

Production of Ethylene Glycol and Its Monoether Derivative from Cellulose

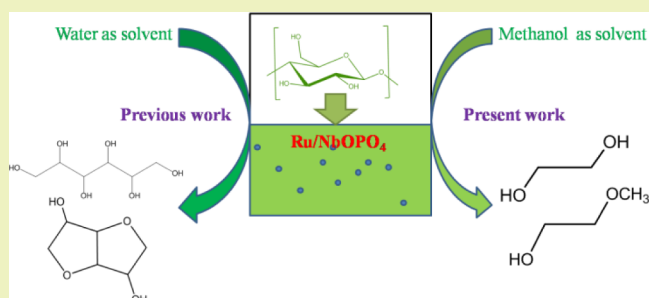
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S Supporting Information

ABSTRACT: The efficient usage of lignocellulosic biomass is of great significance for large-scale low-cost biomass conversion to biofuels and other useful chemicals. Here, an interesting catalytic process was reported related to converting cellulose into ethylene glycol (EG) and ethylene glycol monoether (EGME) in methanol over a Ru/NbOPO₄ catalyst, with the cleavage of a C–C bond by NbOPO₄ and further hydrogenation by supported Ru particles. The influence of reaction temperature, hydrogen pressure, and reaction time was systematically investigated and showed that a 54.5% total yield of EG and EGME could be obtained at 220 °C in 3 M Pa H₂, which was an exciting result. Meanwhile, the effect of solvent was also studied in detail. It was shown that methanol played an important role in the production of EG and EGME, especially in the cleavage of the C–C bond. Methanol could protect the C=O bond in glucose produced from cellulose through acetalization, thus prevent its hydrogenation, and led to the production of EG and EGME. Furthermore, the influence of dopants (W, Sn, Ni, Cu) was further investigated, and it was found that only the Ru–Ni/NbOPO₄ catalyst was more effective through limiting the further hydrogenolysis of products (EG and EGME) to CO and alkanes, and as high as 64% total yield of EG+EGME was achieved. Moreover, the Ru–Ni/NbOPO₄ catalyst showed good reusability, which can be reused at least four times with a little loss in EG and EGME yield.

KEYWORDS: Cellulose, Ru/NbOPO₄, Methanol, Ethylene glycol, Hydrogenation



INTRODUCTION

The production of chemicals or fuels from biomass resources has attracted much attention because of its renewable and carbon-neutral properties. In comparison with starch or corn, lignocellulosic biomass may not compete with the production of edible crops, and its valorization can provide an environmentally friendly alternative for fossil energy.^{1–3} Cellulose, as the most abundant source of biomass and generally accounting for 30–60 wt % of dried plants becomes the first and foremost choice. Many efforts have been devoted to the development of a green and efficient process for cellulose conversion, such as fermentation with enzymes to produce ethanol,⁴ thermo-pyrolysis to bio-oils and syn-gas, and hydrolysis with dilute acids or solid acids to glucose^{5–7} and 5-hydroxymethylfurfural (HMF).^{8,9} Catalytic conversion of cellulose to polyols is particularly noteworthy because of the versatile uses of polyols as chemicals directly or as precursors in the synthesis of fuels and value-added compounds.^{10–12}

As we know, conversion of cellulose to polyols and other fine chemicals in water have been intensively investigated. However, few studies were focused on its conversion in methanol-rich media. In water, conversion of cellulose to polyols involves hydrolysis of cellulose by inorganic acids to glucose and subsequent hydrogenation of glucose to sorbitol and other polyols.^{13–17} Fukuoka and Dhepe first reported the direct

conversion of cellulose to hexitols on Pt/Al₂O₃ in water without use of any mineral acids.¹⁸ In order to improve product selectivity, various bifunctional catalysts with acid and metal sites, including Ni/CNT,^{19,20} Ni₂P/C,²¹ Ru/CNTs,²² Rh–Ni/MC,²³ and Ru/Cs₃PW₁₂O₄₀,²⁴ have been designed and studied. Following the above pioneering work, a novel mesoporous bifunctional catalyst (Ru/NbOPO₄) for cellulose conversion into polyols (mainly sorbitol or isosorbide) in aqueous solution was developed, and good results were obtained in our group.^{25,26} In addition, transition metal carbide catalysts, Ni–W₂C/activated carbon, Ni–W/SBA-15, Ni–WxC/CMK-3, Raney Ni with tungstic acid, and a CuCr catalyst were reported to be active for the production of diols from cellulose.^{27–31} The above systems were all carried out in aqueous media, and ethylene glycol or 1,2-PG was obtained at 6 M Pa above 240 °C. Recently, several groups reported that the cellulose could be converted into alkyl-glycoside with heteropoly acid and Al₅ as catalysts in methanol, and a high product yield could be obtained.^{32,33} It is known that the obtained glucose from cellulose has a tendency to polymerize in acidic aqueous media. Nevertheless, polymerization is undesirable because it dimin-

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ishes the utilization efficiency of xylose and may lead to catalyst deactivation.³⁴ Li et al. showed that methanol can suppress the formation of sugar oligomers and a polymerization reaction compared with the aqueous medium.³⁵ Therefore, methanol as reaction medium for biomass conversion has attracted more and more attention. However, the conversion of cellulose on a bifunctional solid catalyst including cleavage of a C–C bond and further hydrogenation in methanol remain unreported.

Our previous work demonstrated that the Ru/NbOPO₄ catalyst showed high performance for cellulose into sorbitol and isosorbide in the aqueous medium.^{25,26} Nowadays, many chemicals are dependent on petroleum-derived ethylene as a precursor, so ethylene glycol (EG) and its monoether derivative (EGME) are important commodity chemicals due to their extensive application.³⁶ In this paper, a novel route to effectively convert cellulose into EG and EGME in methanol with Ru/NbOPO₄ was reported. Besides that, the effects of reaction temperature, hydrogen pressure, and reaction time on cellulose conversion into EG and EGME in methanol were further investigated. The influence of the addition of a transition metal (W, Sn, Ni, Cu) on the activity of a Ru/NbOPO₄ catalyst for selective production of EG and EGME from cellulose in methanol was also explored. Meanwhile, a series of experiments including the conversion of a methyl glucoside intermediate were designed and conducted in order to clarify the role of methanol and the possible reaction pathway in this process.

EXPERIMENTAL SECTION

Materials. Chemicals including D-glucose (99.5%), D-fructose (99+%), methyl glucosides (95%), cellobiose (99%), 1,2-propanediol (99.5+%), ethylene glycol (99.8+%), 5%Ru/C and RuCl₃·3H₂O (37%) were purchased from Aladdin. Ethanol (99.5%), methanol (99.8%), butanol (99.8%), cyclohexane (99.8%), ethylene glycol monomethyl ether (99.8%), Ni(NO₃)₂ (99.5%), Cu(NO₃)₂ (99.5%) and SnCl₄·4H₂O (99.5%) were provided from Sinopharm Chemical Reagent Co., Ltd. Commercially microcrystalline cellulose powder (PH-101) was provided by Fluka. Sorbitol was purchased from Shanghai Linfeng Chemical Reagent Co., Ltd. H-Beta zeolite was purchased from Nankai University Catalyst Co., Ltd., and γ-Al₂O₃ was provided by BASF Chemical Company. All other chemicals were of analytical grade and were used directly without further purification. The NbOPO₄ catalysts were prepared according to our previous methods.³⁷

Preparation of Catalysts. Nb precursor (Nb-tartrate) was prepared according to the literature.³⁸ Preparation of solid acid support (mesoporous NbOPO₄) was as follows: 1.32 g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 mL water, and the initial pH was adjusted to 2 by using phosphoric acid. With continuous stirring, 20 mL of 0.5 M niobium tartrate (pH 2) was added to the above solution. Then, the mixed solution was dropped into the aqueous solution of cetyltrimethylammonium bromide (CTAB), which was previously prepared by dissolving 1.0 g of CTAB in 13 mL of distilled water. Furthermore, the mixture was stirred for an additional 60 min at 35 °C, and then the transparent solution was aged in a Teflon-lined autoclave for 24 h at 160 °C. After aging, it was cooled, and the obtained solid was filtered, washed with distilled water, and then dried at 50 °C. Finally, the NbOPO₄-pH2 sample was obtained by calcination at 500 °C for 5 h in air to remove the template.

Preparation of Ru/NbOPO₄-pH2 Catalyst. The Ru/NbOPO₄-pH2 catalyst was prepared by the incipient wetness impregnation method. First, the water adsorption of NbOPO₄-pH2 was measured. On the basis of that, the Ru/NbOPO₄-pH2 catalyst was prepared by impregnating the supports with a calculated amount of aqueous solution of 37 wt % RuCl₃·3H₂O (5 wt % Ru/NbOPO₄). After being

dried in air overnight, the obtained sample was directly reduced *ex situ* in a fixed bed flow reactor with pure hydrogen (30 mL/min) at 400 °C for 2 h. Other Ru-based (RuNi, RuCu, RuSn, and RuW) bimetallic catalysts were also prepared by the same method, and the characteristic data is shown in Figure S3 and Table S1 of the Supporting Information, respectively.

Characterization of Catalysts. X-ray diffraction patterns (XRD) were recorded on a Rigaku D/max-2550VB/PC diffractometer by using Cu Kα (λ = 0.15406 nm) radiation. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai F20 s-TWIN instrument, and the electron beam accelerating voltage was 200 kV.

Procedure for Cellulose Conversion and Product Analysis. The ball-milled cellulose samples were obtained using a laboratory ball mill (QM-3SP04). To get the desired sample, about 2 g of microcrystalline cellulose was charged into the grinding cell, and the ball milling was operated at a frequency of 50 Hz with 6 mm agate balls for 10 h. The change of structure of cellulose after ball milling is shown in Figure S1 of the Supporting Information. The conversion of cellulose was performed with a batch-type high-pressure autoclave reactor.

In a typical run, 0.48 g of ball-milled cellulose, 0.15 g of reduced Ru/NbOPO₄, and 16 g of methanol were introduced into the autoclave. Afterward, the reactor was purged with H₂ (>99.99%, Shanghai Pujiang) three times, pressurized with H₂ to 3.0 MPa, and then heated to 220 °C. After the reaction, the reactor was cooled quickly, and the liquid solution was separated from the solid catalyst by centrifugation.

Products were identified on an Agilent 7890 GC-MS with a HP-5 column. Moreover, the reactant and main liquid products were analyzed by gas chromatography (PerkinElmer Clarus 500 GC) with a capillary column SE-54 (50 m × 0.25 mm). The macromolecular species in liquid products were also analyzed by HPLC (Agilent, 1200 series) equipped with a Shodex SUGAR SC1011 column (8 mm × 300 mm) with a refractive index detector (Agilent G1362A) by using high pure water as a mobile phase at a flow rate of 0.8 mL/min at 50 °C. An autosampler (Agilent G1329A) was used to enhance the repeatability of analysis. The yield of products was measured by an internal standard method using benzyl alcohol as the internal standard in GC. The residual solid was washed with ethanol several times followed by drying at vacuum for calculating the cellulose conversion. It was considered that the weight of the catalyst before and after the reaction was unchanged. Then, the conversion of cellulose was determined based on the weight difference of the solid before and after the reaction. The yield of EG and EGME was calculated as

$$Y(\text{EG or EGME})/\% = \frac{\text{moles of EG or EGME}}{(\text{moles of anhydroglucose in cellulose}) \times 3} \times 100\%$$

$$Y(1,2\text{-PG})/\% = \frac{\text{moles of 1,2-PG}}{(\text{moles of anhydroglucose in cellulose}) \times 2} \times 100\%$$

RESULTS AND DISCUSSION

Catalytic Conversion of Cellulose over Various Catalysts in Methanol. According to previous work, cellulose was mainly converted into HMF and levulinic acid (LA) with a solid acid as the catalyst in an aqueous solution.³⁹ However, we were surprised to note that cellulose was converted via another route over a NbOPO₄ catalyst in methanol. Here, cellulose was selectively cracked into the short-chain methyl ether containing 1,1,2-trimethoxyethane, and the possible reaction process is presented in Figure S2 of the Supporting Information. Considering 1,1,2-trimethoxyethane could be converted to other more valuable chemicals, such as EG and EGME by further hydrogenolysis, the hydrogenation catalyst, such as Ru/

Table 1. Catalytic Conversion of Cellulose over NbOPO₄-Based Catalysts in Methanol^a

entry	catalysts	cellulose conversion (%)	yield (%)			
			EG	EGME	1,2-PG	EG+EGME
1	NbOPO ₄ -pH2	74.5	trace	trace	trace	trace
2	1+Ru/C ^b	—	19.4	10.6	1.2	30.0
3	5%Ru/C+NbOPO ₄ -pH2 ^c	92.7	18.6	5.8	2.9	24.4
4	Ru/NbOPO ₄ -pH2	99.5	25.9	28.6	2.5	54.5
5	Pt/NbOPO ₄ -pH2	89.8	20.2	12.8	2.1	33.0
6	Pd/NbOPO ₄ -pH2	95.1	22.3	12.1	1.8	34.4
7	Ni/NbOPO ₄ -pH2	65.5	4.6	2.7	0.9	7.3
8	Cu/NbOPO ₄ -pH2	80.1	5.1	4.2	1.4	9.3

^aReaction conditions: cellulose (0.48 g), catalyst (0.15 g), and methanol (16 g) were put in an 100 mL autoclave and stirred at 220 °C and 3 MPa H₂ for 20 h. ^bThe Ru/C catalyst was put into reaction liquid of entry 1; the yield of products were determined by an internal standard method. ^c5%Ru/C+NbOPO₄-pH2 was mixed mechanically.

Table 2. Catalytic Conversion of Cellulose over Various Ru Catalysts in Methanol^a

entry	catalysts	cellulose conversion (%)	yield (%)			
			EG	EGME	1,2-PG	EG+EGME
1	1%Ru/NbOPO ₄ -pH2	91.9	7.4	14.1	1.9	21.5
2	2%Ru/NbOPO ₄ -pH2	93.2	21.3	9.8	2.4	31.1
3	3%Ru/NbOPO ₄ -pH2	95.9	25.9	28.6	2.5	54.5
4	4%Ru/NbOPO ₄ -pH2	97.4	21.2	22.8	1.8	44.0
5 ^b	3%Ru/NbOPO ₄ -pH2	94.7	26.0	19.2	2.1	45.2
6 ^c	3%Ru/NbOPO ₄ -pH2	100.0	22.4	30.7	2.6	53.1
7 ^d	3%Ru/Al ₂ O ₃	69.6	2.5	7.7	5.4	10.2
8 ^e	3%Ru/H-Beta	68.7	2.3	10.6	4.9	12.9
9 ^f	5%Ru/C	33.9	—	—	—	—

^aTypical reaction conditions: cellulose (0.48 g), catalyst (0.15 g), and methanol (16 g) were put in an 100 mL autoclave and stirred at 220 °C and 3 MPa H₂ for 20 h. ^bThe dose of catalyst was halved. ^cThe dose of catalyst was doubled. ^dSorbitol, oligosaccharide, and methyl glucoside were the main products. ^eMethyl glucoside was the main product. ^fSorbitol was main the product.

C, was put into the reaction system. It is shown in Table 1 that the reaction solution (entry 1) mainly containing 1,1,2-trimethoxyethane was converted to a certain amount of ethylene glycol (EG) and its monoether derivative (EGME) (entry 2, about 30%) when Ru/C catalyst was added. It should be noted that cellulose could be directly converted into EG and EGME in methanol in the presence of Ru/C and NbOPO₄ (entry 3).

On the basis of the above results, a series of NbOPO₄-based bifunctional catalysts (Table 1, entries 4–8) were prepared to test their performance for cellulose conversion into EG and EGME in methanol. It is shown in Table 1 that the Ru/NbOPO₄ catalyst showed the best performance, in which cellulose was completely converted after 20 h, and a 54.5% total yield of EG and EGME was obtained (entry 4). In comparison, the conversion of cellulose could be up to 90% over Pt/NbOPO₄-pH2 or Pd/NbOPO₄-pH2 (entries 5 and 6), but the total yield of EG and EGME over these catalysts was only 20%, which was much lower than that over Ru/NbOPO₄. In addition, as for NbOPO₄-supported non-noble metal catalysts (entries 7 and 8), they showed very low yield for EG and EGME. Among all the cases in Table 1, 1,2-PG was also produced but the amount of 1,2-PG was very low.

In order to determine the optimum loading amount of Ru in the catalysts, a series of Ru/NbOPO₄ catalysts with different loadings of Ru were prepared and tested for cellulose conversion into EG and EGME in methanol (Table 2, entries 1–4). As shown in Table 2, the total yield of EG and EGME increased notably when the amount of Ru increased from 1 to 3 wt %, but the yield dropped from 54.5% to 44.0% after a further

increase to 4 wt %. From the view of economy and efficiency, the 3%Ru/NbOPO₄ catalyst was chosen. The effect of catalyst dosage including 0.075, 0.15, and 0.3 g on cellulose conversion into EG and EGME in methanol was also investigated (Table 2, entries 3, 5, and 6). With 0.075 g of Ru/NbOPO₄, the conversion of cellulose and total yield of EG and EGME were 94.7% and 45.2%, respectively. When the catalyst dosage was increased to 0.15 g, both cellulose conversion and total yield of EG and EGME increased and then remained constant even when the amount of catalyst was increased to 0.3 g. Therefore, 0.15 g of catalyst dosage was considered the optimum dose.

Moreover, in order to investigate the function of NbOPO₄ support on product distribution, the catalytic performances of Ru/Al₂O₃, Ru/H-Beta, and Ru/C were tested, and the results were summarized in Table 2 (entries 7–9). It is shown that they all showed low cellulose conversion and poor selectivity to EG and EGME, with the main product of methyl glucoside (M- α -G) produced by cellulose alcoholysis. This means that these three catalysts were unable to further cleave methyl glucoside to short-chain methyl ether. The above results indicated that the acidity of support was also important for cellulose conversion to EG and EGME, and the Ru/NbOPO₄ showed superior performance to other catalysts.

As mentioned above, solvent played an important role in cellulose conversion over 3%Ru/NbOPO₄. In aqueous solution, sorbitol was obtained,²⁵ while in methanol, EG and EGME were obtained. In order to understand the function of the solvent molecules in cellulose conversion, a series of cellulose conversion experiments were conducted in a variety of solvents. It is shown in Table 3 that EG and its monoether were the

Table 3. Effect of Solvent on Products Distribution from Cellulose Conversion^a

entry	solvent	main product distribution
1	methanol	ethylene glycol; ethylene glycol monomethyl ether
2	ethanol	ethylene glycol; ethylene glycol monoethyl ether
3	butanol	ethylene glycol; ethylene glycol monobutyl ether
4	water	isosorbide; 1,2-hexanediol; 1,6-hexanediol
5	methanol:water = 1:1	isosorbide; 1,6-hexanediol
6	methanol:water = 2:8	isosorbide; 1,6-hexanediol
7	methanol:water = 8:2	isosorbide; 1,6-hexanediol

^aReaction conditions: cellulose (0.48 g), solvent (16 g), 3%Ru/NbOPO₄ (0.15 g), 220 °C, and 3 M Pa H₂ for 10 h.

main products when primary alcohols (methanol, ethanol, and butanol) were used as the solvent. While using water as the solvent or cosolvent (entries 4 or 8), different product distributions were observed, and the polyols containing six carbons were the main products in water. Therefore, solvent was considered to be one of the key factors for cellulose conversion into EG and EGME, and the addition of water would restrain the formation of EG and EGME completely (entries 5–7). It was suggested that methanol likely protects the carbonyl group of glucose through acetalization and thus prevents its hydrogenation into sorbitol (see below).

Investigation of Reaction Conditions and Reaction Route of Cellulose to EG and EGME. Cellulose hydrogenolysis to EG and EGME in methanol was also dependent on the reaction parameters, for example, reaction temperature, reaction time, and hydrogen pressure. The effects of reaction temperature on the activity and product selectivity in cellulose conversion into EG and EGME were examined on the 3%Ru/NbOPO₄ catalyst in 3 M Pa H₂ and are shown in Figure S4(A) of the Supporting Information. With an increase in reaction temperature, the conversion of cellulose increased, and the maximum conversion of cellulose (100%) could be obtained at or above 220 °C, which was related to the large acid amounts of NbOPO₄ support and high temperature.²⁵ Below 210 °C, the total yield of EG and EGME increased successively with an increase in temperature, while further increasing the reaction temperature to 220 °C led to a large decrease in EG yield. However, the EGME yield continued to increase. Likely, the EG obtained further reacts with methanol to produce EGME. The total yield of EG and EGME increased with increasing temperature until 220 °C, while the 1,2-PG yield almost kept constant in the testing temperature range. Therefore, 220 °C was selected as the optimal reaction temperature. Similarly, the effect of reaction pressure in the range of 1–6 M Pa was investigated at 220 °C as shown in Figure S4(B) of the Supporting Information. It is shown that the EG and EGME yield increased with an increase in H₂ pressure below 3 M Pa. When further increasing the H₂ pressure, the EG yield kept increasing, while the EGME yield decreased. This was attributed to the further hydrogenolysis of EGME to EG. However, the total yield of EG and EGME increased with increasing H₂ pressure until 3 M Pa, and the 1,2-PG yield was almost kept constant. So, the optimum hydrogen pressure was set to 3 M Pa and used in further studies.

The possible reaction pathway of cellulose to EG and EGME was investigated by the following experiments at different reaction times. The time curve of the conversion of cellulose on

3%Ru/NbOPO₄ is shown in Figure S4(C) of the Supporting Information. According to the results in Figure S4(C) of the Supporting Information, EG, EGME, and methyl glucoside (M- α -G) were the main products in the reaction effluent. It is shown that the yield of M- α -G decreased with increasing reaction time, while that of EG and EGME both increased within 10 h. The total yield of EG and EGME also increased within 18 h, which indicated that M- α -G was gradually converted into EG and EGME during the reaction. As expected, further extending the reaction time would lead to the conversion of EG and EGME to other byproducts. Therefore, M- α -G was an important intermediate in this reaction system. In addition, the conversion of M- α -G in methanol was also investigated, and the results are shown in Figure S4(D) of the Supporting Information. It is shown in Figure S4(D) of the Supporting Information that the conversion of M- α -G presented a trend similar to that of cellulose, and the main products were also EG and EGME. The conversion of M- α -G could reach 100% in just 6 h, and the maximum yield (74%) of EG and EGME was obtained. The average reaction rates of cellulose and M- α -G conversion were calculated according to Figure S4(C) and (D) of the Supporting Information, which are 0.012 and 0.042 g/h, respectively. This confirmed further that M- α -G was a main intermediate, and the formation of M- α -G from cellulose was the rate-determining step during the process of cellulose to EG and EGME in methanol. The slow conversion of cellulose to M- α -G would be attributed to the solid–solid contact of acid and cellulose; however, the high solubility of M- α -G in methanol could accelerate its conversion.

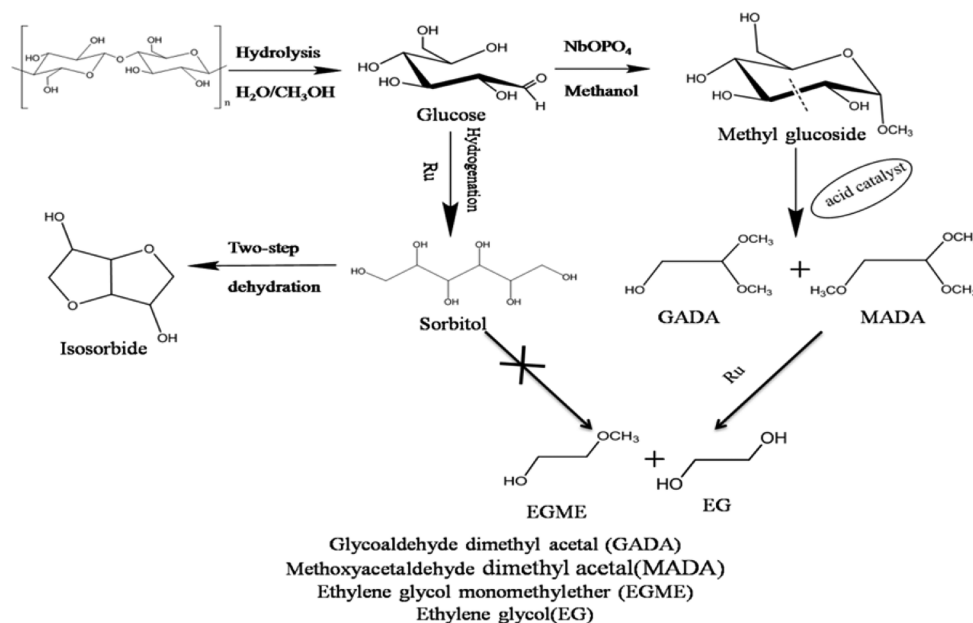
In order to further understand the reaction route of cellulose to EG and EGME, the other possible intermediates in this reaction such as cellobiose, glucose, fructose, and sorbitol were performed on 3%Ru/NbOPO₄ under optimal conditions (at 220 °C and 3 MPa). As shown in Table 4, sorbitol was found to

Table 4. Conversion and Yield in Reactions of Different Possible Intermediates on 3%Ru/NbOPO₄^a

entry	substrates	yield (%)				
		EG	EGME	1,2-PG	EG+EGME	isosorbide
1	cellobiose	30.4	28.1	3.2	58.5	–
2	glucose	36.9	27.6	4.7	64.5	–
3	fructose	15.6	1.3	18.6	16.9	–
4	sorbitol	–	–	–	–	26.8
5	M- α -G	38.7	35.3	1.9	74.0	–

^aReaction conditions: sugar and sorbitol (0.5 g), methanol (16 g), 3% Ru/NbOPO₄ (0.15 g), 220 °C, 6 h, and 3 MPa H₂.

be inactive without the production of EG and EGME (entry 1), while glucose and cellobiose were both readily converted into EG and EGME in 6 h with 64.5% and 58.5% yield of EG and EGME, respectively. In the case of fructose, a small number of EG and EGME (only 16.9%) was obtained, but 1,2-PG was formed dominantly. Combined with the results of M- α -G, it was indicated that M- α -G was a possible intermediate and showed the best yield of EG and EGME. Therefore, on the basis of all of the above results, a possible reaction route was proposed and drawn in Scheme 1. First, cellulose was converted into glucose and then transformed to M- α -G in methanol, which was an important step and also a rate-determining step. Once the glucose obtained was hydrogenated into sorbitol, the main product was isosorbide rather than EG and EGME (Table

Scheme 1. Possible Reaction Mechanism of Cellulose into EG and EGME in Methanol over 3%Ru/NbOPO₄Table 5. Effect of Transition Metal Dopants (W, Sn, Ni, Cu) on Cellulose Conversion and Product Yield over 3%Ru/NbOPO₄^a

entry	catalysts	cellulose conversion (%)	yield (%)			
			EG	EGME	1,2-PG	EG+EGME
1	3%Ru/NbOPO ₄	96.1	25.9	28.6	2.5	54.5
2	3%Ru-0.9%W/NbOPO ₄	92.5	20.1	22.8	2.8	42.9
3	3%Ru-0.9%Sn/NbOPO ₄	90.2	12.7	24.9	2.1	37.6
4	3%Ru-0.9%Ni/NbOPO ₄	89.6	19.9	39.6	1.8	59.5
5	3%Ru-0.9%Cu/NbOPO ₄	88.7	10.3	25.1	1.4	35.4

^aReaction conditions: cellulose (0.48 g), catalyst (0.15 g), and methanol (16 g) were put in an 100 mL autoclave and stirred at 220 °C and 3 MPa H₂ for 20 h.

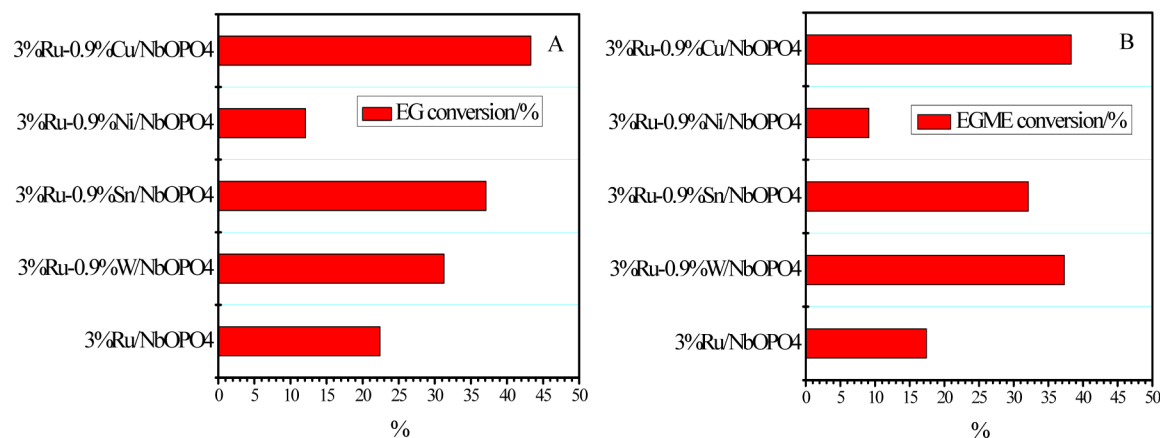


Figure 1. Conversion of EG (A) and EGME (B) in methanol over NbOPO₄-based bifunctional catalysts. Reaction conditions: EG or EGME (0.1 mol), methanol (20 mL), catalysts (0.3 g), 3 MPa H₂, 220 °C, and 3 h.

4, entry 4). Next, *M*- α -G was converted into 1,1,2-trimethoxyethane on a NbOPO₄ solid acid catalyst through the cleavage of a C–C bond (retro-aldol condensation, Table 1, entry 1). Finally, EG and EGME were produced through catalytic hydrogenolysis of 1,1,2-trimethoxyethane over Ru species, which should occur quickly due to only a trace amount of 1,1,2-trimethoxyethane detected throughout the entire process. It was also proved that methanol could protect the carbonyl

group by reacting into *M*- α -G through acetalization, thereby preventing its direct hydrogenation into sorbitol.

Effect of Transition Metal Dopants (W, Sn, Ni, Cu) on Catalytic Performance. It is known from the results described above that the Ru/NbOPO₄ catalyst showed high activity for cellulose conversion into EG and EGME (54.5%) in a methanol solvent. Compared with monometallic catalysts, bimetallic catalysts frequently exhibited superior activity and selectivity.⁴⁰ In order to improve the selectivity of the product

Table 6. Effect of Ru/Ni Ratio on Cellulose Conversion and Product Yield^a

entry	catalysts	cellulose conversion (%)	yield (%)			
			EG	EGME	1,2-PG	EG+EGME
1	3%Ru-0.9%Ni/NbOPO ₄ -pH2	89.6	19.9	39.6	1.8	59.5
2	3%Ru-1.8%Ni/NbOPO ₄ -pH2	98.8	29.6	35.5	1.9	64.1
3	3%Ru-3.6%Ni/NbOPO ₄ -pH2	96.4	23.5	32.3	2.1	55.8
4	3%Ru/NbOPO ₄ -pH2	96.1	25.9	27.6	2.6	54.1

^aReaction conditions: cellulose (0.48 g), catalyst (0.15 g), and methanol (16 g) were put in an 100 mL autoclave and stirred at 220 °C and 3 MPa H₂ for 20 h.

(EG and EGME), W-, Sn-, Ni-, and Cu-modified Ru/NbOPO₄ bimetallic catalysts were prepared by an impregnation method. As shown in Table 5, all catalysts were examined in cellulose conversion using methanol as the solvent and showed a lower cellulose conversion than that of Ru/NbOPO₄. This probably resulted from the coverage of acid sites due to the doping of transition metal.²⁶ However, the selectivity to EG and EGME on these catalysts changed significantly. The selectivity of EG and EGME on a 3%Ru-0.9%Ni/NbOPO₄ catalyst was 66.4% (entry 4), which was higher than that of 3%Ru/NbOPO₄ (56.1%). However, the introduction of Sn, W, and Cu lead to decreases in selectivity to EG and EGME, which were 41.7%, 46.4%, and 40.0%, respectively.

In order to explain the higher selectivity to EG and EGME over 3%Ru-0.9%Ni/NbOPO₄, the experiments with EG and EGME as substrates were performed over 3%Ru/NbOPO₄ and 3%Ru-0.9%Ni/NbOPO₄ catalysts. As shown in Figure 1, it is shown that both EG and EGME could have been hydrogenolysed over NbOPO₄-based bifunctional catalysts in different degrees. The conversion of EG and EGME reached 22.4% and 17.4%, respectively, in 3 h over the 3%Ru/NbOPO₄ catalyst. It was evidenced that the products obtained were mainly CO and C₂H₆ (Figure S5, Supporting Information), and substrate (EG or EGME) was just detected in the liquid phase. The above evidence also indicated that the products (EG and EGME) from cellulose obtained in methanol would be further converted over 3%Ru/NbOPO₄, thus lowering the selectivity of EG and EGME to some extent. When 0.9% Ni was doped into the 3%Ru/NbOPO₄ catalyst, the conversion of EG and EGME dropped to 12.1% and 9.1%, respectively, which indicated that the doping of Ni can prevent the further hydrogenolysis of EG and EGME. This was also in line with the results in Table 5 (entry 4). Similarly, when Sn, W, and Cu were introduced into 3%Ru/NbOPO₄, the conversion of EG and EGME in methanol was higher, and the selectivity of EG and EGME was lower than that over 3%Ru/NbOPO₄, as shown in Table 5 (entries 2, 3 and 5). The results provided clear clues that the doping of transition metals (W, Sn, Ni, Cu) modifies the selectivity to EG and EGME by affecting the further hydrogenolysis of EG and EGME. That is to say, the doping of Ni likely enhanced the selectivity to EG and EGME through preventing further hydrogenolysis of EG and EGME, while the introduction of W, Sn, and Cu all would boost further conversion of EG and EGME to byproducts. Therefore, 3%Ru-0.9%Ni/NbOPO₄ showed better performance for cellulose conversion into EG and EGME than other NbOPO₄-based catalysts.

In order to further probe the effect of Ni on the 3%Ru/NbOPO₄ catalyst for cellulose conversion into EG and EGME, different weight ratios of Ru and Ni were employed for the Ru-Ni/NbOPO₄ catalysts and were investigated for the catalytic conversion of cellulose in methanol. As shown in Table 5, when 0.9% Ni was doped into 3%Ru/NbOPO₄,

cellulose conversion was just 89.6%, and the total yield of EG and EGME was 59.5%. When the amount of Ni increased from 0.9% to 1.8%, cellulose conversion and total yield of EG and EGME both increased to 98.8% and 64.1%, respectively. Further increasing the Ni weight to 3.6% led to a remarkable decline of EG and EGME total yield (Table 6), while cellulose conversion almost remained constant. Therefore, the introduction of 1.8% Ni into Ru/NbOPO₄, that is, the 3%Ru-1.8% Ni/NbOPO₄ catalyst, showed the best performance for cellulose conversion into EG and EGME in methanol.

Stability of 3%Ru-1.8%Ni/NbOPO₄-pH2 for Cellulose Conversion to EG and EGME. Long-term stability of the heterogeneous catalyst is very important in catalytic reactions. Thus, the stability of the catalyst (3%Ru-1.8%Ni/NbOPO₄-pH2) for cellulose conversion into EG and EGME in methanol was tested for several runs. The recovered catalyst was treated by washing and drying before reuse. Figure 2 shows that the

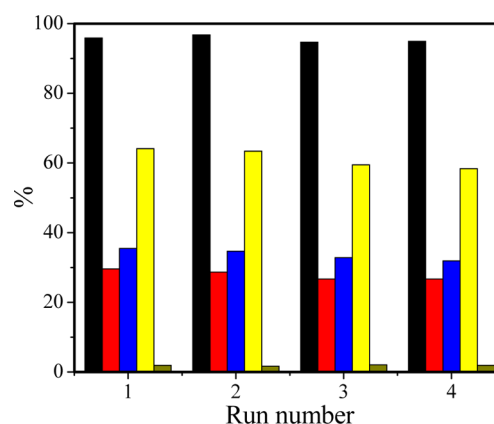


Figure 2. Recycling test of 3%Ru-1.8%Ni/NbOPO₄-pH2 catalyst on cellulose conversion in methanol. Typical reaction conditions: cellulose (0.48 g), 3%Ru-1.8%Ni/NbOPO₄ (0.15 g), and methanol (16 g) were put in an 100 mL autoclave and stirred at 220 °C and 3 MPa H₂ for 20 h. Cellulose conversion (black), EG yield (red), EGME yield (blue), EG+EGME total yield (yellow), and 1,2-PG yield (dark yellow).

reusability of the catalyst is good because the high cellulose conversion was maintained, although the total yield of EG and EGME was slightly decreased from 64.1% to 58.3% after four runs. Inductively coupled plasma spectrometer (ICP) analysis of reaction effluents showed that the leaching of either ruthenium or nickel is negligible (Ru, 0.05%; Ni, 0.02%). The slight decrease in EG and EGME yield may be due to the leaching of P species.³⁷ TEM images in Figure S6 of the Supporting Information shows that the growth or aggregation of the active metal was not observed for the used catalyst compared with the fresh one. The above evidence indicates that

the 3%Ru-1.8%Ni/NbOPO₄-pH2 presents good stability for cellulose conversion into EG and EGME in methanol.

In summary, an interesting catalytic process to convert cellulose into ethylene glycol (EG) and ethylene glycol monoether (EGME) in methanol with Ru/NbOPO₄ as the catalyst was reported, with the cleavage of a C–C bond by NbOPO₄ and further hydrogenation by Ru particles. A 54.5% total yield of EG and EGME could be obtained at 220 °C in 3 M Pa hydrogen pressure, which was an exciting result. It was found that solvent played an important role in the production of EG and EGME, especially in the cleavage of the C–C bond. Methanol could protect the C=O bond in glucose produced from cellulose and produced methyl glucoside rapidly by acetalization, thus preventing its hydrogenation to sorbitol. According to a series of experiment results, the possible reaction route in methanol solvent was provided, which was different from that in water reported by Liu et al.⁴¹ The influence of the transition metal dopants (M = W, Sn, Ni, Cu) on catalytic conversion of cellulose and yield of EG and EGME in methanol were also investigated, and it was found that the Ru–Ni/NbOPO₄ catalyst showed the best performance. The total yield of EG and EGME reached 64%. It was attributed that the Ru–Ni/NbOPO₄ catalyst is likely more effective to prohibit the further conversion of products (EG and EGME) than other catalysts. Moreover, the Ru–Ni/NbOPO₄ catalyst showed good reusability, and it could be reused at least four times with little loss in the EG and EGME yield.

■ ASSOCIATED CONTENT

Supporting Information

Material as mentioned in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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