燃料化学学报
JOURNAL OF FUEL CHEMISTRY AND TECHNOLOGY
ISSN 0253-2409
CN 14-1140/TQ

燃料化学学报 » 2012, Vol. 40 » Issue (09): 1067-1073 DOI:

负载的Ni催化剂上植物油脂加氢脱氧制备第二代生物柴油

左华亮[1,2], 刘琪英[1], 王铁军[1], 史娜[1], 刘建国[1,2], 马隆龙[1]

1. 中国科学院广州能源研究所 可再生能源与天然气水合物重点实验室, 广东 广州 510640;
2. 中国科学院研究生院, 北京 100049

Catalytic hydrodeoxygenation of vegetable oil over Ni catalysts to produce second-generation biodiesel

ZUO Hua-liang[1,2], LIU Qi-ying[1], WANG Tie-jun[1], SHI Na[1], LIU Jian-guo[1,2], MA Long-long[1]

1. Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China;
2. Graduate University of Chinese Academy of Sciences, Beijing 100049, China

- 摘要
- 参考文献
- 相关文章
- 点击分布统计
- 下载分布统计

全文: PDF (1399 KB) HTML (1 KB) 输出: BibTeX | EndNote (RIS) 背景资料

摘要 在半连续反应器中,以棕榈酸甲酯为植物油脂模型化合物,进行了加氢脱氧制取高品质生物柴油燃料的研究。采用浸渍法制备了HY、SiO_2、γ-Al_2O_3及SAPO-11四种载体负载的Ni催化剂,采用XRD、NH_3-TPD、H_2-TPR、BET、SEM等技术进行催化剂表征。结果表明,Ni/SAPO-11催化剂由于SAPO-11表面呈现的弱酸和中强酸性质,在保持较高的加氢脱氧反应性的同时,抑制了裂解反应的发生,具有较好的催化性能。进一步对SAPO-11上不同的Ni负载量、反应温度、反应压力等进行了研究,发现当Ni负载量为7%,反应温度为220℃,压力为2MPa时,催化剂具有较高的催化性能,棕榈酸甲酯的转化率达到了99.8%,$C_{9\sim16}$烷烃的总选择性为92.71%。

关键词: 植物油脂 棕榈酸甲酯 加氢脱氧 Ni基催化剂 第二代生物柴油

Abstract: A series of Ni catalysts supported on HY, SiO_2, γ-Al_2O_3 and SAPO-11 were prepared by incipient-wetness impregnation and characterized by XRD, NH_3-TPD, H_2-TPR, BET and SEM techniques. Their catalytic performance in hydrodeoxygenation (HDO) of vegetable oil to produce the second-generation biodiesel was evaluated in a semi-batch reactor by using methyl palmitate as a model compound. Owning to the weak and medium acidic properties of SAPO-11, the Ni/SAPO-11 catalyst exhibits high activity in the HDO of methyl palmitate and capability of inhibiting the feedstock and long-chain alkanes from being cracked. The effect of Ni loading, reaction temperature and pressure on the HDO behavior over Ni/SAPO-11 catalyst was considered. Under 220℃ and 2 MPa, Ni/SAPO-11 catalyst with a Ni loading of 7% performs best in HDO; the conversion of methyl palmitate and the selectivity towards $C_{9\sim16}$ alkanes reach 99.8% and 92.71%, respectively.

Key words: vegetable oil methyl palmitate hydrodeoxygenation Ni catalysts second-generation biodiesel

收稿日期: 2011-11-09;

基金资助:

国基NSFC/JST重大国际合作项目(51161140331); 国家重点基础研究发展规划(973计划, 2012CB215304)。

通讯作者: 马隆龙,E-mail:mall@ms.giec.ac.cn。 E-mail: mall@ms.giec.ac.cn

引用本文:

左华亮,刘琪英,王铁军等. 负载的Ni催化剂上植物油脂加氢脱氧制备第二代生物柴油[J]. 燃料化学学报, 2012, 40(09): 1067-1073.

ZUO Hua-liang,LIU Qi-ying,WANG Tie-jun et al. Catalytic hydrodeoxygenation of vegetable oil over Ni catalysts to produce second-generation biodiesel [J]. J Fuel Chem Technol, 2012, 40(09): 1067-1073.

链接本文:

http://rlhxxb.sxicc.ac.cn/CN/ 或 http://rlhxxb.sxicc.ac.cn/CN/Y2012/V40/I09/1067

服务
- 把本文推荐给朋友
- 加入我的书架
- 加入引用管理器
- E-mail Alert
- RSS

作者相关文章
- 左华亮
- 刘琪英
- 王铁军
- 史娜
- 刘建国
- 马隆龙

[1] RODOLFO B S. Asphaltene hydroconversion, developments in petroleum science[M]. Chilingarian: Elsevier, 2000: 149-171.

[2] SENOL O I, VILJAVA T R, KRAUSE A. Effect of sulphiding agents on the hydrodeoxygenation of aliphatic esters on sulphided catalysts[J]. Appl Catal A, 2007, 326(2): 236-244.

[3] GLEIM W K T. Role of asphaltene in refining, developments in petroleum science[M]. Chilingarian: Elsevier, 1978: 243-258.

[4] ANCHEYTA J, BETANCOURT G, CENTENO G, MARROQUIN G, ALONSO F, GARCIAFIGUEROA E. Catalyst deactivation during hydroprocessing of Maya heavy crude oil: 1 Evaluation at constant operating conditions[J]. Energy Fuels, 2002, 16(6): 1438-1443.

[5] ANCHEYTA J, CENTENO G, TREJO F, MARROQUIN G. Changes in asphaltene properties during hydrotreating of heavy crudes[J]. Energy Fuels, 2003, 17(5): 1233-1238.

[6] YEN T F, ERDMAN J G, POLLACK S S. Investigation of the structure of petroleum asphaltenes by X-ray diffraction[J]. Anal Chem, 1961, 3(11): 1587-1594.

[7] RYYMIN E M, HONKELA M L, VILJAVA T R, KRAUSE A. Insight to sulfur species in the hydrodeoxygenation of aliphatic esters over sulfided NiMo/γ-Al_2O_3 catalyst[J]. Appl Catal A, 2009, 358(1): 42-48.

[8] BOUHADDA Y, BORMANN D, SHEU E, BENDEDOUCH D, KRALLAFA A, DAAOU M. Characterization of algerian hassi-messaoud asphaltene structure using Raman spectrometry and X-ray diffraction[J]. Fuel, 2007, 86(12/13): 1855-1864.

[9] RYNKOWSKI J M, PARYJJCZAK T, LENIK M. On the nature of oxidic nickel phases in NiO/γ-Al_2O_3 catalysts[J]. Appl Catal A, 1993, 106(1): 73-82.

[10] SCHWAGER I, FARMANIAN P A, KWAN J T, WEINBERG V A, YEN T F. Characterization of the microstructure and macrostructure of coal-derived asphaltenes by nuclear magnetic resonance spectrometry and X-ray diffraction[J]. Anal Chem, 1983, 55(1): 42-45.

[11] SHEU E Y. Petroleum asphaltene properties, characterization, and issues[J]. Energy Fuels, 2001, 16(1): 74-82.

[12] HU C-W, YAO J, YANG H-Q, CHEN Y, TIAN A-M. On the inhomogeneity of low nickel loading methanation catalyst[J]. J Catal, 1997, 166 (1): 1-7.

[13] SHARMA A, GROENZIN H, TOMITA A, MULLINS O C. Probing order in asphaltenes and aromatic ring systems by HRTEM[J]. Energy Fuels, 2002, 16(2): 490-496.

[14] CHANG J, TSUBAKI N, FUJIMOTO K. Effect of addition of K to Ni/SiO_2 and Ni/Al_2O_3 catalysts on hydrothermal cracking of bitumen[J]. J Jpn Pet Inst, 2000, 43(5): 357-360.(in Japanese)

[15] CAMACHO-BRAGADO G A, SANTIAGO P, MARIN-ALMAZO M, ESPINOSA M, ROMERO E T, MURGICH J, RODRIGUEZ LUGO V, LOZADA-CASSOU M, JOSE-YACAMAN M. Fullerenic structures derived from oil asphaltenes[J]. Carbon, 2002, 40(15): 2761-2766.

[16] PARLITZ B, SCHREIER E, ZUBOWA H L, ECKELT R, LIESKE E, LISCHKE G, FRICKE R. Isomerization of n-heptane over Pd-loaded silico-alumino-phosphate molecular-sieves[J]. J Catal, 1995, 155(1): 1-11.

[17] MORDKOVICH V Z, UMNOV A G, INOSHITA T. Nanostructure of laser pyrolysis carbon blacks: Observation of multiwall fullerenes[J]. Int J Inorg Mater, 2000, 2(4): 347-353.

[18] 刘勇军, 刘晨光. 添加剂对渣油加氢脱金属性能的影响[J]. 石油学报(石油加工), 2009, 25(5): 651-654. (LIU Yong-jun, LIU Chen-guang. Effects of additives on hydrodemetallization of residue[J]. Acta Petrol ei Sinica (Petroleum Processing Section), 2009, 25(5): 651-654.)

[19] SNARE M, KUBICKOVA I, MAKI-ARVELA P, ERANEN K, MURZIN D Y. Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel[J]. Ind Eng Chem Res, 2006, 45(16): 5708-5715.

[20] PEREZ-HERNADEZ R, MENDOZA-ANAYA D, MONDRAGO-GALICIA G, ESPINOSA M E, RODRIUEZ-LUGO V, LOZADA M, ARENAS-ALATORRE J. Microstructural study of asphaltene precipitated with methylene chloride and *n*-hexane [J]. Fuel, 2003, 82(8): 977-982.

[21] HAN J, SUN H, DING Y, LOU H, ZHENG X. Palladium-catalyzed decarboxylation of higher aliphatic esters: Towards a new protocol to the second generation biodiesel production[J]. Green Chem, 2010, 12(3): 463-467.

[22] RYYMIN E M, HONKELA M L, VILJAVA T R, KRAUSE A. Competitive reactions and mechanisms in the simultaneous HDO of phenol and methyl heptanoate over sulphided NiMo/γ-Al_2O_3[J]. Appl Catal A, 2010, 389(1/2): 114-121.

[23] MARTENS J A, JACOBS P A, WEITKAMP J. Attempts to rationalize the distribution of hydrocracked products: I Qualitative description of the primary hydrocracking modes of long chain paraffins in open zeolites[J]. Appl Catal, 1986, 20(1/2): 239-281.

[24] MARTENS J A, JACOBS P A, WEITKAMP J. Attempts to rationalize the distribution of hydrocracked products: II Relative rates of primary hydrocracking modes of long chain paraffins in open zeolites[J]. Appl Catal, 1986, 20(1/2): 283-303.

[1] 司兰杰, 王长真, 孙楠楠, 闻霞, 赵宁, 肖福魁, 魏伟, 孙予罕. 制备条件对介孔Ni-CaO-ZrO_2在甲烷三重整反应中催化性能的影响[J]. 燃料化学学报, 2012, 40(02): 210-215.

[2] 胡韬, 杨运泉, 王威燕, 刘文英, 贺恒, 高波. Ni(Co)-W-B非晶态催化剂的制备和加氢脱氧性能研究[J]. 燃料化学学报, 2012, 40(01): 80-85.

[3] 王威燕, 杨运泉, 罗和安, 杨彦松, 胡　韬, 刘文英, 何　兵, 钦柏豪. 复合载体TiO_2-Al_2O_3的制备及其对Ni-Mo-S负载型催化剂加氢脱氧性能的影响[J]. 燃料化学学报, 2011, 39(12): 924-929.

[4] 包建国, 杨运泉, 王威燕, 蒋新民, 李　娅. CoMo/ZrO_2-Al_2O_3催化剂的制备及其加氢脱氧性能[J]. 燃料化学学报, 2011, 39(1): 59-63.

[5] 王威燕, 杨运泉, 罗和安, 王　锋, 胡　韬, 刘文英. La-Ni-Mo-B非晶态催化剂的制备、加氢脱氧性能及失活研究[J]. 燃料化学学报, 2011, 39(05): 367-372.

[6] 王欣, 张舜光, 侯凯湖. 焙烧温度对非负载Ni-Mo-Al_2O_3催化剂加氢脱氧性能的影响[J]. 燃料化学学报, 2010, 38(05): 594-599.

[7] 王威燕, 杨运泉, 罗和安, 包建国, 陈卓. 超声波辅助制备非晶态Ni-Mo-B催化剂及其加氢脱氧性能研究[J]. 燃料化学学报, 2009, 37(06): 701-706.

[8] 任杰, 张怀科, 李永旺. F-T合成油品加工技术的研究进展[J]. 燃料化学学报, 2009, 37(06): 769-776.

[9] 宫立倩,陈吉祥, 李正, 张继炎, 刘季. 还原方式及还原温度对甲烷部分氧化镍催化剂结构和反应性能的影响[J]. 燃料化学学报, 2008, 36(02): 192-196.

[10] 霍立芳, 王雪峰, 侯潇云, 任　杰. Mo、W对Ni/γ-Al2O3催化剂烯烃加氢性能的影响[J]. 燃料化学学报, 2007, 35(05): 595-598.

[11] 王雪峰, , 王　锋, 陈满英, 任　杰. Ni基双金属催化剂加氢脱氧性能的研究[J]. 燃料化学学报, 2005, 33(05): 612-616.