



**HAL**  
open science

## Microwave assisted benzyl alcohol oxidation using iron particles on furfuryl alcohol derived supports

Floriane Mangin, Pepijn Prinsen, Alfonso Yopez, Muhammad Rehan Hasan Shah Gilani, Guobao Xu, Christophe Len, Rafael Luque

► **To cite this version:**

Floriane Mangin, Pepijn Prinsen, Alfonso Yopez, Muhammad Rehan Hasan Shah Gilani, Guobao Xu, et al.. Microwave assisted benzyl alcohol oxidation using iron particles on furfuryl alcohol derived supports. *Catalysis Communications*, 2017, 104, pp.67 - 70. 10.1016/j.catcom.2017.10.003 . hal-04269411

**HAL Id: hal-04269411**

**<https://hal.science/hal-04269411>**

Submitted on 3 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## Short communication

## Microwave assisted benzyl alcohol oxidation using iron particles on furfuryl alcohol derived supports

Floriane Mangin<sup>a</sup>, Pepijn Prinsen<sup>b</sup>, Alfonso Yezpe<sup>b</sup>, Muhammad Rehan Hasan Shah Gilani<sup>c</sup>, Guobao Xu<sup>d</sup>, Christophe Len<sup>a,\*</sup>, Rafael Luque<sup>b,\*</sup>

<sup>a</sup> Sorbonne Universités, Université de Technologie de Compiègne, Centre de Recherche Royallieu, CS 60 319, F-60203 Compiègne Cedex, France

<sup>b</sup> Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, CtraNnal IV, Km. 396, E-14014 Córdoba, Spain

<sup>c</sup> Department of Chemistry, Government College University of Faisalabad, Layyah Campus, Layyah, Pakistan

<sup>d</sup> The State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, Jilin, China

## ARTICLE INFO

## Keywords:

Benzyl alcohol

Oxidation

Iron catalyst

Furfuryl alcohol derived support

## ABSTRACT

This work compares the catalytic activity of iron catalysts supported on porous furfuryl alcohol derived resins for the selective conversion of benzyl alcohol to benzaldehyde using hydrogen peroxide as the oxidant and assisted by microwave irradiation. The catalysts were prepared mechanochemically by ball-milling in the dry state. Initial results showed that the pressure in the reaction medium and the oxidant load are essential to achieve significant conversions. An apparent minimum catalyst load of 0.05 mol% Fe was required for significant reactivity at 132 °C.

## 1. Introduction

Selective oxidations of organic compounds are key transformations in organic synthesis. Whereas in the past strong oxidants (e.g. chrome, manganese and permanganate derivatives), *N*-chlorosuccinimide or hypervalent iodine were used for the oxidation of organic compounds [1–3], currently oxidants including hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), *tert*-butyl hydroperoxide (tBu-OOH) and molecular oxygen (O<sub>2</sub>) are employed to reduce the environmental impacts (as water is in theory the only by-product). The main advantage of using H<sub>2</sub>O<sub>2</sub> over O<sub>2</sub> is that it is a liquid, miscible with water and relatively easy to handle. On the other hand, H<sub>2</sub>O<sub>2</sub> can undergo radical-induced decomposition to H<sub>2</sub>O and O<sub>2</sub>, often catalyzed by metallic impurities [4] and therefore it needs to be added in excess amounts. Alcohols are further classified in aliphatic, allylic, benzylic and heterocyclic groups, as well as in primary, secondary and tertiary alcohols. In general, aliphatic alcohols are more difficult to oxidize [5].

Selective catalytic oxidation has been the subject of numerous publications, in particular from alkanes and olefins (Wacker process) [6]. When starting from alcohols, Ru complexes perform very well [7–9]. Many oxidation catalysts consist of a transition metal, which in reduced form transfers electrons to the substrate and which then is subsequently re-oxidized by the stoichiometric oxidant. However, this process is kinetically constrained and therefore decomposition of the

reduced metal may occur, e.g. formation of ‘palladium black’ [10]. Electron transfer mediators (ETMs) were introduced to overcome these limitations, e.g. CuCl in the conversion of ethylene to acetylene with Pd (II) and air [6]. Another example is benzoquinone which acts as the hydrogen acceptor (oxidant) in the dehydrogenation of benzyl alcohol to benzaldehyde using a homogeneous RuCl(OAc)(PPh<sub>3</sub>)<sub>3</sub> catalyst and Co(salophen) as co-catalyst to re-oxidize the hydroquinone formed, with benzaldehyde yields ca. 60% and turnover number (TON) up to 70 [9]. This catalytic system was also applied for other alcohols, including secondary ones. Besides Pd and Ru, other metals such as Cu and Fe were introduced for aerobic oxidations. However, the catalytic systems that combine Cu with ETMs are rather limited, mainly because they require stoichiometric amounts of base (e.g. KOtBu) [11] or other co-catalysts, e.g. 2,2,6,6-(tetramethylpiperidin-1-yl)oxyl (TEMPO) [12].

When using H<sub>2</sub>O<sub>2</sub> as the oxidant, various metal complexes based on V, Mo, Ti, W, Ru, Os, Pt and Fe have been proposed as catalysts, as well as various (layered) mixed oxides [13]. Whereas homogeneous catalysts (assisted by co-catalysts) are much more effective in the activation of H<sub>2</sub>O<sub>2</sub>, heterogeneous catalysts in turn can be recycled. Studies that use heterogeneous iron catalysts for selective oxidation are limited. Fifteen years ago, FeBr<sub>3</sub> (20 mol%) was proposed for the oxidation of menthol in the presence of 5 eq. of H<sub>2</sub>O<sub>2</sub> [14]. In acetonitrile solvent, menthone yields ca. 92% were reported after 24 h at room temperature. With 15 mol% catalyst, the yield dropped to 72%. Five years later, a catalytic

\* Corresponding authors.

E-mail addresses: [christophe.len@utc.fr](mailto:christophe.len@utc.fr) (C. Len), [q62alsor@uco.es](mailto:q62alsor@uco.es) (R. Luque).

system for the oxidation of secondary benzylic alcohols was reported, consisting of small amounts of  $\text{FeCl}_3$  (2 mol%) with aqueous *t*Bu-OOH (3 eq.) as oxidant in pyridine at 82 °C, with excellent yields (ca. 90%) after 24 h [15]. When using  $\text{H}_2\text{O}_2$  instead of *t*Bu-OOH, the yields were much lower. The authors attributed this to the decomposition of the oxidant on Fe(III). No clear relationship was observed with the iron oxidation state;  $\text{Fe}(\text{ClO}_4)_3$  gave the best results among others ( $\text{Fe}(\text{ClO}_4)_2$ ,  $\text{FeCl}_2$  and  $\text{Fe}(\text{acac})_3$ ).  $\text{FeCl}_3$  was chosen for safety issues (risks related with  $\text{ClO}_4^-$  species). Iron oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ) species also have been reported as effective oxidation catalyst of 0.2 M benzyl alcohol using 1 eq. of  $\text{H}_2\text{O}_2$  [16]. When using 1 mol% catalyst, a conversion ca. 30% with 97% selectivity to benzaldehyde was reported after 12 h at 75 °C. Note that the  $\text{H}_2\text{O}_2$  was added continuously in small amounts over the total reaction course, which can improve the oxidant atom efficiency. Most importantly, conversions ca. 86% were reported when using catalyst nanofractions (3–5 nm) instead of bulky fractions (20–50 nm). However, the selectivity to benzaldehyde dropped to 35%. The authors stated that when using nano  $\gamma\text{-Fe}_2\text{O}_3$ , quasi homogeneous catalyst conditions are approached.

Benzaldehyde is an important organic intermediate used in flavors such as almond and cherry and in various fragrances for soaps and toiletries. It is also used in the manufacture of pharmaceuticals such as ampicillin, pesticides such as dibenzoquat and in phenolbenzaldehyde resins for fire resistant materials. It can be synthesized by the hydrolysis of benzyl chloride or by the oxidation of toluene [17]. This work demonstrates the catalytic activity of small amounts of iron supported on furfuryl alcohol derived resinic materials for the oxidation of benzyl alcohol to benzaldehyde in acetonitrile, using 1.5–2.3 eq. of  $\text{H}_2\text{O}_2$  in relatively short reaction times using microwave irradiation.

## 2. Experimental

### 2.1. Synthesis of furfuryl alcohol based resins

The P500 material was prepared by adding 1.00 g (885  $\mu\text{L}$ ) furfuryl alcohol in 1 L of 5 M  $\text{H}_2\text{SO}_4$  aqueous solution at 20 °C, causing a color change to brown. The suspension was left stirring overnight. Subsequently, the resin particles were three times washed with distilled water and separated by centrifugation (10,000 rpm, 4 °C, 40 min). The P420 resin material was prepared identically, but instead 0.01 g (10  $\mu\text{L}$ ) of furfuryl alcohol was added to 990  $\mu\text{L}$  of water, followed by the addition of 10 mL 9 M HCl. A rapid change of color was observed upon the addition of furfuryl from yellow to violet. The mixture was stirred for 1 h. The resin spheres were purified with distilled water and separated by centrifugation (12,000 rpm, 4 °C, 40 min).

### 2.2. Mechanochemical synthesis of supported nanoparticles

The supported iron catalysts were prepared mechanochemically in dry conditions: 1.0 g solid support and 0.020 g  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (equivalent to 0.5 wt% Fe) were milled together in a planetary ball mill (Retsch 100) under previously reported optimized conditions (350 rpm, 10 min) [18]. The solids were recovered and heated overnight at 120 °C in air.

### 2.3. Catalytic activity in open vessel

Microwave experiments were carried out using a CEM-DISCOVER model with PC control. In a 50 mL round-bottom flask equipped with a cooling system, benzyl alcohol (0.2 mL, 1.92 mmol) was solubilized in acetonitrile (2 mL), followed by the addition of 1.5 or 2.3 eq. oxidant (0.3 mL of a 33 or 50 w/v% aqueous  $\text{H}_2\text{O}_2$  solution) and the catalyst. The reaction was stirred and heated with microwave irradiation at 300 W, achieving temperatures in the 90–132 °C range, as measured by an infra-red probe. After a certain time, the reaction was stopped and upon cooling the mixture was immediately filtered off and subsequently analyzed by GC-FID.

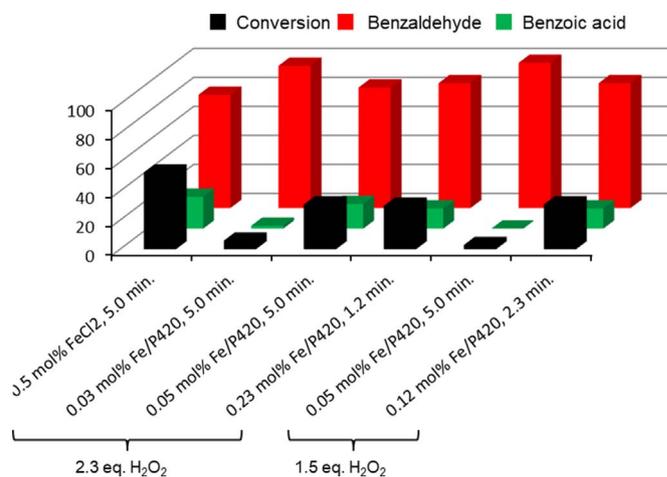


Fig. 1. Benzyl alcohol conversion and selectivity using Fe nanoparticles supported on P420 resin as compared to free dissolved  $\text{FeCl}_2$ , using 1.5 and 2.3 eq.  $\text{H}_2\text{O}_2$ .

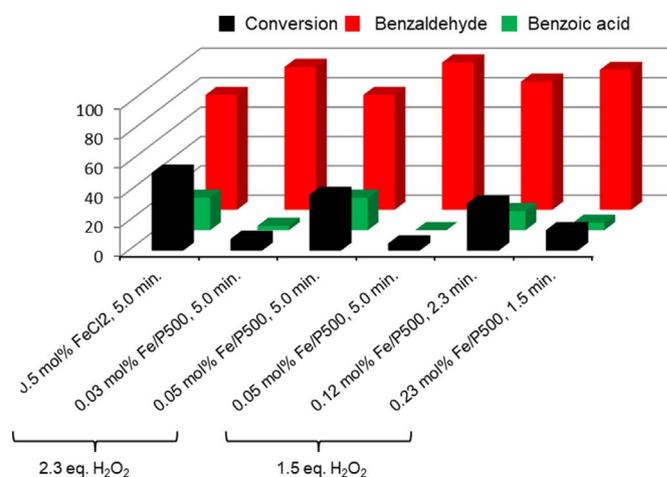


Fig. 2. Benzyl alcohol conversion and selectivity using Fe nanoparticles supported on P500 as compared to dissolved  $\text{FeCl}_2$ , using 1.5 and 2.3 eq.  $\text{H}_2\text{O}_2$ .

### 2.4. Catalytic activity in closed vessel

Microwave experiments were carried out using a CEM-DISCOVER model with PC control. For the experiments performed in closed vessels, the protocol was identically as in the open vessel experiments, except that a pressure controlled closed vessel was used under continuous stirring. The reaction mixtures were stirred and irradiated at 300 W, achieving temperatures in the 90–132 °C range, as measured by an infra-red probe. The autogenous pressure ranged from 5 to 17 bar, with an average of 16 bar.

### 2.5. Product analysis

The filtrates collected from the reaction mixtures were analyzed by GC, using an Agilent 6890N GC model equipped with a Supelco 2-8047-U (60 m  $\times$  25  $\mu\text{m}$   $\times$  25  $\mu\text{m}$  i.d.) capillary column and an FID detector. The temperature of the column was ramped at 10 °C  $\text{min}^{-1}$  to 100 °C (0 min hold time), then at 20 °C  $\text{min}^{-1}$  to 120 °C (20 min hold time) and finally to 180 °C at 20 °C  $\text{min}^{-1}$  (10 min hold time). The nitrogen gas flow was set at 1.8 mL  $\text{min}^{-1}$ . The retention times benzyl alcohol, benzaldehyde and benzoic acid were 1.80, 1.35 and 3.20 min, respectively.

**Table 1**Comparison of the activity of iron particles supported on P500 with other (supported) metal catalysts for the benzyl alcohol oxidation using H<sub>2</sub>O<sub>2</sub> in acetonitrile.

Entry	Cat. (mol%)	H <sub>2</sub> O <sub>2</sub> (eq.)	Conditions	Time (h)	Yield (%)	TON	Ref.
1	FeBr <sub>3</sub> (20.0)	5.0	0.20 M, 25 °C	24	92	5	[20]
2	Fe <sup>3+</sup> /mont-morillonite K10 (1.8)	4.0	1.19 M, 65 °C	4	30	54	[21]
3	Nano-γ-Fe <sub>2</sub> O <sub>3</sub> (1.0)	1.5 <sup>a</sup>	Solvent-free, 75 °C	12	48	12	[16]
4	SiO <sub>2</sub> @APTES-Pd (0.2)	5.0	0.10 M, 80 °C	2	98	490	[22]
5	Fe/MCM-41 (0.15)	2.2	0.77 M, 80 °C	1	24	159	[23]
6	CpMo(CO) <sub>3</sub> (C≡CPh) (20.0)	20.0	Solvent-free, 80 °C	8	79	396	[24]
7	CpMo(CO) <sub>3</sub> (C≡CPh) (20.0)	2.0	0.72 M, 80 °C	8	39	39	[24]
8	Fe (0.5)	2.3	0.77 M, 132 °C	0.08	44	83	This work
9	Fe/P500 (0.05)	2.3	0.77 M, 132 °C	0.08	30	593	This work

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> was added continuously over the reaction course.

### 3. Results and discussion

#### 3.1. Catalytic activity in open vessel

Initially, the experiments were conducted in open vessels. Whatever the nature of the oxidant (H<sub>2</sub>O<sub>2</sub> or *t*Bu-OOH), the amount of catalyst (25, 50 or 100 mg) and the reaction time (5 or 30 min), no significant benzyl alcohol conversion was observed (< 5% in all cases). These results show that high temperature and pressure are required for the reaction to proceed.

#### 3.2. Catalytic activity in closed vessel

First, the free dissolved iron catalyst (0.5 mol% FeCl<sub>2</sub>) was tested for the oxidation of 0.77 M benzyl alcohol with 2.3 eq. H<sub>2</sub>O<sub>2</sub> in acetonitrile. After 5 min microwave irradiation, 53% conversion with 78% selectivity to benzaldehyde was observed. When using an iron catalyst supported on P420 resin, but with 10 times lower Fe content (0.05 mol%), the same selectivity was obtained in the product mixture, but with 22% lower conversion (Fig. 1). Similar results were observed for the iron catalyst supported on the P500 resin (Fig. 2). This was the apparent threshold catalyst load (with 0.03 mol% Fe there was only 6–8% conversion). On the other hand, when the catalyst load was increased to 0.12 mol% or higher, similar conversion and selectivity were obtained, but in 3–4 times shorter reaction times. The question whether conversion increased further in time in those experiments or not remains open, as the reaction was aborted when the pressure limit of the vessel in the microwave equipment was reached. This shows that the as synthesized catalysts were very active in the activation of H<sub>2</sub>O<sub>2</sub>, or to state in another way (i.e. when metal oxides are the actual kinetic active catalytic centers [19]), they were re-oxidized very efficiently with H<sub>2</sub>O<sub>2</sub>.

Next to the catalyst load, the most determining factor was the excess amount of oxidant. The selectivity could be improved using less H<sub>2</sub>O<sub>2</sub> (1.5 instead of 2.3 eq.). This effect is most noticeable in the case of 0.05 mol% Fe (see Figs. 1 and 2). For this reason, the continuous addition of H<sub>2</sub>O<sub>2</sub> might be beneficial to the selectivity in the final reaction mixture, by preventing further oxidation to benzoic acid [16]. Table 1 compares the activity with that of previously reported catalysts for the oxidation of benzyl alcohol with H<sub>2</sub>O<sub>2</sub>. The results clearly show the potential of the presented supported iron catalysts, as the TON was the highest among the studies compared, even after short reaction times, enabled by the use of microwave irradiation.

### 4. Conclusions

This work demonstrates that small amounts of mechanochemically prepared iron particles on a porous furfuryl alcohol derived resin support were very active for the oxidation of benzyl alcohol using 1.5–2.3 eq. of hydrogen peroxide. The use of microwave irradiation allowed the reaction to proceed very fast. An apparent minimum catalyst load of 0.05 mol% Fe was required for significant reactivity. At

this catalyst load and using 2.3 eq. of oxidant, similar selectivity to benzaldehyde was observed as compared to 0.5 mol% of free dissolved FeCl<sub>2</sub> catalyst, however with 15–22% lower conversion.

### Acknowledgements

Rafael Luque gratefully acknowledges MINECO and FEDER funds for funding under project CTQ2016-78289-P.

### References

- [1] M.M. Heravi, D. Ajami, K. Tabar-Hydar, M. Ghassemzadeh, Remarkable fast microwave-assisted zeolite HZSM-5 catalyzed oxidation of alcohols with chromium trioxide under solvent-free conditions, *J. Chem. Res. Synop.* 5 (1999) 334–335.
- [2] A. Shaabani, P. Mirzaei, D. Lee, The beneficial effect of manganese dioxide on the oxidation of organic compounds by potassium permanganate, *Catal. Lett.* 97 (2004) 119–123.
- [3] R.A. Sheldon, J.K. Kochi, *Metal-catalyzed Oxidation of Organic Compounds*, Academic, New York, 1981.
- [4] J. Piera, J.-E. Bäckvall, Catalytic oxidation of organic substrates by molecular oxygen and hydrogen peroxide by multistep electron transfer—a biomimetic approach, *Angew. Chem. Int. Ed.* 47 (2008) 3506–3523.
- [5] C. González-Arellano, J.M. Campelo, D.J. Macquarrie, J.M. Marinas, A.A. Romero, R. Luque, Efficient microwave oxidation of alcohols using low-loaded supported metallic iron nanoparticles, *ChemSusChem* 1 (2008) 746–750.
- [6] A. Heumann, K.-J. Jens, M. Réglie, Palladium complex catalyzed oxidation reactions, in: K.D. Karlin (Ed.), *Progress in Inorganic Chemistry*, 4 John Wiley & Sons, Inc., Hoboken, NJ, USA, 1994.
- [7] K. Fujita, N. Tanino, R. Yamaguchi, Ligand-promoted dehydrogenation of alcohols catalyzed by Cp\* Ir complexes. A new catalytic system for oxidant-free oxidation of alcohols, *Org. Lett.* 9 (2007) 109–111.
- [8] J.B. Johnson, J.E. Bäckvall, Mechanism of ruthenium-catalyzed hydrogen transfer reactions. Concerted transfer of OH and CH hydrogens from an alcohol to a (cyclopentadienone)ruthenium complex, *J. Org. Chem.* 68 (2003) 7681–7684.
- [9] J.E. Bäckvall, R.L. Chowdhury, U. Karlsson, Ruthenium-catalyzed aerobic oxidation of alcohols via multistep electron transfer, *J. Chem. Soc. Chem. Commun.* (1991) 473–475.
- [10] R. Jira, Oxidation of olefins to carbonyl compounds, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1 Wiley-VCH, Weinheim, 2002, pp. 386–405.
- [11] I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Copper-catalyzed oxidation of alcohols to aldehydes and ketones: an efficient, aerobic alternative, *Science* 274 (1996) 2044–2046.
- [12] R.A. Sheldon, I.W.C.E. Arends, Catalytic oxidations mediated by metal ions and nitroxyl radicals, *J. Mol. Catal. A* 251 (2006) 200–214.
- [13] G. Grigoropoulou, J.H. Clark, J.A. Elings, Recent developments on the epoxidation of alkenes using hydrogen peroxide as an oxidant, *Green Chem.* 5 (2003) 1–7.
- [14] S.E. Martín, A. Garrone, Efficient solvent-free iron(III) catalyzed oxidation of alcohols by hydrogen peroxide, *Tetrahedron Lett.* 44 (2003) 549–552.
- [15] M. Nakanishia, C. Bolma, Iron-catalyzed benzylic oxidation with aqueous tert-butyl hydroperoxide, *Adv. Synth. Catal.* 349 (2007) 861–864.
- [16] F. Shi, M.K. Tse, M.-M. Pohl, J. Radnik, A. Brückner, S. Zhang, M. Beller, Nano-iron oxide-catalyzed selective oxidations of alcohols and olefins with hydrogen peroxide, *J. Mol. Catal. A Chem.* 292 (2008) 28–35.
- [17] F. Ullmann, *Ullmann's Encyclopedia of Industrial Chemistry*, 4 Wiley-VCH Verlag, Weinheim, Germany, 2003, pp. 701–707.
- [18] A. Pineda, A.M. Balu, J.M. Campelo, A.A. Romero, D. Carmona, F. Balas, J. Santamaria, R. Luque, A dry milling approach for the synthesis of highly active nanoparticles supported on porous materials, *ChemSusChem* 4 (2011) 1561–1565.
- [19] C.M.A. Parlett, P. Keshwala, S.G. Wainwright, D.W. Bruce, N.S. Hondow, K. Wilson, A.F. Lee, A hierarchically ordered nanoporous Pd/SBA-15 catalyst for the aerobic selective oxidation of sterically-challenging allylic alcohols, *ACS Catal.* 3 (2013) 2122–2129.
- [20] S.E. Martín, A. Garrone, Efficient solvent-free iron(III) catalyzed oxidation of

- alcohols by hydrogen peroxide, *Tetrahedron Lett.* 44 (2003) 549–552.
- [21] U.R. Pillai, E. Sable-Demessie, Oxidation of alcohols over  $\text{Fe}^{3+}$ /montmorillonite-K10 using hydrogen peroxide, *Appl. Catal. A Gen.* 245 (2003) 103–109.
- [22] D. Sahu, C. Sarmah, P. Das, A highly efficient and recyclable silica-supported palladium catalyst for alcohol oxidation reaction, *Tetrahedron Lett.* 55 (2014) 3422–3425.
- [23] C. González-Arellano, J.M. Campelo, D.J. Macquarrie, J.M. Marinas, A.A. Romero, R. Luque, Efficient microwave oxidation of alcohols using low-loaded supported metallic iron nanoparticles, *ChemSusChem* 1 (2008) 746–750.
- [24] A.V. Biradar, M.K. Dongare, S.B. Umbarkar, Selective oxidation of aromatic primary alcohols to aldehydes using molybdenum acetylido oxo-peroxo complex as catalyst, *Tetrahedron Lett.* 50 (2009) 2885–2888.