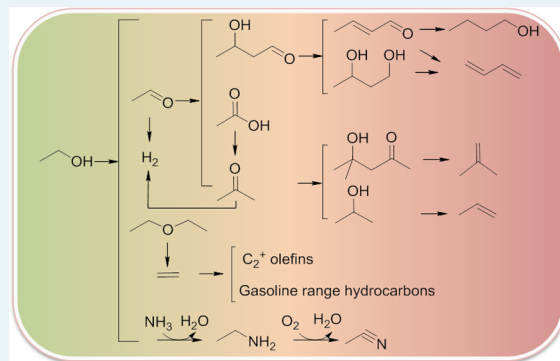


Recent Advances in Catalytic Conversion of Ethanol to Chemicals

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ABSTRACT: With increased availability and decreased cost, ethanol is potentially a promising platform molecule for the production of a variety of value-added chemicals. In this review, we provide a detailed summary of recent advances in catalytic conversion of ethanol to a wide range of chemicals and fuels. We particularly focus on catalyst advances and fundamental understanding of reaction mechanisms involved in ethanol steam reforming (ESR) to produce hydrogen, ethanol conversion to hydrocarbons ranging from light olefins to longer chain alkenes/alkanes and aromatics, and ethanol conversion to other oxygenates including 1-butanol, acetaldehyde, acetone, diethyl ether, and ethyl acetate.



KEYWORDS: ethanol, catalyst, ethylene, isobutene, 1-butanol, hydrogen, oxygenates, gasoline

1. INTRODUCTION

With increased demands for energy, stricter environmental regulations, and continued depletion of fossil feedstock, alternative and renewable energy resources have attracted increased interest in recent research.¹ Due to its renewable nature with low CO₂ emission,² biomass has been recognized as one of the most viable resources to produce biofuels, such as ethanol, which can be readily integrated into the infrastructure of the current end user (i.e., engine).

The conventional fermentation process is a commercial success in the conversion of edible biomass (sugar in Brazil and starch in the U.S.A.) to bioethanol.³ However, due to the competition with food and concerns about ecological systems,⁴ recent research has shifted toward bioethanol production from nonfood biomass feedstocks (i.e., lignocelluloses, hemicelluloses, and cellulose).^{5–7} Currently, bioethanol accounts for almost 90% of global biofuel production. Driven by the latest innovations,^{6,7} world ethanol production is increasing rapidly and anticipated to reach more than 30 billion gallons in 2017.⁸ Blending gasoline with bioethanol is compatible to conventional infrastructures (e.g., combustion engine) and has been mandated to substitute part of fossil fuels for transportation. However, this blending is only limited to 5–10 vol % (E5–E10) in the U.S.A. Based on energy independence and security act (EISA) of 2008, annual ethanol production in the U.S. will go beyond the blending wall of E10 around 2014 (Figure 1). On the other hand, higher blending ratios (e.g., E15–E20) and even ethanol-enriched fuels (e.g., E85) are not likely to be widely practiced, due to the concerns about fuel economy and potential side effects on the conventional end user (e.g., combustion engine). Therefore, it is anticipated that the excess ethanol will become available as a platform molecule for the production of value-added chemicals in the near future.

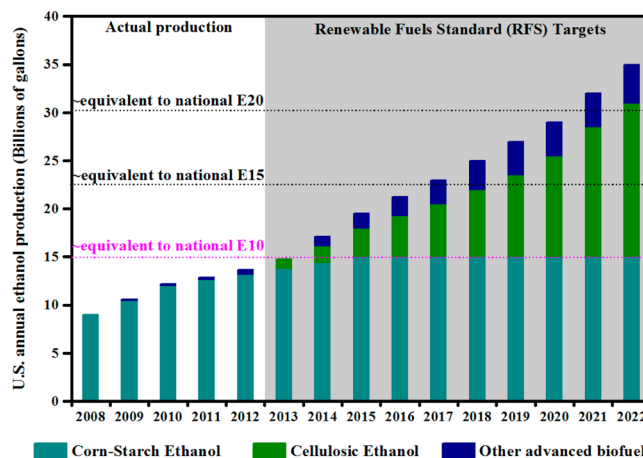


Figure 1. Renewable fuels standard (RFS2) vs EISA-mandated U.S. ethanol annual production since 2008.

Ethanol conversion to 1,3-butadiene in terms of its catalytic mechanism and thermodynamics has been extensively reviewed recently.^{9,10} Catalysts and catalytic processes for ethanol conversion to other chemicals such as hydrogen^{11,12} and small oxygenates like acetaldehyde^{9,13} and 1-butanol⁹ were also summarized. In this review, we provide a comprehensive review of catalytic conversion of ethanol to a variety of chemicals or fuels. Specifically, we briefly introduce the recent advances in the fundamental understanding of the ethanol steam reforming (ESR) process on a cobalt-based catalyst. Then, we extensively

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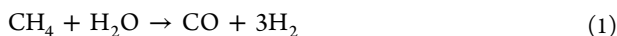
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review the ethanol conversion to hydrocarbons with a focus on the advances of catalysts and fundamental understanding of reaction mechanisms involved in these catalytic processes. Ethanol conversion to other small oxygenates such as 1-butanol, acetaldehyde, acetone, acetic acid, and so forth is also covered in the last parts of the paper. The main purpose of this review paper is to provide a state-of-the-art fundamental understanding of ethanol conversions, and while doing so, to identify a prospective research direction for various reactions.

2. ETHANOL STEAM/AUTOTHERMAL REFORMING TO HYDROGEN FUEL

Hydrogen is a clean energy carrier, which can be used for proton exchange membrane fuel cells (PEMFC) with water being the only product.^{14,15} Today, ~50% global hydrogen production is from steam methane reforming (SMR, eq 1). SMR requires a high temperature (700–1100 °C) steam reforming process combined with a low temperature (200–400 °C) water gas shift (eq 2) to achieve high hydrogen yield. Compared to the SMR, ethanol steam reforming (ESR, eq 3) can be conducted at relatively low reaction temperatures (<600 °C).¹² More importantly, ethanol can be used as a hydrogen carrier for distributed hydrogen production from renewable biomass. It is noteworthy that, thermodynamically, steam reforming of ethanol can occur at temperatures as low as 227 °C (vs 527 °C for SMR),¹⁶ even though current investigations are still limited to a relatively high temperature range (i.e., >400 °C). Development of highly active and stable catalysts that can enable lower temperature ESR is still a major challenge to efficiently provide hydrogen source for on-board fuel cells.

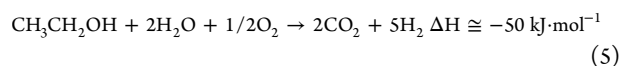
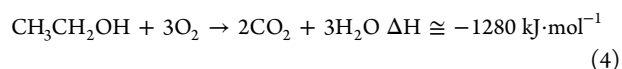


The ESR reaction mechanism and catalyst deactivation have been extensively studied over a variety of supported metal catalysts. Among the metals studied, noble metals exhibit high C–C cleavage activity but low hydrogen selectivity (<70%), due to the high methane selectivity at low reaction temperature (<500 °C).¹⁷ Base metals such as Co show both high C–C cleavage and low methane selectivity at low temperatures (450 °C).^{18,19} The hydrogen selectivity could reach more than 90% with complete ethanol conversion at optimum conditions.¹⁹ However, catalyst deactivation due to coke formation has been identified as a major issue in ESR.²⁰

Numerous reaction pathways have been identified for ESR. Pathways depend on catalyst support, nature of the metal, metal particle size, oxidation state of metal, reaction conditions, and so forth, as summarized in recent reviews.^{11,12,15,20,21} More recent developments in in situ characterization techniques have provided further insight into the reaction mechanisms of ESR. For instance, for cobalt-based catalysts, the effects of reaction feed composition and support on the cobalt oxidation states and thus ESR reaction pathways have been explored by in situ or ex situ XRD, XPS, and XANES.^{22–24} It was found that the oxidation state plays a pivotal role in ESR. Co⁰ has been identified to be responsible for C–C bond cleavage, whereas Co²⁺ is active for an ethanol dehydrogenation and methanation reaction.²⁴ The oxidation state of cobalt was found to be dependent on the support under oxidative atmosphere,²⁴ which ultimately affects the catalyst activity and selectivity.²⁴ For

example, the facile oxidation of Co⁰ by water vapor on Co/ZrO₂ was found to be significantly suppressed with the addition of ZnO (ZnO promoted Co/ZrO₂), manifested by the ex situ XPS characterizations and further confirmed by the catalyst activity studies.²⁴ On the other hand, supports with high oxygen mobility, such as CeO₂, were found to facilitate the gasification of carbon species to inhibit coke formation. In addition, they were also found to facilitate the oxidation of Co⁰, resulting in the decreased activity for C–C bond cleavage.²⁵ Acetone has been identified as an intermediate in ESR, which is prone to coke formation.^{26,27} Our recent experimental and theoretical studies revealed that smaller cobalt particles can effectively dissociate water, leading to facile oxidation of CO/CH_x formed from acetone steam reforming and thus minimizing CO and methane selectivity with enhanced catalyst stability.²⁸

ESR is an endothermic reaction requiring intensive energy input during the operation, however ethanol partial oxidation (EPO) is exothermic albeit with a lower hydrogen yield (eq 4). With an appropriate O₂/ethanol ratio,²⁹ ESR combined with an EPO process (namely, autothermal reforming) provides a thermally neutral operation for hydrogen production (eq 5).³⁰ A thermodynamic analysis revealed that coking could be mitigated when the water/ethanol molar ratio is above 4. Cofeeding with oxygen during ESR also significantly mitigates the catalyst deactivation by suppressing the formation of carbonaceous species.^{29,31} Supported noble^{30,32} and non-noble^{33,34} catalysts have been studied in autothermal steam reforming of ethanol. It was found that both the catalysts and support play important roles in the autothermal steam reforming reactions.^{32,34} Deluga et al. reported an efficient Rh–CeO₂ catalyst, on which >95% ethanol conversion and >3 mols H₂ per reacted ethanol were achieved at a WHSV of ~175 g of ethanol/g of catalyst/h. No carbon formation was observed after 30 h of time-on-stream operation.³⁰ Laosiripojana et al. compared Ni/CeO₂ and Ni/Al₂O₃ catalysts for both ESR and oxidative steam reforming of ethanol at a steam/ethanol molar ratio of 3.³⁴ It was found that cofeeding oxygen significantly suppressed the coke formation on both catalysts. The best hydrogen yields were achieved at oxygen/ethanol (O/E) molar ratios of 0.4 and 0.6 over Ni/CeO₂ and Ni/Al₂O₃ catalysts, respectively. Higher O/E ratios resulted in decreased reactivity and selectivity via the proposed oxidation of Ni to NiO and H₂ to H₂O.³⁴ Ru-doped pyrochlore solid solutions (i.e., La₂Ce_{2-x}Ru_xO₇) were found to show better performances than Ru/CeO₂ in autothermal steam reforming of ethanol (H₂O/ethanol molar ratio = 3) at 600 °C. XPS and TPR studies revealed strong Ru–La and Ru–Ce interaction that lead to the facile reduction of both La and Ce species. La₂Ce_{1.8}Ru_{0.2}O₇ was found to be the optimized catalysts, with r_{H₂} = 2.01 × 10⁻³ mol s⁻¹ g_{cat}⁻¹ at C/O = 0.6,³² which is almost 2 times of that reported on Rh/CeO₂.³⁰



It should be mentioned that due to the relative high operation temperature (550–800 °C), reversed water gas shift is significant, and thus a mixture of H₂/CO is often obtained. A low-temperature section is preferred to achieve higher hydrogen yield via further water gas shift reactions.^{30,35} In addition, a

dedicated control of partial oxidation during the steam reforming is critical to avoid overheating or local hot spots in the reactions.³⁶

3. ETHANOL TO HYDROCARBONS

3.1. Ethanol Dehydration to Ethylene. As the simplest olefin, ethylene has a wide range of applications in society. For example, polymerization of ethylene can produce various polyethylene products, consuming almost half of the ethylene produced worldwide. Epoxidation of ethylene is another important industrial process, which produces ethylene oxide. With increased demand, global ethylene production has expanded from 107 million tonnes in 2005 to 141 million tonnes in 2011.

Currently, ethylene is mainly produced by steam cracking of light hydrocarbons from fossil feedstocks, and its price continuously increases due to the depletion of fossil resources. The climbing ethylene price and decreased bioethanol cost make bioethanol-to-ethylene conversion more attractive, especially from nonfood biomass feedstock. The overall ethanol to ethylene reaction is shown in eq 6.



3.1.1. Reaction Mechanism. Concerning the reaction mechanism, E1, E1cB, and E2 have been proposed for alcohol dehydrations (Figure 2), depending on the catalysts and

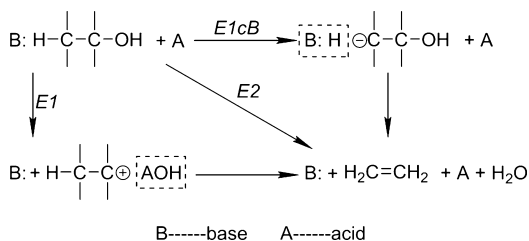


Figure 2. Proposed reaction mechanism for alcohol dehydration reactions.

reactants used.³⁷ The E1 mechanism normally proceeds via a carbocation intermediate on acidic zeolite catalysts, where protonation of alcoholic oxygen is followed by the C–O cleavage to form water and a carbocation intermediate. Then, deprotonation of the adjacent C of the carbocation intermediate on the base leads to the formation of alkene product. The E1cB mechanism, on the other hand, proceeds via a carbanion intermediate on base catalysts, on which C–H bond cleavage takes place first to form carbanion or alkoxy intermediates. This is followed by the elimination of the hydroxyl group on the acid to produce the alkene. The E2 mechanism involves a concerted elimination of both hydroxyl groups by acid and protons by the base. Both E1 and E2 reaction mechanisms have been proposed on secondary and tertiary alcohols (e.g., isopropanol, tert-butanol).^{38–40} Primary alcohols like ethanol typically undergo a concerted E2-type mechanism³⁷ due to the high energy barrier for the formation of primary carbocation intermediate.⁴¹ In addition, kinetic studies revealed that intermolecular dehydration to diethyl ether, followed by dehydration of diethyl ether to ethylene, is another parallel reaction pathway for ethanol to ethylene (Figure 3). Other side reactions include ethanol to acetaldehyde by dehydrogenation and to butylenes by further dimerization of ethylene.⁴² Recently, a combination of kinetic

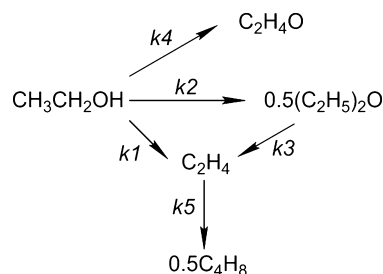


Figure 3. Proposed reaction network in ethanol conversion on alumina. Reproduced with permission from ref 42. Copyright 2011 Elsevier.

and simulation studies showed that ethylene could be formed on metal-based catalysts (i.e., Ni₂P) via a nondirect “rake” mechanism. In this mechanism, an adsorbed ethoxide species is first dehydrogenated to a surface acetaldehyde species that undergoes enolization to a vinyl alkoxide and subsequent hydrodeoxygenation.⁴³

3.1.2. Catalysts for Ethanol-to-Ethylene Reaction. Lab-scale ethanol dehydration to produce ethylene can be traced back to 1795,⁴⁴ with ethanol and sulphuric acid being mixed and heated. Due to its low yield and appreciable byproducts formation, this method has been replaced by a better process using phosphoric acid in either liquid form or dispersed on another solid support.⁴⁵ The gas phase catalytic ethanol dehydration to ethylene over heterogeneous catalysts did not raise much interest until the beginning of last century.^{46–48}

During the last few decades, ethanol dehydration to ethylene has been extensively studied over a variety of heterogeneous catalysts including alumina,^{37,42,46,49–51} zeolites,^{29,52–55} transition metal oxides,⁵⁶ and heteropolyacids.^{40,46,57} Among the catalysts studied, γ -Al₂O₃ and zeolites (e.g., ZSM-5) have received the most attention for their high activity and selectivity. Appreciable dehydrogenation was found on transition metal oxides.^{46,58} Sabatier et al. did a comparative investigation of ethanol dehydration on various oxide catalysts, among which ThO₂, Al₂O₃, and W₂O₃ gave the best performance in terms of ethylene selectivity.⁵⁸ In 1981, alumina-based catalysts (i.e., Syndol catalysts by Holcon SD) were commercially available for ethylene production from ethanol with high stability (>8 months) and one-pass conversion reaching up to 99% with ethylene selectivity up to ~97% at 318 °C. Using bioethanol (~10 wt % ethanol in H₂O) as a feedstock, water was shown to have a significant effect on the ethanol dehydration on alumina-based catalysts. Kochar et al. found that the presence of water, especially at high water content, significantly suppresses the ethanol conversion.⁵⁹ In a microchannel reactor and at lower temperatures (i.e., 380 °C), Chen et al. also found that ethanol conversion decreased from ~86% to ~65% as water content increased from ~5 wt % to 90 wt % over TiO₂/ γ -Al₂O₃, while diethyl ether selectivity increased at the expense of ethylene. However, the effect of water could be eliminated at high temperatures (>420 °C).⁵⁰ From the extensive research efforts,^{50,59,60} it is clear that the reaction temperature on alumina-based catalysts should be kept high (>400 °C, especially in the presence of high water content)^{42,50} to avoid the formation of diethyl ether and achieve high ethylene selectivity.^{42,50}

Zeolites have uniform pore structure, high surface area, and adjustable acidity, which have been widely used in alcohol dehydration reactions. It was found that dehydration reaction

Table 1. Catalytic Data for H-ZSM-5 Zeolite Treated with TFA (2 wt %)^a

catalyst	Si/Al	temp (°C)	WHSV (h ⁻¹)	conversion to hydroc.	product selectivity (%)			
					ethylene	propylene	butenes	others
H-ZSM-5/TFA	10	205	0.9	99.2	95.6	1.3	2.6	0.5
		205	2.4	98.2	99.0	0.3	0.7	
		205	4.5	90.0	99.7	0.1	0.2	
		200	1.1	97.3	99.9	0.1		
		190	0.9	94.8	99.1	0.3	0.5	
		185	1.0	77.3	99.8	0.1	0.1	
		180	1.0	73.9	99.2	0.3	0.4	
		170	1.0	41.9	99.1	0.6	0.3	
H-ZSM-5/TFA	21	200	1.0	95.8	97.7	1.1	0.9	0.3
		285	1.0	73.7	99.3	0.3	0.3	
		200	1.0	72.0	98.1	0.4	1.5	

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temperatures for ethanol are typically lower than 300 °C^{52–55,61–63} and even lower than 200 °C for some cases.⁵² High temperatures (>400 °C) favor the secondary reaction of ethylene (e.g., oligmerization, cracking) to form longer-chain hydrocarbons (e.g., from light olefins to gasoline), which will be discussed in sections 3.2 and 3.3. Among the zeolites studied, ZSM-5 or modified ZSM-5 have shown promising catalytic performance in ethanol dehydration to ethylene due to their surfaces' hydrophobic nature.^{6,52,53}

Similar to γ -Al₂O₃, ethylene is also proposed to form via a simultaneous parallel-consecutive reaction pathway (Figure 3) on zeolites, albeit at a lower reaction temperature. Nguyen and Le Van Mao et al. performed a systematic investigation of bioethanol-to-ethylene (BETE) on H-ZSM5 or modified H-ZSM5 catalysts.^{52,53,61,64} Over the steam-treated ZSM-5 or asbestos-derived ZSM-5, the reaction pathway was found to be dependent on reaction temperatures. Ethylene was mainly formed via a diethyl ether intermediate at lower temperatures (<270 °C, path 2 and 3 in Figure 3), whereas a direct ethanol-to-ethylene reaction pathway dominated at high temperatures (270–350 °C, path 1 in Figure 3).⁶¹

In addition to reaction temperatures, catalyst surface acidity also has a significant effect on catalytic performance in terms of ethylene selectivity and catalyst stability.⁶⁵ It was found that the presence of a high concentration of strong acidic sites, which exist at low Si/Al ratios, would catalyze the secondary reactions of ethylene (i.e., oligmerization, cracking, and coking) to form longer-chain hydrocarbons and even a carbonaceous deposit on ZSM-5 catalysts.^{53,66} Si/Al ratios between 35 and 55 have been suggested to provide high selectivity to ethylene while maintaining high activity and stability.⁶⁴ Surface acidity could also be adjusted using additives to achieve high ethylene selectivity and catalyst stability. The incorporation of Zn and Mg into ZSM-5 was found to lead to enhanced ethylene selectivity by suppressing the formation of other light olefins and diethyl ether.⁵² ZSM-5 (Si/Al = 50) synthesized using X-oil as a template was found to achieve an ethylene selectivity of ~99% even at a reaction temperature of 400 °C.⁶⁷ A recent study also found that the presence of weak acidic sites by addition of more than 3.4 wt % P on ZSM-5 leads to high ethylene selectivity over a wide range of reaction temperatures (300–440 °C). At a P loading of <3.4 wt %, longer chain hydrocarbons were found to form, especially at higher temperatures.⁶⁸ ZSM-5 grafted with trifluoromethanesulfonic acid (TFA) exhibited high activity and selectivity even at a reaction temperature as low as 170 °C (Table 1).⁵³ Similar

behavior was also observed on iron-doped ZSM-5, on which high loading of iron resulted in predominant ethylene production.⁶⁹ Other types of zeolites, such as β , have also been reported to possess moderate acidity, leading to high ethylene selectivity even at high temperatures (e.g., 370 °C).⁷⁰

Different from γ -Al₂O₃, addition of a suitable amount of water was found to increase ethylene selectivity and catalyst stability on ZSM-5 catalysts.^{54,61} A kinetic study by Phillips et al. revealed that water dramatically enhances the rate for direct ethanol-to-ethylene conversion (Figure 3, path 1) and the diethyl ether-to-ethylene reaction (Figure 3, path 3), whereas the ethanol-to-diethyl ether reaction rate is less affected (Figure 3, path 2). The enhanced selectivity and stability were attributed to the possible moderation of surface acidity by water, leading to the suppressed secondary reaction of ethylene toward longer-chain hydrocarbons and coke formation.⁵⁴ The modification of surface Brønsted acidity by water has been further confirmed by theoretical calculations.⁷¹

It should be mentioned that despite the uniform microporous structure, the large primary particle sizes of ZSM-5 (a few micrometers) typically present mass transfer issues for ethanol to access the acidic sites. Micropores can also be readily clogged by bulky molecules, leading to catalyst deactivation.^{72,73} Therefore, different strategies to improve mass transfer and to provide more accessible acidic sites have been attempted.^{74–77} Bi et al. found that decreasing the primary particle size of ZSM-5 results in enhanced catalyst activity and stability with ethanol conversion. Ethylene selectivity was maintained for over 630 h of time-on-stream using a 95 vol % ethanol feed.⁵⁵

3.2. Ethanol to C₃–C₄ Olefins. Similar to ethylene, C₃–C₄ olefins (i.e., propylene, 1- and 2-butene, isobutene, and butadiene) are widely used for the production of various industrial products. Current production of C₃–C₄ olefins still heavily relies on dwindling fossil resources, which is expected to be alleviated by developing renewable ethanol to C₃–C₄ olefins conversion methods.

3.2.1. Reaction Mechanisms. Ethanol conversion to C₃–C₄ olefins has been studied over a variety of catalysts mainly including zeolites/modified zeolites^{78–83} and (mixed) metal oxides.^{84–86} Different reaction mechanisms have been proposed depending on the catalysts employed. Over zeolite catalysts, the formation mechanism of C₃–C₄ olefins has been proposed to proceed via an ethylene intermediate, similar to that of methanol-to-gasoline (MTG).⁸⁷ Specifically, ethanol first dehydrates to form ethylene, followed by the transformation of ethylene to C₃₊ hydrocarbons (including C₃–C₄ olefins) via

Table 2. Product distribution in ethanol to hydrocarbons conversion over H-ZSM5 with varying Si/Al₂ ratios^a

	Si/Al ₂	S _{BET} (m ² g ⁻¹)	product distribution					
			C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ ^b	others ^c
H-ZSM5(30)	30	400	7.0	1.2	10.9	9.8	28.7	42.4
H-ZSM5(80)	80	425	16.5	0.6	16.9	6.9	23.5	27.0
H-ZSM5(280)	280	400	90.7	0.2	3.2	0.0	1.1	4.8

^aReproduced with permission from ref 82. Copyright 2009 Springer. Reaction conditions: catalyst, 0.2g; 0.1 MPa, 673 K; total flow rate, 25 mL min⁻¹; P_{C₂H₅OH} = 20 KPa; time-on-stream, 30 min. ^bThe C₄ included 1-butene, trans-2-butene, iso-butene, butane, and iso-butane. ^cThe others included carbon, CH₄, DEE, C₅₊ aliphatics, and aromatics.

acid catalyzed oligomerization–cracking and oligomerization–aromatization mechanisms.^{79,87} On supported metal oxides (NiO/MCM-41), ethanol dehydration to ethylene followed by ethylene dimerization, isomerization, and metathesis reaction mechanism was proposed on the layered nickel–silicate active phase.^{84,88} Recently, (mixed) metal oxides with balanced acid–base sites have been developed for ethanol conversion.^{85,86,89,90} Propylene^{85,86} and isobutene^{89,90} with high selectivity (>60 mol % vs <30 mol % on zeolites) have been synthesized directly from ethanol via acetaldehyde and acetone intermediates. Ethanol to 1,3-butadiene conversion on (mixed) metal oxides has also been widely studied and summarized.⁹ Although the reaction mechanism is still debatable, dehydrogenation catalyzed by basic sites and then an aldol-condensation reaction pathway have been widely accepted by researchers.^{9,91,92}

3.2.2. Catalysts for Ethanol Conversion to C₃–C₄ Olefins.

a. Production of C₃–C₄ Olefins on Zeolites. Typically, ethanol conversion on zeolites produces a mixture of hydrocarbons including ethylene, C₃–C₄ light olefins, and C₅₊ longer chain hydrocarbons via the oligomerization–cracking mechanism. The distribution of the products mainly depends on the reaction conditions (e.g., reaction temperature) and catalysts' surface acidity controlled by parameters such as Si/Al ratio, additives in zeolites, water content in the feed, and so forth. Stronger acidity and high reaction temperatures favor the secondary reaction of ethylene to form longer chain hydrocarbons. On the other hand, they also favor cracking and coking reactions. A dedicated control of surface acidity and reaction conditions is pivotal to the formation of C₃–C₄ light olefins. Song et al. compared ethanol reaction over H-ZSM-5 of various Si/Al ratios at 400 °C. ZSM-5 with a Si/Al₂ ratio of 80 was found to have an optimum acidity in producing C₃ olefins.⁸² C₅₊ hydrocarbons (Table 2) were mainly produced on ZSM-5 with a Si/Al₂ ratio less than 80 and thus high surface acid density and acid strength. Gayubo et al. investigated the effect of operating conditions on product distributions in the conversion of aqueous ethanol over ZSM-5 (Si/Al = 24). It was found that a suitable residence time and reaction temperatures above 400 °C (e.g., 450 °C) are pivotal to achieve high selectivity to C₃–C₄ light olefins. At 450 °C, longer residence times favor the formation of C₅₊ hydrocarbons, while shorter residence times produce mainly ethylene. Water showed a positive effect on the formation of light olefins, due to its modification of acidic sites and attenuation of oligomerization and cracking.⁷⁸ In terms of catalyst stability, water was found to mitigate the formation of coke;⁷⁹ however, irreversible catalyst deactivation was observed due to the dealumination and deconstruction of microporous structures in the presence of high content of water at high temperatures.^{79,93}

Surface acidity of zeolites could be modified by additives to achieve high selectivity to C₃–C₄ olefins. At high temperatures (i.e., 450 °C), a variety of additives were compared. P and Zr

were found to passivate the strong acidic sites on H-ZSM-5 while maintaining the moderate ones, leading to enhanced propylene selectivity (31–32%). P and Zr were also found to inhibit the dealumination of catalysts and thus enhanced the stability of the catalysts.^{82,83} A recent study combining experimental and kinetic simulations revealed that, upon loading 1 wt % Ni, dealumination of ZSM-5 could be significantly suppressed. Meanwhile, Ni was found to attenuate the strength of acidity on ZSM-5 from 135 to 125 kJ (mol of NH₃)⁻¹, resulting in improved selectivity to C₃–C₄ light olefins.^{80,81} In addition, a more recent study indicates that ZSM-5 (Si/Al = ~7.6) with smaller particle sizes also favors the propylene production at 500 °C, which is attributed to facile mass transfer.⁹⁴

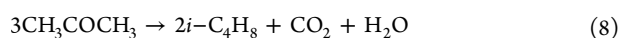
b. Production of C₃–C₄ Olefins on Metal Oxides. Other than zeolites, supported metal oxides (NiO/MCM-41) have also been studied to produce propylene from ethanol. Different from the reaction on zeolites, on metal oxides, ethylene was found to form via two reaction pathways. One is the dehydration via diethyl ether and the other via acetaldehyde and ethyl acetate intermediate.⁸⁴ Ethylene was then converted to propylene through dimerization, isomerization, and metathesis. On Ni/MCM-41 (Si/Ni = 23) and at 400 °C, complete ethanol conversion was achieved with a propylene selectivity of ~30%. Further studies indicated that layered nickel–silicate acts as the active phase for ethanol to propylene conversion, and the presence of water (75 wt % ethanol) has a negligible effect on both ethanol conversion and propylene selectivity.⁸⁸

Despite the extensive research effort on ethanol conversion on zeolites, propylene selectivity is normally low (~20–30%). Iwamoto et al. recently reported that the scandium-modified indium oxide catalyst is highly selective in ethanol-to-propylene conversion (selectivity, 60 mol %) at 550 °C. Such a high selectivity to propylene was attributed to a different reaction pathway from that on zeolites, namely, ethanol dehydrogenation to acetaldehyde, followed by condensation/ketonization of acetaldehyde to acetone. The acetone was then hydrogenated and dehydrated to form propylene.⁸⁵ They later studied CeO₂ modified with different additives and found that yttrium-doped CeO₂ (20 atm% Y/CeO₂) produced 25% propylene and 50% ethylene in the absence of water. Propylene selectivity could be further increased to 30% by suppressing ethanol dehydration. These catalysts also showed much higher stability than zeolites.⁸⁶

c. Production of Isobutene on (Mixed) Metal Oxides. Isobutene is an important intermediate for the production of various industrial products, such as butyl rubber, polyethylene terephthalate (PET), and tri-isobutene, a premium solvent and additive for jet fuel. Ethanol-to-isobutene conversion makes it possible to produce isobutene from the renewable biomass feedstock. To date, two processes have been reported to

produce isobutene from ethanol, namely, a two-step process and a one-step process.

Two-Step Process. A two-step process (eqs 7 and 8) can be used to convert ethanol to isobutene using base metal and acidic zeolite catalysts, respectively. Ethanol to acetone conversion has been studied on various base metal catalysts (eq 7),^{95–98} and the acetone to isobutene reaction has been extensively studied on acidic zeolites (eq 8).^{70,99,100} In the production of isobutene, hydrogen is produced as a valuable coproduct (eqs 7 and 8). In addition, acetone can be used for the production of diversified chemicals such as diacetone alcohol, mesityl oxide, and methyl isobutyl ketone.¹⁰¹



Ethanol to acetone conversion has been widely studied, and its formation mechanism is well understood. This includes base-catalyzed dehydrogenation of ethanol to form acetaldehyde, followed by aldol addition of acetaldehyde and decarbonylation to form acetone^{96,97} or further oxidation of acetaldehyde to acetic acid and ketonization of acetic acid to acetone.⁹⁸ ZnO–CaO was found to give 100% ethanol conversion and ~68% carbon selectivity to acetone at 400 °C with aqueous ethanol (a water/ethanol molar ratio of 4.5) as a feed.^{95,102} Fe–Zn mixed oxide (Fe/Zn = 7:3) exhibited 100% ethanol conversion and ~70% carbon selectivity to acetone at 440 °C. However, the acetone selectivity decreased by 34% during the reaction time of 24 h.⁹⁸ When a higher molar ratio of water/ethanol (9:1) was used, Cu–La₂Zr₂O₇ showed 96% of theoretic acetone yield (equal to 72% carbon selectivity) at 400 °C.¹⁰³ Nishiguchi et al. studied catalytic conversion of aqueous ethanol (water/ethanol molar = 5:1) on CuO/CeO₂ and found that acetone is a main product at 380 °C, whereas acetaldehyde is a main product at 260 °C. It was demonstrated that CeO₂ played an important role as an oxygen supplier.⁹⁶ More recently, we also reported highly selective formation of acetone (~66% carbon selectivity) over ZnO prepared by the hard template method.⁸⁹

Acetone-to-isobutene conversion involves multiple reactions, including condensation, dehydration, and decomposition reactions.^{100,104} Either Brønsted^{70,104} or Lewis acid–base pairs¹⁰⁵ have been demonstrated to catalyze acetone to isobutene conversion. A more recent comparative investigation on zeolites (i.e., ZSM-5 and USY) suggested that both Brønsted and Lewis acid sites are active sites, but they involve different reaction mechanisms.¹⁰⁶ Specifically, initial acetone condensation reaction takes place via one gas phase acetone molecule and one adsorbed acetone on Lewis acid sites, while on Brønsted acid sites via two adsorbed acetone molecules.¹⁰⁶

Isobutene selectivity has been reported to be related to the secondary reactions of isobutylene or mesityl oxide intermediates, which depend on a variety of parameters such as type/strength of acidity and reaction conditions.^{70,99,107} Over ZSM-5, Chang et al. found that ~83% isobutene selectivity was obtained with acetone conversion of ~25% at 329 °C. As temperature increased to 399 °C, isobutene selectivity dropped to ~4% with a concurrent increase of aromatic compounds at acetone conversion of ~95%.⁹³ Over zeolite β with moderate acidity, however, ~87% of isobutene selectivity was still maintained even at 400 °C.⁷⁰ Tago et al. compared the acetone conversion over ZSM-5 (Si/Al = 80) at 400 °C. It was found that acetone conversion decreased rapidly with time-on-stream

(TOS). Meanwhile isobutene selectivity increased with the concurrent decrease of aromatic selectivity. The initial high selectivity to aromatics has been attributed to secondary reactions of olefins on the strong acidic sites. With TOS, the stronger acidic sites were blocked by coke deposition, which led to suppressed secondary reactions and thus increased isobutene selectivity.⁹⁹ It was also found that these secondary reactions can be suppressed by passivating stronger acidic sites on zeolites using alkali additives to improve isobutene selectivity.⁹⁹ These results suggest that the surface acidity, reaction temperature, and residence time play key roles in controlling the secondary reactions of isobutene and thus isobutene selectivity. A major issue for acetone to isobutene conversion on zeolite is the fast coking and deactivation of catalyst. We found that the deactivation was mitigated on nanosized particle size of ZSM-5 at 330 °C, due to less clogging by large-sized molecules.⁷²

One-Step Process. In light of the discussion of the two-step process, one-step conversion of ethanol to isobutene is possible if catalysts with balanced acid/base properties can be designed and synthesized. Recently, we developed Zn_xZr_yO_z mixed oxide catalysts with balanced acid/base properties which were synthesized using a hard template method.⁷⁴ We found that ethanol can be directly converted to isobutene with high yield (>80%, Figure 4) through a cascade catalysis involving

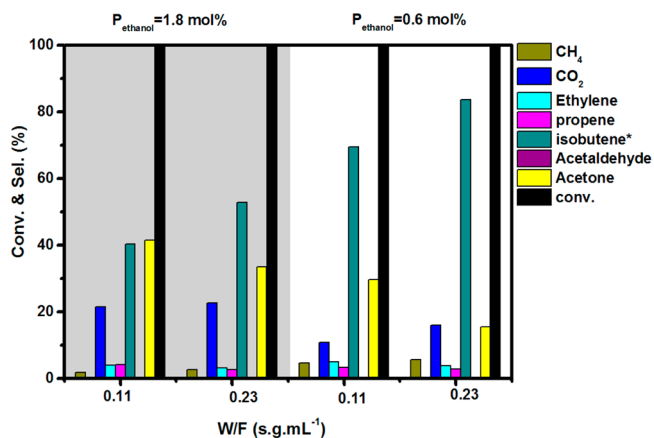
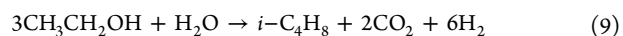


Figure 4. Performance of the Zn₁Zr₁₀O₂ mixed oxide catalyst for the ethanol to isobutene reaction as a function of gas flow rate and ethanol concentration. Reproduced with permission from ref 89. Copyright 2011 American Chemical Society.

dehydrogenation, condensation, dehydration, and decomposition (ethanol → acetaldehyde → acetone → isobutene), with hydrogen being a valuable coproduct (eq 9).^{74,89} Addition of Zn passivated the strong acid sites on ZrO₂ and introduced the basic ones. As a result, ethanol dehydrogenation to acetaldehyde was significantly enhanced by suppressing the direct ethanol-to-ethylene dehydration reaction. The acetaldehyde was then converted to acetone via base-catalyzed aldol addition/ketonization reactions. Weak Brønsted acid sites are likely the active sites required for dehydration of diacetone alcohol to form mesityl oxide during acetone conversion to isobutene, which is the rate-limiting step.⁹⁰



d. Production of 1,3-Butadiene on (Mixed) Metal Oxides. 1,3-Butadiene has been widely used in the production of rubbers with ~25% of global rubber production using 1,3-

butadiene.⁹² Substantial 1,3-butadiene was produced from ethanol during World War II.⁹² The mechanism for ethanol to 1,3-butadiene transformation is complicated and subject to debate. Briefly, it mainly involves the following five principal reactions (Figure 5): (1) ethanol dehydrogenation to

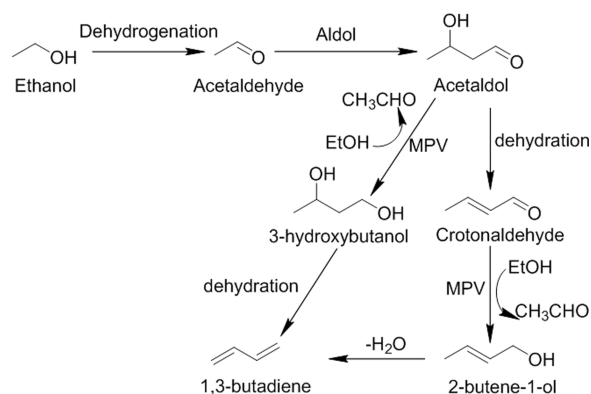


Figure 5. Generally accepted mechanism for the production of 1,3-butadiene from ethanol. Reproduced with permission from ref 91. Copyright 2011 Royal Society of Chemistry.

acetaldehyde; (2) aldol addition of acetaldehyde to acetaldoal; (3) dehydration of acetaldoal to crotonaldehyde or Meerwein–Ponndorf–Verley (MPV) reaction between acetaldoal and ethanol to produce 3-hydroxybutanol; (4) MPV reaction between crotonaldehyde and ethanol to obtain crotyl alcohol and acetaldehyde; and (5) dehydration of crotyl alcohol or 3-hydroxybutanol to 1,3-butadiene.^{9,10,91,92} Similar to the one-step ethanol-to-isobutene⁸⁹ and ethanol-to-propylene⁸⁶ reactions, a dedicated acidity is required to suppress the direct ethanol dehydration and to guarantee the dehydration of crotyl alcohol to 1,3-butadiene. Meanwhile, basicity is equally important to catalyze the dehydrogenation and aldol-condensation reactions.¹⁰⁸

Numerous metal oxide and mixed oxide catalysts have been studied for ethanol to 1,3-butadiene, which have been well-summarized recently.^{9,10} Only those with acid–base bifunctionalities were found to exhibit significant yield for the one-step ethanol conversion to 1,3-butadiene.^{108,109} Silica/magnesia-based materials have received more attention due to their high selectivity to 1,3-butadiene.^{92,110–112} It was found that MgO–SiO₂ catalysts prepared by wet kneading with 0.1 wt % Na reduces the acidity of support and consequently increases 1,3-butadiene yield from 44% to 87%.¹¹¹ Different metal oxide additives have been systematically investigated on MgO/SiO₂, and Cu and Ag oxides showed the best performances in terms of 1,3-butadiene yield. More importantly, the ratio between acid and basic component as well as the nature of redox promoter were found to play important roles in improving 1,3-

butadiene yield and suppressing ethanol dehydration to ethylene.⁹²

Other combinations of various metal oxides have also been investigated in the ethanol to 1,3-butadiene transformation. The most promising catalyst appears to be Zr–Zn supported on silica with a Zr/Zn weight ratio of 1.5/0.5, which showed a 1,3-butadiene selectivity of 66% with cofeeding ethanol and acetaldehyde (a feed ratio of 8:2).⁹¹ Both Zn (II) and Zr(IV) are Lewis acid sites, which were believed to enhance the activity. The enhancement in selectivity was attributed to acetaldehyde that was cofed to favor the aldol-condensation reaction.⁹¹

Given the fact that the ethanol conversion on acid–base catalysts produces a variety of products such as propylene, isobutene, and 1,3-butadiene, it is interesting to identify the nature of active sites and control the reaction conditions and thus, tune the reaction pathway toward a desired product. Table 3 lists the detailed catalysts, proposed active sites, intermediates, and reaction conditions reported for the three typical reactions. It is clear that all the reactions start from the basic-site-catalyzed ethanol dehydrogenation reaction toward acetaldehyde (Table 3). Subsequently, acetaldehyde to acetone has been proposed in the ethanol-to-propylene⁸⁶ and ethanol-to-isobutene⁸⁹ reactions. However, the aldol addition of acetaldehyde to acetaldoal followed by dehydration of acetaldoal to crotonaldehyde was proposed for the 1,3-butadiene formation.⁹¹ From the reaction conditions for the three reactions, it suggests that H₂O and reaction temperature might play a critical role in determining the acetaldehyde reaction pathways. Cofeeding H₂O and relatively higher reaction temperature (>673 K) favor the acetaldehyde-to-acetone conversion,^{86,89} while aldol-condensation of acetaldehyde at relatively lower temperature (<673 K) seems favored.⁹¹ H₂ was found to play a key role in the acetone conversion to propylene and isobutene. Without hydrogen or in the presence of small amount of hydrogen,^{89,90} the acetone-to-isobutene reaction is predominant, however propylene was significantly enhanced in the presence of high-concentration hydrogen (e.g., 30 mol %) at the same reaction conditions.^{85,86} Selective hydrogenation of crotonaldehyde toward crotyl alcohol formation instead of hydrogenation of the C=C bond is required for conversion of ethanol to 1,3-butadiene. There is only very limited information on the identification and correlation of type of acid/base sites and catalytic performances. A detailed fundamental study is still required to further explore the structure, nature of active phase (i.e., acid–base and redox), and reaction kinetics over the (mixed) metal oxides catalysts for ethanol conversion.

3.3. Ethanol to Gasoline (ETG). Gasoline represents a group of hydrocarbons ranging from C₅ to C₁₂, peaked at C₈–C₁₀. Although ethanol can be blended into gasoline for combustion engines, this blending is still limited due to the

Table 3. One-Step Ethanol Conversion to Different Products on (Mixed) Metal Oxide Catalysts

product	catalyst	reaction conditions		reaction mechanism		
		temp (K)	Feed	reaction pathway and key intermediate	active sites	refs
propene	In ₂ O ₃ - and CeO ₂ -based	673–823	co-feeding H ₂ O and H ₂	ethanol to acetaldehyde to acetone to propylene	acid–base and redox	85, 86
isobutene	Zn _x Zr _y O _z	673–753	co-feeding H ₂ O	ethanol to acetaldehyde to acetone to isobutene	acid–base	89,90
1,3-butadiene	(mixed) metal oxides including Zn _x Zr _y O _z	553–698	pure ethanol	ethanol to acetaldehyde to acetaldoal to crotonaldehyde and 3-hydroxybutanol to 1,3-butadiene	acid–base	9,10,91,92

concerns with the potential corrosion of the engine wall and the reduced gas mileage. In most countries, the blending ratios are still limited to lower than E10. Therefore, development of the ETG process is still needed to meet the increased energy requirement and depleting fossil resources.

3.3.1. Reaction Mechanism. The ethanol to gasoline (ETG) reaction is complicated, and mechanistic insights are mainly based on the understanding of methanol to gasoline (MTG).^{61,113} It is worth mentioning that durene (an undesired product for its high freezing point) is always formed during MTG depending on the reaction temperature and pressures.¹¹⁴ However, its formation in ETG has not been reported yet. The ETG process involves three major steps: ethanol dehydration to form ethylene, followed by secondary reaction (i.e., oligomerization) of ethylene to produce aromatics/paraffins via H-transfer.¹¹⁵ Figure 6 shows a detailed pathway for ETG

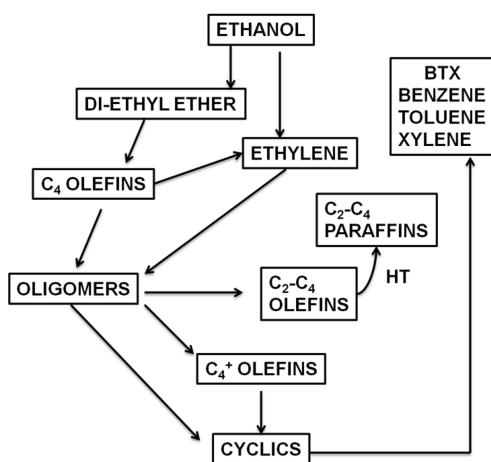


Figure 6. Reaction pathways for ethanol to hydrocarbons.¹¹⁶ Reproduced with permission from ref 116. Copyright 2012 Elsevier.

involving different intermediates/products.¹¹⁶ Brønsted acid sites have been considered as the potential active sites for ETG. In addition, radicals generated under reaction were identified as another type of active sites for secondary reaction of ethylene toward C_{3+} hydrocarbons in the case that Brønsted acid sites of working catalysts were passivated by carbonaceous species.^{21,117}

3.3.2. ETG Catalysts. Among the catalysts studied, ZSM-5-type zeolites have been considered as the most selective catalysts for the ETG process, due to their unique structural properties that selectively produce light hydrocarbon mixtures similar to commercial gasoline.^{31,113,118–120} Numerous studies have been reported on the effects of catalyst acidity, structure, cofeeding water, and reaction conditions on the pathways in ETG over ZSM-5 catalysts. As discussed in sections 3.1 and 3.2, acidic properties and strength on HZSM-5 play a key role in controlling ethanol dehydration to ethylene as well as secondary reactions of ethylene to longer chain hydrocarbons. Tailoring the Si/Al ratio of HZSM-5 is the most common way to adjust the acidic properties. Costa et al. reported that the formation of liquid hydrocarbons, particularly aromatics, is favored on HZSM-5 with low Si/Al ratios.¹¹³ Talukdar et al. also studied the conversion of 50% ethanol aqueous solution over two ZSM-5 zeolites with Si/Al ratios of 20 and 103, respectively. The one with a lower ratio (i.e., 20) showed a higher yield to all liquid fractions, while the other one with a higher ratio (i.e., 103) mainly resulted in high yields to light olefins (C_2 – C_4).¹¹⁵ This suggests that ZSM-5 catalysts with

lower Si/Al ratios and more acidic sites are more suitable for ethanol conversion to C_{5+} hydrocarbons. More recently, HZSM-5 zeolites with Si/Al ratios ranging from 16 to 500 were investigated for ethanol transformation to hydrocarbons. HZSM-5 with a Si/Al molar ratio of 40 was found to exhibit the highest stability and selectivity to longer chain hydrocarbons, due to a balance between the Brønsted acid sites and radicals on the working catalysts, which are considered as active sites for ethanol conversion.¹¹⁷

Although ZSM-5 zeolites with low Si/Al ratio exhibit more acidity and thus high catalytic activity and selectivity in ETG, they usually suffer from deactivation due to coking and dealumination of ZSM-5 catalysts.^{79–81,117} Coking occurs on the strong acid sites, and the control of acid strength has been used to improve the stability of catalysts by modifying ZSM-5.^{69,80,121–124} Modification of HZSM-5 catalysts, such as ion-exchange, affects their acidic properties and textures, leading to different catalytic performances.^{69,80,123} For example, Ni-modified ZSM-5 was observed to possess the optimal acid strength with improved catalyst hydrothermal stability against coking and dealumination in ETG.⁸⁰ Ga- and Zn-doped HZSM-5 catalysts were found to improve catalyst life and increase the yield to hydrocarbons, particularly aromatics, in the conversion of industrial ethanol (88%, v/v, ethanol/water) at 360 °C.¹²² Calsavara et al. prepared iron-doped ZSM-5 zeolites by direct-synthesis and post ion-exchange. It was found that, regardless of the way the iron was incorporated, partial substitution of framework Al^{3+} by Fe^{3+} in ZSM-5 (0.3–0.5 wt % iron) led to extended catalyst life and improved yield to liquid hydrocarbons, which is attributed to the lower acidity of framework Fe^{3+} than that of Al^{3+} .⁶⁹ Tynjala et al. studied the conversion of alcohols (C_1 – C_4) at 370 °C over HZSM-5 and trimethyl-phosphite-modified ZSM-5 zeolites which possess only weak acidity. It was found that ethers were predominantly produced in the conversion of small alcohols (methanol and ethanol) over the trimethyl-phosphite-modified ZSM-5. No further conversion of ethers was observed, due to the fact that weak acid sites are unable to catalyze the formation of longer-chain hydrocarbons.¹²¹

Other studies also suggested that in situ generation of free radicals on the working catalysts, which helps maintain the high activity and stability in terms of secondary ethylene reaction, and a change of the nature of radical species with time-on-stream (TOS) were responsible for the deactivation of catalysts.¹¹⁷ HZSM-5 catalysts were also modified with tetraethyl orthosilicate (TEOS) and were used to investigate ethanol conversion to hydrocarbons at 350 °C and 30 bar total pressure. Although there was a significant loss of Brønsted acidity and microporosity, these catalysts exhibited a slight improvement in C_{3+} hydrocarbons. This suggests that free radicals might be the active sites for ethanol to hydrocarbon (C_{3+}) transformation on the coked catalyst.¹²⁵

Viswanadham et al. studied the conversion of ETG on ZSM-5 catalysts with comparable acidity but different porosities.¹¹⁶ It was found that both strong acidity and mesoporosity are needed for effective conversion of ethanol to gasoline.

As discussed in section 3.2, water could attenuate the acidity and inhibit secondary reactions. Indeed, ETG was found to be suppressed at high water content. Costa et al. compared the conversion of ethanol diluted with 4, 15, and 30 wt % water at 400 °C and observed that the catalyst life was reduced by half when water content increased from 4 to 15 wt %.¹¹³ Similar results were reported by Talukdar et al., that is, the yield of

liquid hydrocarbons decreased when water content increased from 20 to 80 wt %. However, the yield to liquid hydrocarbons was also low with pure ethanol, which indicates that a proper water content favors the ETG process.¹¹⁵ Aguayo et al. found that water can suppress catalyst deactivation by mitigating coke formation and affect the product distributions and the yield to liquid hydrocarbons.⁷⁹

In addition to water, reaction temperature also plays an important role in ETG. When a moderately low space velocity (WHSV = 0.5) was used in the conversion of 96 wt % ethanol/H₂O, a maximum yield to liquid hydrocarbons (52 wt %) was achieved at 400 °C. At a higher temperature (>450 °C), the yield to liquid hydrocarbons decreased due to further cracking of longer-chain hydrocarbon products.¹¹³ A temperature range between 350 and 450 °C is considered to be preferred for the transformation of ethanol to liquid hydrocarbons.^{79,113}

4. ETHANOL TO 1-BUTANOL

Compared to ethanol, 1-butanol has a higher calorific value (29.2 vs 19.6 MJ/dm³) and higher solubility in gasoline. It is therefore considered as a better drop-in fuel. In addition, butanol is an important building block for other chemicals such as acrylic acid and acrylic esters. The main issue in developing the biosynthesis of 1-butanol is the low concentration of biobutanol fermentation broth. This is limited by the toxic metabolic product of the bacterium *Clostridium acetobutylicum*.¹²⁶ Catalytic production of 1-butanol from ethanol is another route to convert biomass into valuable chemicals. Two reaction pathways have been proposed for the formation of 1-butanol from ethanol. One is a direct bimolecular condensation process, in which one molecule of ethanol with its C–H bond in β -position is activated on the basic sites and condensed with another ethanol molecule by dehydration.^{127,128} Another one is the Guerbet process involving three sequential reactions, namely, ethanol dehydrogenation to acetaldehyde, acetaldehyde aldol-condensation to form crotonaldehyde, and hydrogenation of crotonaldehyde to form 1-butanol (Figure 7).^{129,130} Despite the debate with

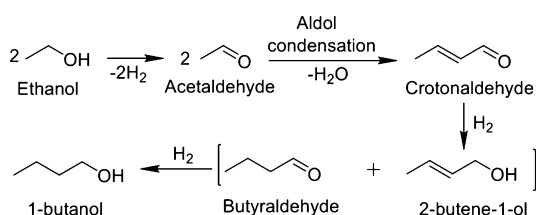


Figure 7. Reaction pathway from ethanol to 1-butanol. Reproduced with permission from ref 129. Copyright 2012 Elsevier.

respect to base or acid/base pair active sites,^{131–133} it has been generally accepted that basic sites are essential to the formation of 1-butanol. Up to now, catalysts such as modified zeolites, metal oxides, and modified hydroxyapatites, among others, have been widely used in the production of 1-butanol from ethanol.^{127,131,134–136}

Yang et al. studied ethanol to *n*-butanol conversion on alkali metal-modified zeolites such as Rb–LiX and found that a selectivity of 43% could be obtained at a reaction temperature of 420 °C. Butanol was proposed to be formed via a direct condensation process.¹²⁷ A recent report revealed that alumina-supported base metal (i.e., Ni) catalysts exhibit high activity and selectivity in ethanol to 1-butanol conversion (i.e., 19% ethanol

conversion with 1-butanol selectivity of up to 64% at a reaction temperature as low as 200 °C).¹²⁸ Using different intermediates like acetaldehyde and crotonaldehyde as reactants, a direct bimolecular dehydration reaction pathway was verified for the growth of the carbon chain. However, the potential effect of hydrogen, a byproduct from the ethanol reactant, was not discussed in the paper.¹²⁸ More recently, different metals (Ru, Rh, Pd, Pt, Au, Ni, Ag) over alumina were reported to produce 1-butanol from ethanol via a one-pot liquid-phase reaction.¹³⁷ Metals have been ranked based on the selectivity toward 1-butanol as follows: Ni > Pt > Au~Rh > Ru \gg Ag, and an ethanol conversion of 25% with a selectivity of 80% to 1-butanol was obtained over 20.7 wt % Ni/Al₂O₃ catalyst at 250 °C.

Basic mixed oxides are another type of catalysts for ethanol conversion to 1-butanol. Cu–Mg–Al mixed oxide catalysts, which were prepared with layered double hydroxide (LDH) precursors, were used to catalyze bioethanol into 1-butanol conversion with 1,1-diethoxyethane as another main product.¹³³ In studies regarding Cu content in the mixed Cu–Mg–Al oxide, it was found that the strong and the total basicities of the catalysts increased with decreasing Cu content. The selectivity to 1-butanol increased with the number of strong basic sites. Recently, different Mg–Al mixed oxides derived from hydrotalcites were investigated. It was found that catalysts with higher concentration and strength of the basic sites lead to high selectively to C₄ products (i.e., 1-butanol), whereas the presence of acid sites promotes ethanol dehydration, leading to decreased efficiency for condensation reactions.¹³² This study suggests that basic sites play an important role in ethanol condensation toward 1-butanol.

The effects of acid/base pairs have also been investigated in ethanol to 1-butanol reactions over Mg–Al mixed oxide catalysts prepared by thermal decomposition of hydrotalcites. Interestingly, besides basic effects, acidic properties of catalysts were also found to be essential for the production of 1-butanol.^{131,132} It was demonstrated that pairs of acid and medium basic sites are present on the mixed Mg–Al oxides. Also, it was demonstrated that adjacent acid and medium basic sites are required to generate the intermediate compounds, which subsequently lead to 1-butanol formation. It was also observed that a higher selectivity to 1-butanol results from the higher concentration of Mg in the catalyst, leading to its higher hydrogenation activity.¹³¹ Another study showed that substitution of Al³⁺ with Fe³⁺ led to a slight decrease of the basic sites but a more dramatic decrease of the acid site concentration on Mg–Al mixed oxides. If the Al³⁺ was completely replaced by Fe³⁺, the resulting Mg–Fe mixed oxide exhibited the highest selectivity to C₄ compounds, especially 1-butanol. It was also observed that the activity for ethanol dehydration was largely suppressed when the acidic sites of the material were passivated, resulting in an increased formation of the dehydrogenation product (acetaldehyde), a key intermediate to form 1-butanol.¹³²

Tsuchida et al. reported that nonstoichiometric hydroxyapatites (HAP), calcium phosphate compounds, are active in one-step selective conversion of ethanol to 1-butanol and their catalytic activity and selectivity increase with the Ca/P molar ratios.^{138,139} More recently, Sr–HAP was found to exhibit a higher selectivity to 1-butanol than Ca–HAP catalysts with activity and selectivity to 1-butanol increasing with Sr/P molar ratios, due to higher densities of relatively strong basic sites.^{129,135} Guerbet reactions have been proposed for the gas

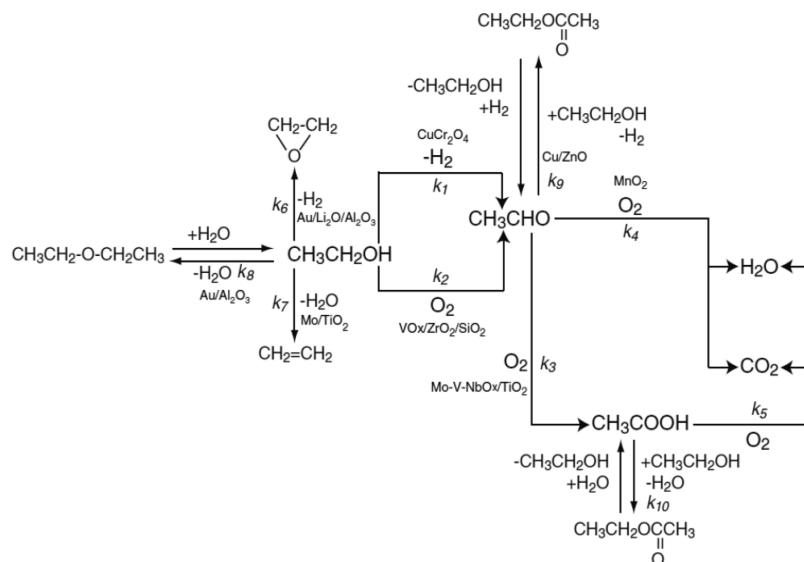


Figure 8. Successive reactions involved in ethanol transformation.¹³ Reproduced with permission from ref 13. Copyright 2011 Springer.

phase conversion of ethanol to 1-butanol on the HAP-based catalysts. The rate-determining step (rds) is postulated to be aldol-condensation, which includes the condensation process itself and the formation of two aldehyde adsorbates on neighboring basic sites prior to condensation.¹²⁹

5. ETHANOL TO OTHERS (ACETALDEHYDE, ACETONE, DIETHYL ETHER, ETHYL ACETATE, AND ACETONITRILE)

Ethanol can also be selectively converted to other chemicals such as diethyl ether, acetaldehyde, acetone, acetic acid, ethylene oxide, ethyl acetate, and acetonitrile. Diethyl ether is widely used as solvent. Currently, most of the diethyl ether is produced from the byproducts of vapor phase hydration of ethylene to produce ethanol. It can also be industrially synthesized via an acid ether process, in which ethanol and strong acid (e.g., sulphuric acid) are mixed and heated. As discussed in section 3.1, vapor phase conversion of ethanol to ethylene proceeds via diethyl ether intermediate on a variety of acidic catalysts. A proper control of reaction conditions can result in selective formation of diethyl ether. For example, vapor phase dehydration of ethanol can lead to diethyl ether yield of more than 80% on γ - Al_2O_3 ⁴⁸ and even 100% on heteropolyacid catalysts.⁵⁷

Production of other oxygenates besides diethyl ether typically proceeds via dehydrogenation or an oxidative dehydrogenation process, with the latter mainly taking place on supported metal catalysts as summarized elsewhere.¹³ The product selectivity was found to be dependent on the reaction conditions and catalysts used (Figure 8). For example, direct oxidation of ethanol to acetic acid takes place on supported noble metal catalysts (such as 1.5% Au/TiO₂). Base metal oxide favors the formation of acetaldehyde. Under a low O₂ concentration, a high selectivity of 88% to ethylene oxide was obtained over Au/Li₂O/Al₂O₃, and the presence of O₂ was found to be important to prevent carbon deposition.¹⁴⁰

Selective conversion of ethanol to acetaldehyde via direct dehydrogenation or oxidative dehydrogenation on supported metal catalysts has also recently been reviewed.¹³ Supported gold catalysts exhibit promising activity in oxidative dehydrogenation of ethanol to acetaldehyde, whereas supported copper

catalysts are active for direct dehydrogenation of ethanol to produce acetaldehyde and hydrogen. Acetic acid is mainly synthesized industrially by the carbonylation of methanol, although acetic acid for vinegar is produced by a biological route. Although current market price does not encourage the conversion of ethanol to acetic acid, fundamental studies have been extensively performed. Ethanol to acetic acid conversion mainly proceeds via acetaldehyde intermediate.¹³ Gold catalysts have been found to be the only active catalysts to produce acetic acid via oxidation of aqueous ethanol. Cu-doped Au/NiO prepared by the coprecipitation method showed good activity at 120 °C with selectivity to acetic acid of above 90%.¹³ Limited reports are available regarding the conversion of bioethanol to acetic acid in the absence of oxygen. Recently, Chu et al. found that ethanol can be selectively oxidized by H₂O to produce acetic acid (~92%) over coprecipitated Co/ZnO catalysts under aqueous phase reaction conditions (225 °C and 2.58 MPa).¹⁴¹ Ethanol to acetone conversion is discussed in section 3.2b and will not be repeated.

Copper-based catalysts (such as Cu/ZrO₂) have been used for the conversion of ethanol to ethyl acetate.^{142,143} It was found that the active site for the coupling of ethanol and acetaldehyde is at the mixed-metal-oxide surface but not at the Cu metal surface.¹⁴³ However, the coexistence of Cu⁰ and Cu¹⁺ over Cu/ZrO₂ was thought to provide a synergistic interaction for the conversion of ethanol to ethyl acetate.¹⁴⁴ One recent study indicates that the combination of the Cu¹⁺/Cu⁰ pair and Cu⁰ interfaced to ZrO₂ is necessary to efficiently transform ethanol to ethyl acetate.¹⁴⁵ It is still unclear regarding the active sites for the conversion of ethanol to ethyl acetate. Further research to develop more selective catalysts is still needed. In addition, amination of ethanol has been widely studied to produce ethylamine,¹⁴⁶ which can be further converted to acetonitrile via oxidative dehydrogenation.¹⁴⁷

6. CONCLUSIONS AND OUTLOOK

Bioethanol is commercially produced from renewable biomass sources. The ethanol “blending wall” coupled with the advancement in production efficiency and feedstock diversification will potentially lead to excess bioethanol, with competitive prices, available for the production of a wide

range of commodity chemicals. Development of efficient catalysts will play key roles for sustainable production of chemicals from renewable biomass. Here, we summarize the recent advances in catalytic conversion of ethanol to chemicals and fuels. This covers hydrogen, small oxygenates, and hydrocarbons ranging from light olefins to longer chain alkenes/alkanes and aromatics.

Development of highly stable and selective catalysts for ESR processes looks promising to produce hydrogen at an industrial scale.¹⁴⁸ Fundamental research on ethanol steam reforming to hydrogen has been extensively focused on less-expensive, non-noble metals such as cobalt-based catalysts, which exhibit promising activities and selectivities at relatively low temperatures (<450 °C). To address the catalyst deactivation issue, support with high oxygen mobility (e.g., CeO₂) has been reported to enhance the gasification of carbon residues and thus, mitigate the coke formation on cobalt.¹⁹ On the other hand, CeO₂ could facilitate the oxidation of metal that leads to reduced catalyst activity.²⁵ Despite the extensive research in the fundamental understanding of reaction mechanism and advancement in catalyst development, design of catalysts with efficient water dissociation and oxidation of carbon species while facilitating the reaction pathways toward hydrogen production is desired for high steam reforming selectivity and catalyst stability.²⁰

Production of ethylene from ethanol using γ -Al₂O₃ is a commercial success. A high reaction temperature (>400 °C), especially in the presence of water, is required to avoid the formation of ethyl ether intermediate while achieving high space-time yields to ethylene. Due to the unique structure and adjustable acidity, zeolite-based catalysts have shown promising applications in low-temperature (<200 °C) dehydration of ethanol to ethylene. A more dedicated manipulation of the nature/strength of acidity, reaction temperature, pressure, and residence time is essential to produce longer chain hydrocarbon fuels/chemicals, while minimizing undesired secondary reactions. Surface acidity could be adjusted by changing Si/Al ratios, doping with additives, and cofeeding with water. In general, relatively low temperatures (<300 °C) favor the formation of ethyl ether and ethylene, and higher temperatures (300–450 °C) lead to the formation of C₃–C₄ hydrocarbons on moderate acidic sites. Formation of bulky hydrocarbons like aromatics normally requires both strong acidic sites and high temperatures (350–450 °C).

Mixed metal oxides with balanced acid–base pairs, such as Zn₁Zr₁₀O₂, has been recently developed for direct conversion of ethanol to isobutene with hydrogen being produced as a useful byproduct. Co-feeding aqueous ethanol with hydrogen on metal oxides such as Sc-modified In₂O₃ and Y/CeO₂ have been reported for more selective production of propylene than that over zeolites. Acid–base catalysts have also been extensively studied for the production of 1-butanol and 1,3-butadiene at different reaction temperatures (200–400 °C). Ethanol to 1,3-butadiene reaction is favored at relatively high temperatures (300–400 °C), although the Guerbet reaction for ethanol conversion to 1-butanol dominates at relatively low temperatures (200–300 °C). In addition, acid–base and redox properties were found to be the key factors in controlling both reactions. Basic sites are believed to catalyze dehydrogenation and condensation reactions for the formation of key intermediates such as acetaldehyde and crotonaldehyde. However, questions such as key intermediates/reaction pathway and kinetics involved in ethanol conversion to 1-butanol/

butadiene/isobutene/propylene on acid–base catalysts and their relationship with the nature of acid–base active sites still remain unanswered. The effects of water in bioethanol have been extensively studied in ethanol conversion to a variety of chemicals and fuels summarized in this review. The studies on the influence of impurities in bioethanol on the catalyst activity and stability are very limited and need to be addressed in order to enable the sustainable production of chemicals from renewable bioethanol.

The depleting fossil fuel resources and the increased availability of bioethanol conversion have made ethanol a platform molecule for the production of value-added chemicals in the near future. However, determination of the promising products is still dependent on the local market as well as a timely sustainability assessment.¹⁴⁹

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Notes

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