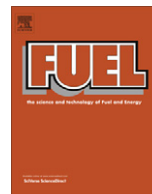


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Support influence on the basicity promotion of lithium-based mixed oxides for transesterification reaction

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HIGHLIGHTS

- ▶ Lithium containing oxides for catalytic transesterification.
- ▶ The support nature strongly affect the basicity promotion of the Li containing oxides.
- ▶ The Li addition onto the catalysts increases the base site number and strength.
- ▶ Li/MgO and Li/Mg(Al)O exhibited high activity under mild reaction conditions (313 K).
- ▶ The reaction occurs through heterogeneous/homogeneous mechanism.

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ABSTRACT

Solid catalysts comprising Li-based oxides were prepared by LiNO₃ impregnation onto supports with different acid/base properties (SiO₂, MgO, Al₂O₃ and Mg(Al)O mixed oxide obtained from hydrotalcite). The materials were characterized by means of XRD, N₂ physisorption, ICP-OES, FEG-SEM and TPD of CO₂. The oxide reactivities were evaluated using the model transesterification reaction between methyl acetate and ethanol under mild reaction conditions (313 K, ethanol/methyl acetate molar ratio = 6/1 and 0.2 wt.% of catalyst). Lithium impregnation onto silica and γ -alumina yielded inactive catalysts for transesterification. On the other hand, the lithium addition onto MgO produced an active catalyst and remarkably high conversions were obtained for Li/Mg(Al)O. The different supports used considerably affected the base site densities and base strengths of the Li-based catalysts. The base properties thus influenced the catalytic performance of the materials. Stability tests revealed the lithium leaching occurrence which resulted in some homogeneous contribution.

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1. Introduction

Transesterification of alkyl esters plays an important function in numerous applications such as biodiesel production. Biodiesel is a promising substitute to fossil diesel fuel because its renewable nature is effective in reducing greenhouse gas emissions. Commercially, biodiesel is produced by transesterification of triglycerides obtained from edible vegetable oils and animal fats with short chain alcohols to produce alkyl esters and glycerol [1]. Transesterification can be accomplished by an acid or base catalyst [1]. A great deal of interest has recently been stimulated by the use of heterogeneous catalysis in place of the homogeneous catalysis industrially employed for biodiesel production [2–4]. The use of solid catalyst has been pointed out as an option for simplifying the biodiesel process, reducing the production cost. The solid

catalyst does not corrode the reactor, can be recycled, and is easily separated from biodiesel, generating an uncontaminated product [5].

Currently, a number of heterogeneous acid and basic catalysts have been developed and applied for biodiesel production, the basic compounds reported to exhibit the highest activity. They include calcium oxide [6], MgAl oxides derived from hydrotalcite [7–9], MgO–La₂O₃ and CaO–La₂O₃ [10,11], Li promoted CaO [12,13], etc. Although intensive investigations have been carried out, the synthesis of an active solid and recyclable catalyst is still a challenge.

In particular, lithium-based catalysts have shown to present a distinctive behavior compared to other alkali (Na, K and Cs) or alkaline earth (Ca, Sr and Ba) based catalysts [14,15]. Lithium incorporation onto MgO is reported to create strong basic sites [15]. In our previous paper, we have shown that MgAlLi mixed oxide is a very active catalyst for transesterification reaction under mild reaction conditions [16].

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Considering this, the motivation for the present investigation has been to elucidate how supports of different acid/base surface properties affect the formation of the active sites for transesterification promoted by lithium-based catalysts. Therefore, the supports chosen were a highly basic MgO, an amphoteric oxide γ -Al₂O₃ and a mixed oxide containing both Mg and Al obtained from hydrotalcite precursor. Furthermore, commercial SiO₂ has been selected as a reference support due to its large surface area and neutral surface properties.

2. Materials and methods

2.1. Synthesis procedure

The Mg–Al hydrotalcite was synthesized by the coprecipitation method at room temperature as described in [16]. Briefly, 100 mL of an aqueous solution containing 20.5 g of Mg(NO₃)₂·6H₂O and 7.5 g of Al(NO₃)₃·9H₂O with Al/(Al + Mg) = 0.2 was added dropwise into another solution containing 2.4 mol L⁻¹ of (NH₄)₂CO₃ under vigorous stirring. The pH during the synthesis was held at 10 by the addition of NH₄OH (30% v/v). The precursors of the Al₂O₃ and MgO (boehmite Al(O)OH and brucite Mg(OH)₂, respectively) were prepared following the same procedure except that magnesium nitrate or aluminum nitrate were absent. The precipitates were aged at 338 K for 18 h and then washed with warm distilled water. The obtained solids were oven dried at 383 K for 24 h. These precursors were decomposed in air atmosphere using a heating rate of 10 K min⁻¹ until 873 K and kept at this temperature for 0.5 h in order to obtain the corresponding oxides. Commercial Aerosil®380 was purchased from Degussa and used as silica source. For comparison, the Aerosil®380 was also “impregnated” with distilled water and calcined under the same conditions as the other support precursors.

The Li-based catalysts were prepared by the wet impregnation method. For that, LiNO₃ was dissolved into 20 mL of distilled water and placed in contact with an appropriated amount of the support precursor, i.g., boehmite – Al(O)OH; brucite – Mg(OH)₂; MgAl hydrotalcite or Aerosil®380 – SiO₂. The amount of the support precursors Al(O)OH and Mg(OH)₂ were stoichiometrically calculated to generate the pure oxides: Al₂O₃ and MgO. The Aerosil®380 is already composed of pure oxide SiO₂. In the case of the Mg(Al)O oxide, the determination of the oxide weight formed by the hydrotalcite calcination was established by hydrotalcite TGA analysis (showed in [16]). Afterwards, the mixture (LiNO₃ aqueous solution + support precursor) was heated at 353 K under magnetic stirring until complete drying. The resulting powder was dried at 383 K overnight.

In our previous study [16], we found that the Li impregnation loading of 10 wt.% onto MgAl hydrotalcite produced the most active catalyst for transesterification reaction. Thus, nominal values of 10 wt.% Li were used for impregnation onto the different supports studied in this work. After LiNO₃ impregnation, the solids were calcined in a tubular furnace under air atmosphere at a heating rate of 10 K min⁻¹ until 873 K and kept at this temperature for 0.5 h.

2.2. Supports and Li-based catalysts characterization

The lithium content in the catalysts was determined with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Varian-Vista). Nitrogen physisorption at 77 K was used for the BET surface area determination (Quantachrome, NOVA – 1200). The materials were also characterized by powder X-ray diffractometry (XRD) in a Rigaku Geigerflex spectrometer using Cu K α radiation (λ = 1.5406 Å). The crystalline phases were identified

using the Powder Diffraction File (PDF) database (JCPDS, International Centre for Diffraction Data). The catalyst morphology was studied by Field emission gun scanning electron microscopy (FEG-SEM) on a Philips XL-30 FEG microscope. The basic properties of the catalysts were investigated by temperature programmed desorption of CO₂ (TPD of CO₂). The samples were previously treated under N₂ flow heated at a rate of 10 K min⁻¹ until 873 K and cooled to room temperature. The CO₂ adsorption was carried out at room temperature using a gaseous mixture of 3% of CO₂ in N₂ until surface saturation (5 min). Physically adsorbed CO₂ was removed by flushing with N₂ for about 1 h. Thus, the CO₂ desorption was performed by increasing the temperature at a rate of 10 K min⁻¹ until 873 K and the flow containing the desorbed CO₂ passed through a methanation reactor. In this step, the desorbed CO₂ was converted into CH₄ on a Ni/Kieselghur catalyst at 673 K. Therefore, the CO₂ desorption was indirectly quantified by the produced CH₄ which was analyzed using a flame ionization detector (FID).

2.3. Catalytic tests

The catalytic activity was evaluated in the transesterification model reaction of methyl acetate and anhydrous ethanol. The use of this model reaction is very useful at this initial step of investigation, in the screening of the active catalysts for transesterification. The model reaction is easier to perform than the reaction involving the triglyceride (vegetable oil) to produce biodiesel and the products are quickly monitored by gas chromatography (4 min run). In addition, the stability tests can be properly carried out when using the model compounds. It is noteworthy that ethanol has been chosen as the alcohol source due to its renewable origin.

The catalytic tests were performed in the low conversion regime in order to better distinguish the catalytic activity. The tests were carried out in a batch jacket reactor of volumetric capacity of 30 mL using magnetic stirring under the following conditions: mol ratio of ethanol/methyl acetate = 6/1, 0.2 wt.% of catalyst and temperature of 313 K. Representative aliquots of the solution were withdrawn periodically and submersed in an ice bath. The solid catalysts were separated by centrifugation and the reaction products analyzed in a gas chromatograph (GC 2010 Shimadzu) equipped with FID and RTx[®]-1 capillary column.

2.4. Stability tests

Chemical analysis of the reaction mixture was performed in order to verify the possible lithium leaching from the catalysts to solution. The lithium content in the reaction mixture was analyzed by SPE-CAA100 Varian flame emission spectrometer. The procedure consisted of solution filtration at the end of the reaction in order to remove the solid catalyst by using syringe filters (0.45 μ m pore size). Thus, an aliquot of 1 mL of the filtrate composed of volatile compounds was evaporated and the residual metals were resuspended with HNO₃ (1% v/v) solution for the chemical analysis. The material stabilities were also investigated by the catalyst reaction with ethanol in order to determine the homogeneous contribution. The catalysts were stirred in ethanol for 150 min at 313 K and filtered. This filtered ethanol was used for transesterification of the methyl acetate. The solution composition was monitored afterwards.

3. Results and discussion

3.1. Structural, textural and chemical characterization of the catalysts

XRD analyses for the materials are presented in Fig. 1. The XRD for Mg(OH)₂ confirmed the formation of brucite structure

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