

## Steam reforming of acetic acid using Ni loaded activated carbons obtained from biomass residues

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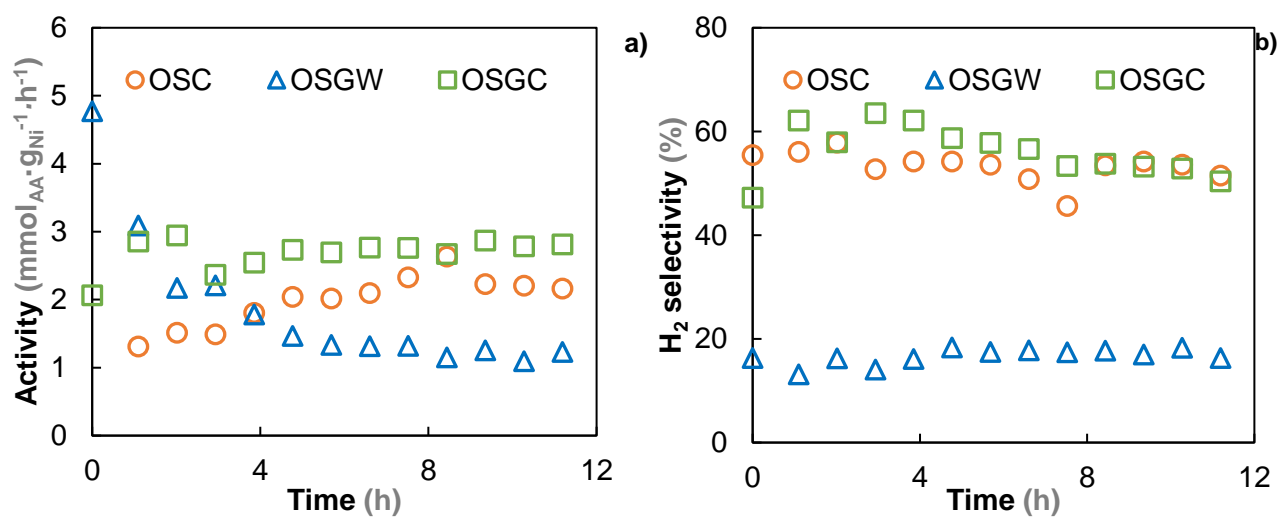
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Steam reforming (SR) of oxygenated compounds in the pyrolysis liquids of biomass residues represents a sustainable path for renewable hydrogen generation. It can be carried out by using nickel catalysts supported over activated carbons (ACs) obtained from the same residues, which enhances the sustainability of the process. The aim of this work consists of the study of the effect of the catalytic support on the performance of nickel catalysts in the SR of acetic acid (AA) as model compound.

For this purpose, nickel supported on AC catalysts with a load of 10% were prepared. ACs were obtained from olive stone (OS) through I) carbonization at 800 °C in a N<sub>2</sub> atmosphere (OSC), II) gasification with steam water of OSC at 850 °C (OSW) and III) gasification of OSC with CO<sub>2</sub> at 780 °C (OSG). Nickel was incorporated by wet impregnation followed by a thermal treatment at 700 °C in an inert atmosphere. The catalysts were reduced in 20% H<sub>2</sub> atmosphere at 600 °C for 2 h prior to the AA SR experiments, and they were characterized before and after the tests (Table 1). OSC and OSGC present a homogeneous nickel distribution (XPS vs ICP content), whereas in OSW nickel seems to be located inside the mesopores. The activity of the catalysts in terms of AA conversion initially follows the sequence OSG > OSW > OSC, with OSG and OSC showing a selectivity to H<sub>2</sub> of 53 and 58%, respectively (Fig. 1). After 12 hours, the activity of OSC increases, reaching values comparable to those of OSG (Fig. 1). However, OSW is deactivated, with a decrease in this activity from 0.4 until 0.1 mol<sub>AA</sub>·g<sub>Ni</sub><sup>-1</sup>·h<sup>-1</sup> due to the production of coke, which hinders the access to the active phase. Even though the microporosity of OSG and OSC catalysts is occluded (Table 1) the formation of carbon nanotubes with accessible nickel nanoparticles, as confirmed by XRD, Raman and TEM (results not shown for brevity sake), and pointed out by the formation of mesopores, contributes to the maintenance of their catalytic activity.

**Table 1.** Characterization of the catalysts before and after used in reaction

	Fresh catalysts					Used catalysts			
	A <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>micro</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	%Ni <sub>XPS</sub> (-)	%Ni <sub>ICP</sub> (-)	A <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>micro</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	V <sub>meso</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	%Ni <sub>XPS</sub> (-)
<b>OSC</b>	488	0.18	0.02	9.9	10.4	270	0.06	0.22	1.4
<b>OSGW</b>	1092	0.32	0.38	3.5	9.0	97	0.01	0.11	0.6
<b>OSGC</b>	736	0.29	0.06	8.3	9.2	119	0.01	0.19	5.3

**Figure 1.** Activity (a) and  $\text{H}_2$  selectivity (b) for the steam reforming reaction of acetic acid. Reaction conditions: 700 °C,  $\text{H}_2\text{O}/\text{AA} = 2$ ,  $C_{\text{AA}} = 3.9\%$ ,  $\text{WHSV} = 288 \text{ mol}_{\text{AA}} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ .

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