



K₂O supported on sol-gel CeO₂-Al₂O₃ and La₂O₃-Al₂O₃ catalysts for the transesterification reaction of canola oil



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ABSTRACT

Heterogeneous supported potassium on promoted CeO₂-Al₂O₃ and La₂O₃-Al₂O₃ sol-gel mixed oxides was used as a catalyst for biodiesel production via the transesterification of canola oil with methanol using a batch reactor. These mixed oxides alone do not show any catalytic activity in the transesterification reaction, and the incorporation of potassium increases the catalytic activity, which is greater in the La₂O₃-promoted catalysts. The improved catalytic activity of the potassium La₂O₃-promoted catalysts was associated with the partial insertion of lanthanum into alumina with a favorable interaction between the potassium and the oxygenated species of the La₂O₃-Al₂O₃ mixed oxide. The larger amount of K₂O species in K₂O/5La₂O₃-Al₂O₃ and the lower acidity explain their large production of biodiesel. Moreover, the leaching resistance of potassium is remarkable, with the K₂O/5La₂O₃-Al₂O₃ catalyst showing < 4% in the first recycle and no more leaching in the four subsequent recycle steps.

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1. Introduction

The industrial production of biodiesel is usually carried out by homogeneous catalytic transesterification reactions using basic alkaline catalysts such as NaOH, CH₃ONa or KOH [1]. Due to the intrinsic problem associated with homogeneous catalysis in terms of separation and recuperation of the catalyst, significant efforts have been carried out for the heterogenization of the alkaline catalysts. For biodiesel, defined as the mono alkyl ester of long chain of fatty acids derived from triglycerides in vegetables oils or animals fats [2], it is highly desirable to use large triglycerides with low polyphenol contents in the starting material. To optimize the biodiesel production and to avoid secondary reactions such as saponification of the triglyceride, it is also desirable for the starting material to have a low water content. Additionally, the differences in the nature of the triglycerides are related to the nature of the alkyl groups; specifically, the length of the chain of the triglycerides is a key issue for the design of the catalyst. Thus, for triglycerides with higher acidity, an acid catalyst being able to esterify fatty acids must be selected. In contrast, if the starting material is a source of triglycerides with a low acidity, a catalyst with basic characteristics to catalyze the transesterification reaction is needed. Recently, new heterogeneous basic catalysts for use in biodiesel production by transesterification reactions have been reported [3–12]. Among

them are the metallic oxides CaO [9,13–17] and MgO [11] that have shown good catalytic activity in the transesterification reaction, as well as other more complex systems, such as KNO₃/Al₂O₃ [18], K₂CO₃/Al₂O₃ [19], Mg/ZrO₂ [20], Ag/Al₂O₃ [21], sodium titanate nanotubes [6], silica [10], resin catalyst [22] and hydrotalcites [11]. Most of them have activity problems, such as the recycling of heterogeneous catalysts, because the leaching of metal is responsible for leading the pathway of the reaction by the homogeneous system [19,23].

Considering that potassium is a promising element in transesterification reactions [13,24], it is here proposed to prepare new heterogeneous basic potassium-promoted alumina-supported catalysts for transesterification reactions. Among the well-known promoters, CeO₂ and La₂O₃ [25–30] have received great attention due to the larger redox properties, high oxygen transport capacity and oxygen storage [31] for the former and large thermal stability and basic characteristics for the latter. On the basis of the above reasoning, we report the effect of the nature (CeO₂ and La₂O₃) and the content (3 and 5%) of sol-gel mixed oxides used as a support to prepare 10 wt% of potassium CeO₂-Al₂O₃ and La₂O₃-Al₂O₃ catalysts and evaluated in a transesterification reaction using canola oil as a model system for the production of biodiesel.

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Table 1
Potassium content, specific area, hydrogen consumption, desorbed oxygen, total acidity and Ce 3d, K 2p and O 1s binding energies of the CeO₂-Al₂O₃ series.

Catalyst	K ^a (%)	S _{BET} (m ² g ⁻¹)	H ₂ consumption (mmol g ⁻¹)	O ₂ desorbed (mmol g ⁻¹)	Total acidity (mmol g ⁻¹)	Ce 3d _{5/2} (eV)	K 2p _{3/2} (eV)	O 1s (eV)
3CeO ₂ -Al ₂ O ₃	–	181	–	0.50	–	–	–	–
5CeO ₂ -Al ₂ O ₃	–	243	–	0.51	–	–	–	–
K ₂ O/3CeO ₂ -Al ₂ O ₃	9.15	72	0.53	0.51	0.073	883.0 (87%)	886.2 (13%)	293.6
K ₂ O/5CeO ₂ -Al ₂ O ₃	9.06	106	0.42	0.52	0.036	883.1 (88%)	886.9 (12%)	293.8

^a Nominal content 10 wt%.

Table 2
Potassium content, specific area, hydrogen consumption, desorbed oxygen, total acidity and La 3d, K 2p and O 1s binding energies of La₂O₃-Al₂O₃ serie.

Catalyst	K ^a (%)	S _{BET} (m ² g ⁻¹)	H ₂ consumption (mmol g ⁻¹)	O ₂ desorbed (mmol g ⁻¹)	Total acidity (mmol g ⁻¹)	La3d _{5/2} (eV)	K2p _{3/2} (eV)	O1s (eV)
3La ₂ O ₃ -Al ₂ O ₃	–	315	–	0.67	–	–	–	–
5La ₂ O ₃ -Al ₂ O ₃	–	270	–	0.69	–	–	–	–
K ₂ O/3La ₂ O ₃ -Al ₂ O ₃	9.12	116	0.45	0.23	0.055	835.4	293.4	531.6
K ₂ O/5La ₂ O ₃ -Al ₂ O ₃	8.95	92	0.62	0.17	0.031	835.1	292.8	531.5

^a Nominal content 10 wt%.

2. Experimental

2.1. Preparation

The syntheses of sol-gel 3%CeO₂/Al₂O₃, 5%CeO₂/Al₂O₃, 3%La₂O₃/Al₂O₃ and 5%La₂O₃/Al₂O₃ mixed oxides were carried out from aluminum trisec-butoxide and the respective lanthanum and cerium acetylacetonates. The procedure consisted of maintaining the respective precursors of Ce and La under reflux and agitation at 70 °C in distilled water and 2-butanol and maintaining a water/alcohol molar ratio of 1:4 at pH 7. The obtained materials were subjected to vacuum drying at 100 °C and subsequent air calcination at 600 °C for 6 h. Subsequently, a potassium impregnation procedure in order to obtain three atoms of K nm⁻² was carried out on the sol gel mixed oxides, followed by another calcination procedure in air at 600 °C for 6 h.

2.2. Characterization

The specific surface areas were calculated using the BET method from the nitrogen adsorption isotherms using Tri Star II 3020 equipment. Diffraction X ray measurements were conducted using a Rigaku diffractometer (CuKαλ=0, 15406 nm and Ni filter), and atomic absorption spectroscopy (AAS) was performed using a PerkinElmer 3100 absorptiometer. Temperature programmed reduction (TPR), temperature programmed desorption of oxygen (O₂-TPD) and ammonia desorption (NH₃-TPD) profiles were performed using a TPR/TPD 2900 Micromeritics system with a thermal conductivity detector (TCD). Prior to the reduction experiment, the samples (50 mg) were thermally treated under a He flow at 110 °C for 30 min to remove water and other contaminants. The reduction profiles were recorded with a 5% H₂/Ar flow at 50 mL min⁻¹ at a heating rate of 10 °C min⁻¹ from room temperature to 700 °C. For the O₂-TPD experiments, the samples were preheated in an O₂ flow for 1 h at 700 °C, cooled to room temperature in the same atmosphere, and then switched to a helium flow with the oxygen desorption monitored using a TCD. For the NH₃-TPD experiments, the catalyst surface was saturated at 100 °C with ammonia pulses and cooled to room temperature, and once the baseline was restored, the temperature was linearly increased to 800 °C. The XPS measurements were performed using a VG Escalab 200R electron spectrometer equipped with a hemispherical electron analyzer and Mg Kα (1253.6 eV) X-ray source. Prior to analysis, the samples were outgassed at 300 °C for 1 h in a vacuum chamber. Charging effects were corrected by taking the C 1s peak of adventitious carbon at

284.8 eV. The peaks were deconvoluted into several components assuming a Gaussian/Lorentzian shape.

2.3. Catalytic activity

The transesterification reaction to produce biodiesel was carried out using commercial canola oil free of impurities and humidity as a model system. The reaction was conducted in a flask reactor under constant reflux of methanol at 65 °C with 1.2 g of catalyst at atmospheric pressure and 230 rpm of agitation. External diffusion was excluded through a series of mass transfer tests, and thus ignored because the particle size was less than 0.4 mm (i.e., 40–60 mesh). The samples taken from the reactor were deposited in a mixture of 1.0 M HCl and eicosane/hexane at a molar ratio of 1:1 and subsequently centrifuged for 2 min at 6000 rpm. From the organic phase, 1 μL was extracted and injected into a Perkin Elmer Gas Chromatography system, Clarus@ 680 model, which includes a Supelco Omega Watt 250 capillary column.

3. Results and discussion

3.1. Atomic absorption spectroscopy

The elemental composition of K in the potassium supported catalysts is compiled in Table 1 for the CeO₂-Al₂O₃ series and Table 2 for the corresponding La₂O₃-Al₂O₃ catalyst. The obtained values are similar to the nominal one (10 wt% K), indicating no potassium loss during the synthesis.

3.2. Surface area

Table 1 compiles the surface area for the CeO₂-Al₂O₃, and Table 2 contains the corresponding values for the La₂O₃-Al₂O₃ series. For the sol gel CeO₂-Al₂O₃ oxides, a specific area of ~200 m² g⁻¹ is observed. Once the alkali is incorporated, a significant decrease is detected in the K₂O/CeO₂-Al₂O₃ catalysts, indicating that after the incorporation of the potassium, the porosity of the support is blocked for K₂O. The same behavior is observed in the La₂O₃-Al₂O₃ series (Table 2) and in previously reported results for 14 wt% CaO/SBA15 catalysts [13]. Despite the larger surface areas (200–300 m² g⁻¹) of the starting sol gel CeO₂-Al₂O₃ and La₂O₃-Al₂O₃ mixed oxides, the decrease upon potassium incorporation produces potassium-supported catalysts with surface areas that are lower and similar to those of the starting materials (~100 m² g⁻¹) and larger than those of other potassium titanate-supported catalysts [13,24].

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