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Cellulose conversion to glycols over DUT-8(Ni) derived nickel-tungsten/carbons: selectivity tuning.

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There have been various studies on the transformation of cellulose to low carbon polyols (C2,3), ethylene glycol (EG), propylene glycol (PG) and glycerol (Gly), which are prevailing intermediates in the manufacture of plastics, pharmaceuticals, food additives, and cosmetics, 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, the sugar isomerization reaction is also involved. Using activated carbon-supported tungsten carbide (W_2C/AC) catalysts, Zhang et al. obtained an EG yield of 76 % starting from cellulose [1]. Besides being a cheap non-noble metal-derived phase, a noteworthy advantage of tungsten carbide over other tungsten species (oxides and metal) is the preferential formation of EG among other polyols due to its Pt-like catalytic behavior. Yang et al. prepared Ni-W/C nanofiber catalysts, in situ fabricated through the pyrolysis of Ni, W-containing metal-organic framework fibers. A large productivity varying from 15.3 to 70.8 $mol_{EG}.h^{-1}.g_W^{-1}$ was reported, which is two orders of magnitude higher than previously reported Ni-W-based catalysts [2]. Interestingly Sun et al. [3] showed the impact of the Sn phase and valence on the catalytic properties of bimetallic systems supported on activated carbon. When powder of metallic Sn was used with Ni/AC, a Ni-Sn alloy formed which promoted retro-aldol cleavage and hydrogenation, finally favoring EG production (58 %). When SnO was used, the catalyst promoted glucose isomerization, leading preferentially to PG (32 %). The above studies inspired our current work. A series of W and Ni-containing metal-organic frameworks were constructed by one-pot assembly of DUT-8(Ni) MOF precursors and $Na_2WO_4 \cdot 2H_2O$. A subsequent pyrolysis of the W@ DUT-8(Ni) materials at 700 °C under nitrogen produced nickel-tungsten/carbon catalysts. The following nomenclature was adopted for the resulting materials: NiW-l-x-C-N$_2$; where x (nW/nNi) was set at 0.06, 0.12, 0.3, and 0.43, respectively. Figure 1 displays the catalytic results of the as-synthesized materials in the cellulose hydrogenolysis at 245 °C in a reaction time of 1 hour. Both materials with low (NiW-l-0.06-C-N$_2$) and high (NiW-l-0.3-C-N$_2$) W content were selective to EG (17 %). A remarkable yield switch to PG (36 %) was obtained at an average W loading (NiW-l-0.12-C-N$_2$). The highest EG molar yield (25 %) was obtained over NiW-l-0.43-C-N$_2$.
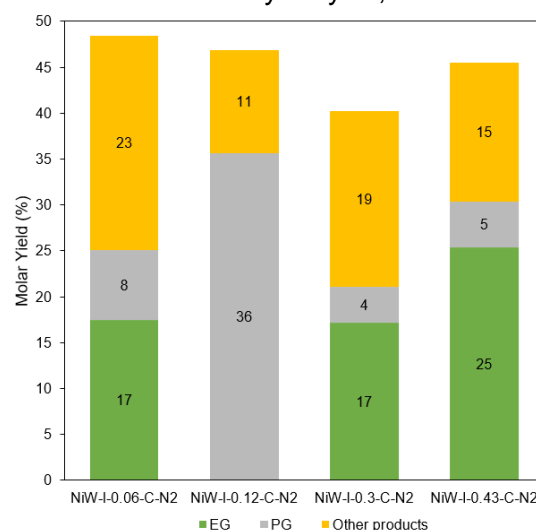

Figure 1. Products' molar yields over NiW catalysts having different tungsten loadings. Reaction conditions: 0.50 g cellulose, 0.15 g catalyst, 50 mL water, 60 bar H2, 1000 rpm, 245°C, and 1 hour.

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[3] R. Sun et al., "Selectivity-Switchable Conversion of Cellulose to Glycols over Ni–Sn Catalysts," *ACS Catal.*, vol. 6, no. 1, pp. 191–201, Jan. 2016, doi: 10.1021/acscatal.5b01807.