Influence of surface acid and base sites on the Guerbet coupling of ethanol to butanol over metal phosphate catalysts

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ABSTRACT

Hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) is a well-recognized catalyst for the Guerbet coupling of ethanol to butanol. In an effort to explore the role of the anion components of the catalyst, steady-state, gas phase catalytic coupling of ethanol to butanol was investigated at 633 K and atmospheric pressure over beta tricalcium phosphate (β-TCP; $β-Ca_3(PO_4)_2$) and fluorine-substituted hydroxyapatite (FAP; $Ca_{10}(PO_4)_6F_2$). Both β-TCP and FAP catalysts were catalytically active for butanol formation, leading to ~35% selectivity at low conversion, suggesting that the PO_4^{3-} group contributes to the active acid-base site pair for butanol formation during ethanol coupling over HAP. Co-feeding water, a product of ethanol coupling, revealed weaker inhibition of the rate over HAP relative to MgO, confirming the potential negative influence of strong base sites on coupling catalysts. Catalytic reactions of ethanol over $Mg_3(PO_4)_2$, β-TCP, and $Sr_3(PO_4)_2$ catalysts demonstrated the importance of Lewis acidity of the metal phosphates on the reaction. Relatively strong Lewis acid sites on the $Mg_3(PO_4)_2$ surface (Mg^{2+} cations) favored undesired ethanol dehydration to ethene (36% selectivity) and diethyl ether (52% selectivity) whereas the $Sr_3(PO_4)_2$ catalyst predominantly catalyzed ethanol dehydrogenation to acetaldehyde (91% selectivity) at a rate significantly higher than that observed over the other catalysts. Evidently, the β-TCP exposes intermediate-strength Lewis acid sites provided by surface Ca^{2+} cations that enable the material to effectively convert ethanol to butanol with 35% selectivity.

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1. Introduction

The catalytic upgrading of bioethanol into value-added fuels and chemicals, such as butanol, has attracted increased interest in recent years due to the many drawbacks posed by ethanol as a gasoline fuel additive. Butanol is a more desirable transportation blend fuel compared to ethanol because it has a lower vapor pressure, a lower solubility in water, and a lower corrosivity [1]. These properties allow butanol to be easily transported using the existing fuel distribution infrastructure and to be blended with gasoline at higher concentrations than ethanol. Additionally, the energy content of butanol is closer to that of conventional petroleum, which allows for improved gas mileage for biofuel blended gasoline [1,2].

The catalytic transformation of ethanol to butanol occurs via the Guerbet coupling reaction – a well-known industrial route for higher alcohol synthesis. A commonly proposed mechanism for Guerbet coupling consists of a multi-step sequence of reactions that involves an initial dehydrogenation step to form acetaldehyde, which then undergoes an aldol self-condensation reaction to cro-

tonaldehyde, followed by hydrogenation of the condensation product to give butanol as shown in Scheme 1 [3,4]. A variety of catalytic materials have been studied for this reaction including solid base metal oxides (such as MgO) [5–7], Mg-Al mixed metal oxides [8–10], basic zeolites [11,12], and more recently hydroxyapatite [13–15].

While the mechanism in Scheme 1 is generally accepted for Guerbet coupling, other reaction paths have been proposed. One alternative mechanism involves the "direct coupling" of ethanol to butanol as suggested by Yang and Meng [12] for coupling over a basic zeolite. A direct coupling path has also been invoked by others [6,16]. Moreover, Scalbert et al. present a thermodynamic argument to conclude the aldol condensation of acetaldehyde is not kinetically relevant at high temperature (above 623 K) during alcohol coupling [15]. Evidently, additional mechanistic studies are needed for the Guerbet coupling reaction.

Calcium hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) has demonstrated exceptional catalytic performance in the Guerbet coupling of ethanol to butanol exhibiting unusually high activity and high butanol selectivity (70%) at significantly lower reaction temperatures than what has been previously reported in the literature for this reaction [17,18]. Recent work from our group has shown that
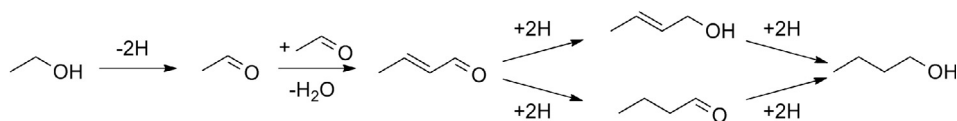
Scheme 1. A commonly proposed mechanism of Guerbet coupling.

the HAP surface exposes a high surface density of acid and base sites of moderate strength that likely facilitate the reaction and account for its high catalytic activity and unique selectivity observed during the reaction [19,20]. However, the nature and composition of the active acid-base site pair on the HAP surface responsible for butanol formation has not been clearly assigned, which continues to complicate future catalyst design and optimization.

In a recent study by Ho et al. [21], *in situ* titration experiments combined with IR spectroscopy revealed the presence of two different active sites on the surface of HAP: surface Ca-O sites responsible for ethanol dehydrogenation to acetaldehyde and Ca^{2+}-PO_4^{3-} site pairs required for butanol formation. Diallo Garcia et al. [22] also investigated acid-base site pairs on the HAP surface and concluded strongly basic surface OH^- groups are likely the active base site involved in catalytic reactions because O^{2-} anions of surface PO_4^{3-} groups were weakly basic and unperturbed during acetylene adsorption studies. Clear consensus regarding the active acid-base site pairs on the HAP surface responsible for butanol formation is lacking and therefore additional investigations are needed.

In this work, the catalytic conversion of ethanol was investigated over beta-tricalcium phosphate (β-TCP; β-$Ca_3(PO_4)_2$) and fluorine-substituted hydroxyapatite (FAP; $Ca_{10}(PO_4)_6F_2$), and results were compared with those using stoichiometric HAP to gain insight into the importance of the OH^- and PO_4^{3-} anions of HAP. The influence of cations in the metal phosphate catalysts was also explored by investigating the catalytic activity of Mg- and Sr-phosphate in ethanol conversion. Additionally, to help elucidate the role of dihydrogen and water that are evolved in the Guerbet reaction, these by-products were co-fed with ethanol during the steady-state gas-phase conversion of ethanol over stoichiometric HAP.

2. Experimental methods

2.1. Catalyst preparation

Stoichiometric HAP was prepared using a controlled co-precipitation method based on the procedure reported by Tsuchida et al. [23], as described in detail in previous work [19]. Briefly, aqueous solutions of 0.5 M calcium nitrate tetrahydrate ($Ca(NO_3)_2$·$4H_2O$, Acros Organics) and 0.3 M diammonium phosphate ($(NH_4)_2HPO_4$, Aldrich, >99.99%), previously adjusted to pH = 10.5 using aqueous ammonia, were simultaneously added dropwise to $100\ cm^3$ of distilled deionized water (DDI) held at 353 K. The resulting suspension was stirred for 24 h at 353 K under reflux. The precipitate was recovered by vacuum filtration, washed 3 times with DDI water, and dried in stagnant air at 400 K overnight. The final HAP powder was calcined at 873 K for 2 h in flowing air using a 10 K min^{-1} heating rate from room temperature and sized to 106–180 μm pellets prior to characterization and reactivity measurements.

The β-TCP catalyst was obtained by heating calcium-deficient hydroxyapatite (Sigma-Aldrich, CAS #7758-87-4, ≥98%) in flowing air to 1073 K using a thermal ramp rate of 2.5 K min^{-1} from room temperature and holding at 1073 K for 2 h. The phase transformation from calcium-deficient hydroxyapatite to β-TCP upon heating occurs according to the following reaction [24,25]:

$Ca_9(HPO_4)(PO_4)_5(OH) \rightarrow 3Ca_3(PO_4)_2 + H_2O$. The resulting powder was sized to 106–180 μm pellets prior to characterization and reactivity measurements.

The FAP catalyst was prepared by solid-state reaction [26]. A stoichiometric mixture (3:1 M ratio) of β-TCP (described above) and calcium fluoride (CaF_2, Sigma-Aldrich) was heated using an electrical tube furnace in flowing argon (UHP, 99.999%) to 1373 K with a 4.5 K min^{-1} thermal ramp rate and holding at 1373 K for 4 h. Pure CaF_2 was placed in the furnace upstream of the reaction mixture to reduce the volatilization of fluorine [26,27].

Magnesium phosphate ($Mg_3(PO_4)_2$) was obtained by heating magnesium phosphate hydrate ($Mg_3(PO_4)_2$·H_2O, Sigma–Aldrich) in flowing air to 873 K using a thermal ramp rate of 10 K min^{-1} from room temperature and holding at 873 K for 2 h. The resulting $Mg_3(PO_4)_2$ powder was sized to 106–180 μm pellets prior to characterization and reactivity measurements. Strontium phosphate ($Sr_3(PO_4)_2$, Sigma-Aldrich) and magnesium oxide (MgO, Ube Material Industries, Ltd) were obtained commercially. The strontium phosphate and magnesium oxide powders were calcined at 873 K for 2 h in flowing air with a 10 K min^{-1} ramp rate. The resulting MgO powder was sized to 106–180 μm pellets prior to characterization and reactivity measurements.

2.2. Catalyst characterization

Crystalline phases of the catalytic materials were confirmed by powder X-ray diffraction (XRD) on a PANalytical X'Pert Pro Multi-Purpose Diffractometer using monochromatic Cu-Kα radiation (λ = 1.54 Å). Scans were collected at 2θ = 10–100° with a 0.05° step size. Specific surface areas were obtained by N_2 adsorption at 77 K with a Micromeritics ASAP 2020 automated analyzer using the BET method after evacuation at 723 K for 4 h. Thermogravimetric analysis (TGA) experiments were conducted using a TA Instruments SDT Q600. Each sample was heated to 1273 K from room temperature with a 10 K min^{-1} thermal ramp rate under 100 cm^3 min^{-1} of flowing He.

Elemental analyses of the catalytic materials were performed by Galbraith Laboratories, Inc. (Knoxville, TN). The metal and phosphorus content of the catalysts were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) and the fluorine content of the fluorapatite sample was determined using a fluoride ion specific electrode. The surface composition of the hydroxyapatite sample was analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Fisher ESCALab 250 apparatus. The signals were corrected using adventitious carbon (C(1)s) set to a binding energy of 284.6 eV.

The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed pyridine was investigated using a Bio-Rad (FTS-60A) FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The DRIFTS experiments were conducted using a high-temperature gas reaction chamber (Harrick Scientific) positioned onto a Praying Mantis diffuse reflectance sample accessory. All spectra were obtained by averaging 100 scans at a spectral resolution of 4 cm^{-1}. The magnesium phosphate sample, diluted in KBr by 50 wt.%, was loaded into the DRIFTS cell and thermally treated *in situ* at 773 K for 1 h in flowing He (30 cm^3 min^{-1}) prior to pyridine exposure. Spectral backgrounds were then collected at 373 and 303 K as the sample cooled in flowing He. Pyridine