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

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Supplementary information

1. Supplementary correlations drawn between *iso*-propanol and ethanol reactivity

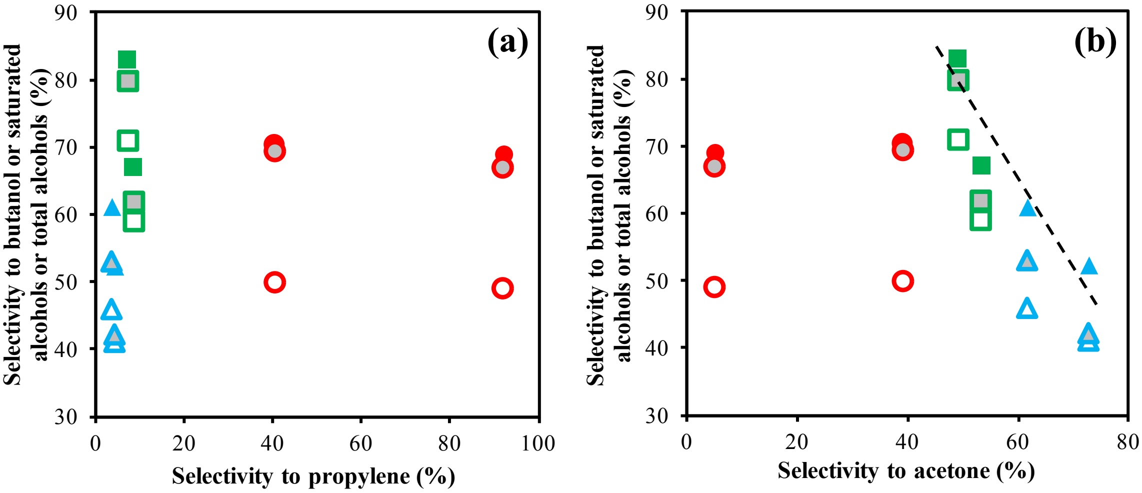

Figure S1(a) Selectivity to butanol or saturated alcohols or total alcohols as a function of the selectivity to propylene, (b) Selectivity to butanol or saturated alcohols or total alcohols as a function of the selectivity to acetone. Selectivity to butanol is represented by open symbols, while selectivity to saturated alcohols (excluding *2*-buten-*1*-ol) is represented by grey-filled symbols and selectivity to total alcohols (thus including *2*-buten-*1*-ol) 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).

No straightforward linear correlation was observed between propylene selectivity (acid character) and any class of Guerbet alcohols (butanol or saturated alcohol or total alcohol) selectivity, as shown in Figure S1(a). However, a sharp increase in the Guerbet alcohols selectivity from carbonate-rich apatites to carbonated apatites was observed for a small increase in propylene selectivity. The behavior of Hap and HapD is deviating from that of the other catalysts due to their higher propylene selectivity, and, hence, to an especially predominant acidic behavior compared to the other catalysts (see also Figure 1). The selectivity to Guerbet alcohols (butanol or saturated alcohols or total alcohols) remained almost similar in HapD and Hap, while the selectivity to propylene over these samples gave a *ca.* 2-fold increase with values of 40.3% and 92%, respectively. This reveals that a too large increase in the acidic character of the solids has definitely no significant effect in the selectivity to Guerbet alcohols. However, it is worth mentioning that the difference between saturated alcohols selectivity (grey filled symbols) and butanol selectivity (open symbols) is higher in HapD and Hap compared to the other catalysts, which shows the ability of these apatites, with predominant acidic behavior, to further condense butanol & ethanol to C6-C10 alcohols. Moreover, the difference between total alcohols selectivity (filled symbols) and saturated alcohols selectivity (grey filled symbols), which is due to the selectivity of *2*-buten-*1*-ol, was more pronounced in carbonate-rich apatites.

A relationship between the selectivities to all the types of Guerbet alcohols (butanol or saturated alcohols or total alcohols) and the selectivity to acetone (dehydrogenation character) is further shown in Figure S1(b). In any case, the Guerbet alcohols selectivity was at least 40%, even for the samples with rather low acetone selectivity (*e.g.*, even for HapD that exhibited an acetone selectivity of 5.8%, and thus a dehydrogenation property which is not predominant). Further, the selectivity to butanol, to saturated alcohols and to total alcohols remained similar in HapD and Hap (group *i*), though acetone selectivity increased from 5% (HapD) to 39% (Hap), thus suggesting that only a ‘slight’ dehydrogenation property might be needed to initiate and smoothly run Guerbet cycles. This dehydrogenation property is supposedly due to the weak or/and medium basic sites since HapD lacks stronger basic sites.[1] All the types of Guerbet alcohols selectivities then reached a maximum when a slight increase in acetone selectivity to 49% in Hap-CO_3 was observed, but this increase is most likely linked with a difference of acid properties. A linear decrease in the total alcohols selectivity (represented by a dashed line) was observed with further increase in acetone selectivity for group *ii* and group *iii* catalysts. A similar trend was also observed for butanol and saturated alcohols selectivities. Since high acetone selectivity represents a highly basic behavior of the catalysts, the above observation of a linear decrease in alcohol selectivity strongly suggests that too much basic behavior had a detrimental effect on the alcohols selectivity. A large difference between the saturated alcohols selectivity (grey filled symbols) and butanol selectivity (open symbols) in HapD and Hap catalysts compared to the other catalysts is clearly observed in Figure S1(b) like in Figure S1(a). The deviation in butanol or saturated or total alcohols and the acetone selectivities away from the line of linear correlation was again confirmed in the case of HapD and Hap.

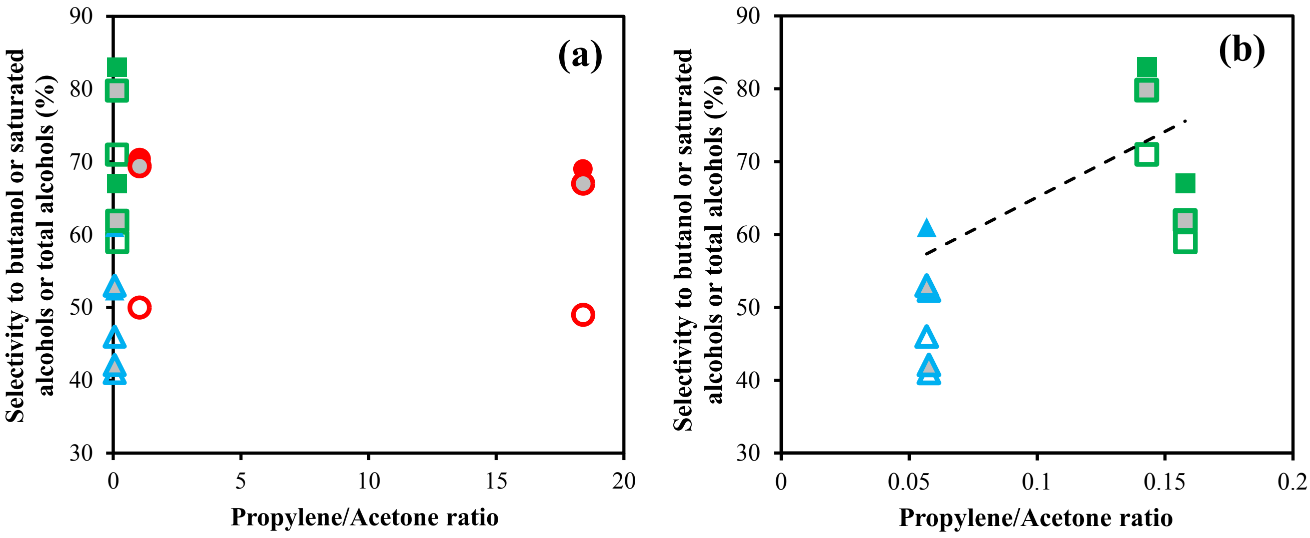

Figure S2 (a) Selectivity to butanol or saturated alcohols or to total alcohols as a function of the propylene/acetone ratio (b) Same figure focused on a narrower range of propylene/acetone ratio (from 0 to 0.2). Selectivity to butanol is represented by open symbols, while selectivity to saturated alcohols (excluding *2*-buten-*1*-ol) is represented by grey-filled symbols and total 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).

Figure S2(a) shows an increase in the butanol, saturated and total alcohols selectivities from carbonate-rich apatites to carbonated apatites, when an increase in the propylene/acetone ratio is observed, from, respectively, 0.05 to 0.15. The selectivity to all the types of Guerbet alcohols (butanol, saturated and total alcohols) then decreased with further increase in the propylene/acetone ratio from 0.15 in carbonated apatites to 1.0 in Hap. Furthermore increasing the propylene/acetone ratio from 1.0 to 18.4 did no yield any effect in butanol or saturated or heavier alcohols selectivities. Figure S2(b) clearly shows that there is a particular narrow range for the propylene/acetone ratio that represents the acid-base behavior in apatites to obtain maximum selectivity to all Guerbet alcohols. The large difference between the saturated alcohols selectivity (grey filled symbols) and butanol selectivity (open symbols) once again underlined that condensation of butanol and ethanol to C6-C10 alcohols is more pronounced over Hap and HapD, over which the acid character is much more predominant than the basic one. Hence this observation really points out the fact that very fine-tuning between the quantities of both antagonist sites is required to promote the Guerbet reaction.

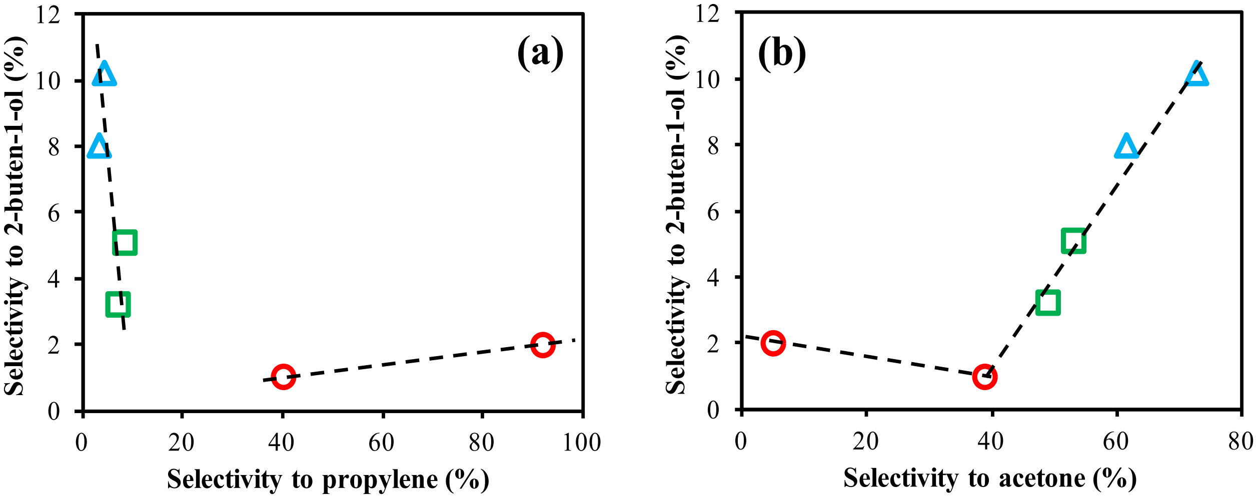

Figure S3 Selectivity to *2*-buten-*1*-ol as a function of (a) the selectivity to propylene and (b) the selectivity to acetone (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Since *2*-buten-*1*-ol is an intermediate in the Guerbet reaction of ethanol to butanol, a direct correlation with catalysts acid-base behavior becomes difficult, as in the case of acetaldehyde. However, to verify the presence of any indirect correlation, the variation in the *2*-buten-*1*-ol selectivity as a function of the propylene and the acetone selectivities was studied, as shown in Figure S3. A linear decrease (represented by a dashed line) in the selectivity to *2*-buten-*1*-ol from 10.2% to 3.2% was observed when the propylene selectivity increased from carbonate rich apatite (4.2%) to carbonated apatite (7%) [Figure S3(a)]. Selectivity to *2*-buten-*1*-ol reached a minimum of 1% with further increase in propylene selectivity to 40.3% in Hap. Further increase in propylene selectivity to 92% did not yield any significant variation of the *2*-buten-*1*-ol selectivity. Since propylene formation is related to the acidic behavior, the above observation reveals that *2*-buten-*1*-ol selectivity was decreased even with a slight increase in the acidic behavior for catalysts that are less acidic in nature (*i.e.*, with a higher relative proportion of basic sites). Further increasing too much the acidic behavior had no effect on *2*-buten-*1*-ol selectivity. Figure S3(a) clearly shows a deviation of two acidic catalysts from the linear behavior of all other catalysts, which is good in agreement with previous observations. Figure S3(b) shows that an increase in acetone selectivity from 5% to 39% could not yield much variation in the *2*-buten-*1*-ol selectivity. However, a linear increase (represented by the dashed line) in *2*-buten-*1*-ol selectivity from 3.2% to 10.2% was clearly observed with further increase in acetone selectivity from 39 % to 72.8%. Hence, the *2*-buten-*1*-ol selectivity over apatite catalysts remains unchanged with increase in the basic behavior up to a certain limit and then starts increasing linearly with the basic character.

2. Supplementary correlations drawn between directly measured acid-base properties and ethanol reactivity

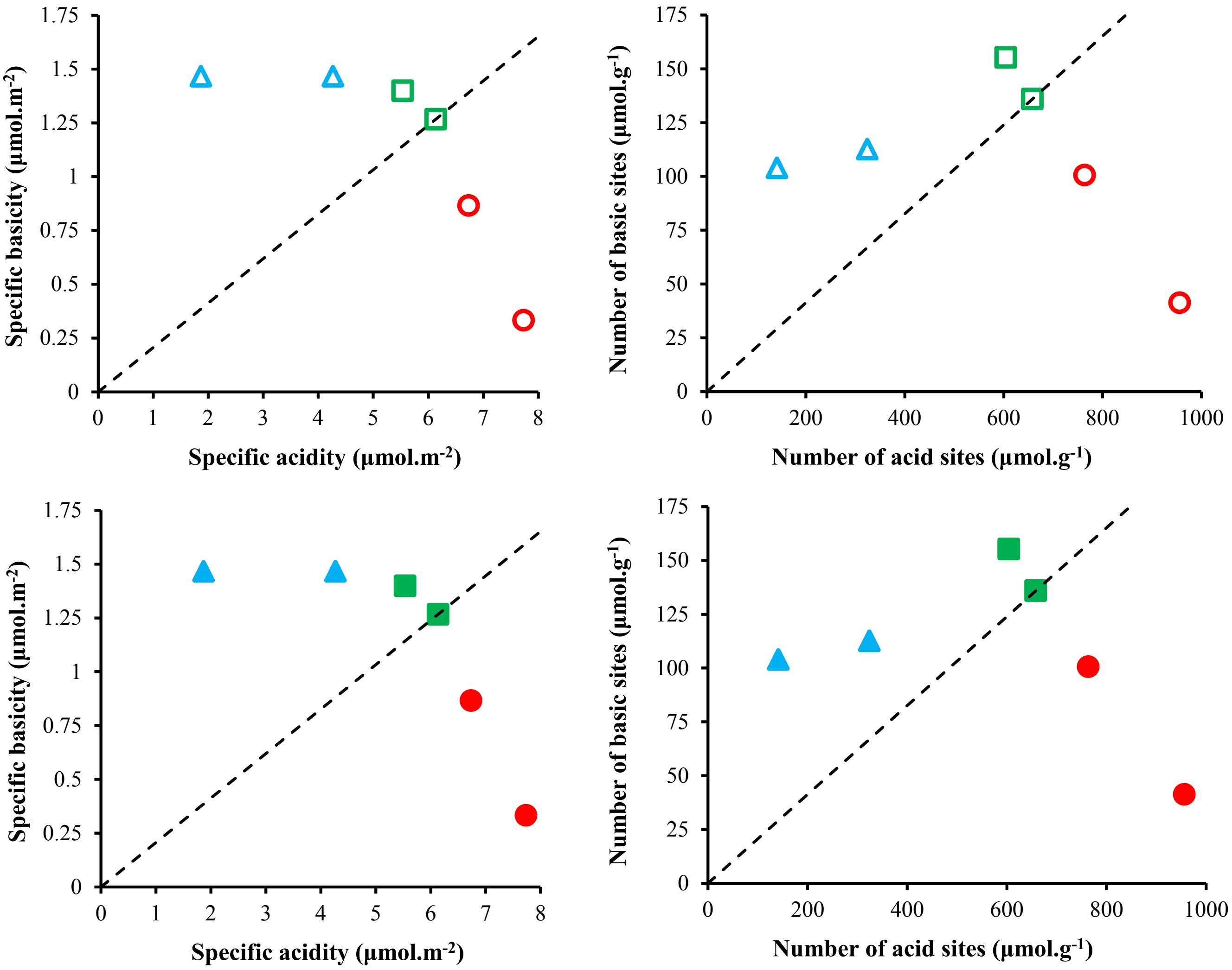

Figure S4 Basicity of apatite catalysts as a function of acidity of the catalysts (both expressed per gram and per m² – specific acidity). (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3). Selectivity to butanol is given in brackets next to open symbols while the value of selectivity to total alcohols is given in brackets next to filled symbols.

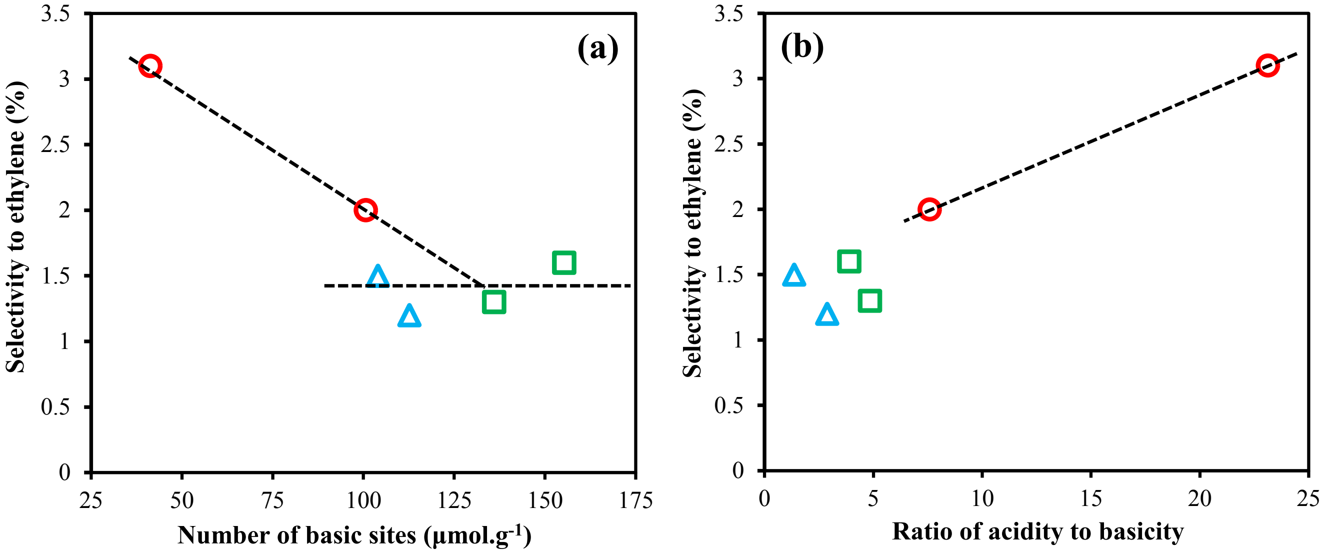

Figure S5 Selectivity of ethylene as a function of (a) the number of basic sites, and (b) the ratio of acidity to basicity in HAPs (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

It is well known that ethylene is formed by ethanol dehydration over acid sites. Thus, while it is obvious that a direct relation between ethylene selectivity and the number basic sites should not exist, a graph was plotted to present the selectivity to ethylene as a function of the number of basic sites [Figure S3 (a)], in order to check about potential indirect correlations. A linear decrease in ethylene selectivity from 3.1% to 2% was observed with an increase in the number of basic sites from 41.3 µmol.g^{-1} in HapD to 100.7 µmol.g^{-1} in Hap. Further increase in the number of basic sites yielded a slight decrease in the ethylene selectivity, which then remained essentially unchanged above all the other apatites, with a value close to 1.5 µmol.g^{-1}. We obviously suppose the initial linear decrease in ethylene selectivity is not related to the increase in the amount of basic sites, but with the higher amount of acid sites above the concerned samples, as explained above. However, this again clearly shows that the behavior of HapD and Hap deviates from that of the other catalysts, underlining the predominant influence of their acidic nature on their chemical properties (reactivity) compared to the other apatites.

Since both acid and basic sites have important roles in Guerbet chemistry, the variation in ethylene selectivity as a function of the ratio of acidity to basicity was studied [Figure S3 (b)]. The ethylene selectivity remained almost unchanged with the increase in the ratio of acidity to basicity from 1.3 (HapE-Na-CO_3) to 4.8 (Hap-CO_3). Further increase in this ratio to 7.6 (Hap) and 20.1 (HapD) yielded a linear increase in ethylene selectivity to 2% and 3.1%, respectively. Hence, the trend observed in the variation in ethylene selectivity with acidity to basicity ratio was found to be similar with the variation in ethylene selectivity with number of acid sites alone (Figure 3), which reflects the predominance of acid sites over basic sites in the apatite catalysts (they possess more acid sites than basic sites).

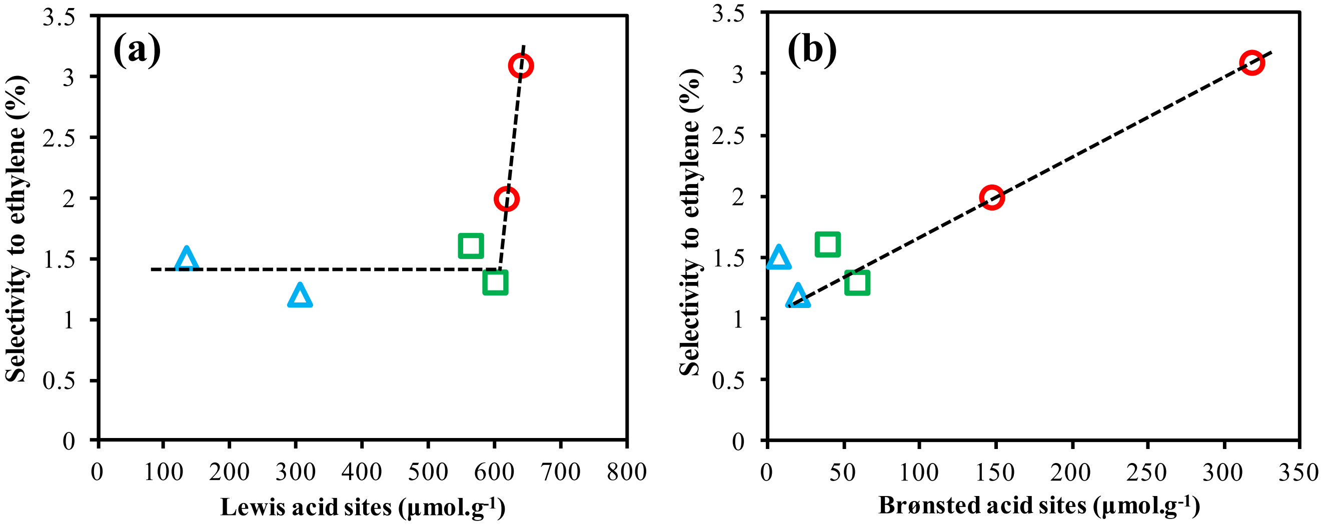

Figure S6 Selectivity of ethylene as a function of (a) the number of Lewis acid sites, and (b) the number of Brønsted sites (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

The selectivity to ethylene as a function of the number of the Lewis and of the Brønsted acid sites is shown in Figure S5. Figure S5(a) shows that ethylene selectivity remained almost unchanged though the amount of Lewis acid sites increased from 134.7 µmol.g^{-1} (HapE-Na-CO_3) to 599.4 µmol.g^{-1} (Hap-CO_3). Further slight increase in the number of Lewis acid sites to 616 µmol.g^{-1} (Hap) and 637.7 µmol.g^{-1} (HapD) was observed related to a sudden increase in the ethanol selectivity to 2% and 3.1%, respectively. Increase in the number of Brønsted acid sites from 6.6 µmol.g^{-1} (HapE-Na-CO_3) to 58.6 µmol.g^{-1} (Hap-CO_3) did not yield any significant variation in the ethylene selectivity. In contrast to a sudden increase in ethylene selectivity with Lewis acid sites, a linear increase in ethylene selectivity to 2% (Hap) and 3.1% (HapD) was observed with further increase in the number of Brønsted acid sites, respectively to 147.3 µmol.g^{-1} and 318.3 µmol.g^{-1}. Since the number of both Lewis and Brønsted acid sites contribute to total number of acid sites, variation in these sites should be equally reflected in total acid sites. Hence, a comparison in ethylene selectivity for both Lewis and Brønsted acid sites (Figure S5) together with total acid sites (Figure 3) can provide the information regarding the nature of sites that contributes mainly towards the ethylene selectivity. Figure S3 shows that ethylene selectivity linearly increased from 2% in Hap to 3.1% in HapD with increase in total number of acid sites from 763.3 µmol.g^{-1} to 956 µmol.g^{-1} (an increase of 192.7 µmol.g^{-1}). For the same increase in ethylene selectivity from 2 % to 3.1 %, the number of Lewis sites increased from 616 µmol.g^{-1} to 637.7 µmol.g^{-1} (an increase of only 21.7 µmol.g^{-1}) and the number of Brønsted sites increased from 147.3 µmol.g^{-1} to 318.3 µmol.g^{-1} (an increase of 171 µmol.g^{-1}). This is a clear indication that it is the Brønsted acid sites that mainly contribute to the ethylene selectivity. If this were not the case, ethylene selectivity would have increased with slight increase in total number of acid sites as observed in the case of Lewis acid sites. Then, we can deduce that ethanol dehydration mainly proceeds over Brønsted acid sites. 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.

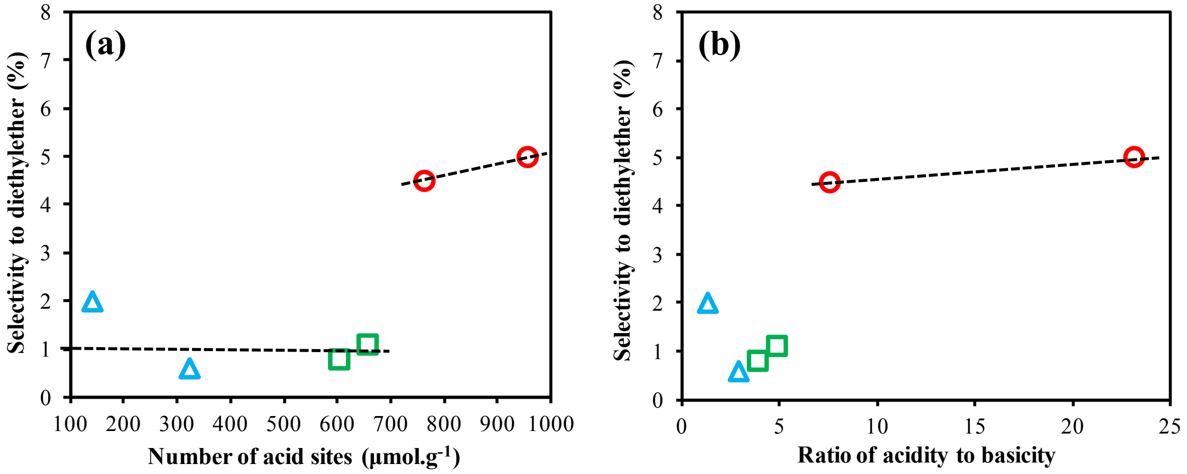

Figure S7 Selectivity to diethylether as a function of (a) the number of acid sites and (b) the ratio of acidity to basicity in HAPs (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Diethylether is formed by intermolecular dehydration of ethanol over the acid sites. Figure S7 (a) shows the variation in selectivity to diethylether as a function of the number of acid sites. The selectivity to diethylether remained almost unchanged (at *ca.* 1%) even with a significant increase in the number of acid sites from 141.3 µmol.g^{-1} to 658 µmol.g^{-1} (note that HapE-Na-CO_3 shows slight deviation). The diethylether selectivity then increased to 4.5% with increase in the number of acid sites to 763.3 µmol.g^{-1} and remained similar for further increase in the number of acid sites to 956 µmol.g^{-1}. This observation indicates that increase in the number of acid sites has no effect on selectivity to diethylether up to a certain limit and, then, a sudden increase in the diethylether selectivity is observed for a further rather small increase in the amount of acid sites. A deviation for catalysts with higher number of acid sites compared to the other catalysts is then clearly observed. Almost similar trend was obtained for the plot of diethylether selectivity as a function of the ratio of acidity to basicity as shown in Figure S7(b). All the above observations are good in agreement with the previous results showing the variation of diethylether selectivity as a function of the *di-iso*propylether selectivity [Figure 1(b)].

To further study the effect of the nature of acid sites on selectivity to diethylether, the variation in diethylether selectivity was plotted as a function of the number of Lewis and of Brønsted acid sites, as shown in Figure S8. The selectivity of diethylether remains almost unchanged with increase in the number of Lewis acid sites from 134.7 µmol.g^{-1} to 599.4 µmol.g^{-1}, as shown in Figure S8 (a). Diethylether selectvity increased from 1.1% to 4.5% and 5%, though the number of Lewis acid sites did not vary much. Figure S8 (b) shows that the diethylether selectivity remains almost same for an increase in number of Brønsted acid sites from 6.6 µmol.g^{-1} to 58.6 µmol.g^{-1}. Selectivity to diethylether then increased to 4.5% with an increase in the number of Brønsted acid sites from 58.6 µmol.g^{-1} to 318.3 µmol.g^{-1}. As aforementioned, variation with respect to the number of Lewis and Brønsted sites will be equally reflected, as in the total number of acid sites. For the increase in diethylether selectivity from 1.1% to 4.5%, the total number of acid sites increased from 658 µmol.g^{-1} to 763.3 µmol.g^{-1} (*i.e.*, an increase of 105.3 µmol.g^{-1}). Comparing this increase in total acid sites number with the increase in the number of Lewis acid sites (of only 16.6 µmol.g^{-1}), and increase in the number of Brønsted sites (of 88.7 µmol.g^{-1}), we could conclude that the Brønsted acid sites are mainly responsible for the formation of diethylether by intermolecular dehydration of ethanol.

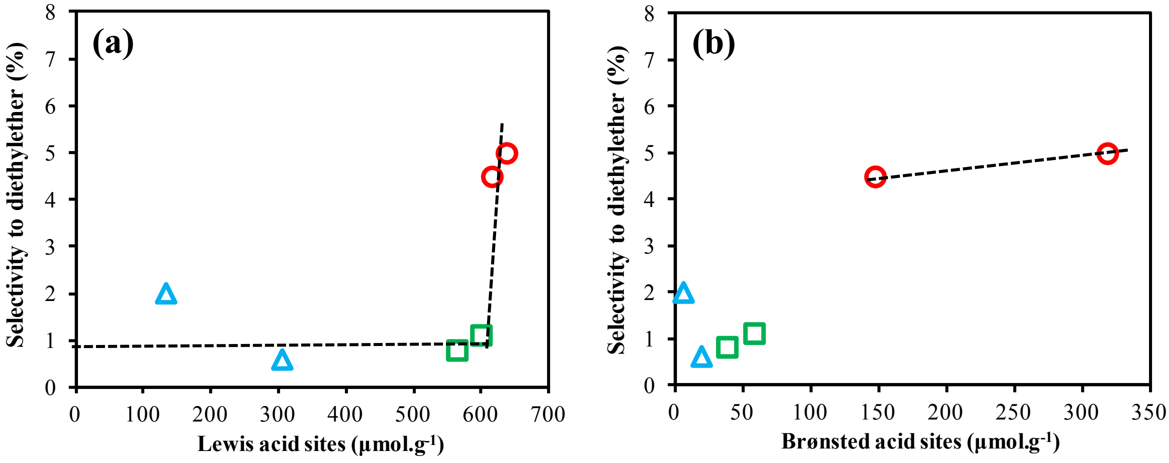

Figure S8 Selectivity to diethylether as a function of (a) the number of Lewis acid sites and (b) the number of Brønsted acid sites in HAPs (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

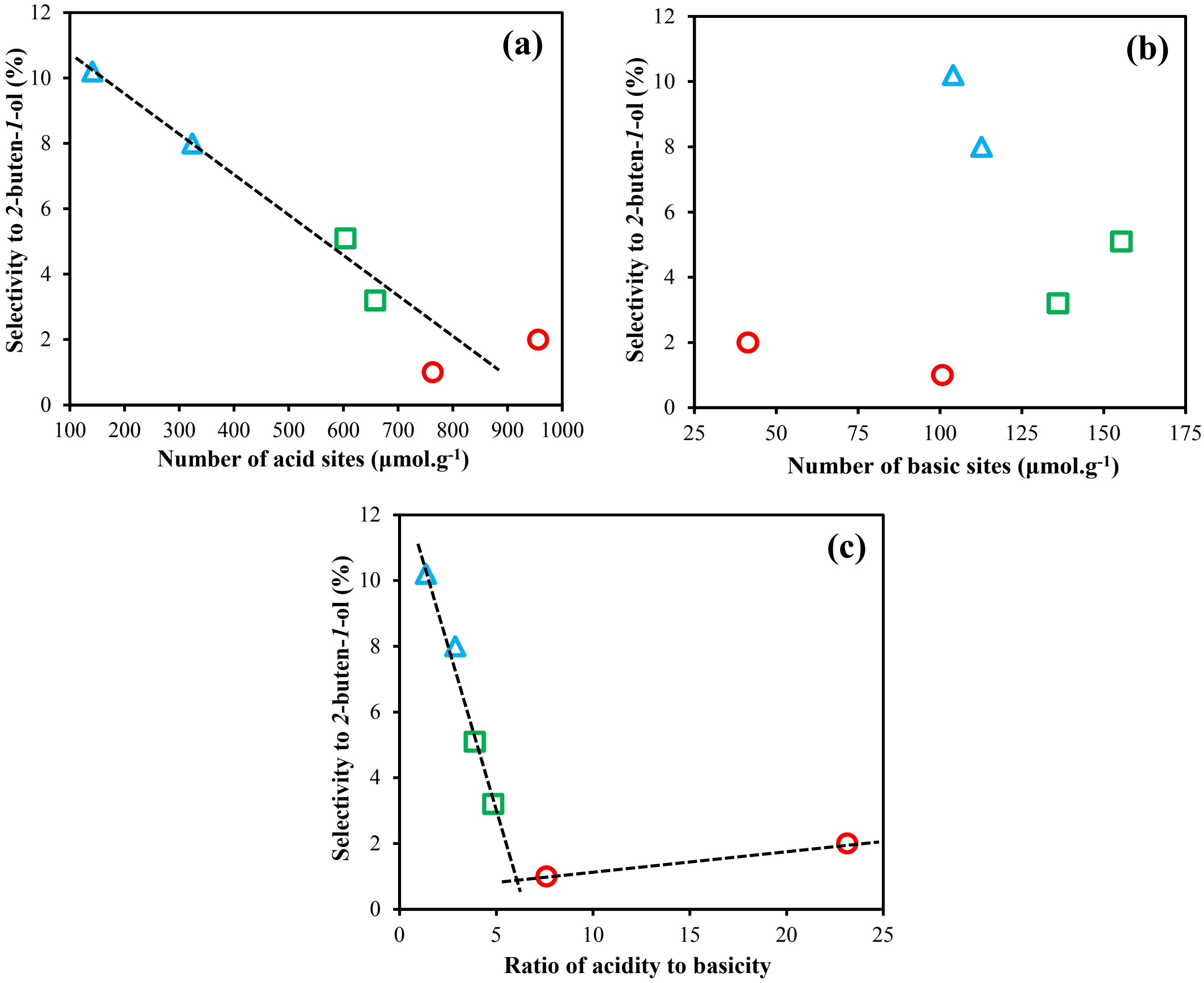

Figure S9 Selectivity to *2*-buten-*1*-ol as a function of (a) the number of acid sites, (b) the number of basic sites, and (c) the ratio of acidity to basicity in HAPs (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

Figure S9(a) shows that the selectivity to *2*-buten-*1*-ol decreased linearly from 10.2 % (HapE-Na-CO_3) to 3.2 % (Hap-CO_3) with an increase in the number of acid sites from 141.3 μmol.g^{-1} to 658 μmol.g^{-1}, respectively. HapD and Hap, which possess higher number of acid sites, showed slight deviation from the linearity like in the previous observations. The variation in *2*-buten-*1*-ol selectivity was not consistent with the number of basic sites, and it was difficult to extract some relation in that case, as shown in Figure S9(b). The plot of selectivity to *2*-buten-*1*-ol as a function of the ratio of the number of acid sites to the number of basic sites [Figure S9(c)] has shown a trend similar to that presented in Figure S9(a), but emphasizing the deviation of HapD and Hap. These results are in good agreement with the results deduced from the plot of *2*-buten-*1*-ol selectivity *vs.* propylene selectivity [Figure S3].

Though indirectly, this above observation clearly indicates that the carbonate-rich catalysts HapE-CO_3 and HapE-Na-CO_3 showing higher selectivity to *2*-buten-*1*-ol due to the lack of a sufficient number of acid sites further transform the intermediate *2*-buten-*1*-ol to butanol during the Guerbet reaction of ethanol. The *2*-buten-*1*-ol selectivity was decreased to 5.1% and 3.2% in carbonated apatites with increase in the number of acid sites, thus confirming the assistance of acid sites in transformation of *2*-buten-*1*-ol to butanol. The catalysts HapD and Hap with higher number of acid sites have also shown lower selectivity to *2*-buten-*1*-ol though they deviate from the linearity of other apatites.

To gain an insight on the nature of the acid sites, which mainly assist in the *2*-buten-*1*-ol transformation to butanol, the selectivity of *2*-buten-*1*-ol as a function of the number of Lewis and Brønsted acid sites was plotted (Figure S10). *2*-buten-*1*-ol selectivity decreased linearly from 10.2% to 3.2% with increase in the number of Lewis acid sites from 134.7 μmol.g^{-1} to 599.4 μmol.g^{-1}, respectively.

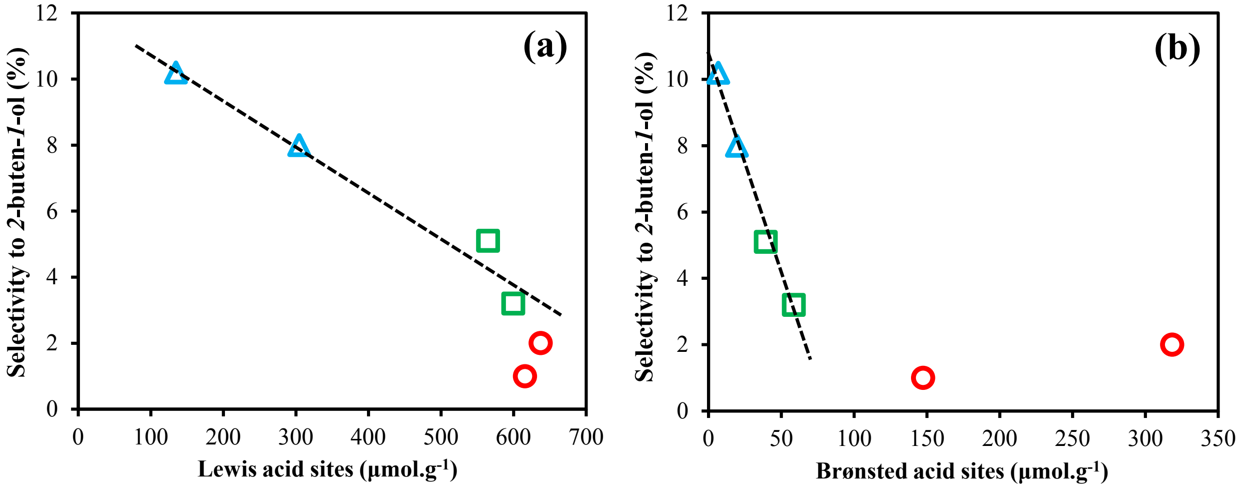

Figure S10 Selectivity of *2*-buten-*1*-ol as a function of (a) the number of Lewis acid sites, and (b) the number of Brønsted acid sites in HAPs (red circles representing HapD and Hap, green squares for carbonated apatites, namely Hap-CO_3 and HapNa-CO_3, and blue triangles for carbonate-rich apatites, namely HapE-CO_3 and HapE-Na-CO_3).

A similar but sharp decrease in *2*-buten-*1*-ol selectivity was observed with a small increase in the number of Brønsted acid sites from 6.6 μmol.g^{-1} to 58.6 μmol.g^{-1}. As aforementioned, by comparing the increase in the number of total acid sites (of 516.7 μmol.g^{-1}), the increase in the number of Lewis acid sites (of 464.7 μmol.g^{-1}) and increase in the number of Brønsted sites (of only 52 μmol.g^{-1}) with the decrease in *2*-buten-*1*-ol selectivity from 10.2% to 3.2%, we could conclude that it is mainly the Lewis acid sites that contribute to the *2*-buten-*1*-ol transformation to butanol.

References

1 L. Silvester,, J.-F. Lamonier, R.-N. Vannier, C. Lamonier, M. Capron, A.-S. Mamede, F. Pourpoint, A. Gervasini, F. Dumeignil, simultaneously submitted to *J. Mater. Chem. A,* 2014, **2(29)**, 11073.