



## Carbonate hydroxyapatite as a catalyst for ethanol conversion to hydrocarbon fuels



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### ABSTRACT

Carbonate hydroxyapatite (CHAP) was successfully used as a catalyst for direct ethanol conversion into hydrocarbon fuels in a single-step gas-phase reaction. The CHAP was synthesized by chemical precipitation method in basic media using an alkali-free system. After heat treatments, it was widely characterized by XRF, XRD, FTIR, XPS, pyridine-TPD, CO<sub>2</sub> chemisorption, and N<sub>2</sub> adsorption at −196 °C. The physical-chemical analysis indicates the formation of B-type CHAP and the presence of acid and basic surface sites being able to act as a bifunctional catalyst. Under optimum conditions of reaction temperature (500 °C) and modified residence time  $W/F_{\text{Ethanol}}$  (40 g h mol<sup>−1</sup>), the ethanol conversion showed a high yield (≈97%) to a mixture of non-oxygenated and oxygenated hydrocarbon fuels with carbon chain lengths in the range from C<sub>4</sub> to C<sub>18+</sub>. After condensation of the reaction products an oily and one aqueous phases were obtained. The net calorific value (NCV) of the oily phase (≈41.3 MJ kg<sup>−1</sup>) was close to those found in conventional fossil fuels.

### 1. Introduction

The constant increase of global energy consumption, particularly the use of fossil fuels for transportation purposes, together with the current environmental preoccupations addressed in the Kyoto protocol have led to rise of proposals for the development of new renewable energy sources. The main available biofuels obtained by direct biomass conversion are ethanol, butanol, and biodiesel. Ethanol is a sustainable fuel widely used either as gasoline additive (anhydrous ethanol) or as gasoline substitute (hydrated ethanol) [1], considered perhaps as the most important renewable fuel, because its origin (e.g., sugar cane, corn) and by having high octane allowing ethanol engines to achieve high torque (1.9%) and high output power (5.4%) in comparison with gasoline engines [2]. Nevertheless, the ethanol still presents some functional disadvantages such as lower NCV (27 MJ kg<sup>−1</sup>) compared to gasoline (44 MJ kg<sup>−1</sup>) [3,4], higher specific consumption and higher hygroscopicity. In addition, at low temperatures (e.g., cold climates) or vapor pressures below 45 kPa, the efficiency of the fuel ignition is not guaranteed [2,5]. Butanol, has a higher NCV (33 MJ kg<sup>−1</sup>) and is better suited to gasoline engines than ethanol. However, it has limited selection of raw materials and produces large quantities of waste products such as acetone. Similarly, biodiesel with NCV (38 MJ kg<sup>−1</sup>) has some limitations such as high hygroscopicity and it dissolves slowly certain materials like rubber and plastics [3,5].

In this regard, new strategic lines of research have been conducted to give greater value to ethanol, using it as raw material for direct synthesis of hydrocarbon fuels with carbon chain lengths close to gasoline-family hydrocarbons (C<sub>4</sub>–C<sub>12</sub>) [5–8]. The latter, involves the vaporization of ethanol into an inert gas stream and its conversion to a mixture of hydrocarbons through a solid catalyst at temperatures between 300 and 500 °C. The energy expended during these processes is comparable to the production of ethanol fuel [5] and somehow coupling these processes could result in lower production costs. In this sense is desirable the development of catalyst with high performance and stability in water.

In the current state of the art, catalysts such as HZSM-5 [5–7] and calcium deficient (nonstoichiometric) hydroxyapatite (HAP) with chemical formula Ca<sub>10-x</sub>(HPO<sub>4</sub>)<sub>x</sub>(PO<sub>4</sub>)<sub>6-x</sub>(OH)<sub>2-x</sub>·nH<sub>2</sub>O (where 0 < x ≤ 1 and 0 < n < 0.25) [8] have been proposed for ethanol conversion to hydrocarbon fuels. HZSM-5 catalysts have been promising for the ethanol conversion to condensable hydrocarbon fuels, predominantly from C<sub>6</sub> to C<sub>9</sub>, and close composition to gasoline attributed to the mesoporous structure and strong acidity that promote mainly the ethanol dehydration reactions [6]. On nonstoichiometric HAP catalysts was also obtained hydrocarbon fuels (up to C<sub>12</sub>) containing, in addition to non-oxygenated hydrocarbons, a fraction of oxygenated hydrocarbons probably due to their unusual property of having both acid and basic sites in a single-crystal lattice with the ability to promote

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dehydration and dehydrogenation reactions of ethanol [8]. Thereby, aiming the development of new renewable energy sources for transport sector, the main purpose of this work was to explore the properties of carbonate hydroxyapatite (CHAP) as a catalyst for direct synthesis of hydrocarbon fuels from ethanol. Actually, the stoichiometric HAP ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) with hexagonal lattice symmetry ( $\text{P6}_3/\text{m}$ ) is the most stable calcium phosphate salt and has a structural flexibility. The HAP lattice can withstand a huge distortion by incorporation of cations and anions that differ in size from the  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions, respectively. The latter allows the alteration of the acid-basic properties of the HAP, and consequently modifies its catalytic activity. There are difference ways to accomplish this. For instance, by substituting their  $\text{Ca}^{2+}$  ions of site I (ninth-coordinated) preferably by  $\text{Na}^+$ ,  $\text{K}^+$  cations or  $\text{Ca}^{2+}$  ions of site II (hepta-coordinated) by  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$  cations as well as the  $\text{OH}^-$  ions by  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\frac{1}{2}\text{O}^{2-}$ ,  $\frac{1}{2}\text{CO}_3^{2-}$  anions and  $\text{PO}_4^{3-}$  ions by  $\text{HPO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{VO}_4^{3-}$ ,  $\text{SiO}_4^{4-}$ ,  $\text{CO}_3^{2-}$  anions [9]. In this way, CHAP can be obtained substituting  $\text{OH}^-$  and/or  $\text{PO}_4^{3-}$  ions by  $\text{CO}_3^{2-}$  anions in the HAP structure. Thus, the  $\text{CO}_3^{2-}$  ions may be located in two different positions of the stoichiometric HAP which in turn depend on the synthesis conditions of the materials. Thus, in CHAPs prepared by heating the HAP in a  $\text{CO}_2$  atmosphere at high temperatures (900 - 1000 °C), the carbonate ions are localized preferably in the  $\text{OH}^-$  ions sites of the HAP producing the A-type CHAP with chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}(\text{CO}_3)_x$  [10–12]. In CHAPs synthesized by chemical precipitation methods and calcined at low temperatures (~400 °C) the carbonate ions preferably substitute the  $\text{PO}_4^{3-}$  ions of the HAP resulting on the B-type CHAP with chemical formula  $\text{Ca}_{10-x/2}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$  [10,13–15]. Also in materials obtained almost exclusively by aqueous precipitation reactions and calcined at temperatures around 900 °C both  $\text{OH}^-$  and  $\text{PO}_4^{3-}$  ions can be replaced, forming an AB-type CHAP with a general chemical formula  $\text{Ca}_{10-x/2}[(\text{PO}_4)_{6-x}(\text{CO}_3)_x][(\text{OH})_{2-2y}(\text{CO}_3)_y]$  [16].

The CHAP is commonly used in biomedical applications being the first time that this solid was used as a catalyst in the ethanol reaction. Therefore, in order to understand the active nature of the CHAP catalyst, the bulk and superficial physicochemical properties of the solid were also investigated. In addition, the performance of the CHAP catalyst and the reactor output gas composition were determined in different conditions of reaction temperature and modified residence time  $W/F_{\text{Ethanol}}$  as well as some kinetic parameters for ethanol conversion and products reaction were obtained. Finally, through procedures of condensation and separation of the reaction products an oily phase has been obtained, the same one that was evaluated by a fast-simulated distillation analysis and calorimetric methods. The results obtained in this study not only show an alternative route for the production of a substitute of fossil fuels, but also constitutes a technical basis for future works with intention to obtain products with greater value than ethanol for specific applications in the petrochemical industry.

## 2. Experimental

### 2.1. Catalyst preparation

The CHAP catalyst was synthesized by chemical precipitation method in basic media using an alkali-free system (without  $\text{Na}^+$  ions). A mixed aqueous solution (100  $\text{cm}^3$ ) of 0.3 M acid ammonium phosphate -  $(\text{NH}_4)_2\text{HPO}_4$  (Merck, 99.4%) and 0.05 M ammonium bicarbonate -  $\text{NH}_4\text{HCO}_3$  (Sigma-Aldrich, 99.5%) was added dropwise (1  $\text{cm}^3 \text{ min}^{-1}$ ) to an aqueous solution (50  $\text{cm}^3$ ) of 1.0 M calcium nitrate tetrahydrate -  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck, 99.9%) under continuous mechanical stirring at 50 °C. The pH ( $\approx 10$ ) of the reaction mixture was monitored and adjusted by adding ammonium solution -  $\text{NH}_4\text{OH}$  (Merck, 26.4%). Completed the mixture, the reaction conditions were maintained for further 2 h resulting in a white precipitate suspension. Then the reaction product was cooled to room temperature and left aging overnight. After that, the white precipitate was filtered, washed

with DD water and ethanol (Merck, 99.9%) and dried in a stove in static air (80 °C). Afterward, the product was crushed, classified in particle sizes between 50 and 150  $\mu\text{m}$  and calcined in a muffle furnace at 600 °C under static air for 2 h. Then, the obtained CHAP catalyst was cooled to room temperature and stored in a silica gel desiccator.

### 2.2. Catalyst characterization

All characterizations of the CHAP catalyst were performed after calcination at 600 °C. Calcium (Ca) and phosphorus (P) contents were determined by X-ray fluorescence (XRF) in a X-5000 XRF Analyzer (Innov-X Canada) and the carbon (C) content was estimated by balance. The powder X-ray diffraction (XRD) pattern was carried out in a Philips Analytical X'Pert PW3050 with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) at 40 kV and 40 mA. The diffractogram was obtained in the range of  $2\theta$  from  $20^\circ$  to  $60^\circ$  with a step size of  $0.02^\circ$  and a time step of 1.8 s. The crystallographic unit cell dimensions were calculated using the CELREF Unit-Cell refinement software. Vibrational spectroscopy analysis was carried out by Fourier transform infrared spectroscopy (FTIR) in a Thermo Scientific Instrument (Nicolet 6700). The sample was previously mixed with dry KBr (1:10) and compressed to form transparent disks. The analysis was performed in transmittance mode, between 4000 and  $400 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  and 32 scans. X-ray photoelectron spectroscopy (XPS) analysis was performed in a Physical Electronics PHI VersaProbe 5000-XPS instrument equipped with a monochromatic Al  $\text{K}\alpha$  source (1486.6 eV) operated at 49.3 W, with a beam diameter of 200  $\mu\text{m}$  and in a high vacuum ( $\sim 10^{-9} \text{ mmHg}$ ). Survey scans in a wide binding energy range from 0 to 1350 eV and high-sensitivity spectra in the C1s, Ca2p, P2p and O1s regions with a pass energy of 23.50 eV were acquired. The binding energies were reported taken as reference the “adventitious carbon” C1s peak at 284.8 eV and the XPS peaks with multiple overlapping components were fit using Gaussian-Lorentzian functions. The acid sites density was determined by temperature-programmed desorption (TPD) of pyridine in a Micromeritics AutoChem II 2920 coupled to a mass spectrometer MKS - Cirrus LM99. Before that, the catalyst ( $\approx 0.15 \text{ g}$ ) was pre-treated at 150 °C in a helium flow ( $25 \text{ cm}^3 \text{ min}^{-1}$ ) for 60 min, followed by exposition to pyridine vapor (Sigma-Aldrich, 99.8%) through consecutive pulses until saturation and purged in helium flow for 30 min at the same temperature. The TPD curve was obtained between 150 and 500 °C at a rate of  $10^\circ \text{ C min}^{-1}$ . For adsorbed pyridine quantification was used a mass spectrometry peak delineated at  $m/z = 79 \text{ amu}$ . The basic sites density was obtained by  $\text{CO}_2$  chemisorption in a Micromeritics ASAP 2020. Prior to the adsorption measurement, ca. 0.5 g of sample was pre-treated at 400 °C under vacuum ( $10^{-5} \text{ mmHg}$ ) for 2 h and cooled to analysis temperature (37 °C). As a result, two isotherms were obtained and the difference of both and their extrapolation to zero pressure was used as the measure of the amount of irreversibly adsorbed gas. The CHAP textural properties were determined from  $\text{N}_2$  adsorption-desorption isotherms at  $-196^\circ \text{ C}$  in a Micromeritics ASAP 2020 analyzer. For this, the sample (ca. 500 mg) was degassed at 350 °C for 4 h. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method in a relative pressure range of  $0.05 < P/P_0 < 0.20$  with a linear correlation coefficient greater than 0.999. Total pore volume ( $V_p$ ) and average pore diameter ( $D_p$ ) were determined by the amount of  $\text{N}_2$  adsorbed at  $P/P_0 \approx 0.995$  and Barrett–Joyner–Halenda (BJH) method from  $\text{N}_2$  desorption isotherm, respectively.

### 2.3. Catalytic tests

Ethanol conversion on CHAP catalysts was carried out in a single-step gas-phase reaction (at atmospheric pressure) using a U-shaped quartz tube reactor (ID  $\approx 5 \text{ mm}$ ) installed inside a vertical muffle furnace (ID  $\approx 2 \text{ inches}$ ). The tests were performed at different reaction conditions of reaction temperature between 300 and 600 °C and

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