Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Sol–gel La_2O_3–ZrO_2 mixed oxide catalysts for biodiesel production

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ARTICLE INFO

Article history:
Received 11 May 2017
Revised 19 October 2017
Accepted 3 November 2017
Available online xxx

Keywords:
La_2O_3–ZrO_2
Sol–gel
Biodiesel
Canola oil
Transesterification

ABSTRACT

Different La_2O_3 contents (0, 1, 2, 3, and 5 wt%) were used to prepared La_2O_3–ZrO_2 mixed oxides calcined at 600 °C by the sol–gel method. The catalytic activity was measured as biodiesel production from canola oil through a transesterification reaction. The characterization results indicate that the La_2O_3 monolayer formation and extent of basicity of m-ZrO_2 have a large influence on biodiesel production. Greater biodiesel conversion (56% at 4 h) was obtained with the 3% La_2O_3–ZrO_2 catalyst in the presence of basic sites and the formation of a monolayer of La_2O_3. The decrease in the catalytic activity for 5% La_2O_3–ZrO_2 resulted from the loss of active sites on the catalyst because of agglomeration, which was suggested by XPS and the isoelectric point. The kinetic data fit to a pseudo-first order constant, and the largest kinetic constant corresponds to 3% La_2O_3–ZrO_2, currently the largest heterogeneous non-alkaline metal catalyst reported for a transesterification reaction.

1. Introduction

The large surface areas obtained in materials synthesized by sol–gel methods allow for the preparation of pure and mixed oxides with desirable properties [1]. Sol–gel synthesis is an effective route to obtain materials with specific and desirable properties because materials are mixed in the atomic level [2]. One of these advantages is obtaining solids with acidic and/or basic properties for use in a diversity of applications [3]. Some acidic solids were prepared by the sol–gel method, such as those by Köse et al. who used this technique to prepare an acidic semiconductor [4], and Surech et al. who synthesized pure $BiFeO_3$ with control over the ferromagnetic properties of the solid [2]. Ben Ali et al. prepared ferrite nanoparticles using the sol–gel route and by modifying the zinc concentration [5]. Yuan et al. studied the pH effect on ZrO films codoped with iron and cobalt, concluding that a tunable pH was capable of controlling the band gap energy of ZrO [3]. Usha et al. studied the photoluminescence of CuO nanoparticles that were prepared by the sol-gel method with control over the crystallinity and size of these nanoparticles [6]. Additionally, the sol–gel method allows for doping of a selected material to improve its catalytic properties by modifying its acid-base properties. Other reports of sol–gel materials address the formation of thin films with aluminum- and copper-like doped agents, allowing the modification of the structural, morphological and magnetic properties of the material [7]. With regard to the La_2O_3–ZrO_2 mixed oxide, which is used as a catalyst and as a support to prepare supported catalysts, a sulfated-ZrO_2 supported in La_2O_3 for the isomerization of n-hexane was reported. In this case, the support was modified to allow for an elevated conversion, and the La_2O_3 effect provided a higher selectivity pathway for the isomerization products [8]. On the another hand, Radwan et al. studied the role of the addition of La_2O_3 and ZrO_2 (from 2 to 10 wt%) as promoters to a CuO/MgO catalyst, modifying the acid–base properties of the catalyst for the CO oxidation reaction [9]. Meanwhile, Tao et al. improved the properties of a Ni/La_2O_3–ZrO_2 catalyst for syngas production by CO_2 reforming of coke oven gas [10], and Li et al. reported the production of dimethyl ether using a Cu–La_2O_3–ZrO_2/γ–Al_2O_3 hybrid catalyst [11]. The previous reports indicate that the strength of the basic sites of supports and the entire support with a considerable thermal stability should have a large influence on the stability of catalysts for biodiesel production [12–14]. For this study, ZrO_2 was selected due to its acidic and/or basic sites, which are dependent on the preparation procedure [15], and

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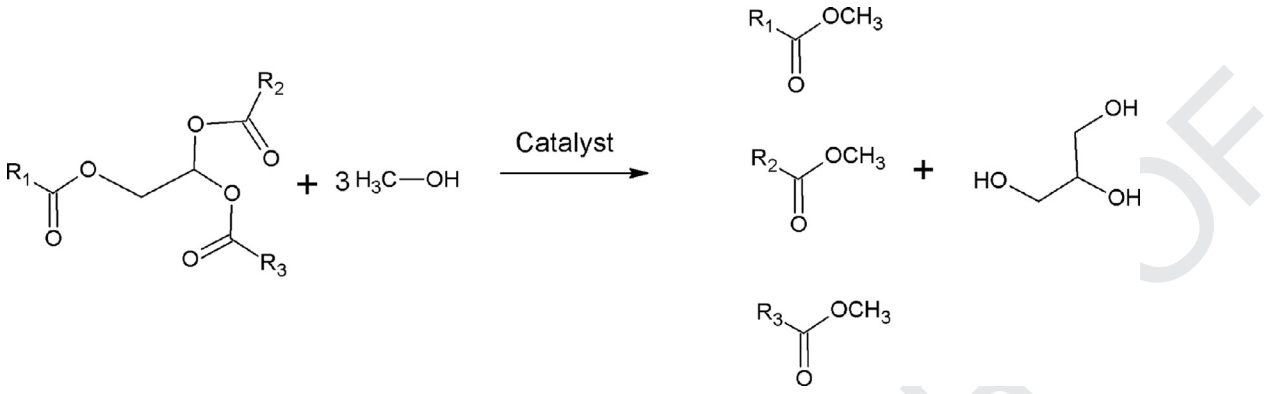
https://doi.org/10.1016/j.jechem.2017.11.003
2095-4956/

Please cite this article as: D. Salinas et al., Sol–gel La_2O_3–ZrO_2 mixed oxide catalysts for biodiesel production, Journal of Energy Chemistry (2017), https://doi.org/10.1016/j.jechem.2017.11.003



Scheme 1. Transesterification reaction.

La_2O_3 was studied as a support for nickel in steam reforming reaction of alcohols and oxidation of CO [16]. However, it is possible to find reports on biodiesel production with La^{3+} ions in zeolite HZSM-5 with oleic acid as a model molecule [17], on esterification and transesterification reactions of Jathopha oil using the binary metal oxide catalyst CaO–La_2O_3 [18,19], on transesterification of Jatropha oil using nano-La_2O_3 [20] and on transesterification of sunflower oil with ZrO_2 supported on La_2O_3 [21]. Moreover, it is of great interest to study random distribution of La_2O_3 over zirconia or the supports and to detect the acid-basic properties and changes produced by La^{3+}ions [9,22–25]. Biodiesel production is gaining attention as a viable substitute for petroleum diesel because of its uncommon characteristics, such as biodegradability, renewability, lower sulfur content, among others, and biodiesel production by a transesterification reaction is defined by the chains of fatty acid methyl ester (FAME) that can be used as an alternative to diesel engine fuel [26]. Moreover, biodiesel can be produced by the chemical reactions of oils and animal fats (triglyceride sources) with an alcohol, mainly methanol, through a transesterification reaction, as can be seen in Scheme 1.

According to reports, bulk metal oxides, such as MgO [27], CaO [18,19,28–30] and zeolites [17,31,32], can serve as active catalysts in transesterification reactions. Some reports show that active supported metal oxides, such as KNO_3/Al_2O_3 [13,33], KI/Al_2O_3 [34], CaO/MCM-41 and CaO/SBA-15 [12], KOH/ZrO_2 [35], strontium oxides [36], modified strontium nanocatalysts supported on ZSM-5 [31], HZSM-5-supported lanthanum, [17] and cesium-impregnated sodium zirconate [37], work as basic catalysts in transesterification reactions. The trend is clear, for the transesterification reaction, it is necessary to use basic metal oxide catalysts, such as Li_2O [38], K_2O and potassium titanate [13,26,33,39], $NaZrO_3$ [14,37], CaO [19,28–30], SrO [31,36], MgO [27] and La_2O_3 [17–21]. To date, studies have been focused on materials that simultaneously carry out esterification and transesterification reactions depending on the starting triglycerides [40–42].

In this work, the effect of the La_2O_3 content (0, 1, 2, 3, and 5 wt%) on the use of sol–gel La_2O_3–ZrO_2 mixed oxides as catalysts in the transesterification reaction of canola oil for biodiesel production is reported.

2. Experimental

2.1. Preparation

Sol–gel La_2O_3–ZrO_2 systems were prepared using 80 wt% zirconium n-butoxide, $Zr[O(CH_2)_3CH_3]_4$, as the zirconium precursor and lanthanum acetylacetonate, $La(acac)_3$, to obtain La_2O_3–ZrO_2 mixed oxides with 0, 1, 2, 3 and 5 wt% La_2O_3. The gelling reaction was carried out for 1 h under reflux at 80 °C in the presence of distilled water and 2-butanol, maintaining a water:2-butanol molar ratio of 1:4. The obtained gels were dried in air for solvent evaporation and calcined at 600 °C for 6 h. The mixed La_2O_3–ZrO_2 oxides were labeled according to the La_2O_3 content, starting at 0% La_2O_3 (pure ZrO_2) and going from 1 to 5 wt% La_2O_3.

2.2. Characterization

The BET specific surface area (S_{BET}) and pore volume were determined from nitrogen isotherms at 77 K in a Micromeritics ASAP 2010. Prior to the measurements, the samples were outgassed at 300 °C for 2 h. The total pore volume (*Vp*) was recorded using nitrogen adsorption at a relative pressure of 0.99. Powder x-ray diffraction (XRD) spectra were obtained using a D4 Endeavor Bruker AXS diffractometer equipped with nickel-filtered Cu $K\alpha_1$ radiation ($\lambda = 1.542$ Å). The standard scan parameters were 1° min^{-1} for a 2θ range of 10°–90°. Identification of the phases was carried out by reference to EVA diffraction file data. The isoelectric point (pH_{IEP}) of the mixed oxides was determined through electrophoretic migration measurements using Zeta-Meter Plus 3.0 equipment. For this characterization, 0.025 g suspension of sample in 200 mL of ultrapure water was used. The pH of the solution was adjusted with 0.1 mol L^{-1} HCl or KOH solutions. The isoelectric point was calculated by the graphical representation of the zeta potential versus solution pH. The apparent surface coverage (ASC) of ZrO_2 by La_2O_3 was calculated from equations previously validated by ion scattering spectroscopy (ISS) and XPS [43–45] as follows:

$$IEP = IEP_{La_2O_3} \cdot X_{La_{2O_3}} + IEP_{ZrO_2} \cdot \left(1 - X_{La_{2O_3}}\right) \quad (1)$$

where, $X_{La_2O_3}$ is the fraction of the zirconia surface covered by La_2O_3. The diffuse reflectance spectra (DRS) of the materials were recorded over the 200–800 nm wavelength range using a UV-visible JASCO V 650 spectrophotometer, to which a diffuse reflectance chamber (with a 60 mm diameter integrating sphere and internal spectral coating) was attached. The FTIR spectra were recorded between 4000 cm^{-1} and 500 cm^{-1}. The IR measurements were acquired using a FTIR Nicolet Nexus, and the spectra were recorded with a 4 cm^{-1} resolution and 250 scans. Temperature programmed reduction (TPR) was carried out in a Micromeritics TPR/TPD 2900 system equipped with a thermal conductivity detector. In the experiment, 0.050 g of the sample was heated from 25 °C to 700 °C at 10 °C min^{-1} under 5% H_2/Ar flowing at 50 mL min^{-1}. Thermal programmed desorption of carbon dioxide (TPD-CO_2) was performed in a TPR/TPD Micromeritics 2900 system with a thermal conductivity detector (TCD). Prior to analysis, 0.050 g of sample was cleaned under a He flow of 50 mL min^{-1} at 110 °C for 30 min. After that, the adsorption of CO_2 at 80 °C and the CO_2 desorption up to 700 °C were carried out under 5%

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