Bioresource Technology 106 (2012) 178–181

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Short Communication

Transesterification of sunflower oil on single step sol–gel made Al_2O_3 supported CaO catalysts: Effect of basic strength and basicity on turnover frequency

Emin Selahattin Umdu, Erol Seker *

Izmir Institute of Technology, Department of Chemical Engineering, Gulbahce Campus, Urla, Izmir 35430, Turkey

ARTICLE INFO

Article history:
Received 7 April 2011
Received in revised form 29 November 2011
Accepted 30 November 2011
Available online 8 December 2011

Keywords:
Sol–gel
Calcium oxide
Alumina
Sunflower transesterification
Turnover frequency

ABSTRACT

The activities of single step sol–gel made calcium oxide on alumina catalysts were studied as a function of CaO loading, methanol/oil molar ratio and the amount of the catalyst in the transesterification of sunflower oil at 50 °C. Also, the turnover frequency (TOF) of the catalysts was calculated to better understand the relationship between the basicity/basic strength and the catalytic activity. From volcano curve (TOF vs. basic strength), it was found that under 50 °C and methanol/oil molar ratio of 9, 60% CaO/Al_2O_3 had the highest turnover frequency, 0.028 s^{-1}, whereas 85% CaO/Al_2O_3 showed the highest biodiesel yield, ~96.6%, but TOF obtained on it was 0.012 s^{-1}. It seemed that 60% CaO catalyst had the proper basic strength to obtain the highest TOF.

1. Introduction

Eighty-eight percentage of the world energy consumption is provided by the carbon based non-renewable fuels, such as petroleum and natural gas with limited reserves and their use causes environmental problems, such as air, water, and soil pollutions (Baruch, 2008). In fact, transportation is responsible for 28% of total CO_2 emission in the world (Zachariadis and Kouvaritakis, 2003). Biodiesel (monoalkyl esters of long chain fatty acids) seems to reduce green house gases (GHG) emission since carbon in the biodiesel are reused by the plants during growth; hence resulting in a near net zero carbon dioxide (CO_2) emission. Biodiesel is commonly produced using a soluble catalyst, such as KOH, in the industry but the major drawback of using soluble catalyst is that it may result in soap formation if oil has high free fatty acid and water (Zhang et al., 2003; Meher et al., 2006).

Acid, base, or supported enzyme catalysts were used as heterogeneous catalysts in the transesterification of vegetable oils (Van Gerpen, 2005; Xie and Li, 2006; Chen et al., 1998). For example, Suppes et al. (2003) reported metal ion-exchanged zeolites were highly active in the transesterification of soybean oil at 100–150 °C temperature range in 4–24 h. Enzymatic catalysts, such as lipases, are environmentally friendly but they are expensive and also decrease of activity was observed when immobilized on a support material (Severac et al., 2011). Commercially available low surface area CaO when used without heat treatment gave 61% biodiesel yield at 65 °C and methanol/soybean oil molar ratio of 12 in 1.5 h whereas commercial CaO when heat treated at 700 °C gave ~94% biodiesel yield, than untreated CaO (Liu et al., 2008; Granados et al., 2007). Calcination temperature effect on other catalyst formulations was also reported (MacLeod et al., 2008). Unfortunately, it is difficult to make sound comparison between the studies in the literature because of the varying preparation methods, calcination temperature and the reaction conditions. In addition, the use of biodiesel yield as the indicative of the catalyst activity seems to be misleading because the catalysts used in comparison do not have the same surface areas. However, to eliminate the effect of the surface areas and pore sizes on the activity of the catalysts, turnover frequency (TOF, s^{-1}) is used to correlate the catalytic activities with the physicochemical properties by plotting TOF vs. the basic strength, known as volcano plot (Boudart, 1995; Ribeiro et al., 1997). In fact, there is no study on the relationship between the basic strength/basicity and the turnover frequency for the heterogeneous transesterification of sunflower oil over sol–gel made alumina supported high CaO loadings at 50 °C in the literature.

In this manuscript, the effect of CaO loading on the basicity (basic site density, μmol/m^2) and the basic strength (the peak temperature, °C) of single step sol–gel made CaO/Al_2O_3 catalysts and also its relationship to the turnover frequency, s^{-1}, (TOF) of the catalysts in the transesterification of sunflower oil at 50 °C were studied. For comparison, pure alumina synthesized with the same sol–gel procedure and also a commercial pure CaO were used.

---

* Corresponding author. Tel.: +90 232 750 6646; fax: +90 232 750 6645.
E-mail addresses: selahattin_umdu@hotmail.com (E.S. Umdu), erolseker@iyte.edu.tr (E. Seker).

0960-8524/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2011.11.135

2. Methods

2.1. Catalyst preparation

CaO/Al_2O_3 catalysts were synthesized using a modified single step sol–gel method (Yoldas, 1975; Umdu, 2008). Briefly, necessary amounts of aluminum isopropoxide (AIP) (98%, from Fluka Inc.), water and HNO_3 were mixed at 85 °C under total reflux for 1 h. Then, a required amount of calcium nitrate tetrahydrate (99.3%, from Fluka Inc.) was added to the alumina sol and stirred for one more hour to achieve the desired CaO loading (e.g. 30, 60, and 85 wt.%) and then excess water was slowly evaporated to obtain the gel. Also, pure Al_2O_3 was synthesized using the same sol–gel procedure without adding calcium nitrate precursor. All the gels were dried at 120 °C for 18 h and calcined at 500 °C for 6 h. Finally, the catalysts were ground and sieved to less than 325 mesh and stored in a desiccator prior to the activity tests. Pure CaO (99+%, from Aldrich Inc.) were used after applying the same heat treatment and sieving.

2.2. Catalyst activity and characterization measurements

The catalytic activities of CaO/Al_2O_3, pure CaO and pure Al_2O_3 catalysts for transesterification of sunflower oil were determined in a batch reactor under total reflux. Before testing, all the catalysts were activated at 500 °C to remove absorbed water and CO_2. After that, to avoid further exposure to atmospheric water and carbon dioxide, all the catalysts were immediately mixed with the required amount of methanol for the transesterification reaction under nitrogen atmosphere as soon as they were removed from the furnace at 500 °C. Commercially available sunflower oil (from Tansas Inc.) were then added. The following reaction conditions were used in all the tests: 50 °C, 3–12 wt.% of the oil used as the catalyst amount, 1100 rpm of the stirring speed and the methanol/oil molar ratio of 4–12. Based on the previous study done on canola oil using heterogeneous catalysts (Umdu, 2008), the transesterification activity tests in this study were done using three replicates; hence, the repeatability at 95% confidence interval was ~4.5%. Two phase formation was observed at the end of the reaction and then, the mixture was centrifuged at 4000 rpm for 30 min to fully separate solid catalyst from two liquid phases. Finally, the upper liquid phase was weighed and analyzed by a GC after separation.

The biodiesel content of the upper phase was determined using a Shimadzu GC-17A gas chromatograph equipped with a FID detector and a DB-WAX 122-7032 (30 m long, 0.25 mm in diameter and 0.25 μm film thickness). Biodiesel yield was defined as:

$$\text{Biodiesel yield (wt.\%)} = 100^{*}[\text{Amount of biodiesel in upper phase (g)}]/[\text{Initial amount of sunflower (g)}]$$

Biodiesel yield (wt.%) is in fact equal to the sunflower oil conversion (mol.%) since the ratio of molecular weight of sunflower to molecular weight of the corresponding methyl esters is equal to the stoichiometric coefficient (i.e. 3) of methyl esters in the transesterification reaction.

Turnover frequency (TOF, s^{-1}) was calculated using the initial reaction rate concept and the total basicity as follows (Ranganathan et al., 2005; Kulkarni and Wachs, 2002):

$$\text{Turnover frequency (TOF}, s^{-1}) = [\text{Initial oil consumption rate}]/[\text{Total basicity}]$$

where the initial rate of oil consumption is in gmol/m^2 s; the total basicity is in gmol/m^2.

Crystalline phases present in the catalysts were determined by X-ray diffraction technique (Philips X'pert Pro XRD, operated at 40 kV and 45 mA) and the average crystallite sizes were calculated from the peak broadening of the diffraction peaks using Scherrer equation. The specific surface areas of the catalysts were found using a standard procedure and Micromeritics ASAP 2010.

Micromeritics AutoChem 2910 equipped with an inline Balzers Thermostar GS300 quadrupole mass spectrometer was used to measure the basicity and the basic strength of the catalysts. 0.15–0.20 g of the catalyst was first degassed under helium flow of 100 ml/min at 500 °C and then was cooled down to room temperature under the helium flow to carry out CO_2 adsorption using the flow of pure CO_2. Following the adsorption, the catalyst was purged with 100 ml/min of helium for 30 min at room temperature to remove gas phase and weakly adsorbed CO_2. Then, TPD was performed under helium flow of 100 ml/min from room temperature to 500 °C at 10 °C/min of a heating rate. Once 500 °C was reached, it was kept at this temperature for 30 min.

3. Results and discussion

3.1. Catalyst characterization

As seen in Table 1, pure Al_2O_3 had the highest specific surface area, 265 m^2/g, among all the catalysts. However, the surface areas decreased from 1.58 to 0.99 m^2/g as CaO was increased from 60 to 85 wt.%. XRD analyses of all the CaO/Al_2O_3 catalysts showed no diffraction peaks corresponding to CaO crystalline phase; i.e. CaO crystallite size was less than 5 nm but the crystallite size of pure CaO showing only CaO diffraction peaks was ~164 nm. Besides, for 60 and 85 wt.% CaO, there were some diffraction peaks (at ~38° and ~42° 2θ) identified as hydrated calcium aluminate and alumina crystalline phases (JCPDS-ICDD, 2000). It was difficult to clearly distinguish the crystalline phases to calculate the average crystallite sizes.

3.2. Effects of CaO loading and the reaction time on the biodiesel yield

In this study, it was found that under 6 wt.% of the oil as the catalyst amount and methanol/sunflower oil molar ratio of 9, the highest biodiesel yields, ~96.6% and ~80%, were obtained on 85 and 60 wt.% CaO/Al_2O_3 catalysts, respectively, in 4 h of the reaction time whereas 30 wt.% CaO/Al_2O_3 and pure CaO showed less than 3% biodiesel yield while pure Al_2O_3 was not active. The effects of methanol/oil ratio and the catalyst amount were studied on 85 wt.% CaO/Al_2O_3 catalyst since it was the most active. As the methanol/oil ratio was increased from 4 to 9, the biodiesel yield increased from ~70% to ~96.6% but then decreased to ~80% at 12 molar ratio. Also, as the amount of the catalyst was increased from 3 to 6 wt.%, the biodiesel yield increased from 57% to ~96.6% and then stayed constant at 12 wt.% catalyst amount.

Fig. 1 shows the biodiesel yield as a function of time for 85 and 60 wt.% CaO/Al_2O_3 catalysts. In 50–60 min, ~96% and ~44% biodiesel yields were obtained on 85 and 60 wt.% CaO/Al_2O_3, respectively. It was also important to find out if the reaction occurred heterogeneously on the solid catalyst surface or homogeneously by dissolved ionic species released from the solid catalysts. From ICP analyses of the liquid phases obtained when using 85 wt.% CaO/Al_2O_3, it was found that the biodiesel yield was ~20% and Ca ion concentration in the upper phase was 256 ppm at the end of 30 min and stayed constant even for 4 h of reaction time within the experimental error. After the centrifugation of the mixture to remove the catalyst, the mixture (without the catalyst) was further kept under the same reaction condition for an additional of 30 min and then, the analysis of the upper phase using the GC showed ~20% biodiesel yield. Hence, this indicated that there was no homogeneous transesterification in the second 30 min due to the presence of dissolved Ca cations in the mixture because ~96% bio-