Available online at www.sciencedirect.com

ScienceDirect

SHORT COMMUNICATION

Catalytic Conversion of Cellulose to Ethylene Glycol over Tungsten Phosphide Catalysts

ZHAO Guanhong[1,2], ZHENG Mingyuan[1], WANG Aiqin[1], ZHANG Tao[1,*]

[1]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China
[2]Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Tungsten phosphide (WP) showed good activity in the selective conversion of cellulose to ethylene glycol (EG). At a H_2 initial pressure of 6 MPa and temperature of 245 ^{o}C, EG yield reached 25.4 mol% over 20%WP/AC (activated carbon) and 46.0 mol% over 2%Ni-20%WP/AC, which demonstrated a remarkable synergy between Ni and WP.

Key words: biomass; cellulose; tungsten phosphide; ethylene glycol

Nowadays, fossil energy depletion and climate deterioration are driving the development of alternative clean energy sources. Among various potential solutions, the converting of biomass to energy chemicals and building block materials is regarded as one of the most attractive approaches because of the carbon neutrality and renewable properties of biomass. Lignocellulose, the most abundant biomass on earth, is widely available in various agricultural wastes. However, the crystalline and compact structure of cellulose makes it difficult to degrade. It remains a significant challenge to efficiently and selectively convert cellulose into valuable chemicals. Among possible routes [1–7], the catalytic conversion of lignocellulose with solid catalysts has unique advantages such as good selectivity for target products, reusability of catalysts, mild reaction conditions, and environmental friendliness [5–7].

Previously, we have reported that cellulose can be converted into polyols with high selectivity over transition metal carbide and phosphide catalysts [8–12]. In particular, over tungsten carbide (W_2C) supported on activated carbon (AC) and mesoporous carbon and nickel-promoted tungsten carbide catalysts, the highest ethylene glycol (EG) yield obtained was 75 wt% [10]. To unravel the unique role of tungsten carbide in the transformation of cellulose to EG, we employed Ni-W bimetallic catalysts instead of Ni-W_2C and found that the Ni-W bimetallic catalysts also exhibited high activity and selectivity

[11]. In contrast to W-based catalysts, with nickel phosphide catalysts, the main product was sorbitol rather than EG [12]. These results suggest that the tungsten component plays an important role in selectively cracking the C–C bond of the reactant, while the nickel component mainly promotes catalytic hydrogenation. To further prove this proposition, in this work, we prepared tungsten phosphide (WP) catalysts supported on AC and silica and investigated their catalytic behavior in the conversion of cellulose.

The preparation of the tungsten phosphide catalysts comprised three steps [13,14]: impregnating the support, AC (Norit, 20–40 mesh, A_{BET} = 709 m^2/g), or silica (Qingdao Haiyang Chemical Company, 20–40 mesh, A_{BET} = 455 m^2/g) with solutions of ammonium metatungstate (AMT) and $(NH_4)_2HPO_4$, drying the sample at 120 ^{o}C for 12 h, and reduction with a procedure in which the sample was heated from room temperature to 350 ^{o}C at a rate of 5.5 ^{o}C/min, then to 850 ^{o}C at a rate of 1 ^{o}C/min, and kept at 850 ^{o}C for 1 h. The hydrogen gas hourly space velocity (GHSV) was 12 000 h^{-1}. After reduction, the phosphide was passivated in 1%O_2-99%N_2 for 4 h. For the preparation of the nickel-promoted tungsten phosphide catalyst, $Ni(NO_3)_2$ was co-impregnated with AMT and $(NH_4)_2HPO_4$, which was followed with the procedure described above, except that the final reduction temperature was 650 ^{o}C. The nominal loadings of tungsten and

nickel were 20 wt% and 2 wt%, respectively.

X-ray diffraction (XRD) patterns were obtained on a PW3040/60 X' Pert PRO (PANalytical) diffractometer. CO chemisorption measurement was conducted on a Calvet-type microcalorimeter (Seteram BT2.15) described elsewhere [15]. Before the measurement, the catalyst was treated in H_2 flow at 650 $^\circ$C for 1 h. Transmission electron microscopy (TEM) analysis was performed on a JEM-2000EX (JEOL) microscope. The catalytic conversion of cellulose (Merck, microcrystalline) was performed in a stainless steel autoclave (Parr Instrument Company, 100 ml) at a H_2 pressure of 6 MPa (measured at room temperature) and 245 $^\circ$C for 30 min. For each reaction, cellulose (0.5 g), catalyst (0.15 g), and deionized water (50 ml) were charged into the reactor and stirred at a rate of 1 000 r/min. The liquid products were analyzed by high performance liquid chromatography. The liquid products were also analyzed by the total organic carbon (TOC) method on an Elementar Liqui TOC instrument. The metal loss from the catalyst after reaction was determined by inductively coupled plasma (ICP) using an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The gas products were analyzed by gas chromatography. Cellulose conversions were determined by the weight change of cellulose before and after the reaction [5,8]. The yields of polyols were calculated by the carbon mole ratio of product and cellulose [12].

As shown in Fig. 1, the AC-supported catalyst 20%WP/AC showed typical XRD patterns of WP. A small amount of tungsten carbide was also formed, which was ascribed to the carbothermal reduction of tungsten by the carbon support to form the carbide during the high temperature preparation of tungsten phosphide. In contrast, for the silica-supported catalyst 20%WP/SiO$_2$, only a very weak peak of the WP phase was observed. The absence of most of the diffraction peaks of WP from the 20%WP/SiO$_2$ catalyst suggested a high dispersion of WP on the silica support. The CO adsorption measurement showed a CO uptake of 18.3 μmol/g by 20%WP/SiO$_2$, which was more than twice that by 20%WP/AC (8.3 μmol/g), which further demonstrated that tungsten phosphide had a higher dispersion on the 20%WP/SiO$_2$ catalyst. The TEM images (not shown) showed that the particle size of tungsten phosphide on
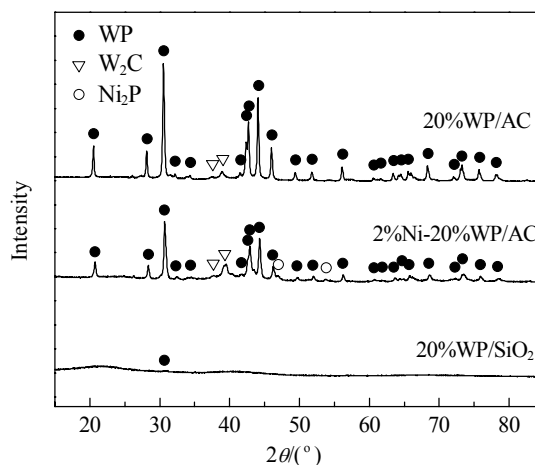

Fig. 1. XRD patterns of different tungsten phosphide catalysts.

20%WP/SiO$_2$ was smaller than that on 20%WP/AC. On the 2%Ni-20%WP/AC catalyst, the main phase was still WP, with small amounts of W$_2$C and Ni$_2$P.

The catalytic conversions of cellulose over the various catalysts are listed in Table 1. Over all the tungsten phosphide catalysts, cellulose was completely degraded in 30 min. EG was the main polyol product. For 20%WP/AC, the EG yield was 25.4 mol%, with a hexitol yield of as low as 2.3 mol%. This result is very close to that over a W$_2$C/AC catalyst [8,9]. As mentioned above, a small amount of tungsten carbide was formed on 20%WP/AC, which may play an important role in EG formation during cellulose conversion. To exclude the influence of tungsten carbide, we used a silica-supported tungsten phosphide catalyst. Again, a good yield of EG was obtained on 20%WP/SiO$_2$, in good agreement with 20%WP/AC. The high selectivity for EG in cellulose conversion should be attributed to the catalytic performance of tungsten phosphide. As compared with nickel phosphide, which we reported recently [12], the product selectivities were quite different even though both were metal phosphides. Cellulose was selectively transformed into sorbitol with a high yield of 48.4 mol% over nickel phosphide, while smaller molecule products, such as EG, were mainly formed over the tungsten phosphide catalyst. By correlating with our previous work on

Table 1 Results of cellulose conversion and polyol yields over the catalysts

Catalyst	Conversion[c] (%)	Conversion[d] (%)	Yield (mol/%)							
			Glycerol	EG	1,2-PG	Sorbitol	Mannitol	Erythritol	CO$_2$	CO
20%WP/AC	100	86.53	1.2	25.4	2.1	1.8	0.5	1.2	1.4	0.2
20%WP/SiO$_2$	100	80.56	1.3	25.0	2.5	1.5	1.0	1.1	1.7	0.2
20%WP/AC[a]	100	—	1.1	21.8	3.0	1.7	2.1	1.2	—	—
20%WP/AC[b]	100	—	0.9	17.4	3.5	2.0	1.9	1.1	—	—
2%Ni-20%WP/AC	100	87.29	1.2	46.0	6.4	3.3	2.6	2.0	0.8	0.03
10%Ni/AC+20%WP/AC	100	—	0.8	34.1	7.6	4.3	2.9	1.7	—	—
10%Ni/AC	74	—	1.1	10.2	4.9	12.3	2.5	1.3	—	—

[a]20%WP/AC in the 2nd run. [b]20%WP/AC in the 3rd run. [c]Cellulose conversion calculated by mass change of cellulose before and after reaction. [d]Cellulose conversion calculated by organic carbon in liquid products divided by total carbon of cellulose put into the reactor.
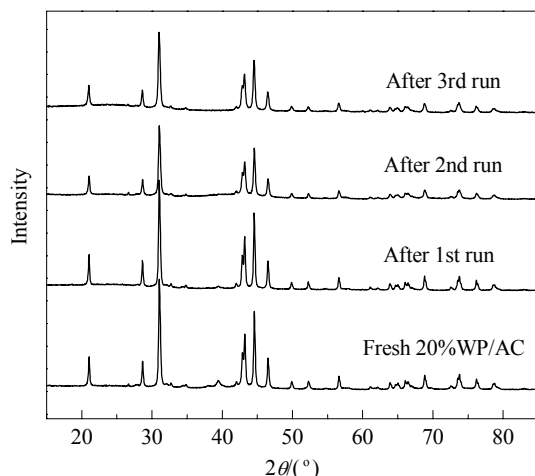
EG—Ethylene glycol; PG—Propylene glycol.

Fig. 2 XRD patterns of fresh and recycled 20%WP/AC catalysts.

tungsten carbide and metallic tungsten catalysts [8–11], we conclude that tungsten phosphide functions as the active site for hydrogenation and also plays an important role in selectively cracking the C–C bond of the cellulose or glucose by some tungsten species.

The gas phase analysis showed that a small amount of CO and CO_2 were produced but there were no methane or other alkanes formed during the reaction. The cellulose conversion was 80%–90% of total organic carbon. The reason for the 10%–20% carbon loss after reaction is not clear yet.

The reusability of the tungsten phosphide catalyst was examined with recycling tests. After three recycling runs, the EG yield over 20%WP/AC decreased from 25.4 mol% to 17.4 mol%, indicating that slight deactivation had occurred. The XRD patterns of the spent catalysts (Fig. 2) showed that the WP phase remained well dispersed after three recycling runs and no tungsten oxide peaks were seen. On the other hand, a comparison of the CO uptake amounts before and after reaction indicated that the CO uptake had slightly decreased (6.4 μmol/g) after the reaction. The ICP analysis of the liquid products showed that 5.2 wt% tungsten from the catalyst was leached into the solution after reaction. This may account for the decrease in catalytic activity. In addition, partial oxidization of the active sites on the catalyst may be another reason for the deactivation.

Activity for catalytic hydrogenation is necessary for a catalyst for cellulose conversion to polyols [10,11]. Thus, we attempted to modify the tungsten phosphide catalyst with nickel to provide more hydrogenating sites on the catalysts. The CO chemisorption measurement showed that the CO uptake amount over 2%Ni-20%WP/AC was 11.9 μmol/g, which was higher than the 8.3 μmol/g over the 20%WP/AC. During cellulose conversion, the EG yield was remarkably increased to 46.0 mol% over the nickel-modified tungsten phosphide,

which showed notable synergy in the 2%Ni-20%WP/AC catalyst. On the other hand, over a mechanical mixture of 10%Ni/AC and 20%WP/AC, an EG yield of 34.1 mol% was obtained. Although this value was higher than that over the individual catalysts, it was still much lower than that from the 2%Ni-20%WP/AC catalyst. This result further demonstrated that a synergistic effect occurred when both Ni and W were present in one catalyst, probably as neighbors to each other. On one hand, the tungsten component in the catalysts degraded cellulose into small molecules of unsaturated C_2 species. On the other hand, tungsten catalyzed the hydrogenation of unsaturated molecules into EG. Thus, with a proper amount of hydrogenating sites or using a novel preparation method to adjust the relative amounts of the two kinds of functions on the catalyst, tungsten phosphide catalysts should give a better performance for cellulose conversion to EG.

In summary, tungsten phosphide catalysts showed good activity for cellulose conversion to EG. Similar to tungsten carbide catalysts, a synergistic effect of duel catalytic sites occurred on tungsten phosphide catalysts for EG formation. The addition of Ni into tungsten phosphide promoted catalytic hydrogenation and led to a remarkable increase in the EG yield to 46.0 mol%. The result is helpful for a better understanding of cellulose conversion into EG over tungsten-based catalysts and provides less expensive catalysts for biomass conversion.

References

1 Lynd L R, Cushman J H, Nichols R J, Wyman C E. *Science*, 1991, **251**: 1318
2 Philippidis G P, Smith T K, Wyman C E. *Biotechnol Bioeng*, 1993, **41**: 846
3 Asadullah M, Kaoru F, Keiichi T. *Ind Eng Chem, Res*, 2001, **40**: 5894
4 Mohan D, Pittman C U, Steele P H. *Energy Fuels*, 2006, **20**: 848
5 Fukuoka A, Dhepe P L. *Angew Chem, Int Ed*, 2006, **45**: 5161
6 Yan N, Zhao C, Luo C, Dyson P J, Liu H C, Kou Y. *J Am Chem Soc*, 2006, **128**: 8714
7 Luo C, Wang S C, Liu H C. *Angew Chem, Int Ed*, 2007, **46**: 7636
8 Ji N, Zhang T, Zheng M Y, Wang A Q, Wang H, Wang X D, Chen J G. *Angew Chem, Int Ed*, 2008, **47**: 8510
9 Ji N, Zhang T, Zheng M Y, Wang A Q, Wang H, Wang X D, Shu Y Y, Stottlemyer A L, Chen J G G. *Catal Today*, 2009, **147**: 77
10 Zhang Y H, Wang A Q, Zhang T. *Chem Commun*, 2010, **46**: 862
11 Zheng M Y, Wang A Q, Ji N, Pang J F, Wang X D, Zhang T. *ChemSusChem*, 2010, **3**: 63
12 Ding L N, Wang A Q, Zheng M Y, Zhang T. *ChemSusChem*, 2010, **3**: 818
13 Shu Y, Oyama S T. *Carbon*, 2005, **43**: 1517
14 Clark P, Wang X, Oyama S T. *J Catal*, 2002, **207**: 256
15 Li L, Wang X, Shen J, Zhou L, Zhang T. *J Therm Anal Calorim*, 2005, **82**: 103