

Ethanol reactivity over $\text{La}_{1+x}\text{FeO}_{3+\delta}$ perovskitesGuillaume Tesquet^a, Jérémy Faye^{a,b}, Fadime Hosoglu^a, Anne-Sophie Mamede^{a,c}, Franck Dumeignil^{a,d}, Mickaël Capron^{a,*}^a Université Lille 1 Sciences et Technologies, UCCS, Unité de Catalyse et Chimie du Solide, UMR CNRS 8181, 59655 Villeneuve d'Ascq Cedex, France^b TEAMCAT Solutions SAS, Ecole Centrale de Lille, Cité Scientifique-CS 20048, 59655 Villeneuve d'Ascq Cedex, France^c Ecole Nationale Supérieure de Chimie de Lille, 59650 Villeneuve d'Ascq, France^d Institut Universitaire de France, Maison des Universités, 103 Boulevard Saint-Michel, 75005 Paris, France

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ABSTRACT

Mixed oxide catalysts composed of mixtures of $\text{La}_{1+x}\text{FeO}_{3+\delta}$ perovskite and La_2O_3 were prepared using the auto-combustion method with glycine as an ignition promoter. A series of samples was prepared with $x=0, 0.1, 0.3, 0.5, 0.8$ and 1 , which were hereafter called La_{1+x}Fe . The as-prepared powders were characterized by XRD, XPS, DTA-TGA and N_2 -physisorption. Their acid-base properties were evaluated from their 2-propanol reactivity. Surface enrichment in La_2O_3 was detected when the lanthanum content increased. For high lanthanum concentrations, lanthanum hydroxide was also formed. The highest ethanol conversion was observed over $\text{La}_{1.3}\text{Fe}$ (32% at 400°C), which contained the largest amount of basic sites. The main reaction products were ethylene, acetone, 2-pentanone and 1-butanol. Other minor products originating from dehydration, reverse aldolization and hydrogenation reactions were also detected. Such a diversity of products was due to the presence of different kinds and distribution of sites on the catalysts surface (acid, base, hydrogenation, etc.). The catalysts activity was depending on their acid-base properties: an increase in the basic character due to the La_2O_3 presence at the surface led to higher selectivities to 1-butanol and 2-pentanone, which were 6 and 31% at 400°C , respectively, over the sample with the highest number of basic sites, which were also stronger ($\text{La}_{1.3}\text{Fe}$). On the other hand, over $\text{La}_{1.8}\text{Fe}$, which contained the highest quantity of $\text{La}(\text{OH})_3$, lower selectivities to 1-butanol and 2-pentanone (4.3 and 22%, respectively) were observed due to a decrease in the number of basic sites, together with a high ethylene selectivity (37%), with thus a predominant action of acid sites.

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1. Introduction

Hundreds of molecules are issued from oil processing. These chemicals are used in several sectors such as textile industry, food-industry, health, transport, chemistry, etc. [1]. However, the progressive depletion of oil resources together with an increasing demand in countries like China, Brazil and India [2] lead to the development of new technologies based on alternative resources, such as biomass.

Biomass can be pre-processed to yield platform molecules such as furfural, various acids or alcohols such as glycerol or ethanol. The ethanol global production has reached 89 billion of liters in 2011. It was mainly produced in the United States and in Brazil, which represent together about 87% of the global production [3]. Ethanol is used in various fields: in organic chemistry as a solvent, in the

cosmetic industry and in paints as a dissolvent, but the main application, which is driving the market, consists in its use as a biofuel [4]. Among the molecules that can be obtained from ethanol, 1-butanol is of particular interest as a solvent in organic chemistry, it possesses various applications in the cosmetic industry, and can be further used as an additive in gasoline and diesel [5,6] thanks to a high octane index and a low saturation vapor pressure compared to that of ethanol [4]. It can be synthesized from ethanol via the Guerbet reaction, which was discovered in the 19th century by Marcel Guerbet [7] and is recognized as a useful synthetic tool to obtain dimer alcohol by a self-condensation of primary alcohol [8]. It is often considered as a multi-step reaction (Fig. 1, given in the case of ethanol as a raw material): (i) dehydrogenation of ethanol over metallic or basic sites (weak or medium) leading to acetaldehyde; (ii) then, aldolization between two molecules of as-formed acetaldehyde on a strong basic site to obtain the associated aldol (i.e., 3-hydroxy-butyraldehyde); (iii) Elimination of one water molecule on acid sites to form an α,β -unsaturated aldehyde. Finally, (iv) double hydrogenation of this aldehyde occurs

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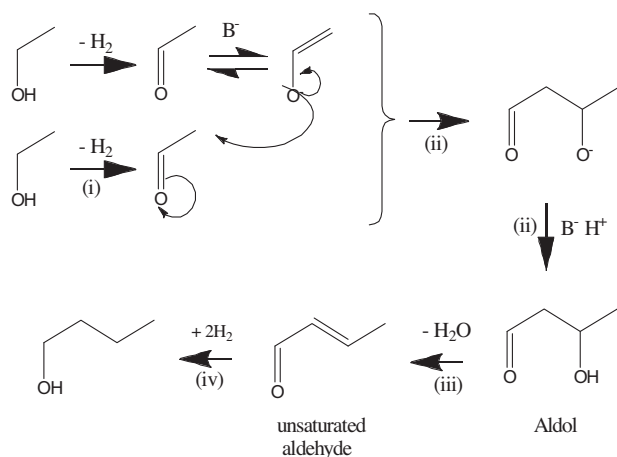


Fig. 1. Guerbet reaction pathway with ethanol as a reactant.

to produce 1-butanol, requiring a hydrogenation or Lewis acid site function on the catalyst.

Due to the complexity of the reaction pathway and to the diversity of catalytic sites needed to realize this reaction, many byproducts, such as acetone, ethylene, ethane, ester, 2-pentanone can be formed from ethanol. However, the Guerbet reaction is not the only reaction pathway to obtain butanol from ethanol. Scalbert et al. [9] have also evidenced 2 other different possible routes. After the first dehydrogenation step, which is the same for both alternative reaction pathways, one molecule of ethanol and one molecule of acetaldehyde react to form butenol or butanediol. In the case of the butanediol formation, this molecule loses a water molecule to obtain the butenol. The last step of both alternative routes is a reaction between ethanol and butenol to yield butanol and acetaldehyde via a hydride transfer according to a Meerwein–Ponndorf–Verley mechanism.

The Guerbet reaction has been realized over heterogeneous catalysts [10], in the liquid phase [11–14] and in the gas phase [15] using alcohol mixtures or alcohols heavier than ethanol as reactants. Only a few studies specifically report the conversion of ethanol, mainly over hydrotalcite [16] or over hydroxyapatites (HAP) [17–20].

Hosoglu et al. [16] have synthesized hydrotalcite-type $Mg_{6-x}Cu_xAl_2(OH)_{16}CO_3 \cdot 4H_2O$ catalysts ($x=0; 1; 3; 5$), in order to evaluate the influence of the copper introduction in the hydrotalcite structure. Such substitution led to an important increase in the ethanol conversion at 300 °C, which reached 80% for x of 5. However, this type of catalysts was selective to acetaldehyde, with a selectivity of almost 60%, but not in 1-butanol, which was detected in only very low quantities.

Tushida et al. [18] have reached a maximum yield to butanol with an ethanol conversion equal to 20% and a selectivity to 1-butanol of 70% at 370 °C using stoichiometric HAP

($Ca_{10}(PO_4)_6(OH)_2$). Authors have proposed a mechanism showing interactions between ethanol and the various active sites of HAP (acidic and basic sites of various strength and nature) during the Guerbet reaction. Then, Ogo et al. [19] have improved the selectivity in 1-butanol (i.e., 75% for 20% of ethanol conversion) substituting partially calcium by strontium ($Ca_5Sr_5(PO_4)_6(OH)_2$). This small 1-butanol selectivity increase has been attributed to the presence of residual sodium, which was included in the strontium precursor, highlighting the benefit effect on butanol formation when the number of basic sites is well tune. Finally, Silvester et al. [17,20] have prepared several HAP, which present various acid/base ratio. The goal was to understand finely the influence of acidic and basic site on ethanol reactivity and butanol production. They have evidenced an optimal acid/base ratio equal to 5, which enabled to reach a maximum butanol and other heavier alcohols selectivity via Guerbet reaction, and minimize the others side reactions. MgO has been also tested to convert ethanol into 1-butanol through the Guerbet reaction [21]. Irrespective of the catalytic system, the best yield reported so far does not exceed 25%.

The guideline followed in this work was to design multifunctional catalytic materials to carry out a one-pot reaction from ethanol. To reach this goal, we have chosen to use perovskite-type materials. Indeed, perovskites present a wide range of modularity owing to their general formula $LnMO_3$, where Ln corresponds to an element of the lanthanide group, and M a transition metal [22,23]. The elementary lattice of the perovskite structure is composed of MO_6 octahedrons linked by their corners. These octahedrons form a tri-dimensional framework and the lanthanide element is located in the cavity induced by the framework. The perovskite structure is obtained if the electroneutrality and the tolerance factor are respected [24]. Perovskites have already been often used in catalytic reactions for their oxidant character [25–31], but also for their reductive properties [32–34].

In this study, non-stoichiometric lanthanum-iron based perovskites were synthesized to investigate the influence of the lanthanum excess, in particular to increase the basic properties of the material, which seem to be the key parameter for the Guerbet reaction.

2. Experimental

2.1. Catalysts synthesis

A series of mixed oxides of the $La_{1+x}FeO_{3+\delta}$ general formula (with $x=0, 0.1, 0.3, 0.5, 0.8$ and 1) was prepared using the so-called auto-combustion method [25,35–37]. This preparation procedure was selected due to its quickness compared with common methods (e.g., co-precipitation or freeze drying [33,38–40]), which further enables obtaining larger specific surface areas.

Lanthanum and iron nitrates precursors [$La(NO_3)_3 \cdot 6H_2O$, purity 99.99%; $Fe(NO_3)_3 \cdot 9H_2O$, purity 99.99%; both from Sigma–Aldrich] were dissolved in a minimum quantity of water. Then, glycine

Table 1
Elemental composition and physical properties of the $La_{1-x}Fe$ catalysts, Binding energies and relative abundances of the elements constituting the $La_{1+x}FeO_{3+\delta}$ samples, and atomic distribution in oxygen-containing surface species obtained from the O1s spectral fitting.

Sample	SSA (m ² /g)	Ratio La/Fea			Surface composition								O1s spectral fitting (at.%) ^b			
		Th	ICP	XPS	C1s		O1s		La3d5/2		Fe2p3/2		O _{LaFeO₃}	O _{La₂O₃}	O _{La(OH)₃+CO₃²⁻}	O _{H₂O}
					BE (eV)	at.%	BE (eV)	at.%	BE (eV)	at.%	BE (eV)	at.%				
LaFe	6	1	1.02	2.04	285.0	30.6	529.3	46.7	834.0	15.0	710.0	7.3	60.0	–	34.2	5.8
La _{1.1} Fe	10	1.1	1.11	3.26	285.0	28.2	529.1	49.3	834.4	17.3	710.1	5.3	42.2	3.5	50.8	3.5
La _{1.3} Fe	9	1.3	1.31	4.36	285.0	23.7	529.0	52.8	834.6	19.2	710.4	4.4	30.3	9.1	59.3	1.3
La _{1.5} Fe	9	1.5	1.50	5.70	285.0	23.5	528.9	53.8	834.5	19.4	709.9	3.4	22.7	7.6	68.5	1.3
La _{1.8} Fe	12	1.8	1.80	6.30	285.0	23.9	528.9	54.2	834.1	18.9	709.9	3.0	17.2	6.8	74.8	1.3
La ₂ Fe	21	2	2.01	6.97	285.0	21.2	529.0	55.7	834.6	20.2	710.0	2.9	17.4	12.1	69.6	1.0

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