Supporting Information

Temperature-controlled Phase-transfer Catalysis for Ethylene Glycol Production from Cellulose

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1. Experiment

1.1 Catalysts

Tungsten acid was provided by Sinopharm Chemical Reagent Co., Heteropoly acid ($H_3O_{40}PW_{12}$) was provided by Aladdin Chemistry Co..

WO_3 was prepared by calcination of ammonium metatungstate (AMT) at 723K for 5h. The activated carbon support (NORIT, surface area 709 m^2/g) was treated with nitric acid solution (33 wt%) at 353 K for 24 h prior to the deposition of active metal component. The Ru/AC catalyst was prepared by incipient wetness impregnation method using $RuCl_3$ as the metal precursor. After drying at RT overnight and at 353 K for 5 h, the sample was reduced in a H_2 flow at 523 K for 1 h. Prior to exposure to air, the as-prepared catalysts were passivated in a flow of 1 % O_2/N_2 for at least 5 h at RT.

Ru-W_2C/AC was prepared by the carbothermal hydrogen reduction (CHR) method. For a typical preparation, activated carbon was impregnated with an aqueous solution of ammonium metatungstate (AMT) and $RuCl_3$, and the mixture was dried at 393 K for 12 h. The sample was then carburized in a H_2 flow at 1073 K for 1 h. Prior to exposure to air, the as-prepared carbide catalyst was passivated in a flow of 1 % O_2/N_2 for 12 h at room temperature.

1.2 Reaction of cellulose

Catalytic conversion of cellulose was carried out in a stainless-steel autoclave (Parr Instrument Company, 100 mL) typically at 6 MPa H_2 pressure (measured at room temperature) and 518 K for 30 min. For each reaction, 0.5 g cellulose, a designated amount of catalyst, and 50 g water were put in an 100 mL autoclave and stirred at 1000 r/min and 518 K for 30 min. For stability tests of H_2WO_4 + Ru/C catalyst, a 300 mL autoclave was employed which contained 1.0 g cellulose, a proper amount of catalyst and 100 g water. The catalysts were recovered after each run by filtration with 0.45μm filter membrane and washing with deionized water for several times, and then were put into the reactor for the next run without any reduction treatment.

1.3 Products analysis

After the reaction, the liquid-phase products were analyzed by HPLC system (Agilent 1200, Shodex Sugar SC1011 column, differential refractive index detector, water as mobile phase, flow rate: 0.6 ml min^{-1}, Inj Vol: 5.0 μl, RID opt *T*: 35 °C, Oven *T*:45 °C), and the gas products were analyzed by gas chromatograph (Agilent 6890N, TDX-1 column, TCD detector). Cellulose conversions were determined by the change of cellulose weight before and after the reaction with an uncertainty of ±3%. The yield of polyols was calculated as: yield (%) = (weight of polyol in the products)/(weight of cellulose put into the reactor) * 100%.

2. Additional discussions

2.1 Chemical state of Ru in the reaction

Concerning the active form of Ru, i.e., Ru or RuO_x, it is difficult to give an unambiguous identification at present. The XPS analysis of the used Ru/AC catalyst showed electron binding energy of Ru $3P_{3/2}$ was 463.0 eV, which is characterized of Ru (III) or Ru (IV). This result seems to suggest that RuO_x is the active form considering that the catalyst was not subjected to reduction treatment before the next run. However, one must keep in mind that the Ru(O_x) nanoparticles are so small that the redox reaction on it should be very fast. As reported by Fukuoka and coworkers (*Applied Catalysis A: General*, 2011, 407, 188–194), the oxidation of Ru nanoparticles can proceed even at RT. Actually, our freshly reduced Ru/AC catalyst must be passivated with 1%O_2/N_2 before exposure to air in order to avoid violent oxidation and combustion. In reverse, the ultrafine nanoparticles of RuO_x should also be reduced into Ru^0 very fast upon exposure to H_2 or other reducing agents. Considering that the reaction of cellulose hydrogenolysis proceeds under high-pressure H_2 atmosphere and the products are polyols (polyols are typical reducing agents and able to reduce RuO_x into Ru^o at certain temperatures), it is reasonable to speculate that the Ru^0 nanoparticles are formed during the reaction and catalyze the hydrogenation reaction of glycolaldehyde to produce EG. Nevertheless, unambiguous evidence for the redox behavior of Ru/AC under reaction conditions is still lacking because it relies on the critical in situ characterizations.

2.2 What determines the yield of ethylene glycol?

The overall yield of ethylene glycol depends on the good match of the two reactions. In other words, if the formation rate of glycolaldehyde in the first step is much faster than the hydrogenation rate of glycolaldehyde in the second step, the excess glycolaldehyde would be consumed by other side reactions such as oxidation, which will decrease the overall yield of ethylene glycol. For instance, although $H_3PW_{12}O_{40}$ afforded a comparable, even a higher yield of glycolaldehyde in the first step than H_2WO_4, it may also promote the oxidation of glycolaldehyde to form acids ($H_3PW_{12}O_{40}$ is also a strong oxidation catalyst) if the hydrogenation catalyst is not active enough to catalyze the hydrogenation of glycolaldehyde. To confirm this point, we replaced Ru/AC with Raney Ni and found that the ethylene glycol yield was increased by 12%, as shown in Table S3. The result provides further evidence that the overall yield of ethylene glycol depends both on the retro-aldol activity of tungsten catalyst and on the hydrogenation activity of transition metal catalyst. Therefore, the good balance between two consecutive reactions is required to obtain a high yield of ethylene glycol. By changing the ratio of tungsten acid to Ru/C, as shown in Table 1, one can reach such a balance between two reactions and therefore a high yield of ethylene glycol.

2.3 Purity and identity of all compounds

Since the chemical transformation of cellulose involves many parallel and consecutive reactions, many compounds are formed as byproducts in addition to the major products listed in Table 1. However, these byproducts are very low in their concentrations, and diverse from acids to polyols. This presents a grand challenge in analytical chemistry. To the best of our knowledge, the identification of all compounds derived from cellulose conversion has not been available as yet. By means of distillation, we concentrated the products and identified some of them by GC-MS and HPLC-MS. These byproducts include alcohols from C1 to C6, diols from C2 to C6, triols from C3 to C6, as well as unidentified acids. In addition to the liquid byproducts, there are also gas byproducts such as light alkanes and CO_2 which account for 5% ~10% of the total carbon depending on the catalyst and reaction conditions.

2.4 The solubility of H_2WO_4 in water

The solubility curve of H_2WO_4 in water is very useful for understanding its catalysis. However, we failed to get this curve in a wide temperature range due to experimental difficulties. Presently, by sampling at different intervals and ICP analysis of the W concentration in water, we can get this solubility curve until the reaction temperature of 160 ^{o}C. As shown in Fig. S6, one can clearly see the solubility of H_2WO_4 increases sharply with the reaction temperature, in accordance with our proposed “temperature-controlled phase-transfer behavior”.

On the other hand, from the change of EG yield with the amount of H_2WO_4, one can estimate the solubility of H_2WO_4 under the reaction conditions, i.e., 518 K, 13 MPa H_2. As shown in Table 1 of the manuscript, EG yield increased with the amount of H_2WO_4 and reached the maximum value when the amount of H_2WO_4 was equal to 50 mg. A further increase in H_2WO_4 amount had little effect on the EG yield. Therefore, it is reasonable to speculate that 50 mg/50 g water will be very close to the solubility of H_2WO_4 under the reaction conditions.

3. Supporting figures and tables

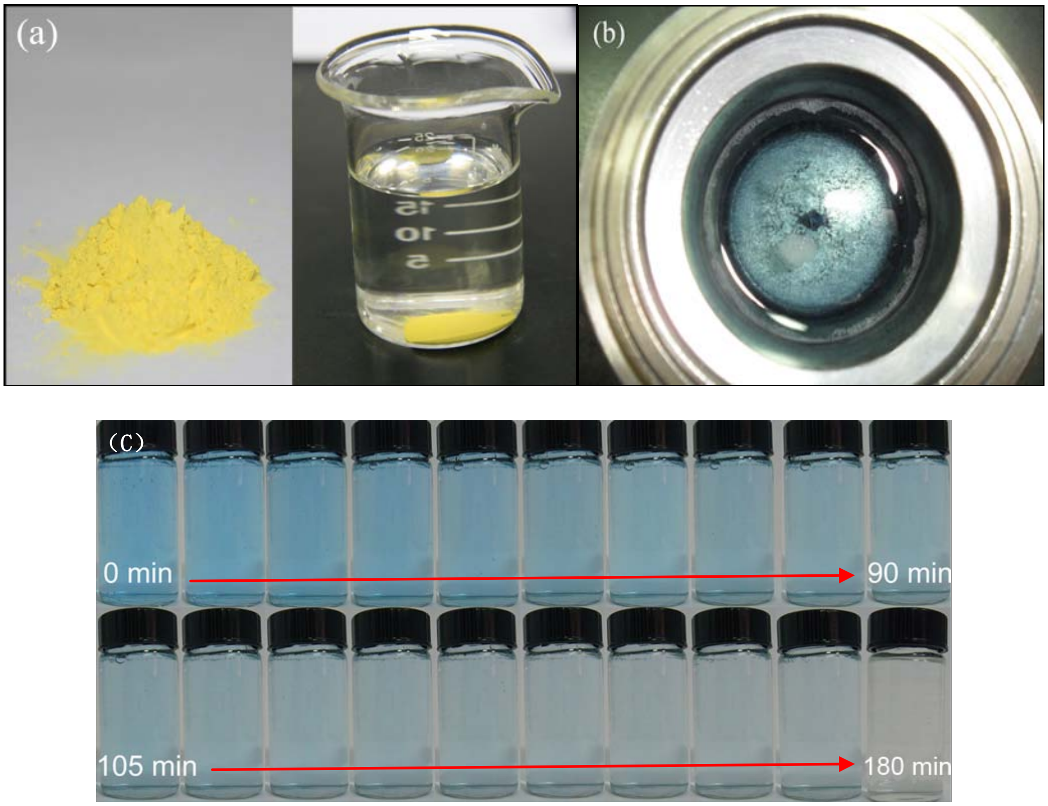

Fig. S1. (a) Photograph of H_2WO_4 powder and H_2WO_4 in water at room temperature. The yellow solid deposited on the bottom indicates H_2WO_4 is insoluble in water at RT. (b) Photograph of H_2WO_4 after hydrothermal reaction at 518 K and 6 MPa H_2 for 30 min. The dark blue solid dispersed on the bottom indicates the dissolved H_xWO_3 was precipitated upon cooling. (c) The color change of the transparent blue solution with time within 3 h, indicating the dissolved H_xWO_3 was gradually oxidized to H_2WO_4 and precipitated from the solution.

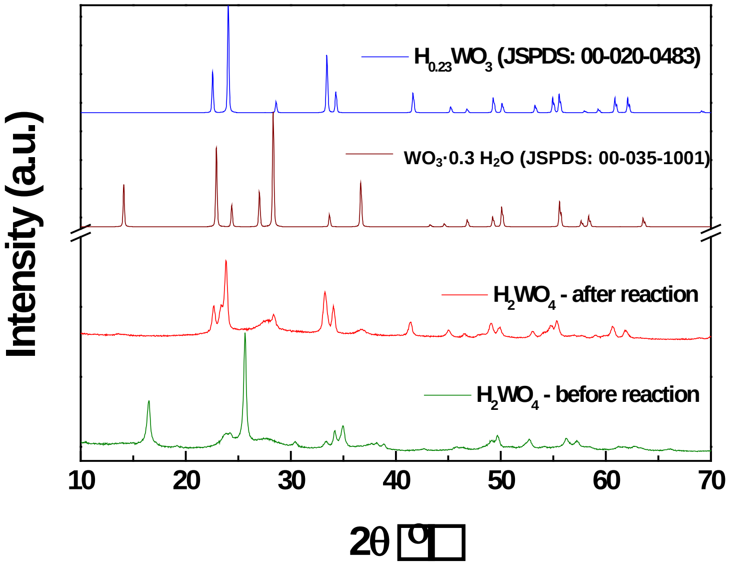

Fig. S2. XRD patterns of H_2WO_4 before and after hydrothermal treatment at 518 K and 6 MPa H_2 for 30 min. It is clear that a major phase of H_xWO_3 and a minor phase of $WO_3 \cdot 0.3\ H_2O$ were formed after the reaction.

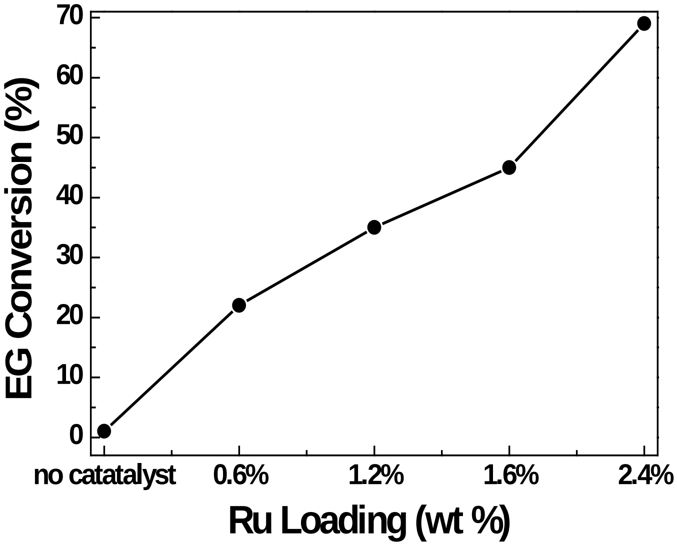

Fig. S3. Hydrogenolysis of EG over Ru/AC. The reaction condition was identical to the conversion of cellulose except for the catalyst amount of 0.15 g and 50 mL 0.5 % (wt.%) EG aqueous solution.

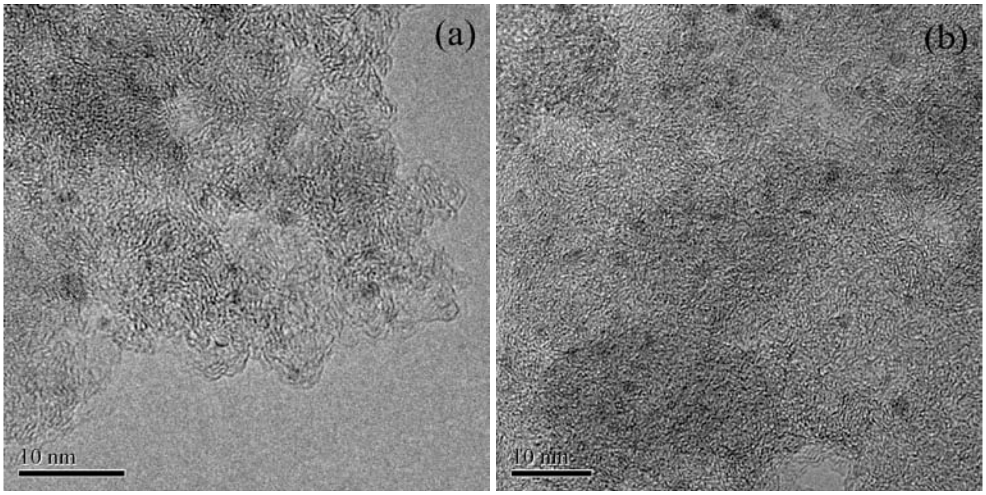

Fig. S4. HRTEM images of 1.2 % Ru/AC catalysts. (a) fresh; (b) used

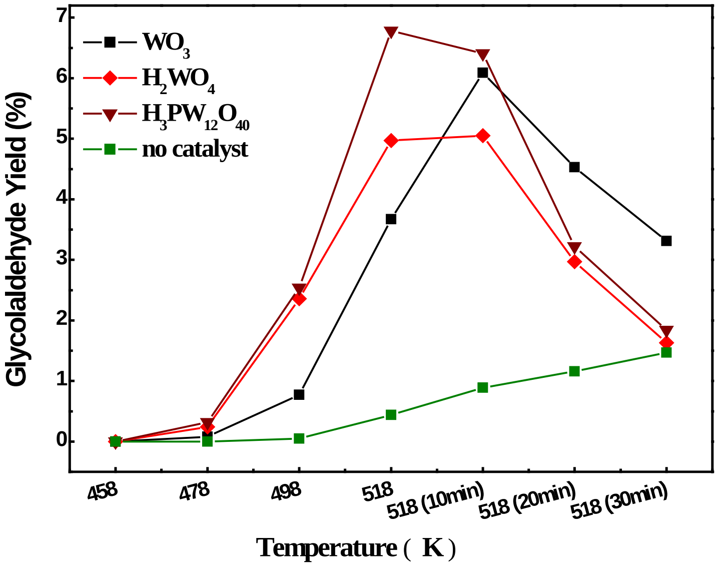

Fig. S5. The conversion of cellulose to glycolaldehyde over different tungsten compounds without hydrogenation catalyst at 518 K and 6 MPa H_2 for 30 min.

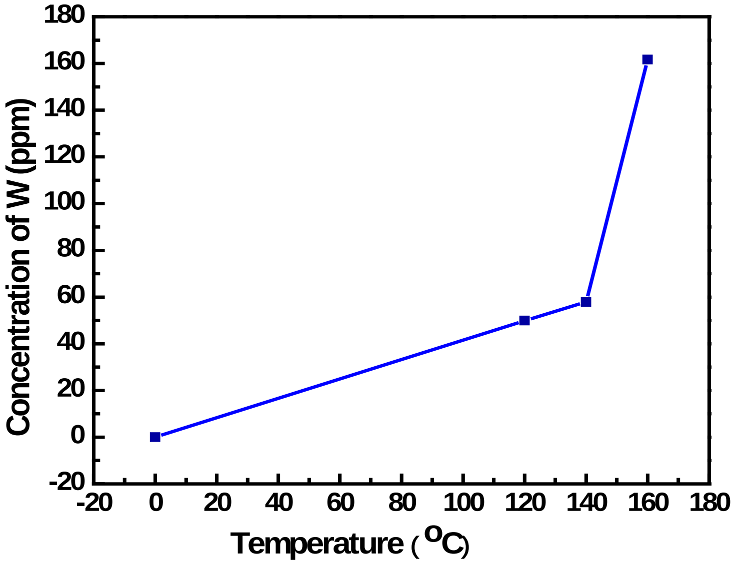

Fig. S6. Solubility of H_2WO_4 in water with temperature.

Table S1. The concentrations of Ru and W in the liquid phase during reuse experiments. The reactions were performed with 1.0 g cellulose and 100 g water at 518 K and 6 MPa H_2 in 300ml batch reactor.

Run number	Ru concentration in the liquid phase (ppm) [a]	Ru leached from the Ru/C catalyst (wt%)[b]	W concentration in the liquid phase (ppm) [a]	Tungsten Recovery (wt%)[c]
1	0	0	130.1	95.5
2	0	0	114.2	95.9
3	0	0	64.6	97.6
4	0	0	68.0	97.4
5	0	0	45.3	98.2
6	0	0	36.5	98.5
7	0	0	38.0	98.5
8	0	0	28.5	98.8
9	0	0	36.4	98.5
10	0	0	30.8	98.7
11	0	0	29.9	98.7
12	0	0	35.5	98.5
13	0	0	29.3	98.7
14	0	0	32.3	98.6
15	0	0	33.0	98.5
16	0	0	30.4	98.6
17	0	0	27.5	98.7
18	0	0	24.4	98.8
19	0	0	23.9	98.9
20	0	0	23.2	98.9

[a] The metal concentration in the liquid phase after each run was determined by ICP. [b] The metal leached from the catalyst was calculated by the equation: metal leached (wt %) = the weight of metal in the liquid phase/the weight of metal on the catalyst * 100%. [c] Tungsten Recovery was calculated by the following formula: [1-(weight of tungsten in the liquid phase / weight of tungsten put in the reactor in each run)] * 100 %.

Table S2. Yields of polyols from the conversion of cellulose over different catalyst combinations at 518 K and 6 MPa H_2 for 30 min.

Entry	Catalyst	Yield (%) [a]						
		Ery	Gly	EG	1,2-PG	Man	1,2-BDO	Sor
1	1.2 %Ru/AC(0.15 g) + $ZnCl_2$ (0.1047 g)	0.6	0	8.3	11.1	1.2	1.2	2.5
2	1.2% Ru/AC (0.15 g) + H_3BO_3 (0.0526 g)	0.9	0	9.8	4.7	3.1	1.9	6.0
3	1.2% Ru/AC (0.15 g) + H_3PO_4 (0.0166 g)	2.1	1.2	8.2	3.3	8.0	4.0	20.4
4	1.2% Ru/AC (0.15 g) + HCl (35.5 μl)	1.5	2.2	7.9	3.8	3.4	2.9	6.9
5	2% Ru-30 %W_2C/AC (0.15 g)	3.2	-	63.5	3.9	2.8	-	5.4
6	5% Ru -25% W/AC (0.3 g) [b]	7.9	-	61.7	3.2	3.1	-	4.1
7	1.2% Ru/AC (0.1509 g) + $H_3PW_{12}O_{40}$ (0.0495 g)	1.9	-	37.0	5.6	1.5	4.3	5.4
8	1.2% Ru/AC (0.1509 g) + WO_3 (0.0445 g)	1.9	-	35.6	3.0	2.2	3.6	5.0

[a] Ery, Gly, EG, 1,2-PG, Man, 1,2-BDO, and Sor are abbreviations of erythritol, glycerol, ethylene glycol, 1,2-propylene glycol, mannitol, 1,2-butanediol, and sorbitol, respectively. The yield of polyol was calculated using the equation: yield (%)=(weight of polyol in the products)/(weight of cellulose put into the reactor) X100%. [b] The result of entry 6 was cited from our published results in *ChemSusChem* 2010, 3, 63–66.

Table S3. Yields of polyols from the conversion of cellulose over different hydrogenation catalyst in combination with $H_3PW_{12}O_{40}$ at 518 K and 6 MPa H_2 for 30 min.

Entry	Catalyst	Yield (%)						
		Ery	Gly	EG	1,2-PG	Man	1,2-BDO	Sor
1	1.2% Ru/AC (0.1509 g) + $H_3PW_{12}O_{40}$ (0.0495 g)	1.9	-	37.0	5.6	1.5	4.3	5.4
2	RaneyNi (0.0448 g)+ $H_3PW_{12}O_{40}$ (0.0500 g)	2.3	-	49.1	4.6	3.3	6.6	4.8