Efficient Mechanochemical Bifunctional Nanocatalysts for the Conversion of Isoeugenol to Vanillin

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A bifunctional nanocatalyst composed of iron containing SBA-15 material modified with sulfonic acid groups was synthesized by a mechanochemical approach. A full characterization of the obtained nanocatalyst was performed by N2 physisorption isotherms analysis, transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and Fourier-Infrared Spectroscopy (FT-IR). The mechanochemically synthesized nanocatalyst displays a high isoeugenol conversion to vanillin under mild conditions using H2O2 as oxidizing agent. Interestingly, this conversion resulted to be higher than that one obtained with the same material synthesized by an impregnation method. Additionally, the nanocatalyst showed excellent reusability over four successive runs under the studied reaction conditions.

Keywords: vanillin, nanocatalyst, catalytic oxidation, sulfonic groups, SBA-15

INTRODUCTION

Nowadays, in the field of Green Chemistry, the conversion of lignocellulosic biomass into value-added chemicals has become a challenging topic in both academic and industrial research areas (Zakzeski et al., 2010; Xu et al., 2014; Behling et al., 2016). Lignocellulosic biomass is composed by three major components (cellulose, hemicelluloses, and lignin), which offers specific opportunities to produce a myriad of valuable chemicals (Rinaldi et al., 2016). Among them, the highly functionalized and aromatic structure of lignin facilitates the designing of desired chemical platforms. In this sense, derived compounds of lignin such as eugenol, isoeugenol, and ferulic acid have been employed to obtain vanillin through a simple oxidation route (Gusevskaya et al., 2012). Vanillin (4-hydroxy-3-methoxybenzaldehyde) possesses a number of valuable applications for food, beverages, perfumery and pharmaceutical industries owed to it represent the principal flavor and aroma component in vanilla. Currently, the major amount of vanillin is obtained from petro-based compounds, especially guaiacol and glyoxylic acid by non-environmental friendly synthetic routes such as Riedel process, Huang et al. (2013) attaining low qualities of the final product. To overcome these drawbacks, greener strategies based on the catalytic oxidation of lignin model compounds have been developed using metal functionalized mesoporous silica material as efficient nanocatalysts (Augugliaro et al., 2012; Franco et al., 2017).

Noteworthy, it have been reported that the anchorage of organic functional moieties like –COOH and –SH can interact with silanol groups of the mesoporous silica framework and control
its surfaces properties and consequently its catalytic performance (Li and Yan, 2010; Rajabi et al., 2011). Among various functionalized groups, sulfonic acid group cause a remarkable increase on the catalytic performance of the catalysts due to its favored interactions with the metal active sites and its surface acid properties (Akiyama et al., 2011). Incorporation of sulfonic groups on the surface of ordered mesoporous such as SBA-15 and MCM-41 is performed generally by two step process (Kapoor et al., 2008): co-condensation or anchoring of -SH containing alkoxide precursors and the subsequence oxidation in the present of H₂O₂, which are somewhat complicate and incomplete routes (Melero et al., 2006). In previous works, the lack of order in few domains of sulfonic groups at the pore surfaces have decreased the catalytic yields caused by the aggregation of nanoparticles on the outer surface of the nanocatalysts (Kim et al., 2009; Jackson et al., 2013). For these reasons, the designing of novel efficient synthetic routes toward the synthesis of high performance nanocatalysts composed of metal containing mesoporous silica modified with sulfonic acids groups is still a challenge.

In this work, we propose an unprecedented one-pot mechanochemical synthesis of bifunctional nanocatalysts (Figure 1) based on iron containing SBA-15 functionalized with sulfonic groups (Fe-SBA15-HSO₃Μ) for the selective oxidation of isoeugenol to vanillin. The methodology used represents a greener and innovative route to construct highly functionalized mesoporous silica nanomaterials taking advantage of their nanochannels with controllable pore size, high surface area and tunable reactivity. Also, we have compared the catalytic performance of the novel nanocatalysts with others synthesized by conventional methods such as the ball milled/ impregnation method (Fe-SBA15-HSO₃Μ−IM).

**EXPERIMENTAL**

**Materials**

All chemicals chloride were obtained from Sigma–Aldrich with pure analytical degree.

**Synthesis of SBA-15**

The ordered mesoporous silica SBA-15 was synthesized following a procedure described in the literature (Jarry et al., 2006). The triblock copolymer Pluronic P123 (0.41 mmol) was dissolved in a HCl aqueous solution (2M) at 35°C. Subsequently, Tetraethyl ortho-silicate (TEOS) (25 mmol) was added drop wise to the solution mentioned above. The resulted solution was agitated for 24 h at 35°C. After that the mixture was subjected to a hydrothermal treatment in an oven at 100°C for 48 h. The resulting material was filtered and dried at 60°C. Finally, the template was calcined at 550°C for 8 h to remove it.

**Preparation of Fe-SBA-HSO₃Μ Nanocatalysts**

Fe-SBA-HSO₃Μ catalyst was prepared using 0.5 g of SBA-15 as silica support, 1.34 g of Fe(NO₃)₃·9H₂O as iron precursor, 0.25 mL of propionic acid and 0.5 mL of sulfuric acid in a planetary ball mill (Retsch PM-1000) at 350 rpm for 15 min, employing a 125 mL reaction chamber and eighteen 10 mm stainless steel balls (Pineda et al., 2012). Subsequently the
obtained composite was heated up slowly to 800°C for 8 h using an extractor to remove the possible gases formed during the calcination process.

### Preparation of Fe-SBA-HSO$_3$\textsuperscript{BM-IM} Nanocatalysts

The Fe-SBA-HSO$_3$\textsuperscript{BM} catalyst was prepared by a two-step protocol. Firstly, 0.5 g of SBA-15, 1.34 g of Fe(NO$_3$)$_3$·9H$_2$O and 0.25 mL of propionic acid were milled in a planetary ball mill (Retsch PM-1000) at 350 rpm for 15 min. The obtained material was calcined at 600°C for 8 h. Secondly, 10 mL of sulfuric acid was added drop wise to 1 g of the obtained Fe-SBA-15. After filtration, the solid was washed with distilled water, was heated up slowly to 800°C for 8 h using an extractor to remove the possible gases formed during the calcination process and dried overnight.

### Catalyst Characterization

Low-angle XRD pattern were recorded on a Bruker D8 Discover diffractometer equipped with a goniometer Bragg Brentano $\theta/\theta$ of high precision, and coupled to a Cu X-ray tube. The surface

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**FIGURE 2** | TEM images of (A) SBA-15, (B) Fe-SBA15-HSO$_3$\textsuperscript{BM} nanocatalyst, (C) Fe-SBA15-HSO$_3$\textsuperscript{BM-IM}, and (D) small-angle XRD patterns of the nanocatalysts.

**FIGURE 3** | N$_2$ adsorption-desorption isotherm for (A) Fe-SBA15-HSO$_3$\textsuperscript{BM} and (B) Fe-SBA15-HSO$_3$\textsuperscript{BM-IM} nanocatalysts.
area and pore volume were calculated from N₂ adsorption–desorption isotherms at liquid nitrogen temperature (77 K) in a Micromeritics ASAP 2000 instrument. The samples were previously degassed for 24 h at 130°C at vacuum conditions ($p < 10^{-2}$ Pa).

TEM analysis was performed in the FEI Tecnai G2 system, integrated to a charge coupling device camera. To the preparation, the samples were diluted in ethanol and deposited on a copper grid.

The FT-IR spectra of both nanocatalysts were recorder on an infrared spectrophotometer (ABB MB3000 with Horizon MBTM software), equipped with an ATR PIKE MIRacleTM sampler and a ZnSe window employing 256 scans at a resolution of 16 cm⁻¹.

The metal content of the catalysts was obtained by ICP–MS in an Elan DRC-e (PerkinElmer SCIEX) spectrometer. Prior to the analysis, the samples ($\approx$25 mg) were digested using an acid mixture of HF/HNO₃/miliQ water up to a maximum of 1% of HF.

Energy dispersive X-ray spectroscopy (EDX) of the obtained materials was carried out using a JEOL JSM-6300 Scanning Microscope with energy-dispersive X-ray analysis (EDX) at 20 kV.

### Oxidation of Isoeugenol to Vanillin

The oxidation reactions were carried in a carousel system using isoeugenol (0.8 mL, 5 mmol), 30% H₂O₂ solution (1.2 mL, 0.04 mmol), 0.10 g of catalyst and acetonitrile (8 mL) as solvent. The reaction mixture was heated at 90°C for 24 h. The progress of the reaction was monitored by withdrawing samples at 20, 40 min, and then every 1 h for 24 h. Samples were analyzed in a HP5890 Series II Gas Chromatograph (60 mL min⁻¹ N₂ carrier flow, 20 psi column top head pressure) using a flame ionization detector (FID). The capillary HP-101 column (25 m x 0.2 mm x 0.2 µm) was employed.

### RESULTS AND DISCUSSION

The synthesized materials showed a typical diffraction pattern of SBA15-like hexagonal structure which displayed a high intensity (100) peaks at 0.95° and additional order (110) peaks at 1.76° (Figure 2D). The transmission electron microscopy (TEM) images (Figures 2B,C) depicted that Fe containing nanoparticles with size ranging between 4 and 5.7 nm were successfully incorporated inside the nanochannels of SBA-15 (Figure 2A) through the two synthetic routes. However, significant changes in the nanoparticles distribution patterns were observed for the two nanocatalysts. The Fe-SBA15-HSO₃BM frameworks have a highly homogeneous and well-dispersed distribution (Figure 2B) which is in agreement with similar materials reported for our group (Pineda et al., 2011); while in the Fe-SBA15-HSO₃BM–IM are highly aggregated. Also, the small shifts to lower diffraction angles of the (100) peaks suggest a slight disordering around the pores while maintaining the hexagonal pore structure upon the synthesis of both nanocatalysts.

The nitrogen adsorption/desorption isotherms were performed to investigate the surface area and pore size properties of the synthesized nanocatalysts. The nanocatalysts possess the typical type IV isotherms and H1 hysteresis loops between 0.6 and 0.75 P/P₀ (Figure 3), which is a representative behavior of mesoporous materials that contain uniform cylindrical pores (Gao et al., 2007). Interestingly, nitrogen adsorption/desorption experiments displayed a pronounced decay of the surface areas and pore volumes of the nanocatalysts in comparison with the SBA-15 (Table 1). These results can be attributed to the occupation of the SiO₂ nanochannels for the iron nanoparticles during the synthesis of the nanocatalysts and possible calcination.

### Table 1 | Textural properties of the synthesized nanocatalysts.

| Material | S_{BET} (m² g⁻¹) | D_{BJH} (nm) | V_{BJH} (cm³ g⁻¹) |
|----------|------------------|--------------|-------------------|
| SBA-15   | 629              | 5.9          | 0.75              |
| Fe-SBA15-HSO₃BM | 194            | 5.3          | 0.27              |
| Fe-SBA15-HSO₃BM–IM | 373       | 5.4          | 0.35              |

S_{BET}, specific surface area was estimated by the Brunauer-Emmett-Teller (BET) equation. D_{BJH}, mean pore size diameter was estimated by the Barret-Joyner-Halenda (BJH) equation. V_{BJH}, pore volume was estimated by the Barret-Joyner-Halenda (BJH) equation.

### Table 2 | Elemental composition of the nanocatalysts.

| Material           | ICP-MS (wt%) | EDX (wt%) |
|--------------------|--------------|-----------|
|                    | Fe  | Fe  | S  |
| Fe-SBA15           | 22  | 21  | –  |
| Fe-SBA15-HSO₃BM    | 16  | 15  | 20 |
| Fe-SBA15-HSO₃BM–IM | 0.10| 0.25| 0.33|
effects for the case of Fe-SBA15-HSO$_3^{\text{BM}}$–IM nanocatalysts (Zhang et al., 2015).

Figure 4 depicts the FT-IR results obtained for the Fe-SBA15-HSO$_3^{\text{BM}}$ and Fe-SBA15-HSO$_3^{\text{IM}}$ nanocatalysts respectively. In the high frequency regions the spectrum displays a broad band in the region of 2,700–3,600 cm$^{-1}$ which corresponds to -OH stretching absorption of the SO$_3$H groups. Bands appeared in the absorption ranges of 1,165–1,248 and 1,007–1,065 cm$^{-1}$ have been ascribed to the O=S=O asymmetric and symmetric stretching modes respectively. Also bands found in the range of 560–608 cm$^{-1}$ were assigned to the S-O stretching mode. All these IR bands strongly support the successful anchorage of the sulfonic groups on both nanocatalysts (Amoozadeh et al., 2016; Kolvari et al., 2016; Veisi et al., 2016).

The elemental composition of the Fe-SBA15-HSO$_3^{\text{BM}}$ and Fe-SBA15-HSO$_3^{\text{IM}}$ nanomaterials was determined by both, ICP–MS and EDX, as complementary techniques (Table 2). The ICP-MS measurements of the Fe-SBA15-HSO$_3^{\text{BM}}$ revealed an iron content of 16 wt%. This result was corroborated by EDX analysis, which displayed 15 and 20 wt% for iron and sulfur, respectively. These values strongly support the successful incorporation of sulfonic groups and iron in the SBA-15 by the applied mechanochemical protocol. Additionally, the elemental content of Fe-SBA15-HSO$_3^{\text{IM}}$ was determined and compared with the values obtained for Fe-SBA15 before the impregnation process. It was observed a decrease in the iron content after the functionalization of the Fe-SBA15, which have been attributed to the leaching of iron. The high incorporation of iron oxide nanoparticles using the BM method suggests that this approach could represent a new option in the design of novel functionalized nanocatalysts.

The catalytic behavior of both nanocatalysts was subsequently investigated to get insights on the effects of their structural variations over the selective oxidation of isoeugenol (Table 3, Figures 5, 6). Low activities were observed in the systems in the absence of the nanocatalysts and in the presence of the

### Table 3

| Entry | Catalyst                  | Time (h) | Conversion (% mol) | Selectivity (% mol) |
|-------|--------------------------|----------|--------------------|---------------------|
|       |                          |          | vanillin           | Diphenyl ether      | Unidentified products |
| 1     | Blank                    | 1        | 18                 | 13                  | 64                  | 23                  |
| 2     | 15-SBA                   | 1        | 34                 | 31                  | 49                  | 20                  |
| 3     | FeSBA-15HSO$_3^{\text{BM}}$ | 1       | 93                 | 50                  | 1.8                 | 47                  |
| 4     | FeSBA-15HSO$_3^{\text{BM}}$–IM | 1   | 22                 | 20                  | 63                  | 11                  |

*Table* Catalytic performances of the nanocatalysts toward the isoeugenol oxidation. The reaction conditions: 0.1 g catalyst, 8 mL acetonitrile, 0.8 mL isoeugenol, 1.2 mL H$_2$O$_2$, $T = 90^\circ$C, time: 1 h.

### Figure 5

Time dependent conversion and selectivity to vanillin profiles for (red circles) Fe-SBA15-HSO$_3^{\text{BM}}$ and (blue circles) Fe-SBA15-HSO$_3^{\text{BM}}$–IM nanocatalysts. Reaction conditions: 0.1 g catalyst, 8 mL acetonitrile, 0.8 mL isoeugenol, 1.2 mL H$_2$O$_2$, $T = 90^\circ$C, time: 1 h.
FIGURE 6 | Recycle activities obtained for (A) Fe-SBA15-HSO₃⁹⁹M and (B) Fe-SBA15-HSO₃⁹⁹M−IM toward the selective oxidation of isoeugenol to vanillin. Selectivity data for both nanocatalysts is inserted by the black squares representation. Reaction conditions: 0.1 g catalyst, 8 mL acetonitrile, 0.8 mL isoeugenol, 1.2 mL H₂O₂, T = 90°C, time: 1 h.

SBA-15 (Table 3 entry 1, 2). Under optimized reaction conditions (Table 3, entry 3), the Fe-SBA15-HSO₃⁹⁹M nanocatalyst showed a remarkable higher conversion and selectivity values of 93 and 51% respectively for the selective oxidation of the isoeugenol to vanillin. The lower conversion of the Fe-SBA15-HSO₃⁹⁹M−IM (Table 3 entry 4) could be associated to both, the leaching of the Fe content during the synthesis of the material and the high aggregation of the nanoparticles on specific areas of the mesoporous silica materials which induces the disorganization of the sulfonic acid groups domains.

The time dependent conversion and selectivity profiles of the nanocatalysts are shown in the Figure 5. The nanocatalyst synthesized by the mechanochemistry approach displayed a high conversion and selectivity which validates its excellent catalytic performance, while the Fe-SBA15-HSO₃⁹⁹M−IM nanocatalyst achieved just a 33% after 8 h of reaction.

The reusability of the catalysts constitutes an important parameter to take into account for future applications. At the optimum conditions, the recycling experiments were performed to investigate the stability of the reused catalysts (Figure 6). Noteworthy, the Fe-SBA15-HSO₃⁹⁹M nanocatalyst could be reutilized for at least four catalytic runs without a substantial decay in the activity, suggesting that there is not leaching of the iron nanoparticles during the reaction process. In summary, it has been demonstrated that the iron containing sulfonic acid-functionalized mesoporous silica framework synthesized by a mechanochemical procedure induces a suitable stabilization of the small iron NPs homogeneously distributed inside of the mesoporous framework favoring the enhancement of the catalytic activity of the nanoreactor.

CONCLUSIONS

In summary, we have prepared an efficient heterogeneous nanocatalyst for the selective oxidation of the isougenol to vanillin composed of sulfonic acid functionalized metal mesoporous silica framework using a one-step mechanochemical approach. The catalyst display a framework formed by a highly disperse small iron nanoparticles on the mesoporous silica stabilized by the sulfonic acids domains which induces the enhancement of the catalytic performance of the nanoreactors toward the selective oxidation of the isoeugenol. The work presented here constitutes a significant contribution, not only in the fabrication of effective bifunctional heterogeneous catalysts for the selective oxidation of the isoeugenol to vanillin, but also unraveling the structure/function relationship of the synthesized bifunctional catalysts.

AUTHOR CONTRIBUTIONS

SO conducted the catalytic reactions and wrote the first draft of the manuscript. AF conducted the synthesis of the catalyst. DR-P performed all the characterization of the materials. AP-S conducted interpretation of the materials and catalytic data. MP-dd revised the manuscript, discussed the results and improved the manuscript for submission. HS and RL conceived the concept of the paper, planned the experiments and revised, rewrote the final manuscript.

ACKNOWLEDGMENTS

RL gratefully acknowledges MINECO as well as FEDER funds for funding under project CTQ2016-78289-P and financial support from the University of Cordoba (Spain). HS gratefully acknowledges Sistan and Balouchestan University of Iran for the financial support of the research as well as Iran Nanotechnology Initiative Council for complementary financial supports. The publication has been prepared with support of RUDN University Program 5-100.
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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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