催化学报 » 2011, Vol. 32 » Issue (11) :1755-1761 DOI: 10.3724/SP.J.1088.2011.10711

研究论文

基于纤维素的固体酸催化剂的制备及其催化高酸值废油脂生产生物柴油

娄文勇 1,2,a, 蔡俊 2, 段章群 1, 宗敏华 1,b

1华南理工大学轻工与食品学院, 广东广州 510640; 2湖北工业大学发酵工程省部共建教育部重点实验室, 湖北武汉 430068

LOU Wenyong1,2,a, CAI Jun2, DUAN Zhangqun1, ZONG Minhua1,b

1College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, Guangdong, China; 2Key Laboratory of Fermentation Engineering (Ministry of Education), Hubei University of Technology, Wuhan 430068, Hubei, China

摘要 以廉价的纤维素为原料, 经不完全炭化和磺化制得含高密度 (1.69 mmol/g) SO_3H 基团的固体酸催化剂 Cellulose-SO_3H. 结果表明, 该催化剂适宜的制备条件为: 在 400 ^oC 炭化 15 h, 再在 150 ^oC 磺化 15 h. 所得催化剂在油酸与甲醇的酯化反应中表现出明显高于其它几种典型固体酸催化剂 (铌酸, Amberlyst-15, 硫酸化氧化锆) 的活性, 同时还能高效地催化棕榈酸或硬脂酸以及高酸值废油脂 (较多脂肪酸) 与甲醇的酯化反应. 在醇/油摩尔比为 25, 催化剂用量为 10% (基于废油脂的质量), 于 85 ° C 反应 10 h 的条件下, 生物柴油收率约为 95%, 明显高于上述三种典型固体酸催化剂. 连续使用 30 批次 (每批次 10 h) 后, Cel-lulose-SO_3H 仍能保持初始催化活性的 90% 以上, 表现出极好的操作稳定性. 可见, 所制 Cellulose-SO3H 催化剂在生物柴油领域具有较好的应用潜力.

关键词: 纤维素 固体酸催化剂 生物柴油 酯化 废油脂

Abstract: A cheap cellulose-derived solid acid catalyst (Cellulose-SO_3H), containing SO_3H groups (1.69 mmol/g), was successfully prepared through sulfonation of incompletely carbonized cellulose. Various preparation variables exerted remarkable effects on the catalytic activity of the prepared catalyst, and the optimal preparation conditions were found as follows: carbonization at 400 ^oC for 15 h and subsequent sulfonation at 150 ^oC for 15 h. The resulting catalyst showed significantly higher activity for esterification of oleic acid with methanol than several typical solid acid catalysts (niobic acid, amberlyst-15, and sulfated zirconia). The Cellulose-SO_3H catalyst was capable of efficiently catalyzing esterification of other higher fatty acids (palmitic acid and stearic acid) with methanol to the corresponding fatty acid methyl esters (biodiesel). Moreover, the conversion of waste oils containing 27.8% free fatty acids to biodiesel catalyzed by Cellulose-SO_3H was investigated. It was found that the optimal molar ratio of methanol to oil, catalyst amount, reaction temperature, and reaction time were 25, 10% (based on the mass of waste oil), 85 ° C, and 10 h, respectively. Under the optimal reaction conditions, the yield of biodiesel obtained catalyzed by Cellulose-SO_3H was much higher than that by the above-mentioned three typical catalysts. Cellulose-SO_3H still retained above 90% of its original catalytic activity even after 30 cycles of successive re-use, indicating excellent operational stability. It can be clearly seen that the Cellulose-SO_3H catalyst displays tremendous potential for biodiesel production.

Keywords: cellulose, solid acid catalyst, biodiesel, esterification, waste oil

收稿日期: 2011-07-20; 出版日期: 2011-10-13

引用本文:

娄文勇, 蔡俊, 段章群等 .基于纤维素的固体酸催化剂的制备及其催化高酸值废油脂生产生物柴油[J] 催化学报, 2011,V32(11): 1755-1761

LOU Wen-Yong, CAI Jun, DUAN Zhang-Qun etc .Preparation of Cellulose-Derived Solid Acid Catalyst and Its Use for Production of Biodiesel from Waste Oils with High Acid Value[J] Chinese Journal of Catalysis, 2011,V32(11): 1755-1761

链接本文:

http://www.chxb.cn/CN/10.3724/SP.J.1088.2011.10711 或 http://www.chxb.cn/CN/Y2011/V32/I11/1755

[1] atanabe Y, Pinsirodom P, Nagao T, Kobayashi T, Nishida Y, Takagi Y, Shimada Y. J Am Oil Chem Soc, 2005, 82: 825

[2] ose O, Tuter M, Aksoy H A. Bioresour Technol, 2002, 83: 125

[3] eljkovic V B, Lakicevic S H, Stamenkovic O S, Todorovic Z B, Lazic M L. Fuel, 2006, 85: 2671

[4] harma Y C, Singh B, Korstad J. Biofuel Bioprod Bior, 2011, 5: 69

[5] elero J A, Iglesias J, Morales G. Green Chem, 2009, 11: 1285

[6] usca G. Chem Rev, 2007, 107: 5366

[7] oda M, Takagaki A, Okamura M, Kondo J N, Hayashi S, Domen K, Hara M. Nature, 2005, 438: 178

[8] ou W Y, Zong M H, Duan Z Q. Bioresour Technol, 2008, 99: 8752

[9] ong M H, Duan Z Q, Lou W Y, Smith T J, Wu H. Green Chem, 2007, 9: 434

[10] 乌日娜, 王同华, 修志龙, 郭峰, 潘艳秋, 银建中. 催化学报 (Wu R N, Wang T H, Xiu Zh L, Guo F, Pan Y Q, Yin J Zh. Chin J Catal), 2009, 30: 1203

[11] Mo X H, Lotero E, Lu C Q, Liu Y J, Goodwin J G. Catal Lett, 2008, 123: 1

[12] Suganuma S, Nakajima K, Kitano M, Yamaguchi D, Kato H, Hayashi S, Hara M. J Am Chem Soc, 2008, 130: 12787

[13] 赵冠鸿, 郑明远, 王爱琴, 张涛. 催化学报 (Zhao G H, Zheng M Y, Wang A Q, Zhang T. Chin J Catal), 2010, 31: 928

[14] Hara M, Yoshida T, Takagaki A, Takata T, Kondo J N, Hayashi S, Domen K. Angew Chem, Int Ed, 2004, 43: 2955

[15] Okamura M, Takagaki A, Toda M, Kondo J N, Domen K, Tatsumi T, Hara M, Hayashi S. Chem Mater, 2006, 18: 3039

[16] Hara M. Top Catal, 2010, 53: 805

[17] Hara M. Energy Environ Sci, 2010, 3: 601

[18] Okuhara T. Chem Rev, 2002, 102: 3641

[19] Semwal S, Arora A K, Badoni R P, Tuli D K. Bioresource Technol, 2011, 102: 2151

[20] Shu Q, Nawaz Z, Gao J, Liao Y, Zhang Q, Wang D, Wang J. Bioresource Technol, 2010, 101: 5374

[21] 舒庆, 张强, 高继贤, 王金福. 现代化工 (Shu Q, Zhang Q, Gao J X, Wang J F. Modern Chem Ind), 2009, 29(8): 21

[1] 李伟, 赵莹, 刘守新.以纳米微晶纤维素为模板的酸催化水解法制备球形介孔 TiO_2[J]. 催化学报, 2012,33(2): 342-347

[2] 方林, 张坤, 李晓红, 吴海虹, 吴鹏.磺酸基团功能化的碳-硅介孔复合材料的制备及其在生物柴油绿色合成中的应用[J]. 催化学报, 2012,33(1): 114-122

[3] 陈崇城 1,2, 陈航榕 1,a, 俞建长 2,b, 叶争青 1, 施剑林 1.多级孔WO_3/ZrO_2固体酸催化剂的制备与表征[J]. 催化学报, 2011,32(4): 647-651

[4] 赵应伟 1,2, 李臻 1, 夏春谷 1.烷基磺酸酯基功能化离子液体的合成、性质及其在酯化反应中的应用[J]. 催化学报, 2011,32(3): 440-445

[5] 陈孝云, 陈星, 洪时伟, 陈筱, 黄彪.碱法纳米纤维素模板剂合成介孔 TiO_2 及其性能[J]. 催化学报, 2011,32(11): 1762-1767

[6] 王建勋 1, 陈洸艟 2, 陈锦章 1,* .K_2SiO_3/C 颗粒催化大豆油酯交换制备生物柴油[J]. 催化学报, 2011,32(10): 1592-1596

[7] 秦丽娜, 喻晓蔚*, 徐岩*.非水相中微生物脂肪酶催化转酯化拆分 (R,S)-α-苯乙醇[J]. 催化学报, 2011,32(10): 1639-1644

[8] 吴树昌 1,2, 王春雷 1, 高勇军 1,2, 张少春 3, 马丁 1, 赵宗保 1,4.离子液体中微波辅助的 Lewis 酸催化纤维素制备 5-羟甲基糠醛[J]. 催化学报, 2010,31(9): 1157-1161

[9] 赵冠鸿 1,2, 郑明远 1, 王爱琴 1, 张涛 1.磷化钨催化转化纤维素制乙二醇[J]. 催化学报, 2010,31(8): 928-932

[10] 邹昀1, 童张法1, 刘琨1, 冯献社2.间歇反应器内醋酸丁酯酯化反应与渗透汽化集成过程的模型计算[J]. 催化学报, 2010,26(8): 999-1005

[11] 李军, 高爽, 奚祖威.反应控制相转移催化研究的进展[J]. 催化学报, 2010,26(8): 895-911

[12] 王连弟 1, 吴小伟 1,2, 赫巍 1, 刘子双 1, 余正坤 1 .钯催化 1,3-丁二烯羧酯化合成 3-戊烯酸甲酯[J]. 催化学报, 2010,26(8): 1044-1048

[13] 张凤;蒋晓原;洪俊杰;楼辉;郑小明.ZnCl2改性离子交换树脂的制备及其催化乙醇和乙酸酯化反应性能[J]. 催化学报, 2010,31(6): 666-670

[14] 沈磊;冷炎;王军;任晓乾;吴雅静;张明珏;许岩 .锚定在杂多酸上的席夫碱锰配合物催化磷酸与等摩尔月桂醇绿色酯化反应[J]. 催化学报, 2010,31(2): 156-162

[15] 刘仕伟 1, 李露 1, 于世涛 1, 解从霞 2, 刘福胜 1, 宋湛谦 1,3.酸性离子液体催化脂肪酸甲酯聚合制备二聚酸甲酯[J]. 催化学报, 2010,31(12): 1433-1438