分子筛负载杂多酸催化大豆油制备生物柴油

黄艳芹

(新乡学院 化学与化工学院,河南 新乡 453003)

摘 要:采用等体积浸渍法制备了负载型催化剂 PW/MCM-41,并以此催化大豆油与甲醇酯交换反应制备生物柴油。考察了磷钨酸负载量和催化剂焙烧温度对催化剂催化活性的影响,以及醇油物质的量比、催化剂用量、反应时间和反应温度对生物柴油产率的影响。结果表明:磷钨酸负载量为30%、焙烧温度为300℃时,催化剂活性最高。酯交换反应的最佳条件是醇油物质的量比为12∶1、催化剂用量为原料油质量的6%,反应时间6 h,反应温度70℃。在此条件下制备生物柴油,其产率可以达到89%以上。

关键词:杂多酸; MCM-41 分子筛;催化;酯交换反应;生物柴油;产率

中图分类号:TQ645.1 **文献标识码**:A **文章编号**:1000-9841(2011)03-0488-05

Preparation of Biodiesel from Soybean Oil Catalyzed by Molecular Sieve Catalyst with Heteropoly Acid

HUANG Yan-qin

(Department of Chemistry and Chemical Engineering, Xinxiang University, Xinxiang 453003, Henan, China)

Abstract: PW/MCM-41 catalyst was prepared by supporting phosphotungstic acid (PW) on MCM-41 molecular sieves via impregnation method. The transesterification of soybean oil and methanol to biodiesel catalyzed by PW/MCM-41 was studied. The influences of PW loadings and calcination temperature on the catalytic activity of PW/MCM-41 was investigated. The effects of molar ratio between methanol and soybean oil, catalyst dosage, reaction time, reaction temperature on yield of biodiesel was researched. PW/MCM-41 catalysted with 30% (mass fraction) PW and calcination temperature 300℃ was preferable. The results showed that the optimum reaction conditions were as following: molar ratio between methanol and soybean oil 12∶1, mass ratio of catalyst to soybean oil weight 6%, reaction time 6 h, reaction temperature 70℃. The yield of biodiesel reached 89% under the optimum reaction conditions.

Key words: Heteropoly acid; MCM-41 molecular sieve; Catalysis; Transesterification; Biodiesel; Yield

生物柴油具有闪点高、十六烷值大、可再生、可降解、对环境友好等优点,将逐渐成为石化柴油的替代品。目前生物柴油生产主要采用酸碱均相催化酯交换法[1-2]。碱催化反应过程对原料中水和游离脂肪酸含量要求高,因为水会降低催化剂的活性,游离脂肪酸含量较高容易发生皂化反应导致催化剂失活。以硫酸、对甲苯磺酸等酸催化酯交换反应,存在腐蚀性大,反应后分离困难,污染环境等问题[3-4]。杂多酸以其独特的酸性、多功能性等特点在催化领域受到广泛关注。杂多酸均相催化反应催化剂表面较小,催化活性较低,同样存在催化剂回收困难。因此,把杂多酸有效的负载于载体上,不仅能提高催化活性,而且还利于催化剂循环利用。中孔分子筛MCM-41具有较大的比表面积和孔容,孔道结构规整,有利于大分子在其孔道内进行有效扩散[5-8]。因此该研究采用浸渍法制备了负载型杂多酸催化剂 PW/MCM-41,并以此催化大豆油和甲醇酯交换反应制备生物柴油。

1 材料与方法

1.1 试剂与仪器

大豆油(市售,食品级),正硅酸乙酯(TEOS)、十六烷基三甲基溴化铵(CTMAB)、NaOH、磷钨酸、甲醇等试剂均为分析纯。

F4-200 晶化釜;250 mL 三口圆底烧瓶;HDM-1000 型电热套恒温搅拌装置;80-2 型离心机;BT-224S 电子天平;RE-52A 旋转蒸发器。D8-FOCUS 型 X 射线衍射仪(德国 Bruker 公司),管电压 40 kV,铜靶 CuKα $\lambda = 0.154$ nm,扫描范围 $2\theta = 3 \sim 90°$,扫描速率 $2° \cdot min^{-1}$。FTS-40 型红外光谱

收稿日期:2011-02-23
基金项目:河南省重点科技攻关资助项目(092102310184);河南省自然科学研究计划资助项目(2008C480002)。
作者简介:黄艳芹(1966-),女,副教授,硕士,主要从事应用化学研究。E-mail: hyq200405@sohu.com。

Ý åúñ Ü b å é ž > Q æâ † æâââ ßã ê

ã%ä, 0 x U * ¹ º

ƒ %r üòü Šæã q m ˆ ďÜ ´ ò üðñ Š ôþ Š ý þ÷ Š÷ä þ í ã Šé%ç Šã%ê Šçââ 0 † q · , ą̂ ò Š üðñT ý þ÷² Â ë @%ú * åG " w W± . … å ¡ T ! õ # û ôþ åð # Ÿ ³ … åÅ äç' 5 Z 9 G " Ñ è ợ / ƒ 0 é û , " [ß à \ ] q p e Z * åÅ ããâ' 5 þ Ý éä åB … Þ éé ^ Ö * ¯ åE Œ ãä åèâ' 5 W2 è åu üòü Šæã g ê

¼Ý ¡ ÿ áü òü Šæã q m ˆ ợ w W· q « V ¨ ² H á w W· q ú * å¿ M w W· A m q üòü Š æã w x åÿ x Õ œÿ w W± . … åããâ' 5 € Œ å å w Wª À 5 W2 å åt u Û w Ð ¼Ý ¡ ÿ áü òü Š æã ê

ã%å, § ^ 2 1 * ¹ º

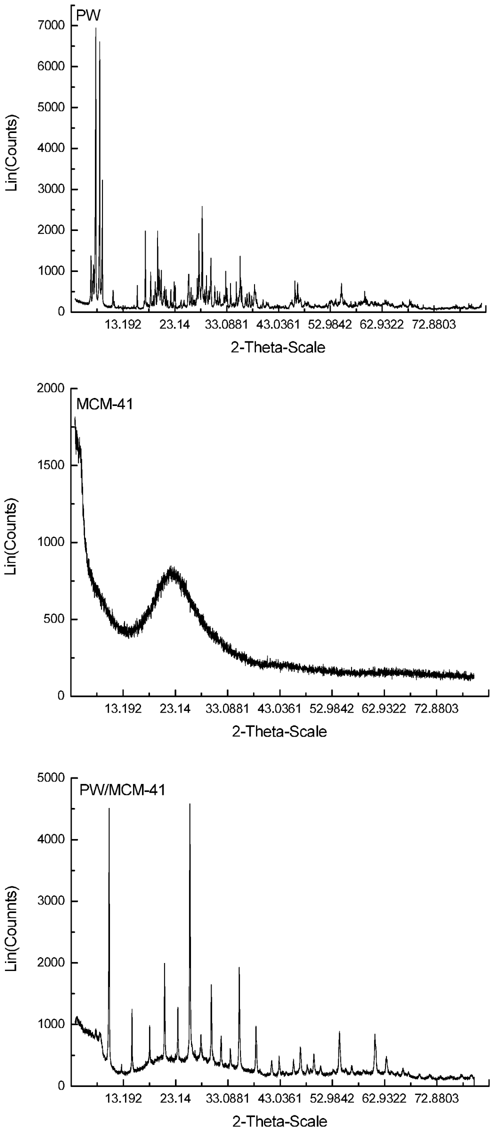
¦ & ' . T ` t ï w W0 † q · , # û Ð ÷ 2 * â å' # û w W· q Û w Ð ¼Ý ¡ ÿ áü òü Š æã ą̂ ˆ C Â ê Ï S G " T Ó • · ì 1 q á ª Ï k Œ* å—- G " T Ó • Ø × åK w Wq ª À 5 € • ì R K p e ê p e ± Ý … å@I ƒ @Ó Ô ¼Ý ¡ ê ¦ ³ • é û ª ¢ ô † š * åò † Ó Ô c · q ` t å- ¦ ² ³ ¢ û ƒ ³ ú _ * Q C ƒ + åõ + Q = . å½ + Q 6 g ˜ 0 U . ê¿ < åÅ æ˜ 0 U . q 6 < ê

ä, WX - € •

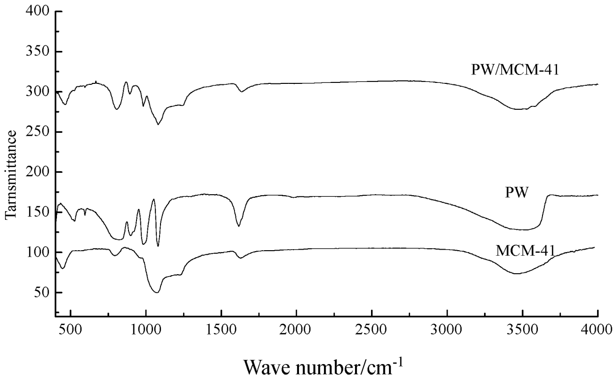
ä%ã, # ‡ * Wú u '

í ãÈ ÿ éw x üòü ŠæãT ÿ áü òü Šæã q ‡ å • í êò í ãÄ Ñ åÿ Q o ¨ K å •) áä·â Q ë%èŽéäè%äŽéåâŽÿ j Å ¹ ˆ Ð q ú ± [q i " » Ô o ê üòü ŠæãK å •) áä·âQ å%èŽéää%êŽ j Þ ‡ å • o åz › ƒ º q ƒ %r Å ¹ üòü Šæã* < ƒ %r q ± [i " ë ê ÿ áü òü Šæã í ³ ´ å : w x = > åÿ » Ô o Þ ‡ q ì C T å • 3 À ¸ ¹ u Ý å¼# —- ú ± [ê Û È ò Â üòü ŠæãÅ ¹ & q , z Ô é& q < \ ï • ÿ Q o ¨ 9 üòü Šæã q z Ô ° 5 ˜ K 9 3 q •) / – åB ï ÿ Q o ¨ Ä ï ¸ 0 ƒ ü K w x üòü Šæã½ ê

í äÈ ÿ éw x üòü ŠæãT ÿ áü òü Šæã q - x , ã í êò í äÄ Ñ å ÿ Q o ¨ K ã âêäéëêâé êëâT êââ ßã j ¹ æ‰i " » Ô o åÈ ò « V ¨ i ¹ q ú ± [Ã v q ôð üòü ŠæãK ã äââé ã âêäé ëçç T êââ ßã j Þ ‡ » Ô o ê K ÿ áü òü Šæã¼Ý ¡ q ø ã í * åÅ ï y ? Ê # á ÿ Q o ¨ q æ‰i " » Ô o åz › ÿ Q o ¨ Û w á ƒ %r üòü Šæã½ … # B —- ú ± [ê



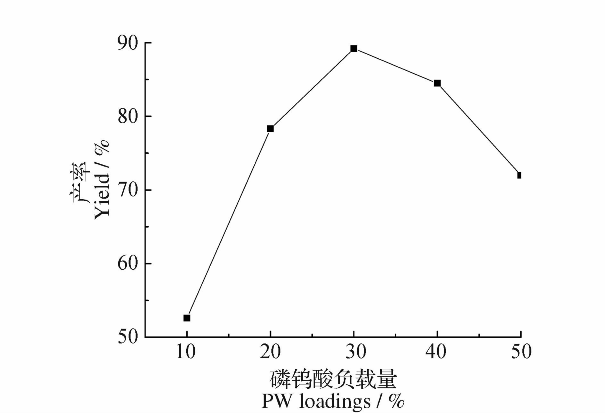
E ã, ÿ éü òü Šæã| ÿ áü òü Šæã* óE
õ àã, ó !! ÿ åü òü Šæã
ÿ áü òü Šæã



E ä, ÿ éü òü Šæã| ÿ áü òü Šæã* õ Šø Ž E
õ àä, õ Šø ! ÿ åü òü Šæã
ÿ áü òü Šæã

ä%ä, \ ]) Ì ©0 x U¥ b * È É

ä%ä%ã, ¿ À Z Á « » åb » ? — â, K ì R K p e * å« m t . 0 † q · , Q ãä Šãé¼ Ý ¡ – · Q ä / . † · q èÛ é þ e ± . è é þ e ª À éâ' å¼Ø « V ¨ Û w · d ¼ Ý ¡ z ¯ q = > å± ² Ñ í åê å æ « V ¨ Û w · q " # å 0 U . q 6 < ñ " & …o ñ åÛ w · Q ååÛ± å6 < } & ê 2 È 6 Q Û w · ã ± å« V ¨ K üòü Šãz Ô ¸ 0 ƒ ü å ¹ › ƒ € û üòü Šã< ° ± [* åå æ « V ¨ Û w · q " # å¼ Ý ¡ z ¯ * I " o åz ¯ " # êõ « V ¨ Û w · ^ c ååÛ± åc o q « V ¨ † ˜ ' , åç V ¸ 0 ƒ ü K üòü Šã½ å® ± › ƒ « V ¨ , ƒ x ` a ® < < ° å0 ¼ Ý ¡ q , z ÔÕ T < —o ñ åz ¯ 8 ã ê 3 ï s Ú « V ¨ Û w · Q ååÛ9 ƒ Õ ê

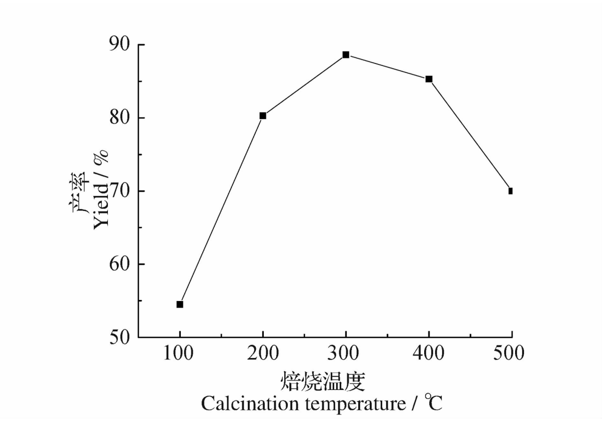


E å, ÿ / Š X ©0 x U¥ b * È É
õ àå, ! ÿ ! ! &!
!#!& ÿ áü òü Šã

ä%ä%ä, Â Ã é Ù , ¼ Ý ¡ W2 ª À d ˆ ¼ Ý z ¯ = > 9 & ê s – « V ¨ Û w · ååÛq ÿ áü òü Šã / ¼ Ý ¡ åK t . 0 † q · , ãä Šãé¼ Ý ¡ – · Q ä / . † · q èÛ é þ e ª À éâ' é þ e ± . è q 3 4 5 € • ì R K p e å¼ØW2 ª À d ¼ Ý ¡ z ¯ q = > å± ² Ñ í æê å æ W2 ª À q º » å 0 U . q 6 < ñ " & …o ñ å0 W2 ª À Q ååâ' ± å 6 < } » ê 2 È 6 Q ª À ã ± ÿ 9 üòü Šã* ç ‹ s ± ƒ ç ë å¼ Ý ¡ ¼ Ý z ¯ 9 ã ð À Q ååâ' ± åÿ 9 üòü Šã* ç ‹ s ± ƒ 9 b A åñ ± þ ú ç @€ ë åÿ # V —- ä L ± [å¼ Ý ¡ q z ¯ 9 » õ W2 ª À » Â ååâ' ± åÿ —@ƒ H ð € ë ± þ ú å ƒ ± [÷ ø ù å¼ Ý z ¯ 5 8 ð À ÷ ó » åÿ 9 ç ‹ s ä Ö å± [÷ ø ù å¼ Ý ¡ z ¯ B ã ê 6 ' ås Ú ¼ Ý ¡ W2 ª À Q ååâ' ê

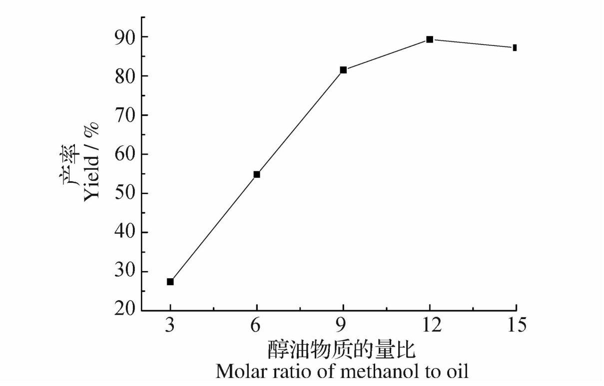
ä%å, \ ]) Ì ©e Ë * È É

ä%å%ã, Ä Å 2 b %» Ì , t . 0 † q · , È = > ˜ 0 U . 6 < q ^ _ 6 þ Þ w ê & ' . 9 ` t q



E æ 3 4 ‡ å ©0 x U¥ b * È É
õ àæ ! ò ! ! !"
! ! &! !#!& ÿ áü òü Šã

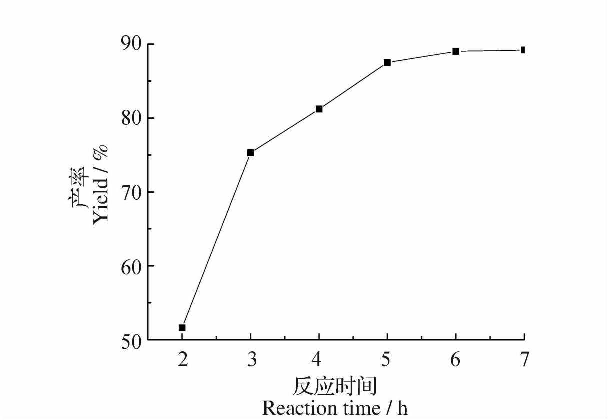
ì R K p e È Ä q p e å' # ` t – · åÄ ï º » & ' . q ¢ Ý < T ˜ 0 U . q 6 < êK ì R K p e * å« m ¼ Ý ¡ – · Q ä / . † · q èÛ é þ e ± . è é þ e ª À éâ' å¼Ø t . 0 † q · , d ˜ 0 U . 6 < q = > å± ² Ñ í çê t . 0 † q · , ã ± åå æ t . 0 † q · , " # å6 0 6 < " & 9 2 å õ t . 0 † q · , & Â ë± å6 < " # 9 Ü åõ t . 0 † q · , Q ãä± å6 < } & åZ 9 " # t . 0 † q · , å6 < p ð ¹ 3 5 8 ê 2 È 6 Q ` t · c & åD À v p e x ÿ å8 ã v p e V { ê{ x ` t · c & å # v Ó Ô ` t q Û ê T º † ê 3 ï å@ ƒ ¾$ ¥ h 6 þ ås Ú t . 0 † q · , Q ãä Šã9 ƒ Õ ê



E ç, 5 1 ^ À * X c © § ^ 2 1 e Ë * È É
õ àç, ! ! !
! &

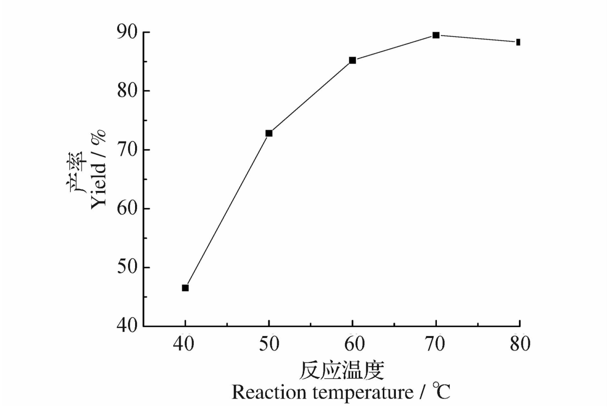
ä%å%ä, ‹ – ' Û , K ì R K p e * å« m t . 0 † q · , Q ãä Šãé¼ Ý ¡ – · Q ä / . † · q èÛ é þ e ª À éâ' å¼Ø p e ± . d ˜ 0 U . 6 < q = > å± ² Ñ í èê å æ p e ± . q È é å 0 U

. 6 < ! ô " # åp e è ± å6 < } & åZ 9 p e å 6 < " # ã Ü ê2 È 6 Q p e ¡ T ± åƒ Ø & 9 1 å3 ï 6 < " # 9 2 åp e è ± åU Õ - Ø & å- È é p e ± . åd p e = > ç & ê3 ï s Ú } * p e ± . Q è ê



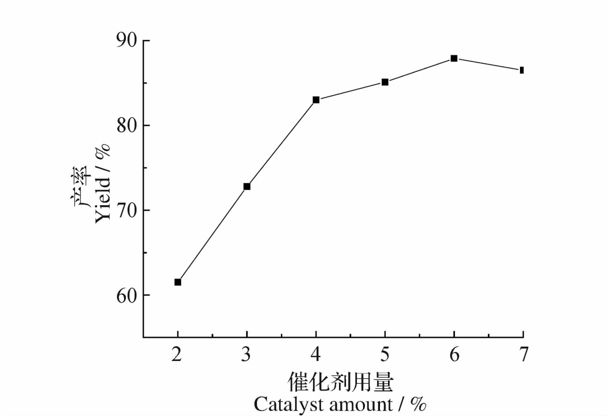
E è, µ ´ è ` © § ^ 2 1 e Ë * È É
õ à è, ! ! !
&

ä%å%å, ‹ – é Ù , K ì R K p e * å‹ mt . 0 † q · , Q ãä Šãé¼Ý ¡ – · Q ä / . † · q èÛ ép e ± . è å¼Ø p e ª À d ˜ 0 U . 6 < q = > å± ² Ñ í éê p e ª À ã ± åp e 3 < 9 Ü å6 0 6 < ñ åå æ ª À º » åp e 3 < # 2 å6 0 6 < " # 9 2 åª À Q éâ' ± å6 < } & åZ 9 º » ª À å6 < ¹ 3 5 8 ê2 È 6 Q E Ü 5 ` t q A j Q èæ%é' åª À c » å& · ` t Ä Ý åp e x ÿ * ` t ž · o C å= > p e > À å3 ï 6 < 8 ã ê6 ' s Ú p e ª À éâ' 9 ƒ Õ ê



E é, µ ´ ‡ å © § ^ 2 1 e Ë * È É
õ à é, ! ! ! !"
&

ä%å%æ, ÆI ¦ ß » , K ì R K p e * å‹ mt . 0 † q · , Q ãä Šãp e ± . è ép e ª À éâ' å ¾Ø ¼Ý ¡ – · d ˜ 0 U . 6 < q = > å± ² Ñ í êê ¼Ý ¡ – · C ± åª Y q z ¯ * I C åp e 3 < Ü å6 0 6 < ã åå æ ¼Ý ¡ – · q " # å6 < ç ä " # å0 ¼Ý ¡ – · Q èÛ± å6 < } & êZ 9 " # ¼Ý ¡ – · å6 < u Ý ç & ê3 ï s Ú ¼Ý ¡ – · Q ä / . † · q èÛ9 ƒ Õ ê



E ê, 0 x U • X © § ^ 2 1 e Ë * È É
õ à ê, ! ! &! " !
&

ä%æ, Ò Ó T V

K ð 6 þ ' Wq 5 • ½ å' t . 0 † q · , é ¼Ý ¡ – · ép e ± . ép e ª À æ‰6 þ Q 1 2 d › å – ûê áåæâÛ R ' W å' ˜ 0 U . 6 < Q^ Š - ç å W} * q = W3 4 ê6 þ ú Ø z Ñ z ãå ' W± ² Ñ z äê

u ã, Ò Ó T V) Ì Í Î u
ã, õ ! # ûê áåæâ ! ! !

	p e ª À	p e ± .	¼Ý ¡ – ·	t . 0 † q · ,
ú Ø	!	!	ò ! &!	ü !
û # !	!" á	! á	" !áÛ	! !
	ð	ñ	ò	ó
ã	èâ	ç	ç	ë Šã
ä	éâ	è	è	ãä Šã
å	êâ	é	é	ãç Šã

ò z ä* B n ƒ „ Ä u ó¥ 6 þ d ì R K p e q = > > À Q ó . 0 † q · , î ¼Ý ¡ – · î p e ª À î p e ± . ê} * = W3 4 Q óp e ª À éâ' åp e ± . è å¼Ý ¡ – · Q ä / . † · q èÛ å . 0 † q · , ãä Šãê K ' : Ý 3 4 5 mˆ ˜ 0 U . å 6 < Ä ï { á êëÛï ½ ê

表2 正交试验结果及极差分析

Table 2 Results of orthogonal experiment and range analysis

序号 No.	反应温度 Reaction temperature A	反应时间 Reaction time B	催化剂用量 Catalyst amount C	醇油物质的量比 Molar ratio of methanol to oil D	生物柴油产率 Yield of biodiesel /%
1	1	1	1	1	84. 35
2	1	2	2	2	84. 79
3	1	3	3	3	78. 43
4	2	1	2	3	82. 78
5	2	2	3	1	89. 53
6	2	3	1	2	81. 00
7	3	1	3	2	87. 17
8	3	2	1	3	81. 06
9	3	3	2	1	87. 98
K_1	82. 55	84. 98	82. 14	87. 29	
K_2	84. 47	85. 16	85. 26	84. 35	
K_3	85. 41	82. 47	85. 04	80. 79	
R	2. 86	2. 69	3. 12	6. 56	

3 结 论

以等体积浸渍法制备了负载型催化剂 PW/MCM-41,并以此催化大豆油与甲醇的酯交换反应。结果表明,磷钨酸负载量为30%,焙烧温度为300℃时,催化剂活性最高。酯交换反应的最佳条件是反应温度70℃,反应时间6 h,催化剂用量为原料油质量的6%,醇油物质的量比12∶1。在此优化条件下制备生物柴油,其产率可以达到89%以上。分子筛负载杂多酸催化剂具有较高的催化活性,易与反应体系分离回收,腐蚀性小,对环境友好,是一类应用前途广阔的催化剂。

参考文献

[1] 鞠庆华,曾昌凤,郭卫军,等.酯交换法制备生物柴油的研究进展[J].化工进展,2004,23(10):1053-1057.(Ju Q H, Zeng C F, Guo W J, et al. Review on production of biodiesel via the transesterification method[J]. Chemical Industry and Engineering Progress, 2004, 23(10): 1053-1057.)

[2] 黄艳芹.餐饮废油催化转化制取生物柴油研究[J].新乡学院学报:自然科学版,2008,25(4):30-32.(Huang Y Q. Study on production of biodiesel by waste oil of restaurant catalytic transformation[J]. Journal of Xinxiang University: Natural Science Edition, 2008, 25(4): 30-32.)

[3] Gerpen J V. Biodiesel processing and production [J]. Fuel Processing Technology, 2005, 86(10): 1097-1107.

[4] Arzamendia G, Campoa I, Arguinarena E, et al. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH [J]. Chemical Engineering Journal, 2007, 134 (3): 123-130.

[5] 张波,付湘清,张汉鹏.介孔分子筛固载Keggin结构钼钨磷杂多酸的制备及表征[J].化学世界,2002,43(5):230-232.(Zhang B, Fu X Q, Zhang H P. Synthesis and characterization of Keggin-type heteropoly acid supported on mesoporous molecular sieve[J]. Chemical World, 2002, 43(5): 230-232.)

[6] 李长海,谷春旭,王国强,等.负载杂多酸 MCM-41 分子筛的制备与性能[J].石化技术与应用,2007,25(6):287-290.(Li C H, Gu C X, Wang G Q, et al. Preparation and property of heteropolyacid supported MCM-41 sieves[J]. Petrochemical Technology & Application, 2007, 25(6): 287-290.)

[7] 温朗友,沈师孔,闵恩泽.二氧化硅负载磷钨杂多酸催化剂的表征及催化性质[J].催化学报,2000,21(6):524-528.(Wen L Y, Shen S K, Min E Z. Physicochemical and catalytic properties of 12-Phosphotungstic acid supported on different silica[J]. Chinese Journal of Catalysis, 2000,21(6): 524-528.)

[8] Mylonas A, Papaconstantinou E. On the mechanism of photocatalytic degradation of cholrinated phenols to CO_2 and HCl by polyoxomatalates [J]. Journal of Photochemistry and Photobiology A: Chemistry, 1996, 94: 77.

[9] Beck J S, Vartuli J C A, Roth W J, et al. New family of mesoporous molecular sieves prepared with liquid crystal templates[J]. Journal of the American Chemical Society, 1992, 114: 10-34.