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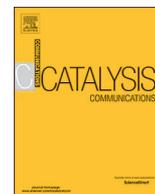
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Short communication

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



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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 (H₂O₂), *tert*-butyl hydroperoxide (tBu-OOH) and molecular oxygen (O₂) are employed to reduce the environmental impacts (as water is in theory the only by-product). The main advantage of using H₂O₂ over O₂ is that it is a liquid, miscible with water and relatively easy to handle. On the other hand, H₂O₂ can undergo radical-induced decomposition to H₂O and O₂, 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)(PPh₃)₃ 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 H₂O₂ 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 H₂O₂, heterogeneous catalysts in turn can be recycled. Studies that use heterogeneous iron catalysts for selective oxidation are limited. Fifteen years ago, FeBr₃ (20 mol%) was proposed for the oxidation of menthol in the presence of 5 eq. of H₂O₂ [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

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system for the oxidation of secondary benzylic alcohols was reported, consisting of small amounts of 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 H_2O_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 ($\text{Fe}(\text{ClO}_4)_2$, FeCl_2 and $\text{Fe}(\text{acac})_3$). FeCl_3 was chosen for safety issues (risks related with 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 H_2O_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 H_2O_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 H_2O_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 μL) furfuryl alcohol in 1 L of 5 M H_2SO_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 μL) of furfuryl alcohol was added to 990 μL 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 H_2O_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.

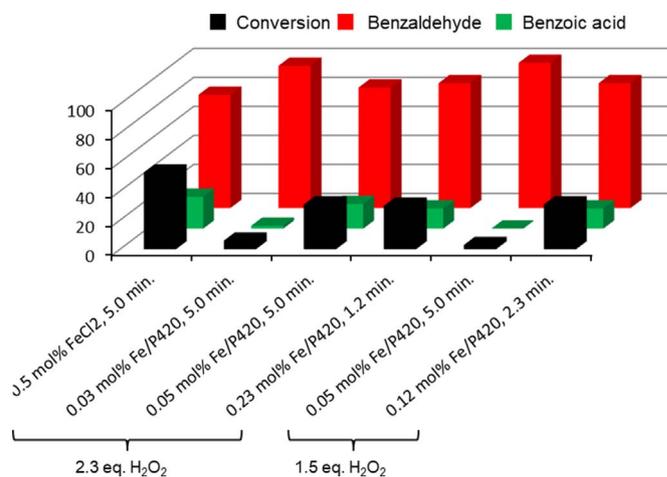


Fig. 1. Benzyl alcohol conversion and selectivity using Fe nanoparticles supported on P420 resin as compared to free dissolved FeCl_2 , using 1.5 and 2.3 eq. H_2O_2 .

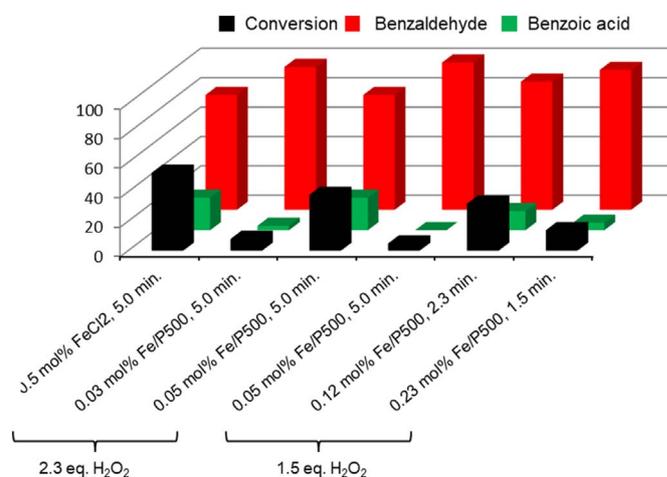


Fig. 2. Benzyl alcohol conversion and selectivity using Fe nanoparticles supported on P500 as compared to dissolved FeCl_2 , using 1.5 and 2.3 eq. H_2O_2 .

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 μm \times 25 μm i.d.) capillary column and an FID detector. The temperature of the column was ramped at 10 °C min^{-1} to 100 °C (0 min hold time), then at 20 °C min^{-1} to 120 °C (20 min hold time) and finally to 180 °C at 20 °C min^{-1} (10 min hold time). The nitrogen gas flow was set at 1.8 mL min^{-1} . The retention times benzyl alcohol, benzaldehyde and benzoic acid were 1.80, 1.35 and 3.20 min, respectively.

Table 1Comparison of the activity of iron particles supported on P500 with other (supported) metal catalysts for the benzyl alcohol oxidation using H₂O₂ in acetonitrile.

Entry	Cat. (mol%)	H ₂ O ₂ (eq.)	Conditions	Time (h)	Yield (%)	TON	Ref.
1	FeBr ₃ (20.0)	5.0	0.20 M, 25 °C	24	92	5	[20]
2	Fe ³⁺ /mont-morillonite K10 (1.8)	4.0	1.19 M, 65 °C	4	30	54	[21]
3	Nano-γ-Fe ₂ O ₃ (1.0)	1.5 ^a	Solvent-free, 75 °C	12	48	12	[16]
4	SiO ₂ @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) ₃ (C≡CPh) (20.0)	20.0	Solvent-free, 80 °C	8	79	396	[24]
7	CpMo(CO) ₃ (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

^a H₂O₂ 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 (H₂O₂ 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% FeCl₂) was tested for the oxidation of 0.77 M benzyl alcohol with 2.3 eq. H₂O₂ 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 H₂O₂, 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 H₂O₂.

Next to the catalyst load, the most determining factor was the excess amount of oxidant. The selectivity could be improved using less H₂O₂ (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 H₂O₂ 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 H₂O₂. 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 FeCl₂ catalyst, however with 15–22% lower conversion.

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