介孔碳负载的 Pd 催化剂催化 β -谷甾醇加氢制备 β -谷甾烷醇

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摘要: 采用液相还原法制备了介孔碳 (CMC) 负载的 Pd 催化剂, 用于 β -谷甾醇加氢制备 β -谷甾烷醇反应. 与活性炭负载的 Pd 催化剂相比, Pd/CMC 的活性更高, 这归因于该催化剂具有较大的孔径, 从而有利于较大分子的催化加氢反应.

关键词: 钯; 活性炭; 负载型催化剂; 介孔碳; 孔径效应; 微量吸附量热; β -谷甾醇; 加氢; β -谷甾烷醇

中图分类号: O643 **文献标识码:** A

收稿日期: 2011-09-06. 接受日期: 2011-10-19.

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基金来源: 国家自然科学基金 (21073089); 国家重点基础研究发展计划 (973 计划, 2005CB221400); 江苏省工业支撑项目 (BE2009145); 中央高校基本科研业务费专项资金.

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 Carbon Supported Pd Catalysts for the Hydrogenation of β -Sitosterol to β -Sitostanol

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Abstract: Supported palladium catalysts on mesoporous carbons (CMC) were prepared by liquid phase reduction and used for the hydrogenation of β -sitosterol to β -sitostanol. Compared to Pd/AC (active carbon), the Pd/CMC catalysts showed significantly higher activity for the hydrogenation of large molecules due to their larger pore size.

Key words: palladium; active carbon; supported catalyst; mesoporous carbon; pore size effect; microcalorimetric adsorption; β -sitosterol; hydrogenation; β -sitostanol

Received 6 September 2011. Accepted 19 October 2011.

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This work was supported by the National Natural Science Foundation of China (21073089), the National Basic Research Program of China (973 Program, 2005CB221400), the Industrial Supporting Project of Jiangsu Province (BE2009145), and the Fundamental Research Funds for Central Universities.

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

胆固醇过高严重威胁人类健康. 相比药物治疗, 膳食疗法更具有吸引力. 研究发现, 天然植物甾醇及其饱和形式甾烷醇能有效降低人体的胆固醇水平, 并可用作功能性食品添加剂^[1~3]. 它们可抑制小肠对胆固醇的吸收, 而其本身则极少被人体吸收^[4]. 人类已经发现超过 40 种植物甾醇, 其中以 β -谷甾醇最为常见, 其饱和形式 β -谷甾烷醇在抑制胆固醇吸收方面更加有效^[5,6], 此外, β -谷甾烷醇具有更好的

抗氧化性能, 不易转化为对人体有害的固醇物质^[7].

但天然存在的 β -谷甾烷醇很少, 需要通过 β -谷甾醇加氢制得. 研究发现, Ni 催化剂并不适于甾醇的选择加氢反应, 负载的 Pd 或 Pt 催化剂则表现出优良的催化性能^[8,9]. 碳材料^[8,10~12]、嫁接高分子化合物^[8,13]以及氧化铝^[9]等都是常用的载体. Pd/C 催化剂用于甾醇酯加氢为甾烷醇酯已见诸报道^[14].

由于 β -谷甾醇分子较大, 因而孔径较大的催化

剂更为适用. 近期研究发现, 与活性碳 (AC) 担载的 Pd 催化剂相比, 介孔碳材料担载的 Pd 催化剂在 β -谷甾醇加氢反应中表现出更高的活性和稳定性^[3].

本课题组开发了一种介孔碳 (CMC) 的制备方法^[15], 所制样品比表面积、孔径和孔体积都较大. 本文以 CMC 为载体, 制备了 Pd/CMC 催化剂, 用于 β -谷甾醇加氢制备 β -谷甾醇反应.

本文所用介孔碳有 CMC (20~40 目)、CMC-200 (200 目) 以及 CMC-200-NA (CMC-200 经浓硝酸处理). 将不同的 CMC 浸润在适量水中, 形成悬浮液, 在不断搅拌的同时, 加入 H_2PdCl_4 水溶液. 用 NaOH 溶液调节悬浮液的 $pH \approx 12$, 加入过量的甲醛水溶液将钯还原为金属, 过滤、洗涤干净后, 即得 Pd/CMC 催化剂, 其中 Pd 的质量含量为 5%. 为了比较, 采用同样方法制备了 Pd/AC 催化剂, 其中 AC 为商用载体 (200 目).

图 1 为 393 K 干燥后碳载体和 Pd/C 催化剂的 XRD 谱. 可以看出, Pd/CMC 样品在 $2\theta = 40.0^\circ$, 46.5° 和 67.7° 处出现衍射峰, 归属于 FCC 金属 Pd (JCPDS 89-4897), 表明该催化剂中 Pd 分散度较差. 而在其他催化剂中未见 Pd 衍射峰, 表明 Pd 在这些催化剂上分散度较高.

图 1 经 393 K 干燥后碳载体和 Pd 催化剂的 XRD 谱

Fig. 1. XRD patterns of carbon supports and supported Pd catalysts dried at 393 K.

表 1 为 393 K 干燥后碳载体和 Pd/C 催化剂的比表面积和孔结构性质. 由表可见, CMC 的孔体积和孔径明显大于 AC. Pd/AC 催化剂主要是微孔结构, 而 Pd/CMC 主要由介孔孔道组成. 另外, 担载金属 Pd 后, 各碳载体的比表面积降低并不大.

表 1 经 393 K 干燥后碳载体及 Pd/C 催化剂的比表面积和孔结构性质

Table 1 Surface area and pore properties of carbon supports and supported Pd catalysts

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Most probable pore size (nm)
AC	1217	0.5	2.6	—
Pd/AC	1128	0.5	2.5	—
CMC	1532	2.2	5.3	6.4
Pd/CMC	1534	2.1	4.9	6.0
CMC-200	1644	2.4	5.3	6.5
Pd/CMC-200	1222	1.6	4.7	5.8
CMC-200-NA	1441	2.0	5.0	5.8
Pd/CMC-200-NA	1339	1.8	5.0	6.1

为了测定催化剂表面金属 Pd 原子的数目, 在室温下进行了 CO 吸附实验, 并假设吸附 CO 与表面金属 Pd 原子的化学计量比为 $CO/Pd = 1$. 根据 CO 吸附量, 还可以计算催化剂的活性金属表面积、金属分散度及其平均粒径, 相关结果见表 2. 由表可见, Pd 在 CMC 上的分散度较低 (18.6%), 表明该催化剂中 Pd 粒径较大, 与 XRD 结果一致. Pd/CMC-200 中金属 Pd 分散度为 27.7%, 而 Pd/AC 和 Pd/CMC-200-40NA 中的相近, 达到 43% 以上. 一般地, 通过 CO 吸附滴定测得的表面 Pd 原子数量决定了催化剂在加氢反应中的催化活性. 还可以看出, 降低载体的颗粒度 (CMC-200) 以及对其进行表面硝酸处理 (CMC-200-NA) 提高了相应催化剂上金属 Pd 的分散度. 硝酸处理可以增加碳载体表面含氧官能团的数量, 从而有利于金属 Pd 的分散^[16].

催化剂表面金属 Pd 的化学性质还可能受载体的影响. 通过 CO 的微吸附量热技术可以了解金属

表 2 各 Pd/C 催化剂上 CO 室温吸附及催化 β -谷甾醇加氢反应结果

Table 2 Results for the adsorption of CO at 298 K and the hydrogenation of β -sitosterol to β -sitostanol on the supported Pd catalysts

Catalyst	CO uptake ($\mu mol/g$)	Pd surface area ^a ($m^2/g-Pd$)	Pd dispersion ^a (%)	Pd diameter ^a (nm)	X_s^b (%)
Pd/AC	208	197	44.3	2.5	39.1
Pd/CMC	87	83	18.6	6.0	70.0
Pd/CMC-200	130	123	27.7	4.1	83.0
Pd/CMC-200-NA	203	192	43.1	2.6	93.8

^aCalculated according to the uptake of CO. ^bReaction conditions: 298 K, 0.5 MPa, 3 h, 0.1 g Pd catalyst, 1.0 g β -sitosterol, 50 ml solvent. X_s — β -sitosterol conversion.

表面的电子密度变化. 图 2 是 308 K 时 CO 在不同 Pd/C 催化剂上的吸附量热结果. 由图可见, 各样品上 CO 吸附量大小顺序为 $\text{Pd/AC} \approx \text{Pd/CMC-200-NA} > \text{Pd/CMC-200} > \text{Pd/CMC}$, 与表 2 结果一致. 然而, CO 在这些催化剂上的初始吸附热相近 (约为 100 kJ/mol), 表明在不同载体上的金属 Pd 的表面电子密度是相近的^[17], 也就是说, 本文所考察催化剂的表面金属 Pd 的化学性质并未受到载体的影响.

图 2 308 K 时 CO 在不同 Pd/C 催化剂上的吸附量热结果
Fig. 2. Differential heat versus adsorbate coverage for the adsorption of CO at 308 K on carbon supported Pd catalysts.

β -谷甾醇的催化加氢反应在 100 ml 微型反应釜中于室温进行, 异丙醇为溶剂, 反应压力为 0.5 MPa, 反应时间为 3 h. β -谷甾醇原料 (植物甾醇的总含量为 98.66%) 中含有 80.86% β -谷甾醇、13.58% 菜油甾醇以及 4.63% 菜籽甾醇. 反应结束后, 催化剂经过滤分离, 并用异丙醇洗涤, 然后将所有滤液收集归并, 通过 Agilent 1200 HPLC (XDB-C18 色谱柱, 示差折光检测器) 进行产物组成分析, 并计算甾醇转化率和甾醇选择性, 结果见表 2. 在所有 Pd/C 催化剂上, 甾醇为唯一产物. 结合表 2 可知, 尽管 Pd/CMC-200-NA 和 Pd/AC 的表面 Pd 原子数目相近, 但 Pd/CMC-200-NA 上 β -谷甾醇转化率远比在 Pd/AC 上的高. 然而, 根据 CO 吸附量热结果, Pd/CMC-200-NA 和 Pd/AC 催化剂的表面 Pd 原子数量和化学性质相似, 因此, 它们的活性差别可归因于孔径差别. 由于反应物分子较大, 因而孔径较大的 Pd/CMC-200-NA 催化剂活性较高, 而 Pd/AC 较小的孔道可能限制了 β -谷甾醇分子的扩散.

还可以看出, 对于 Pd/CMC 催化剂, β -谷甾醇转化率随着 Pd 分散度的增加而增加. 可见, 只要催化剂的孔道足够大, 表面金属 Pd 原子数目越多, 催化活性就越高. 但对于微孔的 Pd/AC 催化剂, 即使具有较多的表面 Pd 活性中心 (显著多于 Pd/CMC), 其活性反而远低于 Pd/CMC. 可见, 催化剂的孔径大小确实是决定 β -谷甾醇加氢活性的重要参数.

本文还发现, 反应温度对 β -谷甾醇转化率的影响较大, 而反应压力的影响较小. 提高反应温度可以减少催化剂用量, 缩短反应时间. 例如, 当反应在 343 K 和 0.5 MPa 的条件下进行时, 只需要使用 0.25% 的 Pd/CMC-200-NA 催化剂, 反应 1 h 后 β -谷甾醇转化率即可达到 96% 以上.

综上所述, 孔径和表面活性中心数目是决定 Pd/C 催化剂在较大分子 (如 β -谷甾醇) 加氢反应中活性的两个重要参数, CMC 具有较大的比表面积和孔径, 非常适合作为贵金属催化剂的载体, 用于较大分子的催化加氢反应.

参 考 文 献

- Hicks K B, Moreau R A. *Food Technol*, 2001, **55**: 63
- Jones P J H, Ntanos F Y, Raeini-Sarjaz M, Vanstone C A. *Am J Clin Nutr*, 1999, **69**: 1144
- Mäki-Arvela P, Martin G, Simakova I, Tokarev A, Wärnå J, Hemming J, Holmbom B, Salmi T, Murzin D Y. *Chem Eng J*, 2009, **154**: 45
- Wärnå J, Geant M F, Salmi T, Hamunen A, Orte J, Hartonen R, Murzin D Y. *Ind Eng Chem, Res*, 2006, **45**: 7067
- Jones P J H, Howell T, MacDougall D E, Feng J Y, Parsons W. *Metabolism*, 1998, **47**: 751
- Miettinen T A, Puska P, Gylling H, Vanhanen H, Vartiainen E. *N Engl J Med*, 1995, **333**: 1308
- Helminen J, Paatero E, Hotanen U. *Org Process Res Dev*, 2006, **10**: 51
- Helminen J, Hotanen U, Paatero E, Hautala M, Kärki A. US 6 147 235. 2000
- Michalson E T, Devore J D. US 6 673 951. 2004
- Lindroos M, Mäki-Arvela P, Kumar N, Salmi T, Murzin D Y, Ollonqvist T, Väyrynen J. In: Morrell D G ed. *Catalysis in Organic Reactions*, Chemical Industries. Vol 89. New York: Marcel Dekker, 2002. 587
- Wong A, Boguski W N. WO 00/59921. 2000
- Augustine R L, Reardon E J Jr. *Org Prep Proced Int*, 1969, **1**: 107
- Eklom J. WO 98/38206. 1998
- Van Amerongen M P, Lievens L C. US 6 106 886. 2000
- Huang Y, Hu S, Zuo S, Xu Z, Han C, Shen J. *J Mater*

Chem, 2009, **19**: 7759

- 16 Hermans S, Diverchy C, Demoulin O, Dubois V, Gaigneaux E M, Devillers M. *J Catal*, 2006, **243**: 239
- 17 Spiewak B E, Shen J, Dumesic J A. *J Phys Chem*, 1995, **99**: 17640

英 译 文 *English Text*

High levels of cholesterol in human bodies are a serious problem for human health. Dietary approaches are considered more attractive than pharmacologic alternatives to lower the levels of cholesterol in general population. Naturally occurring phytosterols and their saturated counterparts, phytostanols, were found to be efficacious to reduce the cholesterol levels in humans and thus used as additives in foods [1–3]. It is believed that phytosterols and phytostanols inhibit the absorption of dietary and endogenously produced cholesterol from the small intestine, while the phytosterols/phytostanols themselves are only very poorly absorbed [4]. There are more than 40 different phytosterols, in which β -sitosterol is most popular. The saturated derivative of β -sitosterol is β -sitostanol, which has been recognized as the more efficacious agent to reduce cholesterol than the un-saturated counterpart [5,6]. Furthermore, β -sitostanol is resistant to oxidation, while β -sitosterol contains double bond and can be oxidized to harmful steroid compounds [7].

However, β -sitostanol is not abundant in nature. Thus, it is desirable to produce β -sitostanol by the hydrogenation of β -sitosterol. Some metal catalysts have been tested, among which nickel catalysts were found to be not suitable for the double bond hydrogenation of sterols. On the other hand, supported Pd and Pt catalysts were found to exhibit good performance for the hydrogenation of β -sitosterol to β -sitostanol [8,9]. Different supports have been used for Pd for the hydrogenation of β -sitosterol to β -sitostanol, including carbons [8,10–12], grafted polymers [8,13], and alumina [9]. The hydrogenation of sterol esters to stanol esters was also performed over Pd/C [14].

Because β -sitosterol is a relatively large molecule, supports with large pores are desirable to support Pd for the hydrogenation reaction. Recently, a mesoporous carbon (Sibunit) was used to support Pd for the hydrogenation of β -sitosterol, which exhibited higher β -sitosterol conversion and stability than the Pd catalyst with microporous carbon as a support [3]. Previously, a method was developed in our lab for the preparation of CMC [15]. In this work, such CMC were used to support Pd for the hydrogenation of β -sitosterol to β -sitostanol.

The CMC treated differently were suspended in water by stirring, during which aqueous solution of H_2PdCl_4 was

added. Palladium was deposited by the addition of aqueous solution of NaOH ($\text{pH} \approx 12$). Formaldehyde solution was then added to reduce palladium. After washing with water, the Pd/CMC catalysts were obtained, which contained about 5% Pd (mass percentage). Three mesoporous carbons, CMC itself (20–40 mesh), CMC-200 (200 mesh), and CMC-200-NA (CMC-200 treated with concentrated HNO_3), were used as supports. A commercial activated carbon (AC, 200 mesh) was also used as the support for comparison.

Figure 1 shows the XRD patterns of carbon supports and Pd/C catalysts dried at 393 K. Three diffraction peaks around 40.0° , 46.5° , and 67.7° were observed for the FCC Pd (JCPDS 89-4897) on Pd/CMC, indicating the poorly dispersed palladium in this catalyst. On the other hand, no diffraction peaks for metallic Pd were observed for the other catalysts, suggesting the highly dispersed Pd in these catalysts.

Table 1 summarizes the textural properties of supports and Pd/C catalysts dried at 393 K. The results showed that the pore volumes and pore sizes were significantly larger for CMC supports than for AC. While the Pd/AC contained mainly micropores, the CMC supported catalysts possessed mainly mesopores. The surface areas did not seem to be decreased a lot upon the loading of Pd for all the catalysts.

The adsorption of CO was conducted at room temperature for the catalysts, which titrates the number of surface Pd sites in the catalysts according to the stoichiometric ratio ($\text{CO}/\text{Pd} = 1$). The surface metal area, metal dispersion, and particle size were also calculated accordingly. Table 2 shows the results. It is seen that the dispersion of Pd on CMC was poor (18.6%), consistent with the XRD result. The dispersion of Pd was increased to 27.7% on the CMC-200. The dispersions of Pd in Pd/AC and Pd/CMC-200-NA were similarly high (44%). The uptakes of CO indicated the numbers of surface Pd atoms in the catalysts, which was an important factor determining the activity for the hydrogenation reaction. Apparently, the small particle sizes of CMC-200 and CMC-200-NA favored the dispersion of Pd. The treatment with HNO_3 increased the surface oxygen-containing groups on carbons that promoted the dispersion of Pd [16].

The chemical properties of surface Pd atoms might be affected by the supports. This effect can be probed by the microcalorimetric adsorption of CO. Figure 2 shows the results of microcalorimetric adsorption of CO on the catalysts. It can be seen that the uptakes of CO followed the same sequence for the catalysts ($\text{Pd}/\text{AC} \approx \text{Pd}/\text{CMC-200-NA} > \text{Pd}/\text{CMC-200} > \text{Pd}/\text{CMC}$) as that titrated by the adsorption of CO (see Table 2). However, the initial heats of CO adsorption on these catalysts were similar (about 100 kJ/mol), demonstrating the similar electron charges on Pd surfaces on different supports [17], i. e., the chemical properties of surface Pd atoms were not affected by the different

carbon supports used in this study.

The catalytic hydrogenation of β -sitosterol was performed by using isopropanol as a solvent in a 100 ml autoclave for 3 h at 0.5 MPa and room temperature. The raw material (98.66% phytosterols) contained about 80.86% β -sitosterol, 13.58% campesterol, and 4.63% brassicasterol. After the reaction, the catalysts were filtered and washed with isopropanol. All the filtrates were collected and analyzed by an Agilent 1200 HPLC with an Eclipse XDB-C18 column and a differential refractometer detector. The results are shown in Table 2. Phytosterols were the only hydrogenation products. It is interesting to note that the conversion of phytosterols on Pd/CMC-200-NA was significantly higher than that on Pd/AC, although the numbers of surface Pd atoms were similar in the two catalysts. This might be due to that the Pd/CMC-200-NA possessed larger pores than Pd/AC, since the numbers of surface active sites and chemical properties of the two catalysts were similar according to the microcalorimetric adsorption of CO. The small pores in Pd/AC might restrict the diffusion of relatively large molecules of β -sitosterols.

The results in Table 2 also showed that the β -sitosterol conversion increased with the increase of Pd dispersion in the mesoporous carbon supported catalysts, indicating that the catalyst was more active with more active surface Pd

sites as long as the pores in catalyst were large enough. However, the Pd/AC with small pores was significantly less active than the Pd/CMC, although the Pd/AC possessed much more surface Pd active sites than the Pd/CMC, indicating that the pore size was a very important factor in determining the activity of hydrogenation of β -sitosterol to β -sitostanol.

Reaction temperature was found to affect the conversion of β -sitosterol, while pressure had little effect. Less catalyst and short time could be used when the reaction was performed at higher temperatures. Specifically, 96% conversion of β -sitosterol was achieved when the reaction was carried out at 343 K and 0.5 MPa for 1 h by using only 0.25% of the Pd/CMC-200-NA.

In summary, the pore size and number of surface Pd active sites were found to be the two important factors in determining the activity for the hydrogenation of large molecules such as β -sitosterol over carbon supported Pd catalysts. Mesoporous carbons such as CMC possessed large surface areas and pore sizes, which were the appropriate supports for the dispersion of Pd for the hydrogenation of large molecules.

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