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# Mechanistic insights into the microwave-assisted cinnamyl alcohol oxidation using supported iron and palladium catalysts

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#### ABSTRACT

The efficient oxidation of alcohols remains a challenge, especially when using solid heterogeneous catalysts. Herein, the catalytic activity of mechanochemically prepared iron and palladium particles on various supports are compared for the oxidation of cinnamyl alcohol to cinnamaldehyde and benzaldehyde in acetonitrile using aqueous hydrogen peroxide as the oxidant assisted by microwave irradiation. Important insights into the mechanism of the reaction towards the differently observed products have been provided.

#### Introduction

Aldehydes and ketones represent an important commercial volume in the market, both as bulk chemicals as well as synthetic intermediates [1] or as end-products, including compounds with biological activity, olfactory properties, etc. [2,3]. The shortest pathway for the synthesis of carbonyls is the oxidation of the corresponding alcohol [4], both in liquid and gas phase. The preparation of aldehydes and ketones through selective oxidations is an important transformation step in organic synthesis [5]. In the past, stoichiometric oxidants based on chrome, magnesium permanganate, manganese or other metal derivatives were used, [6,7] leading to the formation of toxic waste and costly waste disposal/treatment [8]. Research in this field has mainly focused at increasing the atom and energy efficiency, the use of less hazardous solvents, the use of renewable feedstocks and the development of efficient oxidation methods that employ safer oxidants like hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or molecular oxygen (aerobic oxidation with O<sub>2</sub> or air) [9,10]. Both homogeneous and heterogeneous catalysts have been developed; whereas the former generally provide much faster turnover frequencies, optionally aided by co-catalysts, the latter enable an efficient catalyst separation and reduce waste streams. Solid catalysts for selective oxidations are mainly based on supported metal particles [11], such as Pd nanoparticles supported on mesostructured silica (SBA-15) [12], iron oxide (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles [13], (bimetallic) Au particles supported on metal oxides [14,15], Ru supported on alumina [16], zeolites [17], etc. The use of recoverable heterogeneous catalysts for selective oxidations remains a challenging subject, especially when using H<sub>2</sub>O<sub>2</sub> as the oxidant, as reviewed recently by Sheldon (2015) [18]. Solid catalysts for H<sub>2</sub>O<sub>2</sub> directed oxidations generally involve early transition elements, mostly tungsten, molybdenum and vanadium, in high oxidation states and peroxometal complexes. Recently, efficient oxidation of benzyl alcohol (primary alcohol) to benzaldehyde using H<sub>2</sub>O<sub>2</sub> was also demonstrated for small amounts of iron supported on furfuryl alcohol based resin support as alternative to the previously mentioned expensive noble metals (Pd, Au, Ru) [19]. The oxidation of cinnamyl alcohol is way more challenging, at least when one aims the selective production of cinnamaldehyde. Alcohol feedstocks can be classified in aliphatic, allylic, benzylic and heterocyclic alcohols, as well

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as in primary, secondary and tertiary alcohols. In general, primary benzylic alcohols can be converted efficiently, while other alcohols remain more challenging, especially in terms of selectivity [20].

Cinnamaldehyde can be used in a wide variety of applications. Cinnamaldehyde has been reported to exhibit antibacterial and antifungal activity [21,22], as well as anti-cancer-like activity [23], being also employed as a cross-linker in bioplastics [22] and as flavor/odor agent [24]. At one hand, it can be isolated and purified from natural resources such as cinnamon bark and leaves [25,26]. On the other hand, it can be produced by the selective oxidation of cinnamyl alcohol. Previous studies on catalytic cinnamyl alcohol oxidation proposed ruthenium complexes (using N-methylmorpholine-N-oxide, H<sub>2</sub>O<sub>2</sub> and tbutyl hydrogen peroxide as the oxidants) in dichloromethane (reflux) [27] and copper catalysts using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMP) in acetonitrile (20 °C) [28]. Methods which employed only H<sub>2</sub>O<sub>2</sub> (1–5 eq.) were reported using Ag<sub>3</sub>PO<sub>4</sub> photocatalysts in water, [29] Pd(II) complexes in ionic liquids, [30] Pd supported on silica [31,32] and Pt black (20 °C) [33]. The latter gave the highest yields, ca. 90% cinnamaldehyde after 2-3 h at 80 °C. To our knowledge, only Pillai et al. (2003) reported an iron-based catalyst for this reaction, with 19% yield after 4 h at 65 °C using 4.0 eq. of H<sub>2</sub>O<sub>2</sub> [34]. The present work explores the catalytic activity of iron and palladium supported on various supports for the oxidation of cinnamyl alcohol in acetonitrile assisted by microwave irradiation using 1.6-2.8 eq. of aqueous H<sub>2</sub>O<sub>2</sub> as a green oxidant. Fe (transition metal) was selected as compared to Pd (noble metal) to investigate the possibilities of the use of a cheap, environmentally friendly and largely available transition metal for selective oxidations. In addition to this, several supports available from previous research from our group including aluminosilicates, zeolites and a magnetically separable support were also tested in order to investigate the effect of the support in the metal deposition as well as in the catalytic activity in the systems.

#### **Experimental section**

# Catalyst supports

The synthesis of mesoporous aluminosilicate Al-SBA-15 was carried out following the procedure described by Zhao et al. (1998) [35]. The triblock co-polymer Pluronic P123 (0.41 mmol) was used as directing agent and dissolved in aqueous HCl (2 M, pH 1.5) for 2 h at room temperature. After complete dissolution, tetraethyl orthosilicate (0.025 mol) was used as the silica source and the corresponding amount of aluminum isopropoxide (0.01 mol) was slowly added. The mixture was stirred for 24 h at room temperature, followed by hydrothermal treatment in an oven at 100 °C for 24 h. The gel obtained was filtered off, dried and subsequently calcined under nitrogen atmosphere at 600 °C for 2 h, and then under air atmosphere for 4 h. The obtained SBA solids (Si/Al molar ratio 20) were recovered and stored.

The magnetic support MAGSCN was prepared according to the procedure reported by Ojeda et al. (2014): [36] 0.5 g solid SBA-15 silica support was ground with 1.34 g solid Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O in a Retsch PM-100 planetary ball mill in a 125 mL vessel using eighteen 10 mm stainless steel balls. Optimized milling conditions were 10 min. at 350 rpm [37]. Fe-containing SBA-15 was subsequently reacted with propionic acid (10 mL, ca. almost 1:10 material:propionic acid ratio) at 85 °C, 3 h under static vacuum to achieve the magnetic phase. The nanocomposite was slowly heated up to 300 °C under air (1 °C min<sup>-1</sup>) and kept at 300 °C for an additional 30 min.

P420 resin material was prepared according to the procedure reported by Mangin et al. (2018): [19]  $0.01 g (10 \mu L)$  of pure furfuryl alcohol was mixed with 990  $\mu$ L of deionized water, followed by addition of 10 mL 9 M HCl, causing a rapid change of color from yellow to violet. The mixture was stirred for 1 h at 20 °C. The resin spheres were purified with distilled water and separated by centrifugation (12,000 rpm, 4 °C, 40 min.). Fig. S1 shows a SEM image of the purified resin surface.

Commercial MFI zeolites ZSM-5-30 and ZSM-5-50 (ammonium ZSM-5 CBV3024E and CBV5524GE) and FAU zeolites Y-5.2 and Y-60 (ammonium H-60 and H-5.2) were purchased from Zeolytes International (USA). Zeolite materials were calcined at 600 °C during 24 h prior to use to remove ammonia. NC (where appropriate) stands for uncalcined samples.

## Catalyst synthesis and characterization

Fe/Al-SBA-15, Fe/P420, Fe/H-ZSM-5 and Fe/H-Y catalysts were prepared mechanochemically in dry conditions: 1.0 g solid support and 0.020/0.040 g FeCl<sub>2</sub>.4H<sub>2</sub>O (equivalent to 0.5/1.0 wt% Fe to reach a theoretical amount of 0.25 and 0.50 mol% Fe with respect to the cinnamyl alcohol load) were milled together in a planetary ball mill (Retsch 100) under previously reported optimized conditions (350 rpm, 10 min.) [37]. The solids were recovered and heated under air atmosphere during 4 h at 400 °C (Fe/Al-SBA-15). For Fe/P420, the obtained solids were calcined during 48 h at 120 °C. In the case of Fe/H-ZSM-5 and Fe/H-Y, the obtained solids were calcined at low temperature (48 h, 120 °C) or at high temperature (2 h, 800 °C). For Pd/Al-SBA-15 and Pd/MAGSCN catalysts, the same protocol was followed as for Fe/Al-SBA-15, but instead 0.03/0.06 g Pd(acac)<sub>2</sub> was used as metal precursor (to reach a theoretical amount of 0.25 and 0.50 mol% Pd with respect to the cinnamyl alcohol load).

Powder X-ray diffraction patterns (XRD) were recorded on a Bruker D8-advance X-ray diffractometer with Cu K $\alpha$  radiation (0.154 nm) over the 2 $\Theta$  range of 10-80°. For low angle experiments, XRD patterns were acquired at a step size of 0.02° with a counting time per step of 20 s.

 $N_2$  adsorption/desorption isotherms of were determined in the Micromeritics automatic analyzer ASAP 2000 at -196 °C. Samples were previously degassed overnight at 130 °C under vacuum (P <  $10^{-2}$  Pa). The linear determination of the BET equation was carried out to obtain the specific surface area.

Scanning electron microscopy images were recorded with a JEOL JSM-6300 scanning microscope (JEOL Ltd., Peabody, MA, USA) equipped with Energy-dispersive X-ray spectroscopy (EDX) of 15 kV at the Research Support Service Center (SCAI) from University of Cordoba.

Elemental analysis in the Fe loaded zeolites was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using Perkin Elmer Nexion 300X equipment. Prior to analysis, the samples were digested in hydrofluoric acid.

X-ray photoelectron spectra (XPS) were acquired using a Physical Electronics PHI 5700 spectrometer with non-monochromatic MgaKa radiation (300 W, 15 kV, and 12,565 eV) at Universidad de Malaga. C1s line at 284.6 eV from adventitious carbon was used as reference.

HR-TEM micrographs were recorded in a JEOL JEM 2010 microscope (operated at 200 kV) with a resolution of 0.194 nm.

# Catalytic experiments

The experiments were carried out in a closed pressure-controlled vessel under continuous stirring, assisted by microwave irradiation using a CEM-DISCOVER model with PC control. The microwave irradiation of the reaction mixture was power-controlled (300 W), reaching temperatures in the 84–112 °C range (average temperature 98 °C), as measured by an infra-red probe. The pressure in the closed system ranged from 34 to 170 psi, with an average of 100 psi. In a typical reaction, 0.247 mL of cinnamyl alcohol (Sigma Aldrich, 98% purity) was suspended in acetonitrile (3 mL) containing 50 mg catalyst and then H<sub>2</sub>O<sub>2</sub> (0.300 mL of 30 or 50% w/w aqueous solution) was added with catalyst to start the reaction. After the reaction, the mixture was cooled to room temperature and filtered off. Subsequently, the filtrate was analyzed by GC.

#### Product analysis

GC analysis was performed using an Agilent 6890 N GC chromatograph equipped with a Supelco 2-8047-U ( $60 \text{ m} \times 25 \text{ m} \times 25 \text{ \mum}$ ) capillary column and an FID detector. The temperature of the column was ramped at 10 °C min<sup>-1</sup> to 100 °C (0 min hold time), then at 20 °C min<sup>-1</sup> to 120 °C (20 min. hold time) and finally to 180 °C at 20 °C min<sup>-1</sup> (10 min hold time). The nitrogen gas flow was 1.8 mL min<sup>-1</sup>. The retention times of benzaldehyde, cinnamaldehyde and cinnamyl alcohol were 9.6, 17.7 and 25.1 min, respectively. Yield, conversion and selectivity were determined as:

$$Yield \ (mol\%) = \ \frac{Mol_{Product}}{Mol_{Initial}} \times 100$$

$$Conversion (mol\%) = \frac{[Mol_{Initial} - Mol_{Final}]}{Mol_{Initial}} \times 100$$

$$Selectivity (mol\%) = \frac{Mol_{Product}}{Mol_{Mol_{initial}} - Mol_{initial}} \times 100$$

The response factors (RF) relative to a fixed concentration  $(9.04 \text{ mg mL}^{-1})$  of benzyl chloride as internal standard (IS) were experimentally determined by preparing dilution sets of cinnamyl alcohol, dihydrocinnamyl alcohol, cinnamaldehyde and benzaldehyde, which were 1.207, 1.486, 1.189 and 1.047, respectively. The linear regression coefficients of the linear fittings were high in all cases ( $r^2 > 0.99$ ). The RF of the remaining compounds identified in the product mixtures with unknown RF were calculated by the Effective Carbon Method (ECN) [38] relative to a compound with an experimentally determined RF and with a similar structure in terms of total carbon atom number, as the following:

$$RF_{unknown} = RF_{Exp. known} \times \frac{ECN_{unknown}}{ECN_{Exp. known}}$$

Table S1 (see Supporting Information) shows the calculated ECN factors and the corresponding calculated RF. Some compounds (those present in very small amounts) which did not elute in the GC-FID analysis were quantified by comparison of their relative peak area in the GC/MS analysis with the peak area of a compound (both relative to the IS peak area) which did elute in the GC-FID analysis.

A selected set of product mixtures obtained after filtration were also analyzed by GC–MS analysis on a gas chromatograph coupled with a triple quadrupole mass detector (Bruker, GC-436, Scion TQ) working with electron impact ionization and ion detection in the scan range of m/z 35–450 (0.5 s per scan). The chromatograph was equipped with a high-temperature capillary 5% phenylsilicon column (DB-5HT, 30 m × 0.25 mm i.d., 0.25 µm film thickness). Helium was used as carrier gas at a rate of 1 mL min<sup>-1</sup>. The injector temperature was set at 265 °C and the split ratio was 50. The oven was heated from 80 °C to 200 °C at 3 °C min<sup>-1</sup> and finally from 200 to 280 °C at 35 °C min<sup>-1</sup> (3.5 min.). The identification of the compounds was performed by comparison with pure standards, with MS data in the NIST library.

#### **Results and discussion**

Low amounts of iron and palladium (0.5–1.0 wt%) were supported on various well-defined supports via mechanochemical synthesis in dry conditions (ball-milling). Table S2 (see Supporting Information) shows the Si/Al ratio, specific surface area, pore size and pore volume of the aluminosilicate supports used in the present study, as determined experimentally by nitrogen adsorption analysis at -196 °C. The incorporation of such low amounts of iron and palladium onto the different supports did not change significantly the textural properties in the final material as compared with their respective support. Comparison of the XRD spectra of the H-Y-5.2 and Fe/H-Y-5.2 materials (iron on zeolites obtained after calcination at 120 °C) failed in revealing the presence of any FeCl<sub>2</sub> phase (Fig. S2), neither hematite or maghemite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). Neither in the spectrum of the catalysts calcined at 800 °C any phase of magnetite ( $\gamma$ -Fe<sub>3</sub>O<sub>4</sub>) was clearly visible. It was difficult to reveal the iron crystal phase as most of the XRD signals of the zeolite are present at identical diffraction angles compared with pure FeCl<sub>2</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>3</sub>O<sub>4</sub>. Marturano et al. (2001) demonstrated that, upon sublimation of FeCl<sub>3</sub> in H-ZSM-5 zeolite by chemical vapor deposition at 320 °C, FeCl<sub>2</sub><sup>+</sup> species formed in the zeolite framework, at least when no washing step was applied [39]. Similar observations were reported by Kucherov and Shelef [40]. These authors identified a wide range of (active) iron phases depending on the exact synthesis conditions with the aid of advanced characterization techniques including EXAFS, UV–vis and AAS spectroscopy.

In view of the catalytic application, i.e. the oxidation of cinnamyl alcohol, no concise data was found on the actual catalytic active phase. Parlett et al. demonstrated, at least for Pd supported on mesoporous silica, that the metal oxide (and not the metal) nanoparticle is the active phase in the oxidation of cinnamyl alcohol when using O<sub>2</sub> as the oxidant [41,42]. Considerable effects of the support on the selectivity were actually the result of varying dispersions of the metal oxide. The identification of iron phase in the materials synthesized in the present study by XRD was not possible due to, firstly, the low metal loading in the catalysts as well as the high crystallinity of the zeolites whose diffraction lines could overlap those corresponding with the different iron species. XPS measurements, especially useful for these material in which X-ray diffraction is not helpful due to the low metal loading and high crystallinity of the support, were used to identify the metallic species present after the different thermal treatment that these materials underwent (calcination at 120 and 800 °C). Fig. 1 shows the XPS spectrum in the Fe 2p region of Fe/H-ZSM-5-30\_120C sample, exhibiting peaks corresponding with Fe(II) and Fe (III) as a result of partial transformation of Fe(II) from the metal salt into Fe (III) while in the respective spectrum for the material calcined at 800 °C the distinctive peak at 711 eV of Fe  $2p_{3/2}$  corresponding with Fe<sub>2</sub>O<sub>3</sub> can be observed (see also Fig. S3) [43,44].

The nominal metal loading in synthesized catalysts was confirmed by ICP-MS for selected samples (Table S3). An iron content *ca.* 0.4 wt.%was measured for zeolite samples with 0.5 wt% nominal loading. Chloride anions from the metal salt precursor were present in the samples treated at  $120 \degree$ C for 48 h while in the sample calcined at 800 °C for 2 h no Cl was not detected. Additionally, TEM micrographs were recorded of the Fe containing zeolites to search for Fe nanoparticles as well as to evaluate the morphology of the metal functionalized



Fig. 1. XPS spectra in the Fe 2p region for the materials: a) Fe/H-ZSM-5-30\_120C and b) Fe/H-ZSM-5-30\_800C (calcined at 120 °C and 800 °C, respectively).

#### Table 1

Cinnamyl alcohol oxidation after 5 min. at 300 W microwave irradiation (ca. 100 °C) with Fe supported on Al-SBA-15 as compared to the corresponding dissolved counterparts FeCl<sub>2</sub> and compared to Pd/Al-SBA-15.

Entry	Catalyst (% Fe/Pd) <sup>a</sup>	$H_2O_2$ (eq.) <sup>a</sup>	Conversion (%) <sup>a</sup>	Yield (selectivity, %) <sup>a</sup>	
				Cinnamaldehyde	Benzaldehyde
1a	-	1.6	5	1 (34)	1 (26)
1b	-	2.8	9	3 (33)	2 (27)
2a	Al-SBA-15	1.6	12	3 (29)	4 (31)
2b	Al-SBA-15	2.8	16	5 (28)	5 (32)
3a	FeCl <sub>2</sub> (0.80)	1.6	28	8 (30)	13 (45)
3b	FeCl <sub>2</sub> (0.80)	2.8	41	11 (28)	19 (47)
4a	FeCl <sub>2</sub> (1.60)	1.6	29	7 (25)	14 (49)
4b	FeCl <sub>2</sub> (1.60)	2.8	38	9 (24)	19 (50)
5a	Fe/Al-SBA-15 (0.25)	1.6	57	10 (17)	32 (57)
5b	Fe/Al-SBA-15 (0.25)	2.8	79	10 (13)	48 (61)
6a	Fe/Al-SBA-15 (0.50)	1.6	58	11 (20)	32 (55)
6b	Fe/Al-SBA-15 (0.50)	2.8	82	10 (12)	51 (62)
7a	Pd/Al-SBA-15 (0.25)	1.6	24	8 (34)	6 (27)
7b	Pd/Al-SBA-15 (0.25)	2.8	22	10 (45)	8 (38)

<sup>a</sup> In molar percentages on cinnamyl alcohol load.

materials after the milling process. The general trend was that samples of the zeolite materials calcined at 800 °C showed smaller particle sizes compared to those calcined at 120 °C (Fig. S4). Slight dark spots in the TEM images apparently showed the presence of metal nanoparticles.

As-synthesized catalysts were tested for the oxidation of 0.5 M cinnamyl alcohol in acetonitrile using microwave irradiation as a tool to reduce the reaction times drastically. To compare the catalyst activity, reaction times were set at 5 min. The amounts of supported iron (Fe) and palladium (Pd) used in the catalytic experiments corresponded with 0.25–0.50% (molar percentage with respect to cinnamyl alcohol load). Table 1 shows that in the present conditions benzaldehyde is the main product. Blank experiments with 1.6 and 2.8 eq.  $H_2O_2$  (Table 1, entries 1a and 1b) showed low cinnamyl alcohol conversion (5–9%). When using only support (Al-SBA-15), conversions increased slightly to 12–16% (entries 2a and 2b). Fe supported on Al-SBA-15 enhanced the conversion drastically to 57–82%, but with poorer selectivity to cinnamaldehyde (12–20%).

Higher amounts of free dissolved iron (0.8 and 1.6% FeCl<sub>2</sub>) gave only 28–41 % conversion at 24–30 % selectivity to cinnamaldehyde. When changing Fe for Pd (entries 7a and 7b) in the catalyst synthesis procedure, the conversions dropped noticeably to 21–24 %, whereas the selectivity to cinnamaldehyde increased to 34–45 %.

Different supports were subsequently compared (Fig. 2), including a

furfuryl alcohol derived resin (P420), aluminosilicate (Al-SBA-15), zeolite (H-ZSM-5-30) and a magnetic nanocomposite (MAGSNC). At lower oxidant load (1.6 eq., Fig. 2a), the conversions varied between 11 and 33%, except for Fe/Al-SBA-15 (57%). Higher oxidant loads (2.8 eq., Fig. 2b) were required to reach high conversion levels. Interestingly, using small amounts of Fe (0.1%) supported on P420 resin, 52% conversion was achieved, the highest value after Fe/Al-SBA-15 (79%). The use of comparable quantities (ca. 0.4-0.5% Fe) on P420 did not significantly increase the conversion in the systems (ca. 60% maximum conversion achieved for almost identical Fe content). The selectivity to cinnamaldehyde in turn dropped from 41 to 23%. The highest selectivity was observed for Fe/H-ZSM-5-30 and Pd/Al-SBA-15. Their conversions were 42 and 21%, respectively. This result, as the best compromise between conversion and selectivity to cinnamaldehyde, conducted us to further explore H-ZSM-5-30 and other zeolites as support for Fe particles. Fig. 3 compares the catalytic activity of MFI and FAU zeolites (H-ZSM-5 and H-Y), and the activity of the same zeolites with Fe supported on it, obtained after calcination at low temperature (120 °C, 48 h) and at high temperature (800 °C, 2 h).

Zeolites as such gave higher conversion (15–33 %) compared to Al-SBA-15 (16%), with significantly improved selectivity to cinnamaldehyde (29–65 %). When incorporating low amounts of Fe (1 wt%) in the zeolite framework through calcination at low temperature, the



Fig. 2. Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde and benzaldehyde using Fe and Pd catalysts prepared similarly on different supports 50 mg of catalyst (containing 0.5% Fe and Pd, except for P420 support: 0.1% Fe) at (a) 1.6 eq and (b) 2.8 eq. H<sub>2</sub>O<sub>2</sub>.



Fig. 3. Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde and benzaldehyde using 2.8 eq.  $H_2O_2$  using different zeolites as compared to the same zeolites with supported Fe (0.5%) obtained after 48 h calcination at 120 °C and after 2 h calcination at 800 °C.

conversions increased to 42-49 %. Interestingly, the selectivity to cinnamaldehyde was fully retained for the zeolites having low Si/Al ratio (H-ZSM-5-30 and H-Y-5.2) whereas the selectivity decreased for the high Si/Al ratio zeolites (H-ZSM-5-50 and H-Y-60). When incorporating Fe through calcination at high instead of low temperature, the conversions further increased with 6-10% without any significant loss of selectivity. Both the catalyst powders obtained after calcined at 120 and 800 °C exhibited a pink color, whereas the not-calcined samples were pale yellow. While the color of the calcined catalysts was retained after the catalytic experiment (and recovery, washing and drying), the color of the recovered not-calcined catalysts disappeared, leaving behind the bare zeolites (white powder). This indicates that both calcination procedures effectively supported iron on the support, whereas without calcination the iron was leached from the zeolite structure during the catalytic experiment. The low angle XRD spectra (Fig. 4) clearly show that the samples calcined at 120 and 800 °C contained a different active iron phase. The best performing catalyst was 0.5% Fe on H-ZSM-5-30 calcined at 800 °C (16% cinnamaldehyde and 19% benzaldehyde yields, at 50% cinnamyl alcohol conversion after 5 min reaction time).

Some effects of changing reaction conditions were also studied. Fig. 2 already showed that reduced oxidant loadings (1.6 eq.) resulted in higher selectivity to cinnamaldehyde. When dosing 2.4 eq. in 3 steps (after 0, 1 and 3 min.) instead of adding all the oxidant at the beginning, the selectivity to cinnamaldehyde increased from 31 to 42% (using Fe/ H-Y-60 120 °C as catalyst) but at the expense of a decreased conversion (dropping from 44 to 30%). Another way to increase the selectivity to cinnamaldehyde (from 33 to 52%) was decreasing the microwave irradiation power (Fig. 5a), once again conversion with a reduction in conversion from 42 to 26%. When monitoring the course of the reaction between 5 and 30 min (Fig. 5b) for Pd supported on Al-SBA-15, the conversion increased from 21 to 69%, with a however significantly decreased selectivity to both cinnamaldehyde (from 45 to 19%) and benzaldehyde (from 38 to 30%). This means that significant amounts of other products started to form at reaction times over 5 min as discussed hereafter.

An in-depth study of the reaction product composition by GC/MS analysis (Fig. 6a) elucidated the presence of side products, which were not all observable in GC-FID analysis. A product mixture was obtained containing cinnamaldehyde and benzaldehyde (14 and 18% yields, respectively) as the main products using 0.5% Fe supported on H-ZSM-5-30, while *ca.* 6% side products were formed. The same zeolite (H-ZSM-5-30), but without Fe, resulted in 10% cinnamaldehyde and 8% benzaldehyde yields with *ca.* 5% side products. At conversion levels of 42 and 26%, respectively, this means that a slight percentage of the



Fig. 4. Low angle XRD spectra of Fe (0.5 wt%) supported on H-Y-5.2 after calcination during 2 h at 800 °C (top image), Fe (0.5 wt%) supported on H-Y-5.2 after calcination during 48 h at 120 °C (middle image) as compared to the parent H-Y-5.2 zeolite.

mass balance (3–4%) was not covered. This is not surprising, as the oxidative disruption of the propyl chain in cinnamyl alcohol would lead to the release of CO,  $CO_2$ , formaldehyde and/or formic acid, which are not accounted in the mass balance. Interestingly, when repeating the experiments but starting from dihydrocinnamyl alcohol (without insaturation, Fig. 6c) instead of cinnamyl alcohol, the mass balance dropped to 76–85 %. Here, formic acid 3-phenylpropyl ester (compound 12) was present among the side products (2.0 and 0.2% yields for Fe/H-ZSM-5-30 and H-ZSM-5-30, respectively), which supports the hypothesis of formaldehyde or formic acid release upon oxidative



Fig. 5. Conversion of cinnamyl alcohol and selectivity to cinnamaldehyde and benzaldehyde: (a) after 5 min using 0.5% Fe on H-ZSM-5-30\_120C in function of the microwave irradiation power and (b) between 5 and 30 min. at 300 W using 0.5% Pd supported on Al-SBA-15.

disruption. Independent from the starting compound, mass balances were slightly lower when using Fe supported on zeolite as compared to the bare zeolite, in accordance with their higher benzaldehyde yield. Thus, the presence of iron increases the disruption activity in sacrifice of higher selectivity to cinnamaldehyde. This is demonstrated in Fig. 6b, were cinnamaldehyde was oxidized to benzaldehyde and cinnamic acid among other side products. Importantly, when starting both from cinnamyl alcohol and cinnamaldehyde, the corresponding epoxide compounds (compounds 9 and 16) were detected in significant amounts, while it was completely absent when starting from dihydrocinnamyl alcohol. This shows that the epoxidation occurs through interaction of peroxy radicals with the double bound, independent from the functionality of the carbon adjacent to it.

Still, the nature of compound 2 was not fully clear based on its mass

spectrum. It could be phenylaceytaldehyde but also the corresponding epoxide (2-phenyloxirane) and consequently we could not fully exclude the formation of epoxides in the reaction with the corresponding saturated compound (dihydrocinnamyl alcohol). Anyway, this result suggests that when starting from dihydrocinnamyl alcohol (Fig. 4c), less benzaldehyde would be produced, which was experimentally evidenced. However, it did not lead to a higher yield of dihydrocinnamaldehyde (compound 6). Instead, more other side products were produced due to an increased release of formaldehyde and/or formic acid from the terminal carbon in the propyl chain (which leads to higher amounts of compounds 2 and 3) and due to the coupling of radical fragments leading to products such as benzoin and 3,4-dihydro-1-benzopyran (compounds 7 and 8) among others (which were not detected here but which are plausible to be present as seen from the



**Fig. 6.** GC/MS chromatograms, cinnamyl alcohol conversion and selectivity to main and minor oxidation products and the corresponding mass balance obtained in catalytic experiments (2.8 eq.  $H_2O_2$ , 300 W, 5 min) using H-ZSM-5-30 zeolite and 0.5% Fe supported on H-ZSM-5-30 (calcined at 120 °C) starting from 0.5 M (a) cinnamyl alcohol, (b) cinnamaldehyde and (c) dihydrocinnamaldehyde.



Scheme 1. Selective oxidation of cinnamyl alcohol to cinnamaldehyde and disruptive oxidation to benzaldehyde through formation of epoxides as reaction intermediates.

lower mass balance). Recently, the formation of formaldehyde was experimentally evidenced in the gas phase isolated from batch experiments with cinnamyl alcohol by Santos Costa and co-workers (2015).<sup>45</sup> To further improve the selectivity to cinnamaldehyde using Fe based heterogeneous catalysts, the disruptive pathway through epoxidation needs to be suppressed. Scheme 1 shows a tentative illustration of the cinnamyl alcohol oxidation reaction mechanism using aqueous H<sub>2</sub>O<sub>2</sub>, in accordance with the results reported by Santos Costa et al. (2015), [45] who proposed that the oxidation to cinnamaldehyde occurs on the catalyst surface while the disruptive oxidation to benzaldehyde takes place in bulk phase. Accordingly, they succeeded in suppressing the disruptive oxidation by adding a stoichiometric amount of 2,6-di-tertbutyl-4-methylphenol (HBT) as radical trap to the reaction mixture, which strongly suggests that the disruptive oxidation to benzaldehyde indeed is a radical mediated reaction. Similarly, when adding 1 eq. HBT to the reaction medium using the Fe/HZSM-5-30\_800C catalyst in the present study, the conversion after 5 min. dropped from 53 to 30%, whereas the selectivity to cinnamaldehyde increased from 26 to 39% and for benzaldehyde decreased from 39 to 26%. This result confirms that various reaction mechanisms take place, still it remains unclear how effective HBT can suppress the radical mediated pathway. Our results suggest that the supported metals (either as chloride salts or as oxides) catalyze the formation of reactive peroxy radicals which may act as the radical chain initiators in bulk phase (not only the cinnamaldehyde but also the benzaldehyde yields increased upon incorporation of metals into the support). Whereas Santos Costa and coworkers did not detect the formation of any epoxides in the product mixture, [45] the present study does confirm the formation of epoxides.

# Conclusions

Iron supported on various aluminosilicates showed much higher activity for the oxidation of cinnamyl alcohol using hydrogen peroxide as the oxidant as compared to their bulk counterparts (dissolved iron chloride), however, with lower selectivity to cinnamaldehyde. Palladium supported on a magnetic silicate and iron supported on a furfuryl alcohol derived resin showed higher selectivity to cinnamaldehyde in the range of bulk iron particles, but at significant lower conversion levels. Better results were obtained with 0.5% iron supported on MFI and FAU zeolites, which exhibited conversions between 42 and 49% at 26–33 % selectivity to cinnamaldehyde and 26–42 % selectivity to benzaldehyde. Higher conversions (50–55 %) were obtained through fast calcination at 800 °C of the iron/zeolite catalysts instead of slow calcination at 120 °C, without any significant loss in selectivity. Higher activity lead in most of the cases to lower selectivity to cinnamaldehyde as the higher activity was especially noticed in the disruptive oxidation pathway through the formation of the epoxide compounds through addition of oxygen radical species at the double bound of the allylic alcohol, but also through the release of formaldehyde, which lead to benzaldehyde and minor amount of side products.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110409.

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