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Tungsten species supported on natural polymers-derived carbons for One-pot hydrogenolysis of cellulose to diols

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PURPOSE OF THE ABSTRACT

The current demand for energy and the functioning of the chemical industries depend heavily on the use of non-renewable energy sources, resources that are significantly diminishing. As a result, most countries around the world have focused their research on the use of renewable biomass to alleviate resource constraints [1]. So far, several studies have been carried out on the transformation of cellulose into low carbon polyols (C2,C3); ethylene glycol (EG), propylene glycol (PG), glycolaldehyde (GA) and hydroxycaetone (HA), which are major intermediates in the manufacture of plastics, pharmaceuticals, food additives, etc. Cellulose conversion to diols mainly involves 3 types of reactions: cellulose hydrolysis, retro-aldol condensation, and hydrogenation. For the formation of 1,2-PG, sugar isomerization reaction is also needed. A recent report about the catalytic conversion of bamboo pulp to polyols revealed that graphitic carbon nitride (g-C3N4) phase showed a high chemical stability under hydrothermal conditions. This work inspires our study in order to study the potential of natural polymers-derived nitrogen doped carbon catalysts for the cellulose to glycols transformation, knowing that N elements in a given carbon matrix can be pyrrolic, pyridinic and graphitic N [2]. Beyond its eco-friendly nature, the exploitation of renewable biomass-derived materials offers many advantages, including the availability and abundance of the starting materials and provides additional benefits in terms of structural and morphological diversities [3]. Chitosan, for instance, containing 7 wt.% of N, cheap and abundant biomass resource has a real potential for the synthesis of N-doped carbon materials.

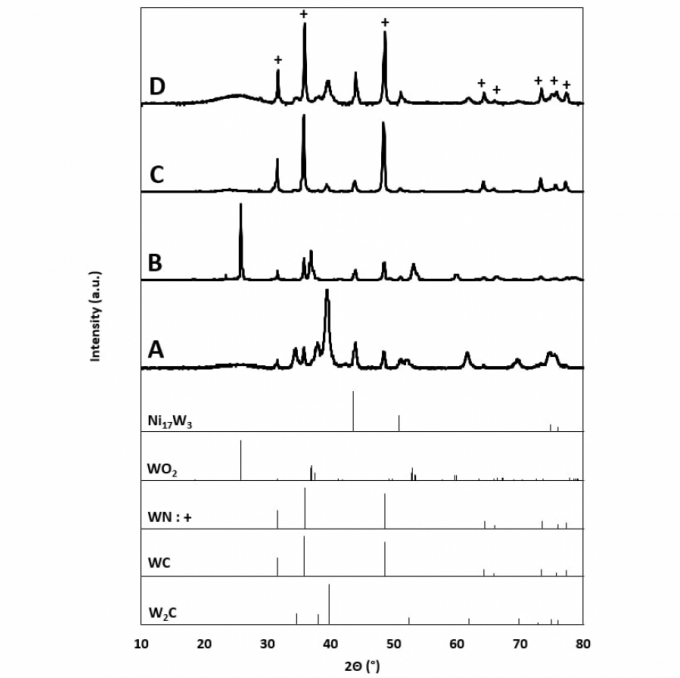
In this study, cheap transition metals (Nickel-tungsten) based catalysts supported on N-doped porous carbon (from chitosan) were synthesized through 2 main routes: (1) Hydrothermal treatment or base-activation treatment of the bio-sourced polymers, followed by pyrolysis under inert atmosphere, and metals' doping by wet impregnation; (2) In situ synthesis of the bifunctional catalysts by hydrothermal treatment of metallic and organic precursors followed by pyrolysis under inert atmosphere.

Amorphous nitrogen-doped carbons with a hierarchical porosity and high surface areas up to 314 m2/g were obtained from the hydrothermal-pyrolysis treatment of chitosan. In addition, the variation of the synthesis conditions (the choice of the polymer, its concentration in the synthesis solution, the synthesis route, the N-additive used?) could yield different phases of tungsten W2C (hexagonal, orthorombic) and WC (hexagonal, cubic); tungsten nitride WN (hexagonal); and tungsten oxides WOx (Fig. 1). For the cellulose to diols hydrogenolysis reaction, molar yields of up to 16% in EG and 6% in PG could be obtained at 250 °C (1 hour, PH2

= 90 bar) with 5%Ni-30%W2C/NC type catalyst. Those yields increased up to 29% in EG and 7% in PG after a further pyrolysis of the catalyst under hydrogen atmosphere (Fig. 2). The impact of pyrolysis step conditions (atmosphere from neutral to reducing) on the material properties and catalytic performances is discussed.

In term of perspectives, better dispersion of the metallic phases, upgrading the materials textural properties as well as synthesis scale-up are aimed by trying other pre-pyrolysis synthesis routes like freeze drying of metal-complexed chitosan monoliths and microspheres, films' casting, and bimetallic functionalization of MOF materials.

FIGURES



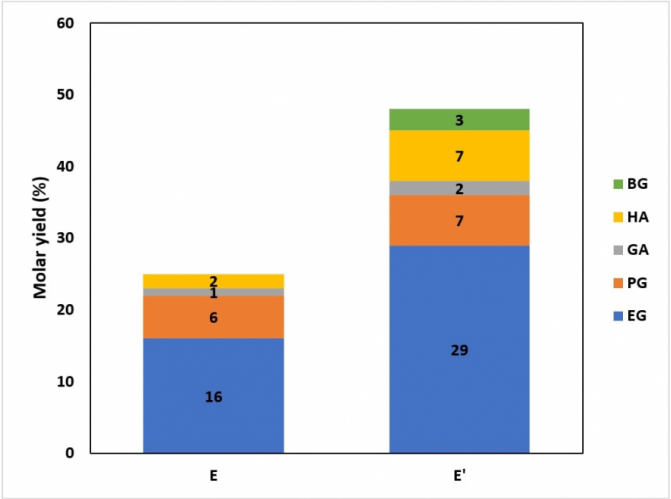


FIGURE 1

Figure 1

XRD spectra of Ni-W functionalized NC supports synthesized by multi-step (A and B) or In-Situ (C and D) hydrothermal method. Nomenclature: A: NiW2C/NC; B: NiWO2/NC; C: NiWC/NC; D: NiWN/NC

FIGURE 2

Figure 2

Cellulose conversion and product yields over a selected catalyst. Conditions: T = 250 °C, PH2 = 90 bars, t = 1 h, 0,5 g cellulose, 0,15 g catalyst, 50 mL water. Nomenclature: E: N-doped NiW2C/NC (A;) E': E further reduced under H2.

KEYWORDS

Nitrogen doped carbons | Hydrothermal treatment | bimetallic tungten carbides catalysts | Hydrogenolysis

BIBLIOGRAPHY

[1] Kumar, A. K.; Sharma, S. Recent Updates on Different Methods of Pretreatment of Lignocellulosic Feedstocks: A Review. Bioresour. Bioprocess. 2017, 4 (1), 7. https://doi.org/10.1186/s40643-017-0137-9.

[2] Xiao, Z.; Zhang, Q.; Wang, X.; Ge, Q.; Gai, X.; Mao, J.; Ji, J. Organic Nitrogen Promotes Stability of Metallic Catalysts in Conversion of Bamboo Pulp to Low Carbon Polyols. Journal of Fuel Chemistry and Technology 2019, 47 (6), 675–687. https://doi.org/10.1016/S1872-5813(19)30029-5.

[3] Yaman, S. Pyrolysis of Biomass to Produce Fuels and Chemical Feedstocks. Energy Conversion and Management 2004, 45 (5), 651–671. https://doi.org/10.1016/S0196-8904(03)00177-8.