介孔氧化钨负载 Pt 催化剂上甘油氢解制备 1,3-丙二醇

刘龙杰^{1,2}, 张艳华¹, 王爱琴¹, 张涛^{1,*}¹ 中国科学院大连化学物理研究所, 辽宁大连 116023² 中国科学院研究生院, 北京 100049

摘要: 采用蒸发诱导自组装法制备了介孔氧化钨 (m-WO₃), 负载 Pt 后应用于催化甘油氢解制 1,3-丙二醇。结果表明, 与商业氧化钨 (c-WO₃) 相比, m-WO₃ 具有高比表面积和易还原的优点, 从而使得 Pt 纳米粒子高度分散于其上。在 180 °C 和 5.5 MPa H₂ 下反应 12 h, Pt/m-WO₃ 催化剂上甘油转化率和 1,3-丙二醇的选择性分别为 18.0% 和 39.2%, 明显高于 Pt/c-WO₃ 催化剂。

关键词: 介孔氧化钨; 铂; 甘油; 氢解; 1,3-丙二醇

中图分类号: O643 **文献标识码:** A

收稿日期: 2012-05-09. 接受日期: 2012-06-12.

*通讯联系人. 电话: (0411)84379015; 电子信箱: taozhang@dicp.ac.cn

基金来源: 国家自然科学基金 (21176235).

本文的英文电子版(国际版)由 Elsevier 出版社在 ScienceDirect 上出版(<http://www.sciencedirect.com/science/journal/18722067>).

Mesoporous WO₃ Supported Pt Catalyst for Hydrogenolysis of Glycerol to 1,3-PropanediolLIU Longjie^{1,2}, ZHANG Yanhua¹, WANG Aiqin¹, ZHANG Tao^{1,*}¹ Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China² Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Mesoporous tungsten trioxide (m-WO₃) was prepared using an evaporation-induced self-assembly method and was used as the support of Pt for hydrogenolysis of glycerol to produce 1,3-propanediol. In comparison with commercial WO₃, the m-WO₃ presents a much larger surface area and better reducibility, which make the Pt particles highly dispersed on the support. At a reaction condition of 180 °C, 5.5 MPa H₂, and reaction time of 12 h, the Pt/m-WO₃ catalyst afforded 18.0% conversion of glycerol and 39.2% selectivity for 1,3-propanediol, both of which are much higher than those on commercial Pt/WO₃ catalyst.

Key words: mesoporous tungsten trioxide; platinum; glycerol; hydrogenolysis; 1,3-propanediol

Received 9 May 2012. Accepted 12 June 2012.

*Corresponding author. Tel: +86-411-84379015; E-mail: taozhang@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (21176235).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

随着生物柴油的日益推广, 其生产过程中产生的副产物甘油大量过剩 (每生产 1 吨生物柴油副产 100 千克甘油)^[1]. 由甘油制备高附加值化学品, 可以增长生物柴油的产业链, 提高其产业经济性. 甘油转化有多种途径, 如氧化生成甘油酸和二羟基丙酮^[2,3], 脱水生成丙烯醛^[4], 氢解生成二元醇^[5~7], 以及水汽重整制备合成气^[8]等. 其中甘油选择性氢解制

备 1,3-丙二醇 (1,3-PDO) 广受关注^[7,9~17]. 1,3-PDO 是生产聚酯材料聚对苯二甲酸丙二醇酯 (PTT) 的单体, 随着 PTT 的发展, 其需求不断增加. 早期报道在均相催化剂, 如铑、钨和钼等贵金属的络合物作用下, 可以将甘油选择氢解生成 1,3-PDO^[18~20]. 由于均相催化剂分离难, 近年来, 人们普遍研究采用多相催化剂.

Chaminand 等^[9]报道了在 Rh/C 和 H_2WO_4 催化剂共同作用下, 以环丁砜为溶剂, 在 $180\text{ }^\circ\text{C}$ 和 8 MPa 氢气压力下反应 168 h , 1,3-PDO 的收率为 4%, 1,3-PDO 与 1,2-丙二醇的摩尔比为 2. Kurosaka 等^[10]以 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 为催化剂, 1,3-二甲基-2-咪唑啉酮 (DMI) 为溶剂, 在 $170\text{ }^\circ\text{C}$ 和 8 MPa 氢气压力下反应 18 h , 甘油氢解产物中 1,3-PDO/1,2-丙二醇的摩尔比为 2, 1,3-PDO 收率为 24%. Qin 等^[14]在固定床反应器上, 采用相同的 $\text{Pt}/\text{WO}_3/\text{ZrO}_2$ 催化剂, 得到 1,3-PDO 的收率为 32%, 1,3-PDO/1,2-丙二醇的摩尔比为 17.7. 龚磊峰等^[11]研究了 $\text{Pt}/\text{WO}_3/\text{TiO}_2/\text{SiO}_2$ 催化剂上甘油氢解反应性能, 1,3-PDO 收率为 7.7%, 1,3-PDO/1,2-丙二醇的摩尔比为 5. Zhu 等^[17]在固定床反应器上, 优化反应条件, 在 $\text{Pt-HSiW}/\text{SiO}_2$ 催化剂上甘油氢解生成 1,3-PDO 收率为 31.4%. 综上所述, WO_3 有可能是催化剂高选择性催化甘油氢解生成 1,3-PDO 不可缺少的组成部分. 因此, 为了研究氧化钨物种对生成 1,3-PDO 的关键作用, 本文制备了介孔氧化钨 (m-WO_3), 负载 Pt 后, 首次用于甘油氢解反应中.

以六氯化钨为前驱体, 嵌段共聚物 $\text{P123}(\text{EO}_{20}\text{PO}_{70}\text{EO}_{20})$ 为结构导向剂, 采用溶剂蒸发诱导自组装法制备 m-WO_3 ^[21]. 模板剂在 $500\text{ }^\circ\text{C}$ 焙烧 1 h 去除得到 m-WO_3 . 将所得的 m-WO_3 等体积浸渍于氯铂酸溶液, 在 $400\text{ }^\circ\text{C}$ 空气气氛焙烧 1 h , $300\text{ }^\circ\text{C}$ 氢气气氛还原 1 h . 作为对比, 制得负载 Pt 的商业氧化钨 (c-WO_3) 催化剂. 上述催化剂中 Pt 负载量均为 2%. 图 1 为 m-WO_3 和 c-WO_3 的 N_2 吸附-

脱附等温线和孔分布曲线. 由图可见, m-WO_3 样品的吸附-脱附等温线为介孔材料特有的 IV 型, 在 $p/p_0 = 0.4\sim 0.9$ 范围内存在 H1 型滞后环, 且孔径分布主要集中在 4 和 7 nm ; 而 c-WO_3 样品的吸附-脱附等温线未出现介孔材料特有的滞后环, 且具有非常广的孔径分布. 测得 m-WO_3 的比表面积为 $22\text{ m}^2/\text{g}$, 是 c-WO_3 的 2 倍多.

图 2 是 $\text{Pt}/\text{m-WO}_3$ 和 $\text{Pt}/\text{c-WO}_3$ 催化剂经 H_2 还原后的 XRD 谱, 由图可见, 各样品均出现 WO_3 (PDF 20-1324) 和 $\text{H}_{0.53}\text{WO}_3$ (PDF 72-1712) 两种晶相, 说明氧化钨在 Pt 的促进作用下部分还原为低价态 WO_x ^[22,23]. 另外, $\text{Pt}/\text{c-WO}_3$ 上还出现微弱的 Pt 衍射峰 ($2\theta = 39.8^\circ$), 而 $\text{Pt}/\text{m-WO}_3$ 上没有, 说明负载在 c-WO_3 上的 Pt 粒子较大. 图 3 为上述两种样品的

图 2 催化剂 $\text{Pt}/\text{c-WO}_3$ 和 $\text{Pt}/\text{m-WO}_3$ 经还原后的 XRD 谱
Fig. 2. XRD patterns of $\text{Pt}/\text{c-WO}_3$ (1) and $\text{Pt}/\text{m-WO}_3$ (2) after reduction.

图 1 不同 WO_3 样品的 N_2 吸附-脱附等温线和孔分布曲线

Fig. 1. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) for different WO_3 samples.

图3 催化剂 Pt/c-WO₃ 和 Pt/m-WO₃ 的 TEM 照片Fig. 3. TEM images of Pt/m-WO₃ (a) and Pt/c-WO₃ (b).

TEM 照片. 可以看出, m-WO₃ 上 Pt 粒子小于 5 nm, 而 Pt/c-WO₃ 上的为 10~30 nm. 这可能是由于 m-WO₃ 具有较高的比表面积所致. 此外, m-WO₃ 样品平均粒径为 30 nm 左右的球形.

本文考察了 Pt/c-WO₃ 和 Pt/m-WO₃ 催化剂上甘油氢解制备 1,3-PDO 的反应性能. 反应条件为 180 °C, H₂ 压力 5.5 MPa, 催化剂与甘油质量比为 1/4, 反应时间 12 h. 液相产物主要包括 1,3-PDO、1,2-丙二醇、正丙醇和异丙醇, 同时含有少量的乙二醇、乙醇和甲醇. 气相产物主要包括过度氢解产物甲烷、乙烷和丙烷, 具体反应结果见表 1, 可以看出, Pt/m-WO₃ 催化剂上甘油转化率和 1,3-PDO 选择性分别为 18% 和 39.3%, 1,3-PDO 与 1,2-丙二醇的摩尔比高达 9.6, 均远高于 Pt/c-WO₃ 催化剂.

表 1 催化剂 Pt/m-WO₃ 和 Pt/c-WO₃ 上甘油氢解反应性能
Table 1 Hydrogenolysis of glycerol over Pt/m-WO₃ and Pt/c-WO₃ catalysts

Catalyst	Conversion (%)	Selectivity (%)				1,3-PDO/1,2-PDO
		2-PrOH	1-PrOH	1,2-PDO	1,3-PDO	
Pt/m-WO ₃	18.0	7.1	33.8	4.1	39.3	9.6
Pt/c-WO ₃	4.5	12.6	23.6	14.1	29.9	2.1

Reaction conditions: 40 g of 10 wt% glycerol aqueous solution, catalyst 1.0 g, initial H₂ pressure 5.5 MPa, 180 °C, 12 h. 2-PrOH: 2-propanol; 1-PrOH: 1-propanol; 1,2-PDO: 1,2-propanediol; 1,3-PDO: 1,3-propanediol.

研究表明^[14,15], H⁺和 H⁻的转移可以催化甘油转化为 1,3-PDO. 而 H₂ 解离形成 H⁺和 H⁻的能力决定于 Pt 分散度和载体氧化钨的还原性. 图 4 给出了两种载体及其负载 Pt 催化剂的 H₂-TPR 谱, 由图可见, m-WO₃ 比 c-WO₃ 更易还原为低价态. UV-Vis 结果表明 (图 5), m-WO₃ 在 600~900 nm 区吸收比 c-WO₃ 大, 说明前者具有更多的氧空位^[24], 这也是它

图4 不同 WO₃ 载体和 Pt/WO₃ 的 TPR 谱Fig. 4. TPR profiles of different WO₃ supports and Pt/WO₃. 图5 不同 WO₃ 载体的紫外-可见光谱Fig. 5. UV-Vis spectra of different WO₃.

易于还原的原因. 负载 Pt 后, WO₃ 在 200 °C 便开始还原, 由于 Pt 在 m-WO₃ 上高度分散, Pt⁴⁺还原为 Pt⁰ 的温度比在 c-WO₃ 上的低. 催化剂上高分散的 Pt 和易还原的 m-WO₃ 有利于生成 H⁺和 H⁻. 生成的 H⁻进攻仲位羟基生成 3-羟基丙醇盐负碳离子, H⁺进攻负碳离子形成 1,3-PDO (见图式 1). Pt 与 m-WO₃ 之间的强相互作用促进了 H₂ 解离形成 H⁺和 H⁻, 因

图式 1 H₂ 极性解离生成 1,3-PDO 的反应机理

Scheme 1. Proposed mechanism for 1,3-PDO formation via heterolytic dissociation of H₂.

此活性和选择性升高。

综上所述, 本文制备了 m-WO₃ 担载 Pt 催化剂, 并首次应用于甘油氢解制备 1,3-PDO 反应中。结果表明, 该催化剂表现出优异的活性和 1,3-PDO 的选择性, 可归结为催化剂上高分散的 Pt 和易还原的氧化钨所致。与其他含钨的混合氧化物相比, 该催化剂将是研究甘油氢解制 1,3-PDO 反应中 Pt 与 WO₃ 协同作用的模型催化剂。

参 考 文 献

- 1 Pagliaro M, Ciriminna R, Kimura H, Rossi M, Della Pina C. *Angew Chem Int Ed Engl*, 2007, **46**: 4434
- 2 Hu W B, Lowry B, Varma A. *Appl Catal B*, 2011, **106**: 123
- 3 Bianchi C L, Canton P, Dimitratos N, Porta F, Prati L. *Catal Today*, 2005, **102-103**: 203
- 4 Kraveva E, Palcheva R, Dimitrov L, Armbruster U, Brückner A, Spojakina A. *J Mater Sci*, 2011, **46**: 7160
- 5 冯建, 熊伟, 贾云, 王金波, 刘德蓉, 陈华, 李贤均. 催化学报 (Feng J, Xiong W, Jia Y, Wang J B, Liu D R, Chen H, Li X J. *Chin J Catal*), 2011, **32**: 1545
- 6 Li B D, Wang J, Yuan Y Z, Ariga H, Takakusagi S, Asakura K. *ACS Catal*, 2011, **1**: 1521
- 7 Nakagawa Y, Shinmi Y, Koso S, Tomishige K. *J Catal*, 2010, **272**: 191
- 8 Luo N-J, Wang J-A, Xiao T-C, Cao F-H, Fang D-Y. *Catal Today*, 2011, **166**: 123
- 9 Chaminand J, Djakovitch L, Gallezot P, Marion P, Pinel C, Rosier C. *Green Chem*, 2004, **6**: 359
- 10 Kurosaka T, Maruyama H, Naribayashi I, Sasaki Y. *Catal Commun*, 2008, **9**: 1360
- 11 龚磊峰, 吕元, 丁云杰, 林荣和, 李经纬, 董文达, 王涛, 陈维苗. 催化学报 (Gong L F, Lü Y, Ding Y J, Lin R H, Li J W, Dong W D, Wang T, Chen W M. *Chin J Catal*), 2009, **30**: 1189
- 12 Daniel O M, DeLaRiva A, Kunkes E L, Datye A K, Dumesic J A, Davis R J. *ChemCatChem*, 2010, **2**: 1107
- 13 Gong L, Lu Y, Ding Y, Lin R, Li J, Dong W, Wang T, Chen W. *Appl Catal A*, 2010, **390**: 119
- 14 Qin L-Z, Song M-J, Chen C-L. *Green Chem*, 2010, **12**: 1466
- 15 Amada Y, Shinmi Y, Koso S, Kubota T, Nakagawa Y, Tomishige K. *Appl Catal B*, 2011, **105**: 117
- 16 Oh J, Dash S, Lee H. *Green Chem*, 2011, **13**: 2004
- 17 Zhu S, Zhu Y, Hao S, Chen L, Zhang B, Li Y. *Catal Lett*, 2011, **142**: 267
- 18 Che T M. US4642394-A. 1987
- 19 Drent E, Jager W W. US6080898-A. 2000
- 20 Schlaf M, Ghosh P, Fagan P J, Hauptman E, Bullock R M. *Angew Chem, Int Ed*, 2001, **40**: 3887
- 21 Yang P, Zhao D, Margolese D I, Chmelka B F, Stucky G D. *Chem Mater*, 1999, **11**: 2813
- 22 Hadjiivanov K, Lukinskas P, Knözinger H. *Catal Lett*, 2002,

82: 73

- 23 Bigey C, Hilaire L, Maire G. *J Catal*, 1999, **184**: 406
- 24 Xi G, Ye J, Ma Q, Su N, Bai H, Wang C. *J Am Chem Soc*, 2012, **134**: 6508

英 译 文

English Text

As the increasing production and application of biodiesel, there is a large surplus of glycerol produced as a byproduct (100 kg glycerol is formed for production of 1 tonne biodiesel) during the transesterification of seed oil with methanol [1]. Transformation of glycerol into value-added chemicals can greatly improve economic viability of biodiesel manufacture and supply chain. Various catalytic transformation pathways have been developed for glycerol utilization, such as oxidation to form glyceric acid and dihydroxyacetone [2,3], dehydration to form acrolein [4], hydrogenolysis to form diols [5–7], as well as steam reforming to produce H₂ and syngas [8]. Among them, the selective production of high-value 1,3-propanediol (1,3-PDO) via hydrogenolysis of glycerol has attracted a great deal of attention from both academic and industrial societies due to the increasing demand of 1,3-PDO for the manufacture of polytrimethylene terephthalate (PTT) [7,9–17]. Although some homogeneous complexes of noble metals such as Rh, Pd, and Ru were found to be active and selective for the formation of 1,3-PDO from glycerol [18–20], the solid catalysts of these noble metals are more preferred owing to their easy recovering.

Various solid catalysts have been developed towards the selective production of 1,3-PDO from hydrogenolysis of glycerol. Chaminad et al. [9] showed that a catalyst combination of Rh/C and H₂WO₄ afforded 1,3-PDO in a yield of 4% and 1,3-PDO/1,2-PDO molar ratio of 2 from a sulfolane solution of glycerol at a reaction condition of 180 °C, 8 MPa, 168 h. Kurosaka et al. [10] employed Pt/WO₃/ZrO₂ as the catalyst and DMI (1,3-dimethyl-2-imidazolidinone) as the solvent to conduct the reaction, and they obtained 1,3-PDO in a yield of 24% and 1,3-PDO/1,2-PDO molar ratio of about 2 under the reaction condition of 170 °C, 8 MPa H₂, and 18 h. Also with the Pt/WO₃/ZrO₂ catalyst, Qin et al. [14] reported a higher yield of 1,3-PDO (32%) and a higher 1,3-PDO/1,2-PDO molar ratio (17.7) using a fixed-bed continuous flow reactor. Gong et al. [11] investigated the performance of Pt/WO₃/TiO₂/SiO₂ in this reaction and obtained 1,3-PDO in a yield of 7.7% and 1,3-PDO/1,2-PDO molar ratio of 5. With optimized Pt-HSiW/SiO₂ catalyst, Zhu et al. [17] obtained 1,3-PDO in a yield of 31.4%. These studies reveal an interesting phenomenon, i.e., tungsten seems to be an indispensable component in various catalyst formulations for achieving a high selectivity for 1,3-PDO. In order to

understand the crucial role of tungsten oxide in the selective production of 1,3-PDO from glycerol hydrogenolysis, we prepared mesoporous tungsten trioxide (m-WO₃) and then deposited Pt on it. The result showed that our Pt/m-WO₃ catalyst was very active and selective for the formation of 1,3-PDO. Under optimal conditions, the selectivity for 1,3-PDO was 39.3% and 1,3-PDO/1,2-PDO molar ratio was as high as 9.6 at the glycerol conversion of 18.0%. To the best of our knowledge, this is the first report that mesoporous WO₃ has been successfully used as the catalyst support for 1,3-PDO production from glycerol.

Mesoporous WO₃ was prepared with an evaporation-induced self-assembly method (EISA) using WCl₆ as the precursor and triblock P123 (EO₂₀PO₇₀EO₂₀) as the structure-directing agent, according to Yang et al. [21]. The m-WO₃ was obtained by calcination of the as-prepared material at 500 °C for 1 h. Pt/m-WO₃ was prepared by incipient wetness impregnation of m-WO₃ with H₂PtCl₆ followed by calcination in air at 400 °C for 1 h and reduction in H₂ at 300 °C for 1 h. For comparison, commercial WO₃ (denoted as c-WO₃) was also employed as the support of Pt. The Pt loading was fixed at 2 wt%. Figure 1 presents the N₂ adsorption-desorption isotherms and pore size distributions of two different WO₃ materials. The m-WO₃ shows a type IV isotherm with a sharp capillary condensation step at $p/p_0 = 0.4\text{--}0.9$ and a well-defined H1-type hysteresis loop, which is characteristic of mesoporous material. It has a bimodal pore size distribution centered at 4 and 7 nm, respectively. On the other hand, the c-WO₃ presents a very broad pore size distribution. The m-WO₃ has a BET surface area of 22 m²/g which is more than twice larger than that of c-WO₃ (9 m²/g).

Figure 2 shows the XRD patterns of Pt/m-WO₃ and Pt/c-WO₃ after H₂-reduction, both of them are composed of two phases: WO₃ (PDF 20-1324) and H_{0.53}WO₃ (PDF 72-1712), indicating WO₃ has been partially reduced with the promotion of Pt [22,23]. In addition, metallic Pt phase is also visible and more prominent in the Pt/c-WO₃, indicating a larger Pt particle size in the latter catalyst. The TEM images in Fig. 3 clearly show the Pt particles in the Pt/m-WO₃ are smaller than 5 nm while they are 10–30 nm in the Pt/c-WO₃ catalyst. Moreover, the m-WO₃ presents a spherical morphology with an average particle size of ~ 30 nm. The smaller Pt particle size in the Pt/m-WO₃ can be attributed to the large surface area of m-WO₃.

The catalytic performance of the two catalysts was investigated for the hydrogenolysis of glycerol, under the reaction condition of 180 °C, 5.5 MPa H₂, 12 h, and a catalyst/glycerol mass ratio of 1:4. The liquid products include 1,3-PDO, 1,2-PDO, 1-propanol, 2-propanol, and a small amount of

ethylene glycol, ethanol and methanol, while the gas products are CH₄, C₂H₆, and C₃H₈ which are formed by excessive hydrogenolysis. For clarity, table 1 only lists the major products. Although the two catalysts are selective for the formation of 1,3-PDO, the Pt/m-WO₃ is much more active and selective. The glycerol conversion on the Pt/m-WO₃ reached 18.0% and the selectivity for 1,3-PDO was 39.3%. In particular, the molar ratio of 1,3-PDO to 1,2-PDO was as high as 9.6, which is more than 4 times that over the Pt/c-WO₃.

It was reported that proton and hydride transfer are involved in the formation of 1,3-PDO from glycerol [14,15]. The ability for H₂ heterolytic dissociation into proton and hydride ion depends both on the dispersion of Pt and on the reducibility of WO₃ support. The H₂-TPR (temperature-programmed reduction) profiles of the two supports before and after loading of Pt are shown in Fig. 4. It indicates clearly that the m-WO₃ is much easier to reduce than the c-WO₃ support. The UV-Vis spectrum (Fig. 5) of the m-WO₃ presents a wide absorption band in the range of 600–900 nm which can be ascribed to the presence of oxygen vacancies [24]. The similar absorption band is not found in the c-WO₃. Therefore, the presence of a large number of oxygen vacancies is probably responsible for the easy reduction of m-WO₃. After deposition of Pt, the reduction of both WO₃ supports is promoted further, but the reduction of Pt⁴⁺ to Pt⁰ occurs at a lower temperature for the Pt/m-WO₃ due to the high dispersion of Pt on the m-WO₃ support. The high dispersion of Pt and the reducibility of m-WO₃ will make it easier to form proton and hydride via heterolytic dissociation of H₂ followed by spillover to the support. Upon formation of hydride (H[−]), it will attack the 2-position of the alkoxide to break the C–O bond and form the 3-hydroxypropoxide carbanion, which is subsequently attacked by proton (H⁺) to form 1,3-PDO (Scheme 1). The strong interaction between Pt and mesoporous WO₃ facilitates the heterolytic dissociation of H₂, with which both the activity for glycerol hydrogenolysis and selectivity for 1,3-PDO are enhanced.

In conclusion, we have developed for the first time the mesoporous WO₃ supported Pt catalyst which is highly active and selective for the production of 1,3-PDO from glycerol hydrogenolysis. The high dispersion of Pt and the good reducibility of mesoporous WO₃ contribute together to the excellent performance of Pt/m-WO₃. In comparison with other W-containing mixed oxides supports, the present catalyst will be a good model to study the synergistic effect of Pt and WO₃ in the hydrogenolysis of glycerol to 1,3-PDO.

Full-text paper available online at Elsevier ScienceDirect
<http://www.sciencedirect.com/science/journal/18722067>