

ROLE OF PHOSPHORUS ON ACTIVATED CARBONS USED AS CATALYTIC SUPPORTS IN STEAM REFORMING OF PYROLYSIS LIQUIDS

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Hydrogen production from steam reforming (SR) of the liquids resulting from biomass waste pyrolysis with nickel catalysts is a sustainable alternative for decarbonization. Chemical activation with H_3PO_4 provide activated carbons (ACs) with high surface area and porosity development, improved surface oxidation/gasification resistance and acid character due to the presence of stable surface phosphorus groups. In addition, they can be prepared from the same biomass waste making them sustainable supports for steam reforming Ni catalysts. However, little is known about the role of surface P groups on the activity of nickel. In this work ACs, with different amounts of P, have been used as support for steam reforming Ni catalysts in order to study the effect of P on the catalytic activity and stability.

Pistachio shell (PS), a non-edible agroforestry waste, has been used as feedstock for both the preparation of the activated carbons (ACs) and the pyrolysis liquids. P-containing AC was obtained by chemical activation of PS with 3:1 acid to precursor mass ratio and activation temperature of 500 °C, named PS3P sample. The amount of surface P in PS3P was partially decreased by hydrogen treatment at 600 °C for 4 h (PSLP sample). P-free AC was also prepared by CO_2 physical activation of PS at 800 °C for 3 h (PSG sample). 10 % wt. Ni nominal loading were supported onto the ACs by the incipient wetness impregnation method with $Ni(NO_3)_2 \cdot 6H_2O$ and thermal annealing in N_2 atmosphere at 700 °C for 2 h. The resulting catalysts have been evaluated on SR of a mixture of oxygenated hydrocarbons (ethanol, acetone and acetic acid) usually found in pyrolysis liquids. Each of them was fed with a 0.75 % volume concentration, while the steam to carbon ratio was set on the stoichiometric value. The reaction was carried out in a fixed bed tubular reactor at a temperature ranging from 500 to 800 °C and using a space time of 50 $g_{cat} \cdot s \cdot mmol^{-1}$.

All the catalysts have different P amounts and share similar A_{BET} and microporosity (V_{micro} , Table 1); however, mesopore volume (V_{meso}) is larger in P-containing catalysts. SR of model compounds started to be relevant at 500 °C for the three catalysts, showing the formation of hydrogen along with CO, CO_2 , methane and ethylene as the main products, Figure 1. These carbon compounds and H_2 yields are referred to carbon and hydrogen in the inlet, respectively. The H_2 yield at low TOS seems to be negatively impacted by the presence of P (H_2 yield_{1h}, Table 1). However, as TOS increased to 15 h (H_2 yield_{15h}), P-free catalyst faced severe deactivation, which was not found on P-containing PS3P catalyst. This feature seems to be related with gasification of the carbon support, which is hindered in the presence of surface P groups. Therefore, the presence of P seems to be beneficial for the stability of AC-based Ni SR catalysts, which could otherwise suffer of surface gasification during SR operation.

Table 1. Characterization and SR performance at 700 °C of AC catalysts

| Sample | A_{BET} $m^2 g^{-1}$ | V_{micro} $cm^3 g^{-1}$ | V_{meso} $cm^3 g^{-1}$ | P_{XRF} % wt | H_2 yield _{1h} $g H_2/g_{H,feed}$ | H_2 yield _{15h} $g H_2/g_{H,feed}$ |
|--------|---------------------------|------------------------------|-----------------------------|-------------------|---|--|
| PS3P | 985 | 0.32 | 0.82 | 0.50 | 0.11 | 0.16 |
| PSLP | 935 | 0.32 | 0.73 | 0.25 | 0.24 | 0.16 |
| PSG | 940 | 0.36 | 0.06 | 0.00 | 0.29 | 0.13 |

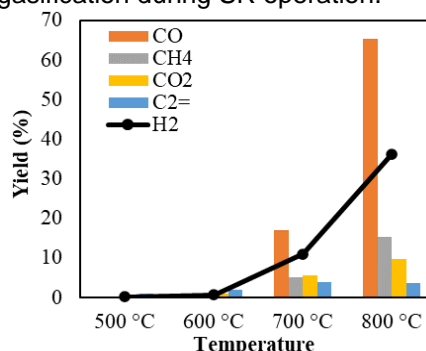


Figure 1. PS3P yields at different T (TOS: 1 h)

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