Steam Reforming of Model compounds of Pyrolysis Liquids Using P-containing Activated Carbon as Ni Catalyst Support

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INTRODUCTION

Fossil fuels still represent the main source for obtaining primary energy and plenty of chemical products, despite all the greenhouse gases emission problems related to these uses. New directives and plans for decarbonization of energy propose the use of green hydrogen, obtained in a sustainable way from renewable sources, as an energetic vector and an industrial raw material. One alternative to produce green hydrogen lies in steam reforming (SR) of the liquids resulting from biomass waste pyrolysis. Nickel based catalysts were regarded as the most active for SR. However, their low stability and sustainability needed to be addressed (Li and Gong, 2014). The latter could be increased by using activated carbons (ACs) as catalytic support, prepared from the same biomass waste used as pyrolysis feedstock. However, they might suffer from gasification, when operating at high temperatures or high steam content. In this sense, chemical activation with H_3PO_4 of lignocellulosic waste generated surface phosphorus functionalities with acid character (Rosas *et al.*, 2009). These P groups also governed the carbon reactivity with oxygen, conferring strong oxidation resistance to ACs (Rosas *et al.*, 2012; Valero-Romero *et al.*, 2017). In this work, the effect of P surface groups on the activity and stability of Ni-AC catalysts for steam reforming of model compounds of pyrolysis liquids was studied.

MATERIALS AND METHODS

Pistachio shell was chosen as the activated carbon precursor since it represents a non-edible and abundant agroforestry waste. A P-containing activated carbon, named PS3P, was obtained by chemical activation with H_3PO_4 of the raw material using a 3:1 acid-to-precursor mass ratio and an activation temperature of 500 °C, followed by a washing stage. P surface groups in PS3P were reduced by applying a hydrogen treatment at 600 °C for 4 h, obtaining the corresponding PS3LP sample. Finally, a P-free AC was also prepared by partial gasification of pistachio shell char with CO_2 at 800 °C for 2 h (PSG sample). 10 % wt. Ni nominal loading was supported onto the ACs by incipient wetness impregnation method, with $Ni(NO_3)_2 \cdot 6\,H_2O$ and thermal annealing in N_2 atmosphere at 700 °C for 2 h.

Resulting catalysts have been evaluated for steam reforming of an equimolar mix of ethanol, acetone and acetic acid, as model compounds of pyrolysis liquids, at 700 °C, using a space time of 50 $mg_{cat} \cdot s \cdot \mu mol^{-1}$ and a concentration of 0.75 % for each model compound. Steam to Carbon (S/C) molar ratio was set to the stochiometric value.

Bulk and surface chemical composition and oxidation state were determined by XRF and XPS. In addition, the porosity and the crystalline composition of the catalysts were analysed by N_2 adsorption-desorption and X-ray diffraction (XRD) analyses, respectively.

RESULTS AND DISCUSSION

The three obtained catalysts showed a very similar specific surface area with values around 950 m^2/g, although PSG sample presented mainly a microporous structure (V_{micro}=0.36 cm^3/g and V_{meso}=0.07 cm^3/g), whereas PS3P and PS3LP were mostly mesoporous catalysts (V_{micro}=0.32 and 0.37 cm^3/g and V_{meso}=0.82 and 0.88 cm^3/g, respectively). Bulk phosphorus content varied from 0.5 down to 0.25 and 0.00 wt.% for PS3P, PS3LP and PSG support, respectively. After nickel loading, the Ni2p XPS region of P-free PSG catalyst showed the highest peak intensity at 852.5 eV, indicative of the presence of metallic nickel content. Differently, the PS3LP and PS3P catalysts showed a lower peak intensity of this band. Both catalysts also showed a small band at 128 eV in P2p XPS spectra, related to the presence of phosphide. The XRD patterns of the catalysts are shown in Figure 1. According to these results, nickel in PSG sample appears as metallic nickel, meanwhile, in PS3P catalysts, nickel phosphides are the main species formed, probably as a consequence of the interaction of surface phosphorus with nickel. PS3LP, which shows a lower P content, presents an intermediate behaviour, showing an incipient contribution of nickel phosphides, being the metallic nickel the most abundant compound.

The results of steam reforming of model compounds at stoichiometric S/C ratio (Figure 2) revealed that PSG catalyst needs a 3-hours induction period during which nickel was *in situ* reduced before starting to produce H_2. This period was not necessary when using PS3P, which was probably related to the presence of nickel phosphides as active phase. When a previous reduction was carried on, PSG provided a greater initial H_2 yield, followed by PS3LP. However, PSG catalyst, with and without previous reduction, suffered from a strong deactivation with time on stream, whereas PS3P showed a very stable H_2 yield at the operation conditions studied. A fast initial deactivation was also observed for PS3LP, from which a stable yield value was observed. This value was similar to that observed for PS3P.
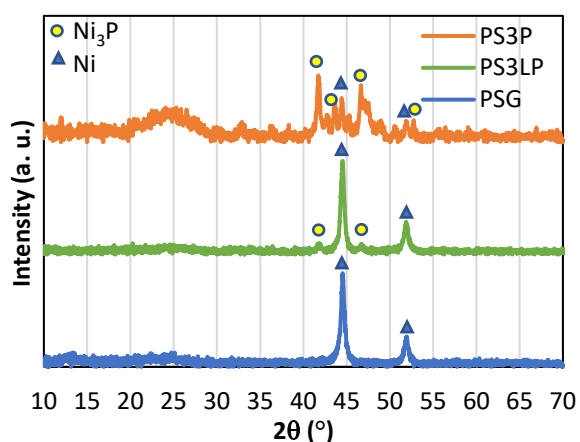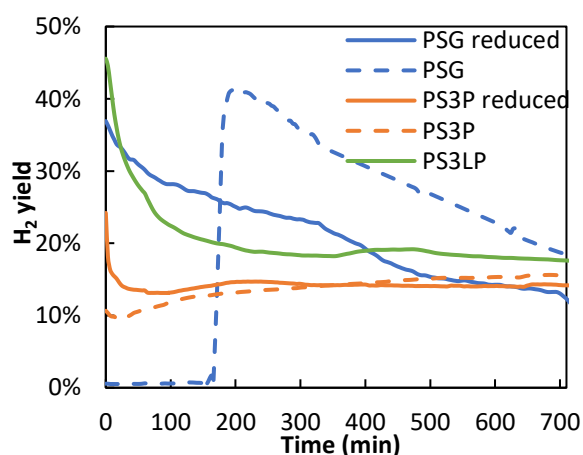

FIGURE 1: XRD profiles of Ni-AC catalysts

FIGURE 2:. H_2 yield during reaction at 700 °C

CONCLUSIONS

The presence of phosphorus in ACs support for nickel catalysts promoted the formation of nickel phosphides. As a result, the reduction of the active phase before steam reforming reaction of pyrolysis liquids became unnecessary. Despite pre-reduced, P-free carbon support initially showed a larger hydrogen yield. However, a more stable activity was observed for P-containing catalysts. These results suggested that nickel phosphides as active phases provided a better long-term stability of the catalysts.

References

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