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MOF [(4,4-Bipyridine)$_2$(O_2CCH_3)$_2$Zn]N as Heterogeneous Acid Catalysts for the Transesterification of Canola Oil

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Abstract : Biodiesel has emerged as a material with great potential as a renewable energy replacement to current petroleum-based diesel. Recently, biodiesel production is focused on the development of more efficient, sustainable process with lower costs of production. In this sense, a “green” approach to biodiesel production has stimulated the use of sustainable heterogeneous acid catalysts, that are better alternatives to conventional processes because of their simplicity and the simultaneous promotion of esterification and transesterification reactions from low-grade, highly-acidic and water containing oils without the formation of soap. The focus of this methodology is the development of new heterogeneous catalysts that under ordinary reaction conditions could reach yields similar to homogeneous catalysis. In recent years, metal organic frameworks (MOF) have attracted much interest for their potential as heterogeneous acid catalysts. They are crystalline porous solids formed by association of transition metal ions or metal–oxo clusters and polydentate organic ligands. This hybridization confers MOFs unique features such as high thermal stability, larger pore size, high specific area, high selectivity and recycling potential. Thus, MOF application could be a way to improve the biodiesel production processes. In this work, we evaluated the catalytic activity of MOF [(4,4-bipyridine)2(O_2CCH_3)2Zn]n (MOF Zn-I) for the synthesis of biodiesel from canola oil. The reaction conditions were optimized using the response surface methodology with a compound design central with 24. The variables studied were: Reaction temperature, amount of catalyst, molar ratio oil: MetOH and reaction time. The preparation MOF Zn-I was performed by mixing 5 mmol 4´4 dipyridine dissolved in 25 mL methanol with 10 mmol $Zn(O_2CCH_3)_2 \cdot 2H_2O$ in 25 mL water. The crystals were obtained by slow evaporation of the solvents at 60°C for 18 h. The prepared catalyst was characterized using X-ray diffraction (XRD) and Fourier transform infrared spectrometer (FT-IR). The prepared catalyst was characterized using X-ray diffraction (XRD) and Fourier transform infrared spectrometer (FT-IR). Experiments were performed using commercially available canola oil in ace pressure tube under continuous stirring. The reaction was filtered and vacuum distilled to remove the catalyst and excess alcohol, after which it was centrifuged to separate the obtained biodiesel and glycerol. 1H NMR was used to calculate the process yield. GC-MS was used to quantify the fatty acid methyl ester (FAME). The results of this study show that the acid catalyst MOF Zn-I could be used as catalyst for biodiesel production through heterogeneous transesterification of canola oil with FAME yield 82 %. The optimum operating condition for the catalytic reaction were of 142°C, 0.5% catalyst/oil weight ratio, 1:30 oil:MeOH molar ratio and 5 h reaction time.

Keywords : fatty acid methyl ester, heterogeneous acid catalyst, metal organic framework, transesterification
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