

Mechanochemical functionalization of mesoporous carbons for the catalytic transformation of trans-ferulic acid into vanillin

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ABSTRACT

Mesoporous carbonaceous materials were functionalized with iron or copper by a mechanochemical approach. The structural and textural properties of these catalysts were characterized by N₂ physisorption, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The synthesized materials were evaluated in the transformation reaction of trans-ferulic acid using H₂O₂ as a green oxidant and acetonitrile as a solvent. Furthermore, all the materials were evaluated during three reaction cycles to study their stability and reusability. Inductively coupled plasma mass spectrometry (ICP-MS) was employed to demonstrate that there was no significant metal leaching in the reaction mixture. A 50% selectivity to vanillin was obtained under optimum conditions (remaining at similar values) after 3 subsequent reaction cycles of 6h for Cu/C catalyst at 0.5 wt.% copper load.

Keywords: Mesoporous Carbon; Mechanochemistry; Trans-ferulic acid; Vanillin.

INTRODUCTION

Research faces the challenge of decreasing the consumption of fossil fuels and finding alternatives to such non-renewable substances. The Twelve Principles of Green Chemistry focus on designing processes to achieve environmental sustainability¹. On this point, the conversion of renewable biomass-derived substances into added-value products and materials has become a common subject worldwide, which aims to avoid the use of edible biomass precursors that would compete with the food production industry^{2,3}. In this sense, the complex structure of lignocellulosic biomass, composed by three major components, cellulose, hemicellulose, and lignin^{2,5-7}, turns it into a promising source of many products of industrial interest^{2,5-7}. For example, lignin-derived compounds such as isoeugenol or trans-ferulic acid have been employed to obtain vanillin by means of different strategies⁸⁻¹¹. Alternatively, to catalytic protocols for vanillin production, biosynthetic routes have been studied, for example through the use of different families of bacteria^{12,13}, immobilized enzymes¹⁴ or by the Solvay Process through fermentation¹⁵. Although these processes are environmentally friendly, it has several disadvantages such as the difficult separation of the reaction medium and the need for specific strains that increase the cost of the process^{12,14}.

Ferulic acid is the most abundant hydroxycinnamic acid found in plant cell walls¹⁶, as monomer, homodimers or esterified or esterified with proteins or polysaccharides¹⁵ in order to confer rigidity by crosslinking through covalent bonds¹⁶. Among others, it has many important applications in the field of medicine to prevent thrombosis, atherosclerosis¹⁷ or cancer¹⁸. In addition, ferulic acid is used by food and cosmetic industries as preservative due to its antioxidant and antimicrobial properties^{19,20}, and also as precursor of interest compounds such as vanillin. Vanillin (4-hydroxy-3-methoxybenzaldehyde) is a major compound of vanilla bean extract, being widely used in the pharmaceutical, cosmetic, medical or food industries²¹. The global consumption of vanillin is around 18,000 ton/year²² from which only 1% is obtained by natural extraction²³, the remaining percentage is chemically synthesized, mostly employing the non-environmentally friendly Riedel Process²¹.

Biomass-derived polyphenolic molecules (i.e. condensed tannins) have been proven as excellent alternatives to substances of petrochemical origin conceived to synthesize carbonaceous materials. In particular, mimosa tannin (MT) is a type of condensed tannin extracted from the *Acacia mearnsii* tree, mainly composed by flavan-3-ol moieties with a resorcinol and pyrogallol ring linked by a heterocyclic ring. MT exhibits

a reactivity similar to that of resorcinol, which, together with its autocondensation potential allows synthesizing various types of carbon materials including gels, foams, spheres and mesoporous materials²⁴. These materials exhibit excellent properties such as high surface areas, resistance to highly acidic or alkaline media, good recycling characteristics, surface hydrophobicity, low density and ease of functionalization²⁴. All these properties provide organic and carbon materials with a versatility to be employed in a wide range of applications including catalysis²⁵⁻²⁸, energy storage, adsorption and biosensing²⁹.

Besides, the incorporation of copper and/or iron on carbonaceous materials as supports could increase the catalytic activity in double bond oxidations, particularly useful for the transformation of trans-ferulic acid into vanillin based on its reaction mechanism^{11,30-33}.

In view of aforementioned aim for eco-friendly and sustainable development of processes, this study proposes the use of mimosa tannin-derived mesoporous carbon materials functionalized with either iron or copper as heterogeneous catalyst for the trans-ferulic acid transformation into vanillin. Ordered and disordered mesoporous carbonaceous materials (OMCs and DMCs, respectively) containing 0.5% wt. iron and copper were synthesized via simple, fast and green two step mechanochemical synthesis/incorporation approach, with relevant insights observed on the stability of synthesized materials depending on final calcination temperature.

MATERIALS AND METHODS

Synthesis of OMC and DMC materials

The mesoporous carbon materials were synthesized following a surfactant-water-assisted mechanochemical mesostructuration (SWAMM) method³⁴. Briefly, MT (SilvaChimia) is used as a carbon precursor and Pluronic® F127 (P) as a pore-directing agent, both mixed in together with a small quantity of water (W) in a planetary ball mill (PM 100 from Retsch, 50 mL agate vessel, agate 10 balls of 10 mm diameter) during 60 minutes at 500 rpm. The obtained mesophase was directly carbonized at 900 °C (temperature increasing rate of 1 °C/min, holding final temperature for 1h) under N₂ flow (100 mL/min). To obtain the DMC material a ratio of 2:2:2 mass ratio of MT:P:W was used, while the OMC material was synthesized using a 2:0.75:1.75 mass ratio.

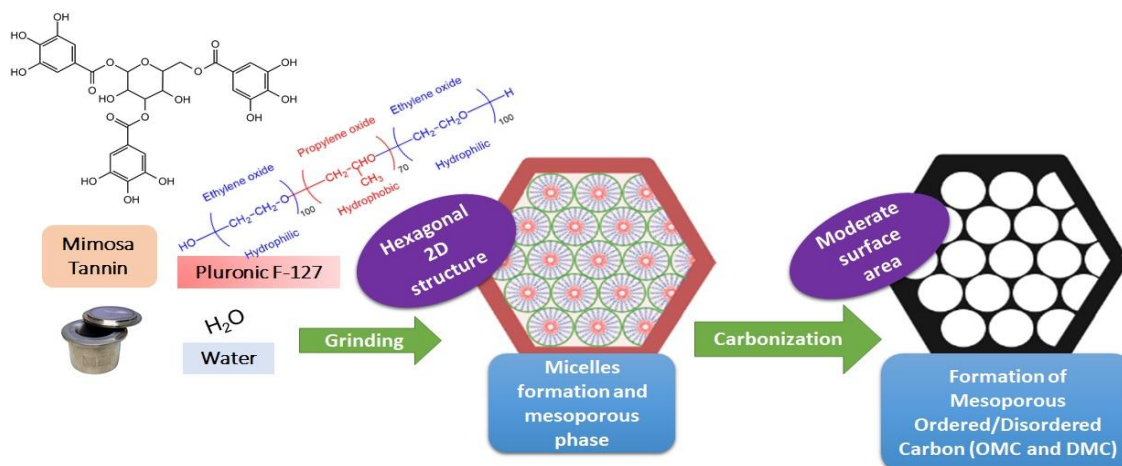


Figure 1. Scheme of the surfactant-water-assisted mechanochemical mesostructuration (SWAMM) synthesis approach.

Material functionalization

The functionalization was carried out following the method previously described by Pineda et al.³⁵. In a 25 mL steel vessel (with 8 steel balls of 10 mm diameter), 0.5 g of mesoporous carbon (ordered or disordered) were ground with a metal precursor salt, either 5.7 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or 9.5 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, during 10 minutes at 350 rpm in a Planetary Ball Mill (PM 100 Retsch). After grinding, the recovered material was calcined at 300, 400 or 500 °C for 2h.

Calcined materials were labelled “*M/C sT*” where “*M*” refers to the functionalization metal, Cu or Fe, “*s*” corresponds to the ordered or disordered mesoporous structure of the carbon material, O or D, respectively; and “*T*” corresponds to the calcination temperature.

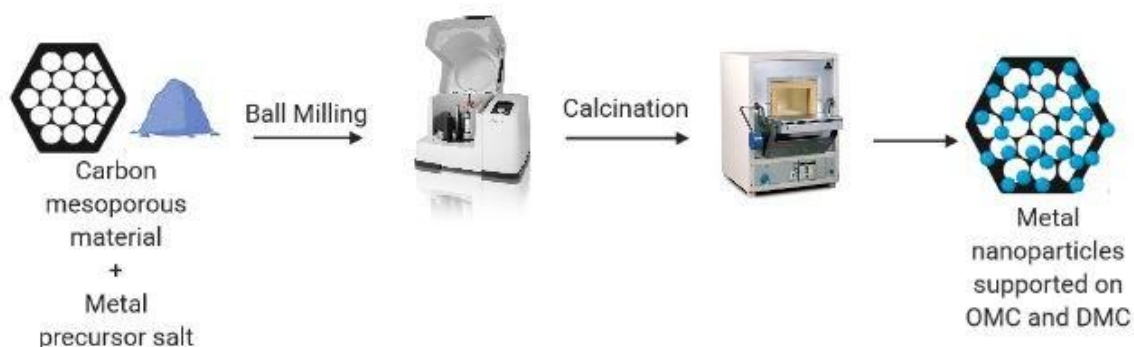


Figure 2. Mechanochemical functionalization of the mesoporous carbons.

Catalyst Characterization

Textural properties of the materials were evaluated by N₂ adsorption-desorption measurements using an ASAP 2000 device (Micromeritics). Samples were outgassed at 130 °C for 24 h ($p < 0.1$ Pa) prior to analysis. Textural properties were calculated using the software MicroActive and SAIEUS, both provided by Micromeritics.

XRD diffractograms were acquired in a DISCOVER D8 diffractometer (Bruker), equipped with a Cu X-ray source (K- α line, $\lambda = 1.5406$ Å), able to scan 2θ angles between 10° and 80° at speed of 0.5 °/min.

Elemental analysis (EA) and element mapping of the composition of synthesized materials were performed using a scanning electron microscope JSM 7800 F (JEOL) equipped with an X-max 150 microanalysis system a Si/Li detector allowing a detection range from boron to uranium and a resolution of 127 eV.

Transmission electron microscopy (TEM) photomicrographs were obtained using the JEM 1400 High-Resolution Transmission Electron Microscope (JEOL) which irradiates a thin sample with an electron beam of uniform current density and energy within the range of 80 to 200 keV. Preparation of samples for TEM acquisition of images consisted on dispersing the carbon material in ethanol and depositing the obtained suspension on a copper grid.

For the semiquantitative determination of the possible catalysts leaching in the reaction solution, inductively coupled plasma mass spectrometry (ICP-MS) was used. The equipment used for ICP-MS analysis is an ElanDRC-e spectrometer (PerkinElmer NexionX) equipped with a sample introduction, Argon plasma ionization and quadrupole ion detection systems; in addition, the device is equipped with collision/reaction cells to eliminate some polyatomic interferences.

Catalytic activity

The transformation reaction of trans-ferulic acid into vanillin was carried out in a carousel system (Reaction Station TM, Radleys Discovery Technologies) using 5 mmol trans-ferulic acid (Sigma Aldrich), 1.2 mL H₂O₂ 50% (Sigma Aldrich), 8 mL acetonitrile (ACN, Sigma Aldrich) and 0.1 g of the synthesized catalyst; the reaction

mixture was heated at 90 °C for 6 hours. The progress of the reaction was monitored by withdrawing samples every 15 min to be analyzed by gas chromatography (GC) using a 7890 chromatograph system (Agilent) equipped with a Petrocol® DH 100 m x 0.25 m x 0.5 µm capillary column and flame ionization detector (FID). In order to identify the obtained products by GC-MS, a coupled 7820A GC-5977B/MSD (Agilent) was employed.

RESULTS AND DISCUSSION

Figure 3A depicts XRD diffractograms of synthesized materials calcined at 300 °C where two broad Bragg peaks at 22° and 45° 2θ values can be observed. These broad peaks are characteristic of amorphous carbons with small sp² domains whose (002) and (100) planes correspond to a graphitic hexagonal structure^{36,37}. These characteristic peaks were more intense for ordered mesoporous carbons (OMCs) calcined at the lowest temperature. As the calcination temperature increases, corresponding CuO and Fe₂O₃ oxide diffraction peaks appeared at 400 °C when disordered mesoporous carbons (DMCs) used as support (Figure 3A and 3C) and not until 500 °C for the case of OMC (Figure 3B and 3D). This is due to the fact that OMC is more resistant to oxidation than DMC, as recently demonstrated when OMC and DMC were activated by CO₂ (similar carbon yield and A_{BET} were obtained after 45 and 75 min for DMC and OMC, respectively)³⁸.

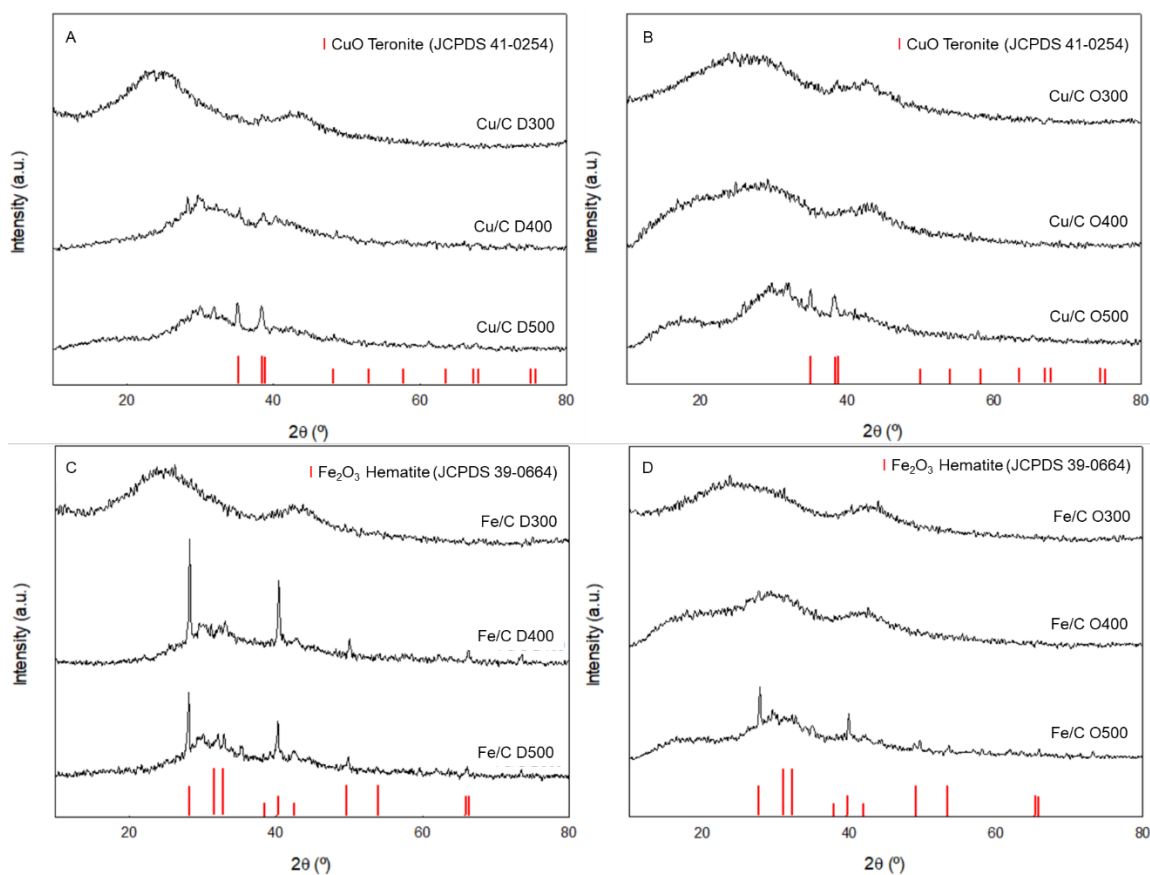


Figure 3. XRD diffraction patterns of synthesized materials at different calcination temperatures (300, 400 and 500 °C). A: Copper-based disordered materials; B: Copper-based ordered materials; C: Iron-based disordered materials; D: Iron-based ordered materials.

N_2 adsorption-desorption isotherms of the synthesized materials calcined at 300 and 400 °C respectively, shown in Figure 4, can be classified according to IUPAC³⁹ as type IV corresponding to mesoporous materials. Materials calcined at 500 °C exhibited type III isotherms, corresponding to almost non-porous materials. Textural properties are listed in Table 1. Figure S1 shows that as a general trend, BET area (S_{BET}) of non-functionalized materials increased after calcination at 300 °C and further decreased after thermal treatment at higher temperatures, with a drastic loss of surface area ($A_{BET} < 35m^2/g$) at 500 °C due to an almost complete oxidation of the carbonaceous support. Similar behavior was observed in pore size distributions (PSDs) of Figure S2, where porosity gradually disappears at increased calcination temperatures.

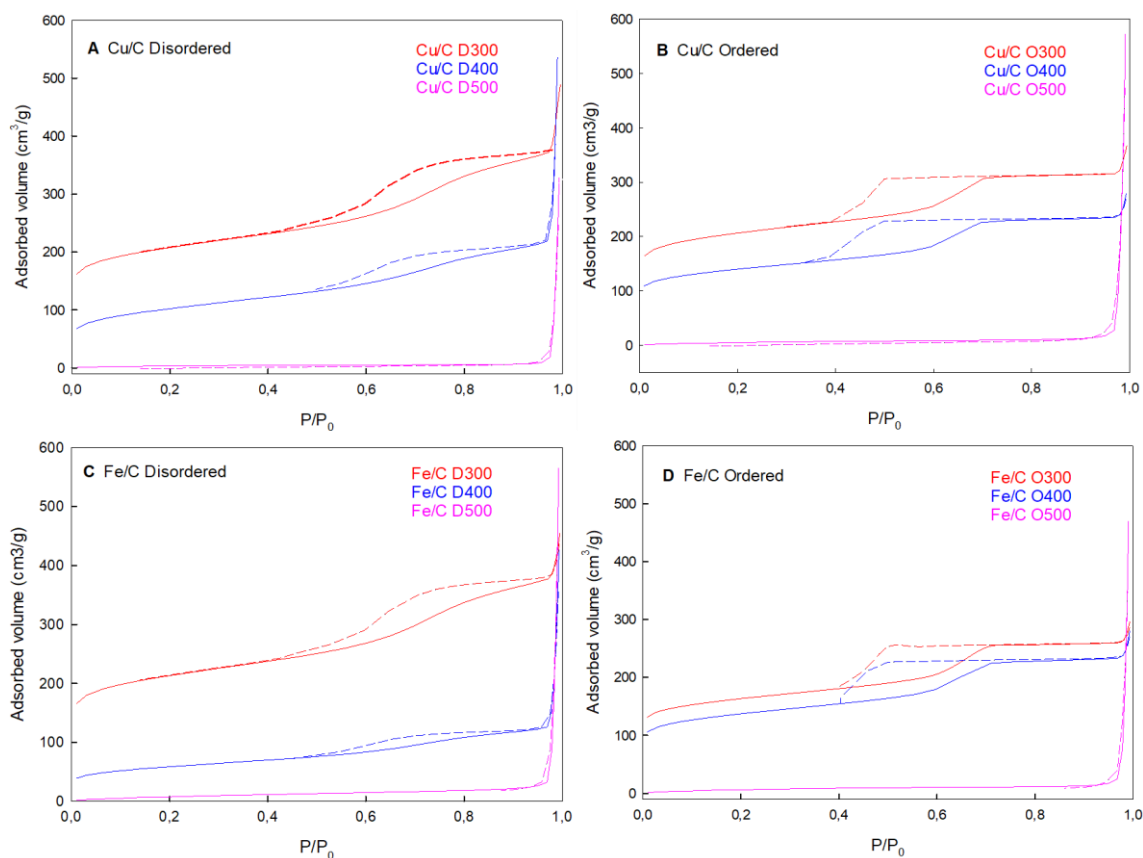


Figure 4. N₂ isotherms of A: Cu/C disordered; B: Cu/C ordered; C: Fe/C disordered; D: Fe/C ordered.

Furthermore, values of Table 1 also show the expected evolution of micro- and mesopore volumes (V_{μ} and V_{meso} , respectively) and average mesopore diameter ($D_{\text{av,BJH}}$), in agreement with the aforementioned gradual loss of porosity.

TEM images shown in Figure 5 and Figure S3, corroborate the findings of the textural analysis by physisorption of N₂, while metal loading (0.5 wt.%) was confirmed by SEM/EDX technique.

Table 1. Textural properties of synthesized materials.

Material	A_{BET} (m²/g)	V_{meso} (cm³/g)^a	V_μ (cm³/g)^b	D_{av,BJH} (nm)
OMC	515	0.16	0.19	4.6
Cu/C O300	769	0.23	0.26	5.3
Cu/C O400	515	0.20	0.17	5.5
Cu/C O500	22	0.05	-	-
Fe/C O300	607	0.20	0.20	5.5
Fe/C O400	502	0.20	0.16	5.6
Fe/C O500	26	0.04	-	-
DMC	490	0.24	0.16	6.5
Cu/C D300	768	0.32	0.25	7.3
Cu/C D400	367	0.24	0.10	17.4
Cu/C D500	12	0.02	-	-
Fe/C D300	789	0.32	0.26	7.1
Fe/C D400	210	0.14	0.06	20.0
Fe/C D500	34	0.05	-	-

^a $V_{\text{meso}} = V_{0.97, \text{N}_2} - V_{\mu}$, where $V_{0.97, \text{N}_2}$ is the adsorbed volume at a relative pressure of 0.97;

^b Calculated by applying 2D-NLDFT to N₂ adsorption isotherms.

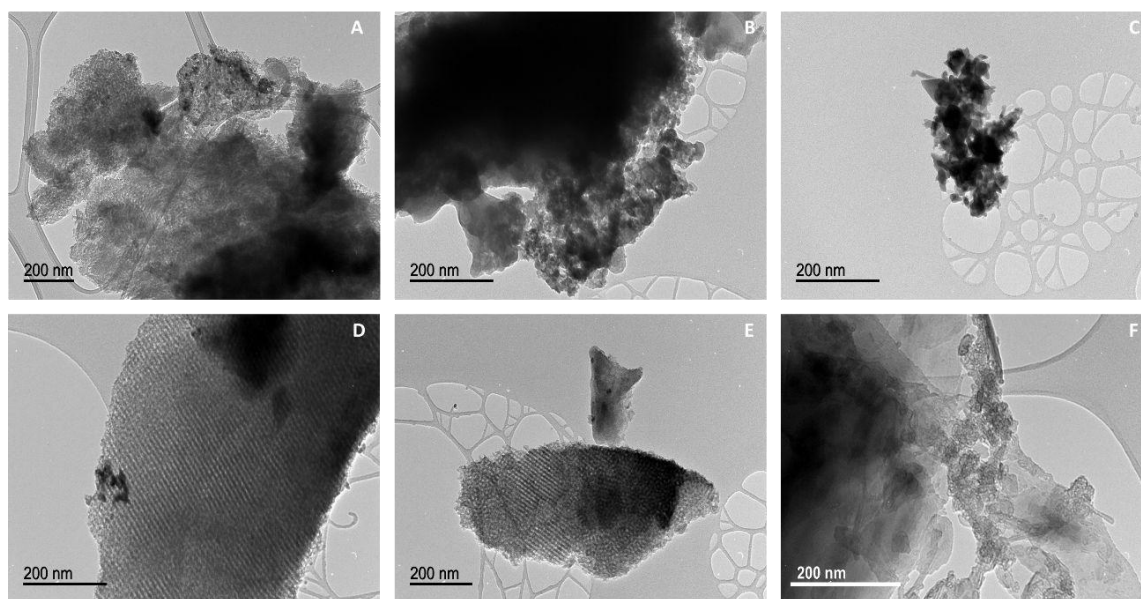
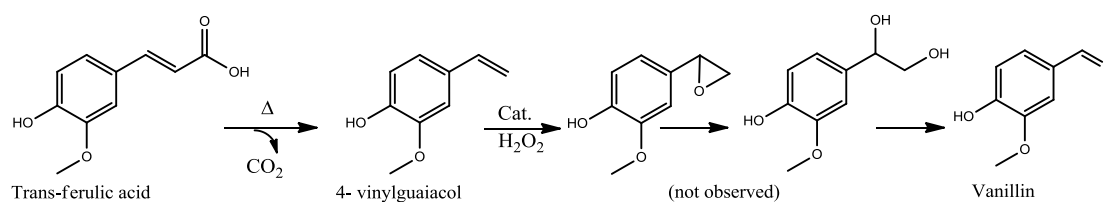


Figure 5. TEM images of A: Cu/C D300; B: Cu/C D400; C: Cu/C D500; D: Cu/C O300; E: Cu/C O400; F: Cu/C O500.

Figure 6 summarizes the experimental results for the transformation of trans-ferulic acid into vanillin using Cu and Fe based materials. The reaction (Scheme 1) takes place in two steps via free radical mechanism³¹⁻³³. In the first step, trans-ferulic acid is thermally decarboxylated to form 4-vinylguaiacol (2-methoxy-4-vinylphenol), which has high value in the food industry as a flavouring and preservative agent⁴⁰, followed by subsequent oxidation of the double bond to form the corresponding epoxide (not observed in this study), which may be subsequently hydrolyzed to form the corresponding diol (also not observed in this study) to then generate vanillin.

Blank runs (in absence of the catalysts) were also performed, with a complete conversion of trans-ferulic acid into 4-vinylguaiacol (> 99%) without detecting any additional product/s. Product confirmation was obtained by GC-MS (see Figure S4).



Scheme 1. Transformation of trans-ferulic acid into vanillin via formation of 4-vinylguaiacol as intermediate.

Materials calcined at 300 and 400 °C, presenting higher BET surface values, provided lower vanillin selectivity values as compared to materials calcined at 500 °C, which could be due to the presence of most carbonaceous support providing the material with higher hydrophobicity (resulting in lower interaction between the active centers of the catalyst and the reaction mixture)⁴¹. No general trends could be observed for Cu or Fe-containing materials with the exception of the aforementioned improved vanillin selectivity for higher temperature calcined materials (500 °C), where most of the carbonaceous support was removed (ca. 70%, TG-DTA, results not shown).

Materials were subsequently tested for stability in various reaction cycles, with Cu-based catalysts generally preserving improved vanillin selectivities (and stability) as compared to Fe-based counterparts. As example, Cu/C O500 provided a very good vanillin selectivity at complete trans-ferulic acid conversion in the first cycle (ca. 47%), well preserved after three reuses (ca. 50%). Similar results were obtained for Cu/C D500, despite an overall reduced selectivity after reuses (53% first use vs 34% after three reuses). 4-vinylguaiacol was obtained as sole additional product under the investigated reaction conditions. Comparably Fe-based materials provided significantly reduced vanillin selectivities after reuses (only a good vanillin selectivity was obtained in the first use, observed even for Fe/C D400), after which 4-vinylguaiacol was observed as exclusive major product (essentially same results as for the blank reaction). ICP-MS did not detect significant amounts of Fe and Cu leaching into solution after the first reaction (all metal quantities remaining below 0.5 ppm for 500 °C calcined materials, with the exception of Cu/C O500), and insignificant quantities for any catalytic system after subsequent reuses (all metal quantities below 0.5 ppm).

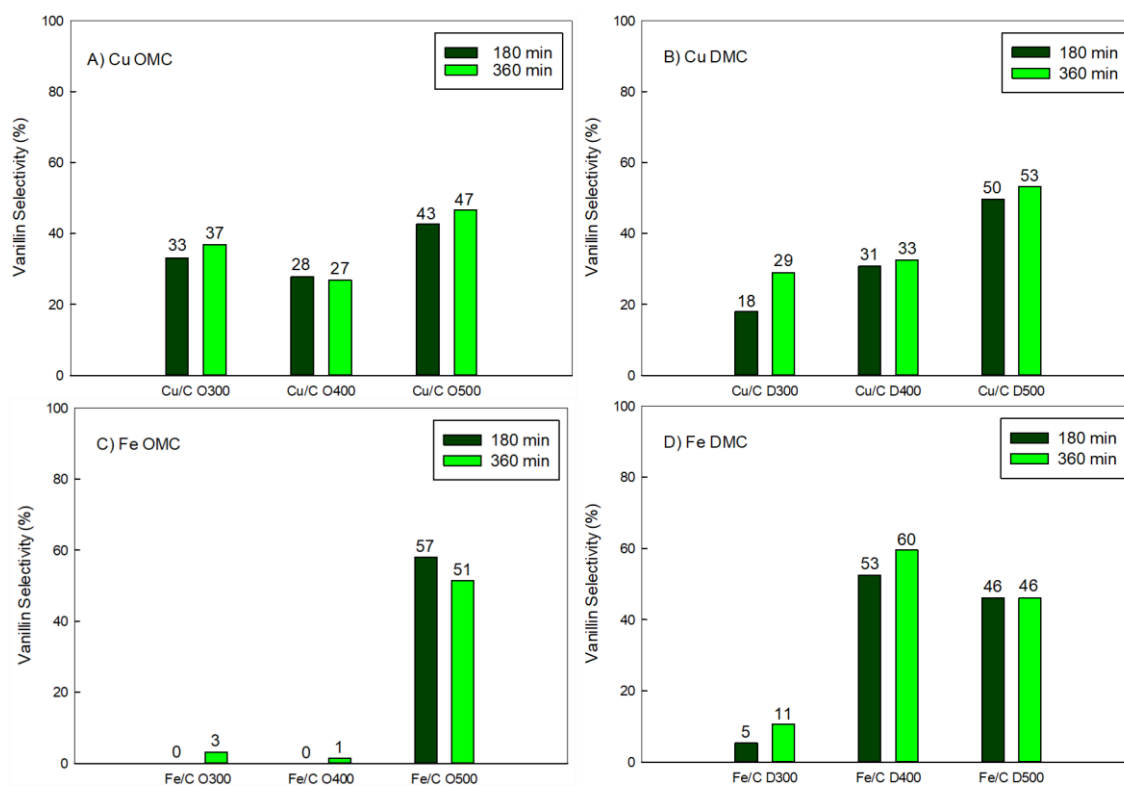


Figure 6. Vanillin selectivity obtained at different reaction times using Fe and Cu-containing OMC and DMC synthesized materials.

Table 2. Vanillin selectivity (%) using synthesized materials as catalyst (first use vs

Material	First use	Recycle 1	Recycle 2	Recycle 3	Cu and Fe concentration (ppm)*
<i>Cu/C O300</i>	37	13	10	10	6.7
<i>Cu/C O400</i>	27	8	8	12	1.7
<i>Cu/C O500</i>	47	70	53	50	6.7
<i>Fe/C O300</i>	3	1	-	3	0.4
<i>Fe/C O400</i>	1	1	1	2	0.8
<i>Fe/C O500</i>	51	5	4	< 1	0.4
<i>Cu/C D300</i>	29	9	3	29	0.5
<i>Cu/C D400</i>	33	32	50	3	0.9
<i>Cu/C D500</i>	53	41	36	34	0.5
<i>Fe/C D300</i>	11	6	-	2	0.2
<i>Fe/C D400</i>	60	4	7	14	9.7
<i>Fe/C D500</i>	46	5	5	4	0.2

subsequent reaction cycles) in the conversion of trans-feruli

c acid to vanillin.

* Reaction mixture ICP-MS after the first reuse (recycle 1)

Reaction conditions: 0.1 g of catalyst; 0.5 mmol of trans-ferulic acid; 1.2 mL H₂O₂ (50% v/v solution); and 8 mL acetonitrile at 90 °C, 360 min reaction.

CONCLUSIONS

Mesoporous carbonaceous materials functionalized with 0.5% wt. Cu or Fe loading were synthesized via mechanochemistry. Calcination temperature and the ordered/disordered mesoporous nature of the carbon support were found to have a relevant influence on both textural properties and selectivity to vanillin in the conversion of trans-ferulic acid. Upon calcination temperature increasing, the carbon support was progressively removed (up to 70-80%), with the ordered mesoporous carbon being more resistant to oxidation/removal. Optimum vanillin selectivity (47-50%) was obtained for Cu/C O500 after three-hour reaction time, with an excellent stability after several reuses (6-hour reaction time each reuse).

Supporting Information

Textural properties graphics, TEM images, GC-MS spectra, catalytic activity comparison. Supporting information available online at XXXXXXXX.

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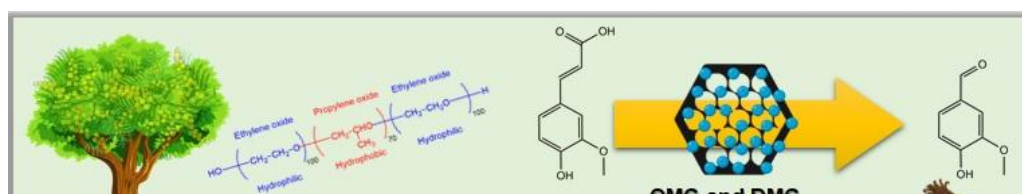
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TOC



Synopsis

Mechanochemically synthesized ordered and disordered Fe and Cu-containing materials exhibited a good vanillin selectivity (up to 70 %) and stability (after three reuses) in the conversion of trans-ferulic acid.