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Deactivation insights of mesoporous acid catalysts in fatty acids esterification

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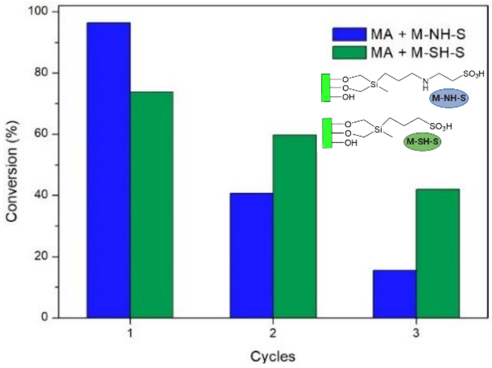
Currently, there are several protocols for biodiesel's production, but very few of them respond to the principles of green chemistry. This work focuses on the preparation of two sustainable MCM-41 type mesoporous acid materials, and the evaluation of their catalytic activity in the Fischer esterification with methanol of three model fatty acids (FAs). The materials were prepared by functionalizing the mesoporous surface in two ways. The first method involved the use of aminopropyltriethoxysilane, which was subsequently modified with 3-propanosultone (sample labeled M-NH-S) [1]. The second method employed mercaptopropyltrimethoxysilane, which was then oxidised with hydrogen peroxide (sample labeled M-SH-S) [2]. The solids were fully characterized by different techniques (XRD, FT-IR, TG, and ICP-AES). In addition, an infrared study of pyridine adsorbed was performed to determine the nature of the acid sites. The conversion kinetics of the FAs to methyl esters was monitored by gas chromatography with FID detection. The stability of the catalysts in terms of reuse was evaluated, observing that M-NH-S is deactivated by more than 80 % after 3 recovery cycles, while M-SH-S loses less than 30 % of its activity under the same experimental conditions.

In order to rationalize this behavior, the possible deactivation mechanism of the synthesized materials was studied through the characterization of the catalyst after the reaction. The deactivation of the materials was attributed to the formation of methyl sulfonates on the catalyst surface, with a more marked trend in M-NH-S. This result could be explained in terms of an increase in the acidity of the sulfonic group of the M-NH-S catalyst by the inductive effect of the NH substituent. This fact would stabilize the sulfonate anion by increasing the dissociation of the O-H bond, leading to a consequent increase in the rate of the O-methylation reaction.



Reusability study of M-NH-S and M-SH-S in the myristic acid (MA) esterification (reaction time: 120 min).

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References

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[2] M. Ziarani *et al*., J. Mol. Catal. A Chem., 397, 166 (2015).