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磷化钨催化转化纤维素制乙二醇

赵冠鸿[1,2], 郑明远[1], 王爱琴[1], 张 涛[1]

[1]中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连 116023
[2]中国科学院研究生院, 北京 100049

摘要: 首次将磷化钨 (WP) 催化剂应用于纤维素的催化转化反应. 结果表明, 与碳化钨催化剂类似, WP 催化剂也可高效地实现纤维素转化. 在 H_2 初始压力为 6 MPa, 反应温度为 245 °C 时, 20%WP/AC (活性炭) 催化纤维素高选择性地生成乙二醇, 其收率为 25.4 mol%. 2% 镍的加入使得该催化剂上乙二醇收率增至 46.0 mol%, 表明 Ni 与 WP 之间存在着明显的协同作用.

关键词: 生物质; 纤维素; 磷化钨; 乙二醇

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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 °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

随着化石能源的日渐枯竭和气候环境的不断恶化, 寻找清洁的替代能源成为人类的重要课题. 由于生物质具有碳平衡和可再生的优点, 在新能源开发诸多途径中, 由生物质转化为能源化学品和大宗平台化合物备受人们关注. 木质纤维素是地球上最丰富的生物质资源, 广泛存在于各种农业废弃物中, 但它的结构致密复杂, 因此, 实现其高效、特别是高选择性转化是一项极具挑战性的课题. 在各种可能的转化途径中[1~7], 利用固体催化剂催化转化木质纤维素具有反应条件较温和、选择性高、催化剂易于回收、环境友好等优点, 因而成为近年来的研究热点之一[5~7].

本课题组曾利用过渡金属碳化物和磷化物类似于贵金属的催化性质, 将纤维素高选择性地转化为多元醇[8~12]. 特别是在活性炭 (AC) 以及介孔炭负载的镍-碳化钨 (W_2C) 催化剂上, 纤维素高选择性地转化为乙二醇 (EG), 其收率最高可达 75 wt%[10]. 为了进一步阐明 W_2C 在该反应中独特的催化作用, 我们使用金属 Ni-W 的组合代替 Ni-W_2C 催化剂, 发现其仍可高选择性地催化纤维素转化为 EG[11]. 而以磷化镍为催化剂时, 纤维素主要转化为山梨醇, 而非乙二醇[12]. 由此可见, W 物种在纤维素的 C–C 键选择性断裂过程中起着非常关键的作用, 而另一活性组分 Ni 则主要起加氢作用. 为进一步验证上述推断, 本文分别制备了 AC 和 SiO_2 负载的磷化钨 (WP) 催化剂, 考察其在纤维素转化中的催化行为.

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联系人: 张 涛. Tel: (0411)84379015; Fax: (0411)84685940; E-mail: taozhang@dicp.ac.cn
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采用还原磷酸盐法制备 WP 催化剂[13,14]. 配制一定浓度的偏钨酸铵 (AMT) 和 $(NH_4)_2HPO_4$ 溶液, 等体积浸渍于 AC (Norit, 20~40 目, 比表面积 709 m^2/g) 或 SiO_2 (青岛海洋化工厂, 20~40 目, 比表面积 455 m^2/g) 上, 于 120 °C 干燥 12 h, 在 H_2 中首先以 5.5 °C/min 升至 350 °C, 然后以 1 °C/min 升至 850 °C, 并保持 1 h, H_2 空速 (GHSV) 为 12 000 h^{-1}. 还原结束后, 待温度降至室温, 通入 $1\%O_2$-$99\%N_2$ 混合气钝化 4 h. 采用 $Ni(NO_3)_2$, $(NH_4)_2HPO_4$ 和 AMT 共浸渍的方法制备 Ni-WP 样品, 除了最终还原温度为 650 °C之外, 其他过程同上. 制得的催化剂中 W 和 Ni 的理论含量分别为 20 wt% 和 2 wt%.

使用 PW3040/60 X' Pert PRO (PANalytical) 型 X 射线衍射仪对催化剂物相进行分析. 催化剂的 CO 化学吸附实验在法国 Seteram 公司的 BT2.15 型微量热量计上进行[15]. 测试前, 催化剂在 H_2 中于 650 °C 原位还原 1 h. 催化剂的透射电镜 (TEM) 表征在 JEM-2000EX 型透射电子显微镜上进行. 纤维素催化转化反应在 100 ml 不锈钢高压釜 (Parr 仪器公司) 中进行. 加入 0.5 g 微晶纤维素、0.15 g 催化剂和 50 ml 去离子水, 搅拌速率为 1 000 r/min, H_2 初始压力为 6 MPa (室温下) . 在 245 °C 反应 30 min. 反应后液体产物用液相色谱仪分析. 有机总碳由 Elementar Liqui TOC 型总碳测定仪测定. 反应前后催化剂上金属流失量由 IRIS Intrepid Ⅱ XSP 型电感耦合等离子体发射光谱仪测得. 气相产物由气相色谱仪分析. 反应转化率由反应前后纤维素质量变化求得[5,8]. 产物收率以反应产物与投入釜内纤维素的各自 C 的摩尔比计算[12].

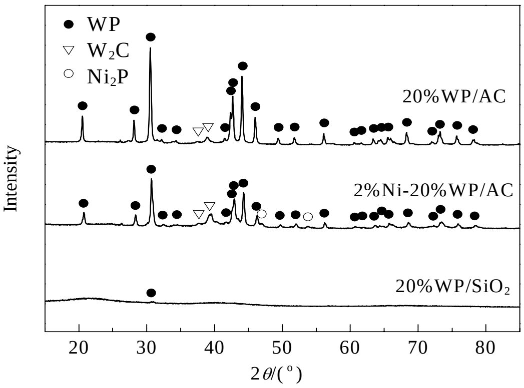

图 1 不同磷化钨催化剂的 XRD 谱

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

图 1 为不同磷化钨催化剂的 XRD 谱. 由图可见, 20%WP/AC 催化剂上出现典型的 WP 特征峰以及少量的 W_2C 晶相. 这是由于在 WP 高温还原制备过程中, 炭载体的碳热还原作用使催化剂中形成了 W_2C 物相. 而在 20%WP/SiO_2 催化剂上, 只观察到一个很微弱的 WP 特征峰, 这可能是由于 WP 高度分散于 SiO_2 载体上. CO 化学吸附实验表明, 20%WP/SiO_2 上的 CO 吸附量为 18.3 μmol/g, 而 20%WP/AC 上仅为 8.3 μmol/g. 这进一步表明前者的活性组分分散度更高. TEM 结果 (未示出) 表明, WP/SiO_2 样品的 WP 粒径明显小于 WP/AC. 2%Ni-20%WP/AC 催化剂主要晶相仍为 WP, 同时还存在少量的 W_2C 和 Ni_2P 物相.

各催化剂纤维素催化转化反应结果见表 1. 由表可见, 在各 WP 催化剂上, 纤维素反应 30 min 后均完全转化, 其中, 20%WP/AC 催化剂上所得的各种多元醇产物中, EG 的收率最高, 为 25.4 mol%, 而六元醇收率则仅为 2.3 mol%. 这与我们早前报道的纤维素在 W_2C/AC 催化剂上反应结果十分类似[8,9].

表 1 不同催化剂上纤维素的转化率及多元醇的产率

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.

由于 20%WP/AC 催化剂制备过程中载体 AC 的碳热还原作用而使催化剂中出现少量 W_2C, 这可能对 EG 的生成起到重要的催化作用. 为排除这种影响, 本文考察了 20%WP/SiO_2 催化剂的反应性能. 结果显示, 该催化剂性能与 WP/AC 非常类似, 纤维素主要转化为 EG, 收率为 25.0 mol%. 这表明 WP 确实可直接催化纤维素转化为 EG. 相比于我们最近所报道的磷化镍催化剂[12], 两者虽然同样是磷化物, 但在纤维素转化反应中生成的产物却明显不同. 纤维素在磷化镍催化剂上高选择性地生成山梨醇, 收率达 48.4 mol%, 而在 WP 催化剂上得到的主要是小分子产物 EG. 结合我们前期对 W_2C 以及金属 W 催化剂上纤维素催化转化的研究结果[8~11], 我们认为, WP 催化剂不仅在纤维素降解转化过程中具有催化加氢作用, 同时催化剂中 W 物种的存在对反应物分子内 C–C 键的断裂具有重要的催化作用.

气相产物分析结果显示, WP 催化剂上纤维素能够转化生成很少量的 CO 和 CO_2, 但未检测到烃类产物. 通过液体产物中的有机总碳量计算纤维素转化率为 80%~90%, 造成反应后出现 10%~20% 碳损失的原因尚不清楚.

通过循环反应考察了 20%WP/AC 催化剂的稳定性. 结果表明, 循环使用 3 次后, 乙二醇收率由 25.4 mol% 降至 17.4 mol%. 图 2 为反应后催化剂的 XRD 谱. 由图可知, 使用 3 次后, 虽然 WP 衍射峰强度略有下降, 但其晶相仍保持良好, 没有检测到氧化钨. 另一方面, 反应后催化剂的 CO 吸附量由 8.3 μmol/g 降为 6.4 μmol/g. 液体反应产物中 W 元素的 ICP 测定结果显示, 反应过程中催化剂中的 W 流失了 5.2 wt%. 因而, 我们推测, 催化剂活性的下降与 W 的流失有很大的关系. 另外, 催化剂表面的部分氧化也可能是失活原因之一.

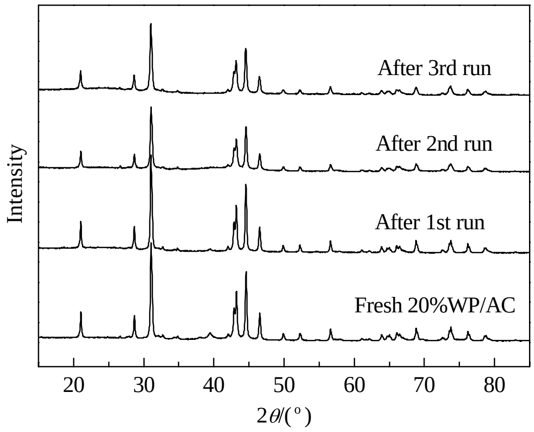

图 2　新鲜和循环反应后的 20%WP/AC 催化剂 XRD 谱

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

在纤维素转化为多元醇的过程中, 催化剂的加氢能力至关重要[10,11]. 因此, 本文利用 Ni 来修饰 WP 催化剂, 以形成更多的加氢活性中心. CO 化学吸附测量结果显示, Ni 的添加使得 20%WP/AC 催化剂上 CO 吸附量由 8.3 μmol/g 增至 11.9 μmol/g. 纤维素催化转化反应结果表明, Ni 的添加使得催化剂上 EG 产率显著增至 46.0 mol%. 当将 10%Ni/AC 和 20%WP/AC 机械混合后用于反应时, EG 产率虽然较两种催化剂单独使用时有所提高, 但远低于 2%Ni-20%WP/AC 催化剂. 这表明, Ni 和 W 间存在显著的协同作用. 一方面, W 物种的存在使纤维素发生选择性 C–C 断裂而降解为小分子的 C_2 不饱和化合物; 另一方面, WP 自身以及 Ni 等催化加氢活性中心催化不饱和分子加氢反应生成 EG. 因此, 可以通过适宜的加氢组分修饰或借助新的制备方法, 调变催化剂上两种催化能力的相对强弱, 使 WP 催化剂在纤维素催化转化为 EG 的反应中表现出更好的催化性能.

WP 催化剂在催化纤维素转化制 EG 的反应中表现出了良好的性能, 在 Ni 的促进下, EG 产率可以增至 46.0 mol%. 与 W_2C 催化剂相类似, WP 催化剂中同样存在两种催化中心的协同作用. Ni 作为催化加氢助剂可显著提高 EG 产率. 该结果有助于加深理解含 W 催化剂中 W 在纤维素转化成乙二醇反应中的作用, 同时为发展新型廉价的生物质转化催化剂提供有益的参考.

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英译文

English Text

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 °C for 12 h, and reduction with a procedure in which the sample was heated from room temperature to 350 °C at a rate of 5.5 °C/min, then to 850 °C at a rate of 1 °C/min, and kept at 850 °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 °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 °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 °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 a 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 20%WP/SiO_2 was smaller than on 20%WP/AC. On the 2%Ni-20%WP/AC catalyst, the main phase was still WP, with small amounts of W_2C and Ni_2P.

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_2C/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 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 C_2 unsaturated 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 of 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.

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