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Structural and surface study of calcium glyceroxide, an active phase for biodiesel production under heterogeneous catalysis

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ABSTRACT

Calcium diglyceroxide has been reported as a very active phase in the transesterification of triglycerides with methanol for biodiesel production. This work reports on the determination of the crystal structure of Ca diglyceroxide by Patterson-based direct methods from synchrotron X-ray powder diffraction (XRD) data in combination with characterisation by Differential Thermal Analysis-Thermogravimetry (DTA-TG), Scanning Electron Microscopy (SEM) and X-ray Photoelectron and Fourier Transform-Infrared spectroscopies (XPS and FT-IR). Its crystal structure is formed by molecular tetramers held together by a complex H-bond network. Both the XRD structural determination and the O1s XPS core level indicate the presence of a basic non-protonated O^- anion at the surface of Ca diglyceroxide. Along with the presence of surface lipophilic CH_x units, this O^- anion may be the origin of this molecule's high activity relative to CaO.

1. Introduction

The synthesis of a calcium glyceroxide was first reported by Grün and Bockish [1], who obtained the triglyceroxide phase, whereas Wheeler in 1931 described the preparation of calcium mono- and diglyceroxides by heating calcium oxide with excess glycerol at 60 and 110 °C, respectively [2], demonstrating that these two glyceroxides can be interconverted at a suitable temperature. Later, Fujii and Kondo undertook the study of the CaO-glycerol system from approximately 10 to 150 °C, aiming to clarify the identity of the different calcium glyceroxide phases and their thermal stabilities [3]. Additionally, calcium glyceroxide has been demonstrated to be an active phase in the transesterification of triglycerides of vegetable oils with low-molecular-weight alcohols (methanol and ethanol) to produce biodiesel.

Calcium oxide (CaO) is one of the most promising solid basic catalysts for the production of biodiesel [4–7]. At the beginning of the transesterification, calcium oxide is the active phase. However, once glycerol is produced as a by-product of the reaction, it reacts with CaO producing, calcium diglyceroxide (CaD):

$$\mathrm{CaO} + 2\mathrm{C_3H_8O_3} \rightarrow \mathrm{Ca(C_3H_7O_3)2} + \mathrm{H_2O}.$$

Kouzu et al. [8,9] verified that this compound is the active phase of the collected catalyst rather than other unknown calcium compounds present as minor constituents. CaD prepared as a reference sample was proven to be as active as the catalyst recovered after the transesterification process. They found that glycerol was more reactive with CaO than methanol, as the immersion of CaO in methanol reflux in the presence of glycerol only produced CaD. To facilitate the handling of the solid base catalyst, Kouzu et al. recommended the previous conversion of CaO into CaD by immersion in a methanol solution of glycerol [8].

Further support of the hypothesis that CaD is the active phase comes from the work of López Granados et al. [10], who demonstrated that the activity of Ca oxide can be increased by creating Ca glyceroxide sites at the surface of Ca oxide. Different synthetic strategies were used to create progressively higher numbers of Ca glyceroxide surface sites by the utilisation of increasingly large amounts of either diglycerides or monoglycerides or glycerol. A relationship between the prevalence of Ca glyceroxide surface sites and the improvement of the reaction rate was observed. Beyond a certain point, no improvement was achieved, indicating that the surface becomes fully covered by Ca glyceroxide species.

Despite the importance of CaD as the active phase for biodiesel production in the presence of CaO and although the synthesis of calcium glyceroxides has been known since 1910 [1], to our knowledge, no structural information about these compounds has been published. The purpose of this paper is to present a detailed study

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of the CaD crystal structure to provide a possible explanation of its outstanding catalytic activity. For this purpose, synchrotron X-ray powder diffraction data have been collected to solve its crystal structure following an *ab initio* procedure. The use of this high-resolution radiation has been essential to its determination due to the complexity of the structure, with a unit cell volume close to 4000 Å^3 and light atoms as main components.

2. Experimental section

2.1. Synthesis of calcium diglyceroxide

Fresh CaO was obtained by the calcination of $CaCO_3$ (Sigma–Aldrich, >99.5%) under dry air at 800 °C for 2 h (heating rate 10 °C min^{-1}) in a quartz reactor. Next, 500 mg of this fresh CaO was poured directly into a flask containing 100 mL of MeOH and 35 mL of glycerol. To avoid exposure to ambient air in this step, the flask had been previously flushed with a N_2 flow to remove the ambient air therein and the CaO was directly incorporated from the reactor in which $CaCO_3$ had been calcined. These precautions were taken to prevent the carbonation and hydration of the fresh CaO with the CO_2 and H_2O present in ambient air. Once CaO was poured over the methanol–glycerol mixture, the flask was hermetically closed to prevent contact with ambient air. Next, this mixture was heated at 50 °C and left under agitation overnight. Initially, the CaO solid dissolved slowly into the mixture. After few minutes, some turbidity was visible and a pale yellow solid gradually became apparent and more concentrated. This solid was recovered by filtration and washed twice with methanol. The solid was stored under nitrogen to prevent extensive carbonation and hydration.

2.2. Transesterification of sunflower oil with methanol

The catalytic performance of the solid prepared (CaD) was evaluated in the methanolysis of sunflower oil. The recovered solid was added to a 500 mL bolted closure autoclave reactor from Autoclave Engineers (with a magnet-driven agitator and a thermostatically controlled heating jacket) containing 135 mL of methanol (Scharlau, Reag. Ph. Eur. >99.8% GC, $H_2O < 0.005\%$). Considering that approximately 1 mg CaO_{eq} mL^{-1} is solubilised in mixtures methanol–glycerol at 60 °C [11] and that we started from 500 mg of CaO, it can be estimated that the reaction was performed with approximately 0.7 wt.% catalyst (referenced to the oil mass employed). The reaction started when 220 mL of sunflower oil (methanol/oil molar ratio of 14) preheated at 60 °C was added to the methanol and catalyst mixture under vigorous agitation (1000 rpm). The reaction was conducted at 60 °C under autogenous pressure.

The catalytic behaviour of CaD was compared with that of CaO. To this end, 500 mg of fresh CaO (obtained by the calcination of $CaCO_3$) (0.23 wt.% of catalyst referred to the oil mass) was tested in the methanolysis of sunflower oil following the procedure described above.

Aliquots for sampling analysis were neutralised with a slight excess of 0.1 M HCl to stop the reaction, and the resulting solution was washed with dichloromethane. This washing step with HCl and dichloromethane was performed twice. The alcohol phase (water, glycerol, methanol, HCl, and $CaCl_2$) was separated from the ester phase (glycerides, dichloromethane, and methyl esters) by decantation, and the residual dichloromethane in the methyl esters phase was removed by evaporation at 80 °C. Once the methyl esters were purified, quantitative analysis was carried out following a procedure described elsewhere [4]. Briefly, the fatty acid methyl esters (FAMEs) content was determined in accordance with the European regulated procedure EN 14103 using a gas chromatograph (Agilent 6890GC) connected to a flame ionisation detector (FID) equipped with an HP INNOwax capillary column.

2.3. Characterisation techniques

Elemental analyses (C, H, N) were conducted using a Perkin–Elmer 240 analyser. Thermogravimetric and Differential Thermal Analysis (TGA and DTA) data were recorded on a SDT-Q600 analyser from TA instruments. The temperature was varied from room temperature to 1000 °C at a heating rate of 10 °C min^{-1}. The measurements were carried out on a sample in an open platinum crucible under air flow. Scanning electron micrographs (SEM) were obtained using a JEOL SM 840. The sample was placed over an aluminium drum and covered with a gold film using a JEOL Ion Sputter JFC 1100.

X-ray photoelectron spectroscopy (XPS) studies were performed with a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyser (model 80-365B) and a Mg Kα (1253.6 eV) X-ray source. High-resolution spectra were recorded at a 45° take-off angle by a concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV using a 720-mm-diameter analysis area. Charge referencing was performed against adventitious carbon (C 1s 284.8 eV). The pressure in the analysis chamber was kept below $5{\cdot}10^{-6}$ Pa. PHI ACCESS ESCA-V6.0 F software was used for the data acquisition and analysis. A Shirley-type background was subtracted from the signals. The recorded spectra were always fitted using Gauss–Lorentz curves to accurately determine the binding energy of the different element core levels.

The Fourier transform infrared (FTIR) spectra were recorded at room temperature at a resolution of 4 cm^{-1} with a Nicolet 5700 Fourier transform spectrophotometer equipped with an Hg–Cd–Te cryodetector working in the range of 4000–650 cm^{-1}. For the glycerol spectrum, KBr was impregnated with glycerol and the mixture was loaded into the cup of a DRIFT accessory. The DRIFT spectrum was taken as the spectrum of glycerol. Further details are given in Ref. [10]. In the case of CaD, it was mixed with KBr and used to make a self-supported wafer. In this case, the IR spectrum of the wafer was recorded in transmittance mode.

A high-resolution powder pattern of CaD was collected on the ESRF ID31 powder diffractometer (Grenoble, France) (λ = 0.2998 Å). The Debye–Scherrer configuration was used, with the sample loaded in a rotating borosilicate glass capillary of 1.0 mm diameter. The overall measuring time was selected as ≈100 min to obtain good statistics over the angular range of 2.3–17° (in 2θ). The data from the multianalyser Si(1 1 1) stage were normalised and binned into 0.003° step sizes using local software.

3. Results and discussion

3.1. Catalytic behaviour

The catalytic performance of the prepared solid was tested in the methanolysis of sunflower oil. Its activity was compared with that obtained by the same amount of CaO (500 mg) used for preparing the CaD. Fig. 1 displays the kinetics of the reaction with both catalysts. The prepared solid was much more active than CaO, achieving a biodiesel yield above 80 wt.% after 2 h of time-on-stream, whereas that for CaO was ca. 20%. After 5 h, the FAME yields of both solids were close to the equilibrium value, which was reached asymptotically. The curve representing CaO is sigmoid, which indicates an induction period during the reaction: the reaction rate is quite small initially, but after ca. 90 min, the rate increases remarkably. As the reaction progresses and glycerol