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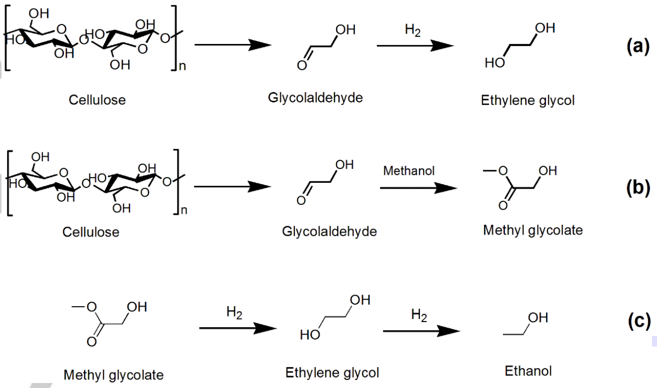
Chemocatalytic Conversion of Cellulosic Biomass to Methyl Glycolate, Ethylene Glycol and Ethanol

Gang Xu,[a,b] Aiqin Wang,*[a] Jifeng Pang,[a] Xiaochen Zhao,[a] Jinming Xu,[a] Nian Lei,[a] Jia Wang,[a] Mingyuan Zheng,[a] Jianzhong Yin[b] and Tao Zhang*[a]

Dedication ((optional))

Abstract: Production of chemicals and fuels from renewable cellulosic biomass is important to construction of a sustainable society, and it critically relies on the development of new and efficient transformation route starting from cellulose. Here we report a chemocatalytic conversion route from cellulosic biomass to methyl glycolate (MG), ethylene glycol (EG) and ethanol (EtOH). Under the catalysis of tungsten-based catalyst, cellulose is converted into MG with a yield as high as 57.7 C% in one-pot reaction in methanol at 240 °C and 1 MPa oxygen, and the obtained MG can be easily separated by distillation and then nearly quantitatively converted to EG at 200 °C and to EtOH at 280 °C with a selectivity of 50% through hydrogenation over Cu/SiO_2 catalyst. By this approach, fine chemical MG, bulk chemical EG, and fuel additive EtOH can all be efficiently produced from renewable cellulosic materials, thus providing a new avenue to mitigating the dependence on fossil resources.

The high demand for energy and the increasing concerns over global climate change have motivated great interest in utilization of lignocellulosic biomass, a renewable, abundant and nonedible carbon source, as an alternative to fossil resources for production of fuels and chemicals.[1] The recalcitrance of cellulose, however, presents great challenges in oriented depolymerization under mild and environmentally benign conditions. Traditional mineral acid-catalyzed hydrolysis of cellulose suffers from serious environmental issues while the emerging enzymatic hydrolysis is still a costly and low-efficiency method.[2] Chemocatalytic approach, on the other hand, offers new opportunities in one-pot conversion of cellulose to chemicals, especially when a multi-functional catalyst is used to promote a series of cascade reactions towards the target product meanwhile minimizing side reactions arising from unstable intermediates.[3-9] Previously, we reported the one-pot conversion of cellulose to ethylene glycol (EG) in water with Ni-W_2C/AC catalyst.[10] In spite of a high yield of EG obtained, the employment of water media not only adds more cost to the separation and purification of the polyols due to the formation of azeotropic mixtures, but also presents greater challenges to the hydrothermal stability of the catalysts. The latter concern necessitates the employment of more durable yet expensive noble metal catalysts to replace nickel.[11a] Considering that glycolaldehyde is a key intermediate in the EG formation from cellulose (Scheme 1a),[11] and it is highly reactive towards alcohols to form esters,[12] we envisage that by coupling the two reactions in one pot, i.e., cellulose conversion to glycolaldehyde and esterification of glycolaldehyde with methanol, methyl glycolate (MG) would be produced directly from cellulose (Scheme 1b).



Scheme 1. Chemocatalytic conversion of cellulose via intermediate glycolaldehyde. (a) One-pot conversion of cellulose to ethylene glycol; (b) one-pot conversion of cellulose to methyl glycolate; (c) Methyl glycolate conversion to ethylene glycol and ethanol via hydrogenation.

MG is not only an important intermediate widely used in synthesis of biodegradable polymers;[12a] more importantly, it can be regarded as a platform molecule for production of EG and ethanol (EtOH),[13] as shown in Scheme 1c. Currently, the production of MG relies exclusively on fossil resources and involves multi-step reactions and complicated separation processes. We conceive that once MG can be produced from renewable lignocellulose, a new chemocatalytic, nonenzymatic route for the production of cellulosic EtOH will be available, that is highly desirable and even competitive to the current high-cost enzyme-catalyzed cellulosic EtOH. The key to this route is the one-pot conversion of cellulose to MG in methanol.

Depolymerization of cellulose in methanol has been reported to proceed smoothly in methanol, producing methyl glucoside, methyl levulinate, as well as methyl lactate, and the predominance of one specific ester was strongly dependent on the catalyst as well as the reaction temperature.[14] Generally, glucoside and levulinate are formed at relatively milder reaction conditions with the promotion of Brønsted acid catalysts,[14a,b] while the lactate requires a higher reaction temperature due to the involvement of C-C bond cleavage and it is usually catalyzed

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by Lewis acid such as Sn-substituted zeolites, mixed Bronsted/Lewis acid such as Sn-triflate catalyst, or basic catalysts.[14c-e] In comparison with these three esters, MG has never been reported to yield in an appreciable amount from cellulose although glycolic acid was reported to produce from cellulose or bio-oil.[15] We suppose that the challenge for the selective transformation of cellulose to MG lies in the kinetic manipulation, which should enable the selective C-C cleavage of cellulose-derived sugars and the subsequent conversion of glycolaldehyde to proceed in such a manner that their reaction rates match well with each other; otherwise, side reactions will rapidly occur due to extremely unstable glycolaldehyde. In our earlier studies, we found that W-containing compounds were a type of highly active and selective catalyst for the C-C cleavage of cellulose to produce glycolaldehyde,[11] and that a higher activation energy required for the C-C cleavage (140-150 kJ/mol) allowed the reaction to proceed more selectively at elevated temperatures (above 200 °C).[16] The knowledge established on the cellulose conversion to EG leads us to believe that the same catalysts would be effective for the selective formation of MG directly from cellulose as long as the solvent is changed from water to methanol.

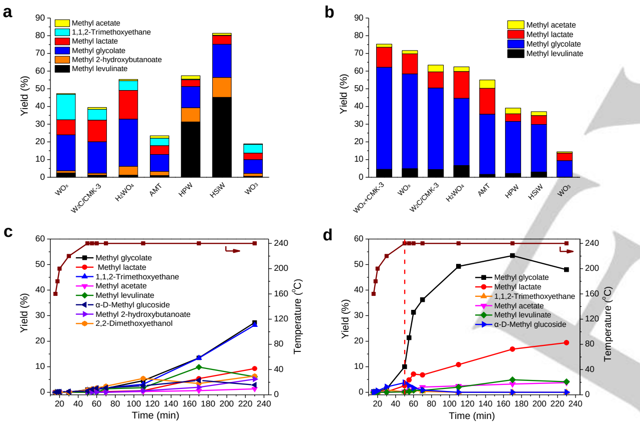

Figure 1. Catalytic performances of various W-based catalysts (a, b) and the evolution of products with the reaction time (c, d) under N_2 (a, c) and O_2 (b, d) atmosphere. Reaction conditions in N_2: 0.5 g cellulose, 4×10^{-4} mol W, 50 mL methanol, 260 °C, 2 h, 800 r/min, 2 MPa N_2. Reaction conditions in O_2: 0.5 g cellulose, 4×10^{-4} mol W, 50 mL methanol, 240 °C, 2 h, 800 r/min, 1 MPa O_2. AMT, HPW and HSiW are abbreviations of ammonium metatungstate, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, respectively. The yield in Y axis is based on carbon (C%)

Our practice began with the reaction of cellulose in methanol in N_2 atmosphere with various tungstic compounds as the catalysts. However, the MG yield was not satisfactory (< 30 C%) although the catalysts and reaction conditions were optimized (Fig. 1a, and Figs. S1-S3). Meanwhile, the formation of an appreciable amount of 1,1,2-trimethoxyethane suggests that the MG formation reaction proceed too slowly to match with the preceding C-C cleavage reaction. Considering that oxygen could greatly accelerate the transformation of glycolaldehyde to MG even without any catalyst (Fig. S4), we consequently turn to conducting the reaction of cellulose under oxygen atmosphere. To our delight, in O_2 atmosphere all the W-containing catalysts behaved selective towards MG (Fig. 1b); the best result was obtained with a physical mixture of WO_x and CMK-3 (noted as WO_x+CMK-3 wherein CMK-3 is a mesoporous carbon material [17]) as the catalyst which afforded MG yield as high as 57.7 C%. Following the WO_x+CMK-3 catalyst, pure WO_x as well as the supported W_2C/CMK-3 also gave excellent MG yields (> 50 C%), almost doubled that in N_2. Even those heteropoly acid catalysts (HPW and HSiW), which were selective for methyl levulinate in N_2 due to their strong Brønsted acidity, evolved to become selective for MG in O_2. Of particular interest is the disappearance of 1,1,2-trimethoxyethane in elevated O_2 pressure while it was the major product in either N_2 or air atmosphere (Table S1). These results demonstrate that oxygen atmosphere play an important role in directing the reaction towards MG, either by manipulating the reaction kinetics or by changing the catalyst property or both. In addition to oxygen pressure, other operation parameters also affected the MG selectivity; slightly lower reaction temperature (e.g., 220 °C) or reduced amount of catalyst appeared to favor methyl lactate while the presence of water in methanol solvent decreased the MG selectivity by forming more methyl acetate (Figs. S5-S7).

To clarify the reaction pathway from cellulose to MG as well as the key role of O_2, we then studied the reaction kinetics over WO_x catalyst in N_2 and O_2, respectively. Comparing the products profiles with the reaction temperature and time in different atmospheres (Figs. 1c, 1d), one can clearly see the following differences: (i) (hemi)acetalization products of glycolaldehyde such as 2,2-dimethoxyethanol and1,1,2-trimethoxyethane were absent in O_2 while they were formed in significant amounts in N_2, suggesting that they could be converted into MG in O_2, and this assumption was proved by control experiments (Table S2); (ii) the reaction rate in O_2 is two orders of magnitude faster than in N_2 (7.7 mmol/mol$_W$.s in O_2 vs. 0.07 mmol/mol$_W$.s in N_2), demonstrating that oxygen accelerates the whole reaction, not merely the final oxidation step; (iii) the MG selectivity is greatly enhanced in O_2 via suppressing a variety of side reactions, particularly the formation of 1,1,2-trimethoxyethane, 2,2-dimethoxyethanol and methyl 2-hydroxybutanoate; (iv) when the reaction proceeds in N_2, the concurrent increase of 1,1,2-trimethoxyethane and MG in almost equal amounts with the temperature rise indicates the former cannot transform into the latter in the absence of O_2. Moreover, methyl glucoside was detected while glucose was not irrespective of atmosphere, indicating the former is more stable than the latter. [18] Our control experiments with glucose and methyl glycoside respectively as the substrates showed that both of them could be transformed into MG, in almost identical yields (Table S2). Taking these results together, we propose the reaction pathway from cellulose to MG shown in Scheme S1. It consists of three tandem reactions: (1) methanolysis of cellulose to glucose and glycoside, and the latter can transform to the former reversably, (2) C-C cleavage of glucose via retro-aldol condensation to produce glycolaldehyde as well as its (hemi)acetalization products 2,2-dimethoxyethanol and 1,1,2-trimethoxyethane, and (3) conversion of glycolaldehyde as well as its (hemi)acetols in O_2 to form MG. Among the three steps, the first step to form glucose is the slowest step; upon its formation, the subsequent C-C cleavage proceeds rapidly under the catalysis of WO_x

because it is kinetically favored at elevated temperatures.[16] Immediately after the C-C cleavage, the further transformation of glycolaldehyde to MG occurs rapidly with the promotion of both acidic WO_x and O_2 atmosphere.

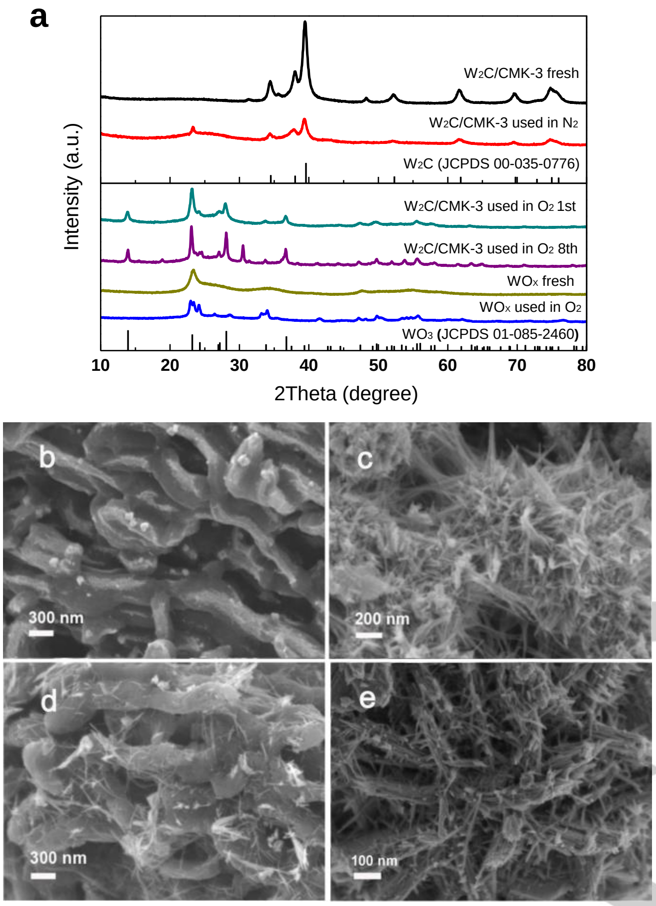

Figure 2. XRD patterns of W_2C/CMK-3 and WOx catalysts before and after the reaction in different atmosphere (a) and SEM images of the W_2C/CMK-3 (b, d) and WOx (c, e) before (b, c) and after the reaction (d, e).

The nature of the catalytically active sites was probed by characterizations of the most efficient catalysts W_2C/CMK-3 and WO_x before and after the reaction. Both XRD and electron microscopy (SEM and TEM) revealed that W_2C nanoparticles on the CMK-3 support were transformed into needle-like WO_3 phase after the reaction in O_2 (Fig.2 and Fig. S8). Concurrent with this phase transformation was a great enhancement in both activity and selectivity to MG. Akin to the WO_3 derived from W_2C, the highly active WO_x ($x = 2.8$) catalyst used here was also poorly crystallized, with a needle-like morphology and a large surface area (126 m^2/g). Both of them are quite different from the commercial WO_3 which is highly crystallized, low-surface-area (17 m^2/g), and poorly active in reaction. All these results point to the poorly crystallized, large-surface-area WO_3 and WO_x as the active phase in the reaction. They catalyze the reaction either via the low-coordination sites which are abundant on the poorly crystallized WO_3 and WO_x surface,[19] or through a homogenous mechanism by forming dissolved WO_x or its hydrate,[11] or both. The homogeneous mechanism could be approved by the reusability test of W_2C/CMK-3 catalyst. As shown in Fig. S9, the catalyst could be reused for at least 6 times without appreciable deactivation; in the 7th and 8th runs the MG yield declined gradually. Concomitantly, significant leaching of W component occurred (W content dropped from 34.4 wt% to 17.3 wt%) and the W_2C phase transformed into highly crystallized WO_3 phase after the consecutive 8 runs (Fig. 2a). These results suggest that upon the poorly crystallized WO_3 or WO_x becomes highly crystallized in supercritical methanol solvent during the reaction, they are robust against leaching meanwhile the number of coordinately unsaturated sites is reduced greatly, both of which lead to activity loss. Fortunately, the dissolved W species could be recovered by distillation of the products.

One issue associated with the practical application is the catalyst adaptability to raw biomass feedstock. To our delight, when raw cellulosic biomass materials, such as birch, cornstalk, and miscanthus were simply pretreated with hot water and then used as the feedstock, satisfactory MG yields (birch gave MG yield as high as 49.1 C%, cornstalk gave 33.3 C% and miscanthus gave 46.2 C%) were obtained (Table S3). Compared with the conversion of pure microcellulose, the lignin component in the biomass did not much negatively affect the conversion of cellulose; instead, it was also converted into phenolic compounds (Fig. S10) in accordance with the previous report.[20]

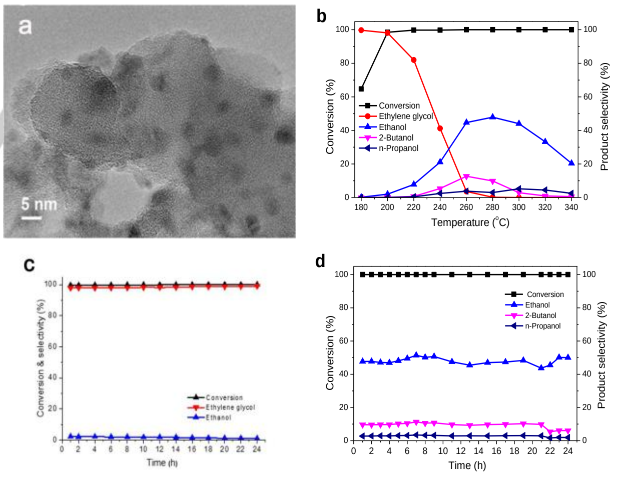

Figure 3. Hydrogenation of MG into EG and EtOH. (a) TEM micrograph of Cu/SiO_2 catalyst; (b) temperature dependence of the product distribution; (c) time course of MG conversion and product distribution at 200 ºC; (d) Time course of MG conversion and product distribution at 280 ºC. Reaction conditions: 10% MG in THF solution was continuously fed into a fixed bed reactor packed with 2 mL catalyst. The liquid flow rate was 2 ml/h corresponding to a LHSV of 1 h^{-1} and the H_2 gas flow rate was 33.3 ml/min corresponding to a GHSV 1000 h^{-1}, H_2/MG = 46.

The MG obtained from renewable biomass was further tested for hydrogenation over Cu/SiO_2 catalyst with a fixed bed reactor under the reaction condition of 3 MPa H_2, 180 ~ 340 °C. The Cu/SiO_2 catalyst was prepared with ammonia evaporation hydrothermal method[13c] and the resultant Cu nanoparticles with an average size of 2-3 nm are highly dispersed on the SiO_2 support (Fig.3a). Over this catalyst, MG was almost quantitatively converted to EG at 200 °C, and to EtOH at 280 °C with a selectivity of 50% (Fig. 3b). The catalyst was stable during 24 h-run, steadily producing EG and EtOH at their respective optimum temperatures (Fig. 3c-d). Thus, MG serves as a platform molecule for the production of EG and EtOH from renewable cellulosic biomass. In comparison with the one-pot production of EG from cellulose we developed earlier,[10,11] the current cellulose-MG-EG two-step route has the advantage of saving separation cost (boiling points of the main and side products are listed in Table S4), and is more flexible by the facile switching between valuable fine chemical MG and bulk chemical EG depending on the market. More importantly, the two-step cellulose-MG-EtOH approach provides a non-fermentation pathway to the renewable cellulosic ethanol which are currently the only established biofuel as an additive up to 10% in gasoline.[21]

In summary, we have developed a new chemocatalytic approach for production of MG, EG, and EtOH from renewable lignocellulose. In the first step, MG was produced up to a yield of 57.7 C% from the one-pot transformation of cellulose in methanol with the catalysis of WOx and the assistence of oxygen. Then, both EG and EtOH were produced with a high selectivity in the second step via hydrogenation/hydrogenolysis of MG. This approach will pave a new way for the biomass conversion since MG can serve as a new biomass platform molecule for production of a variety of bulk and fine chemicals.

Acknowledgements

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Keywords: Methyl glycolate • Ethylene glycol • Ethanol • supported catalysts • biomass

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Layout 1:

COMMUNICATION

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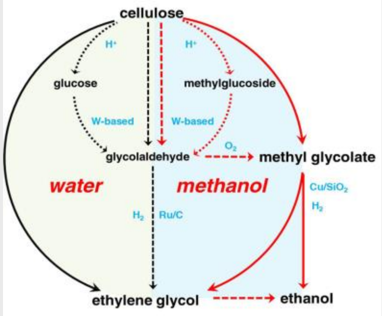

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