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Cellulose conversion to ethylene glycol by tungsten oxide-based catalysts

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Abstract

The conversion of cellulose into ethylene glycol remains a significant challenge in the biobased domain. Here we explored the activity of various bulk and mesoporous (doped) tungsten oxides in combination with carbon-supported ruthenium for obtaining ethylene glycol from cellulose. Tungstite and sub-stoichiometric tungsten oxides are more active and selective than monoclinic WO$_3$. Doping tungstite with early transition metals enhanced the rate of cellulose depolymerization to glucose through a higher Brønsted acidity, although this did not improve the overall performance as the higher acidity resulted in a higher rate of humin formation. The increased acidity of mesoporous sub-stoichiometric tungsten oxide compared to tungstite had a similar adverse effect. Doping this material with niobium improved ethylene glycol selectivity at similar conversion. Kinetic studies showed that the majority of ethylene glycol is produced in the first hour for three optimized catalysts, with undoped bulk tungstite being the most efficient catalytic material. Impregnation of these materials with ruthenium instead of using carbon-supported ruthenium as a co-catalyst was most beneficial for tungstite, as it showed improved ethylene glycol selectivity and lower polyol yields after 1 h of reaction time.

1. Introduction

Ethylene glycol (EG) is an important chemical, which is mainly used for anti-freeze purposes and as a raw material for the production of polyester fibers [1]. The annual global production was estimated at 26.9 million tonnes in 2016, which is primarily obtained by hydrolysis of ethylene oxide [2]. Ethylene oxide is exclusively obtained by selective oxidation of fossil-based ethylene. In recent years, production of fuels and chemicals from renewable sources has become a target in order to supplement or replace fossil feedstock on which society currently relies. Cellulose is the most abundant renewable source of biomass and processing it into valuable commodities has attracted much interest from both academia and industry [3-5]. Unlike starch, cellulose is inedible, which makes it a good feedstock for industrial utilization without endangering food supplies.

Cellulose is a linear polymer of repeating glucose units, which contains many hydroxyl groups rendering it a potent feedstock for the industrial production of EG, sorbitol and other polyols. The large number of intra- and interchain hydrogen bonds make cellulose recalcitrant to depolymerization to glucose, which is considered the first step towards valorization of cellulose [6-8]. Its depolymerization usually involves harsh conditions (high temperature) and reagents such as strong Brønsted acids are employed [8,9]. The release of glucose under these conditions results in rapid further conversion into humins [10,11]. One approach to cope with this is to rapidly further convert the glucose intermediate. Upgrading glucose to EG involves two basic reaction steps, namely step-wise retro-aldolization of glucose to glycol aldehyde followed by its hydrogenation to EG. The obtained product distribution is governed by the chosen reaction conditions and type of catalyst used [10-14]. The predominant reactions to produce EG and related side-products are laid out in Scheme 1.

The occurring reactions can be classified into cellulose hydrolysis, retro-aldolization of glucose and other saccharides, hydrogenation of aldehydes and ketones, and dehydrogenation of polyols and hydrogenation of the resulting C=C bonds. Cellulose hydrolysis is preferably promoted by Brønsted acids, either generated in situ through increased autoprotoysis of hot water or from an external source. Lewis acidic species are responsible for retro-aldol reactions to form shorter aldehydes and can also catalyze isomerization reactions. Hydrogenation of C=O and C=C species is performed by a metal function using gaseous hydrogen. The metal function can either be present as a separately supported catalyst [10,13], or alternatively is deposited on the retro-aldol catalyst [11,14,15]. Our recent work regarding bulk and mesoporous doped tungsten oxides has shown that these materials possess strong Lewis and Brønsted acid sites [16-18]. This, in theory, makes them potentially suitable to carry out retro-aldolization and to aid in cellulose
hydrolysis. These reactions have been evaluated already for supported and unsupported monoclinic WO$_3$ [11,13–15,19]. Our earlier investigation on glucose valorization to 5-hydroxymethylfurfural demonstrated that (doped) tungstite (WO$_3$.H$_2$O) and sub-stoichiometric tungsten oxides are significantly more active compared to monoclinic WO$_3$ [20]. We tested these materials using ruthenium as a hydrogenation co-catalyst, both supported on carbon and directly impregnated on our catalysts. While impregnation of monoclinic WO$_3$ with different metals has already been explored, this has not been studied using tungstite as a support to the best of our knowledge [14,21].

In this work, we explored the activity of various bulk and mesoporous (doped) tungsten oxides in tandem with carbon-supported ruthenium for cellulose conversion into EG. We investigated the influence of temperature and reaction time on the cellulose conversion and the product distribution. We also optimized the ruthenium loading towards optimum EG yield.

2. Experimental methods

2.1. Chemicals

Tungsten hexachloride (WCl$_6$, 99%), niobium pentachloride (NbCl$_5$, 99.9%), titanium tetrachloride (TiCl$_4$, 99%), titanium tetrabutoxide (Ti(OBu)$_4$, 99%), zirconium tetrabutoxide (Zr(OBu)$_4$, 80 wt% in 1-butanol), vanadium trisopropoxide oxide (VO(OiPr)$_3$, 96%), ruthenium (III) nitrosyl nitrate (Ru(NO)(NO$_3$)$_2$, 31.3 wt% Ru) and ruthenium (III) chloride hydrate (RuCl$_3$, 99.9%) were obtained from Alfa Aesar and kept in an MBraun glovebox under an inert argon atmosphere. n-butanol (n-BuOH, 99.8%) and tert-butanol (t-BuOH, ≥99.5%), procured from Sigma-Aldrich, were distilled over CaH$_2$ and stored on freshly activated 3 Å molsieves (Merck) under inert atmosphere.

Microcrystalline cellulose powder (cellulose), ruthenium on carbon (Ru/C, 5% wt. loading) and tungsten oxide (WO$_3$, 99.9%) were bought from Sigma-Aldrich. Ethane-1,2-diol (ethylene glycol, 99%), propane-1,2-diol (propylene glycol, 99%), propane-1,2,3-triol (glycerol, 99%), meso-erythritol, (erythritol, 99%), D-mannitol (mannitol, 99%), D-sorbitol (sorbitol, 98%), butane-1,2-diol (1,2-BD, 98%), hexane-1,2-diol (1,2-HD, 98%) and D-(-)-glucose (glucose, 99) were received from Alfa Aesar and used as chromatography standards. Hydrogen (H$_2$, 5.0), nitrogen (N$_2$, 5.0), helium (He, 5.0) and carbon monoxide (CO, 4.7) were acquired from Linde Gas.

2.2. Catalyst preparation

Bulk tungsten oxide (b-WO$_3$) was prepared by hydrolysis of WCl$_6$ (3.97 g; 10.0 mmol) in 160 mL deionized water kept at 50 °C overnight while stirred. The yellow precipitate was collected by filtration and washed several times with deionized water until neutral pH of the filtrate was reached. The residue was then dried at 60 °C in vacuo overnight. b-NbW5 (W/Nb atomic ratio of 5) was prepared in a similar fashion using a physical mixture of appropriate amounts of WCl$_6$ and NbCl$_5$. b-TiW5 (W/Ti atomic ratio of 5) were prepared by adding an appropriate amount of WCl$_6$ to 160 mL water first and injecting the correct amount of TiCl$_4$ within 10 s using a Finn pipette with the tip submerged in the water. After drying, the materials were used without further treatment.

Mesoporous tungsten oxide (m-WO$_3$) was prepared using a modified literature procedure [22]. Under inert conditions, WCl$_6$ (7.20 g, 18.2 mmol) was dispersed into a cooled (0 °C) mixture of n-BuOH (10.8 mL) and t-BuOH (10.8 mL). The mixture was stirred vigorously for 10 min until a dark blue solution was obtained, which was then poured into a Teflon-lined autoclave and aged at 100 °C for 24 h. Dark blue solids were collected by filtration, washed several times with
ethanol and dried overnight at 110 °C under vacuum to remove residual organics.

Doped variants of m-WO₃ (m-TiW₅, m-VW₅, m-ZrW₅) were prepared by mixing the appropriate amount of metal alkoxide into the alcohol mixture prior to adding the WCl₆ to achieve W/dopant atomic ratios of 5. m-NbW₅ was obtained from dispersing a physical mixture of NbCl₃ and WCl₆ into the alcohol mixture. The mixtures acquired after full dissolution of the metal precursors were treated similarly as for the preparation of m-WO₃.

Supported Ru catalysts were prepared by wet impregnation. In a typical procedure, an appropriate amount of RuCl₃ (for mesoporous oxides) or Ru(NO)(NO₃)₃ (for bulk oxides) was dissolved in 10 mL de-mineralized water. The required amount of support was added and the resulting suspension was homogenized for 3 h before evaporation to dryness at 85 °C. The solids were dried further at 110 °C under vacuum overnight, thoroughly ground and pressed into a sieve fraction (125μm–500μm). The sieve fractions were reduced at 200 °C, ramp 2 °C/min, under a flow of 10% H₂ in He (100 mL/min) for 4 h, followed by passivation in 1% O₂/He (100 mL/min) at room temperature for 6 h.

2.3. Characterization

Nitrogen sorption data was acquired from a Micromeritics Tristar 3000 in static measurement mode at −196 °C. The samples (typically 150 mg) were pretreated at 120 °C under a gentle N₂ stream overnight prior to the sorption measurements. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area (S_BET) from the adsorption data (p/p0 = 0.05–0.25). Mesopore volumes (V_{meso}), if applicable, were calculated by applying the Barrett-Joyner-Halenda (BJH) method on the adsorption branch.

Powder X-ray diffraction (XRD) patterns were obtained from a Bruker Endeavour D2 Phaser diffractometer using Cu Kα radiation with a scanning speed of 0.6 °/min in the range of 5° ≤ 2θ ≤ 60°. Crystal phases were identified using the DIFFRAC.EVA software package and the PDF-2 crystallographic database (version 2008).

X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific K-alpha equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Initial pressure was 8·10⁻⁸ mbar or less which increased to 2·10⁻⁶ mbar due to the active argon charge compensation dual beam source during measurement. For a typical sample preparation, fresh catalyst was pressed down on carbon tape supported by an aluminium sample plate. Spectra were recorded using an Al Kα X-ray source (1486.6 eV, 72 W) and a spot size of 400 μm. Survey scans were taken at a constant pass energy of 200 eV, 0.5 eV step size, region scans at 50 eV constant pass energy with a step size of 0.1 eV. XP spectra were calibrated to the C1s carbon signal (284.8 eV) obtained from adventitious carbon and deconvoluted with CasaXPS. The peak areas thus obtained were used to estimate surface chemical composition.

Infrared (IR) spectroscopy was used to evaluate acidic properties of the materials, using pyridine as probe molecule. Spectra were recorded in the range of 4000 – 1200 cm⁻¹ at a resolution of 2 cm⁻¹ on a Bruker Vertex V70v Fourier-Transform infrared spectrometer equipped with a DTGS detector and CaF₂ windows to separate the environmental cell from the vacuum part. A total of 64 scans were averaged for each spectrum. Typically, finely powdered material was pressed into self-supporting wafers with density ρ = 25 mg cm⁻³ using a pressing force of 3000 kg and placed inside a variable temperature IR transmission cell coupled to a closed gas circulation system. The samples were then outgassed at 70 °C in vacuo until a pressure of 2·10⁻⁸ mbar or lower was reached. Prior to pyridine adsorption, the sample was kept at 70 °C and a sample background was recorded. Pyridine was then introduced into the cell until saturation was reached, and physiosorbed pyridine was removed in vacuo for 1 h. A second spectrum was recorded at this point. Difference spectra were obtained by subtraction of the sample background from the recorded spectra. Processing and deconvolution of the signals in the 1600 – 1400 cm⁻¹ region was performed with Fityk curve fitting program using molar extinction coefficients determined by Datka et al. [23] such that

$$N = \frac{A}{ερ}$$

where N is the density of respective acid sites (μmol mg⁻¹), A the integrated peak area (cm⁻¹), ε the integrated molar extinction coefficient (cm μmol⁻¹) and ρ the wafer density (mg cm⁻²).

Elemental analysis was performed on a Spectroblue EOP ICP optical emission spectrometer with axial plasma viewing, equipped with a free-running 27.12 MHz generator operating at 1400 W. Prior to the measurement, the samples were digested using a 4 M KOH solution. For Ti and Zr containing samples, 8 vol. % HF was added to dissolve the dopant under heating (40 °C). Samples for ruthenium analysis were prepared by melt fusion of approximately 25 mg of fresh sample to a mixture of KNO₃ (1 g) and KOH (0.3 g). Initial solutions are prepared in 2 M KOH and must immediately be diluted further in 0.5 M HCl. Authors advise to analyze the samples immediately after preparation as ruthenium tends to form precipitates in alkaline solutions, while tungsten oxide precipitates from solutions that are too acidic. Calibration lines were prepared using commercial standards. Care was taken that the calibration solutions contained the same concentration of auxiliaries as the analytic solutions.

Temperature programmed reduction (TPR) plots were recorded on a Micromeritics Autochem II 2920. Powdered catalyst (100 mg–150 mg) was loaded between two quartz wool plugs in a quartz glass U-tube. Samples were pretreated in a 10 mL/min He flow at 130 °C for 2 h to remove physisorbed water and other adsorbates. TPR was then performed in a 50 mL/min flow of 4% H₂ in N₂ at a temperature range of 50 °C–750 °C, 10 °C/min.

CO chemisorption data was obtained from a Micromeritics ASAP 2020. Powdered Ru-impregnated catalyst (100 mg–150 mg) was loaded between two quartz wool plugs in a quartz glass U-tube. Prior to measurement, the samples were reduced in situ at 200 °C for 4 h, ramp rate 2 °C/min in a flow of pure H₂. CO chemisorption was then performed at 35 °C. Ru dispersion was calculated assuming an adsorption stoichiometry of 1.5 CO per surface ruthenium atom.

Transmission electron microscopy (TEM) images were obtained in bright field mode from a FEI Tecnai 20 (type Sphera) operating with a LaB₆ filament at 200 kV and a bottom mounted 1024 × 1024 Gatan msc 794™ CCD camera. Suitable samples were prepared by dropping a suspension of finely ground material in analytical grade absolute ethanol onto Quantifoil R 1.2/1.3 holey carbon films supported on a copper grid.

2.4. Catalytic activity tests

All reactions were performed in a 100 mL high-pressure batch re-actor. For a typical experiment, 300 mg of cellulose, an amount of catalyst and 40 mL of water were loaded into the reactor. The catalyst portion either consisted of 50 mg tungsten oxide and 10 mg 5 wt% Ru on carbon, or 50 mg Ru-impregnated tungsten oxide. After sealing, the reactor was purged several times with hydrogen and then pressurized to a final pressure of 45 bar. Stirring was set at 600 rpm and temperature was maintained at 210 °C, 225 °C or 240 °C for 30 min–180 min. The starting point of the reaction was set to when the reaction temperature was reached. After completion, the reactor was cooled to room temperature naturally. Gaseous products were captured in a pre-purged gas cylinder and reactor contents were recovered after addition of n-BuOH as internal standard, added for GC analysis. Solids were separated from the reaction liquor by centrifugation and dried at 110 °C under vacuum overnight.
2.5. Product analysis

Cellulose conversion was determined by mass difference of cellulose before and after the reaction. Volatile reaction products (ethylene glycol, 1,2-propylene glycol and glycerol) were analyzed on an Interscience Focus GC-FID over a Stabilwax-DA column (30 m × 0.53 mm I.D., dp = 1.00 μm) and Shimadzu HPLC equipped with a Rezex-RPM monosaccharide column (300 × 7.8 mm) and ELSD, and milliQ grade water as mobile phase. Quantification was based on mass response factors determined by five-point calibration lines of commercial compounds. Volatile products were additionally referenced to n-ButOH as internal standard. Gaseous products were quantified on an Interscience Compact GC using a Molsieve 5 Å and Porabond Q column, each connected to a TCD, and an Al2O3/KCl column linked to an FID. Identification and quantification of gaseous products was based on a calibration gas standard containing known quantities of a standard gas mixture. Carbon product yields and selectivities, and total carbon balances were calculated from Eqs. (2)–(4). In these calculations, cellulose is regarded as a linear condensation polymer of glucose repeat units having a molar mass of 162 g/mol each.

\[
Y_i(\%) = 100\left(\frac{k_i^{*}n_i}{C_{\text{glucose}}n_{C_{\text{glucose}},i}}\right)
\]

(2)

\[
S_i(\%) = 100\left(\frac{k_i^{*}n_i}{C_{\text{glucose}}n_{C_{\text{glucose}},i} + n_{C_{\text{glucose}},i}}\right)
\]

(3)

\[
Y_C (\%) = 100\left(\frac{\sum k_n^{*}n + k_C^{*}n_{C_{\text{glucose}},f}n_{C_{\text{glucose}},i}}{k_C^{*}n_{C_{\text{glucose}},i}}\right)
\]

(4)

Here, \(Y_i\), \(S_i\), \(k_i\) and \(n_i\) are the yield, selectivity, carbon number and moles of the respective products. \(Y_i\) represents the carbon balance. \(n_{C_{\text{glucose}},i}\) and \(n_{C_{\text{glucose}},f}\) are the initial and final moles of cellulose, computed as moles of glucose repeat units.

3. Results and discussion

(Doped) bulk and mesoporous tungsten oxides were synthesized using previously established procedures [16,17,20,22]. These materials have been used to catalyze the upgrading of glucose to 5-HMF and in-depth characterization and related discussions can be found in our earlier works. Main findings relevant to the present study are discussed below.

Bulk compositions of the doped materials were determined by ICP and the results are given in Table 1. We find that the measured tungsten/dopant levels are close to the desired ones. Sorption measurements (Table 1 and Fig. S1) show the difference in surface area and available pore volume between the sets of bulk and mesoporous materials. Lewis and Brønsted acid densities were analyzed by IR spectroscopy with pyridine as a probe molecule and molecular absorption coefficients as established by Datka et al. [23]. Lewis acid densities of the undoped materials (b-WO3 and m-WO3) are similar when normalized by surface area. Upon doping, the LAS density drops significantly as a result of replacing Lewis acidic W6+ cations by dopant cations. The largest decrease in LAS density was observed for m-WV5. The BAS density increases significantly for the doped bulk materials (b-NbW5 and b-TiW5) as a result of introducing elements with a lower valance state than W6+. This introduces a charge defect which is compensated with an acidic proton. This effect, however, was not observed for the mesoporous doped materials and the BAS density instead dropped after doping. We surmise that this particular effect is induced by additional charge compensation effects induced by varying levels of dopants present on the surface. Note that b-WO3 and m-WO3 themselves already possess a substantial number of BAS, resulting from partial reduction of W6+ cations to W5+.

TEM micrographs of the bulk and mesoporous oxides are displayed in Fig. 1 and present layered phases for all three bulk materials. The sheets which build up b-WO3 and b-NbW5 have clearly defined plane edges, while the sheet edges of b-TiW5 are very corrugated. XRD analysis (Fig. 2) of the bulk materials shows that tungstite constitutes b-WO3 as crystal phase, while b-NbW5 and b-TiW5 mainly consist of hydrotungstite.

In contrast to the sheet-like structure of the bulk materials, all mesoporous oxides consist of an aggregation of irregularly shaped nanoparticles, ranging in size between 5 nm–10 nm. The mesoporous materials mainly comprise sub-stoichiometric β-W2O5OBr. This phase comprises a significant fraction of W5+, which is formed during the synthesis procedure. In addition, m-TiW5 and m-VW5 contain a ribbon-like phase. We suspect this might be tungstite, which can also be observed in XRD measurements.

Direct upgrading of cellulose to EG is a complex process with many possible undesired side reactions. Cellulose is recalcitrant to depolymerization or perhaps its hydrolysis to glucose fragments can be considered the rate determining step. This, however, is beneficial as it keeps the glucose concentration low during the reaction, which prevents its degradation to humins to a significant degree. The retro-aldol functionality of tungsten oxide plays a critical role in converting glucose liberated from cellulose to glycol aldehyde (Scheme 1), which is then hydrogenated to EG. From previous research on tungsten oxide materials, we discovered that tungstite was significantly more active catalyst than monoclinic WO3 [20]. As such, we compared the activity of these two materials (Table 2, entry 1 and 3). We indeed found the performance of tungstite to be superior, both in activity and selectivity towards EG. Monoclinic WO3 contains very few Brønsted acid sites for its surface area, which itself is significantly smaller than that of b-WO3.

| Catalyst | \(S_{\text{BET}}\) \(\text{m}^2 \text{g}^{-1}\) | \(v_{\text{pore}}\) \(\text{cm}^3 \text{g}^{-1}\) | \(W/\text{dopant}\) | \(N_{\text{LAS}}\) \(\text{mmol g}^{-1}\) | \(N_{\text{BAS}}\) \(\text{mmol g}^{-1}\) |
|---------|-----------------|-----------------|------------------------------|-----------------|-----------------|
| WO3     | 5.0             | –               | –                            | 0.026           | 0.006           |
| b-WO3   | 17              | –               | –                            | 0.058           | 0.029           |
| b-NbW5  | 35              | –               | 5.0                          | 0.099           | 0.079           |
| b-TiW5  | 3.9             | –               | 4.4                          | 0.005           | 0.039           |
| m-WO3   | 135             | 0.071           | –                            | 0.46            | 0.29            |
| m-NbW5  | 148             | 0.090           | 4.9                          | 0.12            | 0.098           |
| m-TiW5  | 195             | 0.33            | 5.6                          | 0.14            | 0.17            |
| m-VW5   | 193             | 0.31            | 5.7                          | 0.068           | 0.02            |
| m-ZrW5  | 233             | 0.30            | 4.7                          | 0.26            | 0.33            |

* \(W/\text{dopant}\) ratio determined by ICP.

1 Lewis acid site density.

2 Brønsted acid site density.
These factors combined result in its poor activity compared to b-WO₃. The difference in activity of tungstite and monoclinic WO₃ can also be observed in the distribution of side products. C4 and C6 products are obtained with both catalysts, but the product distribution is different. Monoclinic WO₃ produces polysols as C4 and C6 side products, whereas tungstite is more selective towards the corresponding 1,2-diols. The 1,2-diols are formed from their respective polyols by successive dehydration and hydrogenation. It must be noted that all reaction mixtures were faintly blue in color immediately after recovering the reaction mixture, which is probably caused by finely divided catalytic material, but can also result from soluble tungsten oxide species as reported by Tai et al. among others [24]. Soluble HₓWO₃ species and meta- and paratungstates are known to catalyze the depolymerization and hydrolysis of cellulose [25–27]. This implies that these processes could also be partially homogeneous in nature in our case. However, heterogenic processes cannot be discarded as there is a clear relation between the Brønsted acidity of the material and the level of conversion. This was shown by doping b-WO₃ with niobium or titanium, which increases the Brønsted acidity of the material by inducing charge defects which are compensated by acidic protons, which is reported in earlier work [16,17].

Comparing entries 6 and 9 to 3, doping of tungstite indeed accelerated conversion of cellulose. However, the increased acidity had a negative impact on EG selectivity. This is likely caused by humin formation, as the carbon balance is also negatively affected. Increasing the temperature to 240 °C (entries 4, 7 and 10) equally increased conversion while decreasing the EG selectivity and the carbon balance. Lowering the temperature to 210 °C (entries 2, 5 and 8) was beneficial to EG selectivity and improved the carbon balance significantly, but none of the doped materials exceeded the performance of tungstite. b-WO₃ was therefore used to perform a kinetic study (Table 3). The majority of the EG production occurs in the first hour and the reaction reaches a stable plateau as there is no remarkable change in selectivities towards different side products past one hour of reaction time. A plausible explanation is that during the first half an hour, the amount of free glucose and short-chain cellulose oligomers is still very low, and the catalyst is still active enough to convert these to non-humin forming species. The selectivity to the various hydrogenated species is therefore still high in the first 30 min to 1 h. During the course of the reaction, the amount of soluble short chain cellulose oligomers keeps increasing and so will the apparent conversion, which is purely based on the mass loss of recovered solids. However, these short chains

![Fig. 1. Representative images of bulk and mesoporous materials. Bulk materials are contained in the dashed outline with their corresponding mesoporous oxide displayed below the image.](image1)

![Fig. 2. XRD measurements of bulk and mesoporous materials. Hydrotungstite is abbreviated to H-tungstite.](image2)

**Table 2**

| Entry | Catalyst | Temp. °C | Conv. % | EG % | PG % | BD % | HD % | C4 % | C6 % | CB % |
|-------|----------|----------|---------|------|------|------|------|------|------|------|
| 1     | b-WO₃   | 225      | 39.7    | 29.5 | 0.0  | 0.0  | 10.4 | 11.3 | 68.3 |
| 2     | b-WO₃   | 210      | 44.5    | 70.2 | 0.0  | 8.4  | 4.4  | 12.7 | 74.5 |
| 3     | b-WO₃   | 225      | 75.0    | 50.6 | 2.2  | 8.0  | 4.2  | 2.6  | 6.8  | 67.4 |
| 4     | b-WO₃   | 240      | 100.0   | 43.2 | 6.4  | 8.2  | 2.6  | 1.0  | 3.1  | 64.4 |
| 5     | b-NbW5  | 210      | 46.9    | 66.8 | 0.0  | 7.4  | 0.0  | 4.1  | 11.4 | 72.8 |
| 6     | b-NbW5  | 225      | 80.1    | 44.3 | 3.3  | 7.6  | 3.0  | 1.7  | 4.6  | 61.6 |
| 7     | b-NbW5  | 240      | 100.0   | 37.9 | 7.0  | 8.0  | 2.4  | 1.0  | 2.8  | 59.0 |
| 8     | b-TiW5  | 210      | 56.7    | 45.9 | 5.5  | 7.3  | 0.0  | 1.2  | 3.0  | 63.5 |
| 9     | b-TiW5  | 225      | 95.6    | 34.3 | 5.3  | 7.1  | 1.9  | 0.7  | 2.1  | 51.5 |
| 10    | b-TiW5  | 240      | 100.0   | 29.2 | 9.4  | 10.6 | 1.5  | 0.0  | 1.0  | 51.6 |

* Reaction conditions: 0.3 g cellulose, 0.05 g retro-aldol catalyst, 0.01 g 5 wt % Ru/C (1 wt% Ru w.r.t. WO₃), 40 mL H₂O, 45 bar H₂, 600 rpm, 2 h.

* EG, PG, BD, HD, C4 and C6 refer to ethylene glycol, 1,2-propylene glycol, 1,2-butanediol, 1,2-hexanediol, erythritol and mannitol + sorbitol, respectively.

* Carbon balance.
are expected to deposit on the catalytic surface, form humins in the process, and will so deactivate the catalyst. The kinetic data enables us to estimate overall turnover frequencies based on cellulose conversion, assuming that the required Brønsted acidity only stems from the catalyst. With these assumptions in mind, we find an overall TON of 1277 mol cellulose / mol BAS and an overall TOF of 425 mol cellulose / (mol BAS - h).

Next, the influence of surface area on the conversion and EG selectivity was evaluated by screening a series of (doped) of mesoporous tungsten oxides using temperatures of 210 °C and 225 °C and a reaction time of 1 h, as longer reaction times were not beneficial for EG production. The results are presented in Table 4. For this series, we additionally measured the formation of gaseous products, as ethylene and propylene glycol could in theory be dehydrated and hydrogenated as well, forming a number of C1 to C3 gaseous products in the process. m-WO3 is indeed more active than b-WO3 (Table 4, entries 1 and 2), but its use is accompanied with a significant drop in EG selectivity and carbon balance. The higher BAS density of this material is potentially the cause of the unwanted degradation of glucose and glucose oligomers to humins. The benefit of increased surface area is less than expected, but this is likely caused by the inaccessibility of a significant fraction of the material by larger cellulose fragments. Comparing the various dopants to m-WO3, V-doping is most beneficial when operating at 210 °C (entries 2 and 8), as a selectivity of 89% is reached at comparable conversion. At 225 °C, doping with Nb is most effective (entries 3 and 5) as conversion is traded for selectivity. Gaseous products are indeed formed, but only in low quantities and these neither seem to be influenced by temperature nor by dopant. Overall, the temperature has a remarkable effect on the retro-aldol activity of the various materials. At 210 °C, m-WO3 produces C4 and C6 polyols as side-products; at 225 °C, their dehydrated and hydrogenated 1,2-diol analogues are produced. Also of interest here is that m-WO3, m-NbW5 and m-VW5 (entries 6 and 10) produced 1,2-butanediol already at 210 °C, but m-WO3, m-NbW5 and m-VW5 (entries 2, 4 and 8) did not. We surmise that tetra-valent cations might provide alternative routes to form diols, which are not possible for pentavalent and tungsten cations.

Deeming m-WO3 and m-NbW5 the best-performing materials at 225 °C and 1 h, we subjected these oxides to a similar kinetic study as b-WO3. The results are presented in Table 5 and these show trends comparable to tungstite. The majority of EG is again produced in the first hour in either case. C4 and C6 polyols are produced in the first hour and are converted further to 1,2-diols. Here, interest is higher where m-WO3 seems to outperform b-WO3 in the first 30 min of reaction time as the selectivity towards EG is higher (71% vs. 63%). Comparing the selectivities towards 1,2-diols and C4 and C6 polyols of these materials, m-WO3 produces less of these side products in the first half hour. Only aldehyde or carbonyl-containing fragments can be retro-aldolized into shorter fragments. When these functional groups are hydrogenated prematurely, they will contribute to the yield of C4 and C6 polyols or their 1,2-diol analogues after dehydration and hydrogenation. From this, we can conclude that the retro-aldolization rate of m-WO3 is higher than the hydrogenation rate in this time period when compared to b-WO3.

Using the same assumptions as used for TON and TOF calculations of b-WO3, TON and hourly TOF values of m-WO3 and m-NbW5 are respectively 128 mol cellulose / mol BAS and 43 mol cellulose / (mol BAS h), and 378 mol cellulose / mol BAS and 126 mol cellulose / (mol BAS h).

After formation, glycol aldehyde needs to migrate to a metal function for hydrogenation to EG. The distance between retro-aldol and hydrogenation functions will therefore affect the likelihood for the aldehyde to degrade. To shorten the migration time, we impregnated our best-performing materials (b-WO3, m-WO3 and m-NbW5) with ruthenium (0.2 wt%, 0.5 wt%, 1 wt% and 2 wt%). Actual weight loadings, particle sizes and dispersions are summarized in Table 6. For b-WO3, the measured weight loadings are in good agreement with the desired ones. However, the actual weight loadings for both mesoporous materials deviate significantly from the intended ones. The reason for this is unclear as we could not find any relation between intended and obtained loadings. More importantly, at a loading of 0.25 wt%, particles on b-WO3 are already quite large at 8 nm, exceeding 20 nm at a weight loading of 2.28 wt%. We surmise this is due to the

### Table 3

| Catalyst | Time (min) | Conv. | EG | PG | BD | HD | C4 | C6 | CB |
|----------|------------|-------|----|----|----|----|----|----|----|
| b-WO3    | 30         | 47.4  | 63.1| 0.0| 6.8| 0.0| 4.4| 9.8| 72.3|
| m-WO3    | 60         | 62.3  | 69.2| 2.7| 4.0| 2.3| 8.3| 72.0|
| m-WO3    | 120        | 75.0  | 50.6| 2.2| 8.0| 2.6| 6.8| 67.4|
| m-WO3    | 180        | 87.8  | 50.3| 1.9| 6.6| 3.8| 7.6| 68.0|

a Reaction conditions: 0.3 g cellulose, 0.05 g retro-aldol catalyst, 0.01 g 5 wt% Ru/C (1 wt% Ru w.r.t. WO3), 40 mL H2O, 45 bar H2, 600 rpm, 225 °C.

### Table 4

| Catalyst | Temp. °C | Conv. % | EG | PG | BD | HD | C4 | C6 | CB |
|----------|----------|---------|----|----|----|----|----|----|----|
| b-WO3    | 225      | 62.3    | 60.9| 2.7| 7.7| 4.0| 2.3| 8.3| -  |
| m-WO3    | 210      | 34.6    | 82.7| 0.0| 0.0| 0.0| 1.5| 4.2| 3.9|
| m-WO3    | 225      | 66.7    | 49.5| 5.5| 7.7| 3.1| 0.6| 1.7| 2.7|
| m-NbW5   | 210      | 34.7    | 78.8| 0.0| 0.0| 0.0| 1.1| 6.5| 2.9|
| m-NbW5   | 225      | 64.0    | 56.7| 3.4| 7.4| 4.3| 1.8| 8.5| 2.2|
| m-TiW5   | 210      | 36.2    | 81.4| 0.0| 3.7| 0.0| 1.0| 3.4| 2.2|
| m-TiW5   | 225      | 70.3    | 49.0| 6.8| 9.8| 3.1| 1.1| 2.7| 1.5|
| m-VW5    | 210      | 31.9    | 89.1| 0.0| 0.0| 0.0| 1.6| 5.1| 2.8|
| m-VW5    | 225      | 57.2    | 38.6| 1.7| 4.5| 1.9| 2.3| 9.4| 2.1|
| m-ZrW5   | 210      | 38.6    | 59.5| 0.0| 8.4| 0.0| 2.2| 4.7| 5.5|
| m-ZrW5   | 225      | 74.3    | 45.0| 4.2| 6.1| 2.4| 0.7| 1.4| 1.6|

a Reaction conditions: 0.3 g cellulose, 0.05 g retro-aldol catalyst, 0.01 g 5 wt% Ru/C (1 wt% Ru w.r.t. WO3), 40 mL H2O, 45 bar H2, 600 rpm, 1 h.

b EG, PG, BD, HD, C4 and Glu refer to ethylene glycol, 1,2-propanediol, 1,2-butanediol, 1,2-hexanediol, erythritol, mannitol + sorbitol and glucose respectively.

c Combined selectivity towards gaseous products based on total carbon.
limited surface area of b-WO₃ as the average ruthenium particle sizes on the mesoporous materials are small in comparison, i.e. 1.42 nm for m-WO₃ and 1.75 nm for m-NbW₅. The particle sizes similarly increase with higher weight loadings, but this effect is far less apparent.

The effect of ruthenium impregnation and subsequent pretreatment in reducing conditions at elevated temperatures on the support was evaluated with XRD and TPR. Diffractograms are displayed in Fig. 3. m-WO₃ and m-NbW₅ stay relatively unaffected with regard to crystal phase and that the peaks become slightly sharper. In contrast, b-WO₃ undergoes significant changes in crystal phase under the applied conditions. Tungstite transforms into the same β-W₂O₅₈ phase when exposed to the pretreatment conditions and the extent of this transformation seems to depend on the ruthenium loading. This suggests reduction of the tungstite support by hydrogen spillover from the ruthenium metal as a plausible mechanism. A similar mechanism has already been described by Khoobiar et al. for Pt/WO₃ [28].

TPR profiles (Fig. 4) show that ruthenium reduces earlier on the mesoporous materials than on the bulk tungstite. Ru reducibility on the mesoporous materials depends on the ruthenium loading as peak maxima shift to lower temperatures with increasing ruthenium loading. In contrast, reducibility of the support from β-W₂O₅₈ to WO₂ (temperature range from 750 °C to 850 °C) increases with increasing Ru loading. For tungstite, ruthenium is reduced in two consecutive steps. This phenomenon is not observed for the mesoporous materials. We then screened these materials using reaction conditions of 225 °C and 1 h. The results are presented in Table 7.

Overall, the Ru-impregnated catalysts achieve lower conversions than the non-impregnated materials + Ru/C. However, impregnating b-WO₃ with increasing levels of Ru results in higher EG selectivity (Table 7, entries 1–5), and even exceeds the EG selectivity of the system using separate retro-aldol and hydrogenation functions. Additionally, low loadings of Ru suppress formation of C₄ and C₆ polyols, but this becomes more favored with increasing Ru loadings, as expected. Interestingly, selectivity towards 1,2-PG also increased with larger Ru amounts. This is likely caused by isomerization reactions promoted by b-WO₃. The m-WO₃ series (Table 7, entries 6–10) behaves comparable to the b-WO₃ series as cellulose conversion drops and EG selectivity increases with increasing Ru loadings. C₄ and C₆ selectivities are also

Table 5

| #   | Catalyst | Time | Conv. | EG (%) | PG (%) | BD (%) | HD (%) | C₄ (%) | C₆ (%) | Glu (%) | Gas (%) | CB (%) |
|-----|----------|------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1   | m-WO₃   | 30   | 46.6  | 71.6   | 0.0    | 5.1    | 0.0    | 0.9    | 4.3    | 3.9    | 0.8    | 72.2   |
| 2   | m-WO₃   | 60   | 66.7  | 49.5   | 5.5    | 7.7    | 3.1    | 0.6    | 1.7    | 2.7    | 2.3    | 74.9   |
| 3   | m-WO₃   | 120  | 82.1  | 49.8   | 2.3    | 7.3    | 2.9    | 0.5    | 1.6    | 1.0    | 1.4    | 66.6   |
| 4   | m-WO₃   | 180  | 89.3  | 41.2   | 1.6    | 6.8    | 1.9    | 0.5    | 1.8    | 1.0    | 1.5    | 72.7   |
| 5   | m-NbW₅  | 30   | 50.0  | 64.7   | 3.1    | 6.6    | 3.3    | 1.8    | 8.1    | 3.9    | 0.9    | 72.9   |
| 6   | m-NbW₅  | 60   | 64.0  | 56.7   | 3.4    | 7.4    | 4.3    | 1.8    | 8.5    | 2.2    | 1.8    | 71.1   |
| 7   | m-NbW₅  | 120  | 83.5  | 50.8   | 3.8    | 8.2    | 4.1    | 1.1    | 5.9    | 2.0    | 1.4    | 70.0   |
| 8   | m-NbW₅  | 180  | 95.2  | 39.5   | 2.4    | 5.7    | 2.5    | 0.8    | 4.8    | 1.4    | 1.3    | 57.8   |

* Reaction conditions: 0.3 g cellulose, 0.05 g retro-aldol catalyst, 0.01 g 5 wt% Ru/C (1 wt% Ru w.r.t. WO₃), 40 mL H₂O, 45 bar H₂, 600 rpm, 225 °C.

** EG, PG, BD, HD, C₄, C₆ and Glu refer to ethylene glycol, 1,2-propylene glycol, 1,2-butanediol, 1,2-hexanediol, erythritol, mannitol + sorbitol and glucose respectively.

* Combined selectivity towards gaseous products based on total carbon.

Table 6

| Catalyst | Ru loadinga | d° | D° |
|----------|-------------|----|----|
| b-WO₃    | 0.25        | 8.00 | 16.0 |
|          | 0.51        | 15.3 | 8.39 |
|          | 1.08        | 20.9 | 6.15 |
|          | 2.28        | 20.4 | 6.29 |
| m-WO₃    | 0.23        | 1.42 | 90.6 |
|          | 0.47        | 1.99 | 64.4 |
|          | 0.86        | 2.45 | 52.3 |
|          | 1.34        | 2.64 | 48.5 |
| m-NbW₅   | 0.16        | 1.75 | 73.9 |
|          | 0.40        | 2.36 | 54.4 |
|          | 0.78        | 2.52 | 51.1 |
|          | 1.28        | 2.86 | 44.8 |

* Determined by ICP.

b Calculated from CO chemisorption.
reduced by impregnation and equally increase with increasing Ru loadings, as does 1,2-propylene glycol selectivity. Impregnation of m-NbW5 (entries 11–15) does not show such an increase in selectivity towards EG, although the trend of the initially low but increasing selectivities towards C3, C4 and C6 compounds is preserved.

From this screening, we can conclude that impregnation of b-WO3 with 2 wt% offers significant advantages over separate hydrogenation and retro-aldol functions. Although the conversion is lower, this is more than compensated by lower C4 and C6 side product formation, which facilitates separation of EG from the reaction mixture. A kinetic study was performed to probe the activity of this catalyst over time and the results are displayed in Table 8. Very little side products are formed within the first half hour of reaction time, with comparable carbon balances as other reactions ran for this time period. The amount of polyols stays low, even after 3 h of reaction time, very different from the separate tungsten oxide and Ru/C systems tested in this work. However, we find here that the majority of EG production again takes place in the first hour of reaction time, with decent carbon balance and low side product formation.

4. Conclusion

We investigated the influence of doping tungstite and mesoporous tungsten oxides with early transition metals on the depolymerization of cellulose to glucose and the retro-aldolization of glucose to C2 aldehydes. Both tungstite (b-WO3) and mesoporous tungsten oxide (m-WO3) were more active and EG selective than monoclinic WO3, using carbon-supported ruthenium that provided the hydrogenation function to convert intermediate C2 aldehyde to EG. Monoclinic WO3 reached 40% cellulose conversion with 30% EG selectivity after 2 h of reaction time and was easily surpassed by b-WO3 and m-WO3 in performance, which reached 62% and 67% conversion with EG selectivities of 61% and 50%, respectively, after only 1 h of reaction. Kinetic studies performed with b-WO3 and m-WO3 show that their cellulose conversion rates are comparable, but m-WO3 initially has a higher EG selectivity than b-WO3 (72% vs. 63%). After 1 h, the EG selectivity of m-WO3 drops to 50%, while the EG selectivity of b-WO3 remains steady at 61%. Longer reaction times have a negative effect on EG selectivity, dropping to 50% and 41% for respectively b-WO3 and m-WO3 after 3 h of reaction time.

Table 7

Cellulose conversion activity of Ru-impregnated materials.

| #  | Catalyst     | Ru\(^{\text{b}}\) wt% | Conv. | EG\(^{\text{c}}\) | PG\(^{\text{c}}\) | BD\(^{\text{c}}\) | HD\(^{\text{c}}\) | C4\(^{\text{c}}\) | C6\(^{\text{c}}\) | Glu\(^{\text{c}}\) | Gas\(^{\text{d}}\) | CB\(^{\text{e}}\) |
|----|--------------|----------------------|-------|---------------|----------------|--------------|--------------|-------------|-------------|--------------|-------------|-------------|
| 1  | b-WO3        | Phys\(^{\text{f}}\)  | 62.3  | 60.9          | 2.7            | 7.7          | 4.0          | 2.3         | 8.3         | 2.5          | 2.1         | 72.0        |
| 2  | b-WO3        | 0.2                  | 60.7  | 50.0          | 0.0            | 3.6          | 0.0          | 0.8         | 0.7         | 3.6          | 2.4         | 65.0        |
| 3  | b-WO3        | 0.5                  | 59.3  | 51.2          | 3.3            | 3.5          | 0.0          | 0.6         | 0.3         | 2.3          | 1.8         | 62.0        |
| 4  | b-WO3        | 1.0                  | 49.1  | 60.2          | 4.4            | 4.8          | 0.0          | 1.1         | 0.7         | 3.1          | 2.3         | 60.0        |
| 5  | b-WO3        | 2.0                  | 50.5  | 65.7          | 5.2            | 5.9          | 0.0          | 1.0         | 0.5         | 2.0          | 1.3         | 70.3        |
| 6  | m-WO3        | Phys                 | 66.7  | 49.5          | 5.5            | 7.7          | 3.1          | 0.6         | 1.7         | 2.7          | 2.3         | 74.9        |
| 7  | m-WO3        | 0.2                  | 50.1  | 33.1          | 0.0            | 0.0          | 0.0          | 0.4         | 0.0         | 5.5          | 0.6         | 59.8        |
| 8  | m-WO3        | 0.5                  | 49.8  | 46.9          | 0.0            | 0.0          | 0.0          | 0.5         | 0.6         | 5.2          | 1.4         | 63.8        |
| 9  | m-WO3        | 1.0                  | 50.5  | 56.5          | 4.6            | 4.3          | 0.0          | 1.0         | 1.7         | 5.2          | 3.1         | 69.0        |
| 10 | m-WO3        | 2.0                  | 52.5  | 55.8          | 7.9            | 6.6          | 5.2          | 1.6         | 5.8         | 5.6          | 2.9         | 72.7        |
| 11 | m-NbW5       | Phys                 | 64.0  | 56.7          | 3.4            | 7.4          | 4.3          | 1.8         | 8.5         | 2.2          | 1.8         | 71.1        |
| 12 | m-NbW5       | 0.2                  | 55.0  | 20.3          | 0.0            | 0.0          | 0.0          | 0.3         | 0.0         | 2.8          | 0.4         | 52.2        |
| 13 | m-NbW5       | 0.5                  | 58.6  | 30.8          | 0.0            | 0.0          | 0.0          | 0.4         | 0.3         | 2.8          | 0.8         | 53.4        |
| 14 | m-NbW5       | 1.0                  | 58.7  | 48.0          | 4.3            | 3.8          | 0.0          | 0.7         | 0.9         | 2.8          | 1.2         | 61.6        |
| 15 | m-NbW5       | 2.0                  | 63.0  | 44.0          | 8.9            | 5.5          | 3.5          | 1.3         | 3.9         | 3.7          | 2.3         | 66.1        |

\(^{a}\) Reaction conditions: 0.3 g cellulose, 0.05 g retro-aldol catalyst, 40 mL H2O, 45 bar H2, 600 rpm, 225 °C.

\(^{b}\) Intended Ru loading.

\(^{c}\) EG, PG, BD, HD, C4, C6 and Glu refer to ethylene glycol, 1,2-propylene glycol, 1,2-butanediol, 1,2-hexanediol, erythritol, mannitol + sorbitol and glucose respectively.

\(^{d}\) Combined selectivity towards gaseous products based on total carbon.

\(^{e}\) Carbon balance.

\(^{f}\) Phys refers to separate retro-aldol and hydrogenation catalysts, 0.05 g retro-aldol catalyst, 0.01 g 5 wt% Ru/C (1 wt% Ru w.r.t. WO3).
increased cellulose conversion, but neither dopant increased EG selectivity, especially in the observed when using tungstite. While the total EG formation, especially noticeable when using niobium (m-NbW5) or titanium (m-TiW5) with varying levels of ruthenium showed that a weight loading of 2% on tungstite rendered the most effective catalyst, based on EG selectivity and carbon balance. While the total EG yield of the impregnated material is lower (33% vs. 38%), the EG selectivity and significantly lower polyol yield make tungstite impregnated with 2 wt% of ruthenium the promising catalyst in our study.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110400.

Table 8

Cellulose conversion activity of 2 wt% Ru/b-WO3-α.

| # | Catalyst | Time min | Conv. % | Selectivity |
|---|---------|---------|---------|-------------|
|   |         |         | EG | PG | BD | HD | C4 | C6 | Glu | Gas | CB |
| 1 | b-WO3  | 30      | 37.1 | 61.2 | 0.0 | 0.0 | 0.0 | 1.8 | 1.6 | 1.4 | 0.7 | 72.1 |
| 2 | b-WO3  | 60      | 50.5 | 65.7 | 5.2 | 5.9 | 0.0 | 1.0 | 0.5 | 2.0 | 1.3 | 70.3 |
| 3 | b-WO3  | 120     | 72.3 | 45.2 | 1.8 | 7.0 | 1.6 | 0.8 | 0.6 | 2.3 | 1.2 | 59.6 |
| 4 | b-WO3  | 180     | 82.9 | 37.0 | 1.7 | 7.0 | 1.6 | 0.6 | 0.6 | 2.2 | 1.0 | 52.9 |

α Reaction conditions: 0.3 g cellulose, 0.05 g retro-aldol catalyst, 40 mL H2O, 45 bar H2, 600 rpm, 225 °C. 

β EG, PG, BD, HD, C4, C6 and Glu refer to ethylene glycol, 1,2-propylene glycol, 1,2-butanediol, 1,2-hexanediol, erythritol, mannitol + sorbitol and glucose respectively.

δ Combined selectivity towards gaseous products based on total carbon.

Doping of b-WO3 with niobium (b-NbW5) or titanium (b-TiW5) enhanced the rate of cellulose depolymerization to glucose through a higher Brønsted acidity, but this did not increase the retro-aldol performance as the higher acidity resulted in an increased rate of humin formation, especially noticeable when using b-TiW5. Doping of m-WO3 with niobium (m-NbW5) or titanium (m-TiW5) did not significantly improve the conversion, although a slightly higher EG selectivity was observed when m-NbW5 (57%) was used, compared to m-WO3 (50%). Doping with vanadium (m-VW5) or zirconium (m-ZrW5) lowered and increased cellulose conversion, but neither dopant increased EG selectivity. Since m-NbW5 was slightly more efficient regarding EG selectivity than m-WO3, we also subjected that material to a kinetic study and found that its performance was comparable to that of b-WO3 and m-WO3, especially in the first hour. Impregnation of these three materials (b- and m-WO3 and m-NbW5) with varying levels of ruthenium showed that a weight loading of 2% on tungstite rendered the most effective catalyst, based on EG selectivity and carbon balance. While the total EG yield of the impregnated material is lower (33% vs. 38%), the EG selectivity and significantly lower polyol yield make tungstite impregnated with 2 wt% of ruthenium the promising catalyst in our study.

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