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高酸值生物柴油原料甘油酯化脱酸研究

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Deacidification of high-acid biodiesel feedstock by esterification with glycerol

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摘要 利用共沉淀-浸渍法制备了Al改性固体酸催化剂SO_4^{2-}/ZrO_2,考察了催化剂在甘油酯化脱酸制备生物柴油原料反应中的催化活性、重复利用性和再生性能,并对使用前后的催化剂进行了红外光谱分析。研究表明,添加适量Al(1%,以Al_2O_3的质量分数计)不但提高了催化剂的活性,还改善了催化剂的重复利用性和再生性能。添加Al使ZrO_2上SO_4^{2-}的量增加,SO_4^{2-}结合强度增强,减少了在酯化脱酸反应过程中SO_4^{2-}的流失。在SO_4^{2-}/ZrO_2-Al_2O_3催化剂用量为7%、甘油与酸物质的量比为6:1、反应温度为140 ℃、反应时间为4 h的条件下,酯化率可达91%以上,可将高酸值油脂的酸值从31 mg_{KOH}/g降低到2.8 mg_{KOH}/g以下,可满足生物柴油原料的要求。

关键词: 高酸值生物柴油原料 甘油酯化脱酸 固体酸催化剂

Abstract: Solid acid catalyst SO_4^{2-}/ZrO_2 modified by doping Al was prepared by co-precipitation-impregnation method and characterized by infrared spectrum. The activities of fresh, reused and regenerated catalysts were investigated by esterification with glycerol for deacidification of high-acid biodiesel feedstock. The activity of the catalyst SO_4^{2-}/ZrO_2 modified by 1% Al_2O_3, whatever the catalyst was in fresh or reused or regenerated condition, was better than that of non-modified SO_4^{2-}/ZrO_2. Al can increase the amount of SO_4^{2-} on the catalyst, strengthen the combination between S and O, and decrease the loss of SO_4^{2-} in the esterification process. The conversion of esterification was above 91% under the conditions of atmospheric pressure, 140 ℃ for 4 h, glycerol and fatty acid mole ratio of 6, and SO_4^{2-}/ZrO_2-Al_2O_3 catalyst dosage (catalyst/oil) of 7%.The acid value of the oil was reduced from 31 mg_{KOH}/g to 2.8 mg_{KOH}/g after esterification under above optimum conditions. This low-acid oil is suitable as the raw material of biodiesel.

Key words: high-acid biodiesel feedstock deacidification by esterification with glycerol solid acid catalyst

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