



and its application for alcohol oxidation reaction with molecular oxygen in neat water.

Experimental section

General information

3-Aminopropyl-functionalized silica gel (APTES@SiO₂: 1 mmol g⁻¹ of silica gel; 200–400 mesh) was purchased from Sigma-Aldrich. Acetamide and anhydrous FeCl₃ 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.

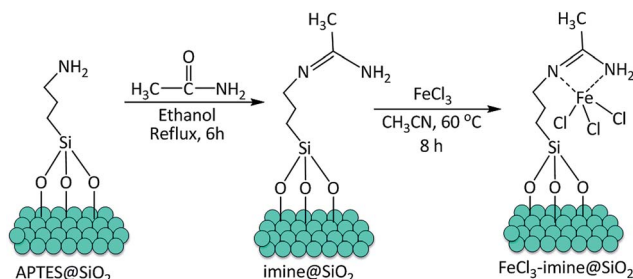
The Fourier transform infrared (FTIR) spectra (KBr; 1800–1400 cm⁻¹) of the materials were recorded on a Shimadzu IR spectrophotometer (prestige-21). X-ray powder diffraction (XRD) was performed with a Bruker diffractometer (model AXS D8) with Cu-K α (1.541 Å) radiation. The scanning electron microscope (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 N₂ 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 °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-K α 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@SiO₂. In a suspension of 3 g of APTES@SiO₂ 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 h. 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 °C for 24 h and designated as imine@SiO₂.

Immobilization of FeCl₃ onto imine@SiO₂: FeCl₃-imine@SiO₂. 2.5 g of imine@SiO₂ was added to a solution of 2.5 mmol of anhydrous FeCl₃ in 40 mL of acetonitrile and the reaction mixture was stirred at 60 °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 FeCl₃-imine@SiO₂.



Scheme 1 Synthesis of the silica supported iron catalyst, FeCl₃-imine@SiO₂.

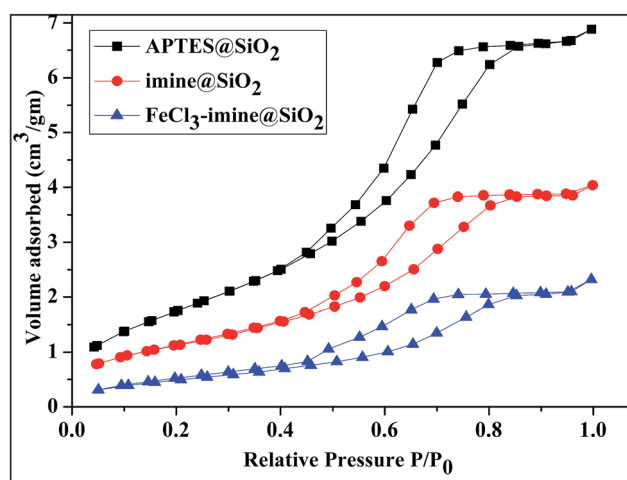


Fig. 1 N₂ adsorption-desorption isotherms of silica-based materials.

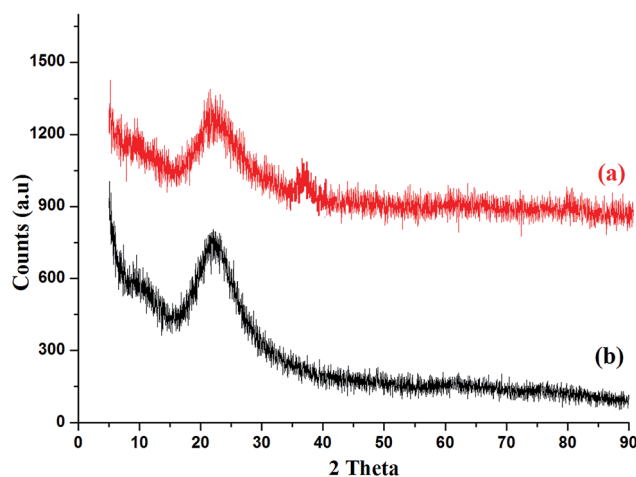


Fig. 2 Powder XRD patterns of (a) FeCl₃-imine@SiO₂ and (b) APTES@SiO₂.

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 O₂ (1 atm.) was bubbled into the mixture for the required time and the reaction mixture was heated at 80 °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 Na₂SO₄. 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, FeCl₃-imine@SiO₂, has been prepared in two steps (Scheme 1). Firstly, commercially available 3-aminopropyltriethoxysilane functionalized silica gel (APTES@SiO₂) underwent a condensation reaction with acetamide to get an imine-functionalized silica gel (imine@SiO₂) which subsequently treated with anhydrous FeCl₃ to get the iron-catalyst.

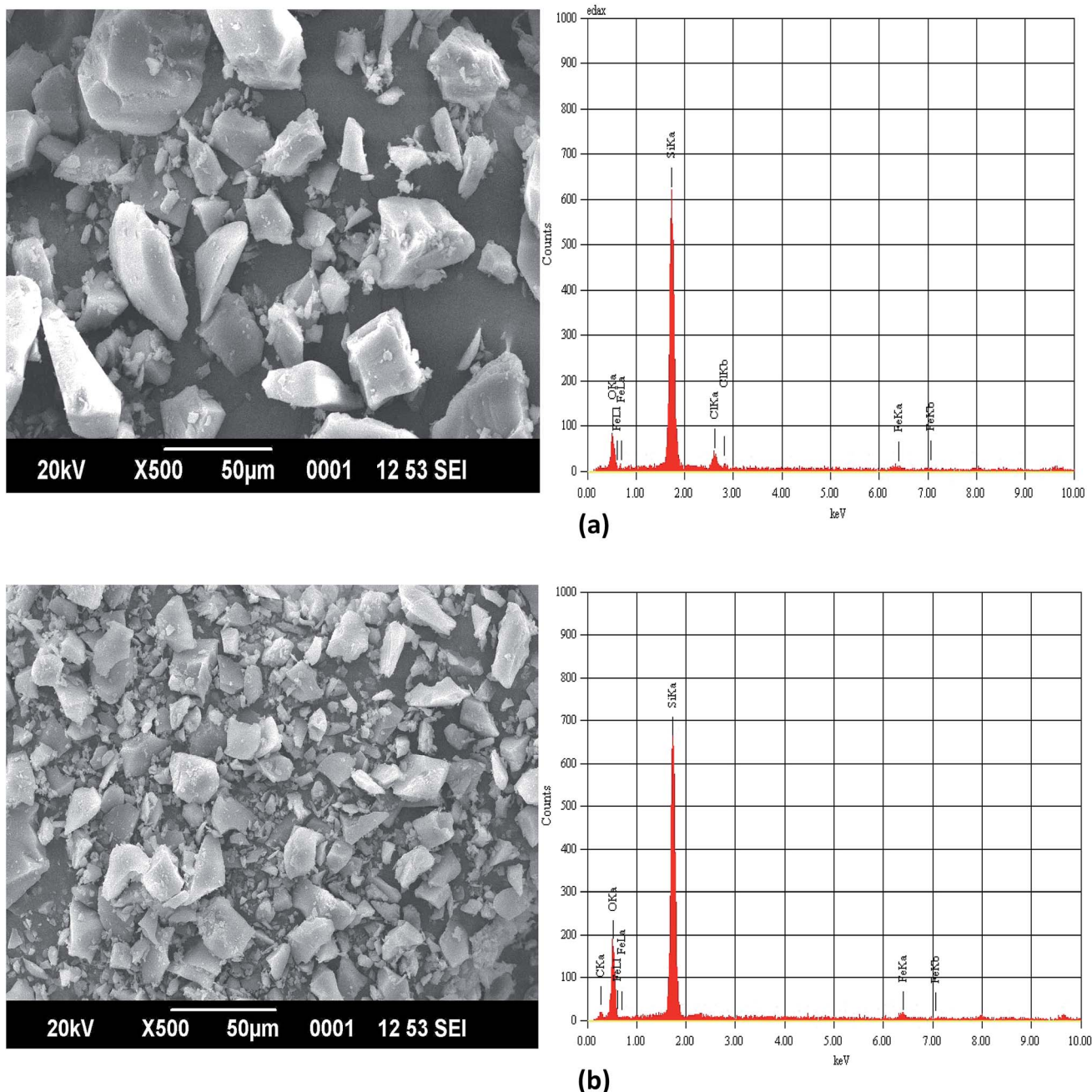


Fig. 3 (a) SEM-EDX spectra of FeCl₃-imine@SiO₂ (before catalysis). (b) SEM-EDX spectra of FeCl₃-imine@SiO₂ (after 5th use).

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 FeCl₃-imine@SiO₂ was confirmed by the shift of $\nu_{\text{CH-N}}$ band from 1646 cm⁻¹ to 1630 cm⁻¹ and ν_{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@SiO₂) studies reveals a high specific surface area of about 416 m² g⁻¹ with specific pore volume of 0.65 cm³ g⁻¹ (Table S1, ESI[†]). These values upon metal immobilization (FeCl₃-imine@SiO₂) decreases significantly to 283 m² g⁻¹ and 0.43 cm³ g⁻¹ which is consistent with successful immobilization of iron onto silica matrix.

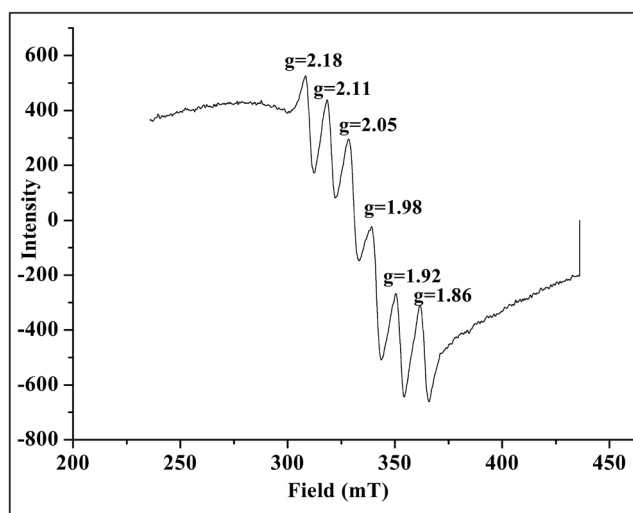


Fig. 4 ESR spectra of FeCl₃-imine@SiO₂ recorded at liquid nitrogen temperature.

The XRD patterns (Fig. 2) of the imine@SiO₂ material exhibit a broad peak centered at $2\theta = 22.48^\circ$ for silica which upon immobilization of FeCl₃ does not show any prominent shift ($2\theta = 22.13^\circ$), except a slight decrease in intensity. No crystalline phases related to metallic iron or iron oxides were observed in the spectra of FeCl₃-imine@SiO₂. However, a prominent peak at $2\theta = 35.9^\circ$ was observed which matched well with the XRD patterns of FeCl₃ or FeCl₃ doped polymer,¹⁵ suggesting the presence of FeCl₃ 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 FeCl₃-imine@SiO₂ displays six lines (Fig. 4) with an average *g* value of 2.01, typical for a Fe³⁺ 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 eV 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.^{14e,16}

Catalytic activity

The catalytic activity of the material FeCl₃-imine@SiO₂ 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

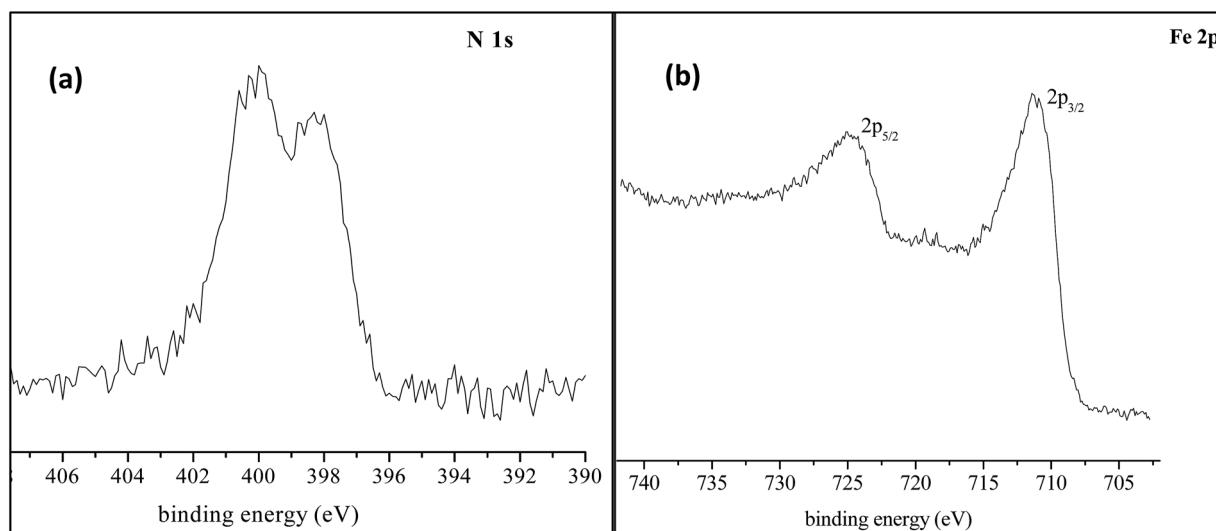


Fig. 5 XPS spectra of FeCl₃-imine@SiO₂.

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), O₂ (1 atm., bubbling), iron catalyst, water (6 mL). ^b GC yield.

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 O₂ (1 atm.) for 8 h moderate improvement in benzaldehyde formation was noticed (entry 2). On increasing temperature to 80 °C, significant improvement in the product yield was observed (entry 4). Interestingly, under similar experimental condition, homogeneous FeCl₃ as catalyst gave only 36% benzaldehyde (entry 5). 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 FeCl₃-imine@SiO₂ compared to homogeneous FeCl₃ 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 °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 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, O₂, water) will make this system a sustainable alternative to expensive platinum metal based catalysts.

Table 2 Oxidation of various alcohols in aqueous media catalyzed by FeCl₃-imine@SiO₂ using molecular O₂^a

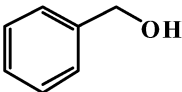
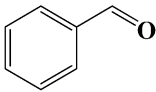
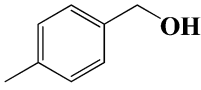
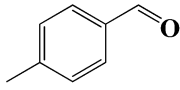
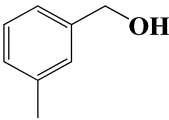
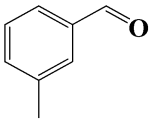
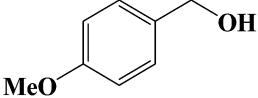
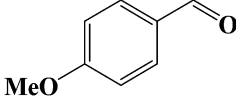
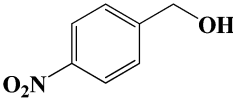
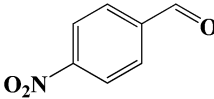
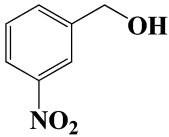
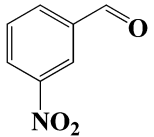
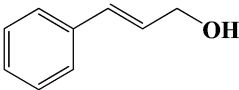
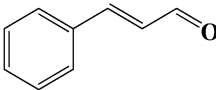
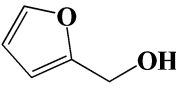
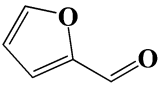
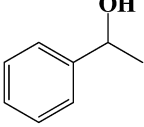
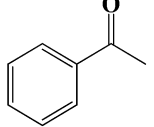
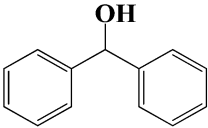
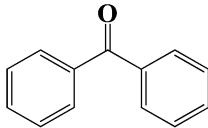
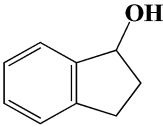
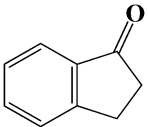
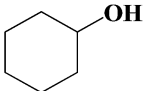
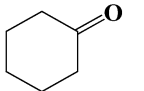
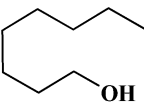
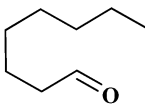
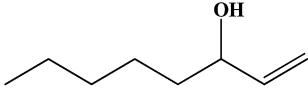
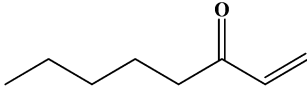
Entry	Substrate	Product	Time (h)	Yield ^{b,c} (%)
1			6	96 (93)
2			6	92 (88)
3			6	73 (68)
4			6	89 (86)
5			7	65 (63)
6			7	46 (44)
7			6	89 (87)
8			6	78
9			6	90 (87)
10			6	91 (90)
11			7	73
12			7	51
13			8	62

Table 2 (Contd.)

Entry	Substrate	Product	Time (h)	Yield ^{b,c} (%)
14			8	56

^a Reaction conditions: alcohol (1 mmol), O₂ (1 atm.), H₂O (6 mL), catalyst (2 mol%), 80 °C. ^b GC yield. ^c Isolated yield in the parenthesis.

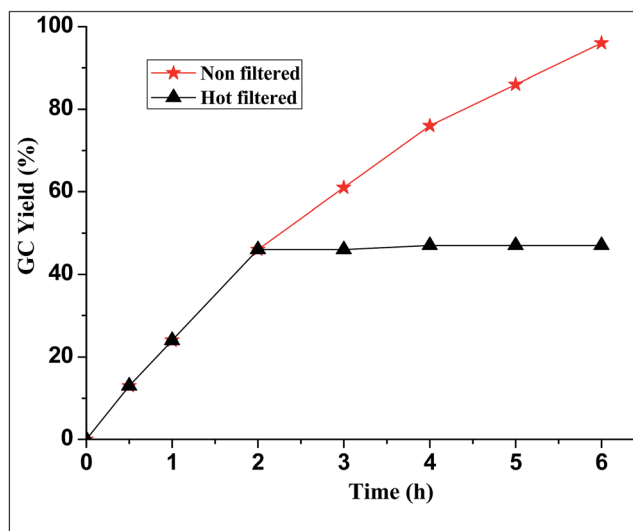


Fig. 6 Hot filtration test for the benzyl alcohol oxidation using FeCl₃-imine@SiO₂.

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References

- (a) R. A. Sheldon, *Catal. Today*, 2015, **247**, 4; (b) C. Parmeggiani and F. Cardona, *Green Chem.*, 2012, **14**, 547; (c) Z. Shi, C. Zhang, C. Tang and N. Jiao, *Chem. Soc. Rev.*, 2012, **41**, 3381; (d) Q. Cao, L. M. Dornan, L. Rogan, N. L. Hughes and M. J. Muldoon, *Chem. Commun.*, 2014, **50**, 4524; (e) M. J. Schultz and M. S. Sigman, *Tetrahedron*, 2006, **62**, 8227.
- (a) Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang and Y. Yang, *Chem. Soc. Rev.*, 2014, **43**, 3480; (b) S. E. Devis, M. S. Lde and R. J. Davis, *Green Chem.*, 2013, **15**, 17.
- M. Hajimohammadi, N. Safari, H. Mofakham and F. Deyhimi, *Green Chem.*, 2011, **13**, 991.
- (a) K. M. Gligorich and M. S. Sigman, *Chem. Commun.*, 2009, 3854; (b) Y. Ye, M. D. Johnson, T. Diao, M. H. Yates and S. S. Stahl, *Green Chem.*, 2010, **12**, 1180; (c) B. Karimi, S. Abedi, J. H. Clark and V. Budarin, *Angew. Chem., Int. Ed.*, 2006, **45**, 4776; (d) B. Karimi, A. Zamani, S. Abedi and J. H. Clark, *Green Chem.*, 2009, **11**, 109; (e) D. Sahu, C. Sarmah and P. Das, *Tetrahedron Lett.*, 2014, **55**, 3422; (f) S. F. J. Hackett, R. M. Brydson, M. H. Gass, I. Harvey, A. D. Newman, K. Wilson and A. F. Lee, *Angew. Chem., Int. Ed.*, 2007, **46**, 8593; (g) H. Wu, Q. Zhang and Y. Wang, *Adv. Synth. Catal.*, 2005, **347**, 1536; (h) X. Ye, M. D. Johnson, T. Diao, M. H. Yates and S. S. Stahl, *Green Chem.*, 2010, **12**, 1180; (i) B. Karimi, D. Elhamifar, J. H. Clark and A. J. Hunt, *Org. Biomol. Chem.*, 2011, **9**, 7420; (j) H. Yang, X. Han, Z. Ma, R. Wang, J. Liu and X. Ji, *Green Chem.*, 2010, **12**, 441; (k) C. M. A. Parlett, D. W. Bruce, N. S. Hondow, A. F. Lee and K. Wilson, *ACS Catal.*, 2011, **1**, 636; (l) J. Chen, Q. Zhang, Y. Wang and H. Wan, *Adv. Synth. Catal.*, 2008, **350**, 453; (m) B. Karimi, A. Zamani and J. H. Clark, *Organometallics*, 2005, **24**, 4695; (n) M. J. Schultz, C. C. Park and M. S. Sigman, *Chem. Commun.*, 2002, 3034.
- (a) A. Wusiman and C.-D. Lu, *Appl. Organomet. Chem.*, 2015, **29**, 254; (b) J. Olguin, H. Muller-Bunz and M. Albrecht, *Chem. Commun.*, 2014, **50**, 3488; (c) L. Liu, M. Yu, B. B. Wayland and X. Fu, *Chem. Commun.*, 2010, **46**, 6353.
- (a) K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2002, **41**, 4538; (b) Z.-W. Yang, X. Zhao, T.-J. Li, W.-L. Chen, Q.-X. Kang, X.-Q. Xu, X.-X. Liang, Y. Feng, H.-H. Duan and Z.-Q. Li, *Catal. Commun.*, 2015, **65**, 34; (c) D. Canseco-Gonzalez and M. Albrecht, *Dalton Trans.*, 2013, **42**, 7424.
- (a) P. Miedziak, M. Sankar, N. Dimitratos, J. A. Lopez-Sanchez, A. F. Carley, D. W. Knight, S. H. Taylor, C. J. Kiely and G. J. Hutchings, *Catal. Today*, 2011, **164**, 315; (b) Y. Li, Y. Gao and C. Yang, *Chem. Commun.*, 2015, **51**, 7721; (c) X. Yu, Y. Huo, J. Yang, S. Chang, Y. Ma and W. Huang, *Appl. Surf. Sci.*, 2013, **280**, 450; (d) R. H. Adnan, G. G. Andersson, M. I. J. Polson, G. F. Metha and V. B. Golovko, *Catal. Sci. Technol.*, 2015, **5**, 1323; (e) T. Wang, X. Yuan, S. Li, L. Zeng and J. Gong, *Nanoscale*, 2015, **7**, 7593; (f) C. D. Pina, E. Falletta, L. Prati and M. Rossi, *Chem. Soc. Rev.*, 2008, **37**, 2077.
- (a) Y. Hong, X. Yan, X. Liao, R. Li, X. Xu, L. Xiao and J. Fan, *Chem. Commun.*, 2014, **50**, 9679; (b) T. Lu, Z. Du, J. Liu, H. Ma and J. Xu, *Green Chem.*, 2013, **15**, 2215; (c) T. Wang, H. Shou,

- Y. Kou and H. Liu, *Green Chem.*, 2009, **11**, 562; (d) K. Kon, S. M. A. H. Siddiki and K.-i. Shimizu, *J. Catal.*, 2013, **304**, 63; (e) T. Wang, C.-X. Xiao, L. Yan, L. Xu, J. Luo, H. Shou, Y. Kou and H. Liu, *Chem. Commun.*, 2007, 4375.
- 9 (a) B. Xu, J.-P. Lumb and B. A. Arndtsen, *Angew. Chem., Int. Ed.*, 2015, **54**, 4208; (b) L. Vanoye, M. Pablos, C. D. Bellefon and A. Favre-Reguillon, *Adv. Synth. Catal.*, 2015, **357**, 739; (c) B.-T. Chen, K. V. Bukhryakov, R. Sougrat and V. O. Rodionov, *ACS Catal.*, 2015, **5**, 1313; (d) G. Zhang, C. Yang, E. Liu, L. Li, J. A. Golen and A. L. Rheingold, *RSC Adv.*, 2014, **4**, 61907; (e) P. Gamez, I. W. C. E. Arends, J. Reedijk and R. A. Sheldon, *Chem. Commun.*, 2003, 2414–2415; (f) G. Zhang, X. Han, Y. Luan, Y. Wang, X. Wen, L. Xu, C. Ding and J. Gao, *RSC Adv.*, 2013, **3**, 19255; (g) S. Samanta, S. Das, P. K. Samanta, S. Dutta and P. Biswas, *RSC Adv.*, 2013, **3**, 19455.
- 10 K. Junge, K. Schroder and M. Beller, *Chem. Commun.*, 2011, **47**, 4849.
- 11 S. E. Martin and D. F. Suarez, *Tetrahedron Lett.*, 2002, **43**, 4475.
- 12 W. Brackman and C. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, 1966, **85**, 257.
- 13 (a) N. Wang, R. Liu, J. Chen and X. Liang, *Chem. Commun.*, 2005, 5322; (b) A. Al-Hunaiti, T. Niemi, A. Sibaouih, P. Pihko, M. Leskela and T. Repo, *Chem. Commun.*, 2010, **46**, 9250; (c) J. Liu and S. Ma, *Org. Lett.*, 2013, **15**, 5150; (d) J. Liu and S. Ma, *Tetrahedron*, 2013, **69**, 10161; (e) M. Lenze and E. B. Bauer, *Chem. Commun.*, 2013, **49**, 5889; (f) S. Chakraborty, P. O. Lagaditis, M. Forster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones and S. Schneider, *ACS Catal.*, 2014, **4**, 3994; (g) C.-X. Miao, J.-Q. Wang, B. Yu, W.-G. Cheng, J. Sun, S. Chanfreau, L.-N. He and S.-J. Zhang, *Chem. Commun.*, 2011, **47**, 2697; (h) V. V. Namboodiri, V. Polshettiwar and R. S. Varma, *Tetrahedron Lett.*, 2007, **48**, 8839; (i) J. Liu and S. Ma, *Org. Biomol. Chem.*, 2013, **11**, 4186; (j) J. Liu and S. Ma, *Tetrahedron*, 2013, **69**, 10161; (k) D. Sahu, B. Banik, M. Borah and P. Das, *Lett. Org. Chem.*, 2014, **11**, 671.
- 14 (a) A. Rezaeifard, M. Jafarpour and A. Naeimi, *Catal. Commun.*, 2011, **16**, 240; (b) F. Rajabi, A. Pineda, S. Naserian, A. M. Balu, R. Luque and A. A. Romero, *Green Chem.*, 2013, **15**, 1232; (c) L. Geng, X. Zhang, W. Zhang, M. Jia and G. Liu, *Chem. Commun.*, 2014, **50**, 2965; (d) G. S. Machado, F. Wypych and S. Nakagaki, *Appl. Catal., A*, 2012, **413–414**, 94; (e) S. Fan, Y. Luan, J. Wang, H. Gao, X. Zhang and G. Wang, *J. Mol. Catal. A: Chem.*, 2015, **404**, 186; (f) D. Obermayer, A. M. Balu, A. A. Romero, W. Goessler, R. Luque and C. O. Kappe, *Green Chem.*, 2013, **15**, 1530; (g) M. Mahyari and A. Shaabani, *Appl. Catal., A*, 2014, **469**, 524; (h) F. Shi, M. K. Tse, M.-M. Pohl, J. Radnik, A. Bruckner, S. Zhang and M. Beller, *J. Mol. Catal. A: Chem.*, 2008, **292**, 28; (i) L. Wang, J. Li, X. Zhao, Y. Lv, H. Zhang and S. Gao, *Tetrahedron*, 2013, **69**, 6041; (j) A. Rezaeifard, M. Jafarpour and A. Naeimi, *Catal. Commun.*, 2011, **16**, 240; (k) P. Shejwalkar, N. P. Rath and E. B. Bauer, *Dalton Trans.*, 2011, **40**, 7617; (l) G. S. Machado, O. J. de Lima, K. J. Ciuffi, F. Wypych and S. Nakagaki, *Catal. Sci. Technol.*, 2013, **3**, 1094; (m) G. S. Machado, F. Wypych and S. Nakagaki, *Appl. Catal., A*, 2012, **413–414**, 94.
- 15 E. M. Abdelrazek, *Phys. B*, 2007, **400**, 26.
- 16 A. R. Silva, M. M. A. Freitas, C. Freire, B. de Castro and J. L. Figueiredo, *Langmuir*, 2002, **18**, 8017.