Applied Catalysis A: General 390 (2010) 26–34

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

One-pot synthesized mesoporous Ca/SBA-15 solid base for transesterification of sunflower oil with methanol

Hui Sun[a,b], Junxing Han[a,b], Yuqi Ding[a,b], Wang Li[a,b], Jinzhao Duan[a,b], Ping Chen[a,b], Hui Lou[a,b,*], Xiaoming Zheng[a,b]

[a] Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, PR China
[b] Key Laboratory of Applied Chemistry of Zhejiang Province, Hangzhou 310028, PR China

ARTICLE INFO

Article history:
Received 22 June 2010
Received in revised form
10 September 2010
Accepted 15 September 2010
Available online 27 October 2010

Keywords:
Ca/SBA-15
CaO
Solid base
Transesterification
Biodiesel

ABSTRACT

A series of Ca/SBA-15 samples with Ca/Si atomic ratios of 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared by using a one-pot synthesis method. They were used in the transesterification of sunflower oil with methanol. For comparison, 0.3Ca/SBA-15 was also synthesized by an incipient impregnation method (0.3Ca/SBA-15-IM). Small-angle XRD, N_2 adsorption, TEM, SEM, TG-DTA, FTIR, CO_2-TPD techniques were used to determine the textual structure and physicochemical properties of Ca/SBA-15 samples. The mesoporous structure of SBA-15 was well preserved with Ca/Si ratios up to 0.5. Compared with 0.3Ca/SBA-15-IM sample, the Ca/SBA-15 showed not only a better calcium species distribution, but also higher BET surface area and larger medium basic sites. A biodiesel yield of as high as 99.1% was achieved on the 0.5Ca/SBA-15 catalyst at a reaction temperature of 200 °C for 8 h. In the meantime, no deactivation was found after five cycles on Ca/SBA-15 sample prepared by one-pot synthesis method in the transesterification reaction, which showed a much better stability than that of prepared by conventional impregnation method. Besides, a water content of up to 5% and/or free fatty acids (FFAs) content of 3% did not affect the catalytic activity of Ca/SBA-15 catalyst in the transesterification reaction.

1. Introduction

Petrochemical sources such as coal and natural gases, which are finite and will be exhausted shortly, are supplying the majority of the energy needs of the world nowadays. The utilization of alternative renewable fuels is therefore being more and more attracting. Biodiesel, a mixture of alkyl esters obtained from vegetable or animal oils, is a promising nontoxic and biodegradable fuel arising from biomass [1,2]. Biodiesel is usually produced by the transesterification of triglycerides with methanol and/or ethanol in the presence of a catalyst [3]. Alkaline catalysts are more widely investigated because the rate of transesterification reactions catalyzed by alkaline catalysts is much faster than those of reactions catalyzed by the acid catalysts [4,5].

Homogeneous basic catalysts such as sodium or potassium hydroxide are conventionally used for the transesterification reaction because these traditional homogeneous catalysts have certain advantages, including high activity (complete conversion within 1 h) and mild reaction conditions (65 °C and 1 atm). However, the removal of these catalysts is technically difficult, and a large amount of wastewater was produced during biodiesel separation and cleaning [6]. Heterogeneous basic catalysts have been widely studied in the last decades in order to circumvent the difficulties with homogeneous catalysts. They have some outstanding advantages, such as simpler separation and no toxicity, no corrosion, or no environmental pollution [7].

Many kinds of solid bases have been investigated for this purpose, including alkali and alkali earth metal oxides [8,9], rare earth metal oxides [10–13], calcined hydrotalcites [14,15], alkali earth metal oxide and rare earth metal oxide complexes [16,17], zeolites [18], anion exchanged resins [19,20]. A leaching problem has been raised up in most of the catalysts just in the past several years [8,9,21,22]. CaO is the most attractive catalyst among the insoluble alkali and alkali earth metal oxides because of its high transesterification activity [23–25]. A large amount of leached species, however, was also observed because of the formation of Ca diglyceroxide when glycerol is present [26]. Because extensive leaching may threaten the reusability and the environmental sustainability of catalyst, pure CaO seems not adaptable for industrial applications. Thus, it is important to investigate novel heterogeneous basic catalysts that are both active and stable for the transesterification reaction.

New opportunities have been opened up in many areas of chemistry and material science since the discovery of mesoporous

* Corresponding author at: Institute of Catalysis, Department of Chemistry, Zhejiang University, Tianmushan Road No. 138, Zhejiang, Hangzhou 310028, PR China. Tel.: +86 571 88273593; fax: +86 571 88273283.
E-mail address: hx215@zju.edu.cn (H. Lou).

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doi:10.1016/j.apcata.2010.09.030

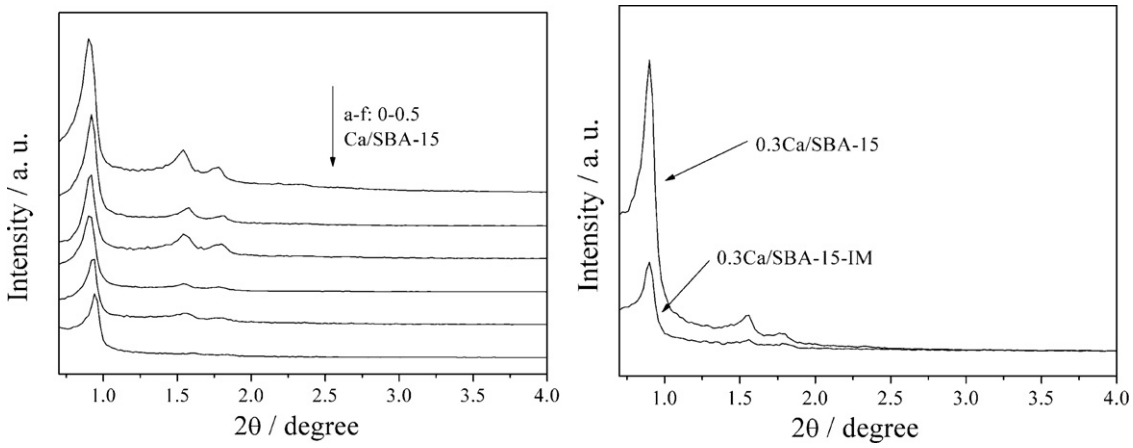

Fig. 1. Small-angle XRD patterns of (a–f) 0–0.5Ca/SBA-15 and 0.3Ca/SBA-15-IM calcined at 550 °C.

silica molecular sieves [27,28]. Due to its desirable features, e.g. tailorable pore size, high degree of structural ordering, ease of synthesis, larger pore size, thicker pore walls and higher hydrothermal/thermal stability, SBA-15 has been extensively studied in the last decade [29,30]. Nowadays, SBA-15 has achieved numerous applications in the fields of catalysis, adsorptions, separations, water purification, and advanced optical devices because of its unique physicochemical properties [31–36].

SBA-15 based solid strong bases have been widely studied in the field of catalysis because of their unique property [37–43]. Srivastava et al. synthesized cyclic carbonates by using adenine-modified Ti-SBA-15 solid base as a catalyst [37]. Sujandi et al. also successfully prepared the short-channeled amino-functionalized-SBA-15 catalysts with high performance in Knoevenagel and Claisen–Schmidt condensations as well as in Henry reactions. Both organic and inorganic compounds, including amino [39], magnesium [40,41], and calcium [42] modified SBA-15 have been achieved by Zhu's group. Albuquerque et al. reported the first use of CaO/SBA-15 type solid base catalyst in biodiesel production, but the reusability of the catalyst was not reported [43]. It is worth noting that Mg and/or Ca modified SBA-15 solid base catalyst were all prepared by an impregnation-like method. This required two steps of calcination for the formation of solid base which of course led to more energy consumption. On the other hand, although solid strong/super bases can catalyze various reactions in mild conditions, their industrial applications are limited by the difficulties in synthesis and storage [44]. Thus, preparation of less strong but more stable solid bases seems more promising in industrial applications.

Here, we present a one-pot synthesis method to prepare calcium loaded SBA-15 solid base. The physicochemical properties of the resultant materials are characterized by X-ray diffraction (XRD), N_2 adsorption, transmission and scanning electron microscopy (TEM and SEM), thermogravimetric analyzers (TG), Fourier transform infrared spectroscopy (FTIR), and CO_2-temperature-programmed desorption (CO_2-TPD) techniques. For comparison, Ca/SBA-15 was also synthesized by the impregnation method (0.3Ca/SBA-15-IM). The catalytic activity of these catalysts was tested by the transesterification reaction of sunflower oil with methanol. The differences between samples prepared by the two methods were also identified and discussed.

2. Experimental

2.1. Sample preparation

Ca/SBA-15 samples were synthesized according to standard literature procedures [29,30]. In a typical synthesis, 2 g of triblock copolymer P123 was first dissolved in 75 g of 1.6 M HCl, then a calculated amount of $Ca(NO_3)_2$ was added under stirring for 0.5 h. Thereafter, 4.25 g of TEOS was added under stirring at 40 °C. The resultant solution was stirred for 24 h at 40 °C, then transferred to a 100 ml autoclave and heated at 120 °C for another 24 h under static condition. Finally, the mixture was evaporated in a rotating evaporator under 55 °C and calcined at 550 °C in air for 6 h. The obtained sample was denoted as *x*Ca/SBA-15 where *x* represents the Ca/Si atomic ratio. For comparison, another Ca/SBA-15 sample was synthesized by an incipient impregna-

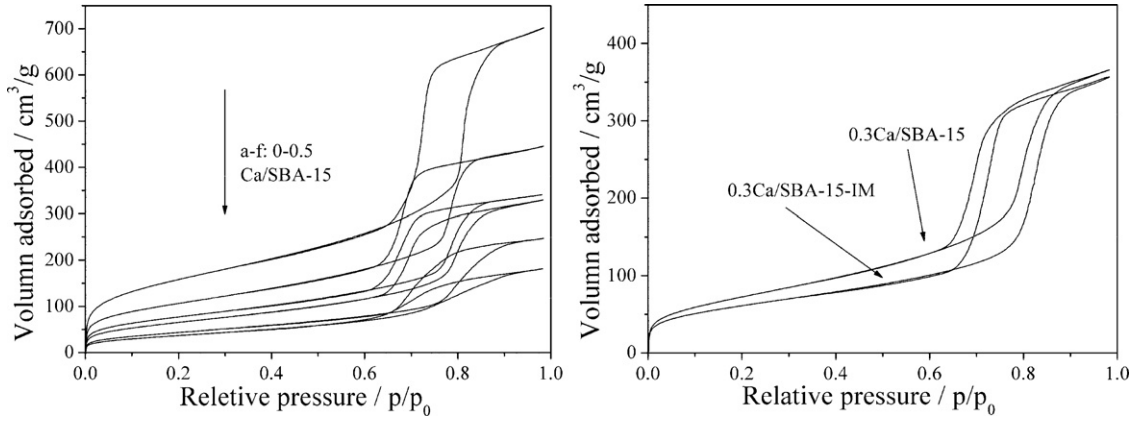

Fig. 2. Nitrogen adsorption–desorption isotherms of (a)–(f) 0–0.5Ca/SBA-15 and 0.3Ca/SBA-15-IM calcined at 550 °C.