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Transesterification of sunflower oil to biodiesel on ZrO_2 supported La_2O_3 catalyst

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ABSTRACT

ZrO_2 supported La_2O_3 catalyst prepared by impregnation method was examined in the transesterification reaction of sunflower oil with methanol to produce biodiesel. It was found that the catalyst with 21 wt% loaded La_2O_3 and calcined at 600 °C showed the optimum activity. The basic property of the catalyst was studied by CO_2-TPD, and the results showed that the fatty acid methyl ester (FAME) yield was related to their basicity. The catalyst was also characterized by TG–DTA, XRD, FTIR, SEM and TEM, and the mechanism for the formation of basic sites was discussed. It was also found that the crystallite size of support ZrO_2 decreased by loading of La_2O_3, and the model of the solid-state reaction on the surface of La_2O_3/ZrO_2 catalyst was proposed. Besides, the influence of various reaction variables on the conversion was investigated.

1. Introduction

Petrochemical sources, such as coal and natural gases are supplying the majority of the energy needs of the world, but all of these sources are finite and will be consumed shortly. Therefore, research is now being directed towards the use of alternative renewable fuels. Biodiesel, a mixture of alkyl esters obtained from vegetable or animal oils, is a promising nontoxic and biodegradable fuel arising from biomass (Laforgia and Ardito, 1995; Srivastava and Prasad, 2000). Biodiesel is usually produced by the transesterification of triglycerides with short-chain alcohols (generally methanol and ethanol) in the presence of a catalyst (Ma and Hanna, 1999). Although both acids and bases can be used for the transesterification reaction, alkaline catalysts are more widely investigated because the rate of transesterification reaction by alkaline catalysts is much faster than that by acid catalysts (Freedman et al., 1984, 1986).

Conventionally, homogeneous basic catalysts, such as sodium or potassium hydroxide dissolved in methanol, are used for the transesterification reaction. These traditional homogeneous catalysts have certain advantages including high activity (complete conversion within 1 h), and mild reaction conditions (65 °C and 1 atm). The removal of these catalysts is however technically difficult, and a large amount of wastewater was produced during biodiesel separating and cleaning (Zhang et al., 2003). In order to circumvent the difficulties with homogeneous catalysts, heterogeneous basic catalysts have been widely studied in the past decades. They have some outstanding advantages, such as simplifying of separation and no toxicity, no corrosion, or no environmental pollution (Kim et al., 2004).

Many kinds of solid bases have been investigated for this purpose, including alkali and alkali earth metal oxides (Ebiura et al., 2005), calcined hydrotalcites (Cantrell et al., 2005; Xie et al., 2006a,b), zeolites (Peterson and Scarrah, 1984), and anion exchanged resins (Leclercq et al., 2001). CaO is the most attractive catalyst among the alkali and alkali earth metal oxides because of its high transesterification activity (Gryglewicz, 1999a,b; Reddy et al., 2006; Granados et al., 2007). The effects of H_2O and CO_2 to the surface property of CaO are also fully studied (Granados et al., 2007). However, a recent study has shown that a large amount of leached species was observed because of the formation of Ca diglyceroxide when glycerol is present (Granados et al., 2009). Therefore, CaO catalyst seems not adaptable for industrial application as extensive leaching may threaten the reusability and the environmental sustainability of catalyst. In view of it, it is important to investigate novel heterogeneous basic catalysts that are both active and stable for the transesterification reaction.

Rare earth oxides (REOs) have similar basicity as CaO (Sato et al., 2009), there were however only a few reports on rare earth oxides used as the transesterification catalysts. Bancquart et al. (2001) reported the first use of REOs as a transesterification catalyst in the preparation of monoglycerides from fatty methyl esters and glycerol. Yan et al. (2009a,b) studied $ZnO–La_2O_3$ mixed oxides

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as a transesterification catalyst by developing a single step method. However, it was only active at elevated temperature and pressure, which leads to a higher operation cost. MgO–La_2O_3 and CaO–La_2O_3 complexes were also investigated recently (Babu et al., 2008; Yan et al., 2009a,b), they both showed high activity on biodiesel production, but CaO–La_2O_3 deactivated rapidly when exposed to air.

As researches on mixed rare earth oxides increase, it is also important to study the role of supported REOs in biodiesel production. Li et al. (2007) prepared the Eu_2O_3/Al_2O_3 solid superbase catalytic performance for the transesterification of soybean oil to biodiesel production, but the conversion only reached 63% after a reaction time of 8 h. In previous work, we investigated the KF/Eu_2O_3 catalyst in the transesterification of sunflower oil with methanol to biodiesel. Though a high activity was found with a reaction time of 1 h, the catalyst could only be used once (Sun et al., 2008). These are the mere studies of supported REOs on transesterification reaction. In view of it, finding novel supported REOs catalysts, which are adaptable for biodiesel production, can be quite challenging.

In present work, we report the first study on supported La_2O_3/ZrO_2 catalyst in the transesterification of sunflower oil with methanol to biodiesel production. The relationship between transesterification activity and surface basicity of La_2O_3/ZrO_2 catalyst was discussed. The model of the morphology change during calcination of the catalyst was also proposed.

2. Methods

2.1. Materials

Commercial edible grade sunflower oil (palmitic acid 6.3%, stearic acid 5.6%, oleic acid 24.3%, linoleic acid 62.7% and others 1.1%) was purchased from supermarket. Ammonia solution (25%) and methanol (99.5%) were purchased from Changzheng (Hangzhou, China) and Juhua (Quzhou, China), respectively. $ZrOCl_2{\cdot}8H_2O$ ($\geqslant$99.0%), $La(NO_3)_3{\cdot}6H_2O$ ($\geqslant$99.0%) were purchased from Sinopharm (Shanghai, China). La_2O_3 ($\geqslant$99.0%) was purchased from Jiahua Rare Earth Metal Ltd. (Jiangyin, China).

2.2. Catalyst preparation

The support ZrO_2 was prepared by a convenient precipitation method. Briefly, 0.1 mol of $ZrOCl_2{\cdot}8H_2O$ was dissolved in 200 ml of deionized water, and ammonia solution was then added dropwise to the aqueous solution with stirring. The final pH value of the aqueous solution was controlled around 9.0 after stirring for 12 h at room temperature. Then the solution was filtered and washed with deionized water until no Cl^- was detected. After dried at 110 °C overnight, the precipitate was calcined at 600 °C for 4 h at a heating rate of 5 °C/min.

The La_2O_3/ZrO_2 catalyst was prepared by an incipient wetness impregnation method with an aqueous solution of $La(NO_3)_3{\cdot}6H_2O$, followed by drying at 110 °C overnight. The catalyst was calcined at 600 °C for 4 h in air before used for the transesterification reaction.

2.3. Catalyst characterization

X-ray diffraction patterns (XRD) of the samples were recorded on a RIGAKU D/MAX 2550/PC diffractometer using Cu $K_{\alpha1}$ radiation (λ = 1.540 56 Å) at 40 kV and 100 mA, over a 2θ range of 10–80° with a resolution of 0.02° at a scanning speed of 6°/min. The phases were identified using the power diffraction file (PDF) database (JCPDS, International Centre for Diffraction Data). Fourier transform infrared (FTIR) spectra of the samples were recorded on a Nicolet MAGNAIR-560 spectrometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. A standard KBr technique was used for the sample preparation. Raman spectra were performed with a 325 nm line of a He-Cd laser (LabRAM, HR-800) with a resolution of 2 cm^{-1} at room temperature. The incident laser power at the sample was 2 mW. The morphologies and dimensions of catalysts were observed by scanning electron microscopy (SEM, HITACHI S-4700) and transmission electronic microscopy (TEM, JEOL-2020F) using an accelerating voltage of 200 kV.

CO_2-temperature-programmed desorption (CO_2-TPD) was used to determine the basic strength and basicity of the samples. About 0.2 g of activated catalyst was filled in a silica tube (ca. 4 mm i.d.), treated under 600 °C for 1 h in Ar (20 ml/min), and then CO_2 was introduced for 1 h at room temperature. After purged with Ar for 1 h to remove CO_2 in the gas phase, the sample was heated from room temperature to 900 °C with a ramp of 10 °C/min. The desorbed CO_2 was detected by a mass analyzer (Dymaxion Mass Spectrometer, AMETEK, the mass signal at $m/e = 44$ was used to determine the amount of desorbed CO_2). To determine the effect of different calcination temperature on the basic property of catalyst, about 0.25 g of fresh 21% La_2O_3/ZrO_2 catalyst was treated at desired temperature for 2 h in Ar before CO_2 adsorption.

2.4. Transesterification of sunflower oil

All experiments were performed in a 100 ml autoclave. It was charged with approximately 20 ml of sunflower oil, 22 ml of anhydrous methanol (stoichiometrically 1:30), and 0.8 g of catalyst (5% weight of sunflower oil). The solid–oil–methanol mixture was heated to 200 °C under magnetic agitation. After the transesterification reaction, the mixture was filtered to remove the catalyst and the residual methanol was separated from the upper liquid phase (the lower phase is glycerin) via rotary evaporation. After that, the reaction products were washed three times with distilled water for removal of the formed glycerin. Fatty acid methyl esters (FAME), triglycerides (TG), and intermediate products (monoglycerides and diglycerides) were analyzed by reserved-phase high performance liquid chromatography (RP-HPLC, Agilent 1100 Series) with a C18 Hypersil BDS column (150 mm × 4.6 mm, 5 μm particle size) using UV/Visible detection at 210 nm (Holcapek et al., 1999; Nicola et al., 2008). A linear gradient from 100% methanol to 50% methanol + 50% isopropanol–hexane (5:5, v/v) in 15 min was employed. Prior to analysis, the biodiesel samples were dissolved in isopropanol–hexane (5:5, v/v), obtaining a sample-to-solvent ratio of 1:30 (W/W). The injection volumes of 5 μl and a flow rate of 1 ml were used in all experiments. Conversion of sunflower oil (CSO) was calculated as the (percent) diminution of the sum of the areas of all TG HPLC peaks, and the FAME yield as the fraction (percent) of the sum of the areas of all FAME HPLC peaks relative to that of samples with maximum conversion. (A typical HPLC separation of a reaction mixture of sunflower oil after transesterification is shown in Supplementary material Fig. S1.)

3. Results and discussion

3.1. Physicochemical properties of ZrO_2 and La_2O_3/ZrO_2

In the TG–DTA curves of ZrO_2 (the TG–DTA curves of ZrO_2 and La_2O_3/ZrO_2 are shown in Supplementary material Fig. S2), the weight losses were concentrated to two ranges (50–150 °C, 150–300 °C). The DTG peak around 100 °C was assigned to the loss of physical adsorbed H_2O, while the other one around 210 °C could be attributed to the decomposition of OH^- on the surface of $Zr(OH)_4$. The exothermic peak around 430 °C in the DTA curve of ZrO_2 was due to the phase transformation from tetrahedral to