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Glycerol dehydration over calcium phosphate catalysts: Effect of acidic–basic features on catalytic performance

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ABSTRACT

This work focuses on investigation of calcium phosphate compounds with different Ca/P ratios (1.39–1.77). Additionally, hydroxyapatite impregnated with tungsten oxide was also investigated. The structural, textural, and surface properties of these materials have been fully characterized using appropriate techniques (low-temperature adsorption–desorption of nitrogen, X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and temperature-programmed reduction (TPR)). Adsorption microcalorimetry of NH_3 or SO_2 was used to estimate the population, strength and strength distribution of acid and basic sites. The nature of acidic sites was determined through the adsorption/desorption of pyridine, followed by infrared spectroscopy. Catalytic performance of the catalysts was tested in the gas phase dehydration of glycerol with the intention of finding correlations between catalytic activity and surface acid–base features. Results show that Ca/P ratio, beside the already known influence on acidic/basic features, also influences red-ox properties of these materials. The investigation performed here proved that, in order to get acrolein – with high selectivity – which is formed on acid sites, it is not only necessary to provide acidity, but also to hinder basic sites. Our results also show that reducing of number and strength of acid centers increases the yield of other desired product, acetol.

1. Introduction

Glycerol is the main by-product obtained in triglyceride methanolysis for biodiesel production [1]. During this process glycerol is normally generated at a rate of 1 mol of glycerol for every 3 mol of methyl ester synthesized, which accounts for approximately 10 wt% of the total product [1]. It is estimated that by 2015, 1.54 million tons of glycerol will be generated worldwide [2], all of which could be efficiently processed in order to increase the value generated from biodiesel production and to achieve a sustainable industry.

Glycerol has a multifunctional structure and properties that give numerous opportunities for chemical and biochemical conversions to produce value-added chemicals. More detailed information is available in recent review articles [3–8]. Therefore, using glycerol for the synthesis of value-added chemicals is of great industrial importance, not only because glycerol can be formed in large amounts during the biodiesel process, but also because glycerol is a nontoxic, edible, renewable and biodegradable compound [9,10].

One of the promising route to glycerol valorization is its catalytic dehydration to produce acrolein and hydroxyacetone (acetol), which are important industrial intermediates for the chemical and agrochemical industries [7,8]. The acidity of the active phase is considered as a crucial factor that influences the catalytic performance in this process to produce acrolein [11,12]. Especially Brønsted acid catalysts give high acrolein selectivity [13]. On the other hand, catalysts that showed higher selectivity to acetol possess significant Lewis acidity, but also possess strong basic sites on their surface [14–18]. Direct correlation between selectivity to acetol and catalyst basicity or Lewis acidity has not been found. Therefore, it remains very challenging topic to explain in more detailed way the selective catalytic conversion of glycerol to hydroxyacetone [19].

Calcium phosphates are compounds of significant interest in an interdisciplinary field of sciences involving chemistry, biology, medicine and geology. Hydroxyapatites [HAP; $Ca_{10}(PO_4)_6(OH)_2$], are the most stable among known calcium phosphates at normal temperatures [20,21]. In the field of catalysis these materials gained

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increasing interest in catalysis due to their unusual property of containing both basic and acid sites in a single crystal lattice [22–24]. The stoichiometric form of HAP is presented as $Ca_{10}(PO_4)_6(OH)_2$ with Ca/P ratio of 1.67 [25]. The ionic radius of HAP's constituent elements (Ca, P) allows a fair degree of transfer or loss of ions within its crystal structure [26]. Thus HAP is a highly nonstoichiometric calcium phosphate compound with a Ca/P molar ratio ranging from 1.50 to 1.67. It is known that at a Ca/P ratio 1.5, highly crystalline HAP acts as an acid catalyst, while at a Ca/P ratio of 1.67 it acts as a basic catalyst [22,23]. If this ratio is between 1.50 and 1.67 HAPs possess both acid and basic character [22,23]. The ability to finely tune the acidic–basic properties of these materials by changing Ca/P ratio makes them appropriate catalysts for investigation of reactions where the yield and selectivity to desired products is largely governed by the balance between acidic and basic active sites. Furthermore, the properties of hydroxyapatites can be tuned by modification of the $Ca_{10}(PO_4)_6(OH)_2$ lattice composition through the numerous possible ionic substitutions [27], on either the Ca cationic position (Ba, Mg, Cd, Sr, etc.), or the ionic sites, PO_4^{3+} (VO_4^{3-}, HPO_4^{2-}, CO_3^{2-}) or OH— (CO_3^{2-}, F^-). These substitutions influence the thermal stability, textural properties and catalytic activity. Due to all of these appropriate properties calcium phosphate materials have been used as catalysts in various reactions; in dehydration and dehydrogenation [28–30] of alcohols, in oxidation of alkanes [31], and for water gas shift reaction [32], for Knoevenagel condensation [33] and Friedel–Crafts alkylation [34].

In the present work calcium phosphates with different Ca/P ratios have been characterized with respect to their structural, textural and red-ox properties. Acidic/basic features of these materials are thoroughly explored here by microcalorimetry of ammonia and sulfur dioxide adsorption, as well as by FTIR (Fourier Transform Infrared Spectroscopy) of pyridine adsorption. Additionally, in order to investigate the influence of wolframate species on acidic–basic properties and catalytic activity of hydroxyapatites; HAP impregnated with tungsten oxide was also investigated in this work. It is known that the presence of wolframate species on the surface of solid catalysts causes both an increase of the Lewis acidity, almost full disappearance of the surface anions acting as basic sites, and the appearance of a very strong Brønsted acidity [35], Catalytic behavior of studied materials was tested in the gas phase dehydration of glycerol. Special attention is given to the correlation between catalytic activity and surface acid–base properties, which are essential to the mechanism of the reaction. Understanding the nature of active sites for dehydration reaction could help in development of more efficient solid catalysts for a sustainable use of biomass-derived glycerol by chemical industry.

2. Experimental

2.1. Sample preparation

Hydroxyapatite samples with Ca/P ratios of 1.50 (product reference: nanoXIM.TCP202) and 1.66 (nanoXIM.HAp402) were commercial samples purchased from Fluidinova S.A. They were calcined in air at 450 °C for 5 h before use.

Sample 1.66 HAP was modified by incipient wetness impregnation, at room temperature, with aqueous solutions of calcium acetate and phosphoric acid to form a Ca-rich (Ca/HAP) and a Ca-deficient (P/HAP) calcium phosphates respectively. Subsequently, samples were dried in air at 110 °C overnight, followed by calcination in air at 450 °C.

W/HAP sample was prepared by incipient wetness impregnation, at room temperature, with an aqueous solution of tungstic acid on 1.66 HAP. The sample was dried in air at 110 °C overnight and calcined in air at 450 °C.

2.2. Characterization

Chemical compositions of investigated materials were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an ACTIVA spectrometer from Horiba JOBIN YVON, after they were digested using a mixture of inorganic acids (H_2SO_4 and HNO_3).

Surface areas were determined by low temperature nitrogen adsorption performed at −196 °C, on a Micromeritics 2020 apparatus, after pretreatment performed for 2 h at 300 °C under vacuum. The BET method was used to derive surface areas (S_{BET}) from the resulting isotherms.

The structural characteristics of samples were examined by XRD, Raman and DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectroscopy techniques. XRD patterns were recorded on a Bruker (Siemens) D5005 diffractometer at room temperature using Cu Kα radiation (0.154 nm) from 4 to 70° in 0.02° steps with 1s per step. Raman spectra were collected under the ambient conditions on a LabRAMHR (Jobin Yvon) spectrometer. The excitation was provided by the 514.5 nm line of an Ar^+ Kr^+ ion laser (Spectra Physics), keeping the sample under microscope. The power of the incident beam on the sample was 100 μW. Because the laser beam can be precisely focused, it was possible to perform quantitative evaluation of band intensities between the samples studied. The laser beam was focused through microscope objective lenses (100×) down to a 1 μm spot on the sample. The acquisition time was adjusted according to the intensity of the Raman scattering. The wavenumber values reported from the spectra are accurate to within 2 cm^{-1}. For each solid, the spectra were recorded at several points of the sample to ascertain the homogeneity of the sample; the averages of these spectra were plotted and presented in this paper. Diffuse reflectance infrared (DRIFT) spectra were collected with a Nicolet 8700 THERMO SCIENTIFIC instrument by co-addition of 100 scans at 2 cm^{-1} resolution. The instrument was equipped with a Praying Mantis accessory (Harrick) and a liquid nitrogen-cooled MCT detector. The samples were diluted in KBr, and a spectrum of KBr was used as a reference.

Surface concentrations of Ca, P and O were determined by means of XPS technique, which was done using KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical electron analyzer and an Al anode (Al Ka = 1486.6 eV) powered at 150 W, with a pass energy of 20 eV, and in a hybrid lens mode. The detection area analyzed was 700–300 μm. Charge neutralization was required for all samples. The peaks were referenced to the C—(C, H) components of the C 1s band at 284.6 eV. Shirley background subtraction and peak fitting to theoretical Gaussian–Lorentzian functions were performed using an XPS processing program (vision 2.2.6 KRATOS). The residual pressure in the spectrometer chamber was 5×10^{-9} mbar during data acquisition.

Red-ox properties of investigated samples were revealed by TPR technique using a TPD/R/O-1100 (ThermoFisher) instrument. Prior to the TPR run, the fresh sample was treated in a O_2/He stream (0.998% v/v, with a flow rate of 20 ml min^{-1}), ramping the temperature at 10 °C min^{-1} from room temperature to 350 °C and maintaining it at this temperature for 60 min. Subsequently, sample was cooled down to 40 °C. The TPR measurements were carried out using H_2/Ar (4.98% v/v) as reducing gas mixture, with flow rate of 20 ml min^{-1}. The heating rate was 10 °C min^{-1} from 40 °C to 850 °C. The consumption of H_2 was detected by a thermal conductivity detector (TCD). The TPR peak areas were calibrated with given H_2/Ar (4.98% v/v) mixture injections.

The acid–base properties were studied by adsorption microcalorimetry of NH_3 and SO_2. Experiments were performed at 150 °C in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus equipped with a Barocel capacitance manometer for pressure measurements. The samples