Acid-base catalyst supported on mesoporous silica and anchored in organocomposites for the processing of biodiesel

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1. Introduction

An interesting possibility to process biodiesel from raw materials with a high acidity index is the immobilization of sulphonic acid and amino functions on the surface of mesoporous silica such as MCM-41 and SBA-15. These materials show excellent catalytic activity and less deactivation along the esterification-transesterification of vegetable oils and animal fats with high acidity index [1]. The development of a bifunctional catalyst, having external acid sites, capable of promoting esterification of free fatty acids, and internal basic sites for transesterifying triglycerides is an economically feasible solution. In a single step, and without the need for catalyst exchange, the low quality raw material can be esterified and transesterified simultaneously having the advantage of the two types of catalysis: acid for esterification and basic for transesterification [2].

The final cost of biodiesel production can be reduced considerably with the inclusion of low-cost raw materials such as frying oils, inedible oils and animal fats. The great challenge is to implement technologies capable of enabling the productive process of this energy input [3,4]. The objective of this work was to synthesize, characterize and catalytically test a propylsulfonic acid and piperazine functionalized support bifunctional catalyst to obtain biodiesel from the native oil of macaúba pulp (Acrocomia aculeata).

2. Experimental Part

The bifunctional catalyst supported by MCM-41 and anchored with propylsulfonic acid and piperazine (pr-HSO3 / MCM-41 / PPZ) was synthesized from the dissolution of Cetrimonium bromide (CTAB) in deionized water and sodium hydroxide solution. Then 1.0 g of pre-prepared basic catalyst (MCM-41 / PPZ), 0.0369 mol tetraethyl orthosilicate (TEOS) as silica source and 0.011 mol (3-Meraptopropil) trimethoxysilane (MPTMS) as sulfonic acid precursor were added. The surfactant was extracted with boiling acidic methanolic solution. The thiol was oxidized to HSO3-moiety with the addition of H2O2. The product obtained then was dried calcined for characterization by SAXS, FTIR and NMR of 28Si. Its catalytic activity was investigated through esterification-transesterification reaction to obtain biodiesel from the native oil of macaúba pulp (Acrocomia aculeata) which contained 34% of free fatty acids. The catalytic test were performed in a Parr 4848 reactor of 100 mL capacity. The reaction system consisted of 0.0142 mol of oil, 0.11 mol of methanol, 0.8 g of catalyst, molar ratio of 1: 8 (oil:methanol), temperature 120°C and reaction time was 180 min.

3. Results and discussion

Figure 1 shows the spectra in the IR spectra for the mesoporous support and for the bifunctional catalyst. Both materials showed absorption bands between 1836-1723 cm⁻¹ indicative to H2O bonds, as well as condensed bands between 3452-3421 cm⁻¹ attributed to the OH group. The silanols groups reacted with the functional groups giving rise to the bifunctional catalyst. Besides the axial deformation of the bond CH2= 2124-2860 cm⁻¹ the catalyst, pr-HSO3 / MCM-41 / PPZ, showed absorption bands at 1401 cm⁻¹ alluding to the SO3 group and at 3262 cm⁻¹ attributed to the NH bond confirming the acid and alkaline character.
condensation and evaluated in the simultaneous esterification-transesterification reaction of macaúba oil in a yield-range of 27-97% of methyl ester. The characterization of the pr-HSO3/MCM-41/PPZ revealed, that the immobilization of pr-HSO3 and piperazine influenced the removal of Si-OH groups

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References

Table 1 - Yield of esterification-transesterification reaction of macaúba oil

<table>
<thead>
<tr>
<th>Bifunctional Catalyst</th>
<th>Amount of catalyst (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>pr-HSO3/MCM-1/PPZ</td>
<td>27</td>
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4. Conclusions
The acid-base heterogeneous catalytic supported on MCM-41 and anchored with propylsulfonic and piperazine groups was synthesized by co-

Figure 1 - FTIR spectra of the bifunctional catalyst.

Figure 2 illustrates the $^{29}$Si NMR spectra for the bond the functionalized and modified catalyst. Pure MCM-41 revealed sites of type Q2, Q3 and Q4. The comparing with the spectra of pr-HSO3 / MCM-41 / PPZ reveal in addition to the Q-sites of the support material T-sites indicative of the C-Si type bonds. The propylsulfonic and piperazine groups influenced the reduction of Si-OH groups and though the appearance of covalent bonds.

Figure 2 - $^{29}$Si NMR spectra for the bifunctional catalyst and MCM-41