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Full Length Article

One-step biodiesel production from waste cooking oils over metal incorporated MCM-41; positive effect of template

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ABSTRACT

MCM-41 materials modified with Mg, Co, and Zn were prepared by direct synthesis method. The template-containing catalysts as bifunctional catalysts were evaluated for simultaneous esterification and transesterification reactions of waste cooking oil. All catalysts showed high FAME yield (≥92%) with methanol to oil mass ratio of 8:1, after 3 h. It was also found that [CTA]MCM-41 had a high catalytic activity achieving a maximum FAME yield of 93%. It might be because of the basicity and hydrophobicity induced by organic template. Furthermore, these catalysts can be reused without loss of catalytic activity due to the stability of organic template (CTA^+) inside the pores.

1. Introduction

Biodiesel (Fatty Acid Methyl Ester) is an alternative fuel similar to conventional or fossil diesel. Various edible oils are investigated by different researchers as potential feedstock for biodiesel production. These raw materials are not entirely suitable, due to the limited supply and high cost associated with their application, as well as competition with the food chain [1]. Therefore, low cost, non-edible oils such as Jatropha oil, animal fat and waste cooking oil (WCO) have been suggested and tested as alternatives [2–5]. However, the main disadvantage of these non-edible types of feedstock is the high content of free fatty acid (FFA) within the oils, which poses problems in the production process. FFA reacts with the basic catalyst (NaOH, KOH) and forms soaps. This soap formation complicates the glycerol separation, and drastically reduces them ethyl ester yield [6]. Consequently, biodiesel from high FFA content feedstock is conventionally produced by a two-stage process. In the first stage, esterification of FFA present in WCO is carried out using an acid catalyst and in the second stage transesterification of neutral WCO is performed using a basic catalyst [7]. Therefore, it is advantageous to develop a new class of heterogeneous catalysts, which can simultaneously catalyze both the esterification and transesterification reactions. Heterogeneous bifunctional catalysts can provide a continuous range of functional groups and offer advantages, such as an enhancement of reactivity and stability of antagonist functional groups [8].

Mesoporous material (such as MCM-41, SBA-15) have attracted growing interest as heterogeneous catalysts owing to their high surface area, uniform pores, and relatively high thermal stability. These materials are prepared by using ionic surfactants [9]. Generally, the residual templates inside the pores are removed by calcination or extraction. Based on our experience, template-containing catalysts exhibited more basicity than their calcined counterparts [10]. In continuation of our previous work, template-containing Mg/MCM-41, Co/MCM-41 and Zn/MCM-41 were synthesized via direct synthesis method. Mg^{2+} as a weak Lewis acid, Co^{2+} as a good Lewis acid and Zn^{2+} as a strong Lewis acid were selected. Simultaneous transesterification and esterification of WCO was carried out in the presence of prepared catalysts which strong acidic and basic sites co-exist on their surface and compared to metal free MCM-41.

2. Experimental

Cetyltrimethylammonium bromide (CTA) (≥98%), Tetraethyl orthosilicate (> 98%), $Zn(NO_3)_2$ $4H_2O$ (≥98), $Co(NO_3)_2$ $6H_2O$ (≥98.5), and $Mg(NO_3)_2$ $6H_2O$ (≥98.5) were purchased from Merck and used as received. The waste canola oil was collected from household cooking activities (Acid value = 2.2 mg KOH/g, determined by titration with KOH as ASTM D 664 test method).

XRD measurements were performed on a STOE-STAD diffractometer with Cu Kα radiation over the 2θ range 1–10°. The elemental chemical compositions of the samples were determined by EDX (MIRA3\\TESCAN-FEG, Czech Republic). FTIR spectra were recorded on a Bruker Tensor 27 instrument using KBr pressed powder discs.

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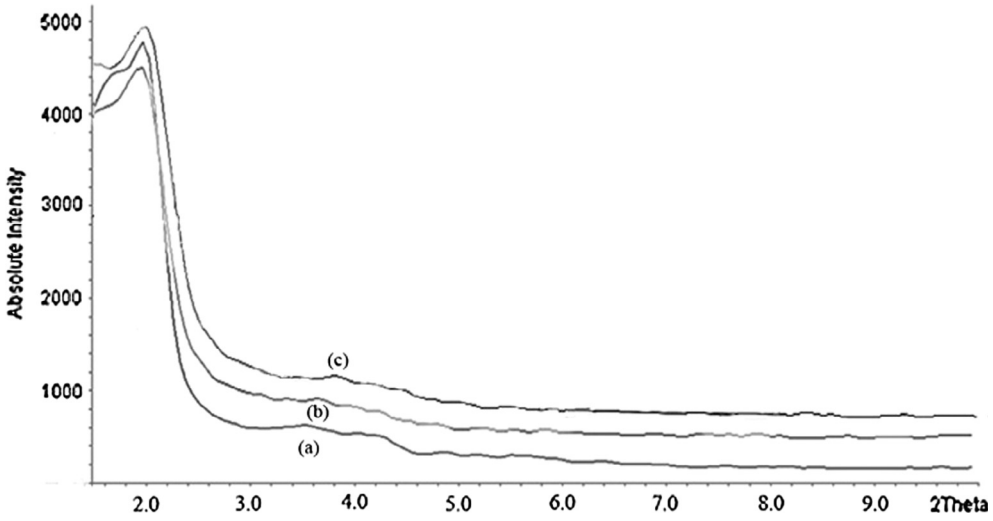

Fig. 1. Low-angle XRD patterns of a) [CTA]Mg/MCM-41, b) [CTA]Co/MCM-41 and c) [CTA]Zn/MCM-41.

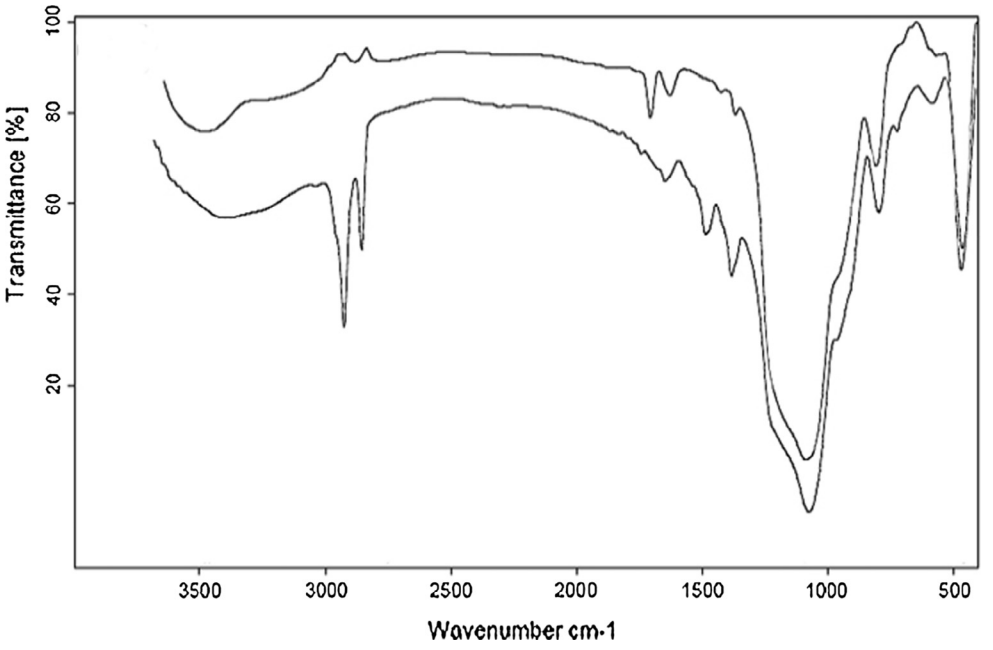

Fig. 2. FT-IR spectra of a) [CTA]Co/MCM-41, b) calcined Co/MCM-41.

2.1. Catalyst preparation

In a typical synthesis [11], 2.74 mmol of cetyltrimethylammonium bromide (CTA) were dissolved in 480 mL of NaOH aqueous solution (15.0 mM), followed by a drop wise addition of 22.4 mmol of tetraethylorthosilicate (TEOS). Then, a solid powder of metal nitrate (2.24 mmol) was slowly added. The mixture was vigorously stirred and heated to 80 °C for 2 h. Subsequently, the product powder was isolated by hot filtration, washed with water and air-dried.

Table 1
The metal content of prepared catalysts.

Catalysts	[CTA]Mg/MCM-41	[CTA]Co/MCM-41	[CTA]Zn/MCM-41
M* (σ**)	2.76 (1.42)	4.6 (0.50)	3.85 (1.47)

* Determined by EDX analysis (wt%).
** Standard deviation.

2.2. Measurement of Lewis acidity

The number of catalytically available Lewis acid sites of the catalysts was determined according to the following process [12]:

A pH electrode was introduced in 20 ml of NaOH 0.005 M standardized solution, until no pH variations were observed (pH = 12). Then 1 g of the catalyst fresh sample was added and pH evolution as a function of time was measured for 1 h.

2.3. Catalytic conversion of WCO to FAME

Catalytic conversion of oils was carried out according to a previously reported procedure [13]. In a typical reaction 1 g oil sample was taken with methanol (8 g) in a 1:8 w/w ratio, followed by catalyst addition (0.1 g) and then the reaction mixture was held at 80 °C for 3 h. After the reaction is completed, the mixture was rotary evaporated at 50 °C to separate the methyl esters. The conversion yield of the oil to the corresponding methyl ester was calculated using Eq. (1):

$$Y = 100 \times (2AME/3ACH_2) \quad (1)$$