BIOETHANOL AS A SUSTAINABLE PLATFORM MOLECULE FOR THE SYNTHESIS OF CHEMICAL COMMODITIES

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ABSTRACT: The upgrading of renewable bio-based ethanol to valuable platform chemicals is a cornerstone of the transition to a more sustainable development. Here, ethanol production technologies are briefly presented. From this, catalytic routes for the upgrading of ethanol to value-added chemicals are reviewed. We focus on arguably the most important bioethanol-derived platform chemicals: acetaldehyde, ethylene, 1-butanol and 1,3-butadiene. Heterogeneous catalyst developments are described in relationship with the production process. This chapter highlights both the opportunities to take and the ongoing challenges to tackle, in order to transform academic research in this field into an industrial breakthrough in integrated biorefineries.

KEYWORDS: bioethanol, acetaldehyde, ethylene, butanol, butadiene, heterogeneous catalysis

1. INTRODUCTION

Humankind consumes energy, chemicals and materials; most of these are still obtained from fossil resources (crude oil, natural gas, coal). In the economic system that has been established since the Industrial Revolution, petro-refineries are the corner stones to produce fuels and chemical commodities (used in a variety of market sectors). However, fossil-based anthropogenic activities (in particular combustion and the associated CO_2 emissions) have enormous detrimental repercussions on the environment (Belgrano et al., 2023). In the perspective of fulfilling the demand for energy and materials, alternatives to the oil economy are undoubtedly needed. Thus, especially in the last twenty years, the World is coveting a gradual transition from a petro-refinery approach to an emerging biorefinery approach (Brienza et al., 2024; Cherubini, 2010; Deuss et al., 2015; Lahive et al., 2016).

Biorefining is an overall concept of processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products ("Industrial Technologies Reports and Analysis | Department of Energy," 2023). The overarching idea is to target the complete use of biomass feedstocks for the sustainable production of different fuels, chemicals, and materials, while also reducing waste to the minimum. The concept involves converting the various molecules found in biomass (carbohydrates, fats, proteins, aromatics) into not only biofuels but also drugs, pulp, paper, polymers, solvents, etc. In the biorefinery scenario, one platform molecule is playing a crucial role to produce biofuels or/and chemical commodities: bioethanol.

Ethanol, a primary alcohol, is a volatile liquid with boiling point = 351.3 K and energy density equal to 19.6 MJ/L. Bioethanol production can contribute to the economic viability of a biorefinery by generating a highly marketable product. It can be sold as a fuel or as an industrial chemical. Moreover, its production can be integrated into a larger biorefinery scheme where multiple products are derived from biomass (holistic approach). Interestingly, despite the fact that most of bioethanol derives from corn cultivations (1st generation bioethanol), in the EU bioethanol production form lignocellulosic biomass (2nd generation bioethanol) is progressively taking off, from 4% of 2018 to 13.4 % of 2022 ("Home - ePURE," 2023).

The main application of bioethanol is as a biofuel for transportation, serving as a cleaner and more sustainable alternative to conventional fossil fuels. It can be blended with gasoline or used as a standalone fuel in certain types of vehicles. Bioethanol is blended with gasoline in varying volume

fractions, specifically at 5%, 10%, and 85%, denoted as E5, E10, and E85 on the consumer market. While E85 is limited to flexible fuel vehicles (FFV), E5 and E10 can be utilized without requiring any modifications to the engine. In Europe, the maximum ethanol content in commercial motor gasoline is 10% (E10) ("Overview of biofuels obligations in the EU - ePURE,"2023).

The production of bioethanol is continuously increasing and its larger availability and decreasing cost (Melendez et al., 2022; Pascoli et al., 2021) also stimulate the exploration of different upgrading options. Furthermore, the need to reduce fossil dependence in other downstream sectors of the chemical industry created a market for bioethanol-based building blocks. Therefore, intense efforts have been made to efficiently convert bioethanol into chemical commodities of industrial interests. This chapter first deals with the ways to produce bioethanol and then focuses on the bases of ethanol catalytic transformation to some of the most important value-added chemicals: acetaldehyde, ethylene, 1-butanol, and 1,3-butadiene.

2. BIOETHANOL PRODUCTION

Ethanolic beverages are known since the earliest times. In fact, the distillation of fermented biomass to produce alcoholic drinks was reported in China approximately 9000 years ago (Halder et al., 2019). Also, the production of beer through alcoholic fermentation was already applied in ancient Egypt. Nowadays, alcoholic beverage global market is still significant; its value in 2022 surpassed 2 billion $. Even though ethanol has been produced for centuries through the fermentation of sugars by yeast, its isolation and industrial production on a large scale began only in the 20th century. First industrial fermentation process to recover ethanol was the ABE process, developed by the scientist C. Weizmann. In this process selected bacteria produced a mixture of acetone, ethanol, and butanol. Next, with the advent of petrochemistry different routes have been developed (Figure 1). Nowadays, bio-based ethanol regains interest.

2.1 Chemical routes to ethanol using non-renewable resources

Around 1930 the ethanol indirect hydration process was introduced. In this reaction ethylene reacted with sulphuric acid to produce ethyl sulphate which was then hydrolysed to ethanol. Instead, in 1947 Shell introduced the direct ethylene hydration process. The reaction was conducted in the gas phase at temperatures between 523 K and 573 K, and high pressure (usually 8 atm) to favour product formation. This reaction is an exothermal equilibrated reaction with an enthalpy of reaction of -43.4 kJ.mol^{-1} (at 298 K, 1 atm). To avoid several parallel and series reactions (i.e. from diethyl ether to higher alcohols), the equilibrium conversion of ethylene is maintained at 7-22% to achieve high ethanol selectivity, and the unreacted ethylene is recycled (Hidzir et al., 2014).

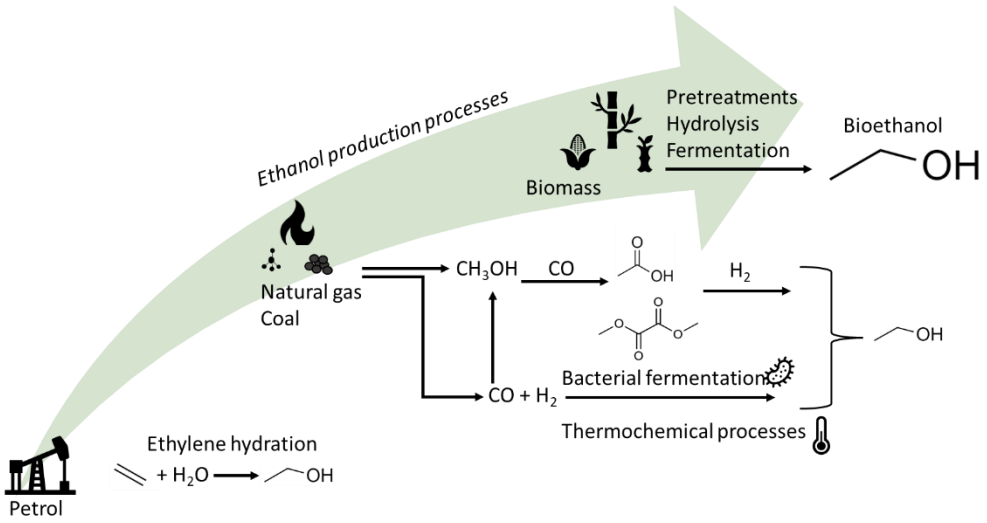


Figure 1: Development of the different ethanol production processes during the last century. First industrial process for ethanol involved the direct hydration of petrol derived ethylene. Besides, several processes have been developed to produce ethanol directly from natural gas or coal, via different intermediates (i.e. acetic acid or dimethyl oxalate), or directly via bacterial fermentation or thermochemical routes. Routes involving intermediates such as acetic acid or dimethyl oxalate are essentially studied at the academic level. Nowadays, because of the low cost, most of ethanol is effectively bio-based. Besides, it must be noted that (bio)syngas can be obtained from biomass. Thus, renewed interest is found in the catalytic conversion of (bio)syngas to ethanol.

Ethanol can also be produced from syngas, a mixture of carbon monoxide and hydrogen (+ carbon dioxide and other impurities) which can be obtained by gasification of coal, petroleum, and natural gas (and nowadays also recalcitrant biomass streams). A common approach involves subjecting the syngas to high-pressure (approximately 200 bar) and temperatures surpassing 573 K in the presence of Cu-based catalyst. The reaction unfolds through a series of sequential steps: i) hydrogen dissociative adsorption and carbon monoxide (CO) dissociation, yielding surface carbon (C*) and oxygen species, ii) formation of adsorbed CH_x species, iii) insertion of non-dissociated CO into an adsorbed acyl species. The final step involves the hydrogenation of the acyl species, culminating in the production of ethanol (Luk et al., 2017).

Syngas can also be fermented by acetogenic bacteria to produce ethanol. The fermentation process follows the reductive acetyl-CoA pathway, which was proposed by Wood and Ljungdahl in the sixties (Ljungdahl and Wood, 2003; Wood, 1991). Several bacteria such as Acetobacterium and Clostridium have proven to be effective for syngas conversion (Drake et al., 2008; Mohammadi et al., 2011). Minimal pretreatment is required for CO-rich syngas feedstock, offering high flexibility in gas composition and impurities, excluding small amounts of specific compounds such as NO and acetylene. Typically, this biological process is carried out under conditions of pH 4–6, 308–315 K, and 0–5 bar (Pang et al., 2019b). The resulting bioconversion yields not only ethanol but also acetic acid and other metabolites such as 2,3-butanediol, butanol, or butyrate (Molitor et al., 2016). Generally, the concentration of the produced ethanol in the fermentation broth is only 2% (Richter et al., 2013). To increase the ethanol yield, several operating parameters still need to be optimized (Pang et al., 2019b). Following downstream processing (i.e. advanced distillation and dehydration), fuel-grade ethanol is obtained.

It is possible to produce ethanol from dimethyl oxalate, ethyl acetate, or acetic acid. However, these routes are mainly investigated at the academic level because of the lower market price of ethanol with respect to dimethyl oxalate, ethyl acetate, acetic acid. For example, starting from syngas, CO reacts with methanol to produce dimethyl oxalate (DMO), followed by the hydrogenation of DMO to ethanol with the produced methanol being recycled back to the feedstock (Pang et al., 2019b; Shang et al., 2019). It is usually carried out by means of a dual catalytic bed. While the first step (DMO production)

can be catalyzed by Pd- and Fe-based catalysts, the second step (DMO hydrogenation) is catalyzed by Cu-based catalysts (Shang et al., 2019; Yue et al., 2014). At low reaction temperature, the process leads to high ethylene glycol (EG) selectivity (up to 95%) (J. Lin et al., 2012; Zheng et al., 2013), but working above 553 K allows pushing the dehydration process further, leading to high ethanol selectivity (Gong et al., 2012). The carbonylation of methanol to acetic acid, followed by its hydrogenation to ethanol, represents another alternative pathway. Different metal-based catalysts have been tested for this reaction but Ru-based catalyst showed the highest ethanol selectivity at low conversion of acetic acid(Shangguan et al., 2016). Other researchers studied the ethyl acetate hydrogenation to ethanol using copper-based catalysts direct (Ye et al., 2016; Zhang et al., 2021; Zhu and Shi, 2014).

2.2 Bio-based routes to (Bio)ethanol

Looking at the biorefinery scenario, bioethanol production relies on the fermentation of sugars. A general scheme to produce ethanol form biomass is depicted in Figure 2. One defines three generations of bioethanol, depending on the starting resource. Depending on the feedstock, various pretreatments may be applied (e.g. milling, extraction, ozone, steam etc..). The latter stages of the production process, however, always consist of i) fermentation to transform sugars into ethanol and then ii) distillation and purification to achieve high grade bioethanol. It must be noted that hydrolysis (saccharification) and fermentation, in some cases are run together in a simultaneous process (Ishola et al., 2013).

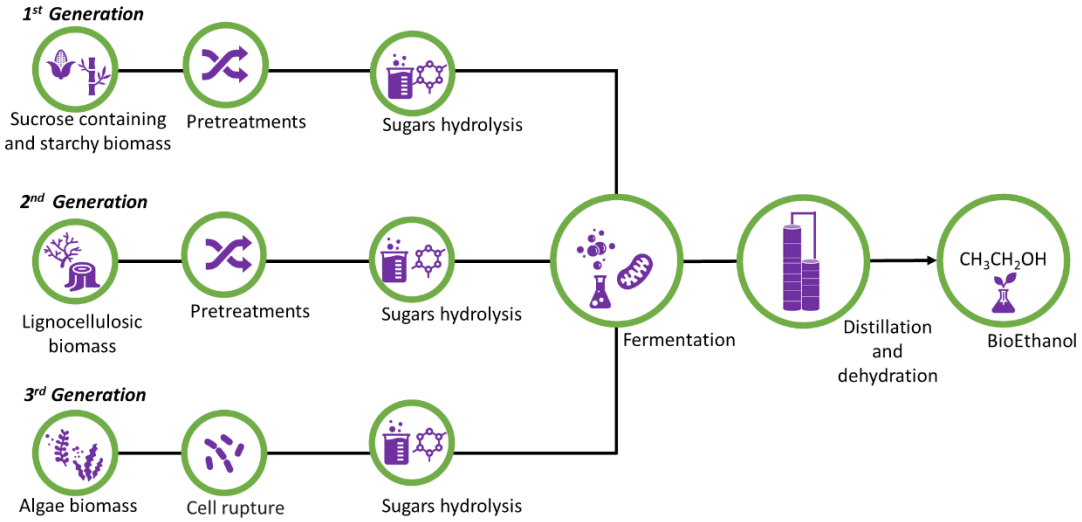


Figure 2: 1st, 2nd and 3rd generation biomass processes for the production of bioethanol

First-generation bioethanol is produced through the fermentation of glucose, that is itself obtained directly from sugary crops (e.g. fructose from sugar cane, beetroots etc.) or from the hydrolysis of starch (derived from corn, wheat, rice, etc.). The technology is well-developed and well-mastered, but it obviously poses a threat to food supply. Second-generation bioethanol is derived from non-edible lignocellulosic biomass such as corn stover, sugarcane bagasse, wheat straw, wood residues, etc.; Its production involves additional processes because lignocellulose needs to be pre-treated first to obtain fermentable substrates (i.e. sugars). Furthermore, the hydrolysis of crystalline cellulose fibres through the breakage of the β-1,4-glycosidic bond is still challenging. Third-generation bioethanol utilizes algae, offering a potential alternative with high carbohydrate content and limited land usage. It must be noted that these types of algae differ from those ones employed to produce biodiesel (that are indeed rich in triglycerides content and not is sugars) (Martinez-Villarreal et al., 2022). Nowadays, bioethanol from 1st generation biomass still accounts for more than 80% of global ethanol (bioethanol and petro-chemical derived ethanol) production (Pang et al., 2019b).

A typical 1st generation ethanol production process starts with the hydrolysis of sucrose or starch, using hydrolytic enzymes or acid hydrolysis. Sugary crops need only a milling process for the extraction of the sugars which are then sent to fermentation, and here ethanol can be produced directly from juice or molasses. Looking at starchy feedstocks, the grain is first ground into flour, which is then mixed with water to form a mash. Heat is first applied to reduce bacteria levels in the mash and then hydrolysis is started by introducing enzymes. In the end, yeast is added to initiate the fermentation process, transforming carbohydrates into ethanol. Fermentation of biomass to ethanol is typically operated with the *Saccharomyces cerevisiae* strain (Inal and Yiğitoğlu, 2011; Zhang et al., 2014). The fermentation process takes up to 50 hours at around 308–313 K with a pH of 4.0–5.0 and a variable sugar concentration (Y. Lin et al., 2012; Torija et al., 2003). The main limitation is the toxicity of ethanol to yeast; indeed, it limits the ethanol concentration to around 10–12 wt%. However, some ethanol-tolerant strains of yeast, such as "Turbo Yeast," or “Red Star Pasteur Champagne”, can increase the ethanol concentration up to 20 v/v% (Baeyens et al., 2015). After fermentation, the broth is filtered, and the filtrate is transferred to distillation columns for separation. In the final stage, the spirit (ethanol-water mixture close to the azeotropic composition) is further dehydrated either over molecular sieves or through azeotropic or pressure-swing distillation to obtain anhydrous ethanol.

Ethanol derived from lignocellulosic biomass is referred to as 2nd generation bioethanol. The disassembly of complex structures based on intertwined lignin, cellulose, and hemicellulose poses several challenges. First, preliminary mechanical pretreatment such as crushing, milling, extrusion allows reducing particle size, homogenizing the samples, and reducing the degree of polymerization (Yoo and Pan, 2015). Then, several pretreatments (i.e. via alkaline/acid steam explosion, organic solvolysis) are conducted to remove lignin from the carbohydrate polymers (Brienza et al., 2024). Next, the pulp (i.e. cellulose fibres) undergoes hydrolysis, wherein acids or enzymes are employed to break it down into mono and/or oligosaccharides. Subsequently, fermentation is carried out using yeast strains. The efficiency of ethanol production from lignocellulosic biomass hinges significantly on the recovery percentage of C_6 or C_5 sugars following pre-treatments and/or hydrolysis, as well as on the formation of inhibitors during these processes (Pang et al., 2019a). Throughout this entire sequence, the conversion of cellulosic components into fermentable sugars stands out as the primary technological and economic bottleneck (Singh et al., 2014; Yang and Wyman, 2008). Furthermore, it has been reported that the rate for co-fermentation of C_5 sugars is lower than the C_6 counterparts. Thus, the process effectiveness strongly depends on the type of feedstock employed (chemical composition). Despite notable advancements in the field, pre-treatment processes typically contribute to over 20% of the overall cost of lignocellulosic biomass ethanol (Pang et al., 2019b; Rodrigues Gurgel da Silva et al., 2019).

Ethanol produced from algae is denoted as 3rd generation bioethanol. In fact, due to their ability to synthesize substantial quantities of carbohydrates for energy storage, algae can serve as a source for alcohol production. Algae, categorized into macroalgae and microalgae based on their morphology and size (ranging from lengths of micrometres to 70 m), are eukaryotic organisms that can be photosynthetic or heterotrophic. Macroalgae, such as brown seaweeds (Phaeophyceae), red seaweeds (Rhodophyceae), and green seaweeds (Chlorophyceae), are primarily found in marine environments. Microalgae, including diatoms (Bacillariophyceae), green algae (Chlorophyceae), golden algae (Chrysophyceae), and cyanobacteria (Cyanophyceae), can be found in both freshwater and marine settings. Carbohydrate content varies markedly among species (Debnath et al., 2021). Microalgae (Chlorella, Spirulina) can have carbohydrate concentrations up to 70 wt.% (DeRose et al., 2019). Among macroalgae, red seaweeds stand out with a carbohydrate content ranging from at least 56 wt.% to more than 77 wt.%, making them one of the richest natural sources of carbohydrates (Müller et al., 2023). The main steps to produce bioethanol from algae are the cultivation, harvesting, cell rupture, saccharification, and fermentation (Müller et al., 2023). Macroalgae cultivation employs vertical or horizontal kelp systems, while microalgae cultivation mainly relies on the autotrophic method, utilizing

inorganic carbon sources and light. Microalgae growth occurs through batch, semicontinuous, or continuous operational modes in open systems or closed photobioreactors. Harvesting macroalgae is straightforward through manual or mechanical means, but harvesting microalgae, with sizes below 20 µm, poses challenges due to high colloidal stability and to the density that only slightly exceeds that of water. Microalgae harvesting costs can represent 20-30% of the total biomass production costs, acting as a bottleneck for commercialization (Tan et al., 2020). To convert sugars from algae to bioethanol, the cell walls must be broken using physical (ultrasound, high-pressure homogenization), chemical (acid and base solutions), or enzymatic methods and then filtrated. Saccharification then occurs using concentrated acids and/or commercial enzymes (Rempel et al., 2018). After hydrolysis, the monomers can undergo ethanol fermentation using routes closely resembling the consolidated production from starch cultures. It is worth noting that the yeast mostly used in the ethanol industry (Saccharomyces cerevisiae) has only a limited ability to ferment the other sugars that are present in algae hydrolysates. This limitation leads to decreased efficiency compared to processes involving biomass derived from starch.

Overall, it must be noted that the two most energy demanding (and thus expensive) steps of the biomass conversion to bioethanol are common among the different type of feedstock. The first is the classical distillation to concentrate bioethanol from 10-15 vol.% (after fermentation) to 95-96% vol.% (i.e. close to the azeotropic point). The second one is the dehydration to obtain an anhydrous bioethanol (at least 99.8%), using azeotropic distillation (Gomis et al., 2007; Vasconcelos and Wolf-Maciel, 2000), pressure swings distillation (Knapp and Doherty, 1992; Mulia-Soto and Flores-Tlacuahuac, 2011), dehydration with molecular sieves (Cartón et al., 1987; Chen et al., 2014; Fujita et al., 2011), or membrane processes (Cai et al., 2016; Ma et al., 2012).

Once “pure” bioethanol is obtained, it can either enter the biofuel marked or be upgraded to various platform molecules. The catalytic conversion towards useful bulk chemicals is nowadays of great academic and industrial interest. Among the various bioethanol drop in products, we reckon that acetaldehyde, ethylene, butanol, and butadiene will (continue to) play a crucial role (Fig. 3). Thus, this book chapter discusses the main insights and recent trends on the synthesis of these four target products.

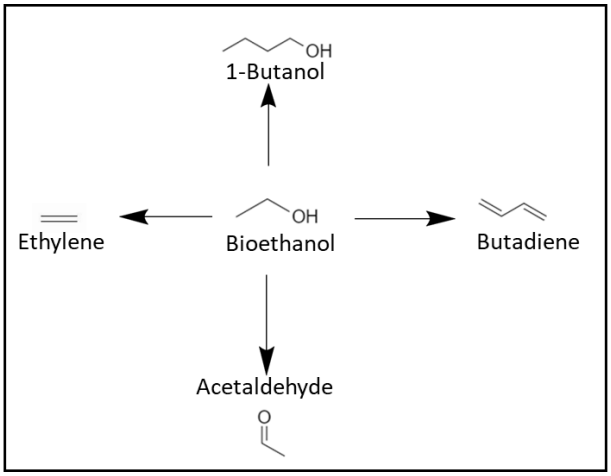


Figure 3: platform molecules that can be obtained from bioethanol and that are discussed in this manuscript

3. ACETALDEHYDE

Acetaldehyde (ethanal) was discovered in 1774 by Scheele during the reaction of black manganese dioxide and sulfuric acid with ethanol. Its composition was only determined in 1835 by Liebig who prepared pure acetaldehyde by oxidation of ethanol with chromic acid and named this substance

“aldehyde,” a contraction of the term “alcohol dehydrogenatus” (Fleischmann et al., 2000). Initially used for acetic acid production (Weissermel and Arpe, 1997), today acetaldehyde serves as an intermediate in diverse chemical commodities. For example, it reacts with primary amines to form Schiff bases, that are employed in optical computers and imaging systems (Berhanu et al., 2019). Additionally, imine complexes derived from the reaction between primary amines and acetaldehyde, exhibit antitumor and antibacterial properties (Brodowska et al., 2014) [11]. Acetaldehyde contributes to the synthesis of pyridine derivatives, crucial in the synthesis of flavouring agents and food additives. Monochloroacetaldehyde, finds applications in pharmaceuticals; for example it is an intermediate for the synthesis of the drug 2-Aminothiazole (Dahlmanns and Müller-Gärtner, 2000). Acetaldehyde's role extends to fertilizer production, where it condenses with urea to form crotonylidenediurea (Fleischmann et al., 2000). Furthermore, acetaldehyde gives rise to polymers such as paraldehyde and metaldehyde. The former is utilized in pyridine production and the latter serves as a molluscicide (Fleischmann et al., 2000).

Acetaldehyde can be industrially produced via various processes: i) acetylene hydration ii) ethylene partial oxidation (Wacker Hoechst process) iii) ethanol dehydrogenation iv) syngas reaction. As the price of ethylene dropped in the 1960s, ethylene saw use as a raw material in the process of acetaldehyde production. The main process, developed by Wacker and Hoechst in the years 1957-1959, can be described as an exothermic catalytic oxidation realized in the liquid phase with homogenous catalysts [18].

However, acetaldehyde can be obtained via the dehydrogenation of (bio)ethanol, over heterogeneous catalysts. The oxidative dehydrogenation of ethanol is an exothermic reaction; considering the Gibbs free energy, it is thermodynamically favoured at any temperatures. In the commercial process (developed by VEBA-Chemie), ethanol is catalytically oxidized with air in the vapour phase.

$$CH_3CH_2OH + 0.5\ O_2 \longrightarrow CH_3CHO + H_2O \qquad \Delta H^0_{298} = -173.0\ kJ/mol$$

From a process point of view, oxidation reactions are difficult to control. Since complete oxidation of organic compounds to CO_2 and H_2O is even more thermodynamically favoured, the production of carbonyl compounds requires precise thermo-kinetic control. The main challenge is to carefully control reaction conditions, especially temperature, using optimized reactor design to prevent selectivity loss. The alternative is to operate in non-oxidative conditions:

$$CH_3CH_2OH_{(g)} \longrightarrow CH_3CHO_{(g)} + H_{2(g)} \qquad \Delta H^0_{298} = +68.6\ kJ/mol$$

The non-oxidation dehydrogenation of ethanol is an endothermic process; thus, it is favoured at relatively high temperatures, where reaction rate is also faster. The process suffers from high energy consumption and equilibrium limitations (i.e. conversion is still limited at moderate temperatures preferred to minimize side-reactions). Dehydrogenation reactions are run at temperatures between 473 and 773 K, typically corresponding to moderately low conversion, depending on the employed catalyst and contact time. In one of the first works published on this topic, in 1886, ethanol was passed through glass tubes at 533-563 K in the presence of metals such as copper, zinc, or cobalt (Buchholz-Meisenheimer, 1967). The first patents on the reaction issued in the first decades of the 20th century described catalysts consisting of copper sponge or copper activated with chromium oxide in a tubular reactor.

Production of acetaldehyde from ethanol is mainly carried out in the gas phase by means of heterogeneous catalysts with redox properties. Looking at this oxidative dehydrogenation (ODH) reaction, many types of catalysts have been tested and supported on different types of materials. Idriss and Seebauer studied metal oxides such as CaO, TiO_2/Fe_3O_4, Fe_3O_4, SiO_2 and Fe_2O_3; acetaldehyde was generally the main products at low conversion regimes (<20%) (Idriss and Seebauer, 2000). It was found that the higher the basicity and the temperature, the lower the selectivity. In fact, at high temperatures, products such as crotonaldehyde or ethyl acetate became predominant. More recently,

Mn based catalysts have been studied for the ODH reaction (Dotsenko et al., 2020; Oxidation et al., 2017; Trawczyński et al., 2005), and the best result was obtained when using titania as the support. However, acetaldehyde selectivity remained moderate (~70%) at a maximum conversion of ~90% at 500 K.

Noble metals are often used as heterogeneous catalysts for their thermal stability and capability to selectively guide the reaction towards the hydrogenation or dehydrogenation products (Busca, 2014a). Many studies report on the effects of different noble metal catalyst characteristics (support type, dispersion of the metals, size and shape of metal particles and role of additives) (Anderson and García, 2011; Geoffrey C. Bond., Springer Link, 2005; Hutchings et al., 2017; Liotta, 2010). Au based catalysts tend to have high selectivity and low desorption energies of acetaldehyde (Grim et al., 2019). Furthermore, it is reported that this metal is very active in the presence of small percentages of O_2 (Behravesh et al., 2021), leading to acetaldehyde selectivity up to 90 % at a conversion of 20% at 473 K (Guan and Hensen, 2009). Simakova et al. investigated the catalytic activity of gold nanoparticles supported on titania, silica and alumina (2% Au/TiO_2, 1% Au/SiO_2 and 2% Au/Al_2O_3) (Simakova et al., 2010). These catalysts have been tested between 353 and 603 K with a volumetric ethanol flow of 2% (He balanced for a final GHSV of 3600 h^{-1}). The best results were obtained with 2% Au/TiO_2, in the temperature range between 353 and 403 K, reaching 60% conversion and an acetaldehyde selectivity of 80%. However, a common behaviour to gold-based catalysts is their tendency to further oxidize ethanol to acetic acid (detected as the main by-products with ethyl acetate). Over 523 K supported Ag (and Cu) catalysts also tend to totally oxidize ethanol to CO_x [8,69–72]. To sum up, noble metal-based catalysts show high selectivity but are generally restricted to operate at relatively low temperature and low conversion levels, due to the strong competition with total oxidation reactions. Furthermore, these catalytic materials are costly. Thus, efforts are also directed towards cheaper catalytic systems that would operate in different reaction conditions.

In this perspective, vanadium-based catalysts have been largely investigated in the partial oxidation of ethanol to acetaldehyde. Vanadium oxide species have been dispersed on supports such as TiO_2 and Al_2O_3 (Beck et al., 2012; Gatt et al., 2010; Hidalgo et al., 2016; Lakshmi et al., 2000; Quaranta et al., 1994), ZrO_2 (L. Jhansi Lakshmi et al., 1999; Lakshmi et al., 2001; Lin et al., 2008; Miller and Lakshmi, 1999) or SiO_2 (Lin et al., 2008)(Botková et al., 2016; R. Tesser et al., 2004; Santacesaria et al., 2003; Wachs, 2010) or their mixed oxides. In particular, silica-based supports have attracted interest because of their well know ability to combine relatively good hydrothermal stability with widely tuneable textural and acid-base properties (Čičmanec et al., 2017). Recently, Autthanit et al. reported a V(2 wt.%)-Zr-La/SBA-15-HT which catalysts showed high catalytic activity: full conversion of ethanol and moderate acetaldehyde (about 40%) at 573 K (Autthanit et al., 2018). VO_x-TiO_2 catalysts also showed high performance (Gliski and Kijeski, 1992; Herrera et al., 2012; Kaichev et al., 2016; Quaranta et al., 1997; Rodella et al., 2002). In particular, bare VO_x-TiO_2 catalysts tend to achieve high acetaldehyde selectivity but only at temperatures lower than 473 K. Instead, V_2O_5 onto TiO_2 coated silica supports allowed improving the catalyst performance, achieving ~80% ethanol conversion and a 74% acetaldehyde yield at 473 K.

Mo-based catalysts also have the ability to catalyse the ethanol oxidative dehydrogenation to acetaldehyde (Chen et al., 2001; Chumbhale et al., 1998; Gonçalves et al., 2000; Pinthong et al., 2019a, 2019b; Villarreal et al., 2018; Zhang et al., 1995). MoO_x supported on SiO_2, SiO_2-Al_2O_3, or γ-Al_2O_3 are generally employed for their suitable surface properties and cheapness for a large-scale use. SnO_2 is a useful support that is employed to produce acetaldehyde or acetic acid. The active phase is made by dispersed tetra-coordinated molybdates (Gonçalves et al., 2000). The same work reported that the main product is acetaldehyde with a selectivity of 70% at a conversion of 90% at 473 K. The highest the temperature, the highest the production of acetic acid (over-oxidation of ethanol). Interestingly for this system, the addition of Ce enhances selectivity to acetaldehyde because it modifies dispersion of molybdate species (Gonçalves et al., 2001). Villareal et al. (Villarreal et al., 2018) found that 12 wt.%

MoO_3/Al_2O_3 has the best performance with high acetaldehyde yields at 573 K and almost total ethanol conversion. The limit in these cases is the low selectivity at both low and high conversion regimes, which entails the coproduction of acetals and dehydration products (ethylene, ethyl ether) on the one hand (Pampararo et al., 2021a, 2021b) or more oxidized products such as acetic acid, ethyl acetate and CO_2 on the second hand.

As said above, ethanol non-oxidative dehydrogenation is the other possibility to selectively produce acetaldehyde. Atomically dispersed gold supported on nanostructured $ZnZrO_x/ZnZr_{10}O_x$ supports acted as an efficient catalyst for the low-temperature ethanol dehydrogenation. Wang et al. found that optimized ZnO distribution preserves the gold active sites for dehydrogenation and suppresses undesired dehydration reactions, driving the reaction close to full selectivity, at temperatures below 573 K (Wang et al., 2016). In particular, Au-$ZnZr_{10}O_x$ showed a stable ethanol conversion 80% and a similar acetaldehyde yield during a 11 h test. Moreover, in the presence of 2 v/v% of water vapour, the yield only decreased slightly (to 75%). Au can also be supported on TiO_2 for ethanol dehydrogenation (Cornejo-Romero et al., 2017; Mai et al., 2015; Nadeem et al., 2012). However, it seems that condensation reactions are favoured, especially when reaction temperatures are higher than 573 K. Liu and Hensen studied $MgCuCr_2O_4$ and Au/$MgCuCr_2O_4$ (Au = 0,9 wt%) catalysts between 373 and 623 K (Liu and Hensen, 2013). The gold containing catalyst has an acetaldehyde selectivity between 95% and 80% (maximum conversion of 55%). While silver has been scarily studied for the non-oxidative dehydrogenation of ethanol (Sushkevich et al., 2013)(Mamontov et al., 2016), copper-based catalysts are known as very promising candidates also for this reaction. In fact, Cu catalysts are very selective for dehydrogenation reactions, minimizing overoxidized products. Thus, it possible to achieve high conversion profiles with high acetaldehyde yields. Also, Cu is cheaper than noble metals, making the evident choice for ethanol dehydrogenation reactions, as documented abundantly in literature (see recent reviews on the topic by Huang et al., Kumar et al., and Phung et al. (Huang et al., 2021; Kumar, 2021; Phung, 2022)).

Bueno's team found that Cu-ZrO_2 catalytic activity depends on particle size and interface with the support: with ZrO_2 supports, the main product was ethyl acetate, with 20% Cu/SiO_2 catalyst at 498 K, acetaldehyde was the main product with only 41% conversion and 87% selectivity (Freitas et al., 2014; Sato et al., 2013, 2012). Also, Hanukovich et al. found that at high ethanol partial pressure, the Cu surface becomes poisoned with reactive intermediates, and supports with Lewis acidity can promote the rate of ethanol conversion, if compared to less acidic support (i.e. ZrO_2) (Hanukovich et al., 2019). Copper-based catalyst supported on Al_2O_3, $ZnAl_2O_4$, $MgAl_2O_4$, have also been extensively investigated (DeWilde et al., 2014a; Garbarino et al., 2019, 2018; Pampararo et al., 2020; Vidya Sagar et al., 2006). These catalysts can reach selectivity to acetaldehyde >90% at almost total conversion but they are progressively deactivated by carbon deposition. Regeneration is possible by burning in oxygen. However, the support itself unavoidably plays a negative role in catalysing unwanted dehydration reactions (Pampararo et al., 2023). Cassinelli et al. obtained highly dispersed copper supported on porous alumina by a sol–gel method (Cassinelli et al., 2015). Cu/Al_2O_3 catalysts presented ~90% ethanol conversion and acetaldehyde selectivity of 80% at 573K, the main by-product was ethyl acetate. Cu-carbon based catalysts (Conesa et al., 2019; Morales et al., 2016; Ob-eye et al., 2019) revealed also to be promising. Ob-eye obtained ethanol conversion of 65% with almost full acetaldehyde selectivity at 623 K over copper-graphene based catalysts (Ob-eye et al., 2019). Morales et al. obtained high selectivity to acetaldehyde at high conversion with Cu-graphene catalysts (Morales et al., 2016). However, products of dehydration were found, associated with the presence of oxygen-containing acidic groups on the carbon surface. Cu-SiO_2 is also a promising candidate: through the tailoring of copper loading and synthesis method it is possible to obtain highly dispersed copper nanoparticles that are strongly active (Dixit et al., 2013; Dong et al., 2016; Finger et al., 2020). For example, Xu et al. found that by coating Cu microparticles with mesoporous SiO_2, catalytic activity was boosted (Xu et al., 2018). Zhang et al. obtained by ammonia evaporation efficient and robust Cu-SiO_2 catalysts (Zhang et al.,

2020). The best sample (10 wt.% Cu/SiO_2) showed an ethanol conversion over 90%, with acetaldehyde selectivity up to 98%.

The main catalytic systems for the upgrading of ethanol to acetaldehyde via dehydrogenation are summed up in Figure 4, together with some of the key features needed to obtain good performance. Metal oxides catalysts are mainly employed in oxidative conditions, that are useful to achieve stable reaction conditions and high conversion profile even at low temperatures (T < 573 K). However, current trends in research seem to favour catalysts development (essentially based on metal nanoparticles supported on suitable supports) for the non-oxidative route. This is mainly because selectivity can be more effectively boosted, by opportune choice of catalysts and reaction conditions, to obtain acetaldehyde and hydrogen as the sole products. Yet, crucial issues such as catalyst deactivation, regeneration, and re-uses often remain over-looked (Martín et al., 2022). Therefore, a real alternative to the currently available industrial processes to produce acetaldehyde is not available yet.

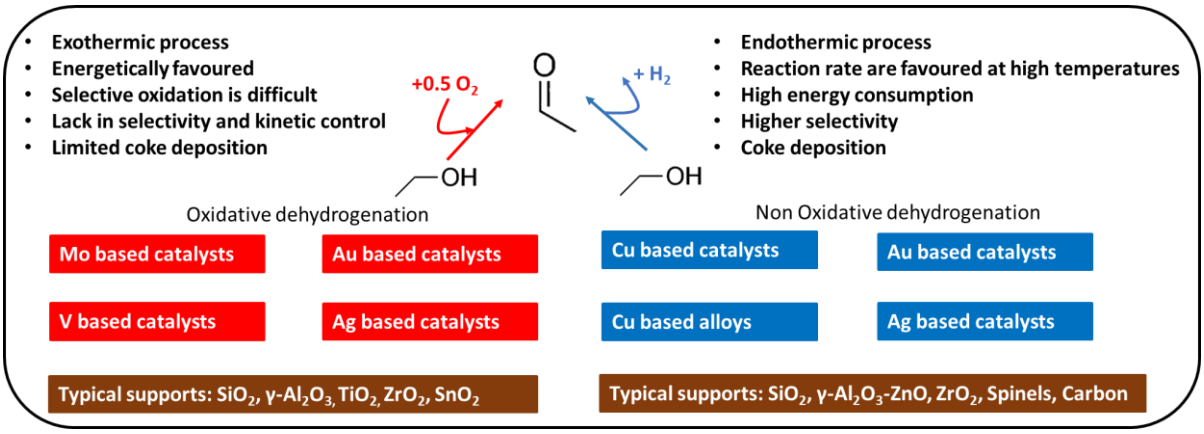


Figure 4: main features of the oxidative and non-oxidative paths to acetaldehyde, with a summary of the most studied catalytic systems

4. ETHYLENE

As the simplest olefin, ethylene has a wide range of applications in society. For example, ethylene is a crucial raw material to produce polyethylene, one of the most ubiquitous plastics globally. Polyethylene has applications in packaging, containers, pipes, etc. Ethylene is used to produce a variety of chemical intermediates, such as ethylene oxide, ethylene dichloride, and ethylbenzene. These intermediates serve as building blocks for the synthesis of other chemicals and plastics. Ethylene is a key component in the production of synthetic rubber, such as ethylene-propylene rubber (EPR) and ethylene-propylene-diene rubber (EPDM). It is employed in the production of solvents, including ethyl alcohol and ethylene glycol. Ethylene is commercially produced by fluid catalytic cracking (crude oil) or through steam cracking of paraffinic hydrocarbons (Gao et al., 2019). However, in addition to being based on fossil resources, these processes are highly energy demanding and emit large amounts of greenhouses gas (Nicholson et al., 2023). An alternative is represented by the dehydration of bioethanol to ethylene, that is mainly carried out in the vapor phase (1).

$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O \qquad \Delta H^0_{298} = +\,44.9\ kJ/mol \quad (1)$$

Alumina-based catalysts have been employed until the 1960s for the ethanol dehydration to ethylene (Phung and Busca, 2020). γ-Al_2O_3 has been commercially employed by Lummus Co., achieving 99% ethanol conversion and an ethylene yield of 94% (Yakovleva et al., 2016). Besides, phosphoric acid impregnated on clay or carbon was among the first catalysts to be employed (Pearson et al., 1981; Zhang and Yu, 2013). Despite the high ethylene yield obtained with these catalysts, deactivation by

coking was fast. In the 1980s, Le Van Mao et al.(Le Van Mao et al., 1989) explored zeolites to convert ethanol to ethylene. Nowadays, an important commercial catalyst is the SynDol ("Products – Scientific Design Company", 2023.) catalyst based on $MgO–Al_2O_3/SiO_2$ developed by Halcon (Fan et al., 2012). Petrobras Co. (Brazil) has developed a process involving several parallel adiabatic reactors with a fixed bed of an aluminosilicate catalyst ("US4232179A - Process for preparing ethene - Google Patents," 2023.). In China, HZSM-5 catalysts are preferred (Li et al., 2010).

The ethanol dehydration process is an endothermic reaction, and the reaction temperature plays a crucial role in determining the ethylene yield. Optimal selectivity for ethylene is achieved within the temperature range of 573–773 K. In general, elevated temperatures tend to favor acetaldehyde production, whereas lower temperatures lead to the formation of diethyl ether. Both isothermal and adiabatic modes of operation have been proposed (Mohsenzadeh et al., 2017). Ethylene is formed via diethyl ether breaking or via direct ethanol dehydration (Tripodi et al., 2019). The further oxidation of the ethoxide into acetaldehyde leads to acetic acid or, eventually, decomposes to methane and carbon monoxide (Wang et al., 2009). On γ-Al_2O_3, kinetic measurements revealed that acetaldehyde and subsequent hydrogen production (following a non-oxidative reaction mechanism) can also mediate the ethylene hydrogenation into ethane (DeWilde et al., 2014b).

The Busca group studied various types of γ-alumina catalysts with high ethanol dehydration performance (Phung et al., 2014a, 2014b; Phung and Busca, 2015a). Main findings revealed that the morphology of the catalysts strongly influences the catalytic activity. Thus, lamellar and faceted Al_2O_3 crystals seemed to have the strongest Lewis acid sites with respect to more bulk-like samples. In fact, highly uncoordinated sites located on corners and edges of the crystal surface have been revealed as the most active species in ethanol dehydration. Nevertheless, alumina-based materials are generally efficient toward ethanol dehydration to ethylene only at temperature higher than 623 K. Active sites are mainly attributed to Lewis acidic sites of unsaturated Al atoms (Zhang et al., 2008). Over these materials, while diethyl ether formation is favored at temperatures lower than 573 K, at higher temperature ethylene is the main product. Researchers developed also preparation methods to obtain nanocrystalline χ- and γ-Al_2O_3 mixtures (Janlamool and Jongsomjit, 2017), but also solvothermal and sol-gel methods to produce nanocrystalline aluminas (Wannaborworn et al., 2015) or high-energy facets exposed gamma alumina (Lv et al., 2023) achieving for example 99% ethanol conversion and 99% ethylene selectivity at 613 K.

Progressively, silica-aluminas attracted more attention due to the possibility of obtaining more active catalysts (Phung and Busca, 2015b; Roca et al., 1969). Industrial silica-alumina catalysts with a broad range of Si/Al molar ratios (5–87 wt% SiO_2) had a comparable activity to pure alumina but displayed a relatively low rate of coking and therefore a better stability with time on stream (TOS) (Tripodi et al., 2019). However, if prepared by classical methods and with low SiO_2/Al_2O_3 ratio, these materials favored the production of diethyl ether (Busca, 2014b; Phung and Busca, 2015b). More recently, advanced synthesis techniques such as non-hydrolytic sol gel have been employed to synthesize highly porous aluminosilicates with intermediate acidity in terms of acid site strength and nature between HZSM-5 and commercial silica-alumina (Styskalik et al., 2020b). The absence of strong Brønsted acid sites limited oligomerization reactions and coke formation and gave promising stability in ethanol dehydration reaction. Alternatively, another possibility to achieve selective and stable catalysts is to functionalize aluminosilicate with CH_3Si groups (Styskalik et al., 2020a). In fact, Styskalik et al. found that $Si–CH_3$ groups were successfully incorporated within the aluminosilicate matrices, leading to a decrease in the Brønsted/Lewis acid sites ratio and to an increase in the ethylene yield with respect to the benchmark catalysts.

Zeolite catalysts are also widely employed, HZSM-5 being the most studied (Wu and Wu, 2017); but HBEA, HFAU, HFER, and HMOR zeolites (de las Pozas et al., 1993; Takahara et al., 2005) have been widely investigated too. Protonic zeolites exhibit higher activity compared to silica-alumina and

alumina in the conversion of ethanol to DEE and ethylene. This activity is attributed to the exclusive presence of Brønsted acidic bridging hydroxyl groups within the zeolite cavities (Phung et al., 2015). For example, H-FER and H-USY catalysts achieved stable 99.9% yield to ethylene at 573 K with no deactivation during 7 hours on stream. Over H-MFI, under full conversion regime, selectivity to ethylene drops while several higher hydrocarbons and high yields to aromatics are obtained (Phung et al., 2015). HZSM-5 generally presented the best performance with selectivity to ethylene higher than 98%, and ethanol conversion of 98%, T = 548 K (Sheng et al., 2013). A prominent limitation associated with HZSM-5 catalysts is their susceptibility to rapid deactivation caused by coke formation. In fact, the Brønsted acid sites in HZSM-5 not only facilitate ethanol dehydration but also induce ethylene oligomerization, thereby resulting in the accumulation of carbonaceous by-products on the catalyst surface (Bi et al., 2010; Nash et al., 2016; Xia et al., 2017).

Thus, water is often added to the feed to reduce coke formation (Phillips and Datta, 1997), yet this limits the catalytic activity because of competitive adsorption between water and ethanol molecules on active sites (Bates et al., 2020; Karimi et al., 2019). To reduce deactivation by coking, multistep and laborious procedures to tune down the acidity and take down the typical microporous structure of HZSM-5 catalysts have been developed. For example, ion exchange (of iron) significantly decreased the strong Brønsted acid sites of the zeolite, which extended the catalyst lifetime due to the decrease of the generation of carbonaceous species (Chen et al., 2016). Phosphorous addition was also beneficial (Ramesh et al., 2009). In fact, its addition led to the partial dealumination and the formation of $AlPO_4$ like species. Consequently, a decrease in total acidity of ZSM-5 upon P addition was found and the P-modified catalysts also showed higher stability (up to 110 h) and resistance to coke formation. Selective and stable ethylene yield was also achieved by hierarchical HZSM-5 (Pornsetmetakul et al., 2023); by reducing nanosheet/plate size of zeolite domains it was possible to increases mesopore volume and external surface areas. These modifications led to almost full ethanol conversion and 95 % of ethylene selectivity for 48h time on stream. In the end, post treatments such as desilication with sodium hydroxide, dealumination with oxalic acid finely tuned the amounts of weak and strong acid sites in the zeolites, which affected catalyst selectivity to ethylene and stability (Xin et al., 2014).

Heteropolyacids (HPA) such as tungstophosphoric acid, silicotungstic acid and molybdophosphoric acid have been also investigated in ethanol dehydration (Varisli et al., 2007). The catalysts were tested at 413-523 K in a flow reactor at atmospheric pressure. High ethylene selectivity (over 75%) was obtained at 523 K with tungstophosphoric acid. At temperatures lower than 453 K the main product was diethyl-ether. Also, silica-supported HPA have been investigated (Al-Faze et al., 2020). The HPA catalysts exhibited strong Brønsted acid sites that effectively transformed ethanol into ethylene. Nevertheless, rapid deactivation occurred because of coke deposition (Verdes et al., 2021).

To sum up, over heterogeneous catalysts, strong acid sites are essential to achieve high ethanol conversions to ethylene. However, the strongest the acidity the fastest is the coke deposition. Thus, the tendency is to develop synthesis techniques that lead to acidic catalysts with moderate acidic strength. These materials can efficiently convert ethanol to ethylene at the lowest as possible temperature (T<523 K) for the longest time on stream (TOS).

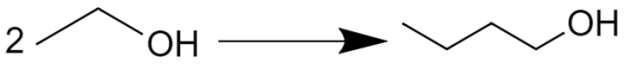
5. 1-BUTANOL

1-Butanol (n-butanol) is a versatile commodity chemical, playing the role of intermediate to various other chemicals, including for example acrylic esters. It possesses high energy density, low water solubility, and a low heat of vaporization (Rana and Parikh, 2020). Two chemical methods are commonly employed for butanol production. The “oxo-synthesis” method (Abdulrazzaq and Schwartz, 2018; Ojima et al., 2000) involves the serial hydroformylation and hydrogenation of propylene as the primary feedstock using homogeneous catalysts based on Co or Rh. Formylation transforms propylene into butanal through reaction with CO and H_2. In the subsequent step, butanal is hydrogenated to

produce a mixture of n- and isobutyl alcohol (Figure 5, reaction A1), which can then be separated by distillation. The "crotonaldehyde hydrogenation" (Abdulrazzaq and Schwartz, 2018) is the alternative pathway, that proceeds via three pivotal stages. Initially, acetaldehyde undergoes aldol condensation and dehydration processes, transforming into crotonaldehyde. Subsequently, supported metal catalysts facilitate the hydrogenation of crotonaldehyde into butanol (Figure 5, reaction A2). This approach typically yields butanol as the exclusive reaction product.

Direct butanol production from biomass fermentation was first reported by Pasteur in 1862. It was exploited during World War I in the so-called ABE (acetone, butanol, and ethanol) process, which employs microorganisms— specifically bacteria from the Clostridia class — to ferment glucose or starch (Ni and Sun, 2009; Veza et al., 2021). Reaction products are mainly ethanol and acetone, with a minor quantity of butanol (Figure 5, scheme B1).

An alternative biomass-based process is based on the upgrading of bioethanol (2). The ethanol-to-butanol (ETB) reaction operates through two identified paths, namely the Guerbet mechanism (Veibel and Nielsen, 1967) and the bimolecular condensation mechanism (Galadima and Muraza, 2015; Ho et al., 2016a). In the Guerbet activation path, ethanol first undergoes dehydrogenation to yield acetaldehyde. Subsequent steps involve the aldol condensation of two acetaldehyde molecules, forming crotonaldehyde as an intermediate and ultimately producing butanol via hydrogenation, (Figure 5, scheme B2). The bimolecular mechanism is a direct coupling that occurs by the condensation of the –OH group of one ethanol molecule with a β-H of another ethanol molecule to eliminate water and produce butanol (Figure 5, scheme B3).



There are some debates asserting that at temperatures below 673 K the reaction proceeds through the Guerbet pathway, whereas at higher temperature it proceeds through the direct bimolecular/coupling mechanism. However, some differences, in terms of reaction intermediates, can be observed depending on the catalyst type and on the reaction conditions (Galadima and Muraza, 2015). Finally, it must be noted that further condensation reactions involving both butanol and acetaldehyde to form higher alcohols or aldehydes can also occur (Tsuchida et al., 2006).

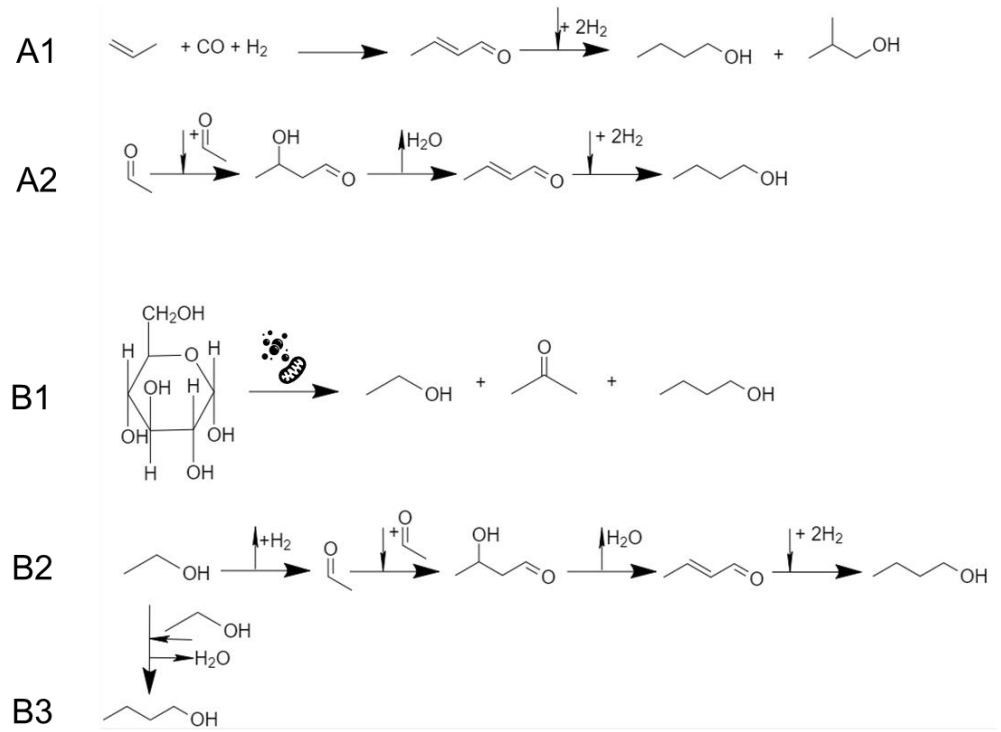


Figure 5: Reaction paths for the production of 1-butanol: A1 represents hydroformylation and hydrogenation of propylene to give n-butanol and iso-butanol. A2 represents acetaldehyde condensation to crotonaldehyde and its consequent hydrogenation. B1 represents the ABE process. B2 represents the ethanol to butanol reaction through the Guerbet mechanism. B3 represents the direct coupling of two ethanol molecules to butanol.

Scientific consensus holds that basic sites play a crucial role in 1-butanol formation. To date, looking at the literature, catalysts such as modified zeolites, metal oxides, supported metals and modified hydroxyapatites have found widespread use in the production of 1-butanol from ethanol (Pang et al., 2019b). Hydroxyapatites (HAP, $Ca_{10}(PO_4)_6(OH)_2$) have been widely studied for this reaction. Meunier et al. employed commercial catalyst at the temperatures of 623-673 K (Meunier et al., 2015). Butanol was obtained as the main reaction product with a maximum selectivity of 55%. In 2006 Tsuchida et al. investigated the influence of reaction temperature on catalytic performance of non-stoichiometric HAP (Tsuchida et al., 2006). At 573 K, nearly 15% ethanol conversion and 76.3% selectivity to butanol were obtained. Increasing temperature, ethanol conversion increased from 15% to 95% but the selectivity of *n*-butanol rapidly reduced from 76% to 6%. Furthermore, they developed a method to tune the selectivity to n-butanol simply by controlling the catalyst's Ca/P molar ratio and thus tuning its acido-basicity (Tsuchida et al., 2008a, 2008b). Replacing Ca in the hydroxyapatite structure by Sr, an increased selectivity to 1-butanol compared to bare Ca-HAP catalysts has been found (Ogo et al., 2012, 2011). High selectivity was correlated with elevated densities of relatively strong basic sites by the increase of Sr content. More recently, experimental but also theoretical results by DFT calculations showed that a balanced distribution of acidic and basic sites on HAP catalysts is critical to accelerate the formation of C–C bonds via aldol condensation, key parameters to achieve high selectivity toward 1-butanol (Brasil et al., 2021).

Riittonen et al. examined a variety of metals (Ni, Pd, Au, Rh, Ru, and Ag) supported on alumina for the liquid conversion of ethanol to butanol (Riittonen et al., 2012). Ni supported on alumina showed the best performance, achieving over 80% selectivity to butanol at 25% ethanol conversion. Dowson et al. investigated a series of ruthenium-based catalysts; the best catalyst achieved 94% selectivity to butanol at ethanol conversions over 20% (Dowson et al., 2013). They suggested that base-catalysed aldol condensation of acetaldehyde is crucial for achieving high selectivity. Improving the rate of aldol condensation led to increased butanol selectivity. Copper based catalysts have also been tested, generally leading to modest results. For example, a Cu/CeO_2 catalyst demonstrated high activity (84%

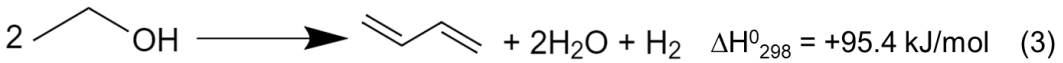
ethanol conversion) but only 31% butanol selectivity (Earley et al., 2015). The high activity of the Cu/CeO_2 catalyst was attributed to the promotion of the aldol condensation step in the Guerbet mechanism. Cu/Al_2O_3 catalysts also achieved high conversion, but the butanol selectivity was limited to 5%. Marcu et al. studied ethanol conversion to butanol with mixed oxide catalysts obtained from layered double hydroxides (Marcu et al., 2013). Pd–Mg–Al catalyst achieved the highest selectivity (40%) to butanol followed by the Cu–Mg–Al catalyst, however, in the reported test conditions conversion was generally lower than 10%. Other researchers (Carvalho et al., 2013, 2012) found promising results on Mg–Al mixed oxides or Ca-Fe modified mixed oxide Mg-Al catalysts (Molina-Ramírez et al., 2022). At 623 K, when the Mg/Al ratio was raised from 1:1 to 3:1 the butanol selectivity markedly increased from 22 to 38%, while maintaining similar conversion levels.

Pristine protonated zeolites such as HZSM-5 or H-BEA are not ideal candidate for this reaction mainly favouring dehydration, oligomerization and aromatization reaction (Ramasamy and Wang, 2013). However, some researchers (Yang and Meng, 1993) have developed modified zeolite catalysts, such as substituted Rb–Li–X and Rb–Na–X catalysts, that demonstrated high selectivity to butanol of 41% and 37%, respectively. More recently, Lu et al. synthesized composite catalysts based on zeolite BEA, reaching selectivity above 80% for the upgrading of ethanol to 1-butanol (Lu et al., 2023). Noticing the crucial effect of acid and basic sites proximity, they claimed that this performance was attributable to a cooperative catalysis effect of the dual-sites, accelerating both kinetically relevant steps of dehydrogenation and C–C coupling.

In summary, considering the Guerbet mechanism (B2), high dehydrogenation activity and as well as condensation activity are the key features a catalyst must have to promote acetaldehyde formation and the condensation reactions that drive the process toward butanol formation. The last hydrogenation step probably relies on the hydrogen produced in the first dehydrogenation, remaining adsorbed on the surface of catalysts (Kozlowski and Davis, 2013). Despite the role of acidic sites is still debated, it seems they play a crucial role in stabilizing the reactive ethoxide and enolate intermediates formed (Ho et al., 2016b) and favouring hydrogenation by the hydrogen obtained through ethanol dehydrogenation (Phung and Busca, 2020). Consequently, the interplay between the acidity and basicity of the catalyst emerges as a pivotal, yet not completely clear, aspect of this reaction. Looking at the direct condensation path (B3), it seems to be preferential on catalysts without transition metals (i.e. hydroxyapatites, hydrotalcites etc.) and at temperatures > 623 K. In fact, the absence of a metallic phase would make very difficult the activation of molecular hydrogen needed to hydrogenate unsaturated intermediates derived from aldol self-condensation (F. C. Meunier et al., 2015).

6. 1,3-BUTADIENE

Butadiene (1,3-butadiene, BD) is a key monomer to produce numerous elastomers, such as styrene-butadiene rubber, polybutadiene, acrylonitrile-butadiene-styrene and others (Grub and Löser, 2011). It is also employed in Diels-Alder reactions, with various dienophiles, to produce other cyclic polymers such as 4- vinylcyclohexene, 1,5-cyclooctadiene or 2,5-dihydrothiophene 1,1-dioxide (Grub and Löser, 2011). Industrially, it is primarily produced by steam cracking of hydrocarbons. In this method, BD is obtained as a by-product of the steam cracking process, which is commonly used to break down larger hydrocarbons into smaller ones (in particular ethylene) at high temperatures (above 1073 K) in the presence of steam. Butadiene is separated from the products mixture through various distillation steps. However, bioethanol can also be a suitable starting point to produce bio-based butadiene (3).



Lebedev pioneered the initial single-step (one reactor, one catalyst) technique to manufacture butadiene directly from ethanol at the beginning of the 20th century. The Lebedev reaction starts with the dehydrogenation of ethanol into acetaldehyde (Dochain et al., 2023a). Subsequently, two acetaldehyde molecules undergo aldol condensation to yield 3-hydroxybutanal, which is then dehydrated to form crotonaldehyde. The final steps involve the reduction of crotonaldehyde to crotyl alcohol (via a Meerwein-Ponndorf-Verley reaction with ethanol) and the subsequent dehydration of crotyl alcohol to produce BD (Figure 6, scheme A). However, it must be noted that there are still debates on the overall mechanism. For example, Chieregato et al. discards the key role of both acetaldol and crotonaldehyde as the reaction intermediates, explaining that instead crotyl alcohol and 3-buten-1-ol are the key intermediates of the Lebedev process and precursors for BD formation (Figure 6, scheme B) (Chieregato et al., 2015). Later, Ostromislensky at Union Carbide developed a "two-step" industrial process characterized by a first reactor where ethanol is dehydrogenated to acetaldehyde that condensates to crotonaldehyde. Next, crotonaldehyde is dehydrated to produce BD in a second reactor (Corson et al., 1950). Industrially speaking, to produce 1,3- butadiene, a mixture of ~69 wt. % of ethanol, 24 wt % of acetaldehyde, and 7 wt. % of water is passed over a Ta_2O_5 catalyst supported on silica gel (2% Ta_2O_5/98% SiO_2) at 623 K (Toussaint et al., 1947). Interestingly, this process provided > 60% of the emergency need of BD for rubber during World War II in the United States.

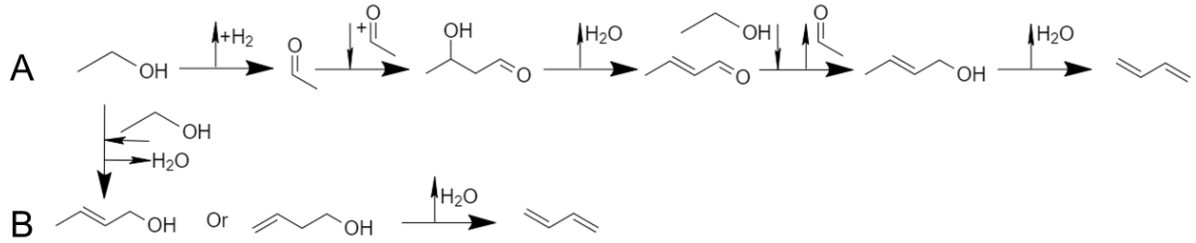


Figure 6: Reaction schemes for ethanol to butadiene reaction. Scheme A represents the first proposed scheme for Lebedev process to obtain 1,3-butadiene from ethanol. Scheme B for the synthesis of 1,3-butadiene from ethanol involves different intermediates.

Despite the complexity of the reaction mechanism and the tailored mix of active sites needed in the Lebedev process – i.e. the catalyst requires a balance of acid, basic, and redox sites (Sushkevich et al., 2014), this one step process is generally considered as less expensive and technically easier than the Ostromislensky process (Abdulrazzaq and Schwartz, 2018). One of the first promising catalytic system for the Lebedev process was a mixture of amphoteric alumina with basic and redox zinc oxide (Al_2O_3-ZnO (60:40)) (Bhattacharyya and Ganguly, 1962) that gave a 56% yield of BD at a temperature of 698 K. However, mixed MgO/SiO_2 formulations are the most studied nowadays (Jones, 2014; Szabó et al., 2020; Zhu et al., 2017). Here, the Mg oxide provides the basic sites while interfacial sites between Mg and Si oxides are thought to be responsible of the slight acid behavior. It seems also that defects generated by supporting MgO on silica enhance the dehydrogenation activity (Zhang et al., 2015). The Mg:Si atomic ratio is a crucial parameter to achieve high BD selectivity, even though contradicting findings have been reported. For example, Ohnishi et al. asserted that a MgO:SiO_2 ratio of 1:1 is the optimum (Ohnishi et al., 1985a), but Makshina et al. showed that a MgO:SiO_2 ratio of two is the most effective (Makshina et al., 2012). Such discrepancies probably arise from the impact of various other parameters, such as the mode of catalyst preparation (which affects the intimacy of the mixing between the two oxides and therefore the abundance and nature of interfacial sites). Cavani et al. utilized a sol gel method to prepare MgO–SiO_2 catalysts (Ochoa et al., 2016). Here, catalysts with a low Si-content (Mg/Si atomic ratio between 9 and 15) yielded superior BD yields. These catalysts featured a coexistence of base and Lewis acid sites, proving crucial for ethanol activation and the dehydration of intermediately formed alkenols to BD. MgO–SiO_2 catalysts prepared by wet kneading (Angelici et al., 2014; Chung et al., 2016; Kvisle et al., 1988) generally achieved >50% ethanol conversion and

moderate (~20-30%) BD selectivity, while classical impregnated catalysts (Angelici et al., 2015; Ohnishi et al., 1985a) gave lower ethanol conversion and lower BD selectivity.

Other elements play a crucial role on catalytic performance. Examples of typical metal oxides are NiO (Kitayama et al., 1996), ZnO (Larina et al., 2015), Zr (Da Ros et al., 2016), Cr_2O_3 (Makshina et al., 2014), CuO (Makshina et al., 2014). Besides, Larina et al. found that La addition had a beneficial effect on ZnO-ZrO_2-SiO_2 catalysts leading to full ethanol conversion and butadiene selectivity of 60% at 673 K (Larina et al., 2016). Since ethanol dehydrogenation to acetaldehyde is one of the key steps for BD production, several metals have been added to the MgO/SiO_2 system to enhance ethanol activation. The best results have been found for Ag (Janssens et al., 2015; Makshina et al., 2012) Cu (Tripathi et al., 2016) Au (Shylesh et al., 2016).

However, aldol condensation of acetaldehyde to crotonaldehyde is recognized to be the rate limiting step (Pomalaza et al., 2020). Metal oxides belonging to group 4 and 5 elements (Zr, Nb, Hf, and Ta) are very active in condensation reactions, owing to their intrinsic Lewis acidity. Optimizing the condensation capacity of these catalysts involves maximizing monoatomic dispersion, specifically in the configuration of tetrahedral "open" sites embedded in the framework of the silicate carriers (Pomalaza et al., 2020). Various methods for metal dispersion on catalyst carriers have been explored to achieve this objective, with notable success observed when employing mesoporous silica supports. In this sense, for example, Dochain et al. (Dochain et al., 2023b, 2023a, 2019) developed mesoporous Ag-Ta-SiO_2 and Cu-Ta-SiO_2 catalysts and Gonzalez et al. (Cabello González et al., 2019b, 2019a) prepared Hf-Zn-SiO_2 catalysts with promising performances.

Dai et al. utilized bifunctional Zn–Y clusters incorporated in the beta zeolite framework, achieving a high productivity of 2.33 g_{BD}/g_{cat}/h and a 1,3-BD selectivity of 63% at 673 K (WHSV of 7.9 h^{-1}) (Dai et al., 2017). The Zn-Y/Beta catalysts proved to be effective, thanks to the pore confinement and suitable acid-base sites. Subsequently, they delved into the deactivation mechanism of the Zn-Y/Beta catalyst during ethanol to 1,3-BD conversion. Through various characterizations, they identified that self and cross-condensation of acetaldehyde and acetone led to the production of long-chain unsaturated aldehydes/ketones. These compounds covered the active sites of the catalysts, resulting in catalyst deactivation (Yan et al., 2018). Catalytic activity was recovered via a simple calcination in an oxidizing atmosphere and the complete regeneration of Zn-Y/Beta was realized. Wang et al. (Wang et al., 2019) employed MFI zeolite nanosheets as support, impregnated with Zn/Hf oxides. This approach yielded enhanced BD selectivity and ethanol conversion compared to the classical ZnHf-MFI catalyst, with approximately a 10% improvement in ethanol conversion and BD selectivity. After doping with 1.7% Li, the best catalyst reached 73% BD selectivity at 65% ethanol conversion, at the temperature of 593 K and a WHSV of 0.47 h^{-1}.

To sum up, mainly two catalytic system have been developed for the ethanol to butadiene reaction. The first includes MgO–SiO_2 catalysts, that are active because weak and medium-strength basic sites on the MgO phase catalyze both the dehydrogenation of ethanol and the aldol condensation. The role and character of the acid sites formed by the mixing between MgO and SiO_2 is not completely understood yet. Synthesis procedure has a huge effect and to enhance catalytic activity, many promoters such as transition metals and metal oxides have been investigated but also alkali and alkaline-earth dopants to tune the acid–base properties of catalysts. In the second system, catalytic activity is mainly imputed to bifunctional catalysts featuring a redox functionality to catalyze the first dehydrogenation (Ag, Cu, and Zn have been identified as the most successful) and Lewis acid sites to catalyze the aldol condensation and the further dehydration reactions (Ta, Hf, Y, and Zr catalysts have been identified as the most active). These systems require a fine tuning of the catalyst preparation method to optimize the balance between redox and acid catalysis and drive the process to high BD yields.

7. CONCLUSIONS AND OUTLOOKS

Bioethanol, as a versatile platform chemical, is of crucial importance in most biorefinery scenario. It can be converted to various useful organic intermediates. Among those, ethylene, acetaldehyde, butanol, and butadiene can be highlighted as relevant targets for industrial production. The effectiveness of the respective conversion processes crucially depends on the choice of the catalyst.

To selectively produce ethylene, moderate acidic catalysts are needed while to produce acetaldehyde basic or/and redox sites are desired. Complex reactions to synthesize butanol and butadiene requires a balanced mix of both acid and basic/redox sites. Thus, to tailor activity and selectivity, catalyst preparation science is pivotal. In fact, besides the chemical composition of the catalysts, there are several parameters that must be considered to boost performance. In fact, textural parameters like specific surface area (Bernard et al., 2021), pore diameter (Schneider et al., 2008; Wheeler, 1951), and pore connectivity (Prachayawarakorn and Mann, 2007; Sharma et al., 2002) are of paramount importance to tailor the catalytic behavior and to achieve better diffusion of the reactants and high reaction rates (Ahmed et al., 2015; González-Castaño et al., 2021; Khaleel et al., 2022; Osman et al., 2022; Sun et al., 2010). Additionally, when utilizing supported catalysts, factors such as the size (Gates, 1995; Rostovshchikova et al., 2005; Wang and Lu, 2020), crystalline phase (Zhao et al., 2023), dispersion (Howeizi et al., 2020; Liu and Corma, 2018; Wang et al., 2022) and proximity (Batista et al., 2022) of the active sites (Vogt and Weckhuysen, 2022) become crucial for achieving enhanced catalytic activity, in particular for multifunctional catalysts. Consequently, the scientific community has predominantly directed its attention towards advanced synthesis techniques to develop more efficient catalysts.

Bioethanol based technology to produce chemicals is spreading in the industrial sector. Crop Energies and Johnson Mattey recently developed a technology to produce ethyl acetate from bioethanol in Germany ("CropEnergies AG unveils plans to produce renewable ethyl acetate using Johnson Matthey technology," 2022). Sekab ("Acetaldehyde - Sekab," 2024) produces acetaldehyde trough oxidative dehydrogenation of bioethanol. Clariant ("Clariant launches 100% bio-based surfactants range driving the transition towards renewable carbon," 2022), Braskem ("Press Releases - Braskem and SCG Chemicals join forces to advance in the bio-based Ethylene project in Thailand," 2023), Axens ("Bio Olefins | Axens," 2024) already developed industrial plants for bioethanol dehydration to ethylene. In parallel, butadiene has also started to be industrially produced from bioethanol by Synthos and Lummus technology ("Lummus and Synthos," 2024), and by a Michelin-IFPEN-Axens consortium ("Michelin - Bio-sourced materials: a new milestone!," 2019).

Despite this progress in the bio-based sector, it is still difficult to find chemicals companies with a main portfolio of bio-based chemical commodities built on bioethanol. We suggest this is associated with three main issues: i) high cost of advanced catalysts synthesis procedures ii) poor catalyst stability and difficult regeneration iii) high cost of anhydrous bioethanol. These points represent some challenges that the scientific community should be tackling in the near future.

i) Several catalysts developed by researchers own brilliant performances, but they are often based on time consuming, expensive, multi-step, and non-scalable synthesis procedures. Such limits must be carefully considered during the design of a new catalyst. A compromise between feasibility and control of the crucial catalyst properties must be found to un-lock Technology Readiness Levels (TRL) higher than 3-4. Thus, the scientific community should focus on maximizing the impact of realistic synthesis techniques to develop new promising catalysts (i.e. spray-drying, solvothermal, etc.).

ii) Despite the development of catalysts that are highly selective to the desired products and possess high conversion profiles or productivity, it is often difficult to maintain stable performances. However, performing long terms activity assessments and demonstrating stable and reliable catalytic performance on stream are the foundation of any scale up for a

catalytic process. Understanding catalyst deactivation on the fundamental level is essential and yet often overlooked. We argue that such effort would represent valuable opportunities to develop tailored strategies to prevent or remediate catalyst deactivation. To understand deactivation phenomena, researchers should also focus on a deep characterization of the spent catalyst, on developing dedicated experiments such as transient kinetic analyses (Hanspal et al., 2015) to reveal the involvement of reaction intermediates in deactivation mechanisms, or on leveraging in situ and operando microscopic and spectroscopic techniques (Dou et al., 2017) to track catalyst changes upon time. Only following this direction, the development of stable catalytic processes will pave the way to industrial breakthroughs that are urgently needed in the ongoing transition to a bio-based chemical industry.

iii) Anhydrous ethanol cost is still too high to inspire a wide industrial use. The two most energy demanding (and thus expensive) steps of the biomass conversion to bioethanol remain the distillation (95-96% vol.%.) and the dehydration procedures to achieve purities of 99.8% v/v. Typically, 37% of the total production cost is spent on dewatering activities (Feng et al., 2019). While the first step is needed to concentrate bioethanol, the second one could be avoided if catalysts capable of working and remaining stable in the presence of water are developed. Therefore, it is of great interest to study catalytic conversion of hydrous ethanol with different water concentrations; enabling the direct use of hydrous bioethanol to produce chemicals would dramatically save energy and cost. On the one hand, regarding ethanol dehydration to ethylene, the effect of water is well described in the litterature (Aguayo et al., 2002; Becerra et al., 2018; Bokade and Yadav, 2011; Ouayloul et al., 2023). Water is shown to minimize coke deposition rate, but concomitantly, its competitive adsorption (vs. ethanol) on the dehydration sites tend to negatively impact catalyst productivity (Ouayloul et al., 2023; Pahari et al., 2022). On the other hand, scientific reports addressing the effect of water remain rare as far as the catalytic upgrading of ethanol to acetaldehyde (Rahman et al., 2016), butanol (Landau et al., 2021), or butadiene (Ezinkwo et al., 2014; Kyriienko et al., 2019) is concerned.

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