Fe_3O_4 and Fe_3O_4@SiO_2-supported guanidine as magnetically recoverable and reusable catalysts for biodiesel production

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Introduction

Biodiesel is typically produced by transesterification process, catalyzed by acids or bases in presence of methanol[1]. Industrial production requires homogeneous basic catalysts to reach high yields. However, the amount of generated waste for catalyst recovery imposes serious limitations to the process[2]. To overcome this problem, new strategies to immobilize homogeneous catalysts onto several solid supports to facilitate the retrieve of the catalyst are need. Considering the above points, in this work we successfully anchored the guanidines TBD and TMG onto silica-coated and -uncoated magnetic supports, resulting in three (MNP-TBD, MNP-TMG and MNP@SiO_2-TBD) recoverable basic nanocatalysts. The materials were characterized by several techniques and their performance in biodiesel production was evaluated.

Results and Discussion

The catalysts were prepared according to the procedure represented in Figure 1.

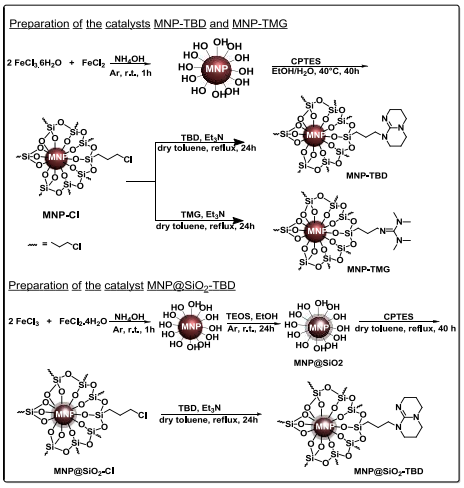

Figure 1: Preparation of the catalysts.

The amount of guanidine immobilized onto the MNP surface (0.20 mmol of TBD per gram of catalyst for MNP-TBD, 0.16 mmol of TMG per gram of catalyst for MNP-TMG and 0.30 mmol of MNP@SiO_2-TBD) were estimated using CNH elemental analysis.

The magnetic measurements of the catalysts showed the absence of hysteresis, which indicates that its display superparamagnetic behavior at T=300 K (**Figure 2a**). They also exhibited spherical particles with diameters ranging between 13-15 nm (**Figure 2b**). Afterwards, the nanocatalysts were tested in the methanolysis reaction of soybean oil in a closed vessel under different conditions. At the end of each reaction, the catalysts were magnetically recovered from the medium (**Figure 2c**) and the product analyzed and quantified by HPLC. The catalyst MNP-TBD showed the best performance in the first cycle: using 10% (w/w) of the catalyst, a methanol/oil ratio of 30:1 and 24 h of reaction at 120° C, achieving 96% in biodiesel conversion. However, the catalyst MNP@SiO_2-TBD showed better reuse (**Figure 2d**).

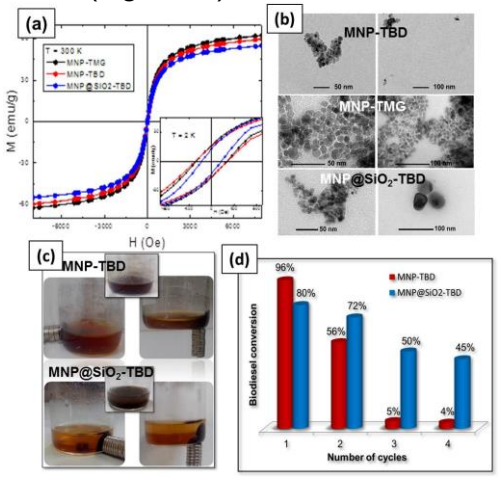

Figure 2: (a) Field dependence of the magnetization measured at 300 K and 2 K, (b) TEM images, (c) recovery and (d) recycling test of the catalysts.

Conclusions

This study showed the advantages of using magnetic nanoparticles as catalytic supports, being useful for a clean and economic biodiesel production.

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