Synergistic Effect of Ni/W/Cu on MgAl$_2$O$_4$ for One-Pot Hydrogenolysis of Cellulose to Ethylene Glycol at a Low H$_2$ Pressure

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ABSTRACT: Nickel and tungsten, combined with copper, were incorporated into a magnesium aluminum spinel to form a multifunctional catalyst (Ni−W−Cu/MgAl$_2$O$_4$). Characterization results suggested that the adjacent Cu not only facilitated the reduction of W$^{6+}$ to W$^{5+}$ with substantial oxygen vacancies but also promoted the reducibility of the Ni species. Besides, the incorporation of Ni, W, and Cu into the support enhanced the catalytic acidity, as well as the L acid sites. The catalyst exhibited a strong synergistic effect between the three metals and the support, resulting in higher catalytic activity for the one-pot hydrogenolysis of cellulose to ethylene glycol. High cellulose conversion (100%) and ethylene glycol yield (52.8%) were obtained, even under a low H$_2$ pressure of 3 MPa.

1. INTRODUCTION

Currently, with the huge consumption and depletion of fossil resources, the production of chemical compounds using renewable biomass as a raw material has received much attention. Lignocellulose biomass is considered a potential feedstock substitute for the fossil resources due to its sustainable properties. The main component of lignocellulose is cellulose.$^{1,2}$ In recent decades, cellulose has been widely converted into various high-value chemicals, such as low-carbon polyols ($C_2$−$C_3$), containing glycerol (Gly), 1,2-propanediol (1,2-PG), and ethylene glycol (EG).$^3$ EG is widely used as a monomer in the plastic industry, as well as in antifreeze products and cosmetics. Moreover, it is considered an essential intermediate for the preparation of diversified chemicals, such as polyester fibers, resins, and polyethylene terephthalate.$^4$−$^6$

Generally, the conversion of cellulose to EG in a one-pot reaction has been widely investigated due to its economic and environmental advantages. The one-pot cellulose conversion to EG contains three main reactions. Cellulose is transformed into glucose by hydrolysis. The formed glucose is then transformed into glycolaldehyde by retro-aldol condensation. Finally, the glycolaldehyde is hydrogenated to EG. Thus, a multifunctional catalyst that contains an acid site for cellulose hydrolysis, active sites to promote the retro-aldol condensation, and active sites to promote hydrogenation is most attractive and efficient.$^7$ Numerous multifunctional catalyst systems have been exploited for the one-pot conversion of cellulose to EG. W-based materials are efficient catalysts for retro-aldol condensation. Noble metals (Pd,$^8$ Ru,$^5$ and Pt$^9$) as well as transition metals (Ni$^{10}$−$^{14}$ and Co$^2$) have been employed for hydrogenation. However, the noble metals have been restricted in their industrial applications due to their high cost and limited availability. By contrast, Ni-based catalysts are preferred in the hydrogenation process. The reaction of C$_6$ intermediate sugars to EG is enhanced by the presence of a basic promoter, such as Cu.$^{15}$ For example, the yields of EG over Ni−W$_2$C/AC$^{12}$ and Ni−W$_2$C/SBA-15$^{13}$ catalysts were as high as 61 and 76%, respectively. Nevertheless, the reaction process is usually performed under 5−6 MPa, which requires expensive and sophisticated instruments. Therefore, it is necessary to develop an efficient catalytic system for cellulose conversion to EG under mild conditions.

In multifunctional catalyst systems, the support is important in the catalytic behavior and it should not be limited by mass transfer and stability. In addition, it facilitates the dispersion and diffusivity of the active species that help to increase the hydrogenation activity. Magnesium aluminum spinel (MgAl$_2$O$_4$) is widely utilized in the catalyst support$^{16}$−$^{18}$ due to its high hydrothermal stability, hydrophobicity, outstanding mechanical robustness, low surface acidity, and large number of empty oxygen sites. These empty oxygen sites lead to higher adsorption of oxygen-containing compounds, such as glucose,
the intermediate compound in the transformation of cellulose to EG. This work represents a systematic investigation of the performances of three metals (Ni, W, and Cu) supported on MgAl2O4.
MgAl$_2$O$_4$ in the one-pot transformation of cellulose into EG at low H$_2$ pressures. The acid sites and metal sites of the multifunctional catalyst were investigated by various characterization methods. The impact of catalyst preparation parameters, such as the metal concentration and Al/Mg ratio of the MgAl$_2$O$_4$ support, on the transformation of cellulose into EG was evaluated. The stability of the catalyst was also investigated. Moreover, the role of each active site and the synergistic effect between the active metals and the support are discussed.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Catalyst.

2.1.1. Crystal Structure. Crystal phases of the catalyst samples were analyzed by X-ray diffraction (XRD). As shown in Figure 1, the characteristic diffraction peaks at 2θ = 19.1, 31.4, 36.9, 44.8, 55.8, 59.3, 65.2, 77.2, and 82.6° assigned to MgAl$_2$O$_4$ (JCPDS 77-0435) are observed in all the catalysts. As shown, the precursor was nearly converted to the spinel with a single-phase cubic structure. The new peaks in 15Cu/MgAl$_2$O$_4$ at 43.2, 50.4, and 74.1° were assigned to Cu (JCPDS 04-0836). Weak peaks at 23.5 and 33.4° attributed to the (010) and (114) facets of WO$_2.83$ (JCPDS 36-1303) were observed in 15W/MgAl$_2$O$_4$, indicating that the W species was well dispersed on the support. Nevertheless, no apparent diffraction peak was attributed to the Ni species, which might be because the metals were amorphous and were well dispersed in the samples or because of low loading. However, with the introduction of Ni to MgAl$_2$O$_4$, the intensity of the diffraction peak at 36.9° increased slightly. This could be ascribed to the interaction between Ni and MgAl$_2$O$_4$, which resulted in a higher crystallinity of the sample. The XRD patterns of 5Ni−15W−15Cu/MgAl$_2$O$_4$ (Al/Mg = 2, 3 and 4) and the post-reaction catalyst are shown in Figure 1b. The increase in the Al−Mg ratio from 2 to 4 significantly increased the crystallinity. After six cycles, the sample [5Ni−15W−15Cu/MgAl$_2$O$_4$ (1:3)] showed the monoclinic WO$_3$ phase and a new CuWO$_4$ crystal phase (JCPDS 21-0307).

2.1.2. Surface Composition. The chemical state and relative quantities of nickel, tungsten, and copper on the catalysts are examined by X-ray photoelectron spectroscopy (XPS), and the results are shown in Figure 2. As shown in Figure 2a, the Ni 2p spectrum showed three major peaks at binding energies of 856.3, 862.0, and 873.0 eV, respectively. The Ni−W−Cu/MgAl$_2$O$_4$ catalysts at binding energies of 852.2, 856.3 eV, and 862.0 were Ni$^0$, NiO, and satellites of Ni$^{2+}$, respectively. Because Ni$^0$ on the catalyst surface was extremely susceptible to oxidation under an air atmosphere to produce Ni$^{2+}$, a large characteristic Ni$^{2+}$ peak still appeared in the spectrum. The W 4f XPS spectra of the Ni−W−Cu/MgAl$_2$O$_4$ (Al/Mg = 2, 3, and 4) catalysts are shown in Figure 2b. Two broad XPS peaks in the 32−40 eV range could be observed for all catalysts, suggesting that tungsten might exist in more than one oxidation state. From the position of the W 4f level, the catalyst samples were deconvoluted by a curve-fitting procedure to distinguish WO$_x$ species in the different chemical states. The peaks at 35.2 and 37.4 eV were attributed to W$^{5+}$ species, while the peaks at 36.1 and 38.2 eV were Ni$^5$, NiO, and satellites of Ni$^{2+}$, respectively. Because Ni$^0$ on the catalyst surface was extremely susceptible to oxidation under an air atmosphere to produce Ni$^{2+}$, a large characteristic Ni$^{2+}$ peak still appeared in the spectrum. The W 4f XPS spectra of the Ni−W−Cu/MgAl$_2$O$_4$ (Al/Mg = 2, 3, and 4) catalysts are shown in Figure 2b. Two broad XPS peaks in the 32−40 eV range could be observed for all catalysts, suggesting that tungsten might exist in more than one oxidation state. From the position of the W 4f level, the catalyst samples were deconvoluted by a curve-fitting procedure to distinguish WO$_x$ species in the different chemical states. The peaks at 35.2 and 37.4 eV were attributed to W$^{5+}$ species, while the peaks at 36.1 and 38.2 eV were attributed to W$^{6+}$ species. As reported by Hamdy, the existence of W$^{5+}$ might be attributed to the presence of oxygen vacancies, leading to a defect in the WO$_3$ structure. When Ni$^{2+}$ or Cu$^+$ (or even positively charged oxygen vacancies from the spinel) are present, the cations of the WO$_3$ association with a lower oxidation state than W$^{6+}$, producing oxygen vacancies. These
oxygen vacancies might be beneficial for the catalytic activity because the defect in the WO₃ structure could act not only as chemisorption sites for the reactants but also as electronically active centers, facilitating surface charge transfer processes. Table 1 shows that the W⁵⁺/(W⁶⁺ + W⁶⁺) molar ratio on the catalyst initially increased and then subsequently decreased as the Mg/Al ratio decreased. For the stoichiometry of the MgAl₂O₄ spinel, the Mg/Al ratio was approximately 1:2. According to Sawai, MgAl₂O₄ with excess Al₂O₃ non-stoichiometry can accommodate a large amount of positively charged oxygen vacancies (F⁺ centers). These F⁺ centers might promote the conversion of W⁶⁺ to W⁵⁺. Nevertheless, the W⁵⁺/(W⁵⁺ + W⁶⁺) molar ratio decreased when the Mg/Al ratio was 1:4. Al₂O₃ was excessive and not all of it contributed in generating MgAl₂O₄ and the excessive Al₂O₃ potentially blocked part of the MgAl₂O₄ surface. As a result, the Mg/Al ratio of 1:3 possessed more oxygen vacancies, which helped to adsorb oxygen-containing compounds such as the intermediate (W⁵⁺ + W⁶⁺) at a Mg/Al ratio of 1:3.

Table 1 shows that the W⁵⁺/(W⁵⁺ + W⁶⁺) molar ratio on the catalyst surface, which implied that the addition of Cu decreased the B acid sites and facilitated the formation of more L acid sites. This result suggested that the adjacent Cu was beneficial to the reduction of W⁶⁺ to W⁵⁺ with substantial oxygen vacancies.

The NH₃ temperature-programed desorption (NH₃-TPD) performance of the catalyst is also characteristic, and the results are shown in Figure 4. The desorption peaks ranging from 100 to 230, 230 to 400 °C, and those above 400 °C were mainly assigned to the weak acid sites, moderately strong acid sites, and strong acid sites, respectively. The support showed broad peaks centered at 120 °C in the range of 70–350 °C and broad peaks at temperatures higher than 400 °C. This indicates that the weak and strong acid intensities were widely distributed on the support surface. With the introduction of Cu to MgAl₂O₄, a large number of moderate and strong acid sites appeared on the catalyst. The results show that the addition of Cu advantageously increased the concentration of moderately strong acid and the total acid intensity of the catalysts. The concentration of the total acid amount per gram of the catalyst increased in the following order: 5Ni–W/MgAl₂O₄ (1:3) < 15W/MgAl₂O₄ (1:3) < 5Ni–W/Cu/MgAl₂O₄ (1:3) < 5Ni–W/Cu/MgAl₂O₄ (1:3) < 15W–15Cu/MgAl₂O₄ (1:3). This indicates that the addition of Cu benefited the reduction of W⁶⁺ to W⁵⁺ with substantial oxygen vacancies.

![Figure 4](https://doi.org/10.1021/acsomega.1c00979)  
**Figure 4.** NH₃-TPD profiles of the Ni–W–Cu/MgAl₂O₄ catalysts.
very small, homogeneous, and existed at the nanoscale, as stated in the literature. The TEM image (Figure 5d) confirmed that the particles of MgAl2O4 (1:3) were nanosized and had an average particle size of approximately 13.5 nm. The high-resolution TEM (HRTEM) image (Figure 5e) showed that the lattice spacing was 0.2 nm for a particular Cu(111) surface. Ni, W, and Cu are well distributed on MgAl2O4 (1:3), as shown in Figure 5f. This observation is consistent with the XRD results, which suggests a fine distribution of W and Ni in atomic closeness to each other and the support.

2.1.5. Reducibility. The reduction performance of the catalyst was examined by the H2 temperature-programed reduction (H2-TPR) technique. As displayed in Figure 6, a limited amount of the solid solution of NiO and MgO (the reduction peak > 700 °C) is formed. This result is in agreement with XRD results; in which, the solid solution of the NiO and MgO patterns was barely detected. For the 5Ni–15W–15Cu/MgAl2O4 (1:3) catalyst, the reduction temperature of nickel oxide was 630 °C, which was attributed to the reduction of NiO interacting strongly with the support. The 5Ni–15W–15Cu/MgAl2O4 (1:3) sample displayed three main peaks: the low-temperature peaks at 220 and 265 °C were attributed to the reduction of Cu2+ and Cu+, respectively, whereas the high-temperature peak at 430 °C represented the reduction temperatures of nickel oxide. The peak of NiO shifted to a lower reduction temperature, suggesting that the addition of Cu facilitated the NiO transformation into Ni0 with weaker interactions between NiO and the support. Moreover, the absorption amount of H2 was larger on the 5Ni–15W–15Cu/MgAl2O4 (1:3) catalyst, indicating higher reducibility. This observation was in good agreement with the XPS results in our previous research, in which the introduction of Cu promoted the conversion of W6+ to W5+ and generated more oxygen vacancies. These vacancies allowed easier NiO activation once the “empty spaces” could interact with the oxygen of NiO and weaken the bond between Ni and O. Thus, the removal of O by H2 was facilitated.

2.1.6. ICP Analysis. The actual loading amounts of Ni, W, and Cu components are investigated, and the results are shown in Table 4. The ICP results showed that the loadings of Ni, W, and Cu on the fresh 5Ni–15W–15Cu/MgAl2O4 (1:3) catalyst were 5.8, 16.0 and 16.7%, respectively, which were not significantly different from the experimental design.
2.2. Synergistic Effect of the Ni−W−Cu/MgAl2O4 Multifunctional Catalyst. To further explore the synergistic effect of Ni−W−Cu and the support in the reaction, three metals (Ni, W, and Cu) were incorporated. From the data in Table 3, no catalyst (entry 1) is used but no polyols are observed. For the bare support MgAl2O4 (entry 2), the cellulose conversion reached 65.5%, which was attributed to the presence of oxygen vacancies in the support. However, only 3.6% EG and 2.0% C2−3 polyols were obtained. In contrast, when adding Ni, even at a minor amount of 5% (entry 3), the EG and C2−3 polyol yields increased significantly to 13.5 and 46.7%, respectively, with glycerol as the primary product. This implied that Ni was efficient for hydrogenation, which was consistent with the results reported by Zheng.34

With the introduction of W (entry 4), the cellulose conversion reached 98.6%. This indicated that the W species has the capability to cleave C−C and C−O bonds. However, only 2.1% EG yield was obtained. With the combinations of W and Ni/MgAl2O4 (entry 6), the main product, EG, dramatically increased to 33.9%. The result provides evidence that the synergy between Ni and tungsten oxide species could tune the selectivity of the reaction toward EG. Furthermore, with the use of the Ni- and W-free catalyst (15Cu/MgAl2O4, entry 5), the EG and C2−3 polyol yields were only 12.0 and 24.6%, respectively, even though the EG was the main product. This result suggests that Cu was also efficient for hydrogenation, but the hydrogenation capability of the C−C cleaved intermediates affected by Cu is weaker than Ni. With the subsequent Cu introduction to 5Ni−15W/MgAl2O4 (entry 7), the EG yield increased to 52.8%, implying that synergistic Ni, W, and Cu were suitable candidates for the conversion of cellulose to EG. It was explained by the Py-IR (Table 2) and NH3-TPD (Figure 3) that the intercalation of Cu into W and Ni enhanced the catalytic acidity, as well as the L acid sites. These findings can be summarized as follows: Ni played a role in the hydrogenation of the cleaved intermediate and W species cleaved the C−C/C−O bond. The adjacent Cu were not only responsible for hydrogenation reactions but also facilitated the cleavage of the C−C/O bond.

Based on the above results, the plausible mechanism of anchoring catalytic sites on the surface of Ni−W−Cu/MgAl2O4 for cellulose transfer to EG is summarized in Figure 7. H2 was decomposed into H radicals on the surface of Cu and Ni at the hydrogenolysis treatment at 245 °C and 3 MPa. EG was the main product. The reaction conditions were 120 min, 3 MPa H2, 245 °C, 50 mL of H2O, 0.5 g of reactant, 0.3 g of catalyst and 250 rpm. EG: ethylene glycol; 1,2-PG: 1,2-propylene glycol; Gly: glycerol; Ery: erythritol; Glu: glucose; and Sor: sorbitol.

Table 3. Conversion of the Cellulose Reactant over Different Catalysts

| entry | catalyst | conv. (%) | yield (%) |
|-------|----------|-----------|-----------|
| 1     | blank    | 53.5      | 0 0 0 0 0 0 |
| 2     | MgAl2O4 (1:3) | 65.5       | 3.6 2.0 0 1.0 3.4 2.5 |
| 3     | 5Ni/MgAl2O4 (1:3) | 86.9       | 13.5 13.0 20.2 4.3 0.9 8.6 |
| 4     | 15W/MgAl2O4 (1:3) | 98.6       | 2.1 1.9 0 0 4.5 4.6 |
| 5     | 15Cu/MgAl2O4 (1:3) | 88.3       | 12.0 8.9 3.7 1.2 0.4 6.2 |
| 6     | 5Ni−15W/MgAl2O4 (1:3) | 97.7       | 33.9 6.9 2.3 0 0 8.5 |
| 7     | 5Ni−15W−15Cu/MgAl2O4 (1:3) | 100       | 52.8 8.0 1.6 1.6 0.4 6.2 |
| 8     | 5Ni−15W−15Cu/MgAl2O4 (1:2) | 84.8       | 16.8 15.9 13.9 4.5 0 1.2 |
| 9     | 5Ni−15W−15Cu/MgAl2O4 (1:4) | 95.8       | 49.7 7.4 1.6 1.4 0.8 2.4 |
| 10    | 5Ni−15W−15Cu/MgAl2O4 (1:5) | 92.9       | 42.9 6.9 1.6 1.2 0 1.8 |

“Reaction conditions: 120 min, 3 MPa H2, 245 °C, 50 mL of H2O, 0.5 g of reactant, 0.3 g of catalyst and 250 rpm. EG: ethylene glycol; 1,2-PG: 1,2-propylene glycol; Gly: glycerol; Ery: erythritol; Glu: glucose; and Sor: sorbitol.

Figure 7. Proposed mechanisms of the anchoring catalytic sites on the surface of Ni−W−Cu/MgAl2O4 for cellulose transfer to EG.
hydrolyzed to glucose by H⁺ formed by water, H⁺ formed by active hydrogen of W⁶⁺ combined with H₂O, and H⁺ formed by Cu and Ni spillovers, respectively. Then, the formed glucose was converted into glycolaldehyde over the active site of W⁵⁺, which was transferred from W⁶⁺ in an easier way promoted by Cu⁰ and F⁺ centers in the MgAl₂O₄ spinel. In this step, the oxygen vacancies absorbed the oxygen of glucose, which facilitated the rapid formation of glycolaldehyde.²⁵ Finally, the obtained glycolaldehyde was reduced to EG over the active site of Ni⁰.

Because the one-pot cellulose conversion to EG contains cracking (the cleavage of the C−C/C−O bond) and hydrogenation, the competition between the two reactions determines the distribution of products. As mentioned above, Ni is essential in the hydrogenation. Therefore, the influence of Ni loading on the catalytic performance is investigated, with the results presented in Figure 8. When the Ni loading increased from 0 to 5 wt %, the yield of EG and the C₂−₃ polyols increased significantly from 24.8 to 52.8% and from 29.7 to 62.4%, respectively. These results suggest that insufficient hydrogenation activity led to lower overall polyol yields and more hydrogenation active sites were generated at higher Ni loadings. However, as the Ni loading increased and exceeded 5 wt %, a slight decline in the yields of EG (38.5%) and the C₂−₃ polyols (51.2%) was observed, as well as the cellulose conversion (from 100.0 to 90.8%). According to Zheng,³⁴ over high activity for hydrogenation led to increased hexitol yield, at the expense of EG. Therefore, a Ni loading of 5 wt % was selected for the next study.

The influence of W loading on the catalytic performance was also evaluated. When W loading increased from 10 to 20 wt % (Ni/W ratio from 1:2 to 1:4), the maximum yields of EG and C₂−₃ polyols were obtained at 15 wt % W loading (Ni/W ratio 1:3). As shown in Figure 8, the EG yield obtained with 5Ni–10W−15Cu/MgAl₂O₄ was only 39.5%, suggesting that insufficient amounts of W species (Ni/W ratio 1:2) prevented the conversion of C₆ sugars to C₂−₃ polyols. On the contrary, a too large number of the W active sites might promote the cracking (the cleavage of the C−C/C−O bond) and make them predominate the hydrogenation reactions, leading to decreases in the yields of EG, C₂−₃ polyols, and even the yield of hexitols. Thus, the Ni/W ratio at 1:3 was the optimum for the competition between the cracking and hydrogenation reactions to obtain a high EG yield.

Figure 8 also illustrates the effect of the loading amount of Cu on the catalytic performance. The yields of EG and the C₂−₃ polyols increased with the increase in Cu loading, and the highest yields (52.8% EG and 62.4% C₂−₃ polyols) were reached at 15 wt %.

The influence of the Mg/Al ratio on the catalytic activity of Ni–W–Cu/MgAl₂O₄ catalysts in cellulose conversion was investigated. The results are shown in Table 3, as the Mg/Al ratio decreased, the cellulose conversion and EG yield initially increased and then decreased. The highest yield (cellulose conversion of 100% and EG yield of 52.8%) was achieved at a Mg/Al ratio of 1:3. As illustrated in Figure 3 (TPD) and Table 2 (Py-IR), there is a substantial improvement in the acid amount and L acid sites when the Mg/Al ratio is 1:3. Table 1 (XPS) also shows that W⁵⁺/(W⁶⁺ + W⁸⁺) was the highest at a Mg/Al ratio of 1:3, indicating that W⁵⁺ is a key factor in the hydrogenolysis of cellulose. From the above results, we conclude that the catalytic activity could be attributed to the
highly acidic center in the magnesium aluminum spinel support, and the synergistic interaction between Ni, W, and Cu.

In summary, the highest EG yield obtained was 52.8% by the synergistic effect of 5Ni–15W–15Cu/MgAl2O4 (1:3:1). This EG yield was lower than the best yield (75%) reported for cellulose conversion to EG, but the reaction process performed in this work (H2 pressure of 3 MPa) was considerably less drastic than that performed to attain a higher EG yield (H2 pressure of 6 MPa).

2.3. Recyclability of the Catalyst. The recyclability of the 5Ni–15W–15Cu/MgAl2O4 (1:3) is investigated, and the results are displayed in Figure 9. After three cycles, no significant decrease in cellulose EG and the C2 polyol yield were observed, demonstrating that the catalyst was stable and reusable under the reaction conditions in this work (at least three cycles). However, the yield of the C2 polyols decreased to 56.1, 48.6, and 41.1% by the fourth, fifth, and sixth runs, respectively, while the yields of sorbitol increased to 9.7, 10.2, and 11.9%. The decrease in the content of C2 polyols and the sharp increase in sorbitol might be because the metal on the catalyst was dissolved and the acidity was decreased, or because of the catalyst structural change. In order to find out the reasons, ICP analysis was carried out to identify the mass fraction of the three metals after six cycles. As shown in Table 4, the loadings of Ni and Cu did not change significantly, but the loadings of W decreased significantly, indicating that the deactivation of the catalyst might be due to W metal leaching. Furthermore, as depicted in the XRD data, the sample after six cycles [5Ni–15W–15Cu/MgAl2O4 (1:3)] showed a new CuWO4 crystal phase. This indicates that the W5+ content decreased. Thus, the capability of the catalyst to cleavage the C–C bond decreased, resulting in an increase in sorbitol and a decrease in C2 polyols. Besides, the formed CuWO4 might promote hydrogenation activity and decrease the acidity of the catalyst, which was in good agreement with the result reported by Liu et al.

3. CONCLUSIONS

The synthesized Ni–W–Cu/MgAl2O4 multifunctional catalyst shows higher catalytic activity for the one-pot hydrolysis of cellulose to EG. The incorporation of Ni, W, and Cu into the support enhanced the catalytic acidity, as well as the L acid sites. The adjacent Cu not only facilitated the reducibility of the Ni species but also promoted the conversion of W6+ to W5+ with substantial oxygen vacancies, which were crucial in cellulose conversion to EG. The cellulose conversion and EG yield could achieve 100 and 52.8% even under a low H2 pressure of 3 MPa.

4. EXPERIMENTAL SECTION

4.1. Materials. Cellulose ((C6H10O5)n microcrystalline) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Aluminum nitrate (Al(NO3)3·9H2O) and magnesium nitrate ([Mg(NO3)2]·6H2O) were purchased from Huaguang Technology Co., Ltd. (Guangdong, China). Propylene oxide (C3H6O), absolute ethanol (C2H5OH), and ammonia metatungstate were purchased from Aladdin Co., Ltd. (Shanghai, China). Finally, copper nitrate hydrate (Cu(NO3)2·3H2O) and nickel nitrate hydrate (Ni(NO3)2·6H2O) were purchased from Xilong Science Co., Ltd. (Guangzhou, China).

4.2. Catalyst Preparation. The catalyst support was prepared by a sol–gel method, as described by Habibi. For the synthesis of the magnesium aluminate, appropriate amounts of Al(NO3)3·9H2O and Mg(NO3)2·6H2O were dissolved in a certain amount of the absolute ethanol solution (C6H10OH/(Al3+ + Mg2+) = 40). After a transparent precursor solution was obtained by stirring at room temperature for 30 min, propylene oxide was added (C3H8O/(Al3+ + Mg2+) = 11). Through the addition of C2H5OH, the gel was formed in a few minutes. After this step, the obtained gel was dried at 85 °C for 24 h and calcined at 700 °C for 3 h, with a 3 °C/min ramp rate.

The supported catalysts were prepared by using a conventional impregnation method. For xNi–yW–zCu/MgAl2O4 preparation: a certain amount of Ni(NO3)2·6H2O, H3PO4·W12·xH2O, and Cu(NO3)2·3H2O were added to deionized water, followed by 1.0 g of MgAl2O4. Subsequently, the pre-catalyst samples were oven-dried at 110 °C for 12 h, and the powder was calcined at 350 °C for 3 h, with a 3 °C/min ramp rate. Finally, the catalyst was reduced under H2/N2 (1/9) flow, with a rate of 20 mL/min at 450 °C for 4 h. The x, y, and z represented the metal loadings of Ni, W, and Cu, respectively.

4.3. Catalyst Characterization. XRD patterns were analyzed by a SmartLab X-ray diffractometer (Rigaku, Japan), with a Cu Kα radiation source (λ = 0.1544 nm) operating at 40 kV in a 2θ range of 10°–90°. XAES were carried out using a Thermo Scientific K-Alpha+ instrument (Thermo Fisher, USA), equipped with a monochromatic Al Kα radiation source (hv = 1486.6 eV). NH3-TPD measurements were performed on an Auto Chem II 2920 system (Micromeritics, USA). Prior to analysis, 0.15 g of the catalyst

![Figure 9. Recycling test of the 5Ni–15W–15Cu/MgAl2O4 (1:3) sample. Reaction conditions: 120 min, 3 MPa H2, 245 °C, 50 mL of H2O, 0.5 g of reactant, and 0.3 g of catalyst. EG: ethylene glycol; 1,2-PG: 1,2-propylene glycol; Gly: glycerol; Ery: erythritol; and Sor: sorbitol.](https://www.acs.org/content/dam/acsorg/acsjournals/acsom/2021/6/11650/11650-37782880496109105201358229688515886971699/s3.png)
was dried in a helium atmosphere from 25 to 200 °C (10 °C/min) for 1 h and then cooled to room temperature under helium flow. Subsequently, the NH3 desorption pattern was recorded from room temperature to 700 °C (10 °C/min). The pyridine-adsorbed Fourier transformation infrared spectra were detected using a Thermo Nicolet 380 (USA). The sample was pressed into a wafer and pre-treated at 300 °C under He for 1 h in the cell, followed by cooling. After the sample background was recorded, the adsorption of pyridine was measured at 200 and 350 °C until saturation. The result was obtained after the desorption of the physically adsorbed pyridine under vacuum for 60 min. Field-emission SEM images were obtained on a Sigma300 (Germany) equipped with energy-dispersive X-ray spectroscopy (EDS). The TEM was performed using an FEI Tecnai G2 F30 microscope (operating at 300 kV). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Titan G2 60-300, USA) was applied to analyze the structure of the catalyst. The homogeneity of elements, including Ni, W, and Cu, was determined by EDS elemental mapping. H2-TPR measurements were performed on an Auto Chem II 2720 system (Micromeritics, USA). The metal leaching was analyzed by inductively coupled plasma–optical emission spectroscopy (Agilent 5110 ICP–OES, USA).

4.4. Catalytic Evaluation. The catalytic evaluation was performed in a 100 mL stainless-steel high-pressure reactor (Dalian Jingyi Autoclave Vessel Manufacturing Co., Ltd., Dalian, China). In each reaction, 0.50 g of microcrystalline cellulose, 0.30 g of catalysts, and 50.0 mL of deionized water were placed inside the reactor. The reactor was sealed and flushed three times with N2 (99.9%) to remove air. Then, H2 (99.9%) filled the reactor until 3.0 MPa at room temperature. The reactor was heated to 245 °C with 250 rpm stirring and held at 245 °C for 2 h. Then, the liquid samples were withdrawn at selected times for high-performance liquid chromatography (HPLC) analysis. Subsequently, the reactor was naturally cooled to room temperature. The hydrogenolysis mixture was separated under a vacuum into the solid and liquid phases through filtration. Solid residues were dried in an oven at 90 °C for 5 h. For the catalyst recycling test, after each run, the catalyst was reused after being filtered from the reaction mixture and washed three times with deionized water.

4.5. Product Analysis. Quantitative analysis of the products was performed using a HPLC system (LC1220, Agilent 1220) equipped with a refractive index detector (RID-10A) and an Xtimate-Ca column (7.8 × 300 mm, 5 μm) at 353 K. The liquid product mixture obtained from the reactor was filtered through a 0.22 μm pore-size filter before HPLC analysis. 20 μL of the liquid sample was injected into the HPLC column, with a flow rate of 0.5 mL/min, and ultrapure water as the mobile phase. The concentration of the target product was calculated based on the standard curve of the concentration of the standards and the peak area. The conversion of cellulose and the yield of products were calculated by eqs 1 and 2. All the concentrations of the target product were analyzed in triplicate, and the calculated yields were presented as average.

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\text{Cellulose conversion (\%)} = \frac{\text{mass of starting cellulose} - \text{mass of cellulose after reaction}}{\text{mass of starting cellulose}} \times 100\%
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\text{yield (\%)} = \frac{\text{mass of carbon in the target product}}{\text{mass of carbon in starting cellulose}} \times 100\%
\]

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Notes
The authors declare no competing financial interest.

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