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ARTICLE TYPE

Reactivity of Ethanol over Hydroxyapatite-Based Ca-enriched Catalysts with Various Carbonate Contents†

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The Guerbet reaction of ethanol to heavier products was performed over a series of extensively characterized carbonate-containing hydroxyapatites (HAPs) with different Ca/P ratios, and thus different densities, strengths and natures of acid and basic sites. These properties were correlated with the reactivity of the solids and an optimal ratio between the amount of acid and basic sites was evidenced (*ca.* 5). The best performances were accordingly obtained over a Hap-CO$_3$ catalyst, which gave a yield of 30% in heavier alcohols at a 40% ethanol conversion.

Introduction

The Guerbet reaction, of which the name originates from the Marcel Guerbet's discovery, is an organic reaction in which a primary aliphatic alcohol is converted to its *β*-alkylated dimer with the loss of one molecule of water. Marcel Guerbet initially found that *1*-octanol, thus a primary alcohol, is transformed to C16 and C24 alcohols when heated at 200 °C in the presence of its sodium derivative or with sodium derivatives of other alcohols.[1] Further, Marcel Guerbet reported that this reaction is also applicable to secondary alcohols by demonstrating the production of higher chain alcohols, namely *4*-methylpentanol and *2,4*-dimethylheptanol, from *iso*propanol, with, *e.g.*, *3*-methylbutyric acid, acetic acid and formic acid formed as by-products.[2] Weizmann *et al.* reported that the presence of an *α*-methylene group in the immediate vicinity of the hydroxyl group is a requisite for the aldol condensation step and hence for the Guerbet reaction. They have also confirmed that the Guerbet reaction between primary and secondary alcohols is predetermined by the fact that an aldehyde condenses with a ketone, most of time giving an alkylidene-ketone even though there are some exceptions.[3,4]

Bioethanol is one of the major compounds produced in large quantities from biomass, but its high vapour pressure, its affinity for water and its lower energy content are hurdles for an extensive application in existing fuels, while this is a major output for this compound nowadays. Biobutanol, which is another primary alcohol that can be used as a fuel or a fuel additive, but also as a platform molecule from which C4 chemistry can be derived, can also be produced directly from biomass, but through routes which are still not economically feasible at the moment (biotech and syngas conversion).[5,6] Then, finding a chemical alternative route to transform ethanol to heavier alcohols such as butanol could represent an attractive option with respect to the biorefinery concept of producing a diversity of chemicals and fuels.[7] Such a transformation is possible through the Guerbet reaction.

Both homogeneous and heterogeneous catalysts have been reported for the production of heavier alcohols through the Guerbet reaction. The Guerbet reaction using homogeneous catalysts was first examined using transition metal complexes such as Rh, Ru, Pt, and Ir under very mild conditions of 110-140 °C at atmospheric pressure.[8-11] Catalytic activity of Rh complex was found to be very high compared with that of Ru and Ir complexes. Pd and Au complexes are inactive in the Guerbet reaction because it is difficult to generate stable hydride metal complexes.[8,9] Carlini *et al.* disclosed the Guerbet reaction using homogeneous Ni and Pd-based catalysts in the presence of basic alkoxides, but using a higher reaction temperature of 200 °C.[9,12-14] Catalytic systems based on Cu, Ni, Rh, Ru and Pd metals in combination with soluble alkoxides as basic components were also employed in the Guerbet reaction to synthesize *iso*butanol.[13-16] The main disadvantage of using excess alkoxide is linked to metal leaching, and also to the production of alkali hydroxides like sodium hydroxide, which is not environmental friendly.[11-16] So, in order to make the Guerbet reaction economically feasible for industrial applications, there is a need for developing heterogeneous catalysts, which can also be environmental friendly in terms of catalyst separation and reusability.

As we will comment in the next page, the Guerbet reaction needs multifunctional catalysts, especially behaving both acid and base sites. Ueda *et al.* reported the condensation of various primary alcohols with methanol over solid basic catalysts such as MgO, CaO and ZnO.[17-20] The reaction took place only over MgO, as the other metal oxides were found to be inactive or non-selective. The Guerbet reaction of alcohols has also been studied using various Mg-Al mixed oxides derived from hydrotalcite type precursors.[21-25] The rate of alcohol dehydration to ethers and olefins is higher for Al-rich Mg$_y$AlO$_x$ solids, but dehydrogenation and aldol condensation of ethanol, respectively to corresponding aldehyde and higher alcohols, is favoured over Mg-rich Mg_yAlO_x samples.[21,25] Also, introduction of copper into the hydrotalcite-derived Mg-Al mixed oxide enhanced the activity of catalyst towards the Guerbet reaction.[22,23]

Hydroxyapatite was especially found to be an active catalyst for the heterogeneous gas phase reaction of ethanol.[26,27] To this respect, Tsuchida *et al.* reported the ethanol conversion over hydroxyapatites with different Ca/P ratios up to the stoichiometric value of 1.67.[27] As a result, they obtained about 70% of selectivity to higher alcohols, at an ethanol conversion of 50%. Indeed, the drawback of using hydroxyapatites for the Guerbet reaction is that at higher ethanol conversions, the produced primary alcohols undergo further condensation to produce heavier alcohols and other heavier products.[28] These heavier alcohols can however be used, *e.g.*, as solvents, fuel additives or plasticizers, provided relevant separation operations can be performed.

Concerning the reaction mechanism, it is most largely admitted that the Guerbet reaction proceeds through a series of consecutive steps over multifunctional catalysts (acid, base and/or redox sites), which were especially considered to explain the reactivity of ethanol over the aforementioned HAPs.[27,29] First, dehydrogenation of the alcohol takes place over redox/acid-base sites to form aldehydes, which further undergo an aldol condensation over basic sites to produce the corresponding aldol. The as-obtained aldol then undergoes dehydrogenation over acid sites to form α-β unsaturated aldehyde or ketone that further undergoes hydrogenation over redox/acid-base sites to form higher alcohols. However, Scalbert *et al.*[30] recently showed that over 350 °C and using a commercial HAP of which the Ca/P ratio was not mentioned but which is supposedly stoichiometric, another mechanism is taking place, involving direct condensation of ethanol. Note that the authors have mentioned that their thermodynamic findings may not be applicable at lower temperatures, *i.e.*, below 350 °C.

In this context, the overall objective of the present work was to get a fine understanding of the acid-base functionalities of HAPs involved in the gas phase Guerbet reaction of ethanol. To this respect, we used a previously synthesised and fully characterized series of HAPs (notably with different Ca/P ratios higher than the stoichiometric value of 1.67).[31] Since there are only few reports correlating the structure, textural and acid-base properties of hydroxyapatites (Ca/P > 1.67) with the Guerbet reactivity, we specifically tracked and discussed the correlations between the observed catalytic performances and the physico-chemical properties. This enabled drawing a complete picture of the specific action of the various types of acid/basic sites present at the surface of the solids on the formation of the various Guerbet reaction products.

Experimental

Catalysts

The synthesis method of all the solids used in this study is reported elsewhere.[31] They are further listed in Table 1 together with their main characteristics.

Table 1 List and basic characteristics of the catalytic solids used in the present study (from data of Ref 31).

Type of solid	Name	Ca/P atomic ratio (ICP)	Na (wt.%)	Specific surface area ($m^2.g^{-1}$)
Deficient	HapD	1.62	-	124
Stoichiometric	Hap	1.69	-	114
Carbonated	Hap-CO_3	1.70	-	107
Carbonated	HapNa-CO_3	1.72	0.64	109
Carbonate-rich	HapE-CO_3	1.90	-	76
Carbonate-rich	HapE-Na-CO_3	2.39	< 0.3	72

Characterisations

Extensive physico-chemical characterization of the solids, namely, X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Scanning electron microscopy (SEM), Infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Low-energy ion scattering spectroscopy (LEIS), Hetero nuclear magnetic resonance spectroscopy (2D NMR), Temperature programmed desorption (TPD-NH_3 & TPD-CO_2), XPS after adsorption of *2*-phenylethylamine (PEA-XPS) and pulse liquid chromatographic adsorption technique using benzoic acid, are reported elsewhere.[31] The present paper is then focused on the solids reactivity in the Guerbet reaction, in relation to the aforementioned characterization results.

The Guerbet reaction of ethanol was carried out using 0.20 g (GHSV = 15000 $mL.h^{-1}.g^{-1}$) or 0.60 g (GHSV = 5000 $mL.h^{-1}.g^{-1}$) of sample under the form of a powder with a particle size between 80 and 100 mesh. 20 Vol.% ethanol in He gas were passed through a fixed bed glass reactor at a total flow rate of 50 mL/min. The feed and the outlet products were analyzed online by a gas chromatography equipped with a zebron ZB-Bioethanol capillary column (l = 30 m, id = 0.25 mm) connected to a FID and coupled to mass spectrometer (MS Agilent 5975C).

The ethanol conversion, the selectivity to each product, and the corresponding yields were calculated as follows:

- Ethanol conversion (%) = 100 x [(moles of ethanol before reaction – moles of ethanol after reaction)/moles of ethanol before reaction];
- Product yield (%) = 100 x (moles of C diverted into the considered product / moles of C in ethanol before reaction);
- Product selectivity (%) = 100 x (Product yield / Ethanol conversion).

Results and discussion

Guerbet reaction products observed at iso-conversion

A first series of experiments aimed at studying the intrinsic catalytic properties of the solids by working at iso-conversion. Table 2 shows the selectivity to the main products of the Guerbet reaction of ethanol at the iso-conversion of 14%. This iso-conversion of ethanol was achieved by properly adjusting the temperature between 300°C and 400°C at GHSV's of 5000 $mL.h^{-1}g^{-1}$ and 15000 $mL.h^{-1}g^{-1}$. As aforementioned, the direct ethanol coupling pathway proposed by Scalbert *et al.* may not be applicable at lower temperatures, *i.e.*, below 350 °C.[30] The iso-conversion of 14 % was observed at a temperature is below 350 °C for three HAPs (HapD, Hap, Hap-CO_3; Table 2). The other 3 ones are carbonate-rich samples, with thus properties different from those of Scalbert *et al.*, who used a commercial solid with thus most probably a stoichiometric composition. Moreover Scalbert *et al.* did not consider the mechanism involved in formation of products like ethylene and ether, which are formed by dehydration of ethanol over acid sites. In the present study, *i.e.*, in our conditions and over our specific solids, we will see in the followings that the observed products are on line with the sequential mechanism proposed elsewhere[27,29], which then actually applies here, even if we cannot completely rule out a potential contribution of the direct pathway to the observed products' distribution.

Butanol was the major product over all the catalysts, its selectivity being higher over the carbonated apatites, namely Hap-CO_3 (71%) and HapNa-CO_3 (59%). Formation of ethylene, which is issued from intramolecular dehydration of ethanol, was observed in rather small quantities over all the apatites, and especially over HapD (3.2%) and Hap (2%), its selectivity being less than 1.6% over the other solids. Acetaldehyde, a dehydrogenation product of ethanol was produced over all the catalysts, and especially observed as a final product over the carbonate-rich apatites, namely HapE-CO_3 (15.5%) and HapE-Na-CO_3 (19%). The formation of *2*-buten-*1*-ol, which is produced by dehydrogenation of ethanol followed by aldol condensation and hydrogenation of the C=O bond while leaving the C=C bond non-hydrogenated, was also observed, in quantities increasing when the solids were richer in carbonates. In contrast, only trace amounts of butyraldehyde were observed, which is a compound produced in a way similar to that of *2*-buten-*1*-ol, but by hydrogenation of the C=C bond leaving the C=O bond non-hydrogenated. Small amounts of diethylether, resulting from intermolecular dehydration of ethanol over acid sites, as well as dienes, were also observed over all the catalysts. Further, 'other' compounds were also detected, namely higher aldehydes, higher alkenes and trace amount of aromatics, which are formed by multiple consecutive steps (including Guerbet intermediates), by uncontrolled reaction over the various sites present at the surface of the solids.

Table 2 Selectivity to Guerbet reaction products at 14% of ethanol conversion.

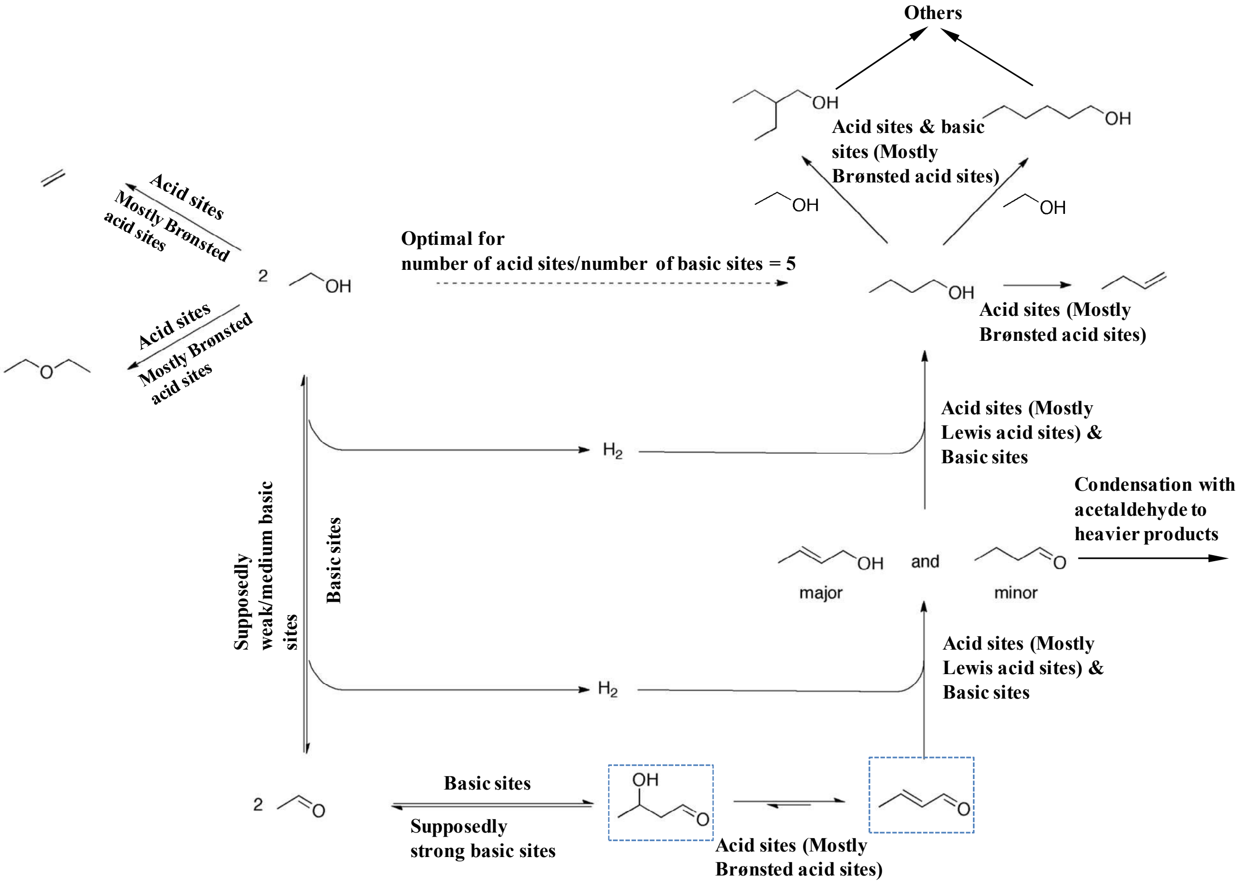
Catalysts	Group *i*		Group *ii*		Group *iii*	
	HapD	Hap	Hap-CO_3	HapNa-CO_3	HapE-CO_3	HapE-Na-CO_3
Ethylene	3.1	2	1.3	1.6	1.2	1.5
Acetaldehyde	5.8	9	7.2	13.1	15.5	19
2-buten-*1*-ol	2	1	3.2	5.1	8	10.2
Butanol	49	50	71	59	46	41
C6-C10 alcohols[a]	18	19.4	8.8	2.9	7	1.1
Total alcohols[b]	69	70.4	83	67	61	52.3
Diethylether	5	4.5	1.1	0.8	0.6	2
Dienes[c]	3.1	1.2	2	2.2	1.5	1.2
Ethyl butyrate	-	-	-	1.5	3.5	10.3
Others[d]	14	12.9	5.4	13.8	16.7	13.7

[a] Hexanol, *2*-ethylbutanol, octanol, *2*-ethylhexanol and decanol;
[b] *2*-buten-1-ol, butanol and C6-C10 alcohols;
[c] *1,3*-butadiene and small amounts of C6-dienes;
[d] Higher aldehydes, higher alkenes, aromatics.
N.B. GHSV = 5000 $mL.h^{-1}.g^{-1}$ for all HAPs but HapNa-CO_3 with 15000 $mL.h^{-1}.g^{-1}$

Due to the high level of complexity of the studied reaction, for sake of clarity we compiled the conclusions deduced from all the results of this study in Scheme 1, which is thus, in fact, a conclusion of this work. Hereafter, we comment Scheme 1, before, in the next part of the paper, detailing the specific set of correlations/conclusions that were gathered to assemble this integrated view of the whole reaction network.

In order for the Guerbet reaction of ethanol to effectively proceed to heavier alcohols, both acid and basic sites are necessary, but the strength, the nature and the relative balance of these sites have a great influence on each step of the Guerbet cycle, and are also involved in the formation of undesirable side-reactions, thereby conditioning the products distribution. The first step of the Guerbet cycle is the dehydrogenation of ethanol over basic sites to produce acetaldehyde. As it was concluded in our previous study on the same solids concerning the reaction of conversion of *iso*propanol to acetone that most probably takes place over weak or medium basic sites (CaO species),[31] we also postulated that this might be the same here for ethanol reactivity, even if we cannot formally exclude the possibility that strong basic sites (OH^-) could also be involved. Scalbert *et al.* proposed a mechanism in which acetaldehyde can further react with unreacted ethanol to form butenol supposedly over stoichiometric HAP at temperatures below 350 °C.[30] However, we used temperatures over 350 °C for the carbonate-containing apatites, which behave different properties compared to those of stoichiometric apatites.

The as-formed acetaldehyde further undergoes aldol condensation over basic sites (probably over stronger basic sites; OH^-) to form an intermediate aldol (never observed in our conditions). Further dehydration of aldol takes place over acid sites (mostly Brønsted acid sites; HPO_4^{2-}) to produce crotonaldehyde, which was also not observed (or in trace amounts). The crotonaldehyde then undergoes partial hydrogenation by proton exchange mechanism over HAP catalysts to form *2*-buten-*1*-ol and butyraldehyde over both types of acid (mostly Lewis acid sites, Ca^{2+} & OH^- vacancies) and over basic sites. These compounds can further undergo hydrogenation over the same acid-base sites in the apatite catalysts to form butanol. Butanol can then further react with ethanol and go through an additional Guerbet cycle involving acid sites and basic sites to form *2*-ethylbutanol or hexanol, depending on the type of attack. The formation of these heavier alcohols was more promoted over catalysts with a larger number of acid sites, and mainly Brønsted acid sites (HPO_4^{2-}). Also, there are some competing reactions, especially dehydration reactions that can form olefins (ethylene, butene etc…) or diethylether, which occur in parallel to the Guerbet cycle (mostly over Brønsted acid sites; HPO_4^{2-}). So, there should be a compromise between the acid and the basic sites number, and also concerning their relative strength and nature to yield a catalyst that is selective towards higher alcohols. We especially identified the best ratio between the number of acid sites to basic sites of *ca.* 5 to reach the maximum selectivity to higher alcohols over the HAP catalysts of the present study. If the amount or the strength of the acid sites becomes too high, the dehydration pathway (producing olefins) becomes more prominent, and if the amount or the strength of the basic sites becomes too high this may preferably lead to the formation of products like aldehydes. In contrast, if there is any deficiency in acid or basic sites, the reaction cannot proceed further towards the butanol or heavier alcohols, thus resulting in increased selectivity to some intermediates of the Guerbet cycle.



Scheme 1 Summary of the role of the acid and basic sites present in the different HAPs towards different pathways. The dashed box represents the intermediates, which were not observed in the reaction. [**Basic sites: PO_4^{3-}, OH^- & CaO, Brønsted acid sites: HPO_4^{2-}, Lewis acid sites: Ca^{2+} & OH^- vacancies (δ+)**]

All these observations are derived from / supported by the conclusions of the following study, which is divided into two main parts, namely, correlation studies between the *iso*propanol test[31] and the Guerbet reaction and the direct correlation study between the Guerbet reaction and the acid-base properties of the HAPs.

Correlation studies between the isopropanol test and the Guerbet reaction

A correlation study was performed between the selectivity to products observed when targeting the Guerbet reaction starting from ethanol (ethylene, diethylether, acetaldehyde, alcohols…) and the selectivity to *iso*propanol reaction products (both taken at iso-conversion; see Ref. 31) to get an indirect insight on the acid-base behavior of all the apatite catalysts. Indeed, the *iso*propanol test on apatite catalysts produced mainly propylene (together with small quantities of *di-iso*propylether) and acetone, which is an indirect representation of the acidic behavior and the basic character, respectively, of the probed solids.[31] In the following figures the catalysts are divided into three groups (corresponding to the groups given in Table 2): *(i)* HapD and Hap represented by circles, *(ii)* carbonated apatite catalysts, namely Hap-CO_3 and HapNa-CO_3, represented by squares, and *(iii)* carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3, represented by triangles (this representation is common with that of Ref. 31).

Since ethylene, diethylether (reaction products from ethanol) and propylene, *di-iso*propylether (reaction products from *iso*propanol) are supposed to be formed by inter- and intramolecular, dehydration reactions over acid sites, a correlation study was performed between these products. As *di-iso*propylether was hardly detected over group *ii* and group *iii* catalysts due to the GC analysis detection limit of *ca.* 0.5%, its quantity was then arbitrarily accounted as 0.25% ± 0.25% over these samples.

Figure 1(a) reveals a good correlation between ethylene and propylene selectivities. The selectivity to ethylene did not vary much for group *ii* & *iii* catalysts, with a value of 1.4 ± 0.2%, but increased for group *i* catalysts, namely Hap (2%) and HapD (3.1%). HapD and Hap exhibited higher selectivity to both ethylene and propylene, thus showing their predominant acidic nature compared to the other solids. A consistent correlation was obtained for the plot of *di*ethylether selectivity as a function of *di-iso*propylether selectivity [Figure 1(b)], with the presence of low amounts of both compounds over group *ii* & group *iii* catalysts, and of more significant amounts over group *i* catalysts. Then, the predominant acidic nature of group *i* catalysts was responsible for both inter- and intra-molecular dehydration of the respective substrates.

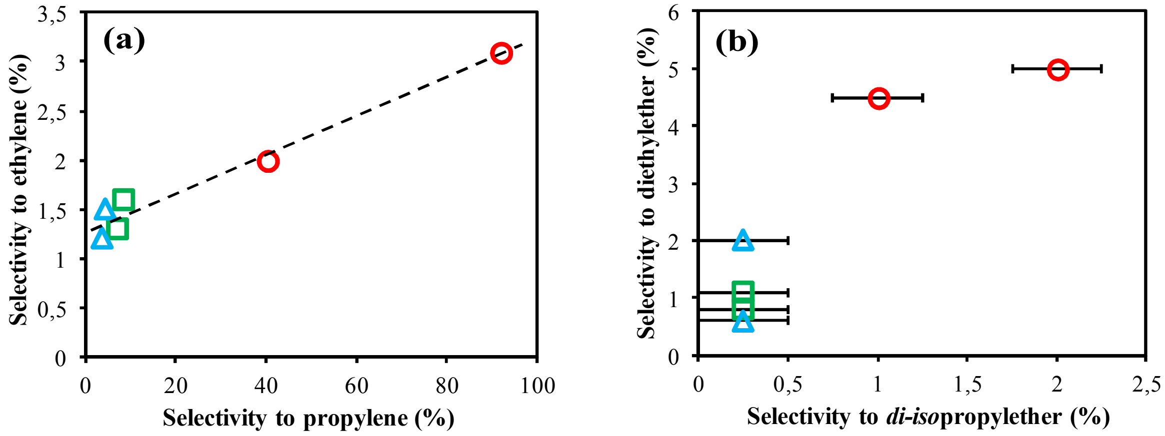


Figure 1 (a) Selectivity to ethylene as a function of the selectivity to propylene; (b) Selectivity to diethylether as a function of the selectivity to *di-iso*propylether (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Figure 2 shows the variation in the acetaldehyde selectivity (dehydrogenation product from ethanol in the Guerbet reaction) with the acetone selectivity (dehydrogenation product of *iso*propanol), both originating from a reaction over basic sites. A rather good correlation is obtained. Selectivity to acetaldehyde increased from 5.8% in HapD (group *i*) to 19% in HapE-Na-CO_3 (group *iii*) along with an increase in the acetone selectivity, respectively from 5% to 72.8%. Higher selectivity to both acetone and acetaldehyde over carbonate-rich apatites (group *iii*) underlined their predominant basic character compared to the other apatites. In addition, a linear increase (represented by the dashed line in Figure 2) was observed especially for the apatites that are highly selective to acetone and acetaldehyde.

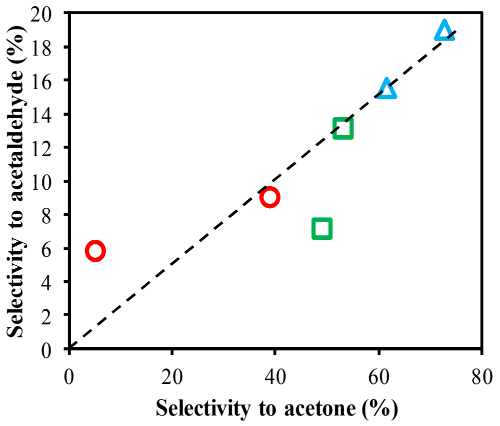


Figure 2 Selectivity to acetaldehyde as a function of the selectivity to acetone (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

However, a direct correlation considering acetaldehyde selectivity is difficult because, at least in the considered cascade mechanism, acetaldehyde is an intermediate in the Guerbet reaction of ethanol that can be further consumed by condensation reaction to heavier products through the whole sequence of Guerbet reaction steps. This is not the case for acetone formation, as this product is a 'dead-end' product in the reaction of *iso*propanol. So, there is a large chance to underestimate the basic nature of a catalyst in the ethanol conversion reaction by only looking at its acetaldehyde selectivity. This may be the reason why some catalysts (*e.g.*, Hap-CO_3, represented by the lower green square in Fig. 2) show deviation from the linearity to lower acetaldehyde selectivity, while supposedly behaving significant dehydrogenation properties.

As a conclusion to this part (including further relevant correlations presented in the ESI file, namely Figures S1, S2 & S3†), interesting correlations were obtained between the Guerbet ethanol reaction and the *iso*propanol test. The selectivities to propylene and *di-iso*propylether were both found to be correlated with the ethylene and the diethylether selectivities, respectively, and their formation confirms the higher acidic behavior of Hap and HapD (group *i*) compared to the other catalysts. The deviation observed for the highly efficient Guerbet catalyst Hap-CO_3 further confirmed the difficulty in the direct correlation of acetaldehyde selectivity, which is an intermediate in the Guerbet reaction. Selectivity to C6-C10 alcohols were larger over group *i* catalysts, which are more acidic in nature, thus revealing the fact that the presence of acid sites facilitates butanol and ethanol condensation. Almost all the observations clearly indicated that very fine tuning of the apatite catalysts is necessary to avoid the competitive side reactions like dehydration and to have a maximum selectivity to Guerbet alcohols.

Direct correlation studies of Guerbet reaction and acid-base properties of the apatites

After indirect correlation with the results of the *iso*propanol test, direct correlation of the Guerbet reactivity with the measured acid-base properties^{31} of the solids was studied.

Figure S4† shows the selectivity to target products (butanol or mix of higher alcohols) on plots reporting the acidity as a function of the basicity of the catalysts (in terms of amount or density). It highlights that Hap-CO_3 is not so far from being an ideal catalyst that possesses well-balanced acid-base properties, enabling a maximum selectivity to butanol or to total alcohols. We plotted a dashed line from the origin to the point representing Hap-CO_3. On this line, the relative density of base to acid sites is 0.2 (slope). Then, we can suppose that any apatite catalyst (or if we may generalize this assumption, that any solid) than lies on this line shows a good compromise between acid and basic sites and can give a maximum selectivity to butanol or to total alcohols. Hence the ideal HAP catalyst should have 5 times more acid sites than basic ones (furthermore, well distributed on the surface to enable the Guerbet reaction sequence, thus using antagonist sites that are supposedly close one to another). Catalysts that are in the region above this line possess too much basic sites. This is the reason why HapNa-CO_3 shows a lower selectivity to butanol or to total alcohols though it possesses a higher amount of basic sites compared to the so-called 'ideal' Hap-CO_3 catalyst. This is the same for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3, with basicity/acidity ratios (slopes) of 0.4 and 0.7, respectively, compared to the 'ideal' 0.2. Moreover, the catalysts that lie below the dashed line possess a too large proportion of acid sites compared to the ideal Hap-CO_3 catalyst. This is the reason why Hap and HapD with basicity/acidity ratios of 0.04 and 0.13, respectively, show lower butanol or total alcohols selectivities compared to Hap-CO_3, though they possess higher amount or density of acid sites than Hap-CO_3. After this first observation, in the followings, we systematically looked for potential direct correlations between the number/nature of sites with the selectivity to the main Guerbet products. This enabled revealing global trends, corroborating the above observations of Figure S4†.

Selectivity to ethylene and to diethylether as a function of acid-base properties of HAP catalysts

Selectivity to ethylene remained almost unchanged, though the number of acid sites increased from 141.3 µmol.g^{-1} (HapE-Na-CO_3) to 658 µmol.g^{-1} (Hap-CO_3), as shown by dashed line parallel to the *x*-axis in Figure 3. In contrast, further increase in the amount of acid sites to 763.3 µmol.g^{-1} (Hap) and 956 µmol.g^{-1} (HapD) yielded a linear increase of the ethylene selectivity to 2% and 3.1%, respectively. This, again, as shown using the comparison with the *iso*propanol reactivity test, clearly indicates the predominant acidic behavior of Hap, and especially of HapD, compared to the other samples.

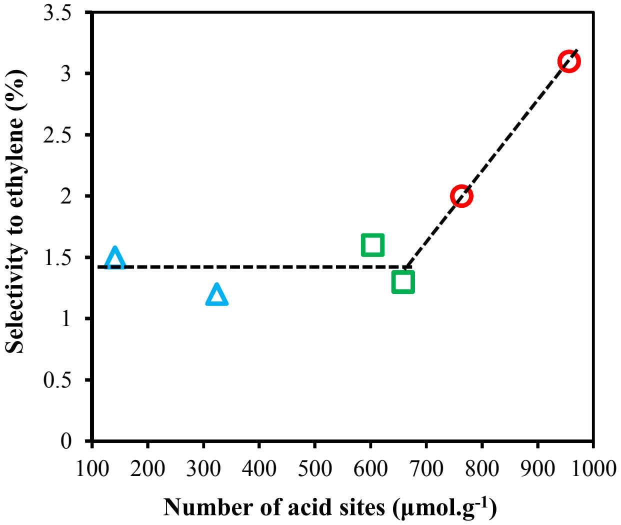


Figure 3 Selectivity of ethylene as a function of the number of basic sites (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

We then deepened the interpretation of the results by taking into account the nature of the acid sites (previously determined in Ref. 31 using PEA-XPS), and the results suggested that ethanol dehydration to ethylene most likely occurs on Brønsted acid sites (HPO_4^{2-}) in HAPs (see Figure S6 and associated comments in the ESI file†).

The same kind of conclusions was drawn for diethylether formation, which also seemed to strongly depend on the presence of Brønsted acid sites in HAPs (see Figure S7 & S8 and associated comments in the ESI file†).

Then, the ethanol inter- and intra-molecular dehydration of ethanol mainly proceeds over Brønsted acid sites (HPO_4^{2-}) in HAPs. To this respect, it is also worth mentioning that the Guerbet reaction releases water. Then, at least some Lewis sites observed during *ex situ* measurements might undergo hydration and be converted to Brønsted sites during the reaction, which can either be used for catalysis or be dehydrated to recover the initial Lewis sites under the reaction conditions. Equilibrium should be reached, but it is very difficult to predict the proportion between species at the steady state.

Selectivity to acetaldehyde as a function of acid-base properties of HAP catalysts

Figure 4 shows the variation in acetaldehyde selectivity with the number of acid and basic sites. It might appear difficult to draw a correlation between acetaldehyde selectivity and acid or basic properties. Indeed, while this reaction occurs on basic sites, as aforementioned acetaldehyde is an intermediate in the Guerbet reaction of ethanol, and should then be further consumed during the reaction over efficient catalysts. This explains why a linear relation could not be observed between acetaldehyde selectivity and the number of basic sites [Figure 4(a)]. In contrast, a very interesting linear correlation between acetaldehyde selectivity and number of acid sites was observed [Figure 4(b)]. The acetaldehyde selectivity was higher over carbonate-rich apatites HapE-Na-CO_3 (19%) and HapE-CO_3 (15.5%) with lower amounts of acid sites (141.3 µmol.g^{-1} and 324 µmol.g^{-1}, respectively) compared to the other solids. We suppose that the carbonate-rich apatites lack in sufficient strong basic sites (OH^- groups) [31], which assists in the condensation of acetaldehyde further to heavier Guerbet products (see Scheme 1). The acetaldehyde selectivity decreased to 13.1% (HapNa-CO_3) and 7.2% (Hap-CO_3) with increase in the number of acid sites to 604 µmol.g^{-1} and 658 µmol.g^{-1}, respectively. The lower acetaldehyde selectivity over Hap and HapD is not only due to the condensation of acetaldehyde, but also to an increased formation of ethylene and diethylether, in competition with the intermediate formation of acetaldehyde over basic sites, which are two reactions primary consuming ethanol. Hence, the amount of acid sites can indirectly influence the apparent acetaldehyde selectivity in two ways.

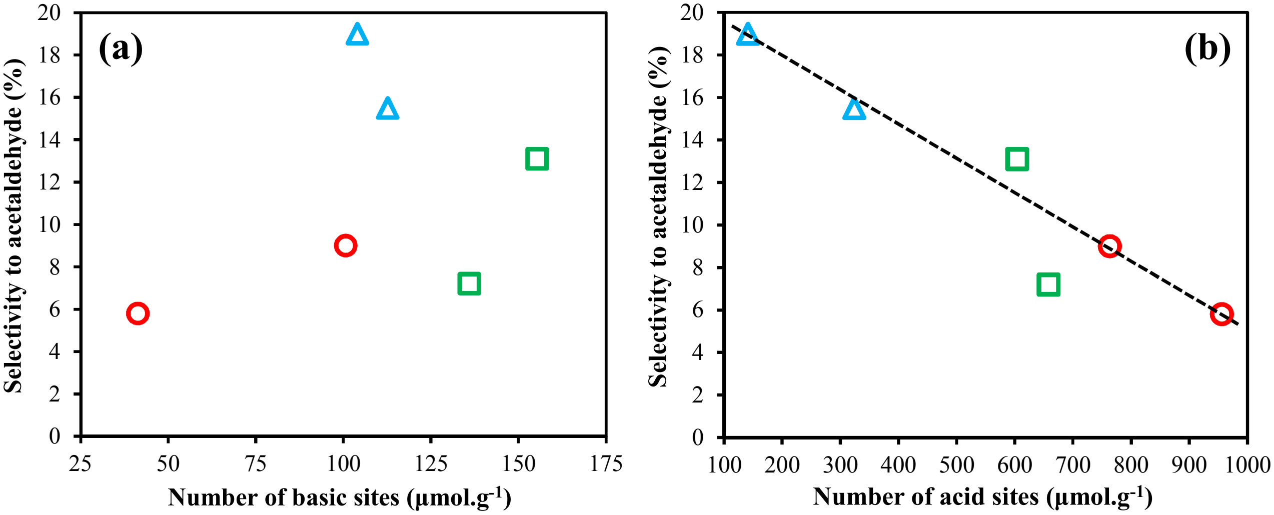


Figure 4 Selectivity of acetaldehyde as a function of (a) the number of acid sites and (b) the number of basic sites in HAPs (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Selectivity to 2-buten-1-ol as a function of acid-base properties of HAP catalysts

Since 2-buten-*1*-ol is an intermediate in the Guerbet reaction of ethanol to butanol, finding a direct correlation of its selectivity with the acid-base properties of the solids is rather difficult as in the case of acetaldehyde. However, to identify if potential indirect correlations can arise, a systematic correlation study was also performed for this compound (Figure S9 & S10 and related comments in ESI†). This study shows that the Lewis acid sites (Ca^{2+} & OH^- vacancies) in HAPs are responsible to the *2*-buten-*1*-ol transformation to butanol (in contrast with the Brønsted sites, which are responsible for dehydration reactions).

Selectivity to Guerbet alcohols as a function of acid-base properties of HAP catalysts

It is difficult to find a direct correlation between the Guerbet alcohols selectivities (butanol, saturated alcohols or total alcohols) and the number of acid sites. However, a rather linear increase (represented by the dashed line for total alcohols) in all the Guerbet alcohols selectivities was observed with an increase in the number of acid sites from 141.3 µmol.g^{-1} (HapE-Na-CO_3) to 658 µmol.g^{-1} (Hap-CO_3), as shown in Figure 5(a).

Hap and HapD again showed deviation from linearity due to their higher number of acid sites (763.3 µmol.g^{-1} and 956 µmol.g^{-1}, respectively). Selectivity to butanol, saturated alcohols or total alcohols remains unchanged even when the number of acid sites increased from 763.3 µmol.g^{-1} (Hap) to 956 µmol.g^{-1} (HapD), which shows that too much increase in the number of acid sites has not much influence on the Guerbet alcohols selectivity. The difference between the grey-filled symbols (saturated alcohols selectivity) and open symbols (butanol selectivity) is the C6-C10 alcohols, and this difference is higher over Hap and HapD compared to other catalysts. It is an indirect representation showing the ability of these apatites with predominant acidic behavior to further condense butanol & ethanol to C6-C10 alcohols. All these observations are in good agreement with Figure S1(a)† showing the relation between Guerbet alcohols selectivity with propylene selectivity. In contrast, a consistent correlation was not obtained between the butanol, saturated alcohols or total alcohols with the number of basic sites, as shown in Figure 5(b). However, a difference between the grey-filled symbols and the open symbols, which represents the formation of C6-C10 alcohols, is clearly observed, though no consistent trend could be revealed.

Since the production of Guerbet alcohols is subjected to the contribution from both acid and basic sites, the Guerbet alcohols (butanol, saturated alcohols or total alcohols) selectivity as a function of the ratio of the number of acid sites to basic sites was plotted [Figure 5(c)]. The trend was similar to that observed when plotting selectivity as a function of the number of acid sites as in Figure 5(a). The selectivity to all the Guerbet alcohols sharply increased from carbonate rich apatite HapE-Na-CO_3 to carbonated apatite Hap-CO_3 with an increase in the acidity to basicity ratio from 1.3 to 4.8. Further increase in the acidity to basicity ratio from 4.8 (Hap-CO_3) to 7.6 (Hap) led to a decrease in the Guerbet alcohols selectivity. The selectivity to butanol, saturated alcohols or total alcohols remains unchanged for an increase in the acidity to basicity ratio to a maximum of 23.1. The above observations are good in agreement with the variation in the Guerbet alcohols selectivity with the propylene/acetone ratio, which is an indirect representation of the acid/base ratio (Figure S2).

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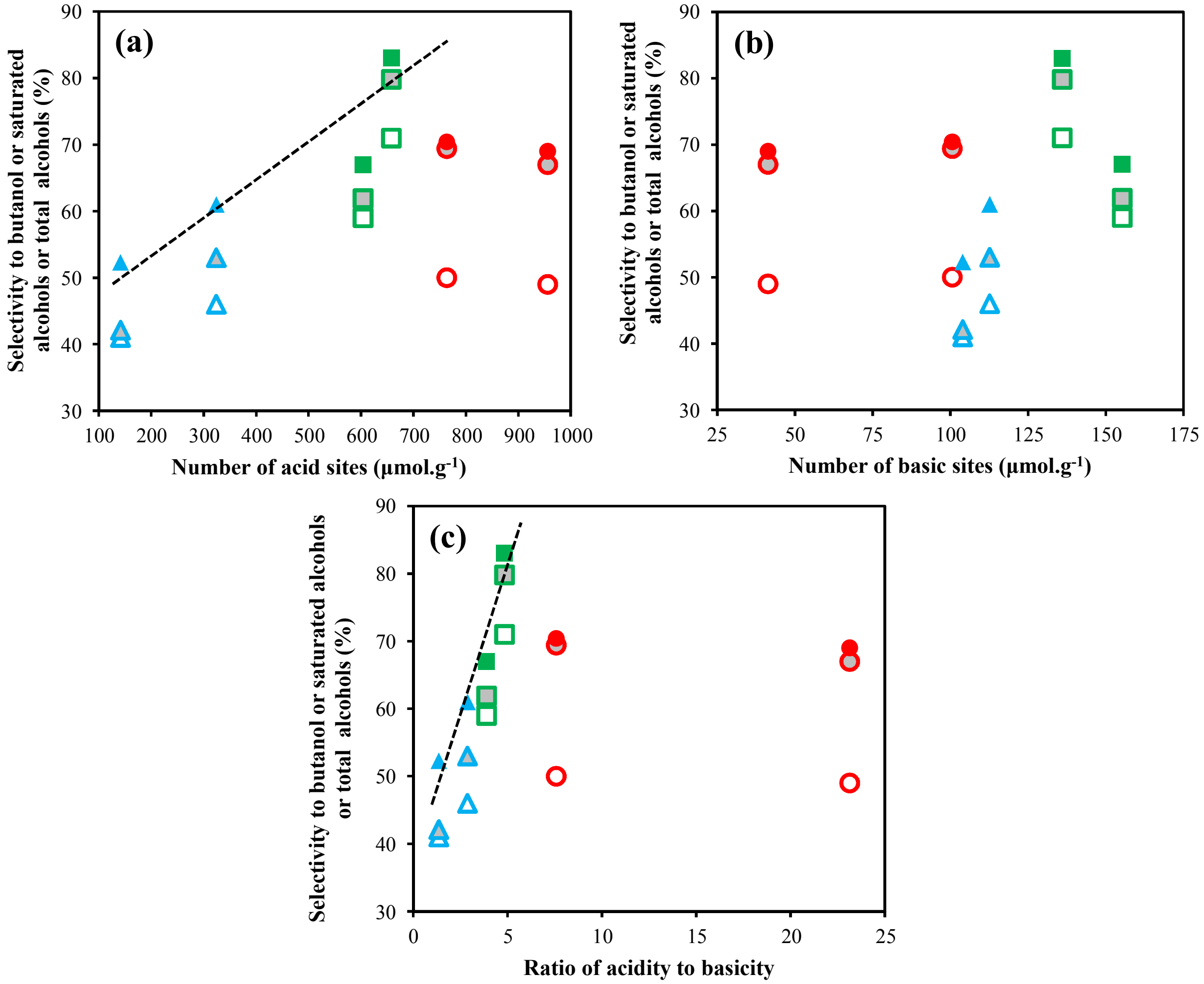

Figure 5 Selectivity to butanol or saturated alcohols or total alcohols as a function of the number of acid sites, (b) Selectivity to butanol or saturated alcohols or total alcohols as a function of the number of basic sites, (c) Selectivity to butanol or saturated alcohols or total alcohols as a function of the ratio of the number of acid sites to the number of basic sites. Selectivity to butanol is represented by open symbols, while selectivity to saturated alcohols (excluding *2*-buten-*1*-ol) is represented by grey-filled symbols and heavier alcohols is represented by color-filled symbols (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Guerbet reaction: Optimization of experimental conditions

In the literature, we can find studies related to the Guerbet reaction of ethanol over hydroxyapatites, but only few studies were reported focusing on maximizing the selectivity to butanol at higher ethanol conversions.[27] Though the authors in Ref. 27 reported similar selectivity to higher alcohols at 50% ethanol conversion, it is difficult to compare with our study since we used different GHSVs and temperatures. The aim of the optimization in the present work was to push the ethanol conversion so as to increase the yield in heavier alcohols, instead of aiming at only synthesizing butanol. This helped us to draw general behavior lines concerning the Guerbet reactivity and the acid-base properties of the solids. In this part, the ethanol reaction was performed at different temperatures and GHSVs in order to approach optimal conditions for the production of heavier alcohols.

As a general summary of the observed results (Figure 6 and Tables 3 & 4), before commenting specific points in the followings, it appears that the reaction products consisted of alkenes, dienes, aldehydes, alcohols, diethylether, ethylbutyrate and aromatics, the major products being ethylene, acetaldehyde, and C4-C10 alcohols including significant amounts of butanol. Condensation products with only even number of carbon atoms like C4, C6, C8, *etc*…, were observed, indicating that the products formed during the reaction were not subjected to any mechanism involving C-C bond cleavage. Only trace amount of light gaseous products such as CO_2 were observed, confirming that the ethanol or the reaction products were not further decomposed over hydroxyapatite catalysts, which is in agreement with previous reports.[26]

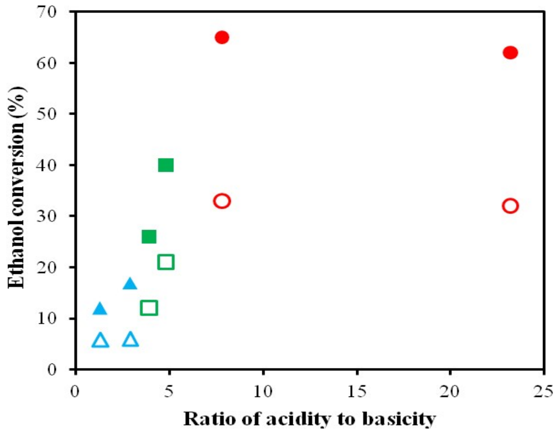

Figure 6 Ethanol conversion as a function of the ratio of acidity to basicity at 400°C; GHSV = 5000 mL.h^{-1}g^{-1} (full symbols); GHSV =15000 mL.h^{-1}g^{-1} (open symbols) (circles representing HapD and Hap, squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Table 3 Conversion and products distribution over hydroxyapatite catalysts at GHSV = 15000 mL.h^{-1}g^{-1}.

	HapD	Hap	Hap-CO_3	HapNa-CO_3	HapE-CO_3	HapE-Na-CO_3
Conversion at						
300°C	4.20	4.50	4.0	3.0	1.0	0.50
350°C	10.40	11.0	8.60	6.70	3.30	2.20
400°C	32	33	21	12	6	5.80
Yield at 400°C						
Alkenes						
ethylene	12.8	5.6	0.44	0.19	0.09	0.06
butene	0.80	1.10	-	-	-	-
hexene	0.10	0.30	0.04	-	-	-
Aldehydes						
acetaldehyde	2.50	2.10	1.20	1.60	1.30	1.40
butanal	0.10	0.26	0.15	0.14	0.13	-
Dienes						
butadiene	3.30	2.70	0.50	0.30	0.10	-
C6-dienes	0.48	1.20	0.11	-	-	-
Alcohols						
butanol	7.80	14.90	12.60	7.0	3.60	3.0
C6-C10 alcohols	0.70	2.50	2.20	1.0	0.2	-
Ethylbutyrate	-	-	0.08	0.18	0.39	0.81
Aromatics	-	-	0.19	0.14	0.12	0.09

The ethanol conversion observed at 400°C and at the two different GHSVs we used (namely, 5000 mL.h^{-1}g^{-1} and 15000 mL.h^{-1}g^{-1}, obtained using 0.2 g and 0.6 g of catalyst, respectively) are shown in Figure 6. The ethanol conversion increased with decreasing GHSV from 15000 mL.h^{-1}g^{-1} to 5000 mL.h^{-1}g^{-1}.

As a general matter, the ethanol conversion increased with the increase in the ratio of the number of acid sites to basic sites from 1.3 (HapE-Na-CO_3) to 7.8 (Hap), and then remained unchanged with further increase to 23.2 (HapD). This is consistent with the results observed at iso-conversion, revealing that a too large increase in the amount of acid sites in the HAP catalysts had no positive effect on the ethanol conversion. We would like to point out that the ethanol conversion can be modulated by the SSA of the HAPs. However, it is clear that the carbonated HAPs (Hap-CO_3 and HapNa-CO_3) and stoichiometric (Hap) having close surface areas showed entirely different conversions (Tables 1, 3 & 4), underlining a preponderant acid-base sites chemical effect.

The yields to minor products such as diethyl ether, ethyl butyrate and aromatics increased with a decrease in GHSV, indicating that dehydration and some dehydrogenation / polymerization reactions were promoted at lower GHSV. Selectivity to acetaldehyde decreased with a decrease in GHSV, suggesting that the aldol condensation of acetaldehyde to heavier products became more prominent due to the increase in the resulting acetaldehyde contact time (Tables 3 & 4). C4-C10 alcohols selectivity increased with decreasing the GHSV for all the catalysts except for HapD and Hap, over which dehydration products like ethylene, diethylether and dienes, resulting from competing side reactions on acid sites, were detected. Since our aim here was to maximize ethanol conversion while yielding a maximal amount of total alcohols, further studies were performed at GHSV = 5000 mL.h^{-1}g^{-1}.

Table 4 Conversion and products distribution over hydroxyapatite catalysts at GHSV = 5000 mL.h^{-1}g^{-1}.

	HapD	**Hap**	**Hap-CO$_3$**	**HapNa-CO$_3$**	**HapE-CO$_3$**	**HapE-Na-CO$_3$**
Conversion at						
300ºC	14.2	13	5.8	5.4	4.8	4.5
350 ºC	27	32.2	15.2	9.5	9	6.8
400 ºC	62.1	65.1	40	26	17	12
Yield at 300 ºC						
Alkenes						
ethylene	0.4	0.1	0.1	0.02	0.1	0.2
Aldehydes						
acetaldehyde	0.8	1.8	0.3	0.5	1.0	1.8
butanal	-	-	-	-	0.01	-
Dienes						
butadiene	0.2	0.2	0.04	0.02	-	-
C6-dienes	0.3	-	-	-	-	-
Alcohols						
butanol	7.1	6.5	4.2	3.7	2.2	1.1
C6-C10 alcohols	3.2	2.6	0.5	0.4	0.4	-
2-buten-1-ol	0.1	0.1	0.2	0.4	0.4	0.5
Diethylether	0.7	0.6	0.04	0.03	-	-
Ethylbutyrate	-	-	-	-	0.1	0.5
Yield at 350 ºC						
Alkenes						
ethylene	2.6	1.4	0.2	0.1	0.1	0.2
butene	0.3	0.5	-	-	-	-
hexene	0.1	0.2	-	-	-	-
Aldehydes						
acetaldehyde	0.8	2.6	0.7	1.1	1.5	2.0
butanal	-	0.3	0.1	-	0.1	-
Dienes						
butadiene	1.4	1.2	0.3	0.1	0.05	0.03
C6-dienes	0.7	0.6	0.1	-	-	-
Alcohols						
butanol	15.1	18.2	10.6	6.2	4.4	2.9
C6-C10 alcohols	3.5	5.4	1.4	0.3	0.7	0.1
2-buten-1-ol	0.2	0.1	0.5	0.5	0.7	0.5
Diethylether	1.6	1.2	0.2	0.1	0.1	0.3
Ethylbutyrate	-	-	-	0.1	0.3	0.7
Aromatics	-	-	0.1	0.3	0.3	0.04
Yield at 400 ºC						
Alkenes						
ethylene	36.7	11.4	0.6	0.4	0.2	0.3
butene	3.0	2.8	0.1	-	-	-
hexene	0.3	2.7	0.04	-	-	-
Aldehydes						
acetaldehyde	1.9	3.1	1.4	1.6	2.6	2.3
butanal	-	0.8	0.5	0.2	0.4	0.2
Dienes						
butadiene	2.4	3.3	1.1	0.7	0.2	0.1
C6-dienes	0.7	5.3	0.3	0.1	0.1	-
Alcohols						
butanol	6.4	21.5	22.4	15.2	7.7	4.9
C6-C10 alcohols	0.2	3.1	6.8	2.6	1.4	0.3
2-buten-1-ol	0.1	0.2	0.8	1.2	1.2	1.1
Diethylether	5.0	2.0	0.2	0.2	0.1	0.2
Ethylbutyrate	-	-	0.1	0.3	0.6	1.2
Aromatics	-	-	0.9	1.0	1.1	0.8

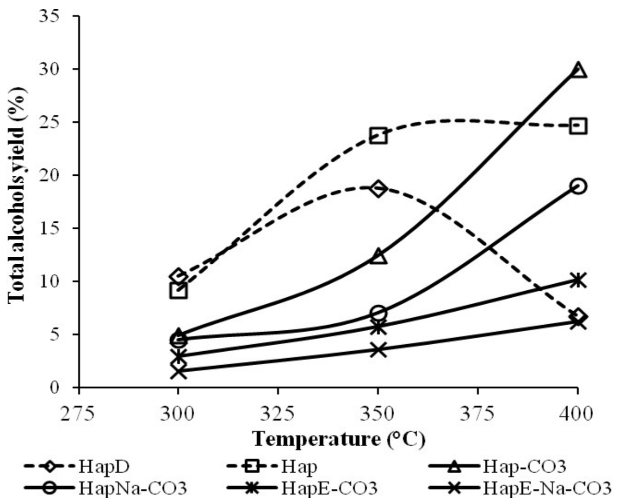

Figure 7 Influence of temperature towards heavier alcohols yield (GHSV = 5000 mL.h^{-1}g^{-1}).

Except for Hap and HapD (represented by the dashed lines), C4-C10 total alcohols yield increased while increasing the temperature up to 400°C (Figure 7). Above this temperature, the yield towards aromatics and olefins severely increased, which subsequently decreased the alcohols yield (data not shown). In Hap, the total alcohols yield remained constant at 350°C and 400°C, whereas in HapD an optimum temperature for the production of heavier alcohols was observed at 350°C. The volcano curve obtained for HapD and the plateau for Hap clearly reflect the highly acidic behavior of HapD compared with Hap. HapD and Hap have shown almost similar selectivity to Guerbet alcohols and the difference in their behaviors was not much evident during iso-conversion studies, where ethanol conversion of HapD and Hap were maintained at 14% at lower temperature (~300°C). It is clearly observed from the dashed lines in Figure 7 that the deviation between the HapD and Hap concerning the total alcohols yield tended to increase with increase in temperature. This observation clearly underlines the enhancement in acidic behavior of HapD, which possess higher number of acid sites, especially Brønsted acid sites, thus leading to higher ethylene yield compared to that in Hap (Table 4).

Further, as aforementioned, the behavior of HapD and Hap (represented by dashed lines) was different from that of the other catalysts. This discrepancy could also be related to the increase in ethylene (and diethylether) yield for Hap and HapD, which is not observed for the other hydroxyapatites (Table 4). This increase is much more pronounced for the HapD catalyst in comparison with Hap. In HapD, the ethylene yield increased from 2.6% to 36.7% and for Hap from 1.4% to 11.4% when the temperature increased from 350°C to 400°C, respectively. This is good in agreement with previous results at iso-conversion, where HapD and Hap showed deviations from other catalyst due to their high acidic behavior. As aforementioned, dehydration of ethanol to ethylene (and to diethylether) is the main competing reaction, which is responsible for the decrease in heavier alcohol yields. The temperature of 400°C was found to be the most favorable temperature for the production of Guerbet alcohols over all the catalysts except for HapD and the following study was focused on this temperature.

Figure 8 shows the variation in the ethanol conversion and in the yield in the major products as a function of the ratio of the number of acid sites to the number of basic sites of the hydroxyapatites, at 400°C and a GHSV of 5000 mL.h^{-1}g^{-1}. As aforementioned, the ethanol conversion increased with increasing the acidity/basicity ratio up to a certain limit and then remained unchanged with further increase in this ratio. The yield to total alcohols increased rather linearly from 6.3% to 30% with increasing the acidity/basicity ratio from 1.3 (HapE-Na-CO$_3$) to 4.8 (Hap-CO$_3$), respectively, and then decreased with further increase in the acidity/basicity ratio. Hence, the Hap and HapD with higher acidity/basicity ratios of 7.8 and 23.2 showed total alcohols yields of 24.8% and 6.7%, respectively. The Hap-CO$_3$ with an acidity/basicity ratio of 4.8 exhibited superior performances in terms of maximum total alcohol yield, which is in good agreement with the results of the iso-conversion study.

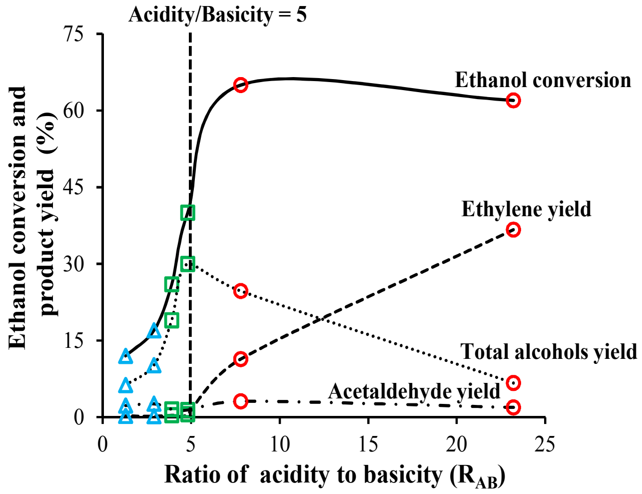

Figure 8 Ethanol conversion and major product yields at 400°C and GHSV = 5000 mL.h^{-1}g^{-1} as a function of the ratio of number of acid sites to the number of basic sites (red color symbols representing HapD and Hap, green color for carbonated apatites, namely Hap-CO$_3$ and HapNa-CO$_3$, and blue color for carbonate-rich apatites, namely HapE-CO$_3$ and HapE-Na-CO$_3$).

The catalysts Hap and HapD obviously deviate from linearity due to their high acidity/basicity ratio (highly acidic behavior), which is represented by the higher ethylene yields of 11.4% and 36.7%, respectively. The ethylene yield was almost similar for all the other catalysts with acidity/basicity ratios ≤ 5. All the above observations are in good agreement with the iso-conversion studies, where Hap-CO$_3$ behaved as an ideal catalyst and Hap and HapD as highly acidic catalysts. It is worth mentioning that the yield to total alcohols over HapD drastically decreased compared to iso-conversion studies, which is explained by the dehydration of ethanol to ethylene over acid sites, which became more pronounced at higher temperature of 400°C. Since ethylene is a product directly formed from the ethanol in the presence of acidic catalysts (primary reaction product), we suppose that it can be formed much easier at higher temperatures, when pushing catalytic reactivity, compared to higher alcohols, which are formed by a multiple steps reaction from ethanol. The yield to acetaldehyde remained almost unchanged with the increase in the acidity/basicity ratio. However, the selectivity to acetaldehyde remained higher over carbonate-rich apatites HapE-CO_3 (15.5%) and HapE-Na-CO_3 (19%) compared to other catalysts, as observed in iso-conversion studies, showing the lack in a sufficient amount of acid sites to condense acetaldehyde further to aldol.

Further, the observed yield in acetaldehyde was low on the left side of the 'ideal' dashed line in Figure 8, because it was consumed through the Guerbet reaction after formation. While its yield is low on the right side of this same line, in part due to Guerbet reaction also, but mainly due to preferential consumption of ethanol by dehydration to give ethylene (and diethylether).

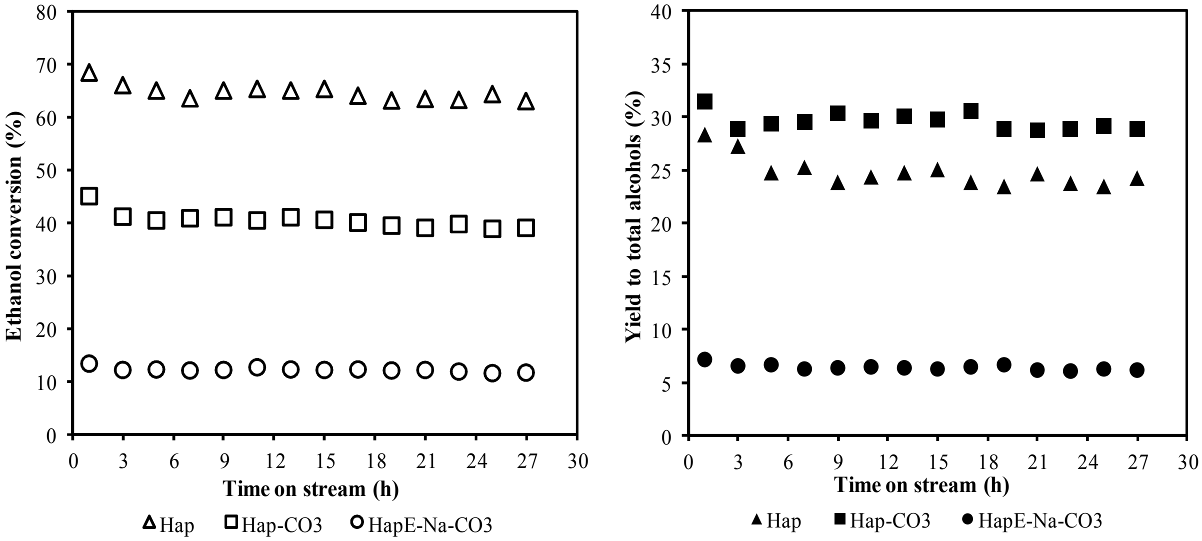

Figure 9 Ethanol conversion and total alcohols yield over stoichiometric (Hap), carbonated (Hap-CO_3) and carbonate rich (HapE-Na-CO_3) hydroxyapatites at 400°C and GHSV = 5000 $mL.h^{-1}g^{-1}$ as a function of time on stream.

In order to get and insight on the effect of carbonate substitution on the catalytic performances stability, ethanol conversion was recorded for more than 24 h over three selected (stoichiometric, carbonate and carbonate-rich) catalysts (Figure 9). We found that all the catalysts were quite stable, without deactivation, which suggests the potential industrial relevance of such systems.

Conclusion

As a conclusion, the ethanol conversion was higher over HapD and Hap due to their acidic behaviors compared to the other catalysts. It was found that the acidic behavior of HapD becomes predominant at higher temperatures and resulted in higher ethylene yield. The ethanol conversion and total alcohols yield were found to be optimum over Hap-CO_3 catalyst with acidity/basicity ratio of nearly 5, which is in good agreement with iso-conversion studies. For the catalysts that possess acidity/basicity ratio < 5, ethanol conversion was lower, which resulted in lower yield to total alcohols. In contrast, catalysts with acidity/basicity ratio > 5 (Hap & HapD) have shown higher ethanol conversion, but were found to be less selective to total alcohols because of increase in ethylene selectivity, thereby decreasing the total alcohols selectivity. Hence, it confirms that a fine-tuning of acid-base sites (both nature and amount) in HAP is necessary to have higher ethanol conversion without losing the Guerbet alcohols selectivity.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Supplementary correlations drawn between *iso*-propanol and ethanol reactivity; Supplementary correlations drawn between directly measured acid-base properties and ethanol reactivity; See DOI: 10.1039/b000000x/

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