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# Design of a new iron catalyst by mechanochemistry using rice husk as a green silica source

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**Abstract:** Biomass has become an alternative to replace petroleum derived materials. Several methodologies for its valorization have been investigated to obtain high value products in a more sustainable way. Rice husk (RH) is an agricultural waste that contains up to 20 wt% of silica. Microwave assisted extraction was employed to remove metal ions from rice husk to obtain a highly pure mesoporous silica. Biogenic silica (RH-Silica) was employed as a support to design a new iron oxide catalyst (Fe/RH-Silica) by an efficient mechanochemical process. Synthesized materials were characterized by different techniques including N<sub>2</sub> physisorption, XRD, TEM, SEM and DRIFT. Materials presented excellent properties and a high activity in organic reactions. Fe/RH-Silica catalyst was tested in the selective oxidation of styrene and the alkylation of toluene under microwave irradiation. High conversion and selectivity were achieved for the desired products.

**Keywords:** Rice Husk ; Silica; Mechanochemistry; Iron oxide; Oxidation; Alkylation.

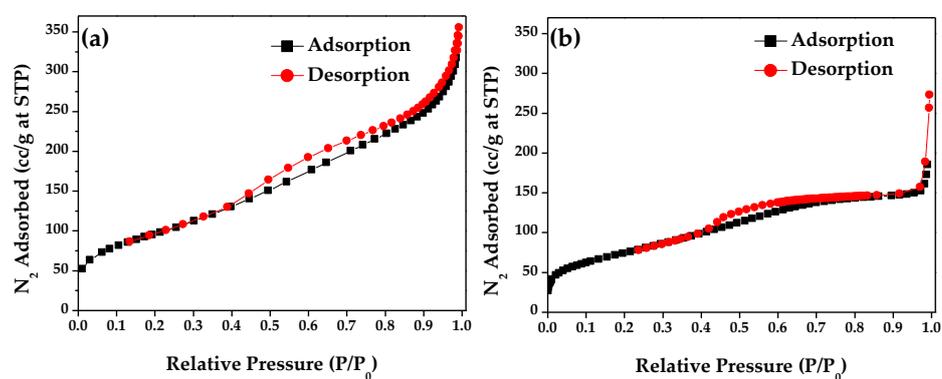
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## 1. Introduction

Fossil fuels and petroleum derived products are sentenced to be replaced. The waste of natural resources and the multiple contaminants released during its production make these procedures not friendly environmental and force to find other sustainable pathways to produce chemicals and materials. Biomass is a current alternative to produce high value products following the principles of Green Chemistry [1]. Food industry produces million of waste residues that have any economic value and it must to be eliminated by long and highly energy processes. Rice is one of the most consumed food item in the world [2]. Rice husk (RH), a waste produced from rice milling, contains a high silica amount in its composition (20 wt%)[3-5]. Microwave assisted extraction makes possible to obtain mesoporous biogenic silica (RH-Silica) from RH and eliminate different metal ions presented in the husk using an acid solution [6]. Mechanochemical process has been reported as an efficient methodology in the preparation of metal oxide catalysts [7]. RH-Silica was used as a support to design a new iron oxide catalyst by mechanochemistry (Fe/RH-Silica). Material synthesized presented iron oxide nanoparticles in its surface and a high Lewis acidity which converted it in an excellent candidate to perform oxidation and alkylation reactions. Fe/RH-Silica was tested in the selective oxidation of styrene to benzaldehyde and the alkylation of toluene under microwave irradiation with excellent results in terms of conversion and selectivity.

## 2. Results

Biogenic silica was extracted from rice husk by an integrated mechanochemical/microwave approach previously reported by our group [8-9]. Fe/RH-Silica was synthesized by mechanochemistry using  $\text{Fe}(\text{NO}_3)_3$  as iron precursor and propionic acid to obtain a Lewis acid catalyst. Figure 1 represents the  $\text{N}_2$  physisorption isotherms of RH-Silica and Fe/RH-Silica. Isotherms can be classified as type IV which is characteristic of mesoporous materials. Textural properties of both materials are shown in Table 1. RH-Silica presented a surface area of  $352 \text{ m}^2\text{g}^{-1}$  with a mean pore diameter of 8 nm and a pore volume of  $0.56 \text{ cm}^3 \text{ g}^{-1}$ . Fe/RH-Silica revealed a decreased in the surface area ( $272 \text{ m}^2\text{g}^{-1}$ ), pore diameter (7.1 nm) and pore volume ( $0.39 \text{ cm}^3 \text{ g}^{-1}$ ). These remarkable changes were consequence of the incorporation of iron oxide nanoparticles in the silica surface by milling process.



**Figure 1.**  $\text{N}_2$  physisorption isotherms of (a) RH-Silica and (b) Fe/RH-Silica.

**Table 1.** Textural properties of RH-Silica and Fe/RH-Silica materials.

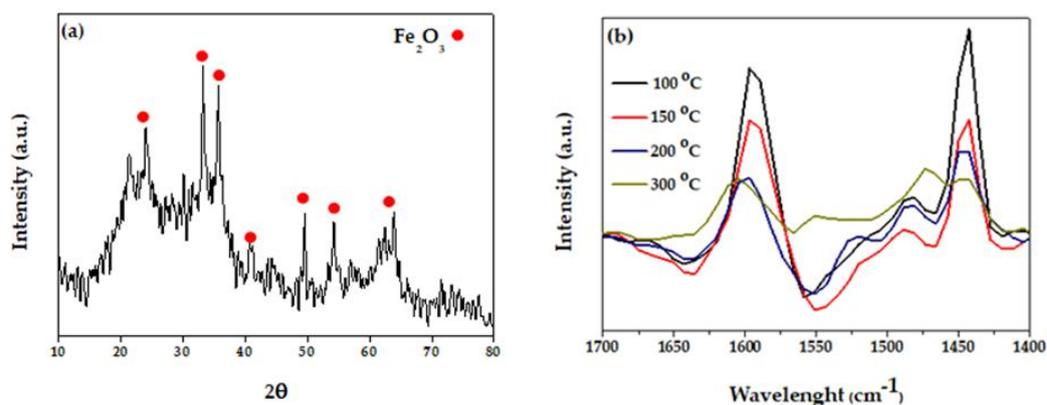
Material	$S_{\text{BET}}^1$ ( $\text{m}^2 \text{ g}^{-1}$ )	$D_{\text{BJH}}^2$ (nm)	$V_{\text{BJH}}^3$ ( $\text{cm}^3 \text{ g}^{-1}$ )
RH-Silica	352	8.0	0.56
Fe/RH-Silica	272	7.1	0.39

<sup>1</sup>  $S_{\text{BET}}$ : specific surface area was calculated by the Brunauer-Emmet-Teller (BET) equation.

<sup>2</sup>  $D_{\text{BJH}}$ : mean pore diameter was calculated by the Barret-Joyner-Halenda (BJH) equation.

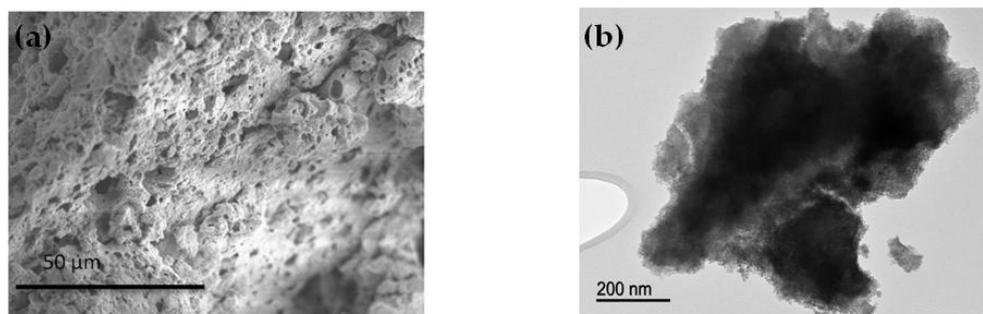
<sup>3</sup>  $V_{\text{BJH}}$ : pore volume was calculated by the Barret-Joyner-Halenda (BJH) equation.

XRD powder pattern of Fe/RH-Silica is shown in Figure 2a. Broad peak detected at  $2\theta$  value of  $22^\circ$  was characteristic of amorphous silica. Other diffraction peaks presented correspond to the iron that it was incorporated as hematite ( $\text{Fe}_2\text{O}_3$ ) [10]. Pyridine adsorption DRIFT is represented in Figure 2b. Two well define peaks at  $1442$  and  $1597 \text{ cm}^{-1}$  were observed in the spectra which confirmed the presence of strong Lewis acid sites in the material. These bands decreased with temperature increased however they are still detected at  $300^\circ \text{C}$ .

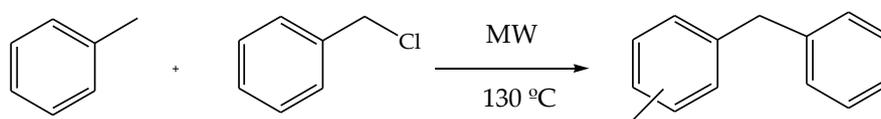


**Figure 2.** (a) Powder XRD pattern of Fe/RH-Silica; (b) Pyridine adsorbed DRIFT spectra of Fe/RH-Silica.

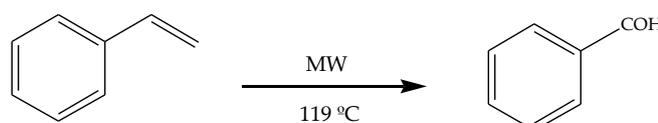
SEM micrograph of Fe/RH-Silica is shown in Figure 3a. An amorphous and compact structure is clearly observed which confirmed the results obtained in XRD. TEM images presented a dense material with different dark areas due the iron incorporation.



**Figure 3.** (a) SEM micrograph of Fe/RH-Silica; (b) TEM image of Fe/RH-Silica.



**Scheme 1.** Mechanim of the alkylation of toluene with benzyl chloride under microwave irradiation.



**Scheme 2.** Microwave assisted oxidation of styrene to benzaldehyde.

Fe/RH-Silica was tested in two organic reactions performed under microwave irradiation. In the oxidation of styrene was obtained a moderate conversion (45%) nevertheless a complete selectivity to benzaldehyde (>99%) was achieved after 1 hour of reaction. The alkylation of toluene with benzyl chloride was also studied. High conversion (>99%) and an excellent selectivity (>99%) to the monoalkylated product was achieved.

**Table 2.** Microwave assisted selective oxidation of styrene to benzaldehyde using Fe/RH-Silica as catalyst.<sup>1</sup>

Material	Conversion (mol%)	Selectivity to Benzaldehyde (mol%)
Blank	- <sup>2</sup>	- <sup>2</sup>
Fe/RH-Silica	45	>99

<sup>1</sup> Reaction Conditions: Acetonitrile = 2 mL, Styrene = 0.2 mL, H<sub>2</sub>O<sub>2</sub> (50% v/v) = 0.3 mL, Fe/RH-Silica = 0.1g, *t* = 60 min, 150 W.  
<sup>2</sup> No Reaction.

**Table 3.** Microwave assisted selective alkylation of toluene with benzyl chloride using Fe/RH-Silica as catalyst.<sup>1</sup>

Material	Conversion (mol%)	Selectivity (mol%)		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
Blank	- <sup>2</sup>	- <sup>2</sup>	- <sup>2</sup>	- <sup>2</sup>
Fe/RH-Silica	>99	57	2	41

<sup>1</sup> Reaction Conditions: Toluene = 2 mL, Benzyl chloride = 0.2 mL, Fe/RH-Silica = 0.025g, *t* = 3 min, 300 W.  
<sup>2</sup> No reaction.

#### 4. Materials and Methods

Biogenic silica from rice husks (RH-Silica) was obtained by an integrated mechanochemical/microwave assisted process. RH was grinding in a Resth-PM 100 planetary ball milling and then it was performed an acid microwave assisted extraction in a ETHOS ONE microwave to obtain RH-Silica. Fe/RH-Silica material was prepared by mechanochemical process using Fe(NO<sub>3</sub>)<sub>3</sub> as iron precursor and propionic acid to obtain an iron oxide Lewis acid catalyst. Materials were characterized using multiple techniques. N<sub>2</sub> physisorption analysis were performed in a Micromeritics ASAP at 77K. Samples were previously degassed under vacuum at 130 °C for 24 hours. Surface areas were calculated from the Brunauer-Emmet-Teller (BET) equation. Barret-Joyner-Halenda (BJH) method was employed to obtain pore size and pore diameter. XRD diffractogram was recorded in a Bruker D8 diffractometer (40 kV, 40 mA) using CuK<sub>α</sub> (λ = 0.15406) as radiation. SEM and TEM images were obtained in a JEOL-SEM JSM-6620 and a JEM 2010F (JEOL) respectively. Catalytic activity were performed under microwave irradiation in a CEM discover microwave reactor. Samples obtained were analyzed by gas chromatography in a Aligent 6890 N chromatograph fitted with an HP-5 capillary column (30 m × 0.32 mm × 0.25 mm). All results were confirmed by GC-MS.

## 5. Conclusions

Biogenic silica (RH-Silica) was obtained from rice husk using an integrated milling and acid microwave extraction. RH-Silica was employed as support to design a new iron catalyst by mechanochemical process. Fe/RH-Silica presented iron oxide nanoparticles in its surface and a high Lewis acidity. Material was tested in two different organic reactions under microwave irradiation. Good results in terms of conversion and selectivity were achieved to the desired products. This work is an example of valorization of a waste product to design a new green material and its application as catalyst.

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**Author Contributions:** R.L., A.M.B and A.A.R. conceived and designed the experiments, together with A.F. who performed the experiment and analyzed the data; A.F. and R.L. wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data, in the writing of the manuscript, and in the decision to publish the results.

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