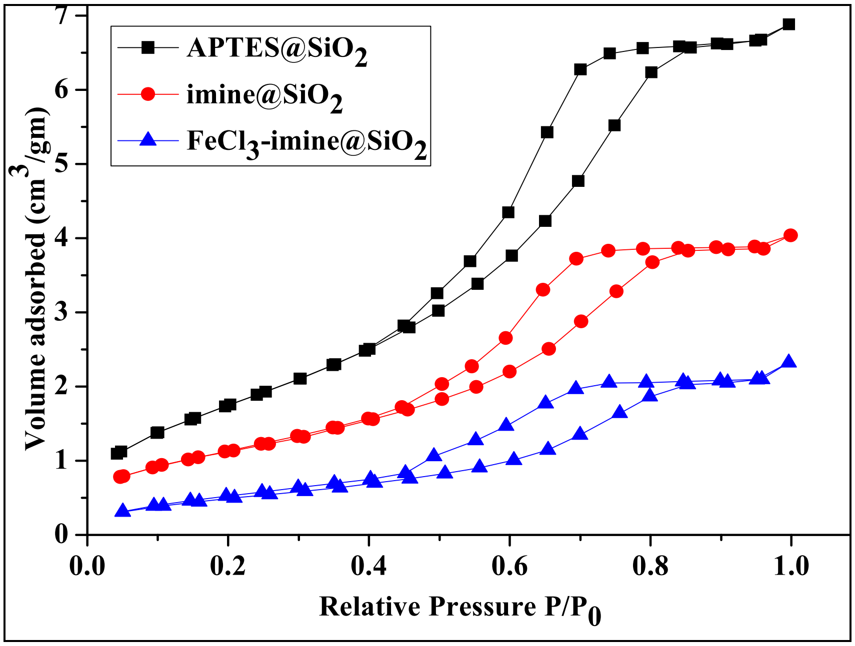

Fig. 1

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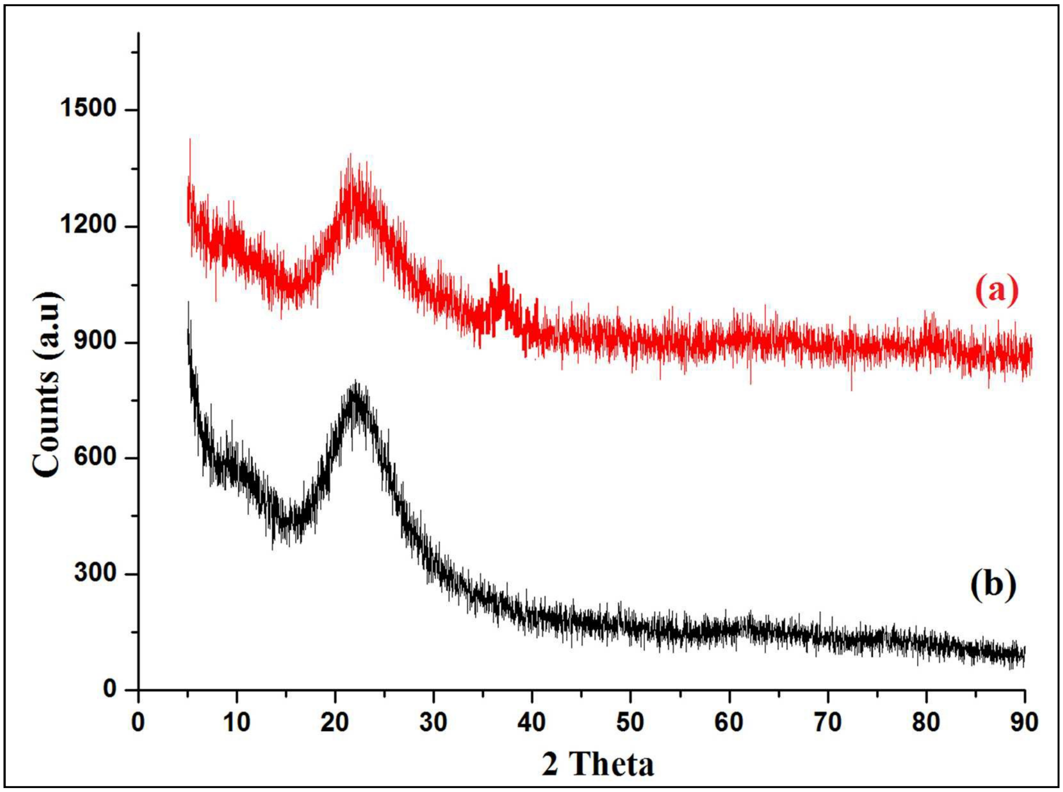

Fig. 2

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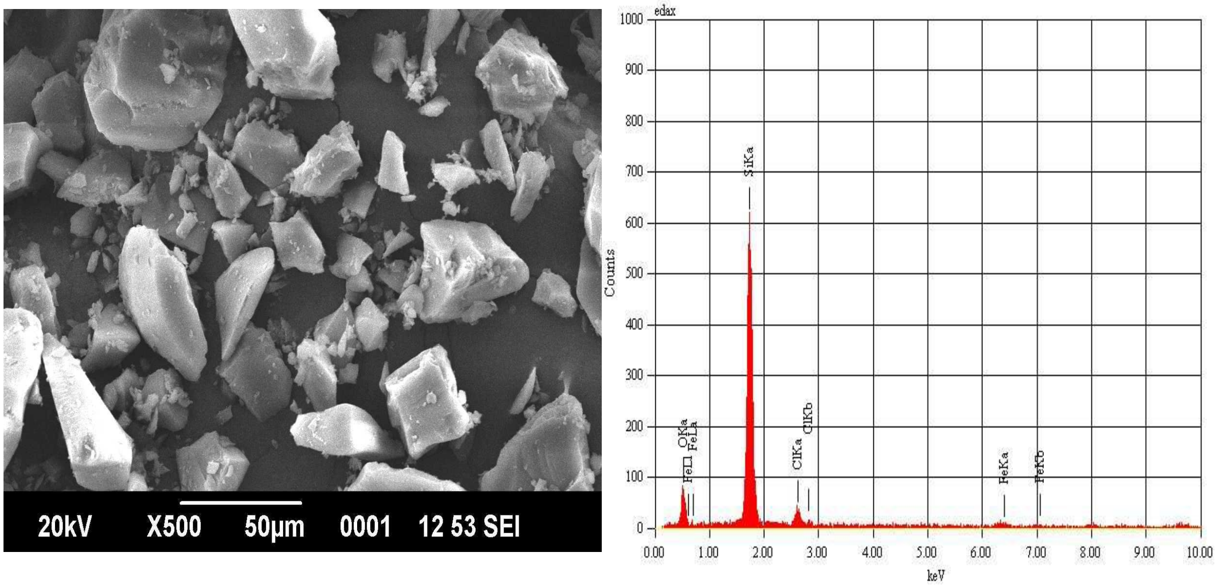

Fig. 3(a)

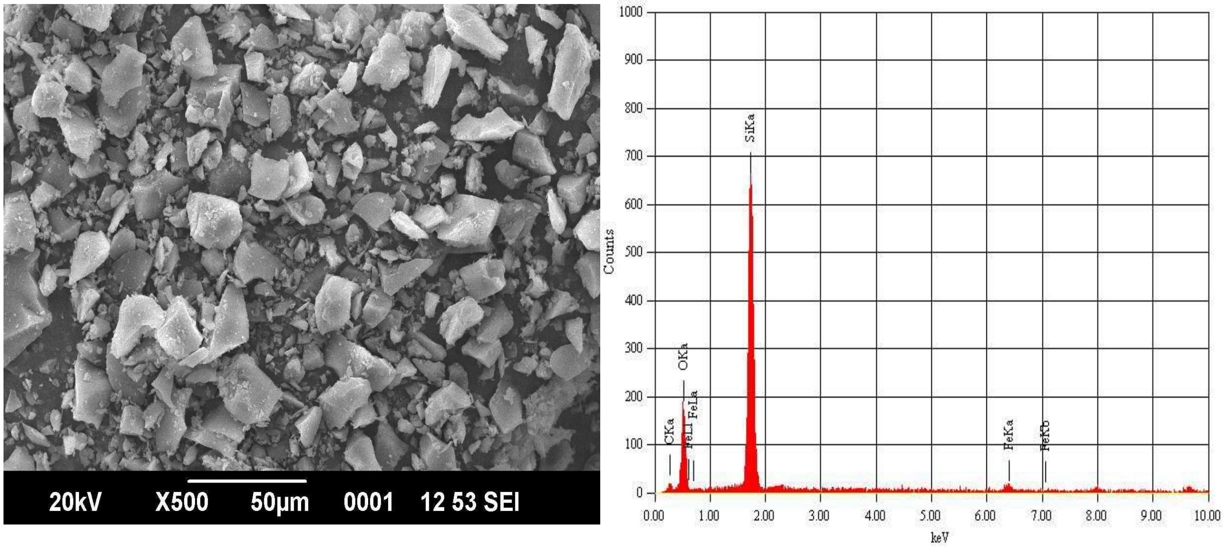

Fig. 3(b)

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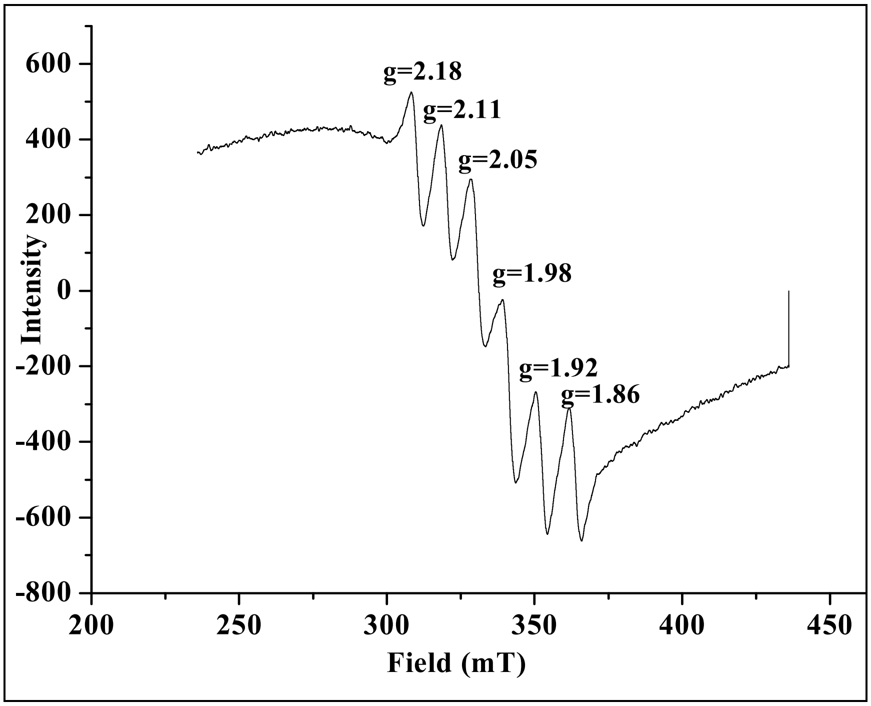

Fig. 4

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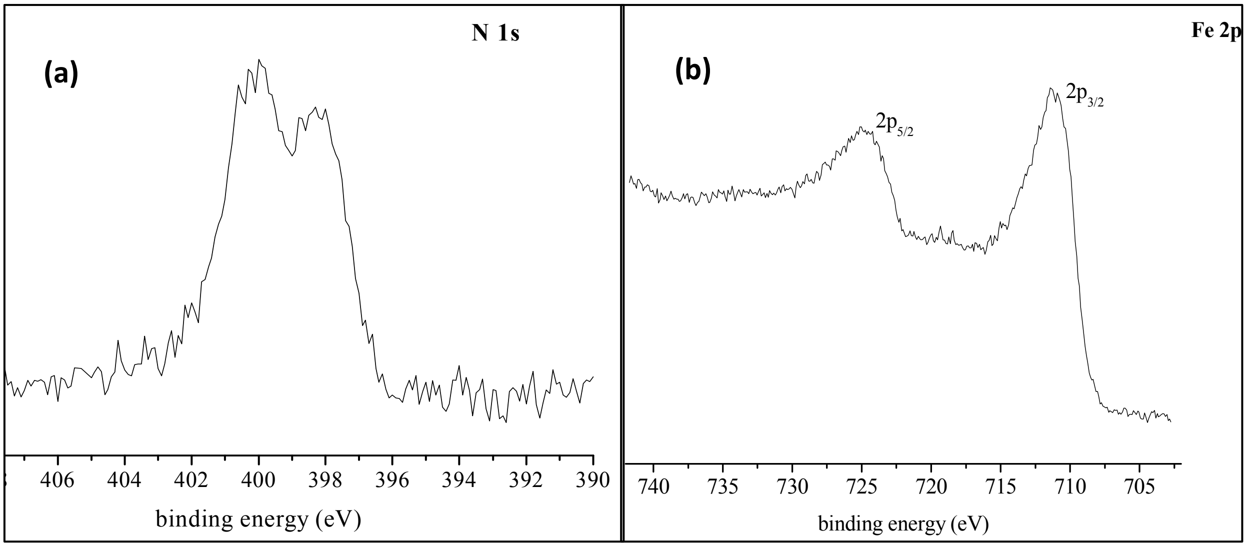

Fig. 5

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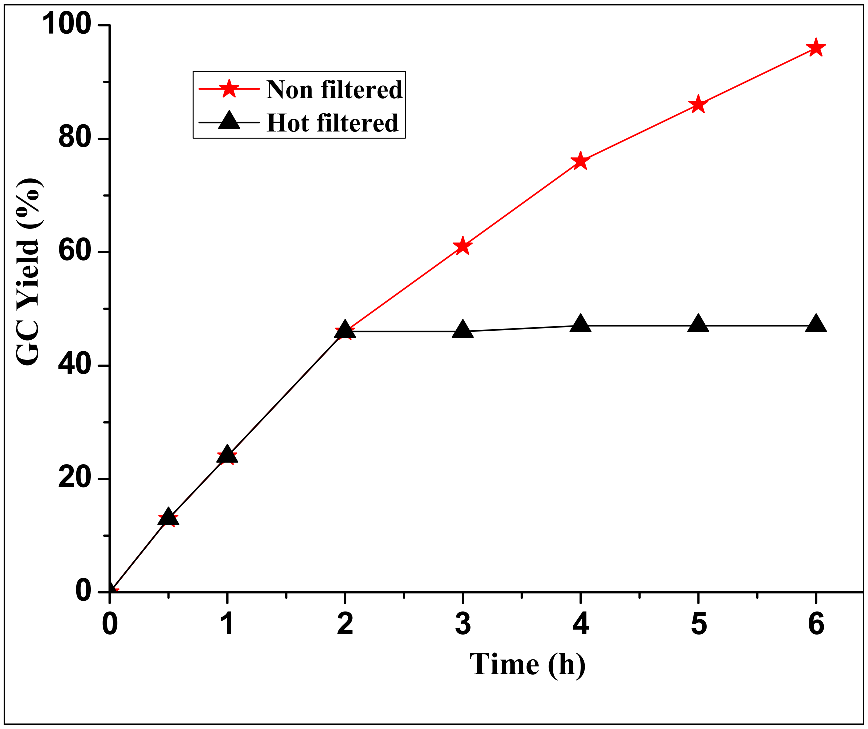

Fig. 6