Selective transformation of cellulose to C<sub>2</sub>-C<sub>3</sub> polyols on M-W/SBA-15 (M = Ni, Pd, Zn, Cu) under low hydrogen pressure

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Abstract. Conversion of cellulose to renewable and valuable chemicals has attracted global interest in order to build up sustainable development. The catalysts M-W/SBA-15 (M = Ni, Pd, Zn, Cu) were prepared to achieve selective conversion of cellulose via hydrogen donors. To be noted, the extra pure H<sub>2</sub> employed in this catalytic system only needed 2.0 MPa and the catalysis results shown a relative high yield of EG, reaching up to 42.2% at 230°C for 5 h. The isopropanol as the suitable hydrogen donor converted to acetone partially and pressurized the space in reaction system. The serial metallic catalysts were characterized and analyzed by H<sub>2</sub>-TPR, XRD, XPS and TEM. Some metal alloys were produced, evidenced by XRD, improved the yields of target products.

1. Introduction

Considering the depletion of fossil resources, searching and developing a suitable and renewable substitute or carbon resource are of paramount urgency and importance. Cellulose, separated from the lignocellulosic biomass, is the most abundant and inedible biomass in nature. And the degradation of cellulose into value-added bio-chemicals, instead of platforms based fossil, has been vigorously explored worldwide<sup>[1-2]</sup>. The average composition of cellulose in lignocellulose is 34~50%. Due to its complex chemical structure, with β-1,4-glucosidic bonds of D-glucose, it is hard to dissolve in water or traditional solvents<sup>[3]</sup>. Those popularly reported transformation routines of cellulose included pyrolysis or liquefaction of cellulose into bio-oil or bio-gas<sup>[4,5]</sup>, selective oxidation of cellulose to some acids or other platforms<sup>[6,7]</sup>, hydrolysis of cellulose to sugar alcohols<sup>[8]</sup>, hydrogenolysis of cellulose to C<sub>2</sub>-C<sub>3</sub> polyols<sup>[9]</sup>. Among these products, C<sub>2</sub>-C<sub>3</sub> polyols including ethylene glycol (EG), propylene glycol (PG) and glycerol (Gly) are the crucial feedstocks in the synthesis of pharmaceuticals and manufacturing of plastics, coating and cosmetics<sup>[10]</sup>. And among the various chemical transformation strategy, the catalytic conversion of cellulose to low carbon polyols has attracted considerable attention both from academic and industrial group.

As the studies reported before, cellulose conversion to C<sub>2</sub>-C<sub>3</sub> polyols relied on three chemical processes such as hydrolysis, hydrogenolysis or hydrogenation including isomerization and retro-aldol reaction steps<sup>[11]</sup>. Some metallic catalysts promoted one or more degradation steps. The tungsten
species promoted retro-aldol condensation reaction leading oligosaccharides converting into unsaturated low carbon intermediates (glucaldehyde, etc), and hydrogenation steps expedited by supported noble or transition metals such as Pt, Ru, Pd, Ni, W catalysts\textsuperscript{[12-15]}. For example, Zhang T. et al used Ni-W/SBA\textsubscript{15} to achieve efficient hydrogenolysis of corn straw to EG with the yield of 55.3%\textsuperscript{[16]}. More importantly, Zhao T. and co-workers had found the tungsten species had the outstanding selectivity for EG indicating that advantage of adopting W was promoting cracking C-C and C-O bonds\textsuperscript{[15]}. Comparatively, transition metals like Ni, Ru, Pt, Pd, and Rh are themselves not effective for the C-C cleavage. Liu H. et al. reported Ni/C catalyst was active for producing EG and PG from xylitol in the presence of solid bases, e.g. Ca(OH)\textsubscript{2}, CeO\textsubscript{2}. Which rendered the Ni particles resistant to leaching and sintering\textsuperscript{[17]}. Fukuoka. A. et al synthesized and developed a Pt/Al\textsubscript{2}O\textsubscript{3} and obtained a maximum sugar alcohol yield of 67%\textsuperscript{[18,19]}. By supporting Ni and W species on SiO\textsubscript{2}, Baek and co-workers were successfully obtained sorbitol, EG, but the yield of target products needed to prove\textsuperscript{[20]}

Based on the literatures reported before, it is known that the issue encountered in cellulose hydrogenolysis needs a high hydrogen pressure ( \( > 4 \) MPa) which requires more robust reactor for performing this reaction. The compressed H\textsubscript{2} with high pressure implies this process occurred with high cost. However, it seems to be a huge challenge which focus on selective C\textsubscript{2}-C\textsubscript{3} polyols synthesis from cellulose with low hydrogen pressures (usually \(< 3 \) MPa). Consequently, developing a efficient catalytic system for cellulose hydrogenolysis to low carbon polyols under a mild hydrogen pressure represents necessity for establishing a eco-friendly and safe chemical process. The hydrogen needed in the hydrogenolysis of cellulose can be generated in one pot under the same catalytic reaction condition when small amount of organic hydrogen donor is added, such as isopropanol\textsuperscript{[21]}, ethanol\textsuperscript{[22-24]}, methanol\textsuperscript{[25]}. Since the existence of compatible metallic catalysts the isopropanol converts to acetone which is also a value-added chemicals. And H\textsubscript{2} can be directly obtained via in situ isopropanol dehydrogenation on metallic catalysts M-W/SBA\textsubscript{15} (M = Ni, Pd, Cu, Zn). This process will be more safe and convenient with a lower extra pure hydrogen pressure.

2. Experimental

2.1 Materials

Cellulose (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. microcrystalline), SBA-15 (Nanjing XFNANO Materials Tech Co., Ltd., Nanjing, China.). Phosphotungstic acid (H\textsubscript{3}PO\textsubscript{4}W\textsubscript{12}·nH\textsubscript{2}O, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.). Nickel nitrate hydrate (Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Energy Chemical Co., Ltd, Shanghai, China.). Cupric nitrate (Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, Shanghai Titan Scientific Co., Ltd., China). Glucose (Sinopharm Chemical Regent Co., Ltd, China.).

2.2 Catalyst preparation

The bimetallic catalysts M-W/SBA-15 (M = Pd, Ni, Cu, Zn) were prepared by equivalent-volume impregnation. 3.0 g glucose was added into the aqueous solutions when the amount of SBA-15 was 3.0 g. The impregnated samples were dried at 80 °C overnight in circulation oven. And then the samples were calcined at pipe calciner in the continuous flow of nitrogen at 500 °C for 5 h with the heating rate of 2 °C/min. The loading percents of active metals were calculated based on the amount of SBA-15. All the catalysts were applied directly in this catalytic system without additional reducing steps.

2.3 Catalyst characterization

BET surface areas were measured by a ASIQC0000-4 instrument (Quantachrome, USA). All the sample were degassed at 100 °C for 1 h and 350 °C for 8 h prior to the measurement.

H\textsubscript{2}-temperature programmed reduction (H\textsubscript{2}-TPR) profiles were recorded by a BEL-Metal-3 commercial micromeritic units (Microtrace BEL, Japan). The catalysts samples were loaded in a U-shaped quartz cell (100 mm × 3.76 mm) heated (10 °C/min) from room temperature to 650 °C under a flow of H\textsubscript{2}/N\textsubscript{2} (5%, 50 mL/min, air liquid) and kept the temperature until the baseline was
stable. H2 consumption was quantified by thermal conductivity detector signals, calibrated by reduction of CuO, ZnO or NiO powder under identical conditions.

X-ray diffraction (XRD) measurements were recorded by a PW3040/60 X’pert Pro type ray diffractometer (PAN-alytical B.V., Netherlands) with Cu Kα radiation (40 kV, 30 mA), and the scanning range was from 10~90° with the speed of 5°/min.

X-ray photoelectron spectroscopy (XPS) was acquired using a spectrometer (Thermo Fisher Scientific, USA) equipped with an Al Kα X-ray source (1486.6 eV, 15 kV, 150 W). The C 1 s peak at 285 eV was used as the reference for the all bonding energies. The areas of the peaks were computed by fitting the experimental spectra to Gaussian curves after the subtraction of the linear spectral background.

Transmission electron microscopy (TEM) analysis used a JEOL 2100 unit with an accelerating voltage of 200 kV.

2.4 Catalytic reaction
Cellulose hydrogenolysis via catalytic transfer hydrogenation reactions were performed in a stainless steel autoclave reactor (YZPR-100, 100 mL. Yanzheng Equipment Co., Ltd., Shanghai, China.). In a typical experiment, 50 mL solution (35 mL water and 15 mL organic hydrogen donor), 0.5 g cellulose and 0.2 g metallic catalyst were loaded in the autoclave, which was the flushed three times with nitrogen to remove the ambient air followed by pressurized 2.0 Mpa H2 into the system. Consequently, the reactor was heated to 230 ℃ and stirred at 500 r/min, and then timing started for 5 h. The reaction liquid was transferred to a sample vial after the pressure was released. Keep the liquid part and the solid residues were filtered off.

2.5 Analytical methods
The liquid products were analyzed by HPLC (Waters, USA.) equipped with a Welch X’mate-Ca (7.8×300 mm, 5μm) column and refractive index detector (RID, Waters 2414, USA.). Samples (injected 20 μL) for the HPLC analysis were filtered through 0.45 μm millipore filter. A mobile phase (deionized water, 0.6 mL/min) was used as eluent at 80 ℃. The cellulose conversion and the polyols yields were calculated based on the following formulas:

\[ X_c = \frac{M_{R0} - M_R}{M_{R0}} \times 100\% \]  
\[ Y_p = \frac{M_p}{M_{R0}} \times 100\% \]

Where \( X_c \) is the cellulose conversion, \( M_{R0} \) and \( M_R \) is the weight of cellulose before and after the reaction respectively. \( Y_p \) is the products yields, \( M_p \) is the weight of products.

3. Results and discussion

3.1 Catalysts characterization

3.1.1 \( H_2 \)-TPR. The TPR profiles of the supported bimetallic catalysts were depicted in Fig. 1. Below 280°C the profiles of Cu-W/SBA-15, Zn-Cu/SBA-15 and Ni-Cu/SBA-15 catalysts essentially exhibited a well-defined diffraction single reduction peaks at nearly the same temperature in the range of 80~280°C. They were related to the reduction process of different metallic oxides including ZnO, NiO and CuO. And the beginning of reduction process of CuO was easier than that of NiO or ZnO. What’s more, it was worth noting that all the samples were prepared by self-reducing method and some of oxides had been reduced already, which led to weak reduction peaks. Comparatively, the Ni-Cu/SBA-15 catalyst shown additional hydrogen consumption at 400°C. However, no obvious hydrogen consumption happened at 80~280°C. This might be caused by hydrogen spillover from Ni (It was reduced partially in preparation.) to CuO, or because the NiO and CuO had been reduced
deeply already. Because of existence of amorphous carbon on the SBA-15 surface, some carbon was
demed to go through partial gasification to produce methane [26]. For Cu-W/SBA-15 and
Ni-Cu/SBA-15 catalysts, the hydrogen consumption peak of Cu-W/SBA-15 was antecedent compared
to the latter. Clearly, the reduction peak of Zn-Cu/SBA-15 appeared at 130°C which was obviously
later. Apparently, the interaction of Cu-Zn and Cu-Ni existed in the samples.

![Figure 1. TPR profiles of supported bimetallic catalysts.](image1)

3.1.2 XRD. XRD patterns of Ni-Zn-W/SBA-15, Ni-Cu-W/SBA-15 and Pd-W/SBA-15 catalysts were
displayed in Fig. 2. The characteristic diffraction peaks of WO3 specie was present for all the samples.
No peaks corresponding to tungsten carbides were detected since the catalysts were calcined in 500°C
and the carbides could not be generated at this temperature. For catalysts Ni-Zn-W/SBA-15 and
Ni-Cu-W/SBA-15, the metal nickel characteristic peaks could be observed at 2θ = 44.3 and 51.5°,
implying that the reducing gas generated from glucose calcination in flow of N2 could reduce NiO to
Ni0. This results was similar to the analysis of Pd-W/SBA-15 which revealed the strong characteristic
peaks for Pd0. The weak peaks at 2θ = 35.6, 29.8° represented CuO and ZnO respectively. It was
reported that CuO and ZnO species were efficient to catalyze C-C bond cracking and transfer
hydrogenation to produce propylene glycol.

![Figure 2. XRD patterns of supported metallic catalysts: (a) 10%Ni-10%Zn-15%W/SBA-15, (b) 10%Ni-10%Cu-15%W/SBA-15, (c) 10%Pd-15%W/SBA-15.](image2)

3.1.3 XPS. Fig. 3 shown the XPS spectra of Pd 3d and W 4f regions for the supported metallic catalyst
10%Pd-15%W/SBA-15. The chemical states of palladium and tungsten on support surface were
measured according to the characteristic binding energy and the metals were reduced at a certain
degree. The results shown that the strong photoelectron peak at 335.1 eV in Pd 3d5/2 region suggesting
the Pd0 specie. The photoelectron peak at 340.8 eV indicated the spin splitting peak of Pd0 shown as in
Fig. 3b. Those peaks were attributed to ruthenium in a completely reduced state ( Pd0). Fig. 3c shown
the W 4f XPS spectra, two broad XPS peaks appeared in range of 34–40 eV. Deconvolution were
performed to distinguish WO3 species in different chemical states from the position of the W 4f level.
by a curve-fitting procedure. The results displayed that two doublets with the W 4f\textsubscript{5/2} B.E. values at 36.8 and 38.8 eV were attributed to W\textsuperscript{6+} atoms which indicated that WO\textsubscript{3} was the main state for tungsten species. It was known that the WO\textsubscript{x} needed tougher reducing condition than that of PdO. As discussion above, it can be confirmed that Pd\textsuperscript{0} and tungsten species were formed after calcination with glucose.

![Figure 3](image_url)

**Figure 3.** (a)10%Pd-15%W/SBA-15 XPS spectra and (b) Pd\textsuperscript{3d} spectra and (c) XPS spectra of W 4f region.

3.1.4 TEM. The TEM images for the 10%Pd-15%W/SBA-15 catalyst were shown in Fig. 4. The support SBA-15 remained the bundle-like structure after the calcination in 500°C, shown in Fig. 4a. Clearly, we could see the active particles which shown clear crystal shape appeared to be well distributed on the SBA-15 support surface exhibited in Fig. 4a and 4b. For a smaller scale, the Pd nanoparticles were narrowly sized (in range of 1-6 nm). As observation above, we could confirm that catalyst particles presented a good dispersion on SBA-15 surface.
3.2 Performance of catalysts

3.2.1 Effect of catalysts on cellulose conversion. During cellulose transformation, adopting appropriate catalyst could potentially improve conversion of cellulose and yield of goal products. The catalytic conversions of cellulose over various catalysts with hydrogen donors were listed in Table 1. The products were mainly water-soluble. The effects of metals sites (Ni, W, Cu, Zn, Pd) on the products yields were examined. At 230°C and 2 MPa H₂, low carbon polyols were generated via hydrogen donor (isopropanol) over bimetallic and multimetallic catalysts after 5 h. Obviously, the EG yields were gained up to 36.3% and 42.2% over bimetallic and multimetallic catalysts respectively. Combined with EG, the total yields of low carbon polyols could reach up to 51.0% as a result of adding Cu sites on catalysts 10%Ni-15%W/SBA-15 to 10%Ni-10%Cu-15%W/SBA-15. Notably, the products distribution changed when the third active metal was adopted; the yield of EG increased dramatically from 17.5% to 42.2%; the conversion of cellulose from 81.3% to 100%. This results shown that adding the third appropriate catalytic role mixed with Ni-W/SBA-15 accelerated the cellulose hydrolysis and C-C/C-O bonds cleavage. It was estimated that the interaction between metals sites happened in process of preparation according to Entry 1, 2 and 7. The XRD characterization (Fig. 3) shown some metal alloys were generated in catalyst Ni-Cu-W/SBA-15. More importantly, this alloys could promote the yields of low carbon polyols remarkably as reported previously [27]. For another hand, we observed that tungsten species could accelerate C-C/C-O bonds cleavage, promoting cellulose conversion compared with Entry 2, 3 and 5.

Table 1. Results of cellulose conversion and yields of main products on various catalysts.

| Entry | Catalyst                  | W/H D | Main liquid products yield/% | Conv. % |
|-------|---------------------------|-------|-----------------------------|---------|
|       |                           |       | EG  | PG  | Gly  | Sor  | Glu  | Aceton |         |
| 1     | 10%Ni-15%W/SBA-1          | 7:3   | 25.3 | 3.8 | 2.3  | 8.7  | 2.4  | 18.6   | 90.3    |
| 2     | 10%Cu-15%W/SBA-1          | 7:3   | 17.5 | 2.5 | 1.2  | 2.1  | 1.9  | 9.8    | 81.3    |
| 3     | 10%Zn-15%W/SBA-1          | 7:3   | 15.6 | 3.2 | 1.3  | 3.2  | 2.3  | 12.3   | 84.5    |
| 4     | 10%Pd-15%W/SBA-1          | 7:3   | 36.3 | 4.7 | 2.8  | 8.4  | 3.1  | 23.6   | 95.9    |
| 5     | 10%Zn-15%Cu/SBA-1         | 7:3   | 6.7  | 0.8 | 0.4  | 1.3  | 0.9  | 3.3    | 64.8    |
| 6     | 10%Ni-10%Zn-15%W/SBA-15   | 7:3   | 27.6 | 4.6 | 2.1  | 8.5  | 3.1  | 18.5   | 92.8    |
| 7     | 10%Ni-10%Cu-15%W/SBA-15   | 7:3   | 42.2 | 5.2 | 3.6  | 9.2  | 2.8  | 25.6   | 100     |
| 8     | 10%Ni-10%Pd-15%W/SBA-15   | 7:3   | 38.8 | 4.5 | 2.7  | 7.9  | 2.3  | 21.6   | 94.6    |

* Water: isopropanol (v/v)=7:3, total volume is 50 mL. * Sorbitol. * Glucose. cellulose, 0.5 g; catalyst, 0.2 g; Reaction temperature, 230 °C; P₁₂= 2.0 MPa; Time, 5 h.
Interestingly, the hydrogen donor (HD) isopropanol had converted into acetone producing H₂ by dehydrogenation reaction. However, the yield of acetone was relatively low, less than 25.6%. The hydrogen generated from HD could enhance the system pressure and possibly participate in cellulose hydrogenolysis in aqueous phase, shown as in Fig. 5. The cellulose was mainly hydrolyzed on tungsten species in pressurized water, but the subsequent hydrogenation of unsaturated intermediates to polyols proceeded because of the active H₂ from isopropanol steam reforming.

![Figure 5. Cellulose conversion to polyols via hydrogen donor.](image)

3.2.2 Effect of ratios of hydrogen donors. Since a number of studies on cellulose hydrogenolysis catalyzed by metals catalysts at relative high H₂ pressure have already reported. One of the objectives of this work was to investigate the performance of supported metals catalysts for depolymerization/hydrolysis/hydrogenation of cellulose to polyols under milder condition. However, the higher H₂ pressure could promote hydrogenolysis of cellulose. This study tried to solve this contradiction and the reaction results for the conversion of cellulose into polyols over different HD ratios were summarized in Table 2. The isopropanol to ethanol volume ratios were from 2:1 to 1:2 in Entry 1, 2 and 3. The water was the reaction media in control group as shown in Entry 4, 5 and 6.

| Entry | Catalyst                  | W/HD /mL | Main liquid products yield/% | Conv./% |
|-------|---------------------------|----------|-----------------------------|---------|
| 1     | 10%Pd-15%W/SBA-1          | 7:3 a    | EG 30.6, PG 2.8, Gly 1.7, Sor 6.5, Glu 2.1 | 92.3    |
| 2     | 10%Pd-15%W/SBA-1          | 7:3 b    | EG 20.5, PG 2.6, Gly 1.3, Sor 5.8, Glu 1.6 | 89.8    |
| 3     | 10%Pd-15%W/SBA-1          | 7:3 c    | EG 15.3, PG 2.1, Gly 1.3, Sor 5.6, Glu 1.8 | 82.4    |
| 4     | 10%Ni-15%W/SBA-1 W=50     | 13.3     | EG 13.3, PG Trac 0.8, Gly 4.3, Sor 2.3 | 95.6    |
| 5     | 10%Pd-15%W/SBA-1 W=50     | 7.6      | EG 7.6, PG Trac 0.3, Gly 3.7, Sor 1.6 | 93.5    |
| 6     | 10%Ni-10%Cu-15%W/SBA-1 W=50| 13.8     | EG 13.8, PG Trac 0.9, Gly 4.1, Sor 1.9 | 89.4    |

*a Water: Hydrogen donor (v/v) = 7:3, isopropanol: ethanol (v/v)=2:1. b isopropanol: ethanol (v/v) = 1:1. c isopropanol: ethanol (v/v) = 1:2, d water = 50 mL.

As shown in Table 2, the effect of hydrogen donor on yield of polyols was obvious. As the increasing of adding ethanol (Entry 1, 2 and 3), the total low carbon polyols yield was plummeting from 35.1% to 18.7%. Fortunately, the only constant was the high EG selectivity, which probably benefited from the tungsten species in catalysts. Compared to Entry 4 in Table 1, as the hydrogen donor and cosolvent, the isopropanol suggested the better effectiveness than ethanol. The results in control group with the 14.7% of low carbon polyols (Entry 6) demonstrated that hydrogen donor could promote the hydrogenation reaction and increase the yield of EG. Such a HD effect may be related to the extra hydrogen generated from HD except 2 MPa pure H₂, which not only increased the amount of H₂ but also improved the pressure in catalytic system. The cellulose hydrogenolysis reaction and isopropanol steam reforming to H₂ were performed in one pot and avoidance of the utilization of high-pressure hydrogen, resulting in more practical feasibility.
4. Conclusions

The selective transformation of cellulose to C$_2$-C$_3$ polyols on M-W/SBA-15 (M = Ni, Pd, Cu, Zn) under low hydrogen pressure was conducted. Because of improved dispersion of active components, the catalysts showed high selectivity in the conversion of cellulose into polyols, especially for EG. The hydrogen-rich polyols isopropanol acted as hydrogen donor and impeller of pressure. The C$_2$-C$_3$ polyols yields could reach up to 51.0% with 42.2% of EG. In this catalysis system, only 2 MPa pure H$_2$ was adopted, which was beneficial to simply apparatus and improve safety. However, to achieve high yield of target products, further investigation about catalysis system was needed to conducted.

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