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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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