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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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A carbon catalyst, which was derived from nanocellulose (NC) and doped with unified size and well dispersed metal nanoparticle, showed the optimal performance on the generation of H_2-enriched (67.4 vol.%) syngas during the catalytic pyrolysis of biomass. The study provides a new route to renewable H_2 production from biomass pyrolysis over green NC-based catalyst.

Cellulose is the most abundant and renewable natural polymer resource on earth with approximately 7.5×10^9 tons produced annually.[1] Native cellulose is composed of a highly ordered crystalline region separated by a disordered amorphous region with lower density and weaker hydrogen bonding.[2] The ordered crystalline region can be extracted, leading to the production of nanocellulose (NC), which has at least one dimension < 100 nm. The fundamental properties of NC, such as dimension, crystallinity, and morphology depend largely on the native cellulose source and the isolation process.[3] These crucial characters greatly determine the end use of the prepared NC. Therefore, continuously increasing interest has been paid attention to the utilization of nanocellulose world widely.

In general, the NC is equipped with various advanced properties such as high surface area (250-500 m^2/g), nanoscale dimension, superior tensile strength (7500 MPa), rigidity, and elastic modulus (100-140 GPa), and low thermal expansion.[4] The biodegradability, renewability, and environmentally friendly nature have made NC an eco-friendly, precious and green alternative material to replace the traditional high-strength source that is largely produced from petroleum fossil fuels.[5] Moreover, due to its excellent and remarkable physicochemical features compared to native cellulosic material, NC has recently become an attractive biomaterial that is widely utilized to fabricate diverse functional materials, such as drug delivery, separation membranes, transparent films, and conductive paper et al.[6,7] As a result, the global market employing NC into cosmetic, paper, food, biomedical and pharmaceutical industry exhibits a promising perspective. It is estimated that the NC market is projected to be USD 250 million by 2020 in the USA.[4]

Recently, the metal nanoparticles-NC hybrid composites as catalysis have attracted extensive attention due to the unique characters of NC. Metal nanoparticles are favourable to offer a bridge between the homogeneous and heterogeneous catalytic systems.[8] As a renewable source, NC used as metal nanoparticle supports can not only provide sustainable alternatives but also display an excellent catalytic property with higher metal nanoparticles stability, reactivity and selectivity when compared to conventional ones.[9] The catalytic application of metal nanoparticles-NC hybrid composites mainly include reductions, oxidations, coupling reactions, electrocatalysis, and photocatalysis. However, the carbon catalysts with nano-scale and rich in surface functional groups provide promising potentials in catalytic conversion of biomass-derived compounds into value-added fuels and chemicals, which needs more effort to obtain success and achievement. Therefore, it is interesting to fill this knowledge gap and study the production of renewable H_2-enriched syngas by catalytic conversion of biomass over metal nanoparticles-NC derived catalysts for the first time. And the current work points out a novel and green route to produce renewable H_2-enriched syngas via catalytic conversion of biomass over NC derived catalysts.

Herein, metal nanoparticle-doped carbon catalyst was synthesized by employing wet impregnation with subsequent pyrolysis, as depicted in Supporting Information. The TEM results showed that the prepared NC showed a spider-web-network structure as shown in Fig. 1. In addition, the length and width of NC was 200-500 nm and around 20 nm, respectively. Metal clusters could be introduced into NC-derived carbon catalyst. Fine particles and good metal

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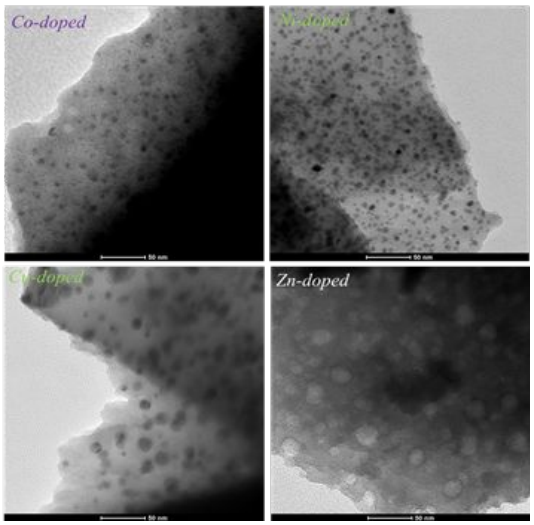

Fig. 1 TEM images of various metal nanoparticle-doped carbon catalysts.

dispersion were achieved for the Co, Ni, Cu, and Zn doped-NC carbon catalysts, respectively. The doped metal crystals were uniformly dispersed with the size ranging from 5~20 nm.

The gas fraction from Douglas fir pyrolysis over metal nanoparticles-NC derived carbon catalyst mainly consisted of CO, H_2, CH_4, and CO_2. In current study, the syngas generation was regarded as the target gaseous product, therefore, the CO_2 was moved into other category to simplify the further analysis. We investigated the effects of metal categories (Co, Ni, Cu, and Zn), carbonization temperature (600, 700, 800 and 900 ºC), metal loading (0.001, 0.005, 0.01 and 0.05) and catalytic temperature (500, 550 and 600 ºC) on product distribution. While studying the effect of various metal nanoparticles (Co, Ni, Cu, and Zn) on gas fraction distribution, catalytic pyrolysis was performed at the temperature of 500 ºC, metal loading of 0.01 and carbonization temperature of 600 ºC. It can be seen from Fig. 2, the metal categories of carbon catalyst significantly affected the gas fraction distribution in biomass pyrolysis process. The concentration of target gases

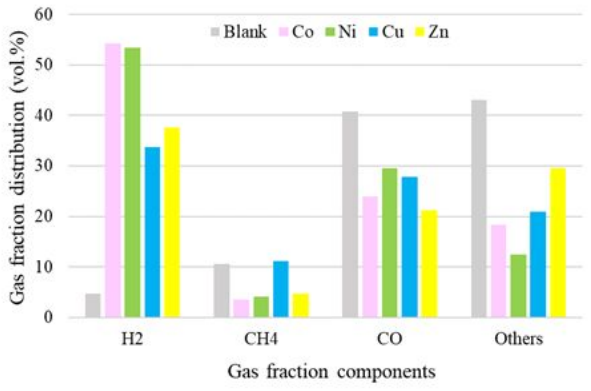

Fig. 2 The distribution of gas fraction components with various metal categories.

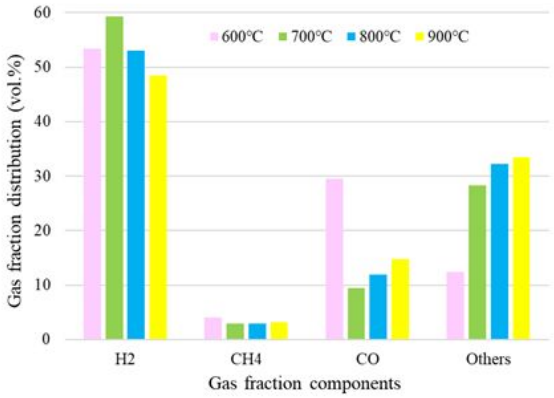

Fig. 3 The distribution of gas fraction components with various carbonization temperatures.

was improved obviously with the loading of various metals compared with blank. The introduction of metals is favourable for changing the acidity of carbon catalyst, which would cause a significant influence on the catalytic performance.[10,11] The results suggested that the generation of the target gases was improved when metal nanoparticles-NC derived carbon catalyst was introduced. When compared with Cu and Zn, the Co and Ni doped NC-derived carbon catalyst caused the highest concentration of H_2 (54.3 vol.% and 53.4 vol.%, respectively). Given that more CO and less CO_2 were generated, Ni was selected as a typical non-precious metal for further investigation on hydrogen production.

Fig. 3 shows that the distribution of gas fraction with different carbonization temperatures of NC-derived carbon catalysts. Carbonization temperature has been demonstrated to be one of the most critical productive elements.[12] In order to investigate the effect of the carbonization temperatures on the gas product distribution, the catalytic pyrolysis of Douglas fir was carried out at a carbonization temperature range of 600-900 ºC with Ni loading of 0.01 and catalytic temperature of 550 ºC. As shown in Fig. 3, the concentration of CH_4 stayed lower than 5 vol.% with the carbonization temperature varying from 600-900 ºC. The concentration of H_2 was firstly increased from 53.4 to 59.3 vol.% then decreased to 48.5 vol.% with elevating carbonization temperature from 600 to 900 ºC. The maximum concentration of H_2 was obtained at a carbonization temperature of 700 ºC. The concentration of CO showed a contrary trend where the minimum value located at the carbonization temperature of 700 ºC. The goal of carbonization process is to improve the carbon content and lead to a porous property of char. It is reported that the increase in carbonization temperature would cause the narrowing and blockage of the micropores entrance.[13,14] The result indicated that 700 ºC of carbonization temperature was the optimal condition for separation of H_2. Therefore, the carbonization temperature of 700 ºC was selected for further investigation.

Fig. 4 shows that the distribution of gas fraction components with various metal loadings of NC-derived carbon catalysts. It is reported that the combination of the metal with

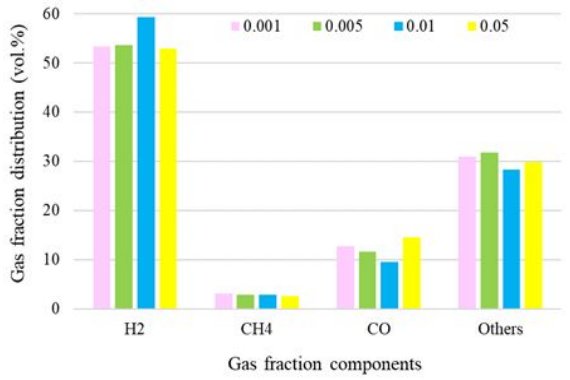

Fig. 4 The distribution of gas fraction components with various metal loadings.

carbon catalyst would improve the performance and selectivity of carbon catalyst by adjusting its surface chemistry.[15] The catalytic pyrolysis of Douglas fir was performed at catalytic temperature of 500 ºC, and carbonization temperature of 700 ºC to investigate the effect of various Ni loadings (0.001-0.05) on gas compositions. The concentration of CH_4 was very low (around 2.9 vol.%) with full range of Ni loadings. The concentration of H_2 and CO showed the opposite trend. The Ni loading of 0.01 resulted in the maximum value of H_2 (59.3 vol.%) concentration and the minimum value of CO concentration (9.5 vol.%). This was due to the fact that introduction of metal enhanced the acid active sites on carbon catalysts, which led to the improvement of catalytic performance of carbon catalyst.[10] However, higher metal loading would give rise to the micropores blockage and decrease of surface area.[15,16]

During the catalytic pyrolysis process, the catalytic temperature has an obvious influence on performance of a catalyst.[17] To investigate the effect of catalytic temperature on gas fraction distribution, the catalytic pyrolysis of Douglas fir was carried out at various catalytic temperatures (500-600 ºC) with carbonization temperature of 700 ºC and Ni loading of 0.01. It can be seen from Fig. 5, the concentration of H_2 increased significantly from 59.3 to 67.4 vol.% with catalytic

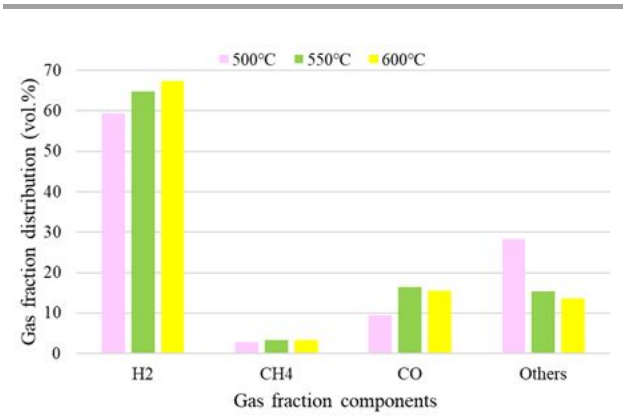

Fig. 5 The distribution of gas fraction components with various catalytic temperatures.

temperature increasing from 500 to 600 ºC. At the meantime, the concentration of CO firstly increased from 9.5 to 16.4 vol.% when the catalytic temperature increased from 500 to 550 ºC, then decreased slightly to 15.5 vol.% with temperature further increased to 600 ºC. The results indicated that the cracking performance of metal nanoparticles-NC derived carbon catalysts was facilitated by increasing the catalytic temperature from 500 to 600 ºC. This was due to the fact that cracking reaction was endothermic process, which can be accelerated by high temperature.

Conclusions

In the present work, the doped metal nanoparticles were uniformly dispersed with the diameter ranging from 5-20 nm. The Co and Ni-doped carbon catalysts exhibited great potential of generating H_2-enriched syngas from catalytic pyrolysis of raw biomass. The excessive carbonization temperature and metal loading were detrimental to generation of H_2-enriched syngas. The high catalytic temperature improved the generation of H_2-enriched syngas (up to 67.4 vol.%) during catalytic pyrolysis process.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract: