Green Chemistry

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Cite this: DOI: 10.1039/c3gc40110c

Aqueous oxidation of alcohols catalysed by recoverable iron oxide nanoparticles supported on aluminosilicates†

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Received 15th January 2013,
Accepted 22nd February 2013

DOI: 10.1039/c3gc40110c

www.rsc.org/greenchem

Supported iron oxide nanoparticles on aluminosilicate catalysts were found to be efficient and easily recoverable materials in the aqueous selective oxidation of alcohols to their corresponding carbonyl compounds using hydrogen peroxide under both conventional and microwave heating. The protocol features an easy work-up, simplicity and the utilisation of mild reaction conditions as well as high selectivity toward aldehydes is highly advantageous compared to alternatively reported methodologies. The supported iron oxide nanoparticles could be easily recovered from the reaction mixture and reused several times without any loss in activity. ICP-MS results proved that there is no metal leaching observed, demonstrating the stability of the catalyst under the investigated conditions.

Introduction

Transition metal nanoparticles (NPs) have recently been of scientific and technological interest to develop readily available, cheaper and more efficient catalysts as alternatives to traditionally employed noble metal catalysts in several catalytic processes.[1] Iron oxide NPs have been recently explored as catalysts for a range of processes including oxidations,[1–3] C–C and C-heteroatom couplings,[4] alkylations,[5] and alkene production from synthesis gas.[6] Their stabilization onto supports *via* alternative methodologies including microwave irradiation (MWI), ultrasounds (US) and ball-mill (BM) are some of the most appealing approaches for the design of well dispersed, small size nanoparticles with enhanced catalytic applications.[2,7]

The selective oxidation of alcohols to their corresponding aldehydes or ketones is a relevant process in synthetic organic chemistry because the products obtained are valuable precursors or intermediates for the production of fine chemicals and pharmaceuticals.[8,9] These processes have been traditionally carried out with stoichiometric amounts of inorganic oxidants such as chromium(VI) and manganese(VII) reagents which are expensive, hazardous and generate great amounts of heavy-metal waste. The design of novel and innovative processes involving environmentally benign oxidants such as H_2O_2 or O_2 (which generate as much as water as a unique reaction byproduct) is highly desirable from both environmental and economic viewpoints.

A range of catalytic systems have been reported to be active in the oxidation of alcohols with H_2O_2. Heterogeneous catalysts based on transition metal oxides[10–15] and noble metals[16–18] have been previously utilised as oxidation materials. Among this wide variety of materials, iron oxide-based materials emerged as green catalytic alternatives due to their low toxicity, abundance and interesting activities that allow the utilisation of mild reaction conditions.[19] Low-loaded supported iron oxide-nanoparticles have also been successfully utilised in microwave-assisted protocols involving production of oxidation products from alcohols.[3,20]

Furthermore, the combination of iron oxide nanoparticles as catalysts in oxidation technologies performed in water offers an additional bonus designing safer and more environmentally friendly processes. Indeed the proposed aqueous approach facilitates the separation of aldehyde and/or ketone products (typically with low solubility in water) that spontaneously separate out from the aqueous phase in contrast to classical methodologies (which utilise organic solvents and require distillation or tedious work-up protocols to separate reaction products).

In continuation of our recent endeavors aimed at the development of heterogeneously catalysed methodologies based on the use of supported iron oxide nanoparticles,[3,5,20] herein we describe a simple and efficient methodology for the mild aqueous oxidation of alcohols to carbonyl compounds with a green oxidant such as H_2O_2. In this work, we have compared reactions carried out both under conventional and microwave

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3gc40110c

heating as well as two different aluminosilicate supports for iron oxide nanoparticles, namely Al-MCM-41 and Al–SBA-15, fully characterised in previous studies.[21]

Experimental

Preparation of catalysts

Al-MCM-41 and Al-SBA-15 supports were prepared as reported by the group in previous work.[21] Tetraethoxyorthosilicate (TEOS) and aluminum isopropoxide were utilised as silica and alumina sources, respectively. Fe oxide nanoparticles were subsequently deposited on the pre-formed aluminosilicate supports by means of a simple microwave-assisted methodology similarly reported for a series of metals and metal oxide nanoparticles.[3,5,7,22] In a typical preparation, 2 g of aluminosilicate was suspended in 20 mL water to which a solution of 1 g of the iron precursor ($FeCl_2 \cdot 4H_2O$) in 2 mL ethanol was added. The mixture was microwaved in a CEM-DISCOVER focalised microwave reactor at 150 W (*ca.* 120 °C, maximum temperature achieved) for 15 min. The final catalyst was thoroughly washed with ethanol and acetone, dried overnight at 100 °C and finally calcined (4 h) at 400 °C under air. The iron loading in both materials was *ca.* 0.5 wt% (Table 1).

Characterisation of materials

X-Ray diffraction patterns were recorded on a Siemens D-5000 (40 kV, 30 mA) diffractometer with Cu K_α radiation ($\lambda = 1.54$ Å). Diffractograms were collected at 0.5 min^{-1} in the $10° < 2\theta < 80°$ range.

XPS measurements were performed in a ultra-high vacuum (UHV) multipurpose surface analysis system (SpecsTM model, Germany) operating at pressures $<10^{-10}$ mbar using a conventional X-ray source (XR-50, Specs, Mg–Kα, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. The survey and detailed Fe high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum ($<10^{-6}$ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. Deconvolution curves for the XPS spectra were obtained using software supplied by the spectrometer manufacturer.

ICP-MS analysis was conducted at the Servicios Centrales de Apoyo a la Investigación (SCAI) from Universidad de Cordoba using an ICP-MS ELAN-DRC-e (Perkin Elmer). Fe was extracted from materials upon treatment with an HNO_3–HCl–HF mixture (5 mL, 2 : 2 : 1 ratio) and then subsequently analysed. A calibration curve was developed with several standards for quantitative purposes.

Table 1 Textural properties [surface area ($m^2\ g^{-1}$), pore size (nm) and pore volume ($mL\ g^{-1}$)], metal content (wt% Fe) and surface acidity [measured by using a gas chromatographic mode using pyridine (PY) and 2,6-dimethylpyridine (DMPY) as probe molecules at 300 °C] of synthesized iron oxide materials compared to their parent supports

Catalyst	Iron loading (wt%)	Surface area ($m^2\ g^{-1}$)	Pore size/volume ($nm\ mL^{-1}\ g^{-1}$)	Surface acidity at 300 °C ($\mu mol\ g^{-1}$) PY (total acidity)	DMPY (Bronsted acidity)
Al-MCM-41 (Si/Al = 30)	—	937	2.3/0.66	102	77
Fe/Al-MCM-41	0.54	970	2.3/0.67	265	102
Al-SBA-15 (Si/Al = 37)	—	747	8.0/0.65	82	61
Fe/Al-SBA-15	0.63	688	7.8/0.63	104	88

Typical procedure for selective oxidations of alcohols to carbonyl compounds (conventional heating)

In a typical oxidation reaction, 50% of aqueous H_2O_2 (0.3 mL) was added to a solution of the corresponding alcohol (2 mmol) and Fe/aluminosilicate (0.05 g) in water. The mixture was stirred at 80 °C for the various reaction times as indicated in Table 1. The reaction was followed by GC and GC/MS as well as by flash chromatography (isolated products). The catalyst was separated by filtration, washed with ethyl acetate and heated at 70 °C prior to its reuse in the next reaction. The combined filtrate and ethyl acetate washing were then washed with water and the organic layer separated and dried over magnesium sulphate. The product was obtained after removal of the solvent. The identity and purity of all final products were additionally verified by elemental analysis as well as by ^1H and ^{13}C NMR (see selected examples from ESI†). H_2O_2 efficiency (%) was calculated as products (mol) per consumed H_2O_2 (mol) × 100. The decomposition of hydrogen peroxide was measured in the final reaction mixture by running it into an acidified solution of potassium iodide, titrating the iodine produced with a solution of thiosulphate using a starch indicator.

Typical procedure for selective oxidations of alcohols to carbonyl compounds (microwave irradiation)

In a typical microwave-heated reaction, 2 mmol of the corresponding alcohol, 0.3 mL of 50% aqueous H_2O_2 and 0.05 g catalyst in 2 mL water or acetonitrile were microwaved for a period of time between 1 and 15 min at 300 W (maximum temperature reached 120 °C, average temperature 80 °C). Samples were filtered off and subsequently analysed by GC and GC/MS.

Reuse experiments (conventional heating)

Upon completion of the first reaction to afford a quantitative yield of the corresponding aldehyde or ketone, the catalysts were recovered by filtration, washed and finally dried at 100 °C. A new reaction was then performed with fresh solvents and reactants under identical conditions.

Results and discussion

Table 1 summarises the characterisation data of the synthesized catalysts from the present work. Iron containing materials featured high surface areas (>650 m^2 g^{-1}) and pore volumes (>0.6 mL g^{-1}), with pore sizes of *ca.* in the 2 to 8 nm range depending on the type of support (Table 1). Iron content in the synthesized materials as measured by ICP/MS was found to be around 0.5–0.6 wt%, with average iron oxide nanoparticle sizes in the 7–8 nm range.[21] XRD of the materials confirmed the presence of the hematite phase (Fe_2O_3, JCPDS card 39-0664) visible even at low metal loadings for Fe/Al-SBA-15 (Fig. 1), which was also confirmed by XPS measurements (typical Fe^{3+} bands at BE 714 ($Fe_{2p3/2}$) and 725 eV ($Fe_{2p1/2}$), Fig. 2).[21] Full characterisation of the materials seemed to point out a synergetic effect Fe/Al which was found particularly useful in the microwave-assisted selective oxidation of benzyl alcohol to benzaldehyde catalysed by iron oxide nanoparticles supported on aluminosilicates as compared to similar nanoentities supported on purely siliceous mesoporous MCM-41 and SBA-15 (fact that could be in principle extended to activated alkenes; *i.e.* styrene).[21,22] A comprehensive study on the observed potential Fe/Al synergy of these materials is currently under investigation by means of a range of techniques including Mossbauer spectroscopy, EXAFS and XAS. Preliminary results seem to point out the existence of electronic-like perturbances, with XAS spectra having significant differences in the low energy domain.[23]

In view of these reported preliminary findings, the catalytic activity in the oxidation of alcohols could in principle be favoured for iron oxide aluminosilicate materials due to the observed beneficial Fe/Al synergy. Results for the catalytic oxidation of a range of alcohols using Fe/Al-MCM-41 and Fe/Al-SBA-15 materials under microwave irradiation have been included in Table 2.

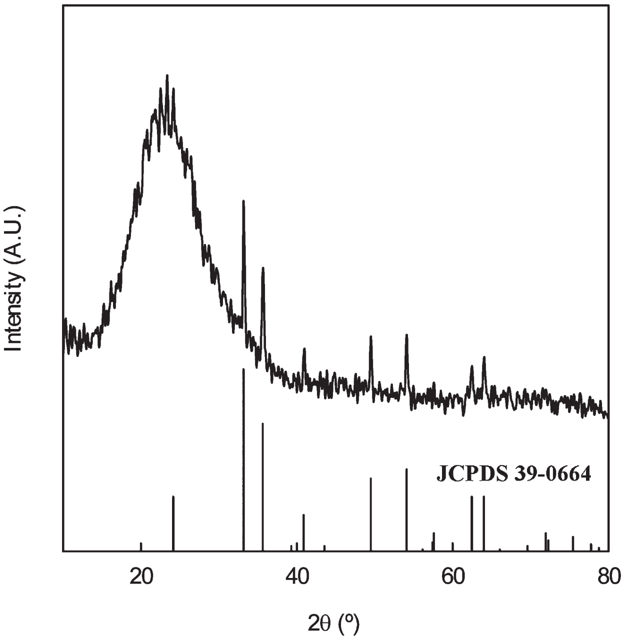


Fig. 1 XRD pattern of Fe/Al-SBA-15. Bottom lines correspond to the JCPDS 39-0664 card of hematite phase Fe_2O_3.

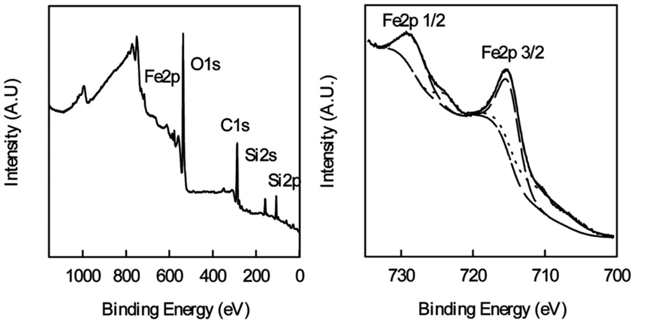
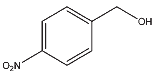
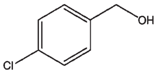
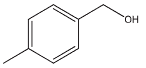
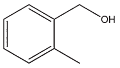
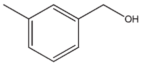
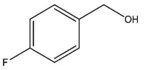
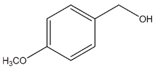
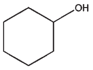
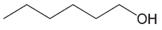
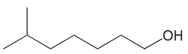
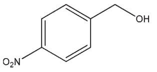
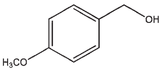
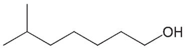


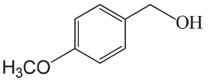
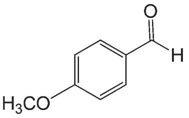
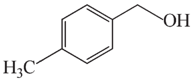
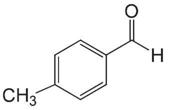
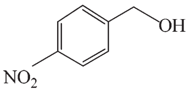
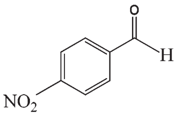
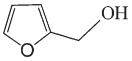
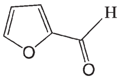
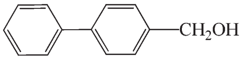
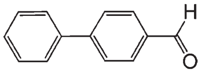
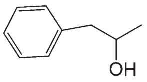
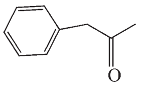
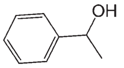
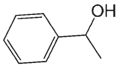
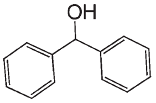
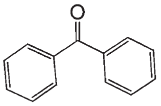
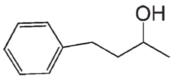
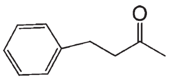
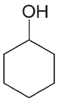
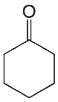
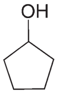
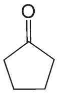
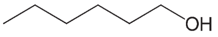
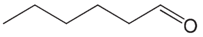
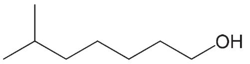
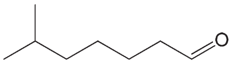
Fig. 2 XP spectra of survey (left figure) and Fe2p (right figure) of Fe/Al-SBA-15.

Table 2 Microwave-assisted oxidation of alcohols using Fe/aluminosilicate catalysts[a]

Entry	Substrate	Catalyst	Conversion (mol%)	Sel. Product (mol%)
1		Fe/Al-MCM-41	69	>99
2		Fe/Al-SBA-15	88	>99
3		Fe/Al-MCM-41	41	92
4		Fe/Al-SBA-15	53	80
5		Fe/Al-MCM-41	56	96
6		Fe/Al-SBA-15	51	>99
7		Fe/Al-MCM-41	46	93
8		Fe/Al-SBA-15	45	90
9		Fe/Al-MCM-41	47	94
10		Fe/Al-SBA-15	45	97
11		Fe/Al-MCM-41	50	90
12		Fe/Al-SBA-15	52	87
13		Fe/Al-MCM-41	57	94
14		Fe/Al-SBA-15	53	93
15		Fe/Al-MCM-41	37	>99
16		Fe/Al-SBA-15	37	>99
17		Fe/Al-MCM-41	15	68[b]
18		Fe/Al-SBA-15	13	63[b]
19		Fe/Al-MCM-41	<15	65[b]
20		Fe/Al-SBA-15	<15	63[b]
21[c]		Fe/Al-MCM-41	>95	>99
22[d]		Fe/Al-SBA-15	>97	90
23[d]		Fe/Al-SBA-15	45	68[b]

[a] Reaction conditions: 2 mmol substrate, 0.3 mL H_2O_2 50%, 0.05 g cat., 2 mL acetonitrile, 300 W, 3 min reaction. [b] The difference of 100 in selectivity corresponds to the main by-products generated in the reaction, dihexylether and di-isoctylether. [c] 15 min microwave irradiation. [d] 30 min microwave irradiation.

Table 3 Selective oxidation of a range of alcohols to the corresponding carbonyl compounds using Fe/Al-SBA-15 catalysts

Entry	Substrate	Product	Time[a] (h)	Yield[a] (%)
1			4 (0.25)	99 (98)
2			4 (0.25)	99 (95)
3			6 (0.25)	97 (97)
4			4 (0.5)	98 (99)
5			6 (0.5)	99 (96)
6			7 (0.5)	95 (98)
7			7 (0.5)	99 (96)
8			12 (0.5)	98 (90)
9			12 (1)	92 (88)
10			12 (0.5)	94 (98)
11			12 (0.5)	96 (90)
12			12 (0.5)	<30 (40)
13			12 (0.5)	<10 (25)

Reaction conditions: 2 mmol substrate, 0.3 mL H_2O_2 50%, 0.05 g cat., 2 mL water, heating at 80 °C or microwave irradiation (300 W, maximum temperature reached 120 °C, average experiment temperature 80 °C). [a] Numbers in brackets correspond to times of the reaction and yields under microwave irradiation.

In principle, the reaction seemed to work under very mild conditions (80 °C, 3 min microwave irradiation in acetonitrile as a solvent) to a reasonable extent with substituted benzyl alcohols, providing moderate to good yields to target aldehyde/ketone products with very high selectivities.

Catalysts seemed to efficiently work both in the presence of electron-donating or electron-withdrawing substituents as well as in less sterically-favoured positions within the aromatic ring (Table 2, entries 7 to 10). The protocol was also amenable to cyclic alcohols (Table 2, entries 15 and 16), although low conversions were observed for linear alcohols (Table 2, entries 17 to 20). Increasing the time of the reaction to 15–30 min, almost quantitative conversion was obtained for most substrates (Table 2, entries 21 and 22) with the exception of linear alcohols that only provided moderate conversions (max. 40–50%; Table 2, entry 23). In the case of linear alcohols, an interesting acid-catalysed intermolecular etherification between 2 molecules of the linear alcohol takes place, competing with the expected oxidation process under the investigated reaction conditions. This is an important reaction that is currently under consideration as alkylethers and derivatives can have relevant industrial applications.[24]

Interestingly, the use of the Fe/Al-SBA-15 seemed to provide slightly improved conversions to target products for certain examples (particularly for electron-withdrawing substituents) with respect to Fe/Al-MCM-41. The difference in acidity between both materials, indication of the slightly different interactions between Fe and Al in the systems, is believed to be responsible for the different activities, which is currently under deeper and thoughtful investigation.[23]

Selecting Fe/Al-SBA-15 as a catalyst, the scope of the reaction was extended to a series of substrates including mono- and di-aromatic alcohols, furfuryl alcohol (an interesting and potentially derived biomass chemical) as well as cyclic alcohols such as cyclohexanol and cyclopentanol. The reaction medium was also switched to water and reactions were compared under both conventional and microwave heating. Results summarised in Table 3 demonstrate the high oxidation activity of the supported iron oxide nanoparticle system, which is able to provide isolated yields in excess of 90% for most of the substrates studied.

The only exception of the protocol was linear alcohols due to the low inherent conversion obtained for these systems as well as to the competing acid-promoted chemistry observed in such cases. In any case, the reaction system was fully compatible with aqueous media under the investigated conditions using the proposed system. In all cases, the hydrogen peroxide efficiency was over 90%, indicating that no significant decomposition of hydrogen peroxide in the systems takes place under the investigated conditions (H_2O_2 is only consumed as an oxidisiding agent), in good agreement with previous results from the group in similar oxidation chemistries.[20,22]

The utilised catalyst was found to be fully reusable under aqueous conditions as clearly shown in Fig. 3, preserving over 90% of its initial activity after 5 cycles. ICP-MS analysis of the reaction mixture indicated no detectable iron leaching (<0.05 ppm) under the investigated conditions, in good agreement with reusability data and previous work from the group that already proved the high stability and activity of similar supported iron oxide nanoparticle systems.[22] In this particular case, the iron oxide nanoparticle species seemed to be particularly stabilised by Al from the mesoporous aluminosilicate network.[21]

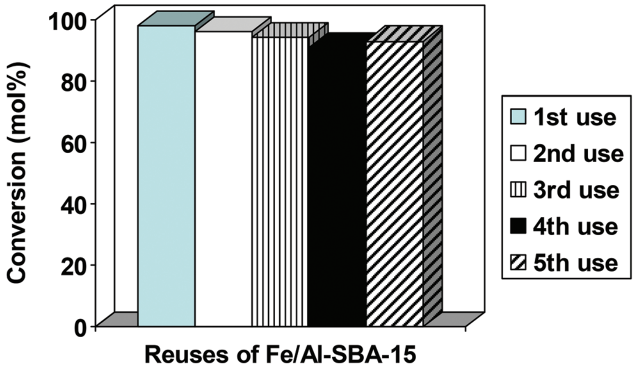


Fig. 3 Reusability studies of Fe/Al-SBA-15 in the aqueous oxidation of benzyl alcohol under conventional heating. Reaction conditions: 2 mmol benzyl alcohol, 0.3 mL H_2O_2 50%, 0.05 g catalyst, 2 mL water, 80 °C, 4 h.

Conclusions

We report a facile route for the synthesis of the carbonyl compounds using supported iron oxide nanoparticles on aluminosilicate materials as efficient, highly selective and active catalysts in aqueous hydrogen peroxide under both conventional and microwave heating. Materials could be easily recovered from the reaction mixture and used five times without any significant activity loss and no metal leaching was observed during the course of the reuses. We envisage the extension of this highly efficient system to related aqueous phase transformations including oxidation of biomass-derived platform molecules (*e.g.* sugars and polyols) to high-added value chemicals, currently under investigation in our laboratories.

Acknowledgements

Rafael Luque gratefully acknowledges support from the Spanish MICINN *via* the concession of a RyC contract (ref. RYC-2009-04199) and funding under projects P10-FQM-6711 (Consejeria de Ciencia e Innovacion, Junta de Andalucia) and CTQ2011 28954-C02-02 (MICINN). Fatemeh Rajabi thanks Payame Noor University and Iran National Science Foundation (INSF) for financial support.

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