PERSPECTIVE

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A perspective on catalytic production of olefinic compounds from biomass

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Chemical syntheses of industrially important olefins and unsaturated oxygenates from biomass are reviewed. Their syntheses are discussed in two aspects: common key reactions and target molecules grouped by the carbon number. Among common key reactions, dehydration of alcohols over acid–base bifunctional solid catalysts, ring-opening dehydration of tetrahydrofurans over acid catalysts, and the deoxydehydration reaction of vicinal diols are especially important. Further, catalyst development is still necessary for all these reactions. In the discussion of each target molecule, the synthesis methods are compared by considering the balance between current demand and the amount of biomass resources. Promising methods have been already developed or proposed for compounds with C4 and more and for C3 unsaturated oxygenates.

Sustainability spotlight

The chemical industry is strongly dependent on the fossil resource both as material source and energy. While there are various sources of renewable energy, biomass is the only renewable organic source. Olefins are one of the most important classes of intermediate substances in the chemical industry and the demand is very large. Here, the chemical syntheses of such important olefins from biomass are reviewed considering both feasibility of chemical conversions and potential supply of each biomass resource. Establishing the chemical synthesis routes to olefins and olefinic oxygenates in large demand from biomass aligns with the following UN sustainable development goals 7, 9, 12 and 13.

1. Introduction

Olefins are an important class of chemicals in industry. Simple olefins such as ethylene, propylene, butadiene, and isobutene are manufactured by thermal cracking of naphtha (typical composition is shown in Table 1).[1–3] The use of catalysts can change the distribution of the products of cracking. Fluidized catalytic cracking (FCC) of heavier oil such as vacuum gas oil is another main method to obtain propylene. Branched olefins as well as aromatics are co-produced in FCC. In addition to the use of the branched olefins as gasoline (FCC gasoline), the petroleum-derived simple olefins are used as-is as monomers of polyolefins or used as reactants for the synthesis of functionalized molecules *via* addition reactions, oxidation, hydroformylation and so on. In view of sustainability, substitution of petroleum with renewable biomass has been a hot topic, especially for the use as chemicals that cannot be replaced by other

renewable energy sources.[4–6] However, the oxygen content of biomass is much larger than those of petroleum and most petroleum-derived compounds. Complete removal of oxygen atoms is necessary for the production of simple olefins from biomass. Meanwhile, some products from petroleum-based olefins contain oxygenated functional groups with retention of the olefinic C=C bond. The production of these compounds from biomass *via* oxygen-free olefins wastes hydrogen, and thus, the synthesis by partial deoxygenation is more atom-efficient.[7,8] The construction of long-chain hydrocarbons from C1 compounds *via* biomass gasification such as BTL (biomass to liquid) and MTO (methanol to olefins) processes is possible; however, these processes are very energy consuming. Altogether, the synthesis of olefinic compounds from biomass requires total or partial deoxygenation reactions, which are not the main reactions in traditional industrial chemistry.

Nowadays, only bio-ethylene by dehydration of bioethanol has been established and commercialized on a significant scale among biomass-derived small (≤C6) olefins.[9,10] The other industrially important olefinic compounds are difficult to synthesize in low cost from biomass; however, the recent large interest in biomass conversion leads to rapid progress in this research field, especially in the development of effective catalysts. Here, we review the recent progress in the synthesis of industrially important C3–C6 olefins and unsaturated oxygenated compounds from biomass.

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Table 1 Distribution (in wt%) of naphtha cracking products[a]

Compounds	Ref. 1 high severity cracking	Ref. 2 high severity cracking	Ref. 3
H_2	3.2a	0.94	1.0
CH_4	15.0	16.5	15.0
C_2H_2	a	1.05	0.4
C_2H_4	31.3	32.8	25.7
C_2H_6	3.4	3.25	3.9
C_3H_4	a	1.08	0.8
C_3H_6	12.1	13.8	13.5
C_3H_8	a	0.29	0.7
C_4H_6	4.2	4.63	5.2
C_4H_8	2.8b	3.49	3.7
C_4H_{10}	b	0.15	0.3
C5 compounds	9.0c	2.58	3.5
Benzene	13.0d	7.1	9.0
Toluene	d	2.35	4.9
C8 aromatics	d	0.73	2.7
C6 – b.p. 473 K or 400 °F (477 K), except C6–C8 aromatics	c	1.29	8.9e
Fuel oil	6.0	4.38	e

[a] a–e: classified as the same group.

2. Key reactions

First, we discuss several key reactions in the conversion of highly oxygenated biomass-derived molecules to olefinic compounds, because these reactions and the catalysts for them can be commonly used for production of many compounds. The target compounds in this review are bulk chemicals, and the reactions cannot use expensive stoichiometric reagents.[11,12] Discharging large amounts of wastes is also unacceptable. Therefore, some reactions commonly used in organic synthetic chemistry such as the Wittig reaction, halogenation–elimination and tosylation–elimination are inappropriate for the complete or partial removal of oxygenated functionalities.

2.1. Dehydration: C=C formation reaction

Dehydration of alcohols is the simplest C=C formation reaction. One OH group and hydrogen atom bonded to the neighboring carbon are removed, providing olefins (Scheme 1). Ideally, the by-product of dehydration is only water, which is acceptable in the synthesis of bulk chemicals. Dehydration of alcohols typically proceeds in the presence of strong Brønsted acid catalysts with an E2 mechanism (primary alcohols) or E1 mechanism (secondary and tertiary alcohols).[13–15] Brønsted-acid-catalyzed dehydration of alcohols is a classical reaction explained in basic textbooks in general chemistry. Sulfuric acid is a typical homogeneous catalyst. Heterogeneous solid acid

Scheme 1 Alcohol dehydration.

catalysts such as acidic resin, silica-alumina and zeolites can be also used. A fundamental issue of the dehydration with Brønsted acid catalysts is low regioselectivity. The sole dehydration product is obtained only when the substrate is ethanol, 1-propanol, 2-propanol or tert-butyl alcohol. Dehydration of other alcohols always produces multiple olefins. The distribution of the produced olefins is mostly governed by the relative thermodynamic stability and is difficult to control by the catalyst: internal olefins, especially trans-olefins, are preferably produced (cf. Saytzev rule). However, the energy difference is generally small, and a mixture of olefins is produced.[14] There are additional side reactions induced by acidic catalysts. One is isomerization by the rearrangement of the carbocation intermediate and this side reaction further complicates the product distribution. Oligomerization of product olefins and C–C cracking can also occur via the carbocation intermediate at too high temperature. Highly polymerized products become coke over solid acid catalysts, which leads to severe problems as explained later.

While the selection of catalysts is not so effective in the control of selectivity among dehydration products, the structure of the substrate much affects the selectivity patterns. The presence of additional functional groups can change the products (Scheme 2). The dehydration of vicinal diols gives carbonyl compounds via keto–enol tautomerization. Aldehydes tend to be more produced than ketones by dehydration of 1,2-diols.[16,17] Aldehydes are reactive molecules and can be further converted to various products such as dioxolanes (acetal of the substrate), carboxylic acids and oligomers. While 1,3-diols do not have special reactivity, the presence of the carbonyl group at the γ-position much increases the reactivity of the OH group toward dehydration because the carbonyl group increases the acidity of the hydrogen atom at the β-position (cf. elimination reaction with the E1cB mechanism and the Michael addition reaction).[18] Functional groups at the δ- or ε-position lead to the formation of cyclization products, such as 1,4-butanediol conversion to tetrahydrofuran instead of 3-buten-1-ol.[19–21]

Dehydration of ethers is a variant of Brønsted-acid-catalyzed dehydration of alcohols (Scheme 3). In the presence of strong Brønsted acids, ethers are first decomposed to olefins and alcohols.[13] In the cases of dialkyl ethers, the produced alcohols are then dehydrated to olefins or returned to dialkyl ethers. In the cases of cyclic ethers with a tetrahydrofuran ring, the reactivity is low and the main path is the direct formation of dienes without a release of alkenols from the catalyst surface.[22,23] Side reactions such as oligomerization and C–C cracking are more likely to occur than simple dehydration of alcohols because severe reaction conditions are required.

Apart from strong Brønsted acids, acid–base bifunctional catalysts can also promote the dehydration of alcohols. Typical catalysts are solid metal oxides such as Al_2O_3 (ref. 24 and 25) and rare-earth oxides.[26] While Al_2O_3 has been widely used in mechanistic studies for a long time, especially during the 1960s and 1970s, recent reports tend to use rare-earth oxide catalysts because of their excellent performance, especially in terms of product yield. While mixing homogeneous acid and base catalysts loses these activities by neutralization, the solid oxide
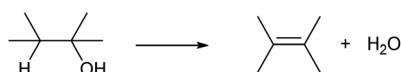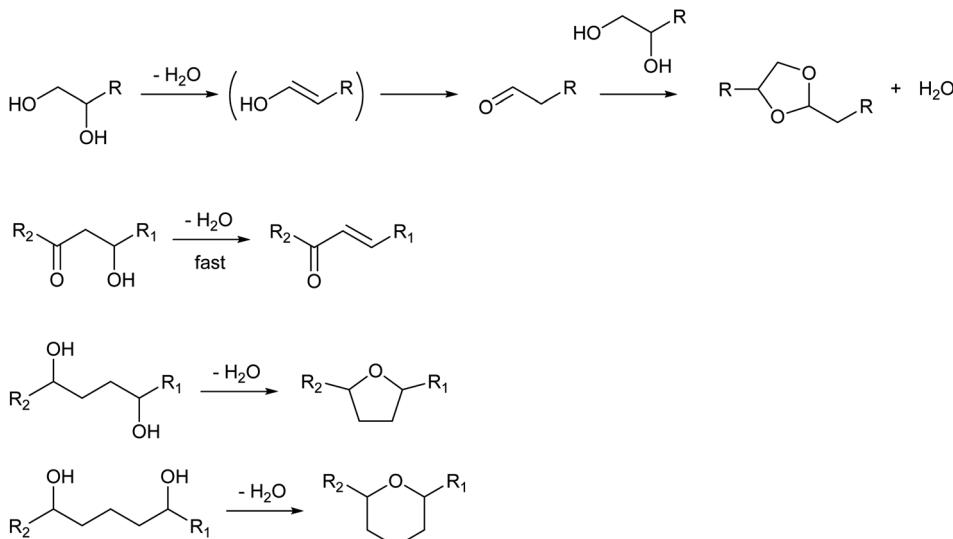
Scheme 2 Effect of other functional groups on dehydration of alcohols.
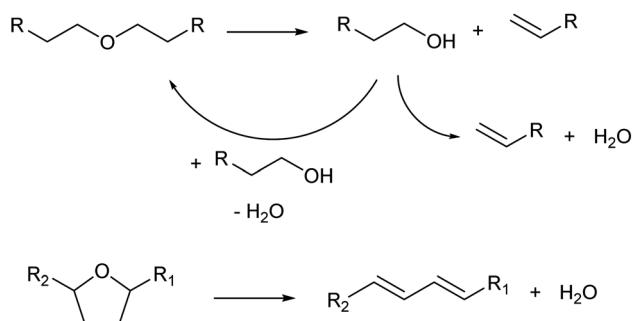
Scheme 3 Dehydration of ethers.

Scheme 4 Dehydration of alcohols over acid–base bifunctional catalysts.

surface can possess acid–base bifunctionality. The proposed mechanism is shown in Scheme 4. Over such amphoteric catalysts, an alcohol substrate is adsorbed on the acid site with the OH group. The vicinal C–O and C–H bonds are dissociated simultaneously, with the acid and base sites, respectively. This is a variant of the E2 mechanism; one difference from the general E2 reaction is that the two bonds are dissociated with *syn* configuration,[27,28] while the general E2 reaction with a strong homogeneous base is the dissociation with *anti* configuration. An important feature of the dehydration over bifunctional catalysts is the suppression of cyclization of diols. With strong Brønsted acid catalysts, only the C–OH group is activated, and the S_N2-type cyclization easily occurs by the reaction between the activated C–OH moiety as a leaving group and another C–OH as a nucleophile. On the other hand, acid–base bifunctional catalysts activate vicinal C–O and C–H bonds simultaneously, and these sites react selectively. Side reactions over bifunctional catalysts are different from those with strong Brønsted acid catalysts. Dehydrogenation to aldehyde, reactions of the aldehydes such as condensation and decarbonylation, and the movement of C=C bonds are typical side reactions. Catalyst development is necessary to suppress such side reactions.

2.2. Deoxydehydration: another C=C formation reaction

Deoxydehydration (commonly abbreviated as DODH) is another reaction for the formation of C=C bonds. Deoxydehydration reductively converts vicinal diols to C=C groups (Scheme 5).[29,30] The term "deoxydehydration" only means the formal change of atoms in the substrate ($-O-H_2O = -2O-2H$); rather, deoxydehydration can be regarded as the reverse reaction of *cis*-dihydroxylation of olefins (*i.e.* oxidation with osmium tetroxide). The merit of deoxydehydration in the production of olefinic compounds is the direct use of the polyfunctionalized substrate.[6] Dehydration reaction of polyfunctionalized substrates has a large number of possible products, and it is generally difficult to obtain high selectivity. In contrast, deoxydehydration gives much simpler product distribution and is sometimes stereospecific.[31] Typically, deoxydehydration is catalyzed by homogeneous Re species, and two-electron reducing agents such as PPh_3 and secondary alcohols are used. The Re-catalyzed deoxydehydration proceeds with a two-electron redox cycle of high-valent monomeric Re species, composed of three steps: coordination of the vicinal diol substrate to Re as diolate species, two-electron reduction of the Re diolate species, and removal of the olefin to leave oxidized Re. The recent development of deoxydehydration systems has enabled the use of heterogeneous catalysts and H_2 as the reducing agent.[32,33] A variant of deoxydehydration is the

Scheme 5 Deoxydehydration (DODH) reaction.

stoichiometric use of formic acid.[34] Formic-acid-based deoxy-dehydration does not use a catalyst and produces CO_2 as a by-product. Although deoxydehydration has not been industrially carried out, the recent rapid development of deoxydehydration systems may lead to industrial use in the future.

2.3. Hydrodeoxygenation: control of the number or position of functionality

Because of the difficulty of the selectivity control in the formation of C=C groups, excess functional groups in substrates should be removed before the formation of C=C groups. The functional groups in biomass-derived molecules are mainly oxygen-containing ones, and their removal (deoxygenation) requires a reductive reaction. Among the reducing agents, H_2 is by far the best one, in view of both atomic economy and cost. Although the use of H_2 may not be convenient in laboratory experiments because of its explosive nature, this does not matter in industrial processes. The selectivity of deoxygenation with H_2 as the reducing agent (hydrodeoxygenation) can be controlled by catalysts.[35–37] Various catalysts with different selectivity patterns have been reported, and the development of catalysts with novel selectivity has been a hot research field in these days.

There are several types of mechanisms of hydro-deoxygenation, depending on catalysts, substrates and even reaction conditions. The mechanisms of hydrodeoxygenation include dehydration + hydrogenation, deoxydehydration + hydrogenation, and direct hydrogenolysis over a metal surface.[38] The dehydration + hydrogenation mechanism over acid + metal bifunctional catalysts is the most typical route. However, it is difficult to obtain very high selectivity with dehydration + hydrogenation due to the same reason as dehydration discussed above. In addition, it is also difficult to combine "dehydration + hydrogenation" with "dehydration" to selectively obtain a single olefin because the C–O bonds that are reactive in dehydration have been removed in the former step. It is easier to obtain high olefin yield when different types of reactions are combined such as the combination of "deoxy-dehydration + hydrogenation" and "dehydration".

2.4. Control of the carbon chain

There are some methods to change the carbon skeletons of organic molecules. However, during the decrease of the carbon chain length, the loss of atom economy is inevitable. It is generally difficult to obtain high selectivity during the extension of the carbon chain (dimerization and oligomerization) or isomerization of the carbon chain. The low selectivity also decreases the atom economy. Considering that biomass is a precious resource in comparison with petroleum, a good atom economy is highly desirable.
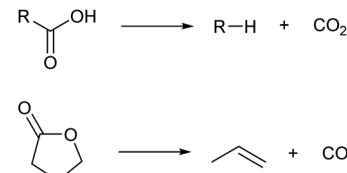

Scheme 6 Decarboxylation reactions.

Among the methods to shorten a carbon chain length, decarboxylation is the most harmless one (Scheme 6).[39] There is no consumption of costly reagents such as H_2. The most oxidized carbon atom in the substrate is removed as carbon dioxide, and the loss of internal energy is minimal if decar-boxylation proceeds ideally. The substrates of decarboxylation are carboxylic acids, esters and lactones, and there are many biomass-derived molecules in these categories.[4,6] Decarboxyl-ation of lactones is especially useful because olefins are directly produced. Various catalysts such as zero-valent metals, acids and bases are applicable to decarboxylation. The reaction temperature for decarboxylation is generally high (such as 523 K) which leads to isomerization of products.

Decarbonylation also decreases the carbon number by one (Scheme 7). Although the loss of free energy is slightly larger than decarboxylation, decarbonylation is also useful in the selective synthesis of hydrocarbons from highly oxidized molecules. Decarbonylation of aldehydes is typically catalyzed by zero-valent noble metals such as Pd.[40] An important variant is decarbonylative dehydration of carboxylic acids which gives olefins directly.[41,42] Decarbonylative dehydration is catalyzed by noble metal complexes via pathways composed of oxidative addition, decarbonylation, β-hydride elimination and reductive elimination. Sacrificial dehydrating agents such as acetic anhydride are necessary in typical systems, and the develop-ment of systems without such requirements is desirable.

Another method worth mentioning for the control of the carbon chain is metathesis (Scheme 8).[43–45] Metathesis is the mutual exchange reaction of two olefin molecules with their alkylidene units. This reaction is useful in the production of olefins with higher demand from those with lower demand and has been already industrialized for the manufacture of some
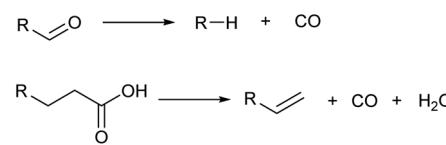
Scheme 7 Decarbonylation and decarbonylative dehydration.
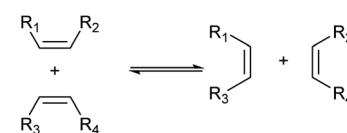
Scheme 8 Olefin metathesis.

olefins such as propylene from 2-butene and ethylene.[44] Typical catalysts are supported high-valent transition metal oxides (MoO_x, WO_x and ReO_x)[46] and homogeneous Ru complexes.[47] The selection of reactants is especially important because both products should be utilized to maximize the atom efficiency of the whole process.

2.5. Catalyst deactivation

Deactivation of catalysts is a frequently encountered problem in the catalytic conversions of biomass-related compounds.[48,49] Coking is the most common cause of the deactivation of solid acid catalysts. Coking is the deposition of carbonaceous material (coke) on the catalyst surface, which leads to catalyst deactivation by covering the active site and/or clogging the pore. Oligomerization and dehydrogenation are the main formation routes of coke for acid catalysts, especially when highly unsaturated compounds are involved in the system. This formation mechanism is similar to the case of FCC[50] where acid catalysts and unsaturated products are similarly involved. Avoiding too strong acids, applying lower reaction temperature and adding water to the feed are effective in suppression of coking; however, these methods tend to decrease the dehydration rate as well. It is difficult to completely suppress coking, and regeneration by calcination is common for solid acid catalysts. Stability during the regeneration, especially against sintering of fully oxidized phases, is also necessary. In view of stability during regeneration, too sophisticated preparation process is not advantageous. Materials obtained by calcination as the final step of preparation are usually stable during regeneration. For the supported catalysts, the selection of support is critical in the stability of the regeneration.

In the liquid phase reaction, leaching of active species to the liquid phase, phase change or sintering during the reaction, and poisoning are major causes of catalyst deactivation. When deactivation is observed, it is necessary to find the cause by characterization of the deactivated catalyst. The hot-filtration test and elemental analysis of the reaction solution are effective methods to detect leaching. Countermeasures against deactivation depend on the cause for the deactivation. Selections of support, solvent and reaction conditions can affect the leaching, and the use in gas-phase reaction can be a solution. Phase change and sintering are difficult problems to solve. It is necessary to find a method to regenerate the catalysts. For poisoning, purification of the substrate, washing the used catalyst, or regeneration of used catalysts is tested depending on the type of poison.

## 3. Specific products

3.1. C3 compounds

While most C3 compounds in petrochemistry are manufactured from propylene, propylene cannot be obtained easily from biomass. The most accessible biomass-derived C3 compound is glycerol, which is a by-product of biodiesel manufacture from triglycerides. Glycerol is co-produced in the ratio of about 10 wt% to biodiesel. The production of waste glycerol reaches 5

million tons per year and is further increasing.[51] As another biomass-based C3 compound, lactic acid has been already industrially produced by fermentation.[52–54] Chemical synthesis of lactic acid from sugars is also possible.[55] The current production capacity of lactic acid (<1 million tons per year as polylactic acid)[56] is significantly smaller than that of the biodiesel industry. The production of acetone by ABE (acetone–butanol–ethanol) fermentation[57] and that of 1,2-propanediol from sugars by hydrogenolysis[58,59] are possible, but these are not regarded as main methods to obtain renewable C3 compounds at present.

3.1.1. Acrolein and acrylic acid. Acrolein and acrylic acid are C3 unsaturated oxygenates synthesized on an industrial scale. They are synthesized by oxidation of propylene (Scheme 9) and are versatile intermediate compounds for many chemicals.[60] One representative use is the source of sodium polyacrylate, which is the most typical superabsorbent polymer. In addition, acrolein is an intermediate of ammoxidation of propylene to acrylonitrile.[61] While the current ammoxidation process is carried out in one step, acrylonitrile can be synthesized from isolated acrolein.

Acrolein can be produced relatively easily from glycerol, by acid-catalyzed double dehydration.[60,62–64] Typical catalysts are W-based ones and zeolitic materials such as heteropolyacids and H-ZSM-5, respectively. The reaction temperature is around 573 K and the acrolein yield is around 80%. Water is usually added to the feed. The role of water includes the retention of Brønsted acidity of catalysts at the high reaction temperature. For zeolitic catalysts including zeolites, the control of pore size distribution is essential. Traditional zeolite crystals with only micropores tend to be deactivated rapidly by the formation of coke. Hierarchical zeolites have been reported to be more durable catalysts.[65,66] Nevertheless, the long-term catalyst durability remains a challenge in the production of acrolein. Lists of reported systems can be found in recent review papers.[63,64]

Oxidization of acrolein produces acrylic acid, which has been an established process in petrochemistry. Therefore, glycerol-based acrylic acid can be obtained by using acrolein as an intermediate.[67–69] Direct production of acrylic acid from glycerol
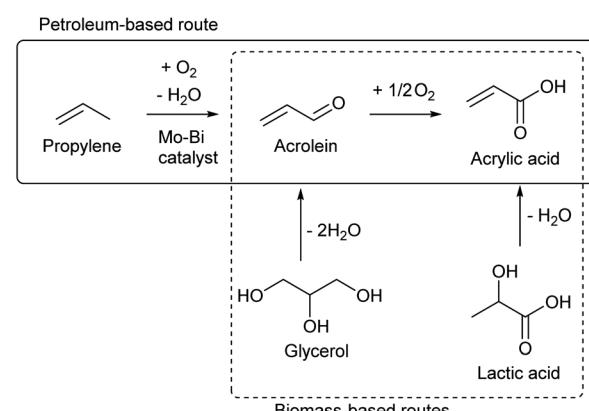
Scheme 9 Synthesis of acrolein and acrylic acid.

is possible by combining oxidation and acid catalysts.[70] Typical component of the former is vanadium oxide and that of the latter is tungsten oxide. The yield of acrylic acid (typically 30–60%) has been significantly lower than that of acrolein in simple dehydration systems. Although coke formation can be suppressed under oxidative conditions, stability is still a problem for the catalyst under (hydro)thermal conditions.

The demand of acrylic acid is over 5 million tons per year.[67] The demand of acrylonitrile, which is also a probable derivative of biomass-based acrolein, is in a similar level to acrylic acid.[71] It is unrealistic for glycerol conversions to cover all the demands of acrolein and acrylic acid, considering that there are many other valuable glycerol conversions. A report on life cycle assessment (LCA) of acrolein production from glycerol revealed that there is a very high environmental load during the agricultural stages.[72] This means that an increase in vegetable oil production only to obtain acrolein is unacceptable. The production methods of acrolein or acrylic acid from sugars are also worth developing. One method is the conversion of lactic acid which is a fermentation product of sugars.[68,69] Stoichiometrically, dehydration of lactic acid can give acrylic acid. This reaction is difficult among dehydration reactions, because the presence of the carbonyl group at the 1-position promotes the removal of groups at the 2-position as a cation ($-H^+$) rather than as an anion ($-OH^-$). High temperature is necessary for the dehydration of lactic acid, and severe conditions promote undesirable side reactions such as decarboxylation. The dehydration of lactic acid requires acid–base bifunctional catalysts such as calcium phosphate,[73–75] alkali salts of zeolites[76–78] and barium sulfate.[79–81] The use of alkali or alkali earth metals is characteristic of the catalysts in this reaction, and these metal sites bind the carboxylic group of lactic acid. The dehydration of the bound lactic acid requires an additional pair of acid and base sites which attack the 2- and 3-positions, respectively. The reactions are typically carried out under flow conditions in the presence of water at high temperature (about 623 K). Some systems obtained about 80% yield of acrylic acid.[73,75,78–81] Dehydration of alkyl lactates has been also reported.[82–84] The co-fed solvent is water or the corresponding alcohol to the alkyl group. When water is used as the co-fed solvent for dehydration of alkyl lactates, the product is acrylic acid. The reactivity over hydroxyapatite (a class of calcium phosphate) was in the order of lactic acid > methyl lactate > ethyl lactate, while the selectivity to acrylic acid was in the opposite order.[83] Long-term stability is a major issue in dehydration of lactic acid and alkyl lactates, like many other catalytic dehydration systems. Sels *et al.* recently reported that the co-feeding of methanol and water is advantageous to the inhibition of catalyst (K–ZSM-5) deactivation in methyl lactate dehydration.[84] Considering that the catalyst requires three sites (alkali/alkali earth metal, acid and base) with appropriate positions, zeolite-based catalysts seem more promising because of the controllable structure.

Feringa *et al.* recently reported another approach to the synthesis of acrylic acid.[85] This approach uses maleic anhydride as the starting compound which can be synthesized from either petroleum or biomass, as described later. Maleic anhydride is hydrolyzed to maleic acid, and then metathesis of maleic acid and ethylene gives two molecules of acrylic acid. Maleic acid was converted quantitatively to acrylic acid with an excess amount of ethylene and the commercially available Ru-based Hoveyda–Grubbs second-generation catalyst.

3.1.2. Allyl alcohol. Allyl alcohol is a useful intermediate chemical. The traditional production method is the hydrolysis of allyl chloride which is synthesized by chlorination of propylene. Isomerization of propylene oxide has been used in industrial plants built recently.[86] The industrial production amount of allyl alcohol is about 1 million tons per year, which means that total substitution of propylene is possible with glycerol as the raw material of allyl alcohol. There are four methods for production of allyl alcohol from glycerol (Scheme 10): acrolein hydrogenation, 1,2-propanediol dehydration, thermal decomposition of glycerol and deoxydehydration of glycerol. Allyl alcohol production by acrolein hydrogenation requires selective hydrogenation of the C=O bond out of the C=C bond. Selective C=O hydrogenation of conjugated α,β-unsaturated aldehydes is a hot topic and many
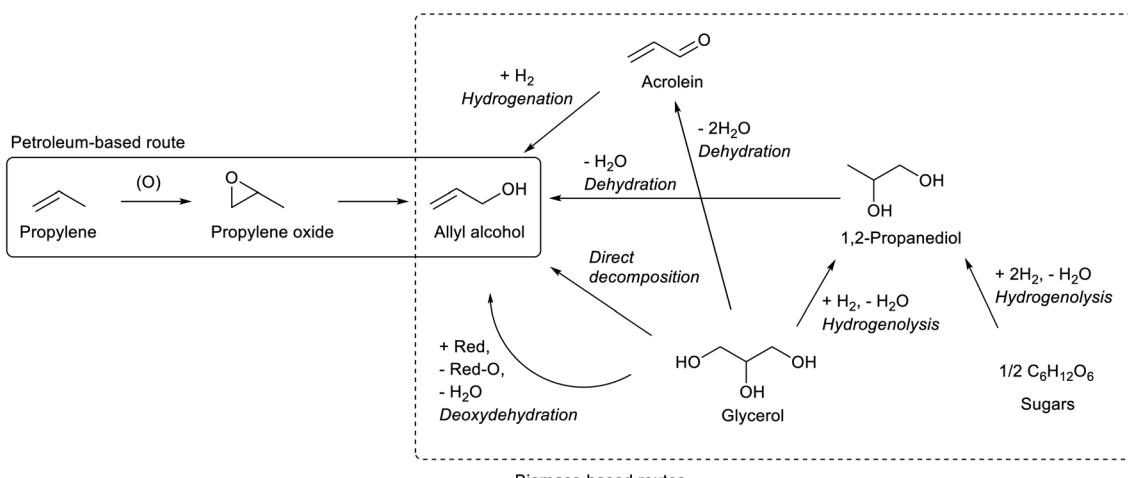
Scheme 10 Allyl alcohol synthesis.

effective systems have been reported.[87] However, acrolein is the most difficult substrate to obtain a high yield of the corresponding unsaturated alcohol because the small steric hindrance around the C=C bond hampers the selective recognition toward the C=O bond. Among hundreds of reports for selective hydrogenation of α, β-unsaturated aldehydes,[87–90] only a few papers reported over 30% selectivity to allyl alcohol, and the activity of catalysts in these reports was low.[91–94] The use of non-H$_2$ reductants (transfer hydrogenation) enables good yield of allyl alcohol more easily;[95–97] but the cost of the reductant and low atom efficiency are severe problems.

1,2-Propanediol can be synthesized from glycerol by selective hydrogenolysis.[98,99] While 1,2-propanediol has been conventionally synthesized by hydration of propylene oxide, glycerol-based 1,2-propanediol has also been already commercialized.[59,98] Hydrogenolysis of sugars to 1,2-propanediol is also possible.[58,59] Dehydration of 1,2-propanediol usually gives propanal; however, with an appropriate catalyst, namely K-doped ZrO$_2$, allyl alcohol was obtained with a significant selectivity (about 50%, at 64% conversion; conditions: 673 K, gas hourly space velocity (GHSV) 9051 h^{-1}, Ar/1,2-propanediol/H$_2$O = 31/1/12).[100] Strong basicity with the appropriate acid/base balance of catalysts is the key to selective dehydration. Severe deposition of the condensation product on the catalyst was observed. This reaction is closely related to the dehydration of 2,3-butanediol which will be discussed below. The catalysts for dehydration of 1,2-propanediol and 2,3-butanediol will be developed at the same time.

The method of thermal catalytic decomposition of glycerol is composed of glycerol dehydration to acrolein and transfer hydrogenation of acrolein with glycerol as the reducing agent. Fe-based catalysts have been mainly reported,[101–104] although why Fe is effective in this reaction is not clarified yet. Other reported catalysts include vanadium- and niobium-based ones.[105,106] However, the severe conditions and consumption of glycerol as the reducing agent limit the selectivity to allyl alcohol below 30% until the 2010s. In 2020, two reports showed higher selectivity by using Mo–Fe catalysts with further modification: MoFe/V-KIT-6 catalyst (31.4% selectivity to allyl alcohol at 92.1% conversion)[107] and CsFeMo–ZSM-5 catalyst (52.0% selectivity at 93.8% conversion).[108] In thermal decomposition, the balance of the reductant and substrate should be considered when high selectivity to allyl alcohol is obtained: the production of one allyl alcohol molecule consumes one hydrogen molecule, and hydrogenolysis such as formations of 1,2-propanediol, propanols, ethanol and acetone also consumes H$_2$ molecules. Without co-feed of H$_2$, the H$_2$ molecules must be supplied by the formation of other glycerol-derived products. Except reforming reactions, it is difficult to supply more than one H$_2$ molecule per one glycerol molecule: C$_3$H$_8$O$_3$ → 3C (coke) + 3H$_2$O + H$_2$; C$_3$H$_8$O$_3$ → 3HCHO + H$_2$; C$_3$H$_8$O$_3$ → $\frac{3}{2}$CH$_3$COOH + H$_2$. It is very difficult to obtain >50% selectivity without co-feed of H$_2$, while with H$_2$ the C=C bond in allyl alcohol is easily hydrogenated over most metal catalysts. Also in 2020, Zhaoyin Hou *et al.* reported very promising results of high allyl alcohol yield from glycerol with H$_2$ and the CoFe alloy catalyst.[109] In this system, Fe can work as the active center for

allyl alcohol formation, and Co is the hydrogenation catalyst of the C=O bond in acrolein (precursor of allyl alcohol) or glyceraldehyde (formed by transfer hydrogenation). Alloying of Co with Fe further decreases the C=C hydrogenation ability. Recent reports for the glycerol conversion to allyl alcohol with or without H$_2$ are summarized in Table 2.

Deoxydehydration of glycerol is another method of one-step production of allyl alcohol from glycerol. Glycerol to allyl alcohol is one of the most attractive applications of deoxydehydration, and there are several reports for catalyst development and the reactor setup.[110–112] While earlier reports used homogeneous catalysts and secondary alcohols as reducing agents,[110,113] we have recently developed heterogeneous ReO$_x$–Au/CeO$_2$ and ReO$_x$–Ag/CeO$_2$ catalysts for the synthesis of allyl alcohol from glycerol with H$_2$ as the reducing agent.[114,115] The yield of allyl alcohol reached over 90%. In these catalysts, atomically dispersed ReO$_x$ species on CeO$_2$ works as the active site of deoxydehydration, and the added metal (Au or Ag) activates the H$_2$ molecule to supply hydrogen species to reduce the ReO$_x$ species. The crystalline CeO$_2$ support is essential in this catalyst, and its roles include stabilizing monomeric high-valent (≥+4) Re species and carrying activated hydrogen species as protons and electrons from added metal sites to Re species.[116] For ReO$_x$–Au/CeO$_2$, the control of the particle size of Au is necessary: around 10 nm of Au particle size is appropriate for selective production of allyl alcohol. Too small Au particles catalyze the hydrogenation of allyl alcohol to 1-propanol in addition to H$_2$ activation, which decreases the selectivity to allyl alcohol at a high conversion level. However, the high selectivity of ReO$_x$–Au/CeO$_2$ with larger Au particle size is obtained at the cost of lower activity because of the limited H$_2$ activation ability of the Au metal surface.[117] On the other hand, Ag species in ReO$_x$–Ag/CeO$_2$ do not have such strong structure sensitivity, and both high activity (comparable to ReO$_x$–Au/CeO$_2$ with small Au particles) and selectivity to allyl alcohol can be obtained without precise control of the Ag particle size.[115] Considering also the lower price of Ag than that of Au, ReO$_x$–Ag/CeO$_2$ is a superior catalyst. Although the catalyst recyclability of ReO$_x$–Au/CeO$_2$ and ReO$_x$–Ag/CeO$_2$ has been confirmed at least three times when they are calcined after use as regeneration,[114,115] long-term stability should be investigated for this type of catalyst.

3.1.3. Propylene. There are several methods to synthesize propylene from biomass-derived compounds (Scheme 11). Propanols can be synthesized from glycerol relatively easily, by dehydration (to acrolein) + hydrogenation,[118,119] deoxydehydration (to allyl alcohol) + hydrogenation,[120–122] and metal-catalyzed hydrodeoxygenation.[123–125] Heterogeneous hydrodeoxygenation catalysts can adsorb polyols more strongly than mono-alcohols, and such preferential adsorption can suppress successive hydrodeoxygenation of propanols until complete consumption of glycerol and propanediols. Acid-catalyzed dehydration of propanols gives propylene. Direct synthesis of propylene by hydrodeoxygenation of glycerol has been also reported typically with Mo-based catalysts.[38,126,127] The yield was about 80% for both multistep synthesis (combined yield) and direct synthesis methods. The direct synthesis method requires a relatively high

Table 2 Selected recent reports for glycerol (G) conversion to allyl alcohol (AA)

Entry	Catalyst	Gas phase or carrier	Liquid phase or feed	Temp. [K]	Time [h]	Conv. [%]	Main products (selectivity [%])	Ref.
1	MoFe/V-KIT-6. 0.5 g	N_2, 0.6 L h^{-1}	35% G aq., 1 mL h^{-1}	613	—[a]	92.1	AA (31.4), acrolein (17.0), acetaldehyde (14.4)	107
2	CsFeMo–ZSM-5, 0.5 g	N_2, 0.6 L h^{-1}	10% G aq., 1 mL h^{-1}	623	—[a]	93.8	AA (52.0), acetol (18), 1,2-propanediol (7), acrolein (5)	108
3	CoFe(1 : 1)-ZIF-reduced, 0.2 g	H_2, 2 MPa	40% G, 1.2 mL h^{-1}, H_2/G = 40	523	—[a]	89.7	AA (68.7), acetol (8.8), 1,2-propanediol (8.7), 1-propanol (7.5)	109
4	ReO$_x$–Au/CeO$_2$, 0.3 g	H_2, 8 MPa	G 0.5 g, 1,4-dioxane 4 g	413	52	>99	AA (91), 1-propanol (5)	114
5	ReO$_x$–Ag/CeO$_2$, 0.3 g	H_2, 8 MPa	G 0.25 g, 1,4-dioxane 4 g	413	12	93	AA (99), 1-propanol (<1)	115

[a] Flow system.

temperature (about 573 K). In either case, the synthesis of propylene from glycerol consumes 2 equiv. of H_2 ($C_3H_8O_3 + 2H_2 \rightarrow C_3H_6 + 3H_2O$). Ethanol is an inexpensive biomass-derived compound, and the synthesis of propylene from ethanol has been investigated.[128] Typical catalysts are metal-modified H-ZSM-5 zeolites. The yield of propylene has been low (typically <30%) because of the difficulty in the control of the carbon chain length. Some petrochemical reactions of ethylene may be also used in the synthesis of biomass-derived propylene.[129] Hydroformylation of (bio)ethylene and hydrogenation gives 1-propanol which can be further dehydrated to propylene. Metathesis of ethylene and 2-butene gives selectively propylene.[46]

Propylene production from biomass is a sore subject in biomass conversion. Propylene is one of the most important key compounds in petrochemistry: a very large amount of propylene is manufactured by naphtha cracking or FCC of heavier oil and is utilized as an intermediate for many chemicals such as polypropylene, phenol (*via* cumene), acrylonitrile and acrolein. The current annual production amount is over 50 million tons for even polypropylene alone, which can be synthesized only from propylene.[130] One major issue of propylene production from biomass is the inherent cost of the reductant. Production of propylene inevitably involves removal of large amounts of oxygen atoms in biomass. If C3 compounds are produced from glycerol, the price (cost) will be in the order of propanediols < propanols < propylene < propane. This order is totally opposite to that in petrochemistry. Large-scale use of glycerol as the source of propylene is thus not realistic; rather, glycerol should be converted to functionalized compounds including those

currently synthesized from propylene such as acrolein, acrylic acid and acrylonitrile in view of the reductant cost. Ethanol or bio-ethylene upgrading is a more promising method for bio-propylene, and lower greenhouse gas emission by bioethanol-based propylene is suggested;[131] however, the gap between the cost of bio-propylene production and the low price of petro-chemical propylene is still large. The use of propylene in the chemical industry should be significantly decreased when biomass becomes the main source of organic chemicals.

3.2. C4 compounds

There are several routes for the synthesis of C4 compounds in petrochemistry. One is the direct recovery from the naphtha cracking products, and such C4 components include butenes, butadiene, and isobutene (Table 3). Yet, the main target products of naphtha cracking are ethylene and propylene, and these C4 compounds are rather minor by-products (Table 1). Therefore, the supply of C4 compounds from naphtha cracking depends on the production amount of ethylene and propylene. The use of lighter hydrocarbon resources such as associated gas than naphtha for ethylene production is a recent trend in petrochemistry, and such a process yields a lower amount of the C4 fraction.[132] Therefore, the use of biomass-derived C4 compounds will be competitive even in the near future. Another synthesis route of C4 compounds in petrochemistry is the use of maleic anhydride as an intermediate. Maleic anhydride is synthesized from *n*-butane or benzene (the former is preferable) by selective aerobic oxidation over the vanadium phosphorous oxide catalyst.[133,134] The use of biomass-derived substrates such
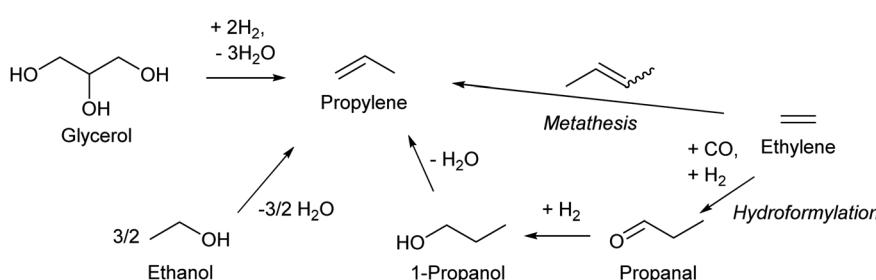
Scheme 11 Synthesis routes of propylene.

Table 3 Example of distribution of the C4 fraction of naphtha cracking products[2]

Compound	Formula	Distribution (wt%)
n-Butane	C_4H_{10}	0.4
Isobutane	C_4H_{10}	0.75
Isobutene	C_4H_8	22.83
1-Butene	C_4H_8	15.40
cis-2-Butene	C_4H_8	3.41
trans-2-Butene	C_4H_8	4.93
1,3-Butadiene	C_4H_6	50.54
1,2-Butadiene	C_4H_6	0.13
Ethylacetylene	C_4H_6	0.18
Vinylacetylene	C_4H_4	1.27

as furfural,[135] 5-hydroxymethylfurfural (HMF)[136] and levulinic acid[137] for maleic anhydride synthesis has been confirmed to be possible (Scheme 12).[138,139] Extension of the carbon chain is another approach to synthesizing C4 compounds in petrochemistry, such as acetaldehyde condensation (C2 + C2) and propylene hydroformylation (C3 + C1). The use of biomass-derived acetaldehyde is possible.

While chemical synthesis of C4 compounds from raw biomass is not easy, fermentation with suitable microorganisms can selectively produce C4 compounds. Such fermentation products include 1-butanol, isobutyl alcohol, butanediols, erythritol, succinic acid and fumaric acid.[4–6,140,141] Fermentation uses substrates themselves as reducing agents, and therefore more oxidized products tend to be obtained in higher yields. The combination of chemical and biological conversions is an effective method to produce a less oxidized C4 compound in high yield.

Because sugar units in biomass resources have C5 and C6 carbon chains, there are several C5 oxygenates that can be relatively easily obtained from biomass. Decarboxylation of C5 compounds is also a useful reaction to produce C4 chemicals.

3.2.1. Butadiene. Butadiene, here we assume 1,3-butadiene, is used as a monomer of synthetic rubber and ABS resin and is the most important C4 olefin in the chemical industry.[142] The demand of butadiene is over 10 million tons per year. Because of the importance and low yield by naphtha cracking, sustainable production of butadiene has been a hot topic in the field of biomass conversion.[142,143] Proposed production routes of butadiene from biomass are ethanol upgrading, dehydration of butanediols, deoxydehydration of erythritol and dehydration of tetrahydrofuran (THF) (Scheme 13).

Ethanol upgrading is the most investigated route and has the longest history (over 100 years).[142,144] The list of recently reported systems can be found in a review paper.[142] This reaction consists of dehydrogenation, aldol condensation, hydrogenation and dehydration (Scheme 14). The hydrogenation step can be coupled with the dehydrogenation step, as transfer hydrogenation with ethanol. Basicity and acidity are necessary for the condensation step and dehydration step, respectively. Although the base sites can catalyze dehydrogenation and hydrogenation steps, metallic species such as Cu and Ag are more effective for these steps. A typical catalyst for ethanol upgrading to butadiene is the combination of MgO/SiO_2 and metal.[145] Supported group 4–5 (Zr, Hf and Ta) metal oxides on SiO_2 with or without metals are also frequently investigated catalysts. The reaction temperature is above 523 K (typically around 623 K) because of the thermodynamic limitation of the dehydration step (crotyl alcohol to butadiene). There are many possible side reactions, such as overhydrogenation to butenes, decarbonylation to C1 + C3 products, ketone formation and polymerization. Because of the high reaction temperature and complicated reaction network, the selectivity is difficult to improve above 70%. The catalyst life is also a serious issue. Coking is a major reason of catalyst deactivation. Designing an appropriate pore structure and the co-feed of water can slow down the coking. The structural stability during hydrothermal conditions and regeneration treatment are remaining issues. Recent techno-economic and
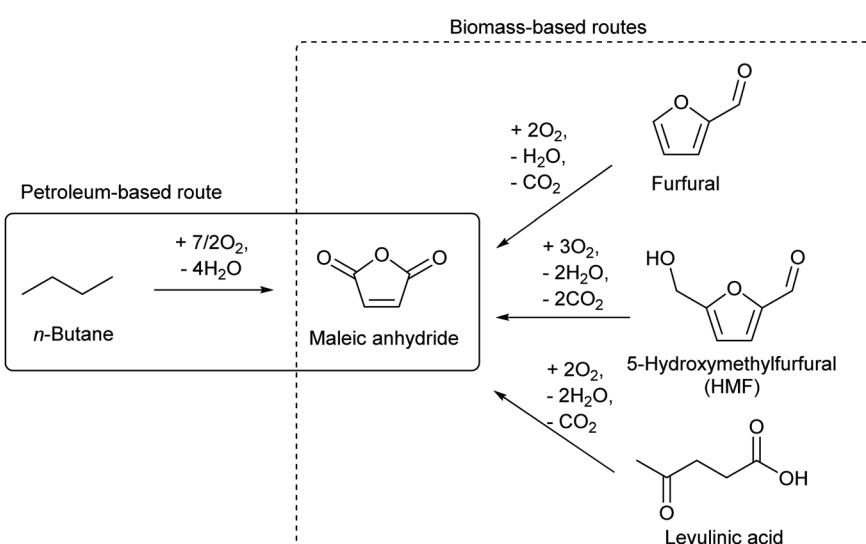
Scheme 12 Synthesis of maleic anhydride.
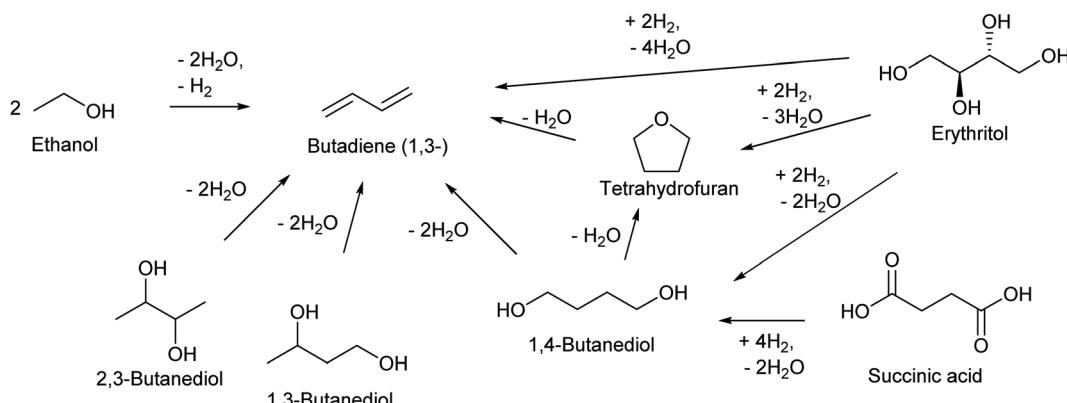
Scheme 13 Synthesis of butadiene from biomass. The displayed compounds except butadiene and tetrahydrofuran are fermentation products.
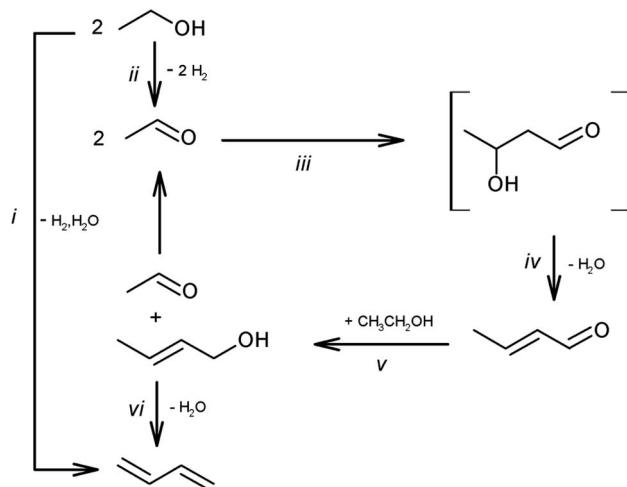
Scheme 14 Pathways of ethanol conversion to butadiene. Reprinted from ref. 145 with permission from the Royal Society of Chemistry.

life cycle assessments demonstrated the potential of ethanol-based butadiene for a large decrease in greenhouse gas emission, and the catalyst performance in the butadiene formation step much affects the results.[146]

Dehydration of butanediols is a simpler route to butadiene than ethanol conversion in a chemical view.[147,148] The main production method of butanediols is fermentation. Each butanediol isomer (1,2-, 1,3-, 1,4- and 2,3-) can be obtained with an appropriate bacterial species. Chemical synthesis of butanediols from biomass-derived compounds is possible, such as hydrogenation of succinic acid[149–152] and hydrogenolysis of erythritol[6,124,153,154] and 1,4-anhydroerythritol.[155–157] The chemically synthesized butanediol is usually the 1,4-isomer, although some methods produce a mixture of isomers. The difficulty and catalyst of butanediol dehydration to butadiene much depend on the position of OH groups in the substrate molecules (Scheme 15). Since dehydration of 1,2-butanediol typically produces butanal, 1,2-butanediol is not usually regarded as a source of butadiene. Most papers for butadiene synthesis by dehydration of butanediols were published within these 10

years. The recent progress in this research area is based on the effectiveness of rare-earth oxide catalysts in the dehydration of diols to unsaturated alcohols which is the first step of butadiene synthesis from butanediols. The findings date back to the report by Sato *et al.* in 2003,[158] and his group has been leading the research field of dehydration of diols.[26,147]

1,3-Butanediol is the easiest isomer to be converted to butadiene because the dehydration itself does not generate by-products. 1,3-Butanediol dehydration proceeds over both strong acid catalysts and acid–base bifunctional catalysts. Strong acid catalysts such as zeolites tend to accompany propylene formation as a side reaction, and the selectivity to butadiene is around 60%.[159,160] Bifunctional catalysts can suppress C–C dissociation reactions, and high yield (>90%; over $Y_2Zr_2O_7$ catalyst) has been
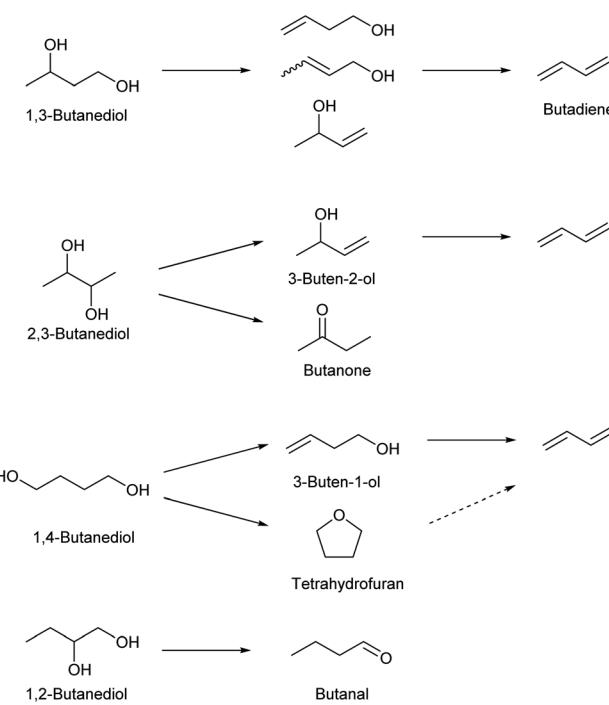
Scheme 15 Dehydration of butanediols. Each arrow represents removal of one water molecule.

reported, although the reaction temperature ($\geq$633 K) was higher than that of the systems of strong acid catalysts (around 573 K).[161,162]

Dehydration of 2,3-butanediol has been more intensively investigated because the fermentative production of 2,3-butanediol is relatively easy. However, simple acid-catalyzed dehydration of 2,3-butanediol produces butanone (frequently called as methyl ethyl ketone or MEK) rather than butadiene or 3-buten-2-ol intermediate.[163] Dehydration to 3-buten-2-ol or butadiene requires removal of hydrogen at the terminal positions (1- and 4-). To obtain such selectivity, the reaction should be driven by a base instead of acid, and the base site is better to be sterically hindered to control the accessibility toward the terminal positions. Solid acid–base bifunctional catalysts with basic nature are effective, such as scandium oxide.[163] The yield of butadiene reached about 90% with scandium oxide-based catalysts.[164] Metal phosphate catalysts have been also tested. Typical phosphate catalysts are less selective than scandium oxide catalysts,[165–167] while one relatively old report using CsH_2PO_4/SiO_2 showed a very high 92% yield.[168] The highest yield (94%) was obtained with a dual bed system composed of Sc_2O_3 and Al_2O_3 catalysts.[169]

Dehydration of 1,4-butanediol has been also investigated, since 1,4-butanediol can be produced either biologically or chemically. Both biomass and fossil resources can be the raw material for the chemical synthesis of 1,4-butanediol. However, the dehydration of 1,4-butanediol to butadiene is not easy. Brønsted acid catalysts easily cyclize 1,4-butanediol to tetrahydrofuran which is much less reactive than the substrate.[170] Acid–base bifunctional catalysts can promote the C=C bond formation. Because the hydrogen atoms that are removed by the base are located at inner positions, activation of more accessible hydroxy groups at the terminal positions is necessary. Therefore, the balance of acidity and basicity and/or even the positions of these sites much affect the catalytic performance.[171] Rare-earth metal oxides have been reported to be effective such as CeO_2 (ref. 170) and Yb_2O_3.[161,172] Yb_2O_3 catalysts show excellent yields of butadiene (commercial Yb_2O_3: 96.6% at 633 K;[161] Yb_2O_3 prepared through hydrothermal aging: 97.4% at 723 K (ref. 172)). The high yields were maintained at a time-on-stream of 10 h ($\geq$95%). There was a slight increase of tetrahydrofuran selectivity at long time on stream, which is due to the accumulation of acidic carbonaceous material. The two-step method, 1,4-butanediol to 3-buten-1-ol as the first step and 3-buten-1-ol to butadiene as the second step, is an option to obtain good performance including long catalyst life.[147,148] The catalyst for the first step should have weak acidity in order to suppress the cyclization to tetrahydrofuran. A high reaction temperature (typically >623 K) is necessary. In the second step, the negative effect of acidity on the selectivity is lower than that in the first step. Acidic catalysts can be used for the second step, enabling the decrease in the reaction temperature.

As described above, tetrahydrofuran can be easily obtained by acid-catalyzed dehydration of 1,4-butanediol. Other production methods of renewable tetrahydrofuran include furfural decarbonylation to furan followed by hydrogenation[173] and 1,4-anhydroerythritol didehydroxylation (one-step deoxydehydration + hydrogenation).[120–122] Dehydration of tetrahydrofuran to butadiene is possible with strong acids but very difficult. The ring-opening of tetrahydrofurans involves carbocation intermediates; however, from tetrahydrofuran the intermediates are unstable primary carbocation species. Tetrahydrofuran is much less reactive than its substituted forms at the 2-position such as 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran.[22,174] The reaction temperature is high (around 623 K) among acid-catalyzed dehydration reactions because of the low reactivity of tetrahydrofuran. The high temperature and strong acidity of the catalyst promote various side reactions including coke formation, and catalyst stability is a serious issue. Recently, the phosphorous-containing siliceous self-pillared pentasil catalyst[175] and ZrO_2 catalyst[174,176] have been reported to show high selectivity to butadiene (about 90% around 50% conversion level) at 623 K and 673 K, respectively. Both catalysts showed significant deactivation in a few hours of time on stream.

Deoxydehydration of erythritol is another production route of renewable butadiene. Erythritol is a more oxidized compound than butanediols and its fermentative production is easier. Double deoxydehydration of erythritol gives butadiene. Because of the importance of butadiene in the chemical industry, erythritol is often selected as a substrate in the reports of deoxydehydration systems including the first report of catalyzed deoxydehydration published in 1996.[177] We have recently reported the deoxydehydration of erythritol with the same heterogeneous catalyst system for allyl alcohol production from glycerol and H_2.[115] The ReO_x–Ag/CeO_2 catalyst is the most effective one among investigated catalysts, and the yield reached 86% in 1,4-dioxane solvent. The reaction can be carried out even without solvent. The melt substrate (erythritol) and intermediates (butenediols) work as solvent, and the formed butadiene easily moves into the gas phase. The over-hydrogenation of butadiene can be suppressed until the total conversion of butenediols. Although the reaction rate without solvent is lower than that with solvent, the selectivity can be higher without solvent, and the maximum yield of butadiene reached 90% (Fig. 1). The solventless condition gives a very good E-factor as low as 3.16, and this value is much lower than those of the other reported systems of deoxydehydration of erythritol to butadiene.

3.2.2.   Linear butenes. Linear butenes (1-butene, trans-2-butene and cis-2-butene) are also currently isolated from naphtha cracking products. The main utilization of linear butenes includes oligomerization to transportation fuel,[178] source of oxygenates (such as 1-pentanol, butanols, and 1,2-butanediol), monomer of polyolefin (using 1-butene) and metathesis with ethylene to propylene (using 2-butene). The utilization in oligomerization to fuel can use a mixture of butenes, while the other main utilizations require pure 1- or 2-butene. Selective production of 1-butene is possible by acid-catalyzed dehydration of 1-butanol,[179] although isomerization to other butenes can occur depending on the catalysts.[180] 1-Butanol can be obtained directly by fermentation, typically by ABE fermentation with a long history.[57,181] Ethanol upgrading to 1-butanol is possible, known as the Guerbet reaction; good
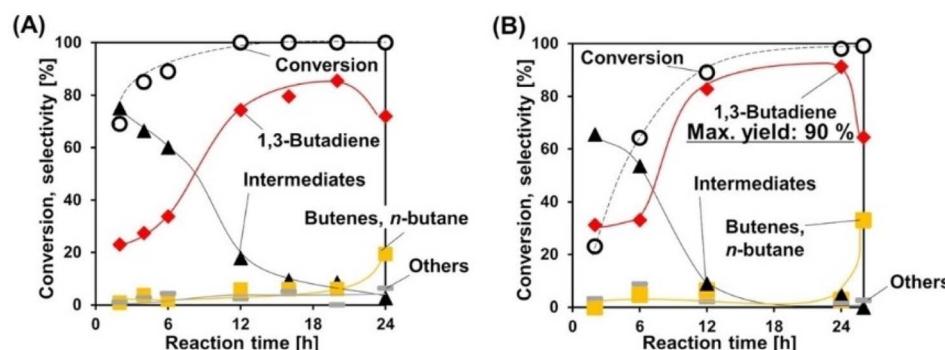
Fig. 1 Time courses in the deoxydehydration of erythritol over ReO$_x$–Ag/CeO$_2$ (A) with 1,4-dioxane solvent and (B) without solvent. Reaction conditions: ReO$_x$–Ag/CeO$_2$ (Re: 1 wt%, Ag/Re = 0.3 [mol mol^{-1}]) 0.3 g, erythritol 0.25 g, 1,4-dioxane 4 g (A) or 0 g (B), 413 K, H$_2$ 8 MPa. Reprinted from ref. 115 with permission from Wiley-VCH.

selectivity (about 80%) can be obtained with weakly basic solid catalysts such as hydroxyapatite at relatively low conversion level (typically <20%).[182] High conversion level inevitably leads to the formation of higher alcohols. Even now bio-butanol (bio-based 1-butanol) is industrially manufactured, although petroleum-based 1-butanol (propylene hydroformylation and hydrogenation) is more common. Because of the competition between bio-butanol and petroleum-based 1-butanol, there are several life cycle assessments or techno-economic analyses of bio-butanol.[183–185] These analyses highlighted the large impact of feedstock and the necessity of the improvement of 1-butanol yield (especially in ABE fermentation). Several systems for selective hydrodeoxygenation of C4 oxygenates to 1-butanol have been reported;[124,154,186] however, the necessity of large amounts of reducing agent hampered the practical use. Production of 2-butene is more difficult. The use of 2-butanol as an intermediate is one approach. Examples of 2-butanol synthesis from biomass include dehydration + hydrogenation of 2,3-butanediol,[187] hydrodeoxygenation of C4 oxygenates (buta-nediols, erythritol and 1,4-anhydroerythritol) with an appropriate catalyst[188,189] and reductive conversion of levulinic acid.[190–192] However, dehydration of 2-butanol always gives a mixture of various butenes[193,194] regardless of the isomerization activity of the catalyst. On the other hand, deoxydehydration can produce one linear butene selectively from each appropriate butanediol: 1-butene from 1,2-butanediol, trans-2-butene from R,R- or S,S-2,3-butanediol and cis-2-butene from meso-2,3-butanediol. Efficient stereospecific production of these butanediols, probably by fermentation, and effective deoxydehydration systems are both necessary.

Dumesic et al. reported an epoch-making method for the production of biofuel via butenes as intermediates in 2010 (Scheme 16).[195] A key step in the process is the decarboxylation of γ-valerolactone to butenes over the SiO$_2$–Al$_2$O$_3$ catalyst. The yield reached 93% at 648 K, with the 1-/2-butene ratio of 33/67. Similar decarboxylation of γ-valerolactone to butenes over SiO$_2$–Al$_2$O$_3$ catalysts has been reported by several research groups, and the reported yields were similarly high.[196–199] The work by Mingyue Ding et al. reported more detailed distribution of produced butenes over SiO$_2$–Al$_2$O$_3$:[198] isobutene : 1-butene : trans-2-butene : cis-2-butene = 2.5 : 22.7 : 43.6 : 31.2 at 648 K. Lower temperature decreased the ratio of isobutene (2.5% → 0.5% at 573 K) and increased that of trans-2-butene (43.6% → 46.6%). Recently, Sihai Yang et al. reported decarboxylation of γ-valerolactone to butenes over the Nb, Al-incorporated MFI zeolite catalyst.[200] The total yield of butenes reached 99.3% (at 593 K). The isomer ratio at a 30% conversion level was iso-butene : 1-butene : trans-2-butene : cis-2-butene = 18 : 19 : 38 : 25. The ratio was more similar to the equilibrium level (45 : 12 : 27 : 16) than that obtained over SiO$_2$–Al$_2$O$_3$, probably due to the stronger acidity of Nb, Al-incorporated zeolite. The raw sources of γ-valerolactone are sugars, cellulose and hemicellulose, and levulinic acid is a common key intermediate.[201,202] The synthesis of γ-valerolactone has been intensively investigated and is becoming more and more practical.

Although there are various production routes of butenes from biomass-derived platforms, all of them are energy-consuming processes because of the very low oxidation level of butenes. This contrasts with the low price of butenes in petrochemistry. Among the current utilization of butenes, the
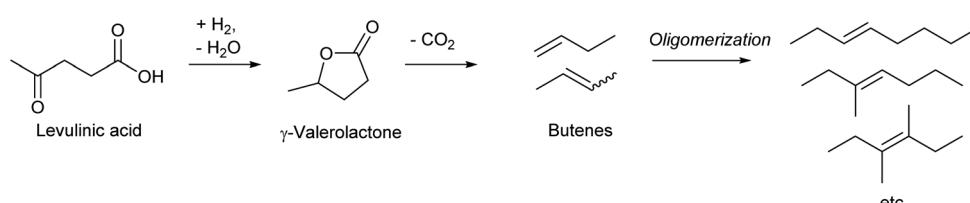
Scheme 16 Biofuel synthesis via butenes.

use for the synthesis of oxygenated chemicals should be replaced with direct synthesis of target oxygenated chemicals from biomass by partial deoxygenation, rather than bio-butene conversions.

3.2.3. Linear C4 unsaturated oxygenates. In comparison with C3 unsaturated oxygenates, the importance of linear C4 unsaturated oxygenates in the petrochemical industry is not large except maleic anhydride, which is manufactured by oxidation of *n*-butane over the vanadium phosphorous oxide catalyst. The current production amount of maleic anhydride is about 2 million tons per year.[134] As described above, biomass-derived compounds such as furfural, HMF and levulinic acid can be oxidized to maleic anhydride over similar vanadium-based catalysts. Furfural is the most attractive substrate among those for maleic acid synthesis because furfural is readily synthesized from lignocellulosic biomass[203] and its oxidation can be carried out in a gas-phase flow process. Recent techno-economic analysis showed that the oxidation of furfural to maleic anhydride can achieve a similar level of maleic anhydride price to the current commercial price.[204]

3.2.4. Branched C4 compounds: isobutene and methyl methacrylate. Isobutene is one of the main components of naphtha cracking products (Table 2) and also one main product of FCC. The main utilization of isobutene is the production of alkylate gasoline and methyl *tert*-butyl ether (MTBE) or ethyl

tert-butyl ether (ETBE) that are used as boosters of the octane number of gasoline.[205] These utilizations are based on two factors: the large supply of isobutene from petroleum and the large demand of gasoline. This situation will be much changed when automobiles only use renewable energy. The main utilization of isobutene except fuel is that as monomers. Poly-isobutylene (PIB) and butyl rubber (isobutylene-isoprene rubber; IIR) directly use isobutene as a monomer. Methyl methacrylate is another important monomer that is synthesized from isobutene.[206] Conversion of isobutene to isoprene by the reaction with formaldehyde has been carried out to compensate for the low yield of isoprene in the naphtha cracking.[207] The demand of renewable isobutene depends on the development of other synthesis methods of renewable methyl methacrylate and isoprene.

Because both lignocellulose and typical triglycerides do not have branches in the carbon chain, the production of branched compounds from biomass on a large scale is generally difficult. Only isobutyl alcohol (2-methyl-1-propanol) is produced commercially by fermentation as a branched C4 compound from biomass.[208] Direct fermentative production of isobutene has been intensively investigated, and this method has the merit of easy separation.[209,210] However, the efficiency of fermentation is limited because isobutyl alcohol and isobutene are less oxidized compounds. The dehydration of isobutyl
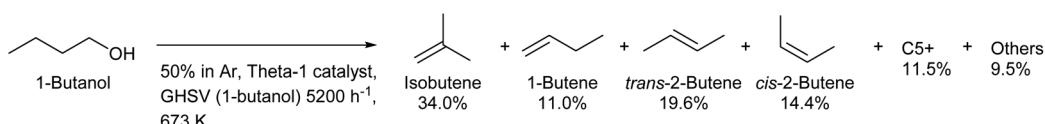
Scheme 17 1-Butanol conversion over the Theta-1 catalyst.[214]
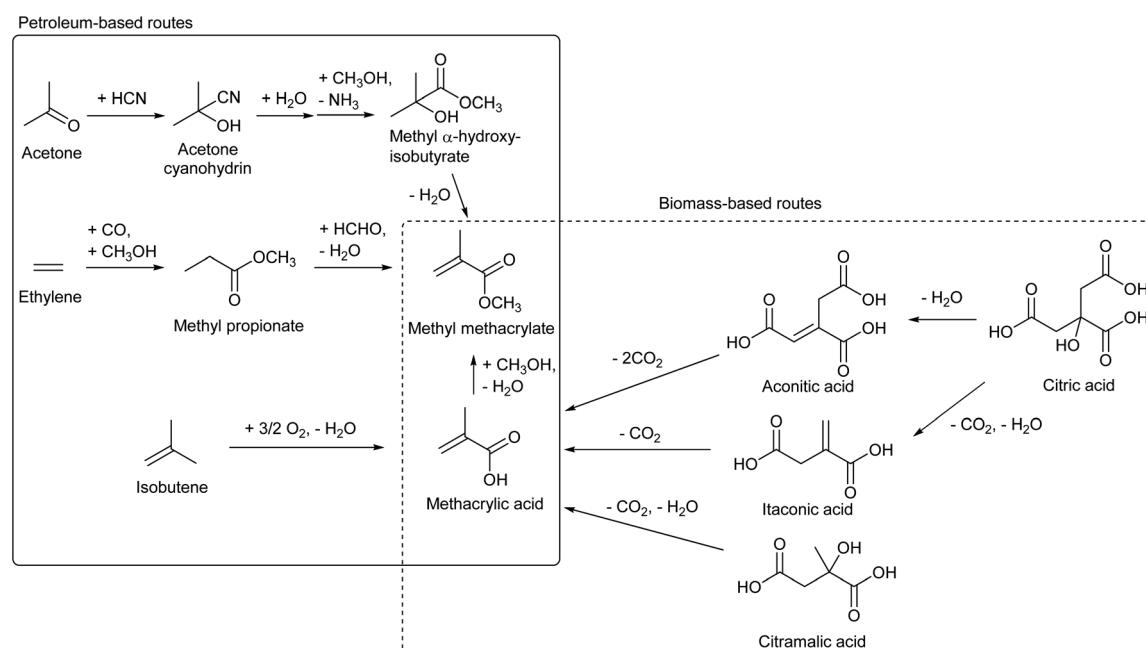
Scheme 18 Syntheses of methacrylic acid and methyl methacrylate.

alcohol to isobutene can proceed over simple acid catalysts such as H-ZSM-5 (ref. 211) and SiO_2–Al_2O_3.[212] The isomerization to linear butenes occurs to some extent, and strong acidity promotes this side reaction. Over 90% selectivity can be obtained with appropriate catalysts and conditions.[212] Inversely, the production of isobutene from linear butanol by dehydration–isomerization is possible,[213,214] although the isobutene formation is limited by equilibrium (theoretical limit: around 40%).[200] Over 30% yield of isobutene from 1-butanol with good stability was obtained by using the Theta-1 zeolite catalyst at 673 K (Scheme 17).[213,214] Theta-1 was selected by searching zeolites with 10-ring channels such as ferrierite, ZSM-23, ZSM-5 and SAPO-11; these channels are suitable for skeletal isomerization of linear alkenes with a monomolecular mechanism.

Methyl methacrylate is the monomer of PMMA, acrylic resin. The methacrylate unit is currently produced from various sources such as isobutene, ethylene (+CO, +HCHO) and acetone (+HCN) (Scheme 18).[206,215] Bio-ethylene and bio-isobutene can be directly used in the current processes to replace petroleum. On the other hand, based on the principle that "from biomass, oxidized chemicals should be produced by partial deoxygenation rather than oxidation of hydrocarbons", methacrylate synthesis from biomass without the need of oxidation is attractive. Decarboxylation reactions of itaconic acid,[216–221] aconitic acid[216] and citramalic acid[222] have been proposed as such production methods of methacrylate. These carboxylic acids can be produced directly by fermentation or can be synthesized from citric acid which is a more common fermentation product.[223] These reactions are not easy because it is necessary to suppress overdecarboxylation, and the reported yield of methacrylate was moderate (Table 4). The development of catalysts in these decarboxylation reactions is still in its infancy and better catalysts will be developed in the future.

3.3. C5 and C6 compounds

Carbohydrates including sugars, hemicellulose and cellulose have C5 or C6 carbon chains. Therefore, there are many C5 and C6 biomass-derived compounds that can be used as intermediates of chemicals.[4–6] Some of these compounds contain C=C double bonds, such as furfural,[203] HMF,[224] levoglucosenone,[225] angelica lactone,[226] itaconic acid[227,228] and muconic acid.[229] The chemical conversions of these biomass-derived compounds

have been well explained in recent review papers focusing on each compound. On the other hand, in the petrochemical industry, most C5 and C6 chemicals do not have olefinic (non-aromatic) C=C double bonds. Unsaturated C5 and C6 chemicals, especially oxygenated ones, are mainly specialty chemicals. In this situation, we only focused on the C5 and C6 olefins without oxygen atoms in this section.

3.3.1. Pentenes and hexenes. The main utilization of simple olefins in this range is the direct use of gasoline (FCC gasoline) and co-monomer of polyethylene to decrease the crystallinity. Alpha-olefin (1-alkene) is used for the latter purpose, and 1-hexene is currently manufactured by trimerization of ethylene.[230] Bio-ethylene can be substituted for petrochemical ethylene. Partial hydrodeoxygenation of sugars or sugar-derived compounds to 1-pentanol or 1-hexanol and their dehydration is another approach; however, it is difficult to obtain high selectivity in both the hydrodeoxygenation and dehydration steps. Large H_2 consumption is also a negative point in this hydrodeoxygenation + dehydration approach. This is a similar situation to the production of 1-butene via 1-butanol.

Some utilizations do not require high purity as a single isomer, such as direct use as gasoline and dimerization to jet-fuel-range hydrocarbons. Regioselectivity is not necessary in the dehydration step for this purpose, and simple Brønsted acid catalysts such as H-ZSM-5 show sufficient performance in the dehydration of secondary hexanols or pentanols.[231,232] For the hydrodeoxygenation step, suppression of over-hydrodeoxygenation to alkanes is a key point. Apart from the development of appropriate catalysts, the use of a biphasic solvent system is effective where the produced mono-alcohols are extracted from polar reaction solvent (typically water) to nonpolar solvent. The Ir–ReO_x/SiO_2 catalyst combined with H_2O/alkane biphasic solvent gave 60% yield of hexanols by hydrodeoxygenation of depolymerized cellulose (Scheme 19).[233] The same system was also applied to hydrodeoxygenation of xylan (hemicellulose); however, the obtained yield of pentanols was lower ($\leq$32%).[234] Deoxydehydration can be also used for the synthesis of mono-alcohols from sugar alcohols with an odd carbon number, namely xylitol. Xylitol can be converted to a mixture of 1-pentanol and 3-pentanol in 97% yield from xylitol over the ReO_x–Pd/CeO_2 catalyst which catalyzes both deoxydehydration and hydrogenation (Scheme 20).[120] This catalyst is

Table 4 Methacrylate synthesis by decarboxylation

Entry	Substrate	Catalyst	S/C molar ratio	Solvent	Temp. [K]	Time [h]	Conv. [%]	Yield [%]	Ref.
1	Itaconic acid	Pt/C	40	Water, 1 eq. NaOH	523	1	n.r.	68	216
2	Itaconic acid	$[Ru(CO)_2(C_2H_5COO)]_n$ + PPh_3	1000 + 200	Water	498	1.5	n.r.	33.8	217
3	Itaconic acid	NaOH	5	Water	633	0.0075	99	75	218
4	Itaconic acid	$BaAl_{12}O_{19}$	12	Water	523	3	100	50	219
5	Itaconic acid	Pt/Al_2O_3	60	Water + methanol, 1.6 eq. NaOH	523	3	100	81.2	220
6	Itaconic acid	Ca/Al_2O_3	20	Water	523	1.5	91.6	44.8	221
7	Aconitic acid	Pt/Al_2O_3	40	Water, 1 eq. NaOH	523	1	100	47.5	216
8	Citric acid	Pd/Al_2O_3	40	Water, 1 eq. NaOH	523	1	100	41	216
9	Citramalic acid	Al_2O_3	0.44 (Al)	Water	523	1	93.6	59.2	222
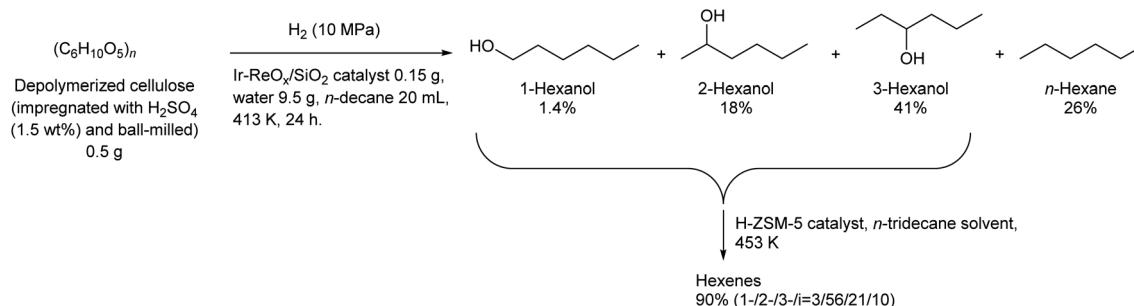
Scheme 19 Synthesis of hexanols and hexenes from cellulose by hydrodeoxygenation and dehydration.[232,233]
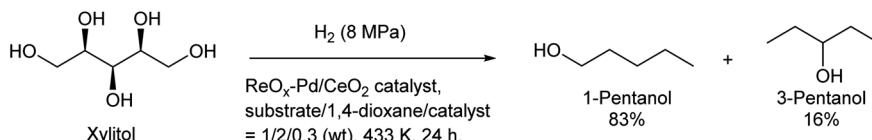
Scheme 20 Synthesis of pentanols from xylitol by deoxydehydration + hydrogenation over the ReO_x–Pd/CeO_2 catalyst.[120]

a variant of ReO_x–Ag/CeO_2 and ReO_x–Au/CeO_2 explained in the above sections for glycerol and erythritol conversions. The difference between ReO_x–Ag/CeO_2 and ReO_x–Au/CeO_2 is the high hydrogenation activity of Pd. This deoxydehydration + hydrogenation approach cannot be applied to sorbitol conversion to hexanols because each deoxydehydration step removes two oxygen atoms at once.

3.3.2. Linear polyenes. Pentadienes and hexadienes, especially those with conjugated double bonds, are used as co-monomers and substrates for fine chemicals.[235,236] In petrochemistry these polyenes are by-products of naphtha cracking obtained in low yields. There are two major routes for the production of these polyenes from biomass: dehydration of diols and dehydration of methyltetrahydrofurans. Various pentanediols such as 1,2-, 1,4- and 1,5-isomers can be synthesized from biomass, *via* furfural (1,2-, 1,4- and 1,5-)[237,238] or levulinic acid (1,4-).[238,239] Among these three isomers, 1,4-pentanediol is the best substrate for dehydration to conjugated 1,3-pentadiene because this dehydration does not involve a hydride shift. Dehydration of 1,5-pentanediol has been more intensively investigated; however, the target product is usually 4-penten-1-ol.[240,241] In a similar manner to dehydration of 1,4-butanediol to butadiene, acid catalysts for dehydration of 1,4-pentanediol promote cyclization to 2-methyltetrahydrofuran which is less reactive.[242] The bifunctional Ce/ZrSi catalyst was reported to be effective (77.5% yield to pentadienes, 1,3-:1.4- = 81:19, at 623 K).[243] The exploration of catalysts has been much less carried out than the dehydration of butanediols. Dehydration of hexanediols to conjugated hexadiene has been rarely investigated[244] because it is difficult to synthesize one specific hexanediol with appropriate positions of OH groups from biomass.

On the other hand, 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran can be relatively easily synthesized from biomass *via* hydrodeoxygenation of furfural and 5-hydroxymethylfurfural (HMF), respectively.[245,246] Furthermore,

dehydration of these methyl-substituted tetrahydrofurans is easier than that of simple tetrahydrofuran because the formation of the unstable primary carbocation is not necessary.[22,174] Over 80% yields of 1,3-pentadiene have been reported for 2-methyltetrahydrofuran dehydration: 86% yield over the B-MWW catalyst at 658 K,[247] 92% yield over the ZrO_2 catalyst at 723 K (ref. 248) and 91% yield over the AlNb-MCM-41 catalyst at 548 K.[249] Although the reaction conditions are less severe than those for tetrahydrofuran dehydration, mild catalyst deactivation has been still observed. Dehydration of 2,5-dimethyltetrahydrofuran has been less investigated than that of 2-methyltetrahydrofuran including the distribution of product isomers; however, several comparative studies showed that the reactivity of 2,5-dimethyltetrahydrofuran is surely higher than those of tetrahydrofuran and 2-methyltetrahydrofuran.[22,174] Very recently, Crossley *et al.* reported dehydration of 2,5-hexanediol over the H-ZSM-5 catalyst at 523 K.[250] The product at short contact time was 2,5-dimethyltetrahydrofuran, and at longer contact time hexadienes were produced. Although it was not tested to fully convert 2,5-dimethyltetrahydrofuran with sufficiently long contact time, the selectivity to hexadienes ([hexadienes]/([all products] − [2,5-dimethyltetrahydrofuran])) was higher than 90%.

In comparison with the synthesis of other olefins, deoxydehydration is not a strong tool in the synthesis of pentadienes and hexadienes, because each corresponding substrate (pentanetetraol and hexanetetraol) cannot be efficiently synthesized at present.[251] Production of hexatriene by deoxydehydration of sorbitol has been already reported, but not with H_2 as the reducing agent.[111,113]

The number of studies for the synthesis of pentadienes and hexadienes has not been large. This is due to the relatively low importance of these compounds in petrochemistry, and the low importance is due to the low yield of these dienes in petrorefinery. On the other hand, the potential of these dienes in biomass conversion is not low.

3.3.3. Isoprene. Isoprene is a co-monomer of synthetic rubber, and the demand is very large. Because of the low yield of isoprene in the naphtha cracking, its synthesis from isobutene and formaldehyde has been widely carried out, as mentioned in the section of isobutene. Nowadays, there is a strong need to use renewable synthetic rubber. The approaches to renewable isoprene are summarized in Scheme 21. Direct production of isoprene by fermentation has been explored intensively.[252,253] It is very difficult to chemically synthesize isoprene from biomass. The combined fermentation and chemical methods include isobutyl alcohol dehydration to isobutene (as mentioned above) and mesaconic acid hydrogenation to 3-methyltetrahydrofuran followed by dehydration.[254] Mesaconic acid hydrogenation proceeds over bimetallic Pd–Re catalysts which are generally effective in the hydrogenation of carboxylic acids to alcohols.[255–257] Dehydration of 3-methyltetrahydrofuran is a similar reaction to that of tetrahydrofuran and 2-methylte-trahydrofuran. The reactivity of 3-methyltetrahydrofuran is low because the C–O dissociation involves the formation of an unstable primary carbocation. Although the largest cost is estimated to be derived from the fermentation step, the efficiency of the dehydration step is still very important. Another multi-step method for isoprene synthesis is the utilization of the aldol reaction of butanone and formaldehyde as the key step.[258] The aldol reaction product, 4-hydroxy-3-methyl-2-butanone, is hydrogenated and then dehydrated to isoprene. The final dehydration step uses acid–base bifunctional catalysts with relatively high basicity such as CeO_2 (ref. 258) and $Y_2Zr_2O_7$,[259] and around 80% of isoprene yield was reported in this step.

It is well known that thermal decomposition of natural rubber (*cis*-1,4-polyisoprene) in an inert atmosphere produces isoprene.[260] This reaction is not practical because natural rubber is more valuable than isoprene. Syntheses of isoprene by decomposition of other natural isoprenoids such as limonene and turpentine are also possible, which were mainly investigated in the first half of the 20th century,[261] but these are also not practical because of the high price of feedstock. Much more recently, large isoprenoid hydrocarbon molecules produced by some microalgae have attracted attention.[262] Typical such molecules are botryococcene (C30–37)[263] and squalene (C30).[264] Thermal cracking of squalene to isoprene has been reported recently, and about 50% yield (at 723 K) was obtained.[265] Because the carbon chain of botryococcene does not consist of pure isoprene units, the synthesis of isoprene by decomposition of botryococcene is not realistic.

3.3.4. Cycloalkenes. Many compounds with a cyclohexane ring have been used on a large scale in the chemical industry. The main sources of these compounds are aromatics such as benzene, toluene and xylenes (BTX). Cyclohexene can be synthesized by partial hydrogenation of benzene, and the subsequent conversion into cyclohexanol and 1,2-cyclo-hexanediol by hydration and oxidation, respectively, has been carried out. Among biomass resources, lignin contains aromatic rings and can serve as the source of cyclohexane ring.[266] Aromatic hydrocarbons such as benzene and toluene can be synthesized from lignin by pyrolysis with or without catalysts in severe conditions; however, the yield of aromatic hydrocarbons in pyrolysis of lignin is low.[267] The combination of pyrolysis at milder conditions to oxygenates and catalytic hydrodeoxygenation is a promising approach to higher yield, and the development of effective catalysts has been intensively carried out.[268] Synthesis of useful oxygenates by partial hydro-deoxygenation without using hydrocarbons as intermediates is a better approach. Selective reduction of guaiacol, which is one of the main components of pyrolysis oil of biomass, into useful oxygenates such as cyclohexanol and phenol has been a very hot topic in biomass conversions.[269,270]

Compounds with a cyclopentane ring have been less used in industry than those with a cyclohexane ring. Nevertheless, cyclopentadiene is a relatively important chemical used as a co-monomer and a precursor of various fine chemicals.[271]
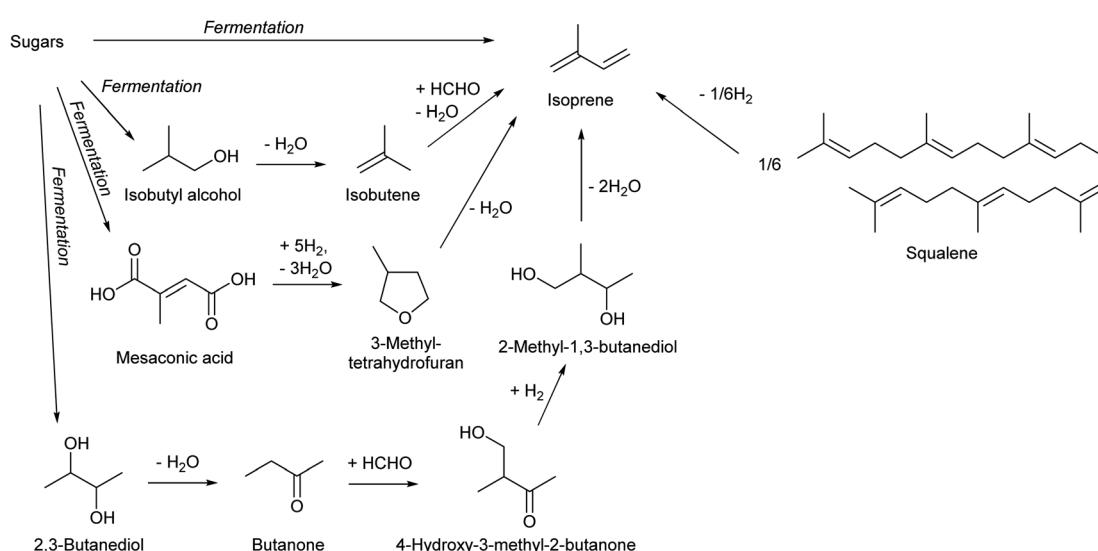
Scheme 21 Synthesis of isoprene from biomass.
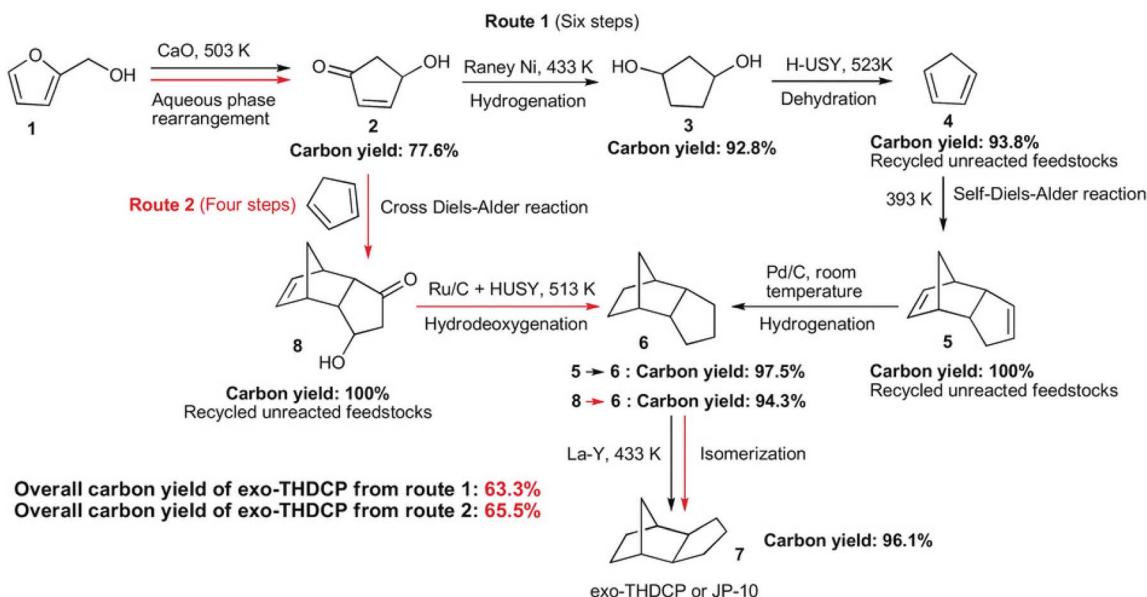
Scheme 22 Synthesis of cyclopentadiene and the dimers from furfuryl alcohol. Reprinted from ref. 275 with permission from Wiley-VCH.

Cyclopentadiene has been isolated from naphtha cracking products or coal tar. The synthesis of cyclopentadiene from biomass requires the chemical formation of the cyclopentane ring because the cyclopentane ring is rare in natural compounds. A useful reaction to produce a cyclopentane ring is intramolecular aldol condensation of 1,4-diones.[272] The dione structure can be formed by hydrolysis of the furan ring which is easily obtained by dehydration of sugars. Direct formation of cyclopentane ring structure from furans is possible, known as Piancatelli rearrangement.[273,274] Tao Zhang et al. reported the stepwise synthesis of cyclopentadiene from biomass (Scheme 22).[275] The starting compound is furfuryl alcohol which is obtained by dehydration of hemicellulose and hydrogenation and has been already synthesized on an industrial scale. Furfuryl alcohol is converted to 4-hydroxy-2-penten-1-one by aqueous phase rearrangement in the presence of a base. The hydrogenation of this unsaturated cyclic compound over the conventional Ni catalyst gives 1,3-cyclopentanediol, and its

dehydration over acidic zeolite gives cyclopentadiene. The overall yield from furfuryl alcohol reached 67.5%, where the dehydration step was repeated with the recovery of the partially dehydrated product and the residual diol. As a related synthesis, that of methylcyclopentadiene has been also reported (Scheme 23).[276–278] The starting compound is 2,5-hexanedione which can be obtained from hexoses such as glucose and its polymer, cellulose, via 2,5-dimethylfuran or 5-(chloromethyl) furfural. Intramolecular aldol condensation of 2,5-dimethylfuran gives 3-methyl-2-cyclopenten-1-one. Reduction and dehydration of this cyclic compound produce 1-methyl-1,3-cyclopentadiene. The yield of 1-methyl-1,3-cyclopentadiene from 2,5-dimethylfuran reached 68% with direct conversion over $ZnO–MoO_x$ catalysts.[277] Zinc oxide helps the formation of oxygen vacancy in the MoO_x phase, and the oxygen vacancy activates the C–O bond in the 3-methyl-2-cyclopenten-1-one intermediate. Improvement of efficiency and catalyst stability for the dehydration step is desirable for both systems.
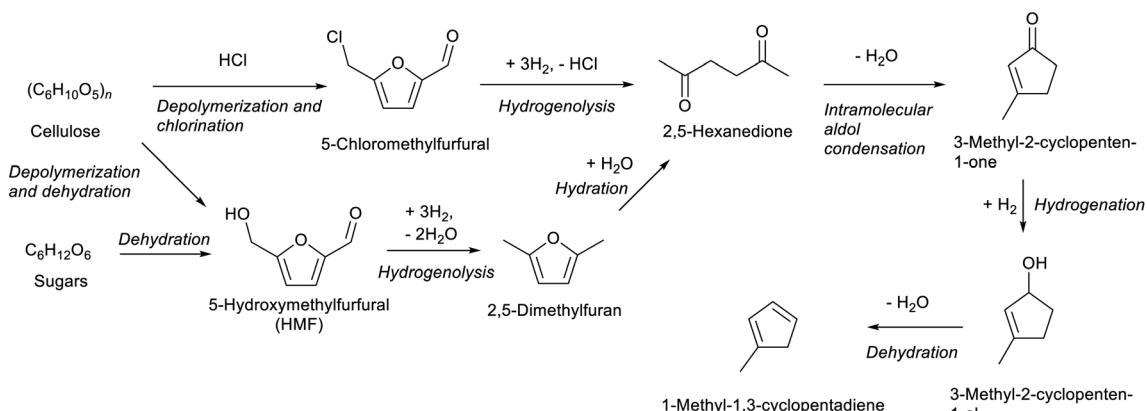
Scheme 23 Synthesis of methylcyclopentadiene from biomass.
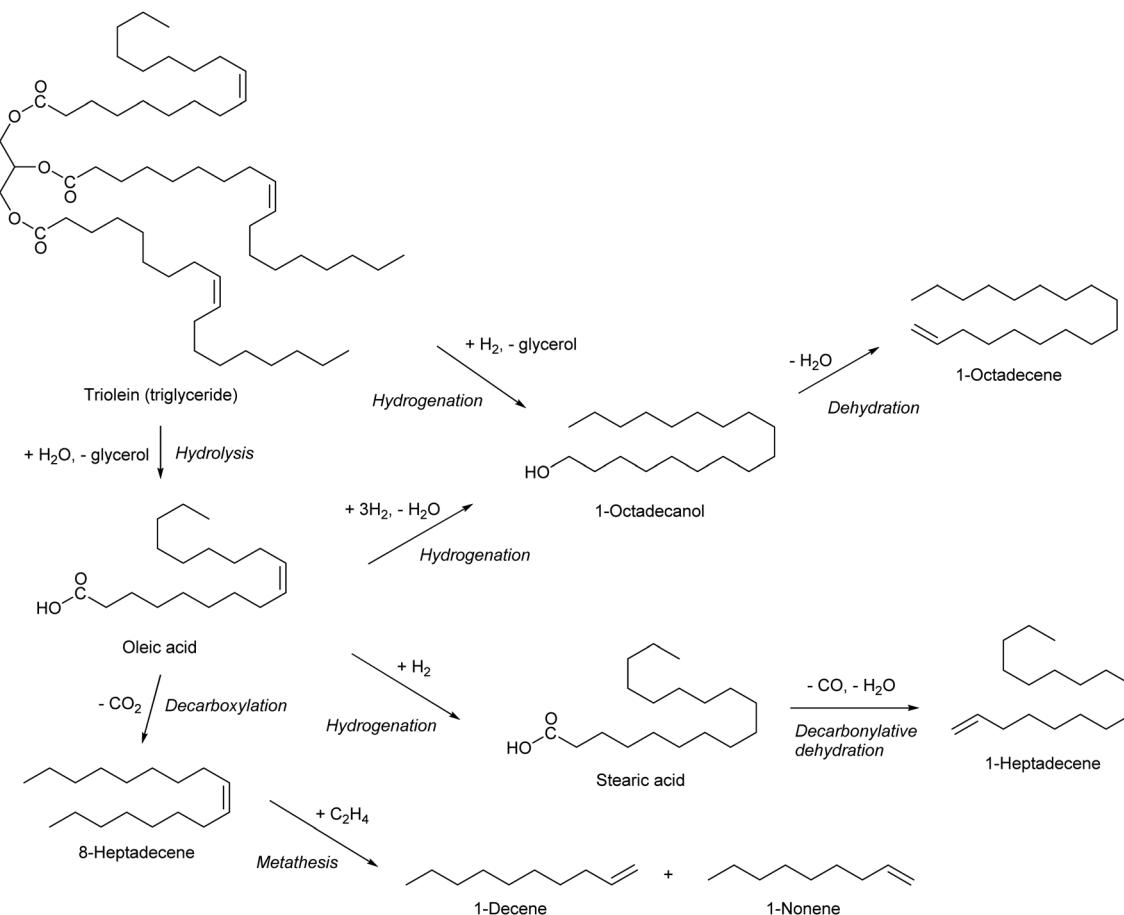
Scheme 24 Synthesis of alpha-olefins from triolein.

3.4. Larger compounds

Olefinic compounds with ≥7 carbon number are specialty chemicals except alpha-olefins which can be obtained by ethylene oligomerization. As described in the section for 1-hexene, the same alpha-olefins can be synthesized by simply replacing the substrate with bio-ethylene. Another method to obtain alpha-olefins is the use of triglycerides as raw material (Scheme 24). Hydrogenation of triglycerides or free fatty acids can produce primary alcohols, and alpha-olefins can be obtained by dehydration. Catalytic hydrogenation of esters or carboxylic acids to alcohols has a long history, but there is still a large room for improvement.[255–257] Decarbonylative dehydration of saturated fatty acids can also produce alpha-olefins.[41,42] Hydrogenation of fatty acids or triglycerides removes the C=C double bonds in the carbon chain. If one wants to utilize the C=C double in the carbon chain, decarboxylation seems to be necessary. However, because of the requirement of severe conditions for the decarboxylation, it is difficult to selectively convert an unsaturated fatty acid to the corresponding olefin, such as oleic acid to *cis*-8-heptadecene, without isomerization, cracking or coking.[279,280] Metathesis is a useful reaction for further conversion of the internal olefins which will be produced by decarboxylation of unsaturated fatty acids.[281,282]

4.   Conclusions and outlook

Most olefinic compounds used in the chemical industry can be now synthesized from biomass. Ethylene can be synthesized by dehydration of ethanol, C3 unsaturated oxygenates can be produced from glycerol, and C4 olefinic compounds can be chemically synthesized from C4 oxygenates obtained by fermentation. Cyclopentadiene production from biomass has been also reported. Catalytic dehydration is frequently used in these syntheses. Conventional Brønsted acids such as acidic zeolites can be used only in limited cases, and recently reported systems tend to use acid–base bifunctional solid catalysts such as rare-earth oxides and alkali metal salts of zeolites. The bifunctional catalysts can suppress cyclization reactions (to tetrahydrofurans and tetrahydropyrans) and rearrangement reactions of the carbon chain. Aldehyde formation and movement of the double bonds are frequently observed in dehydration over bifunctional catalysts. Tuning of catalyst properties is usually necessary for each target reaction, such as the balance of acidity and basicity as well as the pore structure. Zeolite-based catalysts including the alkali-metal salts are advantageous to precisely control the structure and properties. The control of properties of rare-earth metal oxide catalysts is more difficult; however, there is much room for improvement. In particular, mixed metal oxides containing rare-

earth metals have not been explored well. Considering the large number of possible combinations, catalyst informatics may be a strong tool for the future development of rare-earth-metal-based catalysts. Another important dehydration is that of tetrahydrofurans. This reaction is catalyzed by simple acids, but the reported performance, especially for tetrahydrofuran to butadiene, is not sufficient and needs to be improved. Catalyst stability is always a major issue in dehydration over solid acid catalysts since coke formation is inevitable from olefinic compounds over solid acids. Suppressing the activity decrease during time on stream and stability during regeneration are always major topics for catalyst development. For rare-earth metal oxide catalysts, pure compounds synthesized by the calcination of precursors have been mainly used. Appropriate supports will be necessary to improve the stability during the catalytic use and regeneration.

Deoxydehydration is another reaction that produces olefins from biomass-derived oxygenates. Although deoxydehydration has been less investigated than dehydration, recently developed catalysts, namely ReO_x–M/CeO_2 (M = Au or Ag), can very selectively produce olefins from vicinal diols. In contrast to dehydration, tuning of catalyst properties for each substrate is almost unnecessary in deoxydehydration. Although catalyst cost and long-term stability are necessary to be considered, when deoxydehydration is practically carried out, such a catalytic system has great potential to be applicable to a wide range of substrates.

Depending on the structure of target olefinic products, selective partial hydrodeoxygenation and decarboxylation reactions are key steps. These reactions are also very important in the selective synthesis of saturated compounds from biomass, and the current intensive investigation should be continued to obtain higher performance including high selectivity, long catalyst life, and low cost of catalyst.

Because of the difference in oxygen content between petroleum and biomass, simple olefins are generally easier to obtain from petroleum and difficult from biomass. This trend is most prominent in the case of propylene. Propylene is an inexpensive olefin and is utilized on a very large scale in the chemical industry. On the other hand, the production of propylene from biomass requires a large amount of reducing agents and multiple steps. The supply of the C3 biomass source is much smaller than the amount of propylene used in the chemical industry. Renewable propylene is a missing piece of the puzzle of biomass-derived chemicals. Without a drastic breakthrough such as direct high-yield synthesis of propylene by reduction of CO or CO_2, the use of propylene will be much decreased when fossil resources cannot be used. Oxidized compounds are better to be synthesized by deoxygenation than oxidation of simple olefins, especially propylene, in the biomass-based chemical industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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