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Short Communication

One-pot synthesis of calcium-incorporated MCM-41 as a solid base catalyst for transesterification of palm olein

Jonggol Tantirungrotechai [a,*], Pharawee Thananupappaisal [b], Boonyawan Yoosuk [c], Nawin Viriya-empikul [d], Kajornsak Faungnawakij [d]

[a] Center for Catalysis, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Bangkok, 10400 Thailand
[b] Materials Science and Engineering Program, Multi-Disciplinary Unit, Faculty of Science, Mahidol University, Bangkok, 10400 Thailand
[c] National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency, Pathumthani, 12120 Thailand
[d] National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency, Pathumthani, 12120 Thailand

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ABSTRACT

Direct generation of basic sites on mesoporous silica MCM-41 through calcium incorporation was achieved via a one-pot synthesis. The effect of calcium salt precursors was addressed in terms of structure, morphology, and basic property. The catalysts were evaluated for potential application in transesterification of palm olein with methanol to produce biodiesel. Among all of the catalysts tested in this study, the most efficient calcium-incorporated MCM-41 was derived from CaO precursor, affording over 90 wt.% of fatty acid methyl ester after 3 h of reaction at 200 °C.

1. Introduction

Biodiesel is a promising alternative and environmentally friendly biofuel produced by a base-catalyzed transesterification of triglycerides with methanol. Homogeneous base catalysts such as sodium hydroxide and potassium hydroxide are commonly used for the reaction. Even though these homogeneous catalysts provide a rapid reaction rate, the separation and purification of biodiesel product are tedious and a large amount of wastewater is produced in the post-treatment process. On the other hand, heterogeneous base catalysts offer simplification of separation and purification of the reaction products and recycling possibility for the catalysts. Thus, heterogeneous base catalysts become an attractive solution to the problems.

In recent years, many solid base catalysts have been investigated for the transesterification of vegetable oil with methanol, including alkali earth oxides [1–3], supported alkali [4–6] or alkali earth ions [7–9], hydrotalcites [10, 11], and basic zeolites [12]. Alkali earth metal compounds, particularly calcium compounds, are considered very interesting from the economical perspective. Many calcium compounds, for example, calcium carbonate [13], calcium alkoxides [1, 14, 15], and calcium oxide [16–19], have been reported in the literature to be active in biodiesel synthesis. However, the dissolution of these solids in the reaction medium is largely concerned to hinder the benefits of their heterogeneous nature [20]. As a result, many approaches have been adopted in order to enhance the stability of calcium containing solid bases, including the dispersion of calcium species on mesoporous silica supports.

Mesoporous molecular sieves have attracted much interest, especially their applications in catalysis, due to the high surface area, well-defined pore shape, narrow pore size distribution, and high degree of pore ordering. MCM-41 [21, 22] and SBA-15 [23, 24] are mesoporous silica materials that have been widely studied, because their silica framework can be easily modified to achieve active sites of desired purposes. Recently, calcium-containing silicates have been proposed as active solid bases for transesterification [25, 26]. However, there are only a few reports on calcium-containing mesoporous silica; and most of them employed the post-synthesis modification method via incipient wetness [27] or wet impregnation protocols [28]. The one-pot synthesis of calcium loaded mesoporous silica was reported for SBA-15, along with its application in transesterification of sunflower oil with methanol [29]. Nonetheless, due to the different synthetic conditions for SBA-15 and MCM-41, a one-pot synthesis for calcium-incorporated MCM-41 appears equally interesting.

In this study, calcium-incorporated MCM-41 catalysts were successfully prepared by a one-pot synthesis. The effect of calcium precursors on the synthesized catalysts was studied. Their physical

* Corresponding author. Tel.: +66 2 201 5145; fax: +66 2 354 7151.
E-mail addresses: scjjp@mahidol.ac.th, jonggol@gmail.com (J. Tantirungrotechai).

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and basic properties were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), N_2 adsorption-desorption measurement, scanning electron microscopy (SEM), CO_2-temperature-programed-desorption (CO_2-TPD) technique, and Hammett indicator method. The catalytic performance of these solid base catalysts for transesterification of palm olein with methanol was also investigated.

2. Experimental

2.1. Catalyst preparation

In a typical synthesis, 2.74 mmol of cetyltrimethylammonium bromide (CTAB) were dissolved in 480 mL of NaOH aqueous solution (15.0 mM), followed by a dropwise addition of 22.4 mmol of tetraethylorthosilicate (TEOS). Then, a solid powder of calcium precursor (4.48 mmol of CaO, $Ca(OH)_2$, or $Ca(OAc)_2$) 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 methanol, and then freeze dried. Finally, the catalyst was calcined at 600 °C in air for 6 h. Based on the type of precursor, the calcium-incorporated MCM-41 samples are referred to as CaO/MCM-41, $Ca(OH)_2$/MCM-41, and $Ca(OAc)_2$/MCM-41 with a theoretical Ca/Si molar ratio of 0.2. For comparison, MCM-41 was synthesized using the same procedure excluding the addition of calcium source.

2.2. Catalyst characterization

The samples were characterized by TGA carried out on a Mettler Toledo thermogravimeter at a ramping rate of 10 °C/min under a flow of dry air. Powder XRD patterns were recorded on a Bruker D8 ADVANCE diffractometer operating at 40 kV and 40 mA using Cu-$K_{\alpha 1}$ with Ge-crystal (Johansson type) monochromator (λ = 1.540619 Å). The calcium and silicon contents were determined by wavelength dispersive X-ray fluorescence spectrometer, Bruker AXS model S4 Explorer equipped with Rh K radiation operating at 50 kV and 20 mA. The morphologies of samples were observed by SEM (HITACHI S-2500) at 15 kV.

N_2 adsorption–desorption isotherm and pore size distribution measurements were obtained by using Autosorb-1 (Quantachrome); samples were dried at 300 °C for 10 h prior to the measurement. The basic strength of catalyst was studied by Hammett indicator method and CO_2-TPD technique (Thermofinnigan; model 1100). Prior to CO_2 adsorption, 0.4 g of catalyst was pretreated at 120 °C for 30 min under N_2 (20 mL/min). Then, a flow of CO_2 (20 mL/min) was introduced for 150 min at room temperature. After purging the system with N_2 for 60 min, the sample was heated from 40 to 950 °C with a ramp rate of 10 °C/min under He flow (20 mL/min). The CO_2 desorption was monitored by an online gas chromatography instrument equipped with a thermal conductivity detector (TCD). Hammett indicator experiment was performed according to the literature protocols [30], but methanol was employed as a solvent instead of a nonpolar solvent [11]. A sample was added to an approximately 0.5 mL solution of Hammett indicator diluted in methanol, and left to equilibrate for 2 h. The colors of the catalysts were then noted. The Hammett indicators used were Bromothymol blue (pK_{BH+} = 7.2), Phenolphthalein (pK_{BH+} = 9.8), Nile blue chloride (pK_{BH+} = 10.1), and Tropaeolin O (pK_{BH+} = 11.0).

2.3. Catalytic activity for transesterification reaction

The biodiesel production activity of all catalysts was demonstrated through transesterification of palm olein with methanol. The palm olein oil was purchased from Morakot Industries, PCL., Thailand. The fatty acid in the palm olein oil consists mainly of oleic acid (C18:1) (45.8 wt.%), palmitic acid (C16:0) (37.4 wt.%), linoleic acid (C18:2) (11.1 wt.%) and stearic acid (C18:0) (3.6 wt.%). Its acid value is 1.10 mg KOH/g oil. The transesterification reactions were carried out in a 1-L Parr reactor at 200 °C using 1 wt.% of catalyst loading (with respect to weight of oil) and 1:25 of oil to methanol molar ratio. A small aliquot was taken from the reaction mixture at various times in order to follow the product yield. Each aliquot was extracted in a hexane/water system; and the fatty acid methyl ester (FAME) products were determined based on the standard method EN 14103 by gas chromatography (ShimadzuGC-2010) with a capillary column, DB-WAX (30 m × 0.32 mm × 0.25 mm), and a flame ionization detector (FID). The column temperature was programmed from 180 °C to 230 °C with the heating rate of 5 °C/min. Methylheptadecanoate was used as an internal standard for quantification. The biodiesel yield was characterized in term of %FAME as a function of time.

3. Results and discussion

3.1. Catalyst structure

Fig. 1 shows the TG/DTG curves of MCM-41, CaO/MCM-41, $Ca(OH)_2$/MCM-41, and $Ca(OAc)_2$/MCM-41 samples before calcination. The thermal behavior for all samples was similar with the first weight loss of ca. 10% below 120 °C attributed to the evaporation of physisorbed water. The two weight losses at 200–330 and 330–400 °C were due to the decomposition of CTAB. For the calcium-containing samples, the decomposition temperature of CTAB was slightly higher than that of pure MCM-41 and increased in the order of $CaO < Ca(OH)_2 < Ca(OAc)_2$. This result indicated that the introduction of calcium species retarded the decomposition of CTAB. This phenomenon was also observed for MgO- and CuO-modified SBA-15 materials synthesized by an in-situ coating method [31]. The incorporated metal species blocks the decomposition of Pluronic P123. Additionally, the different decomposition temperature is also correlated with the dispersion of calcium species in the catalyst. Among three calcium-containing samples, CaO/MCM-41 exhibited the lowest temperature for CTAB decomposition; thus, the highest calcium dispersion was attained. The weight loss at a higher temperature of 600–700 °C was corresponded to the decomposition of calcium salts.

The XRD patterns of MCM-41, CaO/MCM-41, $Ca(OH)_2$/MCM-41, and $Ca(OAc)_2$/MCM-41 samples are shown in Fig. 2. The intense diffraction peak at 2θ of ~2° as well as the low intensity broad peaks at 2θ of 3.8 and 4.5° are the characteristic (100), (110), and (200) peaks of MCM-41, respectively. For the calcium-incorporated samples, the XRD results suggested that the ordered mesoporous structure of parent MCM-41 was preserved after the introduction of calcium species in the synthesis. However, only the (100) peak was observed with much lower intensity compared to that of pure MCM-41. In general, the introduction of metal oxides may decrease the scattering contrast between pore walls and pore spaces, leading to the decline in diffraction intensity. In addition, a lower degree of pore ordering in the calcium-incorporated MCM-41 samples may also be responsible for the relatively lower intensity. Besides, the 2θ values for (100) peak were shifted to higher angles, implying smaller lattice parameter, *a*, and structural shrinkage after calcium incorporation. At wider angles (Fig. 2b), the XRD patterns show only the characteristic peak of amorphous silica with no appearance of any crystalline calcium-containing phases, suggesting a good dispersion of calcium species in silica framework of MCM-41. Furthermore, the presence of calcium in the samples was confirmed by XRF measurement (Table 1). The Ca/Si molar ratios of the calcium-incorporated MCM-41 samples were 0.27, 0.19, and 0.19 for CaO/MCM-41, $Ca(OH)_2$/MCM-41, and $Ca(OAc)_2$/MCM-41 samples, respectively. These numbers are close to the amount of calcium salt added to the synthetic mixture (calculated Ca/Si ratio = 0.2). The slightly higher calcium