Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information for:

From Douglas fir to renewable H_2-enriched syngas via ex-situ catalytic pyrolysis over metal nanoparticles-nanocellulose derived carbon catalysts

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1. Materials and methods

1.1 Materials

Nanocellulose was purchased from Celluforce Inc., Canada. Douglas fir was purchased from Bear Mountain Forest Products Inc., Cascade Locks, OR. Nickle nitrate, Cobalt nitrate, Copper nitrate, and Zine nitrate were purchased from Alfa Aesar, USA. All chemicals were used without further treatment.

1.2 Preparation of metal nanoparticles-NC derived carbon catalysts

The nano-sized metal-carbon catalysts were synthesis by using wet impregnation with subsequent pyrolysis as displayed in Fig. S1. Various nano-sized metals including Co, Ni, Cu, and Zn were added into NCC (nanocellulose derived carbon) suspension, respectively. Then the suspensions were heated in shaker at 60 ºC with constant stirring at 150 rpm for 6 h. After reaction, the suspensions were cooled to room temperature and frozen dried under vacuum condition. Lastly, the solids were pyrolysis at target temperature by a facile fixed bed reactor. The detail pyrolysis system could refer to our previous study.[1] Then the solid residue was collected as metal doped-NC carbon catalysts when the reaction system at room temperature.

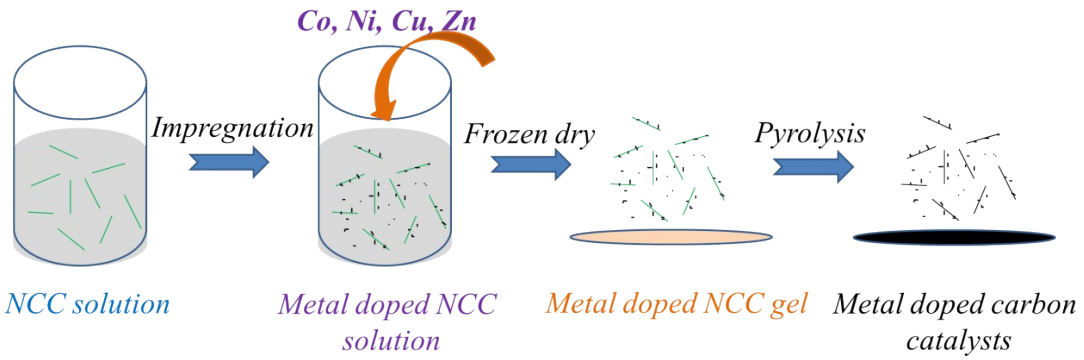

Fig. S1 The procedure of metal nanoparticle-doped carbon catalyst production

1.3 Catalyst characterization

The micromorphology and size of NC suspension and obtained catalyst were characterized by a transmission electron microscope (TEM, FEI Technai G2 20-Twin).

1.4 Catalytic pyrolysis of biomass and analysis of non-condensable gases

The *ex*-situ catalytic pyrolysis of biomass with metal nanoparticles-NC derived carbon catalysts was performed in a facile fixed-bed tube reactor. Firstly, 3 g Douglas

fir was added in a quartz tube with the quartz wool at both ends of the sample. Then 1.5 g carbon catalyst was put into the reactor with the same method. Before reaction, the high purity N_2 was injected at the flow rate of 200 mL/min for 15 min to exclude the O_2 in the reaction system. Then turned on the fixed bed furnace until it reached 500 °C, at the same time, turned on the heating jacket until it reached the target temperature. After that, transferred the quartz tube into the heating device and changed the flow rate of N_2 into 60 mL/min. The function of N_2 is to carry the pyrolysis vapors from biomass passing through the catalyst. After vapors passed through condenser, the non-condensable gas was collected via 1 L Tedlar gas collector.

The resulting gas fraction was analyzed and quantified by Mirco-GC (INFICON inc, Santa Clara, CA, USA) system with a thermal conductivity detector (TCD). The standard gas mixture including H_2, N_2, CH_4, CO_2, and CO was used to calibrate the gas fraction. The gas molecules with more than 2 carbon atoms were negligible.

Reference:

1 Y. Zhang, H. Lei, Z. Yang, D. Duan, E. Villota and R. Ruan, *Green Chem.,* 2018, **20,** 3346-3358.