

# EuroBioRef

**Project acronym:** EuroBioRef  
**Project Title:** EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing  
**Instrument:** Large Scale Collaborative Project  
**Thematic Priority:** FP7-ENERGY.2009.3.3.1  
**Grant Agreement:** 241718  
**Start Date of Project:** 01/03/10  
**Duration:** 48 Months

## SP5 – ADVANCED CATALYTIC CONVERSION PROCESSES TO CHEMICALS AND INTEGRATED SEPARATION TECHNOLOGIES

### WP5.3 – HEAVIER ALCOHOLS AND ALKENES PRODUCTION

## Deliverable report

*Due Date of Deliverable:* M36 - 28/02/2013  
*Actual Submission Date:* M36 - 05/02/2013

#### Deliverable Identification

*Deliverable Number:* D5.3.4  
*Deliverable Title:* Kinetics of the reaction  
*Responsible Beneficiary:* CNRS-UCCS  
*Contributing Beneficiaries:* CNRS-UCCS  
*To be Submitted to the EC:* Yes

#### History

Version	Author	Modification	Date
V1	Jean-François LAMONIER	First version	25/01/2013

#### Approval

	Name	Organization	Date	Visa
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#### Dissemination level

PU	Public	X
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## Executive summary

### *Description of the deliverable objective and content*

The objective of this deliverable was to study the kinetic measurements and reaction pathways based on the acid-base characterization of the catalysts and the performed Guerbet reaction. This deliverable proves the achievement of this objective.

### *Brief description of the state of the art*

The Guerbet reaction is known to proceed through a series of consecutive steps:

- (a) A dehydrogenation of the hydroxyl compounds to carbonyl compounds;
- (b) An aldol condensation between the carbonyl compounds, followed by elimination of water;
- (c) A hydrogenation of the  $\alpha$ - $\beta$  unsaturated aldehydes or ketones formed, the original hydroxyl compounds reacting as hydrogen donors, thus initiating a chain reaction.

Some studies have proposed that the dimerisation of ethanol to butanol also occur through aldol a mechanism in which a C-H bond in the  $\beta$ -position in ethanol is activated by the basic zeolite or metal oxide and condenses with another molecule of ethanol by dehydration. However there is a need of multifunctional catalysts to perform the aforementioned consecutive steps. Since previous studies have reported the performance of heterogeneous catalysts such as MgO, CaO, Mg-Al mixed oxides, hydrotalcites, hydroxyapatites etc...in the Guerbet reaction. Hydroxyapatites which possess both acid-base sites have been found to be active heterogeneous catalysts towards the Guerbet reaction. So the objective of this task is to study the kinetics and the reaction pathways of Guerbet reaction from the conducted reactions.

The gas phase Guerbet reaction of ethanol was performed using hydroxyapatite catalysts whose surface acid-base properties were modulated and characterized using various techniques. We observed that the number of acid-base sites, their strength and nature influence each step in the Guerbet reaction cycle. Considering the products obtained from the Guerbet reaction of ethanol and the acid-base properties of the hydroxyapatite catalysts, correlation studies were done between the Guerbet products and acid-base properties. From these correlation studies, we could successfully propose the Guerbet reaction pathways taking place over hydroxyapatite catalysts.

### *Deviation from objectives and corrective actions*

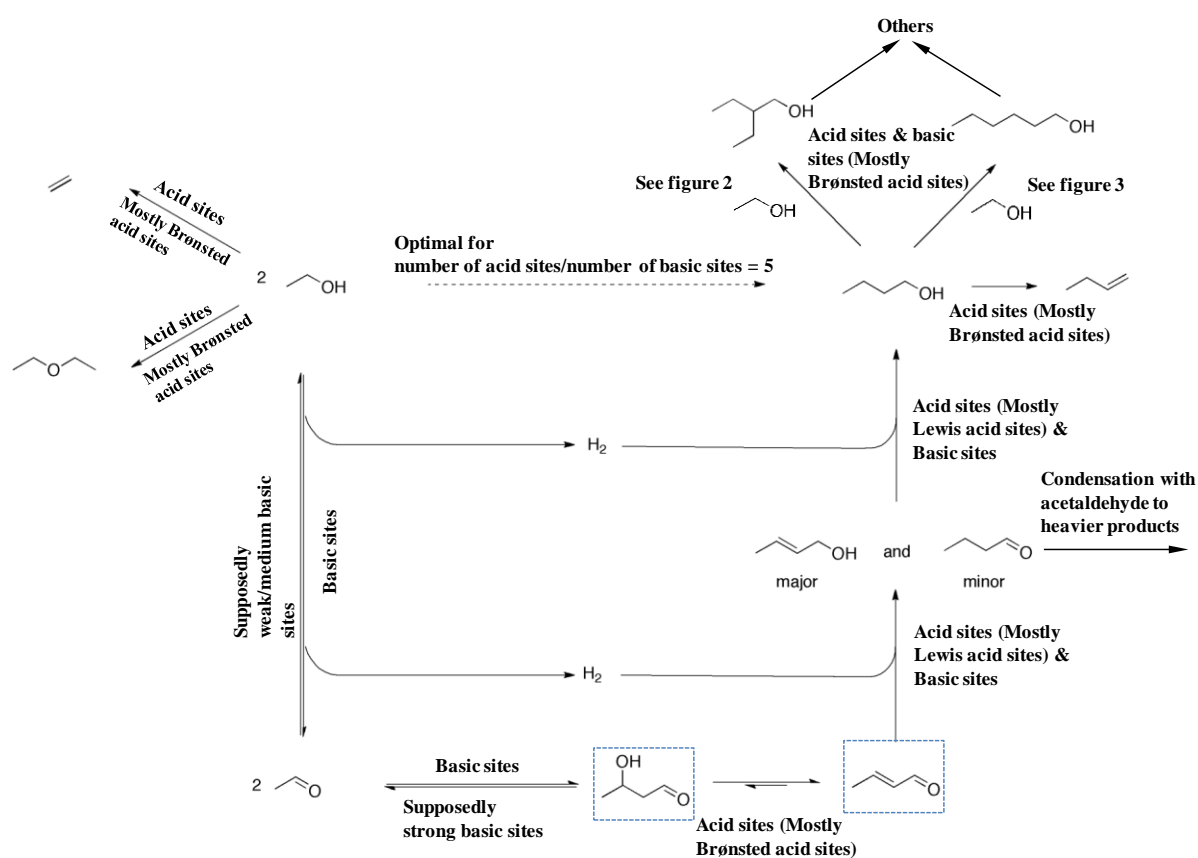
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### *Innovation brought and technological progress*

The abovementioned correlation studies which were done at ethanol iso-conversion of 14% helped us to further modulate the catalysts properties and also to study the reaction pathways at higher ethanol conversions and product yields.

It was found that the acidic behaviour of the deficient hydroxyapatites becomes predominant at higher temperatures and resulted in higher ethylene yield. The ethanol conversion and total alcohols yield were found to be optimum over the catalysts with acidity/basicity ratio of nearly 5. 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.

## Analysis of the results



**Figure 1** Scheme of the role of acid and basic sites in the apatite catalysts towards different pathways. The dashed box represents the intermediates which are not observed in the reaction. [Basic sites:  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$  &  $\text{CaO}$ , Brønsted acid sites:  $\text{HPO}_4^{2-}$ , Lewis acid sites:  $\text{Ca}^{2+}$  &  $\text{OH}^-$  vacancies ( $\delta^+$ )]

The number and strength of acid sites in the apatite catalysts was determined by TPD- $\text{NH}_3$ . Furthermore probing the catalysts with the 2-phenylethylamine (PEA) followed by the XPS analysis allowed us to determine the Lewis acid and Brønsted acid sites over the hydroxyapatite catalysts. TPD- $\text{CO}_2$  was employed to determine the amount and the strength of basic sites. Correlating these characterization results with the Guerbet reaction of ethanol, following results were obtained as shown in the reaction pathway (Figure 1).

The first step of the Guerbet cycle is the dehydrogenation of ethanol over the basic sites to produce acetaldehyde. This dehydrogenation takes place mainly on the weak or medium basic sites. The as-formed acetaldehyde further undergoes aldol condensation over basic sites (probably over stronger basic sites) to form an intermediate aldol (never observed in our conditions). Further dehydration of aldol takes place over acid sites (mostly Brønsted acid sites) 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) 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 further react with ethanol and go through an additional Guerbet cycle of mechanism over acid sites (mostly Brønsted acid sites) and basic sites to form 2-ethylbutanol or hexanol, depending on the type of attack. See Annexe I for the 2-ethylbutanol and hexanol production from condensation of butanol and ethanol. The formation of these heavier alcohols was promoted over catalysts having more number of acid sites, mainly Brønsted acid sites. Also, there are some competing reactions, especially dehydration reactions that can form olefins (ethylene, butene etc...) or diethylether, which occur in

parallel with the Guerbet cycle (mostly over Brønsted acid sites). So, there should be a compromise between the acid and the basic sites number and also concerning their strength and nature over the HAP catalysts to give a global formulation that is selective towards higher alcohols. We especially identified the best ratio between the number of acid sites to basic sites of 5 to attain maximum selectivity to higher alcohols over HAP catalysts. If the amount or the strength or the nature of acid sites becomes too high, the dehydration reactions (producing olefins) become more prominent and if the amount or the strength of basic sites exceeds this may preferably lead to the formation of products like aldehydes. In contrast, if there is any deficiency in the 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.

### ***Impact of the results***

The achievement of this D5.3.4 deliverable (proposed reaction pathways) shows that based on the surface acid base characterization, a multifunctional catalysts is required for the Guerbet reaction. These studies will be useful for catalysts back optimization in tasks 5.3.2 & 5.3.3.

### ***Related IPR***

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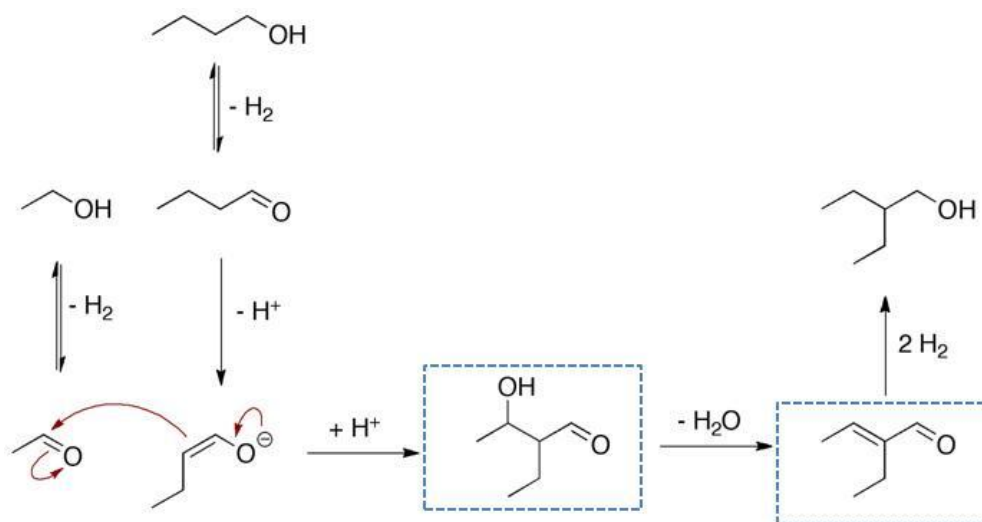
### ***Publishable information***

This deliverable is public.

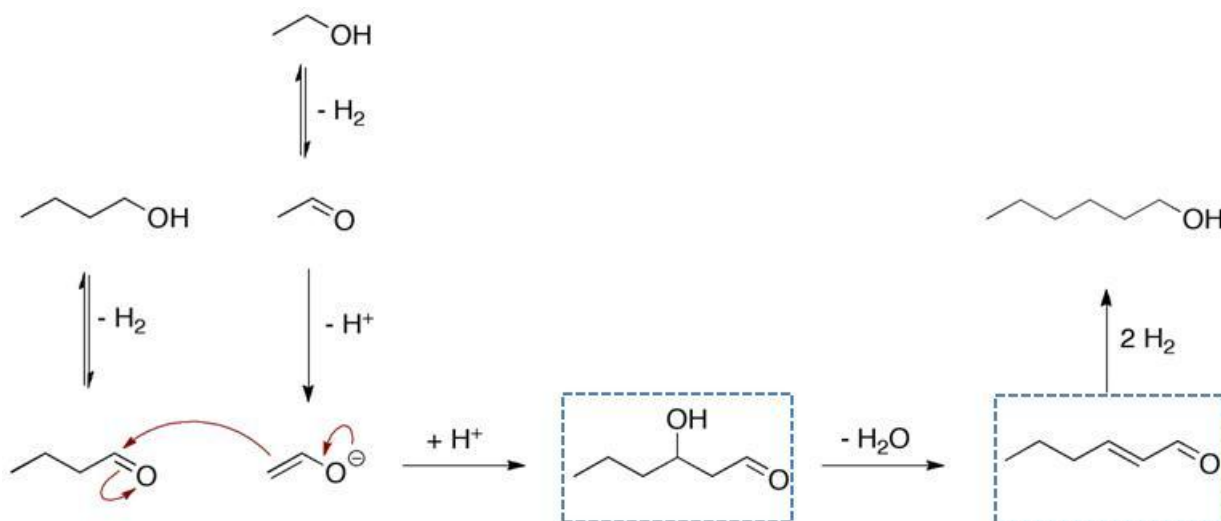
### ***Conclusion***

As results of the work carried out under task 5.3.4, a reaction model based on ethanol reactivity linked to the catalyst surface properties was established. Task 5.3.4 was completed which can be further used in the catalyst back optimization in the Guerbet reaction.

## ANNEX I – Technical content



**Figure 2** Mechanism for the condensation of ethanol and butanol to form 2-ethylbutanol. The dashed box represents the intermediates which are not observed in the reaction



**Figure 3** Mechanism for the condensation of ethanol and butanol to form hexanol. The dashed box represents the intermediates which are not observed in the reaction