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## Short Communication

# Rice straw-based activated carbons doped with SiC for enhanced hydrogen adsorption

S. Schaefer<sup>a</sup>, G. Muñoz<sup>a,b,c</sup>, M.T. Izquierdo<sup>d</sup>, S. Mathieu<sup>a</sup>,  
M.L. Ballinas-Casarrubias<sup>b</sup>, G. González-Sánchez<sup>c</sup>, A. Celzard<sup>a</sup>,  
V. Fierro<sup>a,\*</sup>

<sup>a</sup> Institut Jean Lamour, UMR CNRS - Université de Lorraine n°7198, ENSTIB, 27 Rue Philippe Séguin, CS 60036, 88026 Épinal cedex, France

<sup>b</sup> Department of Renewable Energies and Environmental Protection, Centro de Investigación en Materiales Avanzados (CIMAV S.C.), Chihuahua, Chih, Mexico

<sup>c</sup> Graduate Department, Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua (UACH), Chihuahua, Chih, Mexico

<sup>d</sup> Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán, 4, Zaragoza, E-50018, Spain

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## ABSTRACT

Activated carbons (ACs) based on rice straw (RS) were synthesised using potassium carbonate as activating agent at three different  $K_2CO_3/RS$  weight ratios. Morphological, chemical, structural as well as textural characterisations were carried out in order to establish relationships between the physicochemical properties of the materials and their hydrogen adsorption capacities. The ACs contained potassium and silicon as the main impurities. Si was identified by XRD in both phases of silicon dioxide and silicon carbide. The presence of SiC was particularly surprising due to the rather low activation temperature, much lower than what is usually required for SiC synthesis. ACs exhibited well-developed surface areas (approximately  $2000\text{--}2100\text{ m}^2\text{ g}^{-1}$ ) and high micropore volumes, making them suitable for hydrogen storage applications. RS-based ACs showed higher hydrogen storage capacities than those previously obtained with KOH-activated sucrose. The latter exhibited hydrogen uptakes (excess, 10 MPa, 298 K) up to 0.55 wt. %, whereas 0.65 wt. % was measured for RS-based ACs in the same conditions. The higher hydrogen capacities and isosteric heats of adsorption found here were attributed to the presence of SiC.

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## Introduction

The design of high-efficiency hydrogen storage systems is a bottleneck step in the development of hydrogen as an energy

vector. Solid-state hydrogen storage systems, either by absorption or adsorption, have been investigated for many years. Activated carbons (ACs) are cheap, compared to more sophisticated materials such as Metal Organic Frameworks,

\* Corresponding author.

E-mail address: [vanessa.fierro@univ-lorraine.fr](mailto:vanessa.fierro@univ-lorraine.fr) (V. Fierro).

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and are often biosourced materials exhibiting high hydrogen storage capacities at cryogenic temperatures (around 6.8 wt. % in excess at 77 K) [1]. Hydrogen excess uptake in ACs is most of the time lower than 1 wt. % near room temperature and 10 MPa [1–4]. Several strategies were applied to increase hydrogen – ACs surface interactions. Metal nanoparticle doping is the most widespread approach for inducing hydrogen chemisorption, spill-over or polarised physisorption [5–10]. The second approach consists in introducing heteroatoms for increasing the hydrogen adsorption potential at the surface of the carbon-based materials. Thus, N and B were introduced, forming carbon nitrides, carbon boro-nitrides or even carbides, and their positive effect on hydrogen adsorption was demonstrated [11–15]. The favourable effect of silicon carbide (SiC) on hydrogen adsorption was theoretically [16] and experimentally [17,18] investigated. However, the synthesis of SiC remains uneasy due to the high temperatures required, typically in the range 1600–1900 K [19]. In addition, the interactions between hydrogen and SiC were investigated in carbon-SiC nanotubes [17,18] having low surface areas (i.e., below 100 m<sup>2</sup> g<sup>-1</sup>, according to the BET method based on N<sub>2</sub> adsorption at 77 K). Despite the fact that these studies evidenced the possibility of using SiC-doped materials for hydrogen storage, the low surface areas of those materials limited the hydrogen uptake. Hence, SiC-containing materials of much higher specific areas might be interesting materials for hydrogen storage.

The synthesis of SiC and SiC-containing materials based on rice by-products such as rice husk and rice straw at high temperatures is well known [19–23]. Hydrogen storage in rice-based ACs has been studied at 77 K, a temperature at which pore texture is much more important than electrostatic interactions [24,25]. As far as we know, hydrogen adsorption heats of ACs containing SiC were never determined at near room temperature.

Therefore, the purpose of the present study was to elucidate whether the presence of Si in high surface area-ACs improves hydrogen adsorption near room temperature. ACs were thus prepared by K<sub>2</sub>CO<sub>3</sub> activation of rice straw (RS). The corresponding hydrogen adsorption data were compared with previous results taking into account the surface area and the average pore size of the ACs. We definitely showed that SiC doping has a positive effect on hydrogen adsorption, increasing both excess uptake and heat of adsorption.

## Experimental

### Materials synthesis

20 g of rice straw (RS) were cut, manually ground and then impregnated for 24 h using 300 mL of a solution of potassium carbonate of the appropriate concentration in order to get the desired activation ratio. Then the mixture was left to dry at 393 K. K<sub>2</sub>CO<sub>3</sub> is a better activating agent than Na<sub>2</sub>CO<sub>3</sub> [26,27] and it is also cheaper than KOH. In order to promote the activation effect, the activation temperature was 1173 K, higher activation temperatures being expected to promote the conversion of SiO<sub>2</sub> into SiC. The activation ratio (R) was defined as the K<sub>2</sub>CO<sub>3</sub> to RS mass ratio, and the corresponding

samples were labelled KC-RS\_R, where R was fixed to 3, 4 or 5. After impregnation, RS was put in an oven at 393 K overnight in order to evaporate water. The impregnated, dry, RS was placed in a nickel crucible and then put in a horizontal stainless steel tubular oven flushed by pure nitrogen flowing at 100 mL min<sup>-1</sup>, and heated at 3 K min<sup>-1</sup> up to the final temperature of 1173 K. The latter was held for 2 h, and then the sample was cooled under N<sub>2</sub> flow. The crucible containing the activated material was then removed from the furnace and let to oxidise slowly in air for several hours to avoid violent K oxidation upon washing. Then, the material was washed with hydrochloric acid (1 mol L<sup>-1</sup>), bi-distilled water, and finally in a Soxhlet extractor for 2 days with bi-distilled water again to eliminate the remaining carbonates.

### Characterisation

The textural characterisation of ACs was performed by nitrogen and carbon dioxide adsorption at 77 and 273 K, respectively, using an automatic adsorption apparatus (ASAP 2020, Micromeritics). The samples were degassed under vacuum at 423 K until the pressure stabilised around 0.2–0.4 mPa for more than 48 h. Further degassing was carried out at the measuring port for at least 6 h. Cool and warm volumes were determined after nitrogen or carbon dioxide adsorption to avoid helium entrapment in the narrowest pores. Adsorption data were treated using the Microactive software from Micromeritics. The pore size distributions (PSDs) were obtained using non-local density functional theory (NLDFT) with the Solution of Adsorption Integral Equation Using Splines (SAIEUS<sup>®</sup>) routine. SAIEUS<sup>®</sup> has the advantage of combining both CO<sub>2</sub> and N<sub>2</sub> adsorption data to get more accurate PSDs [28]. The aforementioned NLDFT method was also used to determine the surface areas, S<sub>NLDFT</sub> (m<sup>2</sup> g<sup>-1</sup>), by integrating the PSDs over the whole range of pore sizes [29].

Scanning Electron Microscopy (SEM) observations with secondary electrons (SE) and backscattered electrons (BSE), associated with chemical analysis using Energy-dispersive X-ray spectroscopy (EDX), were carried out. All microscopy studies were made with a FEI QUANTA600FEG equipped with a Bruker Quantax spectrometer. X-ray diffraction (XRD) patterns were collected with a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu anticathode working at 40 kV and 40 mA and a scintillation detector. The diffraction patterns were obtained over a 2θ range from 10° to 80° with a step of 0.02°. The assignment of crystalline phases was performed based on Joint Committee on Powder Diffraction Standards (JCPDS) files. Ash contents were obtained after calcination in air, using a muffle oven heated at 5 K min<sup>-1</sup> until the final temperature of 1073 K, which was held for 45 min.

Hydrogen adsorption experiments were carried out at 298 K using a high-pressure automatic adsorption apparatus (HPVA II, Micromeritics). The temperature was set to 293 K to measure the cold volume, and then it was changed to 298 K to measure the warm volume and to carry out hydrogen adsorption. The pressure range was 0.15–10 MPa for adsorption and 10–2 MPa for desorption. The contribution of the empty cell was systematically measured and subtracted to all data in order to improve the accuracy. The quantity of

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