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Review

Catalytic Transformations of Ethanol for Biorefineries

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Brazil e Estados Unidos são os maiores produtores mundiais de bioetanol e a principal aplicação desse álcool é como combustível. Como o etanol brasileiro é o mais barato do mundo, há um interesse crescente no seu uso como precursor nas biorefinarias para síntese de moléculas maiores. O bioetanol pode ser usado na produção direta de olefinas como etileno, propileno, 1,3-butadieno e hidrocarbonetos maiores, assim como a produção de moléculas oxigenadas, como 1-butanol, acetato de etila, acetaldeído e ácido acético. Nesse review crítico, será discutido o desenvolvimento de catálise heterogênea para a conversão de etanol em produtos com maior valor agregado.

Brazil and the USA are the major bioethanol producers in the world, and the main application of this alcohol is as fuel. Since Brazilian ethanol is the cheapest in the world, there is a crescent interest in its use as a building block for biorefineries. Bioethanol can be used for the direct production of drop-in chemicals, such as ethylene, propylene, 1,3-butadiene and larger hydrocarbons, as well as for the production of oxygenated molecules, such as 1-butanol, ethyl acetate, acetaldehyde, and acetic acid. In this critical review, the development of heterogeneous catalysts for the conversion of ethanol into these commodity chemicals will be discussed.

Keywords: bioethanol, heterogeneous catalysis, biorefinery, drop-in chemicals, oxygenated chemicals

1. Introduction

Before the 19th century, energy and materials were obtained mainly from biomass. Since the upcoming of the industrial revolution and the petroleum-age, biomass has been replaced by non-renewable sources, such as minerals, coal, gas, and petroleum, which were cheap and widely available.[1] Throughout the years, the chemistry of petroleum has been extensively developed and consolidated, and modern society relies on petroleum to meet its needs for energy, transportation fuels, goods and building blocks for commodity and specialty chemicals. Thus, it is not surprising that the petroleum price has been rising, not only because of market regulation, but also for political reasons.[2] The petroleum consumption is significantly higher in developed and emerging countries,[2] and while its worldwide average daily consumption *per capita* is approximately 2 L, in Brazil and in the USA it is around 7.1 and 9.5 L *per* day, respectively.[3,4]

Even though petroleum has been the major source of carbon, in different moments and for different reasons, the discussion of using biomass has emerged. For example, in the 1930s, due to a large agricultural surplus in the USA, the US Department of Agriculture has founded regional laboratories for studying the industrial utilization of "farm products" as feedstock for chemicals.[1] Also, during the Second World War, Europe faced problems in obtaining petroleum, which motivated the use of biomass for the production of fuels, resulting in the so-called biodiesel, produced from the reaction between vegetal oils and alcohols.[5] Later in the 1970s, the Brazilian government was concerned about the country's strong dependence on imported petroleum. Therefore, seeking the energetic independence, Brazil invested in the production of biomass-derived fuels, such as ethanol from sugarcane (ProAlcohol Program) and biodiesel (ProOleo Program).[6] ProAlcohol was very successful and since then, ethanol has been used as fuel or as an additive to gasoline. Nowadays, most Brazilian cars are prepared to run with either hydrated ethanol or with gasoline containing 25% anhydrous ethanol.

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Recently, the interest in using biomass as carbon source for the production of chemicals and fuels has emerged again, mainly due to concerns on petroleum depletion and on environmental issues caused by the chemical and petrochemical industries. Academia, industry, and government agencies have joined forces to promote the development of biomass conversion, which has as ultimate aim producing chemicals and fuels in biorefinaries.

In chemical industry, the main use of biomass is for ethanol production. In this process, the glucose syrup from sugarcane or the glucose obtained from corn starch hydrolysis is fermented to obtain bioethanol. The remaining solid biomass is usually burned to generate heat. Brazil was pioneer in the large-scale production of bioethanol from sugarcane, and for many years, bioethanol has been economically viable only in Brazil. In the 2000s, the USA started investing in the bioethanol production from corn and, in 2005, surpassed Brazil as the main producer (Figure 1). In 2013, Brazil and the USA accounted for 84% of the bioethanol produced worldwide (Figure 2).[7-9] Even if Brazil is not the largest bioethanol producer, the technology developed and improved along the years, makes the Brazilian sugarcane bioethanol the cheapest in the world.[10]

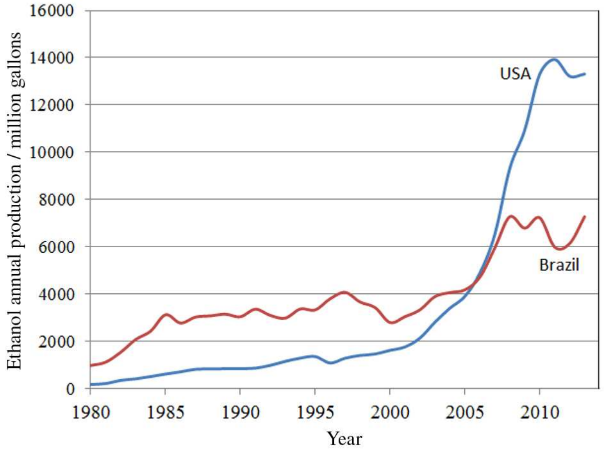

Figure 1. Bioethanol production in Brazil and in the USA since 1980.[11,12]

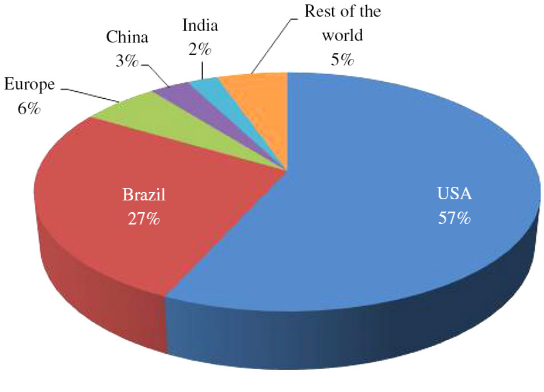

Figure 2. Production of bioethanol *per* country or region in 2013.[9]

In 2004, the US Department of Energy released a report[13] electing the top value-added chemicals from biomass. Surprisingly, ethanol was not in the top 30 chemicals and the justification was that ethanol is a limited building block and would potentially become a super commodity. Clearly, while bioethanol was commercially used in large scale in Brazil for 30 years, for the rest of the world, bioethanol did not seem to be economically viable. Few years later, Bozell and Petersen[14] revised the report and included ethanol as one of the top 10 most valuable chemicals obtained from biomass. The inclusion of ethanol in their list was due to recent technology developments and strategic commercial partnerships, that would have improved its platform potential.[14] However, the fact that the USA triplicated its bioethanol production in the six years gap between the two publications (Figure 1), must have influenced the authors' choice.

Since the 1980s, fuel has been the main use for bioethanol and its consumption has been increasing significantly (Figure 3). In the USA, for example, the Energy Independence and Security Act of 2007 (public law 110-140) mandates that by 2022, 36 billion gallons year^{-1} of transportation fuels will be replaced with biofuels.[15] In Brazil, the large-scale consumption of bioethanol as fuel started in 1938 (law number 737), when adding ethanol to gasoline became mandatory. The Brazilian ethanol has competitive prices compared to gasoline (even without government subsides) and therefore its consumption has been increasing in the last 20 years. For instance, in 2013, according to the Brazilian National Agency for Petroleum, Natural Gas and Biofuels, the total national consumption of bioethanol (anhydrous and hydrated) for fuel purposes was 21.1 billion L, while the gasoline C (for light and medium vehicles) consumption was 41.3 billion L. These numbers revel that, currently, bioethanol accounts for approximately one third of the fuels used in light and medium size vehicles in Brazil.

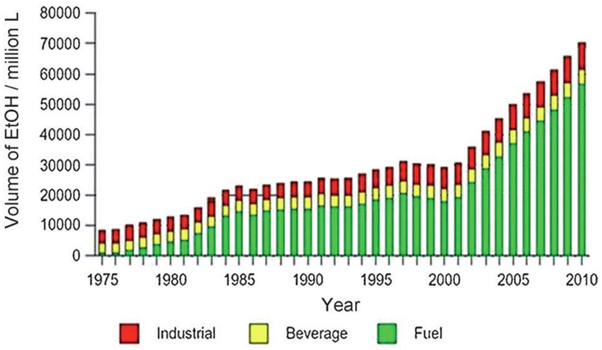

Figure 3. Worldwide production and use of ethanol. Reprinted from reference 16. Copyright 2013 by John Wiley Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

The bioethanol production exceeds significantly its consumption as fuel[8] and, therefore, there is room for its use as a platform molecule for the production of chemicals. As shown in Figure 3, the use of ethanol in the chemical industry almost doubled from 1990 to 2010, however, this increase was not as accentuated as the one observed for fuel. The challenges to increase the use of bioethanol as chemical feedstock are related to the development of novel high performance catalysts and to the cost for replacing well-established processes and products for biomass-derived ones. Bioethanol has an advantage compared to other biomass feedstocks, such as lignin, cellulose, hemicellulose and fatty acids: it can be directly converted, in one-pot processes, into "drop-in" chemicals. This means that bioethanol can be used to obtain some of the same building block chemicals that are currently obtained from petroleum, such as ethylene, 1,3-butadiene, propylene, and higher hydrocarbons. In this case, the changes in chemical industry to incorporate ethanol as feedstock could be minimized. However, the costs for producing these drop-in chemicals from ethanol are still higher than the conventional petroleum-based processes, even though the difference in cost has been decreasing.[16]

In Brazil, due to the low cost of the sugarcane and public incentives, bioethanol has recently been used in the chemical industry for the production of ethylene (or bioethylene). Since 2010, Braskem, chemical company based in Brazil, has a commercial plant with a capacity of producing 200,000 metric tons of polyethylene from bioethylene.[16,17] Dow Chemicals and Solvay also produce or use bioethylene.[14] Recently, Braskem, in collaboration with Genomica, started a new industrial plant for the production of 1,3-butadiene from bioethanol.[18] However, according to the company, the success of this process still depends on public incentives.[17] Besides the drop-in chemicals, other commodity chemicals can be industrially produced from ethanol. For example, Johnson Matthey Davy Technologies has developed in the UK a one-pot process for the partial dehydrogenation of bioethanol into ethyl acetate, using copper supported on chromium oxide.[19,20] According to the company, their plant in South Africa produces 50,000 tons *per* year.[21]

While the direct production of drop-in chemicals from ethanol can sound more interesting due to their broad use in current chemical industry, from the economical point of view, biomass is more suitable to produce oxygenated compounds. Biomass components, such as cellulose and hemicellulose are highly functionalized and present an O/C molar ratio close to 0.8 (Figure 4).[22] Crude oil, on the other side, has an O/C ratio close to zero, due to its non-functionalized nature. Therefore, in a traditional refinery, for the production of oxygenated molecules, oil has to be functionalized, while in the biorefinary, biomass has to be deoxygenated.

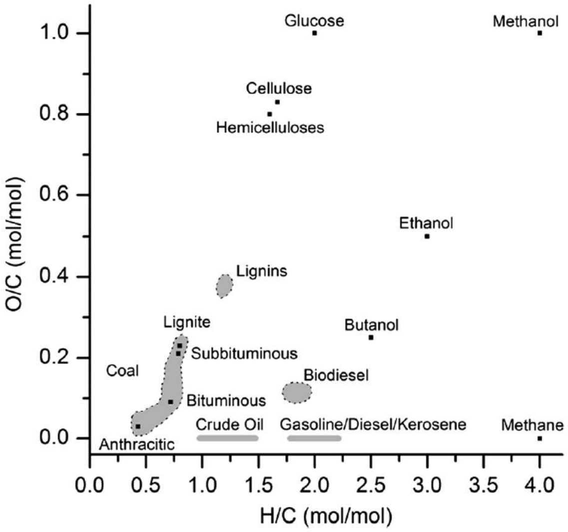

Figure 4. O/C molar ratio for crude oil, biomass fractions, and typical products related to chemical and petrochemical industry. Reproduced from reference 22 with permission from The Royal Society of Chemistry.

Therefore, in an emerging concept, it would be more rational to produce unfunctionalized molecules from oil and functionalized molecules from biomass. In fact, studies show that some oxygenated compounds such as ethanol and acetic acid could be produced at lower costs from biomass, as well as the drop-in chemical ethylene, that can be readily obtained by ethanol dehydration (Figure 5).[23]

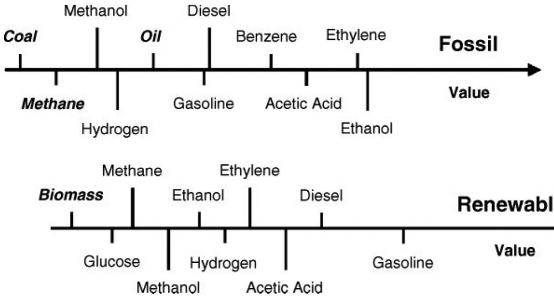

Figure 5. Indication of relative prices for a range of selected chemicals produced from either renewable or fossil resources. Reprinted from reference 23. Copyright 2007 by John Wiley Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

Ethanol is a versatile building block for biorefinaries, and can be used for the direct production of drop-in chemicals, such as ethylene, propylene, 1,3-butadiene and hydrocarbons, as well as for the production of oxygenated molecules, such as 1-butanol, ethyl acetate, acetaldehyde and acetic acid. Figure 6 shows some ethanol-derived organic molecules. In this critical review, the development of heterogeneous catalysts for the conversion of ethanol into commodity chemicals will be discussed.

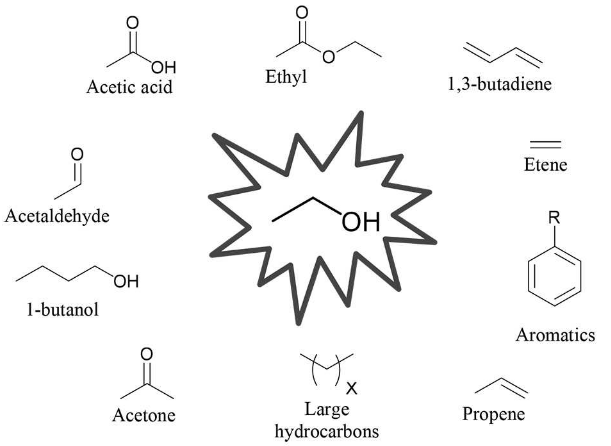

Figure 6. Some organic molecules that can be produced from ethanol.

2. Drop-in Chemicals: Ethylene, Propylene, Butadiene and Larger Hydrocarbons

As previously discussed, converting ethanol into drop-in chemicals would facilitate the integration of the ethanol biorefinary into the current chemical industry processes. Ethylene is probably the most obvious chemical to be obtained from ethanol, first because the reaction involves a simple dehydration, and second because ethylene is the largest-volume petrochemical produced worldwide.[24] In 2006, the ethylene worldwide production was around 113 million tons.[24] Ethylene is used almost exclusively as a chemical building block, and over 80% of the ethylene is used to produce ethylene oxide, ethylene dichloride, ethylbenzene, and polyethylene.[24]

The ethanol conversion into ethylene is endothermic and catalyzed by solid acids. In the reaction, ethanol is directly dehydrated to ethylene or etherified to diethyl ether. The ether can be subsequently converted to ethylene and is therefore considered a reaction intermediate.[25] In general, when the reaction is carried out at temperatures between 150 and 300 °C, diethyl ether is observed as a product, but at higher temperatures, the ether is readily converted to ethylene.[25] The main byproducts of the reaction are acetic acid, ethyl acetate, acetaldehyde, acetone, methanol, methane, propane, propylene, butane, butenes, hydrocarbons, carbon dioxide, carbon monoxide, and hydrogen. A large variety of catalysts has been tested for this reaction, but commercially alumina has been the most used.[25] In the 1960s, there has been an effort to revel the mechanism of ethanol conversion into ethylene and diethyl ether over γ-alumina.[26-32] It has been proposed that ethylene formation should proceed via a surface compound, in which an alcohol molecule is joined by two angular H-bonds to an OH group and an oxygen ion on the surface.[29] However, since alumina is amphoteric, it has also been suggested that the acid sites could lead to ethylene formation, while the basic sites to diethyl ether.[31] A recent density functional theory study proposed that the Brønsted acids in the alumina surface are weak, and therefore the adsorption of ethanol over these sites does not lead to any reaction. Therefore, the Lewis acid sites should be responsible for catalyzing the conversion of ethanol into both ethylene and diethyl ether.[33] Diethyl ether formation happens most probably by a S_n^2 mechanism, by a nucleophilic attack of a free ethanol molecule at an ethanol molecule coordinated to the alumina surface.[33] The decomposition of diethyl ether into ethylene can take place by two mechanisms: the hydrolysis of the ether into two alcohol molecules followed by dehydration or by an elimination mechanism in which the ether would be directly converted into ethylene and an ethoxide coordinated to the catalyst surface.[31-33]

Alumina is indeed a cheap catalyst and therefore interesting for industrial applications. However, for ethanol dehydration, high temperatures (450 °C) are required and the ethylene yield is not particularly high (in the range of 80%).[34,35] Consequently, there has been an interest in finding alternative catalysts. Since alumina has been such a popular catalyst for ethanol dehydration, one alternative is to improve its performance by modification with other metal oxides. Alumina doped with titania has shown to be active for ethanol dehydration.[36,37] When used in a microchannel reactor, alumina doped with 10% of titania led to ethylene yields comparable to pure alumina, however, at reaction temperatures 50 °C or lower. This is attributed mainly to the stronger Lewis surface acidity of the TiO_2-Al_2O_3 catalyst.[37] Amorphous silica-alumina catalysts have also shown ethylene yields comparable to pure alumina (76.7%), but at considerably lower temperature (300 °C),[38] however, amorphous silica is not particularly stable at the reaction conditions. Mixed oxides of Mn_2O_3, Fe_2O_3, Al_2O_3, and SiO_2 at various ratios have also been studied. The catalyst with the molar composition $45Mn_2O_3$:$45Fe_2O_3$:$10SiO_2$ presented the best performance, reaching 66% yield for ethylene at 400 °C.[39] Similar results have been observed for the mesoporous silica MCM-41 modified with vanadium (V/Si molar ratio of 0.04).[40] Using V-MCM-41, however, the reaction follows a dehydrogenative pathway and therefore, oxygen is required (ethanol/oxygen ratio of 2) in order to reduce the dehydration energy barrier. If oxygen is not used, very little ethylene is formed.[40] Between the metal oxide catalysts, one of the most promising results for ethanol dehydration was obtained with WO_x-silicate (W/Si ratio of 0.16), which led to an ethylene yield of ca. 92% at 350 °C.[41] WO_x based catalysts need further studies as dehydration catalysts. This class of catalysts can be an interesting model catalyst to probe the effect of the surface acidity, since their Brønsted/Lewis acid ratio as well as the strength of the acid sites can be finely controlled by the preparation conditions.

In fact, WO_x based catalysts are derived from heteropolyacids, which have been also studied with success for ethanol dehydration. Heteropolyacids, such as tungstophosphoric acid ($H_3PW_{12}O_{40}$, TPA), tungstosilicic acid ($H_4SiW_{12}O_{40}$, STA), and molybdophosphoric acid ($H_3PMo_{12}O_{40}$, MPA) were tested in ethanol dehydration. The best results were obtained with TPA, leading to ethylene yields of ca. 77% (88% ethanol conversion and 87% ethylene selectivity) at 250 °C.[42] Ethylene selectivity using STA and MPA as catalysts were ca. 61 and 27%, respectively. The presence of a small quantity of water (10% of water in ethanol) led to a reduction of the catalysts activity.[42] This is a general problem in ethanol dehydration, since water will compete with ethanol for the active sites. Even though the ethylene yield obtained with TPA as catalyst was similar to that obtained using alumina, the reaction temperature was significantly lower. When the temperature is further reduced to 180 °C and TPA is used as catalyst, the main product was diethyl ether (74% selectivity at 58% conversion). Between the heteropolyacids studied, STA was reported to be the most stable.[42]

In another study, a series of potassium tungstophosphoric acids with the composition $K_xH_{3-x}PW_{12}O_{40}$ (x = 0, 1, 1.5, 2, and 3) were supported on silica and tested as catalyst for ethanol dehydration.[43] For all values of "x", ethanol was fully converted, however, at low temperatures (200 °C), only catalysts with at least one proton in its structure (x = 0, 1 and 2) reached full conversion (selectivities were not reported).[43] From these results, it can be concluded that both Lewis and Brønsted acid sites are active in ethanol dehydration; however, strong Brønsted acids catalyze the reaction at lower temperatures. When the protons of TPA were exchanged with silver ($Ag_3PW_{12}O_{40}$), the catalyst was shown to achieve ethylene yields above 95% at 200 °C.[44] The silver provides redox sites in this catalyst and, under certain reaction conditions, the catalyst is active in dehydrogenation, which is confirmed by the formation of acetaldehyde.[44] Although $Ag_3PW_{12}O_{40}$ has shown promising results, the catalyst is not stable at the reaction temperature and this seems to be a general statement for many heteropolyacids. This class of catalyst presents strong Lewis and Brønsted acid sites, however, questions related to catalyst stability, resistance to water, and effect of the support remain unanswered. Up to now, the results presented for heteropolyacids do not justify considering this catalyst as a replacement for alumina.

By far, the most promising catalysts for replacing alumina as commercial catalyst for ethanol dehydration are zeolites. ZSM-5 with SiO_2/Al_2O_3 ratios of 20-25 has been extensively studied, reaching ethylene yields higher than 95% at temperatures as low as 180 °C.[38] For lower aluminum contents (e.g., SiO_2/Al_2O_3 = 90), temperatures above 300 °C are required.[38,45,46] The stability of this catalyst is not particularly high, and a sharp deactivation is observed (which is comparable with the alumina deactivation). The catalyst deactivation is usually attributed to coke formation, that shields the acid sites,[38,45] but its activity can be fully regenerated by calcination. The formation of coke is due to the high strength of the acid sites, which lead to ethylene oligomerization and subsequently to carbon deposits. The use of small fractions of water mixed into the ethanol feed diminishes the activity of the catalyst since it decreases the surface acid site strength, and therefore, also minimizes the coke formation.[45] A synthetic alternative to improve the ZSM-5 stability involves the modification with 3 wt.% of lanthanum, which doubles the catalyst life time by decreasing coke formation and can be fully regenerated by calcination.[47] The effect of the lanthanum is not completely clear, but it leads to a decrease in the strength of the ZSM-5 acid sites, which should be the reason for a lower formation of carbon deposits. Similar results have been observed for ZSM-5 modified with lanthanum phosphate.[48] Nanosized ZSM-5 has also shown a slower deactivation compared to regular ZSM-5, which has been attributed to a lower residence time of the product (ethylene) inside the catalyst pores, minimizing oligomerization reactions.[49]

Other zeolites, such as mordenite, beta, and Y have also been tested as catalysts for ethanol dehydration, reaching ethylene yields of > 99, 57, and 71% at 180 °C (250 °C for Y zeolite), respectively.[38] Mordenite with SiO_2/Al_2O_3 ratios of 25 and 90 presented similar performance, however, the catalyst with a lower aluminum loading (SiO_2/Al_2O_3 = 90) presented slower deactivation.[38] The silicoaluminophosphate SAPO-34 and its parent form modified with nickel, Ni-SAPO-34 were compared with alumina and ZSM-5 in the dehydration of ethanol into ethylene.[35] Ni-SAPO-34 led to ethylene yields similar to ZSM-5, while the SAPO-34 performance is similar to alumina. The deactivation of the SAPO-34 catalysts was considerable slower than alumina and ZSM-5.[35] The main drawback of SAPOs is the high working temperature required (350 °C).

Zeolites are the most promising catalysts for industrial application in ethylene synthesis from bioethanol, since they are more selective than alumina and allow reaction at much lower temperatures. Zeolites are commercially available and already used in numerous industrial processes, including the traditional refinery. Yet, there are questions to be addressed related to the zeolite stability. It

Table 1. Example of catalysts used for the ethanol dehydration into ethylene

Catalyst	Temperature / °C	Conversion / %	Selectivity / %	Yield / %	Ref.
γ-Al_2O_3	450	85.6	ca. 92	78.7	35
10% Ti/γ-Al_2O_3[a]	410	ca. 90	98.7	ca. 89	37
γ-Al_2O_3[a]	460	ca. 90	ca. 90	ca. 81	37
SiO_2-Al_2O_3	300	–	–	76.7	38
$45Mn_2O_{3:4}5Fe_2O_3:10SiO_2$	400	–	–	66	39
V-MCM-41[b]	400	99	67	66	40
WO_x-silicate (W/Si = 0.16)	350	ca. 92	> 99	ca. 92	41
$H_3PW_{12}O_{40}$	250	ca. 88	ca. 87	ca. 77	50
$Ag_3PW_{12}O_{40}$	200	–	–	95	44
ZSM-5 (SiO_2/Al_2O_3 = 25)	180	–	–	95.9	38
La-ZSM-5	260	98.5	99.5	98	47
Mordenite (SiO_2/Al_2O_3 = 20)	180	–	–	99.8	38
Mordenite (SiO_2/Al_2O_3 = 90)	180	–	–	99.9	38
Beta zeolite (SiO_2/Al_2O_3 = 25)	180	–	–	57.5	38
Y zeolite (SiO_2/Al_2O_3 = 5.5)	250	–	–	71.3	38
SAPO-34	350	91.2	94.3	86	35
Ni-SAPO-34	350	93.4	98.8	92.3	35

[a]Catalysts tested in a microchannel reactor; [b]ethanol/oxygen ratio of 2.

seems that controlling the acid strength is a key factor for the selectivity of the catalyst. Another point to be addressed is related to the presence of water in the reaction feed, which is inevitable for ethanol. Even though small amounts of water in the feed (5-10%) reduce coke formation, the hydrothermal stability of these aluminosilicates is not particularly high. Therefore, systematic studies on the catalyst performance and stability have to be carried out. The performances of selected catalysts for ethanol dehydration into ethylene are summarized in Table 1.

As discussed before, neat ZSM-5 at low temperatures (< 250 °C) is selective to convert ethanol to ethylene. However, at temperatures around 400 °C, ZSM-5 further converts ethylene into heavier hydrocarbons, forming, for example, the so-called BTX (benzene, toluene and xylene) with selectivity of 52.9% (30.9% xylenes, 18.9% toluene, and 3.1% benzene).[51] Ethylene (or butene) formed from ethanol can undergo different reactions, such as oligomerization, aromatization, cracking, transmethylation, etc., forming a large number of saturated and unsaturated hydrocarbons with different carbon chain length. One of the challenges of this process is to tailor the catalyst composition in order to control the product distribution.

Other zeolites, such as USY, mordenite and beta, even at 400 °C, still display selectivities of 86-96% for ethylene.[51] In fact, ZSM-5 is the most studied catalyst for the direct transformation of ethanol into hydrocarbons. The Si/Al ratio has an important effect on the product distribution, as shown in Figure 7.[52] After 1 h on stream, the major products are hydrocarbons with carbon length between C_5 and C_{11} (which could be used as gasoline), followed by C_3-C_4.[52] The selectivity for the C_5-C_{11} fraction is shown to increase with increasing Si/Al ratios, reaching a maximum at Si/Al = 140. After 16 h on stream, ZSM-5 with a Si/Al ratio of 16 and 40 present the highest selectivity for the C_5-C_{11} fraction, i.e., ca. 70%, and ca. 28% for the C_3-C_4 fraction.[52] However, ZSM-5 with a Si/Al ratio of 40 is more selective to paraffins, while ZSM-5 with a Si/Al ratio of 140 is more selective to olefins. By increasing the Si/Al ratio, the selectivity for the lower fraction increases after 16 h on stream, by expense of the heavier fraction, and olefin formation becomes predominant.[52]

Comparison of the methanol to gasoline (MTG) and the ethanol to gasoline (ETG) processes using ZSM-5 as catalyst shows that both processes lead to the same products. However, in the ETG process the compounds trapped inside the zeolite pores are ethyl-substituted aromatics instead of methyl-substituted aromatics common for the MTG process. An assumption is that the heavier products trapped inside the zeolite pores in the ETG process turn more easily into coke, which blocks the zeolite active sites, leading to a faster catalyst

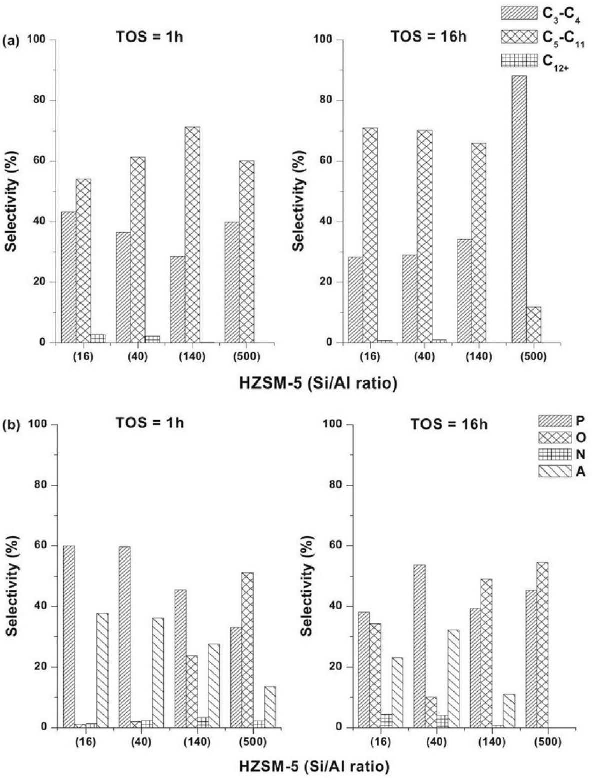

Figure 7. Product distribution as a function of the ZSM-5 Si/Al ratio (a) carbon chain length and (b) type of hydrocarbons [paraffins (P), olefins (O), naphthenes (N), and aromatics (A)]. TOS stands for time on stream. Reaction temperature 350 °C. Reprinted from reference 52. Copyright 2012, with permission from Elsevier.

deactivation.[53] Study of the coke formation shows that the products trapped inside the zeolite pores (mainly alkylbenzenes and akylnaphthalenes) undergo radical reactions, leading to bulkier molecules.[54,55] As mentioned before, the presence of water in the feed attenuates coke formation.[56] However, ZSM-5 does not have a particularly high hydrothermal stability and in the presence of water, catalyst degradation is observed. At high water concentrations (for example 1/1 ethanol/water), the catalyst cannot be regenerated.[57]

A benchmark study showed that modification of ZSM-5 with metal ions affects the product distribution in the ethanol to hydrocarbon reaction.[51] For ZSM-5 ($SiO_2/Al_2O_3 = 29$) containing Mg, Co, Cu, or Re, ethylene remains the main product, indicating that these metals present no activity for converting ethylene. On the other hand, when ZSM-5 is modified with Fe, Ga, Ru, Rh, Pd, Ir, Pt or Au, the main products are BTX (benzene, toluene and xylene). For all these catalysts, xylene is the major product, followed by toluene, while benzene selectivity if low. Ga-ZSM-5 is the most selective catalyst for BTX, reaching 73.6% (46.6% xylenes, 24.5% toluene and 2.5% benzene), but coke formation is considerably high. After reaction, the catalyst had its mass increased by 5.5% due to carbon deposits.[51] With this respect, the Au-ZSM-5 catalyst presented a lower carbon deposition (2.5 weight gain due to coke) and its selectivity for BTX was still considerably high, i.e., 56.8% (30.5% xylenes, 22% toluene, and 4.3% benzene).[51] ZSM-5 modified with iron also presented low coke formation, however the catalyst performance was similar to neat ZSM-5.[51,58] However, using Fe-ZSM-5 and co-feeding hydrogen to the reactor, the selectivity for heavier hydrocarbons increased.[58] The reduction of coke formation in Fe-ZSM-5 has been attributed to modifications of the zeolite surface acidity.[59,60]

Between the several possible products obtained by the reaction of ethanol on ZSM-5 at high temperatures, one has received special attention in the literature: propylene. Propylene is the second most important chemical commodity produced from petroleum and is used as feedstock for chemicals and polymers.[61] Propylene is commercially obtained as a byproduct of ethylene and its production ranges around 30 million tons *per* year,[61] in a market that moved ca. 90 billion dollars in 2008.[62] Braskem, for example, is already investing in polypropylene production from bioethanol-derived propylene. In general, ZSM-5 with high Si/Al ratios are more selective for propylene. For example, ZSM-5 with a SiO_2/Al_2O_3 ratio of 80 leads to a propylene yield of ca. 30%, however after 4 h on stream, the propylene yield starts to drop due to catalyst deactivation.[63] Similar results have been obtained for ZSM-5 with a SiO_2/Al_2O_3 ratio of 280, while lower propylene selectivity is observed for ZSM-5 with a SiO_2/Al_2O_3 ratio of 40.[64] ZSM-5 (SiO_2/Al_2O_3 ratio of 80) modified with Zr,[63] Sr,[65] and P[66] also showed propylene yields of ca. 30%, but the catalyst showed higher stability compared to plain ZSM-5. A mechanistic study proposed that ethanol is first dehydrated to ethylene, which then forms $CH_2{}^*$ carbene species via a π-complex with the ZSM-5 surface. The carbene reacts with an ethylene molecule to form propylene.[67] It has also been proposed that ethylene oligomerizes to polyenes, which undergo acid catalyzed cracking, forming propylene as one of the products.[68]

Since the propylene production from ethanol using ZSM-5 as catalyst is limited to ca. 30% yield, different reaction routes have been studied. For example, ethylene from ethanol is dimerized to butene (Dimersol process). A mixture of ethylene and butene is then subjected to metathesis to form propylene.[69] An example of a metathesis catalyst is the FSM-6 mesoporous silica impregnated with nickel, which leads to a ca. 30% propylene yield at 400 °C.[69]

An alternative reaction pathway involves the dehydrogenation of ethanol to acetaldehyde, which is then converted to acetone. Acetone can be reduced to isopropanol, and the alcohol dehydrated to propylene.[70] This reaction pathway has been gaining attention in recent years. Scandium-modified indium oxide has shown remarkable selectivity for propylene from ethanol, reaching up to 61.8% yield at 550 °C. The main byproducts were butane (14.7%), ethylene (1.2%), acetone (0.1%) and acetaldehyde (2.9%). Bare indium oxide led to only 34% propylene yield.[70] Study of the reaction pathway revealed that it proceeds through acetaldehyde, acetic acid, and acetone as intermediates, with carbon dioxide and ethyl acetate being generated as byproducts. It was found that both acetaldehyde and acetic acid can be converted to acetone. The role of scandium was found to be mainly preventing the reduction of indium oxide, thus prolonging its stability.[71] Indium, however, has a prohibitive price for the application as catalyst for the production of commodities. Other catalysts have been tested, but propylene yields were lower. For example, ceria modified with Y and Nb reached only ca. 32% propylene yield.[72] For a selective propylene production, the reaction pathway though acetone seems to be the most promising, however, catalyst research and development is needed, mainly to further improve the catalyst performance and stability. Further elucidation of the reaction mechanism is also needed.

Another important drop-in chemical produced from ethanol is butadiene. This diene is one of the most important platform chemicals obtained in the petrochemical industry, reaching 9 million tons in 2007.[16,73] Commercially, butadiene is obtained as a byproduct of the ethylene synthesis.[73] In the last years, an increase in butadiene production costs has been observed,[16] and therefore the interest in the production from ethanol has emerged.[16] Recently, two excellent reviews have appeared on the ethanol conversion into butadiene,[16,74] and therefore the discussion in this text will be more practical.

The one-pot process for butadiene synthesis from ethanol is the most studied (Figure 8),[75] since it is more appealing for a large-scale production. The first catalyst for this process was developed and patented in the early 1930 by Sergei Lebedev, and the process was named after him.[16] One decade later, Giulia Natta, identified the catalyst being a mixture of silica and magnesia.[76] Surprisingly, after almost one century, the best catalysts for this reaction are still based on MgO/SiO_2, as shown in Table 2.[16] There is, however, a lack of understanding of the reaction mechanism and of how each of these oxides contributes to the overall performance of the catalyst. For example, studies from the 1970s indicate that the catalyst is extremely sensitive to the preparation method.[75,77-79] When the MgO/SiO_2 catalyst is prepared by wet kneading, it leads to a butadiene yield of 42%. On the other hand, a simple physical mixture of MgO e SiO_2 yields only a few percent of butadiene, similar to the yield obtained with pure MgO.[79] This behavior is justified by the fact that the wet-kneading preparation leads to a higher interaction between the silica and magnesia particles,[80] which is apparently important for the catalyst selectivity. However, when MgO/SiO_2 is prepared by sol-gel methods, which supposedly maximize the silica-magnesia interaction, the butadiene yield is not higher than 10%. Furthermore, variations in catalyst performance are observed even using the wet-kneading method. For example, if the silica used was obtained by the sol-gel method, the optimal $MgO:SiO_2$ ratio is 1:1, while it is 3:1 when Aerosil silica is used.

Therefore, further studies are needed to identify the actual structure and surface properties of the MgO/

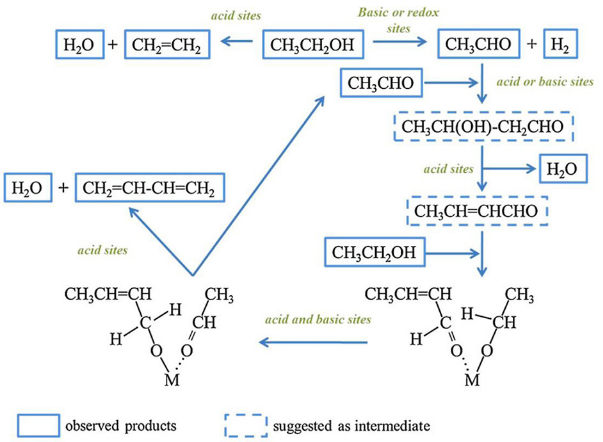

Figure 8. Proposed reaction pathway for ethanol transformation into butadiene. Reprinted from reference 75. Copyright 2012, with permission from Elsevier.

Table 2. Some selected catalysts used for direct ethanol conversion into butadiene. Reprinted/adapted from reference 16. Copyright 2013 by John Wiley Sons, Inc.. Reprinted by permission of John Wiley & Sons, Inc.

Catalyst	Temperature / °C	Yield / %	Reference
$MgO/SiO_2/Cr_2O_5$ (3/2/0.11)	415	41.9	76
$MgO/SiO_2/Cr_2O_3$ (59/39/2)	425	39	81
Mg/sapiolites	300	33.4	82
$NiO/MgO/SiO_2$ (10/27.9/62.1)	280	53	83
MgO/SiO_2 (1/1)	350	42	77
MgO/SiO_2 (1/1) + 0.1% K_2O	350	70	77
MgO/SiO_2 (1/1) + 0.1% Na_2O	350	87	77
MgO/SiO_2 (0.83/1)	350	16	79
Zr(1.5%), Zn(0.5%)/SiO_2	375	11.5	84
Cu(1%), Zr(1.5%), Zn(0.5%)/SiO_2	375	30.1	84
5% CuO em MgO/SiO_2 (2/1)	350	58.2	75
5% ZnO em MgO/SiO_2 (2/1)	350	52.4	75
5% Ag em MgO/SiO_2 (2/1)	350	56.3	75

SiO_2 catalyst in order to understand the real role of each of the oxides in the ethanol conversion to butadiene. This knowledge will be useful to design new and high-performance catalysts for the reaction.

An alternative for the one-pot conversion of ethanol into butadiene is the two step process in which ethanol is first dehydrogenated to acetaldehyde, which is then reacted with ethanol to give butadiene. The reaction mechanism is believed to be the same observed to the one-pot reaction. Therefore, differences between the one pot and the two-step reaction are mainly related to the process itself. This two-step process was commercial in Brazil starting in 1967 at the former Companhia Pernambucana de Borracha Sintética (COPERBO) for the production of rubber with 27,500 tons *per* year capacity and 70% yield.[85] COPERBO shut down the butadiene plant in the 1980th, due to increasing exportation of sugar cane syrup from Brazil and the importation of rubber produced at lower cost from non-renewable sources.

3. Oxygenated Chemicals: Acetaldehyde, Acetic Acid, Ethyl Acetate and Butanol

Acetaldehyde, acetic acid, and ethyl acetate have industrial importance and are typically derived from petroleum or natural gas. The industrial production of these three organic molecules are interconnected, as shown in Figure 9.[86,87]

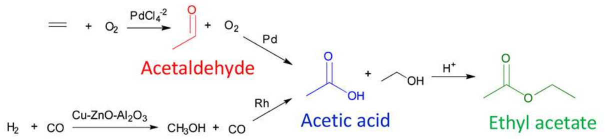

Figure 9. Commercial reaction pathway for acetaldehyde, acetic acid and ethyl acetate production.

Acetaldehyde production in 2003 reached 1 million tons and the commercial process for ethylene oxidation is the so-called Wacker process.[16] The main use of acetaldehyde is the production of acetic acid and esters (mainly ethyl acetate and vinyl acetate), however, other important products such as pyridine and pentaerythritol can be obtained.[87] Acetaldehyde was, for several years, the main precursor for acetic acid, however, nowadays this ester is mostly produced by methanol carbonylation (Monsanto process).[86] The worldwide acetic acid production reached 5 million tons in 2006, and its main use is the production of vinyl acetate and acetic anhydride. Furthermore, acetic acid can also be converted to ethyl acetate or other esters by Fisher esterification.[16,86] Ethyl acetate is an important low-toxic solvent that can replace aromatic solvents in paints and inks.[88] Moreover, it can be used in the pharmaceutical, cosmetics and food industry.[89] The worldwide ethyl acetate production reached 1.3 million tons in 2004 and Rhodia-Brazil is one of the largest producers.[89]

Acetaldehyde and ethyl acetate can be obtained from ethanol by two different routes (Figure 10). In an inert atmosphere, ethanol can be dehydrogenated to acetaldehyde using a redox catalyst. In the presence of a bifunctional redox/acid catalyst, acetaldehyde couples with ethanol to produce ethyl acetate and hydrogen. Under aerobic conditions and in the presence of a redox catalyst, ethanol can be oxidized to acetaldehyde, followed by a second oxidation to acetic acid. If the catalyst also has an acidic functionality, acetic acid readily esterifies with ethanol to ethyl acetate. In the aerobic oxidation, water is formed. The great advantage of the reaction at inert atmosphere is the production of hydrogen, a valuable compound in chemical and petrochemical industry. On the other side, the reaction under aerobic atmosphere can be carried out at lower temperature, and studies have shown that it has one third of the energetic costs and CO_2 emission, compared to the reaction under an inert atmosphere.[90]

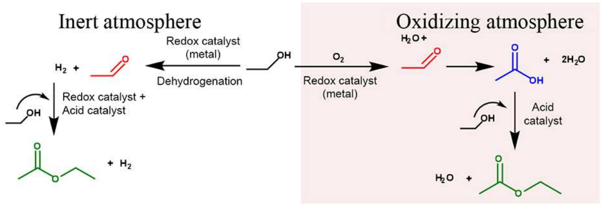

Figure 10. Reaction pathways for ethanol conversion into acetaldehyde, acetic acid, and ethyl acetate.

The dehydrogenation of ethanol to acetaldehyde and subsequently to ethyl acetate has been studied using mainly Cu, Pd and Au based catalysts on different supports. The support, in fact, has an important role in the product distribution, i.e., in a higher selectivity for the aldehyde or the ester. For example, using Cu supported on silica as catalyst, a 87% selectivity for acetaldehyde and only 5.3% selectivity for ethyl acetate has been observed at 41% ethanol conversion at 225 °C (other byproducts include methyl ethyl ketone, butanol, crotonaldehyde, and ethyl ether).[91,92] Using Cu supported on monoclinic zirconia, the selectivity for acetaldehyde and ethyl acetate at 43% ethanol conversion was found to be, respectively, 23 and 73% at 200 °C.[92] Cu^+ species were prevalent over Cu^0 on the metal surface of the Cu/SiO_2 catalyst and the ionic species is more selective to acetaldehyde formation. Using Cu/ZrO_2, the support leads to an increase in the metal electron density, and therefore its surface is dominated by Cu^0 species.[92,93]

Figure 11 shows a proposed reaction scheme for the Cu/ZrO_2 catalyst. Ethanol is activated to $CH_3CH_2O^*$ by Cu^+ sites or on the zirconia surface. When this activation takes place on the Cu^+ sites, the ethanol can be dehydrogenated and transferred to Cu^0 sites as an activated species $CH_3(C^*)O$. This species would undergo coupling reaction with $CH_3CH_2O^*$ found on the Cu^+ or zirconia sites. As already mentioned, the copper surface (when supported on zirconia) is poor in Cu^+, which is mainly involved in dehydrogenation reaction. Therefore it is highly probable that the coupling reaction happens on the surface between the metal and support.[93] This is endorsed by the fact that if the support does not activate ethanol (such as silica), the whole reaction takes place on the Cu/Cu^+ species, which causes a poor ethyl acetate selectivity (ca. 5%).[92,93]

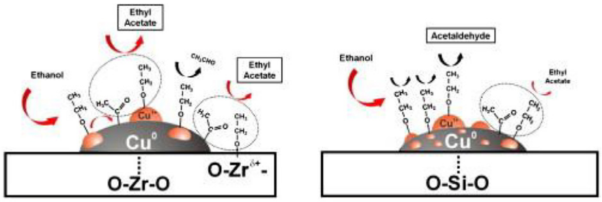

Figure 11. Scheme of the proposed reaction route on the Cu/ZrO_2 and Cu/SiO_2 surfaces. Reprinted from reference 92. Copyright 2012, with permission from Elsevier.

Palladium supported in several metal oxides (such as zinc, tin, silicon, aluminum, and tungsten) has been used for ethanol dehydrogenation.[94] Using Pd/ZnO, 40.9% selectivity for acetaldehyde and 48.5% selectivity for ethyl acetate (40.4% ethanol conversion) was observed at 250 °C.[94] Contrarily, $PdZnO/SiO_2$ was more selective for acetaldehyde, reaching 95.6% at 21.1% of ethanol conversion.[94] In studies using $PdO/ZnO/Al_2O_3$ as catalyst in an inert atmosphere, selectivities of 90.1% for acetaldehyde and only 1.6% for ethyl acetate (16.8% ethanol conversion) were achieved at 175 °C.[95] This catalyst, therefore, is efficient in the dehydrogenation of ethanol, but not in the promotion of the acetaldehyde and ethanol coupling to ethyl acetate. When monoclinic zirconia was physically mixed with this catalyst, selectivities to acetaldehyde and ethyl acetate were, respectively, 51.9 and 42.9% (33.4% ethanol conversion) at 175 °C.[95] Similarly, when a Zn-Zr-Al mixed oxide catalyst was used for this reaction at 220 °C, selectivities to acetaldehyde and ethyl acetate were, respectively, 5.7 and 85% at 66% ethanol conversion.[96] However, to achieve such high ethyl acetate selectivity, the support has to be neutralized with sodium or potassium carbonate. Gold supported on silica showed high selectivity to acetaldehyde in an inert atmosphere.[97] At 250 °C, for example, selectivity to acetaldehyde was close to 100% at ca. 12% ethanol conversion. To achieve high yields, high temperatures have to be used, such as 400 °C, giving acetaldehyde selectivity above 90% at an ethanol conversion of ca. 90%.[97] Studies of the gold particle size showed that ca. 10 nm is the optimal diameter for this reaction.[97]

When the ethanol conversion is carried out under aerobic conditions, acetic acid is also formed as a product (Figure 10). Using PdO/ZrO_2 as catalyst leads to selectivities of 25.1, 32.0 and 34.5%, respectively, for acetaldehyde, acetic acid, and ethyl acetate (32.4% ethanol conversion) at 175 °C.[95] When additional zirconia is physically mixed with the catalyst, there is an increase of the acid sites concentration, leading to the esterification of the acid to ethyl acetate. In this case, the selectivies are 23.9, 2.5 and 63.3%, respectively, for acetaldehyde, acetic acid, and ethyl acetate (41.5% ethanol conversion).[95] Titanium pyrophosphate (TiP_2O_7) modified with Pd showed high activity in ethanol conversion (96%), and the selectivies for the main products were 37.1% of acetic acid and 46.7% of ethyl acetate at 200 °C.[98] Pd supported on Y zeolite showed 50% selectivity to ethyl acetate and 7% to acetic acid (83% ethanol conversion) at 110 °C.[99] These results are particularly interesting, since the reactions were carried out at low temperature. Gold catalysts supported in several metal oxides were tested for ethanol conversion. A recent report shows that 1% gold supported on different oxides, such as molybdenum, lanthanum, strontium, aluminum, titanium, tin, zinc, vanadium, and copper, can reach acetaldehyde yields above 60% at temperatures between 180 and 280 °C, depending on the support. Interestingly, using these catalysts, acetaldehyde was not oxidized to acetic acid.[100] Contradictory results can be found in the literature on the selectivity of gold catalysts for acetaldehyde. For example, one report indicates over 85% acetic acid yield for 1% gold on TiO_2, Al_2O_3 or ZnO at 150 °C.[101] Similarly, 0.07% gold on $MgAl_2O_4$ led to an 83% acetic acid yield at 180 °C.[102] However, Au (0.5%) on SiO_2 showed high selectivity for acetaldehyde and the catalyst performance was dependent on the gold particle size.[103] The optimal particle size was found to be ca. 6 nm, and the acetaldehyde and ethyl acetate selectivities at 200 °C were, respectively, 75 and 20% at 45% ethanol conversion.[103] Increasing the gold loading to 5% on silica and reducing the reaction temperature to 100 °C, an increase in the ethyl acetate selectivity was observed, reaching 90% at 39% ethanol conversion.[103]

1-butanol is an important chemical which is commercially manufactured by propylene hydroformylation (oxo process) with subsequent hydrogenation of the aldehyde formed, using metal catalysts such as Co, Rh, or Ru.[104] In 2002, the global production of this alcohol was around 5.1 million

Table 3. Selected catalysts used for direct ethanol conversion into acetaldehyde, acetic acid, ad ethyl acetate

Catalyst	Atmosphere	Temperature / °C	Product / (% yield)	Reference
Cu/SiO_2	Inert	225	Acetaldehyde (35.7) Ethyl acetate (2.2)	93
Cu/ZrO_2	Inert	200	Acetaldehyde (9.9) Ethyl acetate (31.4)	93
Cu-Zn-Zr-Al-O	Inert	220	Acetaldehyde (3.8) Ethyl acetate (56.1)	96
$PdZn/SiO_2$	Inert	250	Acetaldehyde (20.2)	94
Pd/ZnO	Inert	250	Acetaldehyde (19.6) Ethyl acetate (16.5)	94
$PdO/ZnO/Al_2O_3$	Inert	175	Acetaldehyde (15.1) Ethyl acetate (0.3)	95
$PdO/ZnO/Al_2O_3 + ZrO_2$	Inert	175	Acetaldehyde (17.3) Ethyl acetate (14.3)	95
Au/SiO_2	Inert	250	Acetaldehyde (ca. 12)	–
Au/SiO_2	Inert	400	Acetaldehyde (ca. 80)	–
PdO/ZrO_2	Oxidant	175	Acetaldehyde (8.1) Acetic acid (10.4) Ethyl acetate (11.2)	95
$PdO/ZrO_2 + ZrO_2$	Oxidant	175	Acetaldehyde (9.9) Acetic acid (1.0) Ethyl acetate (25.8)	95
$TiPd_{0.03}PO_x$	Oxidant	200	Acetic acid (35.6) Ethyl acetate (44.8)	98
Pd/Zeolite Y	Oxidant	110	Acetic acid (5.8) Ethyl acetate (41.5)	99
Au/MoO_3	Oxidant	240	Acetaldehyde (94)	100
Au/La_2O_3	Oxidant	260	Acetaldehyde (81) Ethylene (5)	100
Au/ZnO	Oxidant	180	Acetaldehyde (74) Acetic acid (15) Ethyl acetate (2)	100
Au/ZnO	Oxidant	220	Acetaldehyde (44) Acetic acid (46) Ethyl acetate (6)	100
Au/CuO	Oxidant	160	Acetaldehyde (80) Acetic acid (4)	100
Au/TiO_2 Au/Al_2O_3 Au/ZnO	Oxidant	150	Acetic acid (85-90)	101
$Au/MgAl_2O_4$	Oxidant	180	Acetic acid (83)	103
Au (0.5%)/SiO_2	Oxidant	200	Acetaldehyde (33.8) Ethyl acetate (0.9)	103
Au (5%)/SiO_2	Oxidant	100	Ethyl acetate (35.1)	103

tons. The main use of 1-butanol is for the manufacture of butyl acetate used as a solvent for monomers applied in surface coating. The acrylic ester of 1-butanol has also become increasingly important since it is used as essential component of latex.[104] Recently, the use of butanol as fuel has been proposed; however, it has a lower octane number than ethanol.

1-butanol can be produced from ethanol and two reaction pathways are proposed, as shown in Figure 12. One mechanism proposes a dimerization starting with the deprotonation of the C2 carbon of ethanol by the basic catalyst, followed by the coupling of this carbon with the C1 carbon of another ethanol. In the other mechanism, ethanol is dehydrogenated to acetaldehyde, which undergoes aldol-condensation with another acetaldehyde forming 3-hydroxybutanal, which undergoes dehydration and hydrogenation to form crotonaldehyde or butyraldehyde, which are hydrogenated to 1-butanol.[108,109]

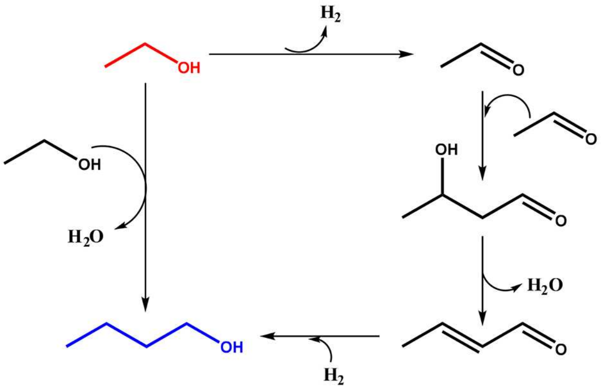

Figure 12. Reaction pathways proposed for the ethanol conversion into 1-butanol.

Mechanistic studies have shown evidences that the preferred mechanism is the ethanol dimerization.[105-107] However, the pathway involving the aldol condensation is still widely accepted, since the expected reaction intermediates are usually found in the reaction mixture.[108,109] In general, the direct transformation of ethanol into 1-butanol is catalyzed by solid bases. A benchmark study using typical solid bases, such as MgO, CaO, BaO, and γ-Al_2O_3, pure or impregnated with metals or mineral acids, has been carried out and MgO has been identified as the most selective catalyst, reaching 18.39% selectivity for butanol with 56.14% ethanol conversion at 450 °C.[106] Typical byproducts were acetaldehyde, butanal, crotonaldehyde, and 2-butanol. Hydroxyapatite, a calcium phosphate, has also been used as catalyst for the reaction. A non-stoichiometric hydroxyapatite with the formula $Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}\cdot nH_2O$ ($0 < z \leq 1$, n = 0-2.5) showed 76.3% selectivity for 1-butanol with 14.7% ethanol conversion at 300 °C.[110] At 350 °C under optimal conditions, 1-butanol yield reached 19.8%, which is significantly higher than the yield obtained with other calcium phosphate catalysts such as $Ca_4(PO_4)_2O$ (3% at 500 °C), or other base catalysts, such as hydrotalcite (12.2% at 350 °C).[110] Hydroxyapatite modified with strontium with a Sr/P ratio of 1.70 led to 11.3% ethanol conversion and 86.4% 1-butanol selectivity. Strontium affects both the densities of the relatively strong acid and basic sites, but the basic site density was found to be significantly higher than the acidic site density.[109] Furthermore, the strontium-modified hydroxyapatite has shown to inhibit coke formation, which could be another reason for its higher selectivity to 1-butanol.[111]

A MgO/Al_2O_3 mixed oxide with a 3:1 ratio led to ca. 33% ethanol conversion and ca. 36% selectivity to 1-butanol at 350 °C.[108] The modification of MgO/Al_2O_3 with a transition metal, such as Pd, Ag, Mn, Fe, Cu, Sm, or Yb improved the selectivity to 1-butanol. The Pd and Sm modified catalysts presented the best selectivities for 1-butanol, 72.7% at 3.8% ethanol conversion and 66.3% at 1.3% ethanol conversion at 200 °C, respectively.[112] The high selectivity of these two catalysts is probably due to the high concentration of basic and low concentration of acid sites. In fact, controlling the basic and acid sites loading has shown to be a major concern for the ethanol to 1-butanol conversion. Zirconia, for example, when impregnated with sodium ions, showed a reduction in the surface acidity and an increase in the basic sites concentration, which, consequently, led to an increase in the 1-butanol selectivity.[113] Importantly, the impregnation with sodium led to an increase in the activation energy for the dehydration reaction (to form ethylene) and a decrease in the activation energy for the dehydrogenation reaction. Ni and Co metal powders and Raney Cu were also shown to be active in the ethanol conversion into 1-butanol in the presence of sodium bicarbonate at 200 °C. The selectivities for 1-butanol were, respectively, 69, 50 and 65%, for ethanol conversions of ca. 4.1, 5.1 and 1.5%.[114] The ethanol conversion into 1-butanol needs serious development of the process design, catalyst development, and further mechanistic study have to be undertaken. It is certainly the poorest developed process discussed in this review.

4. Conclusions

Bioethanol has been used as fuel or fuel additive for several years, being the USA and Brazil responsible for 84% of the worldwide production. Ethanol has also shown to be a versatile platform molecule for the production of drop-in and oxygenated chemicals. Brazilian bioethanol production costs are the lowest in the world, and therefore this molecule can become a cost effective industrial intermediate. The challenges to increase the use of bioethanol as chemical feedstock are related to the development of novel high performance catalysts and to the costs of replacing well-established processes and products by biomass-derived products.

For the production of ethylene, propylene and larger hydrocarbons from ethanol, the ZSM-5 zeolite displays the best results; however, this catalyst still suffers of rapid deactivation and low hydrothermal stability. For propylene production, the alternative route having acetone as intermediate is quite promising; however, the best catalyst is based in indium oxide, which is cost-prohibitive.

For 1,3-butadiene synthesis from ethanol, the best performance is obtained with catalysts similar to the SiO_2/MgO catalyst developed almost one century ago. There is a lack of understanding of the chemistry on the surface of this catalyst. A deeper understanding of the SiO_2/MgO active sites will help to develop new catalysts for this process.

In an atom economy and process cost of view, there is a raising interest in producing oxygenated compounds such as acetaldehyde, acetic acid, ethyl acetate, and 1-butanol from ethanol. Acetaldehyde and ethyl acetate are produced from ethanol by aerobic oxidation or by dehydrogenation. Acetic acid is produced by aerobic oxidation. While acetaldehyde and acetic acid are obtained with high yields, ethyl acetate production still needs to be further developed. In all cases, bifunctional catalyst are needed and a better understanding of the role of support-metal interaction and interface is required. 1-butanol is produced from ethanol with low yields. The process requires both further investigation of the reaction mechanism and catalyst development. However, we believe that in the near future, ethanol will become an important feedstock for the economic production of a larger number of oxygenated chemicals and products.

5. Acknowledgements

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