

Carbon-Increasing Catalytic Strategies for Upgrading Biomass into Energy-Intensive Fuels and Chemicals

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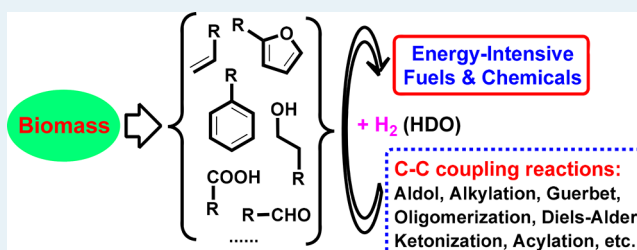
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ABSTRACT: Lignocellulosic biomass is the most abundant organic carbon source and has received a great deal of interest as renewable and sustainable feedstock for the production of potential biofuels and value-added chemicals with a wide range of designed catalytic systems. However, those natural polymeric materials are composed of short-chain monomers (typically C₆ and C₅ sugars) and complex lignin molecules containing plenty of oxygen, resulting in products during the downstream processing having low-grade fuel properties or limited applications in organic syntheses. Accordingly, approaches to increase the carbon-chain length or carbon atom number have been developed as crucial catalytic routes for upgrading biomass into energy-intensive fuels and chemicals. The primary focus of this review is to systematically describe the recent examples on the selective synthesis of long-chain oxygenates via different C–C coupling catalytic processes, such as Aldol condensation, hydroalkylation/alkylation, oligomerization, ketonization, Diels–Alder, Guerbet, and acylation reactions. Other integrated reaction steps including, for example, hydrolysis, dehydration, oxidation, partial hydrogenation, and hydrodeoxygenation (HDO) to derive corresponding key intermediates or final products are also reviewed. The effects of catalyst structure/type and reaction parameters on the catalytic performance along with relevant reaction mechanisms are in detail discussed. Apart from this, the formation of other useful compounds containing C–X bonds (X = O, N, and S) derived from biomass-based substrates for producing fuel additives and valuable chemicals is also briefly reviewed.

KEYWORDS: biomass conversion, high-quality biofuels, C–C coupling, heterogeneous catalysis, catalytic materials



1. INTRODUCTION

Terrestrial biomass, extensively deemed as sustainable, CO₂-neutral, and the most abundant carbonaceous feedstock, has over the past decades developed to be an alternative source of fossil feedstocks for the production of renewable fuels and chemicals.^{1–3} Typically, raw biomass is in a low-density form and must be upgraded by removing oxygen in the form of CO, CO₂, and H₂O to increase its heating value.⁴ In particular, lignocellulose—primarily composed of cellulose, hemicellulose and lignin—is the cheapest biomass component, but it generally contains 40–50% oxygen. Conventional gasification and pyrolysis/liquefaction processes of biomass is one of the promising approaches enabling direct conversion to syn-gas (CO and H₂) and bio-oil, respectively; followed by integrating with other reactions like Fischer–Tropsch (FT) synthesis, condensation, reforming, and hydrogenation capable of further transforming oxygenated hydrocarbons into liquid alkanes.^{5–9}

In those catalytic processes, the formation of C–C chains demonstrate to be the key step for the conversion of light molecules (carbon number ≤5) to biofuels with the carbon chain length matching the gasoline/diesel range (C_{5–13} and C_{10–25}, respectively), and equipped with close physicochemical and fuel properties, including density, boiling point, flash point, viscosity, autoignition temperature, energy density, and cetane number (Table 1).^{10–13} Notably, research octane number (RON) typically in a range of 0–100 is an arbitrary measurement of how resistant a fuel is to autoignition in a spark ignition engine, which is set to a minimum of 95 and 87 by EU and US standard for gasoline present in their regulations, respectively.¹⁰ Similarly, cetane number (CN) on a scale of 0–

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Table 1. Fuel and Physico-Chemical Properties of Gasoline, Diesel, and Linear Alkanes^a

fuel/ <i>n</i> -alkane	carbon no.	$T_{\text{b.p.}}^{10}$ (°C)	T_{flash}^{10} (°C)	T_{AI}^{10} (°C)	density ¹⁰ (g/cm ³)	viscosity ¹⁰ (mm ² /s)	E_{density}^{10} (MJ/kg)	[RON] ¹⁷ / (CN) ¹⁶
gasoline	5–13	50–200	–43	246	0.71–0.77	<2.50	44.4	[>90]
diesel	10–25	200–300	>55	210	0.82–0.85	2.00–4.50	45.1	(>40)
<i>n</i> -butane	4	–0.5	–60	405	--	--	49.1	[94]/(22)
<i>n</i> -pentane	5	36.1	–49	260	0.626	--	48.8	[62]/(30)
<i>n</i> -hexane	6	68.7	–23	225	0.659	0.470	48.5	[24.8]/(45)
<i>n</i> -heptane	7	98.4	–4	215	0.684	0.600	48.4	[0]/(54)
<i>n</i> -octane	8	125.7	9	220	0.703	0.769	--	[–15]/(64)
<i>n</i> -nonane	9	150.8	31	205	0.718	0.700	48.1	[–20]/(72)
<i>n</i> -decane	10	174.1	46	210	0.730	1.254	48.0	[–30]/(77)
<i>n</i> -undecane	11	195.9	60	--	0.740	1.601	47.9	[–35]/(81)
<i>n</i> -dodecane	12	216.3	71	205	0.749	1.974	47.8	[–40]/(87)
<i>n</i> -tridecane	13	234.0	94	--	0.756	2.495	47.8	(90)
<i>n</i> -tetradecane	14	255.0	100	235	0.756	3.020	47.8	(95)
<i>n</i> -pentadecane	15	270.6	132	--	0.769	3.721	47.7	(96)
<i>n</i> -hexadecane	16	287.0	135	201	0.770	4.460	47.7	100

^a $T_{\text{b.p.}}$ = boiling point, T_{flash} = flash point, T_{AI} = autoignition temperature, E_{density} = energy density, RON = research octane number, CN = centane number.

100 is a measurement of how readily a fuel autoignites in a compression ignition engine, and the minimum CN for diesel is allowed to be 51 and 40 in the EU and US, respectively.¹⁰ As a result, fuel with high RON and low CN is suitable for the spark ignition engine, and it also fits the compression ignition engine.¹⁰ Moreover, the boiling points can be used to predict the pressure atomization characteristics of fuels,¹⁴ which are correlated with the number of carbon atoms and ramification.¹⁵ In general, the CN value and boiling point increase by increasing the carbon atom irrespective of ramification,^{10,16} while the RON value decreases with the increase of carbon-chain length.¹⁷ For example, *n*-hexadecane (C_{16}) shows a relatively higher CN of 100 and boiling point of 287.0 °C compared to other *n*-alkanes, and a much higher RON of 94 was observed for *n*-butane (Table 1). When the branched molecule with the same carbon number as a linear one is taken into consideration, relatively lower boiling point and CN with an increased RON are observed.^{10,16,17}

Under aqueous- or liquid-phase reaction conditions, a variety of C_2 – C_6 bioproducts can be attained from hexose and pentose components (cellulose and hemicellulose) via either enzymatic or chemical catalysis (Scheme 1).^{18,19} In parallel, lignin may be degraded into various aromatic compounds via three monolignols: sinapyl alcohol (S), *p*-coumaryl alcohol (H), and coniferyl alcohol (G), as shown in Scheme 1.^{20,21} However, only $\leq C_6$ chain alkanes (e.g., hexane and pentane) from sugars or $\leq C_9$ cycloalkanes from lignin were yielded as dominant products by proceeding subsequent hydrodeoxygenation (HDO), wherein the carbon number was far behind the prerequisite of gasoline and diesel fuels (Table 1).¹⁰ In order to achieve the goal of producing long-chain alkanes, a range of chemo-, bio-, and integrated catalytic approaches were thus developed,^{22–25} as the valorization of bio-oil to high-energy density fuels, typically involving multistep reactions mixed with aldol condensation, ketonization, alkylation, HDO, and so on.²⁶ As such, this Fischer–Tropsch-type transformation process is unable to give good selectivity toward specific products with desirable carbon numbers.²⁷

Much attention has focused on the design of multifunctional heterogeneous catalysts that can perform cascade-type reactions efficiently in order to minimize the number of reaction steps.^{28–31} Among them, zeolites are in particular able to

catalyze the formation of C–C bonds in a controlled fashion, despite the inherent instability in hot water and the site blocking in the vapor phase.^{32–34} On the other hand, a large number of studies have focused on making use of simple biomass-derived substrates (e.g., furanic/aromatic compounds, alcohols, olefins, carboxides, and carboxylic acids or esters) for the efficient production of the gasoline/diesel range biofuels via strategically designed catalytic routes.^{35–48} With regard to this, Scheme 2 illustrates the general C–C coupling reaction pathways primarily including alkylation, acylation, Guerbet, oligomerization, Diels–Alder, Aldol condensation, and ketonization, which have been recently developed for augmenting the carbon-chain length of biomass-derived oxygenates, followed by HDO to produce energy-intensive fuels and/or other relevant reactions to value-added chemicals.⁴⁹

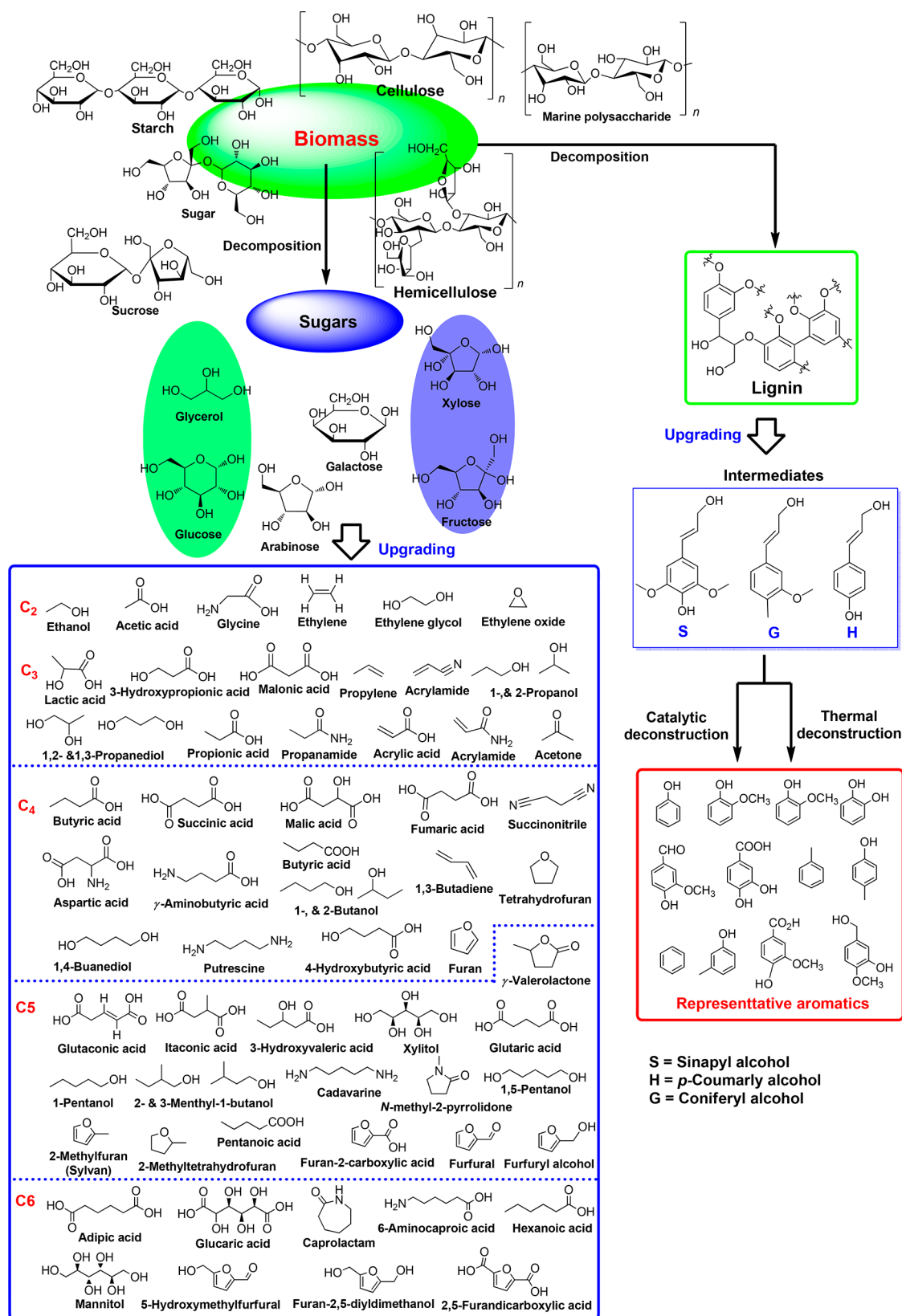
A number of excellent published review articles have emphasized on the application of biomass as sustainable source for producing platform molecules, and their further upgradation to value-added chemicals and potential fuel-additives over a wide range of heterogeneous catalysts, as discussed above.^{18–48} On the other hand, very few reviews briefly focused on upgrading biomass-derived substrates to energy intensive fuels via increasing-carbon using catalytic approaches.^{50–52} This review focuses on systematic descriptions on the selective synthesis of long-chain oxygenates via various C–C coupling reactions followed by HDO to yield corresponding hydrocarbons/alkanes. The influence of catalyst structure/type and reaction parameters on the catalytic performance and relevant reaction mechanism are also delineated. The formation of other potential heteronuclear molecules containing C–X bonds (X = O, N, and S) during the process of biomass upgradation, considered as fuel additives and/or value-added chemicals, is also briefly summarized.

2. ALDOL CONDENSATION

2.1. Biofuranic Aldehydes Condensed with Ketones.

One of the frequently adopted strategies to increase carbon numbers of biomass derivatives for producing energy-rich biofuels is the base-catalyzed aldol condensation of carboxides, followed by subsequent HDO over bifunctional catalysts containing acid and metal sites in appropriate catalytic reactors.^{53–60} In this regard, Dumesic et al. have reported the

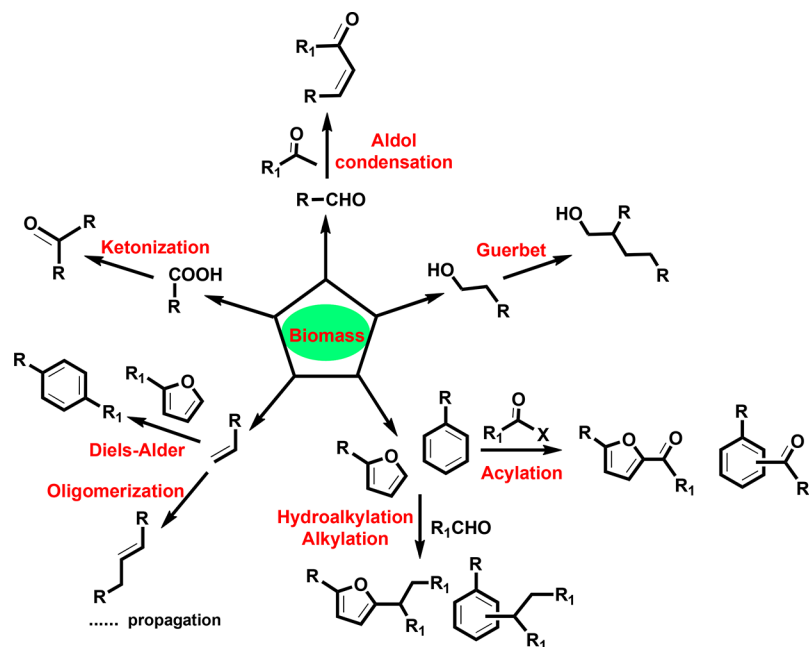
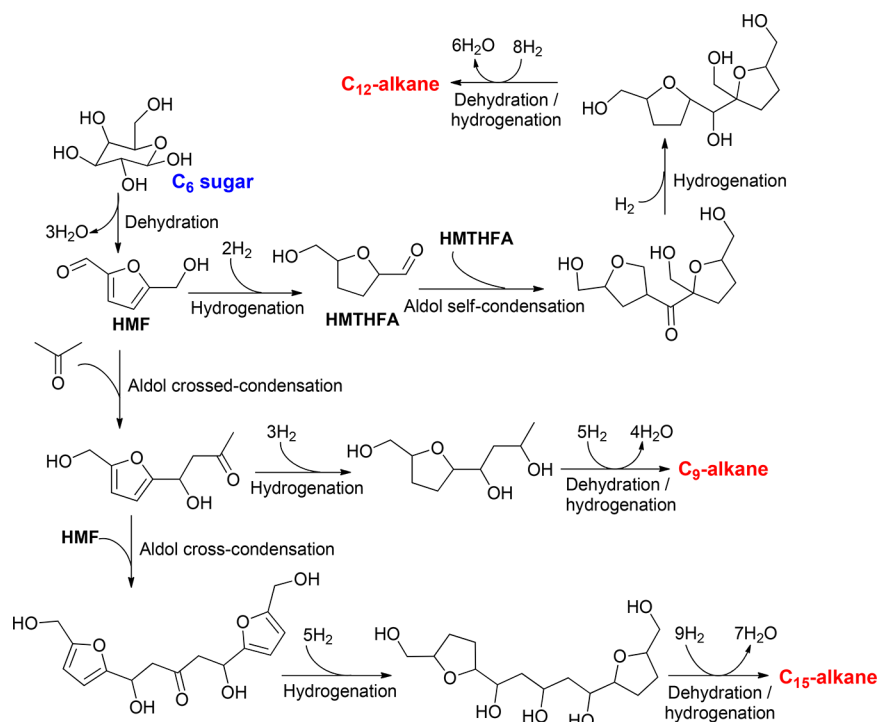
Scheme 1. Representative Biomass-Derived Platform Molecules



production of liquid alkanes with C_7 – C_{15} carbon atoms from hexoses in a four-phase, fixed-bed reactor via a cascade reaction process. This process included acid-catalyzed dehydration to 5-hydroxymethylfurfural (HMF) followed by aldol condensation

over a basic Mg–Al–oxide, prepared by coprecipitation method at room temperature, to produce large organic compounds which further could be transformed into corresponding alkanes by dehydration/hydrogenation over 4

Scheme 2. Carbon-Increasing Catalytic Pathways for Upgrading Biomass through Representative C–C Coupling Reactions

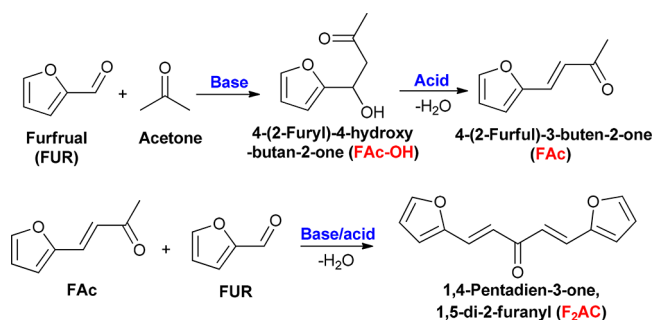
Scheme 3. Reaction Pathways for Transforming Biobased Hexose into C₉–C₁₅ Alkanes⁶¹

wt % Pt/SiO₂–Al₂O₃ at 250–265 °C and 5.2–6 MPa (Scheme 3).⁶¹ The resulting end-product liquid alkanes were demonstrated to retain 90% energy content of hexose and H₂ reactants, and the increase in selectivity toward heavier/lighter alkanes could be achieved by simply increasing/decreasing the molar ratio of HMF to acetone (1:10–1:1), respectively.

2.1.1. Base/Acid-Catalyzed Aldol Condensation. In the aldol-condensation step, the mixed metal oxides containing an optimal acid/base sites ratio of 1:1.1 with medium strength was more favorable for the formation of C₁₅ adduct from HMF and acetone under 2:1 or equimolar conditions at 50 °C.⁶²

Otherwise, retro-aldolization was most likely to take place in the assistance of stronger base sites. In addition, the preparation method and Mg/Al ratio were reported to significantly influence the catalytic performance of Mg–Al hydrotalcite (HT).⁶³ After calcination of Mg–Al HT at 450 °C for 16 h, the resulting mixed oxide having Mg/Al ratio of 3 could afford the condensed product (1,4-pentadien-3-one,1,5-di-2-furanyl; F₂Ac) with >90% selectivity from furfural (FUR) (>95% conversion) and acetone at 100 °C (Scheme 4). Conversely, the rehydration of Mg–Al HT resulted in much lower FUR conversion and selectivity to 4-(2-furful)-3-buten-2-one (FAC)

Scheme 4. Reaction Pathway for Aldol Condensation of FUR with Acetone⁶³



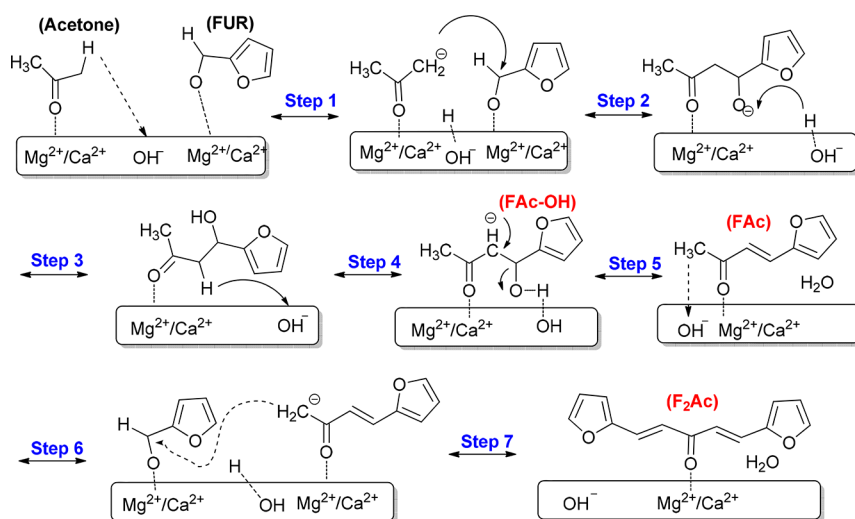
and F₂Ac at 20–100 °C, except the catalysts with Mg/Al ratio of 2 and 3 for ex- and in situ rehydrated HT, respectively.⁶³ The relatively higher crystallinity of Mg–Al HT after calcination as well as lower content of MgO active phase, susceptible to water after rehydration treatment, might have contributed to the superior activity and desired product selectivity. In connection with this, Sádaba et al. comprehensively studied and illustrated that Mg–O–Mg sites at the surface of c-MgO, Mg–O–Zr sites on c-MgO and c-Mg_xZr_{1-x}O_{2-x} of Mg–Zr mixed oxides were predominantly active for aldol condensation of FUR with acetone in water with Mg–O–Zr sites on c-MgO showing the highest activity.⁶⁴ Moreover, the catalyst deactivation might take place by leaching of Mg and Zr species into the solution, hydration of Mg oxides, or deposition of the surface sites with bulky condensed products formed from FUR. Furthermore, Fabá et al. clarified that the primary cause of Mg–Zr deactivation could be its interaction with water to modify the distribution of base sites and the support morphology, rather than the fouling and leaching effects.⁶⁵

Dolomite is a carbonate rock mainly containing Ca²⁺ and Mg²⁺ cations, normally in a chemical composition of CaMg(CO₃)₂. O'Neill et al. illustrated that the activation of dolomite by calcination at 800 °C for 8 h and full hydration in water at 40 °C for 2 h allowed the creation of Brønsted base sites (i.e., hydroxyl sites), exhibiting more activity than relevant Lewis acid sites of mixed metal oxides. This resulted in a high F₂Ac yield of 72.8% and ~90% FUR conversion were attained in water/methanol (2:3, w/w) at 150 °C within 60 min, while

conventional NaOH only gave a maximum of 55.3% F₂Ac yield.⁶⁶ The superior selectivity toward F₂Ac in the presence of activated dolomite could be ascribed to its higher adsorption enthalpy to FAC. In addition, the release of CO₂ during the decomposition of calcium and magnesium carbonates from dolomite at 800 °C resulted in the formation of more porous structure by stresses and ruptures. A domino reaction process was thus proposed (Scheme 5) involving (1) an initial proton abstraction from the α-carbon of acetone by Brønsted base to form a carbanion (Step 1), (2) condensation with the carbon of the carbonyl group in FUR to leave an oxyanion (Step 2) followed by (3) formation of FAC–OH [4-(2-furyl)-4-hydroxybutan-2-one] by fixing a proton abstracted from step 1 (Steps 3–4). The succeeding dehydration step (4) would lead to form FAC, while the recondensation of FAC to F₂Ac would follow the similar catalytic pathways (Steps 5–7).⁶⁶

Unlike Mg–Al HT and activated dolomite, the calcination of nanosized TiO₂ led to decreased catalytic performance for aldol condensation of FUR with acetone, which could be attributed to the dehydration and dehydroxylation of surface active sites.⁶⁷ Although the base strength of Mg–Al HT was higher than that of TiO₂, the latter with the presence of acid sites was more active for the dehydration step after aldol condensation. In other words, the acidic properties of TiO₂ were insufficient to promote dimerization to produce F₂Ac, but were useful for the dehydration of FAC–OH to FAC (up to 72% selectivity). Inconsistently, Kikhtyanin et al. reported that ion-exchanged K-beta zeolite catalysts, with weak basic and strong Lewis acid sites, exhibited poor catalytic activity (5–12% FUR conversion) in the aldol condensation reaction at 100 °C after 2 h. In contrast, appreciable catalytic performance (e.g., FUR conversion: 77.8%, and selectivity: 67.2% FAC, 15.2% FAC–OH and 17.6% F₂Ac) was achieved over the samples prepared by combining ion-exchange with impregnation.⁶⁸ The strong basic centers of the latter, possibly K₂O clusters, were demonstrated to be not only the active sites for aldol condensation but also advantageous for the stability by inhibiting the formation of heavy carbonaceous products. However, it was reported that the visible decrease in the performance of K-beta in consecutive catalytic runs could be caused by the interaction of strong basic sites with CO₂ from the environment and with furoic acid in situ generated from Cannizzaro reaction of FUR.⁶⁸

Scheme 5. Reaction Pathway for Aldol Condensation of Acetone with FUR over Activated Dolomite⁶⁶

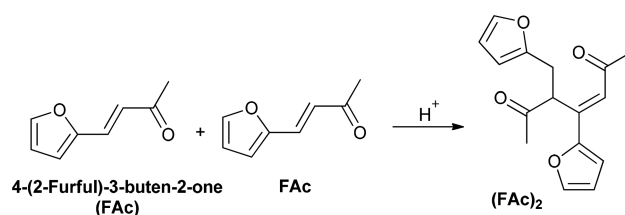


To improve the catalytic performance and reusability of basic catalysts such as Mg–Zr oxides, a nonmicroporous carbonaceous material like high surface-area graphite (HSAG) was used as an inert support to disperse the mixed oxides without interfering the active phase and the diffusion of the reactants, thus creating new basic sites resulting from structural defects.⁶⁹ Encouragingly, Mg–Zr/HSAG prepared by coprecipitation approach afforded a higher catalytic activity in terms of FUR conversion (96.5%) and selectivity toward FAc and F₂Ac (87.8%), as compared with the bulk Mg–Zr oxide (81.4% conversion and 76.2% selectivity) in the cross-condensation of FUR with acetone (1:1 molar ratio) at 50 °C. Importantly, the stability of Mg–Zr/HSAG was significantly enhanced by using HSAG in a pore diameter of 8–17 nm, and F₂Ac selectivity decreased by less than 30% after reusing the catalyst for one cycle at 100 °C in 24 h.⁶⁹ In sharp contrast, more than 85% difference in F₂Ac selectivity was observed over bulk Mg–Zr in two consecutive cycles under identical conditions. Hence, a combination of balanced acid–base sites with an appropriate surface area, and meso-/macroporous structure in the respective materials could be responsible for their predominant activity toward targeted products.⁷⁰

Two wt % Pd incorporated MgO–ZrO₂ preactivated under H₂ pressure of 1 MPa at 50 °C was demonstrated to be an efficient strategy for alleviating the deactivation of the parent catalyst in FUR–acetone aldol condensation after 24 h.⁷¹ Over the Pd/MgO–ZrO₂ catalyst, the selectivity toward F₂Ac decreased by only 25% after two consecutive reaction cycles, while the unmodified MgO–ZrO₂ lost its selectivity greatly corresponding to 90%. The partial hydrogenation of condensed adducts was proposed to improve the solubility in water, thus retarding or even avoiding the formation of deposits largely, thereby diminishing catalyst deactivation. Regarding the selectivity of aldol adducts, Shen et al. reported that MgO–ZrO₂ with three different types of base sites (i.e., Lewis base, Mg²⁺–O^{2–} pair, and surface –OH group) favored for the formation of the dimer (F₂Ac), while N₂-substituted NaY zeolite (Nit–NaY) showed higher selectivity toward the monomer (FAc) due to the relatively smaller and confined cage size in the FAU framework.⁷² Moreover, the addition of water >75 vol % concentration with respect to methanol as solvent led to increase its catalytic performance in terms of dimer selectivity and FUR conversion for both catalysts, although Nit–NaY was not entirely stable under aqueous conditions due to framework N₂ leaching.

Unlike solid bases, solid acids have not been employed as catalysts to the same degree for aldol condensation. Kikhtyanin et al. demonstrated that acidic zeolites (e.g., H-beta(25)) exhibited a remarkable catalytic performance in the formation of corresponding products from FUR and acetone, and 79.5% selectivity to FAc was obtained with 38.5% FUR conversion at 100 °C after 2 h.⁷³ Analogue to the general reaction route over base catalysts, F₂Ac was also formed but with lower selectivity (3.7%). However, further catalytic dimerization of olefinic FAc to (FAc)₂ with a selectivity of 16.8% took place on Brønsted acidic sites of zeolites (Scheme 6). After the first cycle of reaction with H-beta(25), the selectivity toward FAc (88.5%) and F₂Ac (4.6%) slightly increased while the dimer product (FAc)₂ was formed with a poor selectivity (6.9%), possibly due to the deposition of carbonaceous byproducts inside the micropores of zeolites.⁷³ It can therefore be speculated that aldol condensation takes place at both external and internal acid sites of H-beta(25) zeolite, while the formation of (FAc)₂

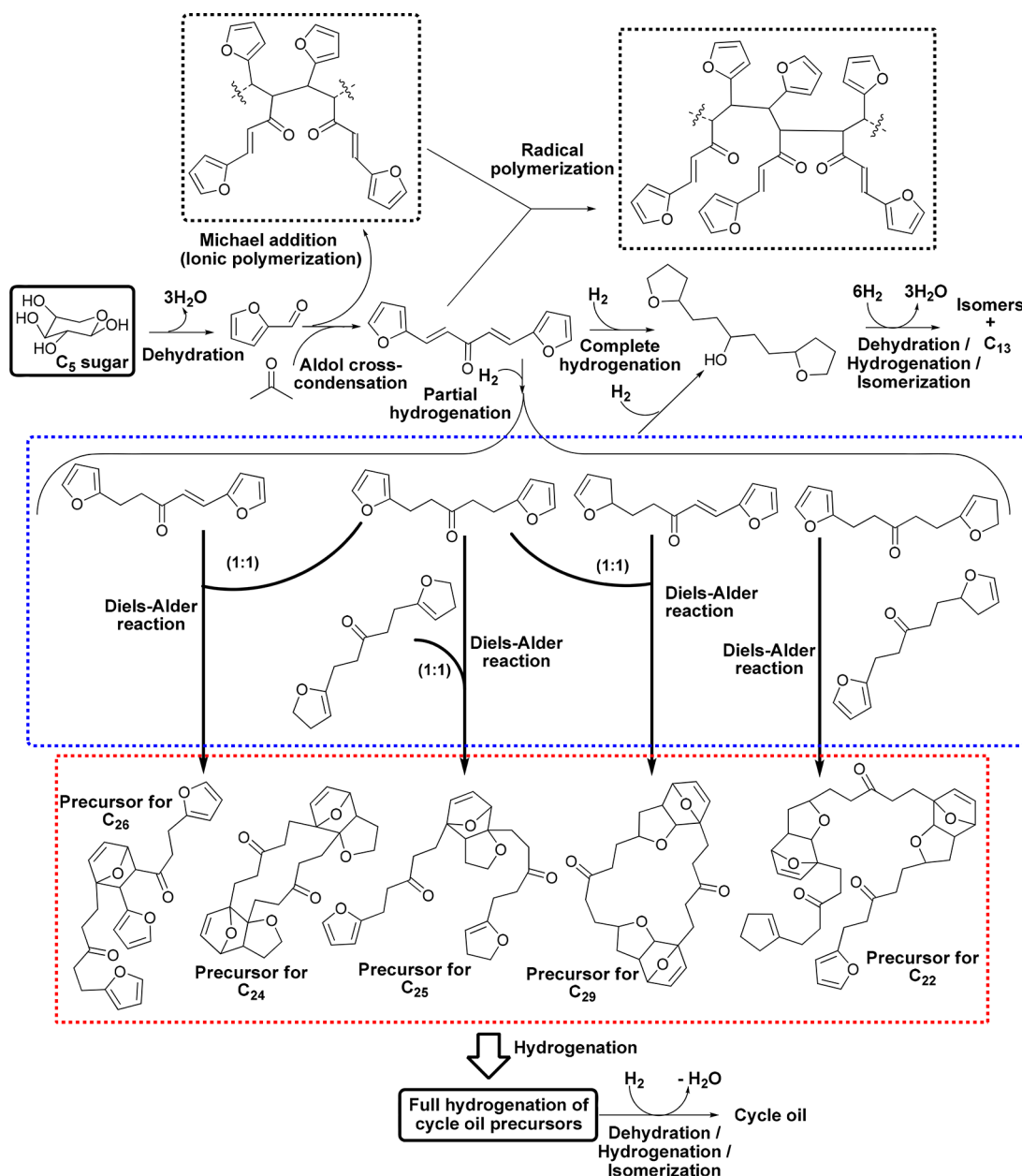
Scheme 6. Reaction Pathway for the Formation of Dimer Product (FAc)₂ from 4-(2-Furful)-3-buten-2-one (FAc)⁷³



predominantly proceeded inside the micropores of the zeolite. However, the role of acidic sites (e.g., intrinsic Brønsted acid sites, in situ generated Brønsted acid sites from Lewis acidic metal species interacted with water molecules, and acid–base paired sites) for the aldol condensation is inconsistent and ambiguous,^{74,75} and further studies are needed to understand the contribution of the type of acid sites toward targeted products.

As aforementioned, the resistance to coking seems to be an intrinsic ability to improve the recyclability of a catalyst for aldol condensation. In general, the active sites of layered two-dimensional (2D) materials with larger external surface area are more accessible than those of three-dimensional (3D) zeolites, thus possessing enhanced activity. However, Kikhtyanin et al. found that the 3D catalyst (e.g., MCM-22:60% FUR conversion, and MCM-49:55% FUR conversion) displayed superior activity to the material with 2D character (e.g., MCM-36:30–35% FUR conversion) at 100 °C after 2 h, probably due to swelling and a pillaring process expanding the interlayer space of 3D materials.⁷⁶ All these MWW family catalysts afforded higher FUR conversion (30–60%) than H-beta(25) (20%) and were more active than other types of zeolites following the order FAU > MOR > MFI.⁷³ Unfortunately, FUR conversion descended by ~12% of all studied MWW materials after the first use owing to coke formation, which is more severe for the 2D catalyst MCM-36 (decreasing from 30 to 35% to 5–7%).⁷⁶ These results apparently indicated that the reaction also occurred in supercages, besides cups located on the external surface, and that the severe coking could be protected by 10 membered-ring openings of the 3D MWW materials.

2.1.2. Aldol Condensation Coupled with Hydrodeoxygenation (HDO). The sequential integration of flow reactors has been demonstrated to be an efficient protocol to produce specific classes of hydrocarbons and/or liquid alkanes with targeted molecular weights from carbohydrates, while a number of acid, base and metal catalysts are often separately involved in different flow reactors.^{77–79} Moreover, a mixture of hydrocarbons (>C₂₂) would be formed via Michael addition, radical polymerization and Diels–Alder reactions (Scheme 7), which closely relied on the content of acid/base sites, reaction temperature, and substrate concentration.⁸⁰ Therefore, efforts were recently made on simplifying the reaction systems to obtain high selectivities. Dedsuksophon et al. reported an integrated catalytic process in one pot consisting of hydrolysis, dehydration, aldol-condensation, and hydrogenation of corn-cobs and tapioca flour for the production of C₅–C₁₅ compounds with a single Pd/WO₃–ZrO₂ catalyst.⁸¹ The WO₃–ZrO₂ moieties could effectively catalyze hydrolysis/dehydration at 200 °C in 5 min and subsequent aldol condensation at 80 °C in 30 h, while the impregnated Pd particles were active for the final hydrogenation at 120 °C in 6

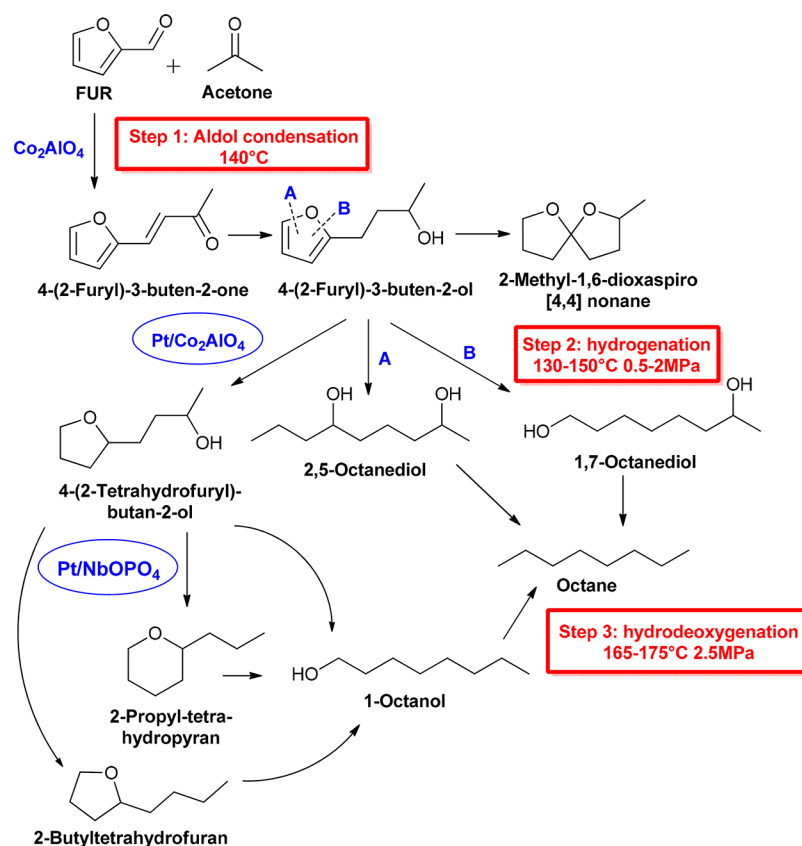
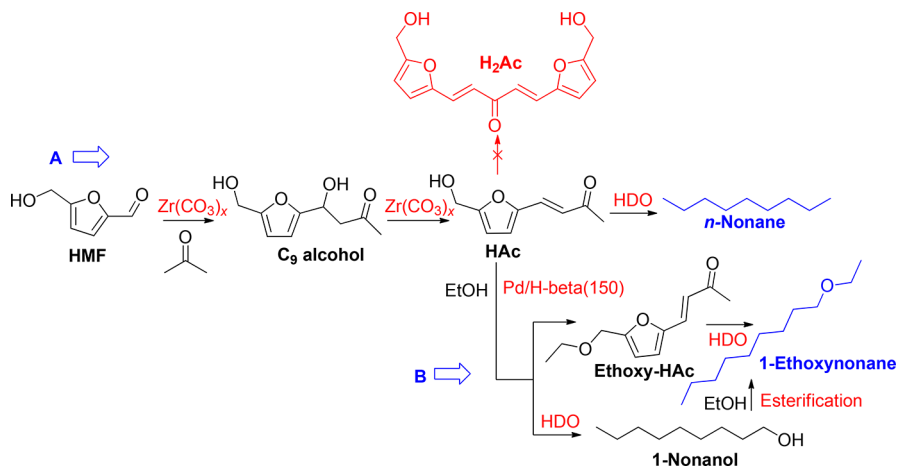
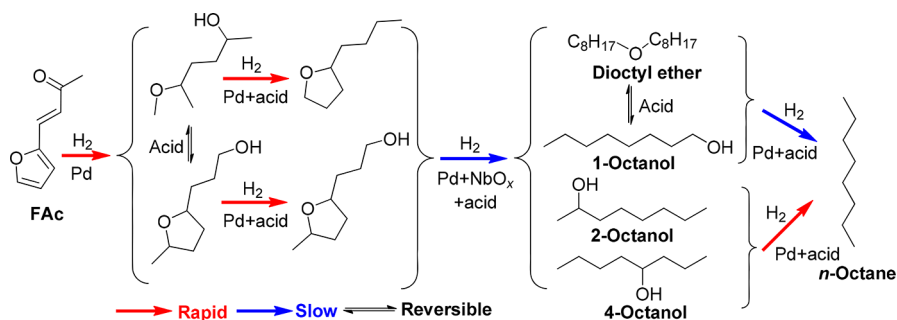
Scheme 7. Reaction Pathways for Transformation of C₅ Sugar into Petroleum Refinery Feedstocks⁸⁰

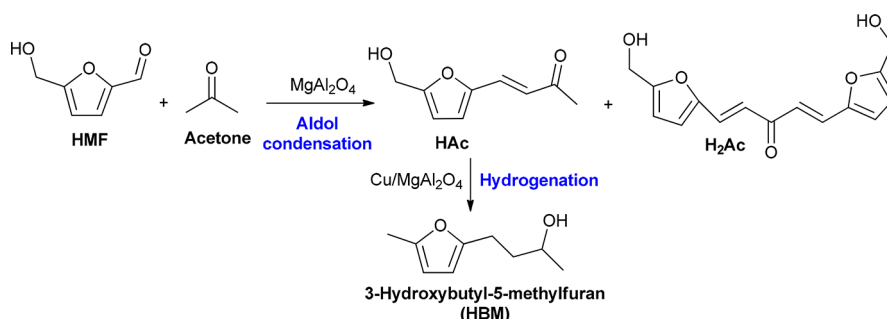
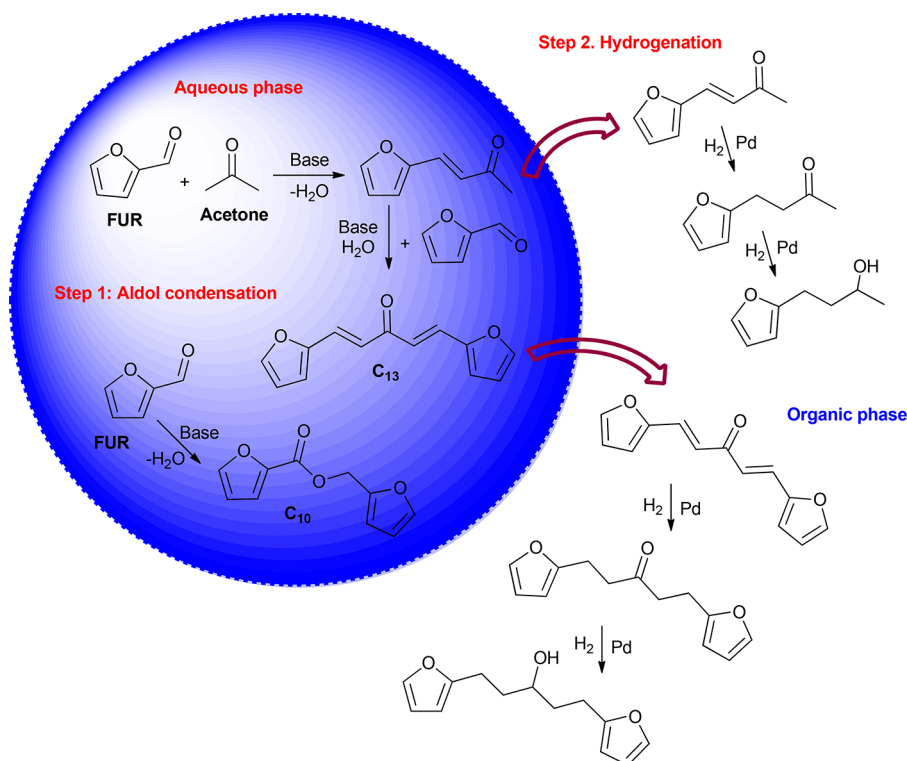
h, giving a total yield of 20.3% C₆/C₉/C₁₅ products from tapioca flour and 14.8% of C₅/C₈/C₁₃ compounds from corncobs. This type of multifunctional catalysts having acid, base, and metal sites exhibited a concerted role in this tandem reaction, thus significantly contributing to its moderate catalytic performance in a single reactor.

Using a bifunctional Pd/MgO-ZrO₂ catalyst in a single reactor, the cross aldol-condensation of acetone with FUR at 53 °C, or with HMF at 80 °C in water, led to the formation of water-insoluble monomer (C₈–C₉) and dimer (C₁₃–C₁₅) species along with water-soluble products in an overall carbon yield of more than 80% after hydrogenation at 120 °C at 5.5 MPa H₂ for 24 h.⁸² Notably, the increase of FUR/acetone molar ratio from 1:9 to 1:1 and 2:1 increased the selectivity toward dimer species by 31% and 43%, respectively. To further improve the selectivity of aldol adducts from FUR being condensed with acetone, Xu et al. developed a catalytic strategy by sequentially using Pt/Co₂AlO₄ (metal-base sites) for aldol

condensation and hydrogenation, and Pt/NbOPO₄ (metal-acid sites) for HDO (Scheme 8).⁸³ This three-step catalytic process gave a high yield of octane of ca. 76% at 175 °C and 2.5 MPa H₂.

Similarly, Bohre et al. reported that a water-tolerant solid base catalyst, Zr(CO₃)_x, could catalyze the reaction of acetone with HMF, yielding 92% of the C₉-aldol adduct (4-[5-hydroxymethyl]furan-2-yl]but-3-en-2-one, HAc) at full conversion at 54 °C after 24 h, and the subsequent HDO was performed over a bifunctional 5 wt % Pd/H-beta(150) catalyst in ethanol at 230 °C and 5.0 MPa H₂ for 8 h, affording *n*-nonane and 1-ethoxynonane with a selectivity of 40 and 56%, respectively.⁸⁴ For the aldol condensation of HMF with acetone, the C₉ alcohol [i.e., 4-(5-hydroxymethyl-2-furyl)-3-butenone] was a key intermediate for producing HAc via dehydration over Zr(CO₃)_x and no dimer of HAc 1,5-bis(2-furanyl-5-hydroxymethyl)-1,4-pentadien-3-one (H₂Ac) was observed (Scheme 9A). Regarding the synthesis of *n*-nonane and

Scheme 8. Reaction Pathways for Transforming Biobased FUR and Acetone into *n*-Octane⁸³Scheme 9. Possible Pathways for Cascade Reactions of HMF and Acetone over $\text{Zr}(\text{CO}_3)_x$ and Pd/H-Beta(150)⁸⁴Scheme 10. Possible Pathway for the Transformation of FAc into *n*-Octane⁸⁵

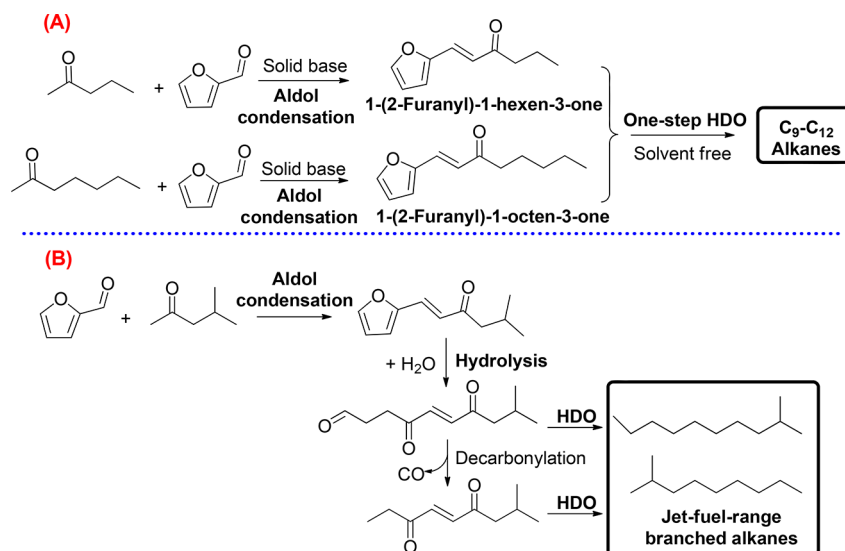
Scheme 11. Aldol Condensation of HMF with Acetone and Subsequent Hydrogenation Catalyzed by Cu/MgAl₂O₄⁸⁷Scheme 12. Schematic Illustration of Cascade Aldol Condensation and Hydrogenation Performed in Water/Oil Interface⁹⁰

1-ethoxynonane from the HDO of HAC catalyzed by Pd/H-beta(150), two plausible reaction pathways was proposed with and without involving opening of the furan ring prior to the HDO or esterification, respectively (Scheme 9B). Notably, Zr(CO₃)_x was reused for five cycles with the yield of HAC slightly decreasing from 91 to 84%, while the deactivation of Pd/H-beta(150) was severe possibly due to coke formation on the catalyst surface blocking the active sites under harsh hydrogenation conditions.

To enhance the yield of the targeted fuel product, Xia et al. prepared a multifunctional catalyst, Pd/NbOPO₄, which efficiently promoted the HDO of FAc to octane with >90% yield in cyclohexane at 170 °C under 2.0 MPa H₂ during 256 h time-on-stream through tetrahydrofuran and octanol intermediates (Scheme 10).⁸⁵ The multifunctionality of Pd/NbOPO₄ can be elucidated as Pd-catalyzed hydrogenation, NbO_x-promoted cleavage of C–O bond (especially for the tetrahydrofuran ring), and dehydration mediated by acid sites of NbOPO₄, which combined enabled excellent transformation of the furan-derived adducts into alkanes. When altering the reaction medium from cyclohexane to water, Xia et al. found

that 1-octanol (up to 62.7% yield) was selectively formed from FAc over the hydrophilic Pd/NbOPO₄ together with trifluoromethanesulfonic acid, via a two-step process involving cascade hydrogenation at room temperature, 2.5 MPa H₂ and 3 h, and at 190 °C and 18 h reaction conditions.⁸⁶ The promising results were attributed to spontaneous separation of in situ generated 1-octanol from the water phase hampering over-hydrogenation to *n*-octane. Importantly, only a slight decrease in 1-octanol yield from 62.7 to 49.1% was observed after four successive cycles with this catalytic system.

Interestingly, a non-noble metal catalyst, Cu/MgAl₂O₄, with basic and metal pair-sites was explored by Pupovac and Palkovits for the efficient transformation of HMF with acetone in a molar ratio of 1:1 and subsequent selective hydrogenation avoiding the furan ring saturation as shown in Scheme 11.⁸⁷ At 140 °C in 7 h, MgAl₂O₄ containing relatively more Brønsted basic sites exhibited a higher activity with regard to the formation of aldol product (HAc) achieving up to 81% yield, which is superior to the systems catalyzed by CoAl₂O₄ (70%) and ZnAl₂O₄ (76%). The introduction of 5 wt % Cu into MgAl₂O₄ by impregnation did not affect its activity (HAc: 78%

Scheme 13. Synthetic Routes to Jet Fuel Range Alkanes Using FUR and Ketones from Lignocellulose^{97–99}

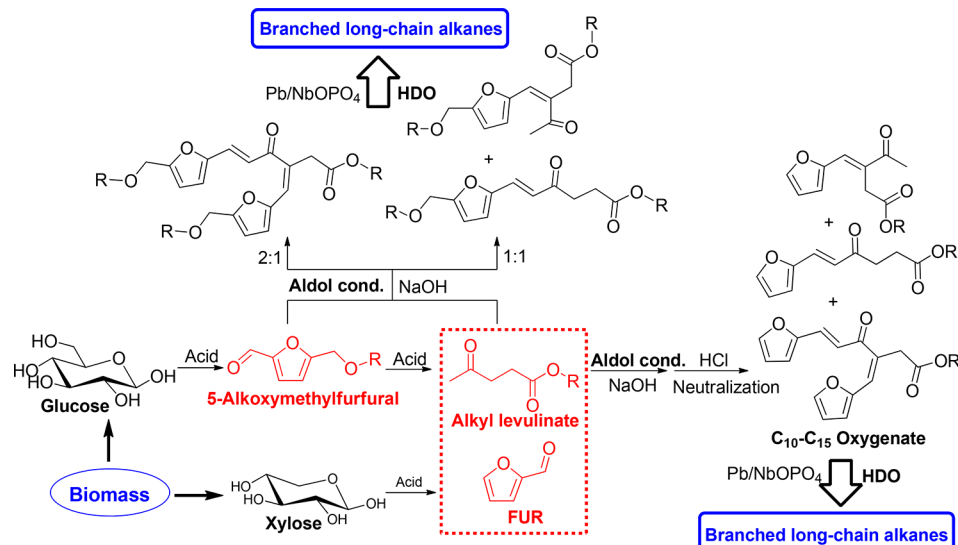
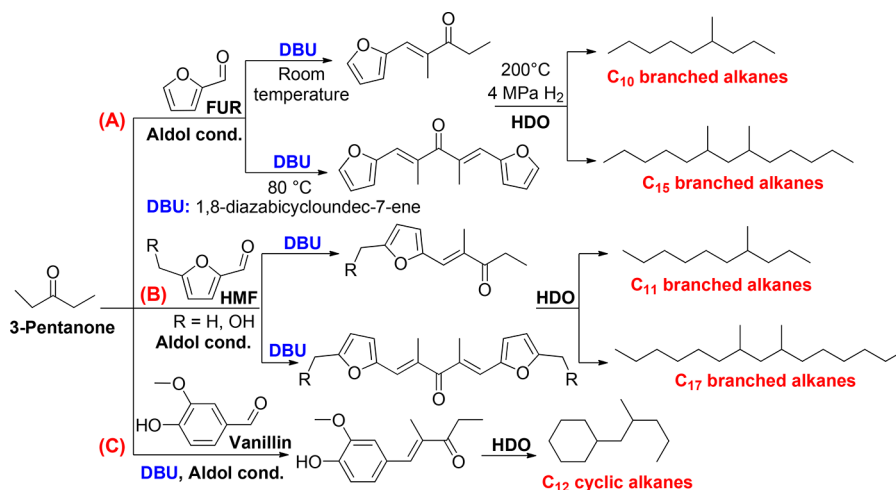
yield), and a very poor yield of H₂Ac (7%) was obtained compared to the pristine support (11%) at complete HMF conversion. Importantly, Cu/MgAl₂O₄ was able to completely convert HAc selectively to 3-hydroxybutyl-5-methylfuran (HBM; 84% selectivity) at 200 °C at 5 MPa after 7 h. The recyclability of Cu/MgAl₂O₄ proved possible due to the intact spinel structure, but in the hydrogenation a significant decrease was observed due to Cu sintering and leaching.⁸⁷ This study revealed that further optimization toward obtaining a robust catalyst structure was required in order to enhance catalyst stability and reusability in the hydrogenation reaction under harsh reaction conditions. In line with this, Xu et al. demonstrated that in situ loading of Pd by coprecipitation of Pd, Co, and Al species could simplify the procedure for the preparation of bifunctional Pd/Co–Al HT-like catalyst with abundant mesopores, which resulted in Pd/Co–Al that was remarkable efficient for aldol condensation of acetone with FUR (ca. 98% conversion) to FAc and F₂Ac (total selectivity of 99%) at 140 °C after 5 h, and subsequent hydrogenation to 4-(2-tetrahydrofuryl)-2-butanol and 1,5-ditetrahydrofuryl-3-pentanol (ca. 91% selectivity) at 120 °C at 4 MPa H₂ after 10 h.⁸⁸ Moreover, the used catalyst was easily regenerated by calcination at 300 °C and exhibiting only a small loss of 2.9 and 6.3% with respect to FUR conversion and completely hydrogenated products, respectively, on subsequent use.

Faba et al. systematically explored a bifunctional Pd/MgO–ZrO₂ catalyst that was meritorious for the production of *n*-octane and tridecane. Hence, the catalyst afforded a total yield of 50% from FUR and acetone in aqueous phase at 220 °C at 4.5 MPa after 24 h in a single-step reaction protocol, which were comparable to the two-step procedure (70% yield) under identical conditions for HDO in combination with preceding aldol condensation at 50 °C for 24 h.⁸⁹ In contrast, a mechanical mixture of bulk MgO–ZrO₂ and Pt/Al₂O₃ only yielded 14.5% of *n*-tridecane (ca. 21% conversion) and a trace amount of *n*-octane in a one-step process due to undesired side reactions.⁸⁹ Moreover, a very small amount of *n*-tridecane (<1%) was obtained with MgO–ZrO₂ and Pt/Al₂O₃ in aqueous phase via the two-step procedure, indicating the solubility of the partially hydrogenated adducts in water might play a promotional role in the single-step catalytic process.

In a biphasic emulsion system consisting of water and decalin, bifunctional nanohybrids prepared by fusing basic oxides (e.g., MgO) to carbon nanotubes were demonstrated to stabilize the water/oil emulsions as well as catalyze the condensation of FUR with acetone, as illustrated Scheme 12.⁹⁰ Although 2-furancarboxylic 2-furanmethyl ester was derived from the products of the Cannizzaro reaction between furfuryl alcohol and furoic acid via esterification, FAc (~66% selectivity) was observed to be the dominant product with nanohybrids at 80 °C after 3 h, which was partially converted to F₂Ac (~31% selectivity) after 24 h. Overall, a relatively higher fraction of FAc and F₂Ac was achieved in the emulsion compared to a single phase of water, and the in situ hydrogenation could be realized by incorporation of an active metal (Pd or Pt) onto the nanohybrids in the emulsion system.⁹⁰ Compared to the reaction proceeding in the monophasic system, an enhanced hydrogen concentration and uniform particle dispersion at the interface of the water/oil biphasic system might in part contribute to its higher activity.⁹¹ In addition, the selectivity toward single or double condensed product could be accordingly controlled by adjusting the ratio of reagents in the biphasic system.⁹²

The aldol condensation of HMF with acetone without a catalyst gave a high yield of >95% to the monoadduct 4-(5-hydroxymethyl-2-furyl)-3-butenone in water at 200 °C at 2.5 MPa CO₂ after 20 h.⁹³ This approach was extended to glucose dehydration to give HMF which further reacted with acetone, yielding 11% of monoadduct in one-pot under identical reaction conditions. Encouragingly, the combined use of supercritical CO₂ (14 MPa) with Pd/Al–MCM-41 at 4 MPa H₂ could produce linear alkane with quantitative selectivity from the monocondensed product of HMF with acetone at 80 °C after 20 h.⁹⁴ It was deduced that the combination of metal (Pd) and acid (CO₂ and incorporated Al species) catalysts facilitated the ring-opening reaction of furan, thus showing the pronounced activity under these reaction conditions.

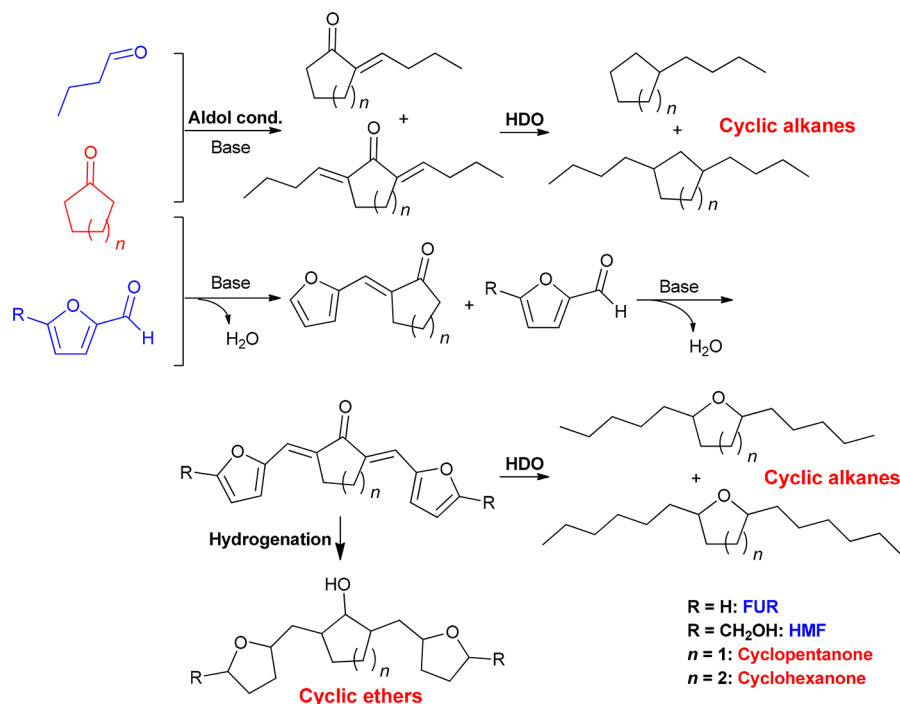
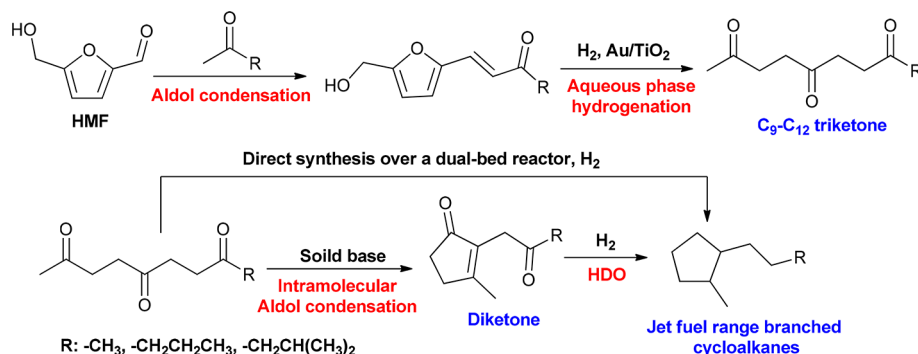
As discussed above, acid and/or base sites with high strength were favorable for the aldol condensation reaction in aqueous phase, while for vapor phase conditions the catalyst might need weak acid–base sites.⁹⁵ Unlike organic amines, mineral bases were unable to catalyze aldol condensation of hydroxycarbonyl

Scheme 14. Reaction Pathways for Transformation of Biobased Platform Molecules into Branched Long-Chain Alkanes^{100–103}Scheme 15. Reaction Pathway for the Synthesis of Liquid Alkanes from 3-Pentanone^{104–106}

compounds (e.g., hydroxyacetone and dihydroxyacetone) due to the generation of alkoxide species as previously reported.⁹⁶ Anyway, the resulting alkanes derived from bioaldehydes (e.g., FUR and HMF) and C₃ carbonyl compounds (e.g., acetone) were commonly straight-chained. When increasing the carbon number (>C₃) of 2-ketones, similar kind of major adducts (e.g., 1-(2-furanyl)-1-hexen-3-one and 1-(2-furanyl)-1-octen-3-one) were derived from bioaldehydes (e.g., FUR) reacting with the C1-position of 2-ketones (e.g., 2-pentanone and 2-heptanone) mediated by a strong base like CaO at 140 °C for 6 h, and the corresponding C₉–C₁₂ linear alkanes (ca. 80% overall carbon yield) were obtained after HDO over Pd nanoparticles using H₂ in a flow rate of 120 mL/min at 260 °C (Scheme 13A).⁹⁷ In this respect, the aldol adducts of bioaldehydes and simple 2-ketones appear to be promising precursors for producing the linear long-chain alkanes. However, branched long-chain alkanes (up to 90% yield of jet-fuel-range alkanes) formed under similar reaction conditions when a substituting 2-ketone (e.g., methyl isobutyl ketone; MIBK capable of being obtained from self-aldol condensation of bioacetone followed by selective hydrogenation) was used instead (Scheme 13B).^{98,99}

Interestingly, the C3-position of levulinic acid (LA) or its ester participated in the condensation with the aldehyde group of FUR or HMF followed by HDO resulted in branched long-chain alkanes (Scheme 14).^{100–103} In this scenario, the aldol adducts, or alkanes with a maximum carbon number of 15 and 17, were achieved from the dimerization of LA (ester) with FUR and HMF, respectively. Moreover, the carbon-chain length of C₁₅ and C₁₇ alkanes was much closer to the range of diesel fuels, showing a great potential to abate the reliance on fossil fuels. Owing to the complexity of the catalytic process, attention should be focused on avoiding unwanted side reactions such as self-Michael additions to mitigate the formation furanic-keto acid polymers.¹⁰³

Under solvent-free conditions, Chen et al. found that biomass-derived 3-pentanone underwent selective aldol condensation with equivalent FUR over CaO or KF/Al₂O₃ and subsequent HDO catalyzed by Ni–Cu/SiO₂ afforded C₉ and C₁₀ branched alkanes; 4-methyl-nonane and 4-methyl-octane (Scheme 15A).¹⁰⁴ On the other hand, the carbon-chain length of the resulting branched alkanes increased to C₁₄–C₁₅ when employing 5-nonanone and FUR/HMF as substrates (Scheme 15B).¹⁰⁵ By altering the carbon-atom number of ketones, the

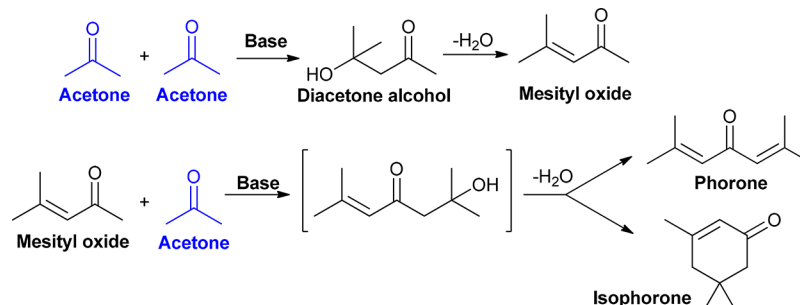
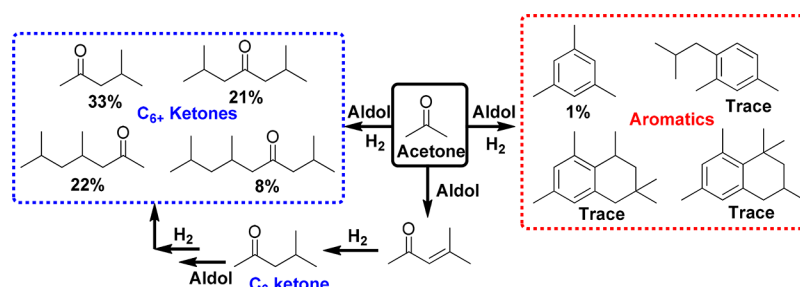
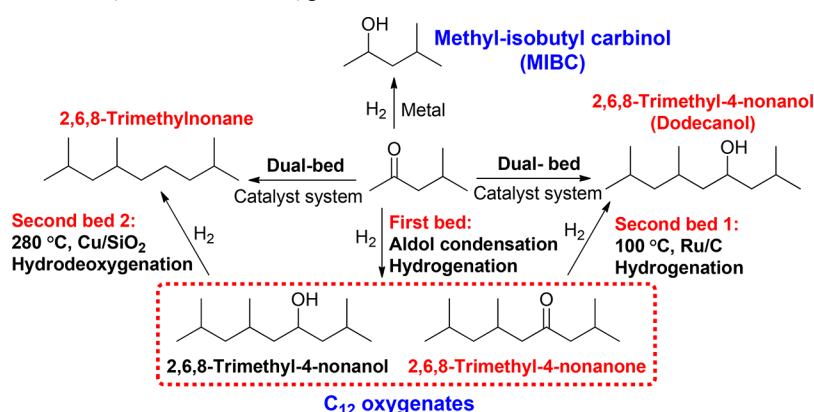
Scheme 16. Reaction Network for the Synthesis of Cyclic Ethers and Alkanes from Bioaldehydes and Cyclic Ketones^{109–113}Scheme 17. Synthesis of C_9 – C_{12} Triketones, Diketones, and Jet Fuel Range Branched Cycloalkanes from Biobased 2-Ketones and HMF¹¹⁶

chain length of the corresponding alkane products can thus be accordingly varied. Instead of using mineral base as catalyst, an organic amine DBU (1,8-diazabicycloundec-7-ene) could efficiently catalyze formation of C_{15} or C_{17} adducts from reaction of one mole of 3-pentanone with two moles of FUR or HMF, respectively (Scheme 15C).¹⁰⁶ It was speculated that DBU not only activated FUR via the formation of hydrogen-bonding network but also facilitated α -H being departed from 3-pentanone to form enolate, thus catalyzing a more complete process for the aldol condensation reaction. In a similar transformation route, vanillin derived from lignin successively proceeded aldol condensation with 3-pentanone and followed by HDO selectively gave C_{12} cyclic alkane (Scheme 15C).¹⁰⁶ The diversity of obtained biobased alkanes in high selectivity reflects the significance and possibility of controlling product distribution. To enhance the recyclability of the catalyst, a postgrafting method was adopted to effectively immobilize organic amines onto silica materials.¹⁰⁷ Gratifyingly, the introduced base ($-\text{NH}_2$) and intrinsic weak acid ($-\text{SiOH}$) sites of the resulting catalysts were found to play a cooperative role in aldol condensations, thus showing a better performance

compared to sole amines such as aminopropane (TOF: 7.8×10^{-4} vs $2.0 \times 10^{-4} \text{ s}^{-1}$).¹⁰⁸

Normally, cyclic alkanes possess higher density and volumetric heating value than straight ones, owing to their strong ring strain.¹⁰⁶ Consequently, the development of efficient catalytic routes for the production of different cyclic alkanes from biomass derivatives has recently attracted a great deal of interest. The aldol condensation of cyclic ketones (e.g., cyclopentanone) with two equivalent of aldehydes (e.g., *n*-butanal, FUR, and HMF) combined with a following HDO process could directly produce cyclic ethers or alkanes (Scheme 16).^{109–113} Similar to alkanes, the cyclic ethers can also be utilized as potential fuel additives.¹⁰⁹ By selecting appropriate metal catalysts (e.g., 5 wt % Pd/C), the selective hydrogenation of exocyclic $\text{C}=\text{C}$ bonds, or also unsaturated $\text{C}=\text{C}$ bonds in furan rings, concurrently avoiding the cleavage of $\text{C}-\text{O}-\text{C}$ ether bonds of the condensed products could be realized.¹¹¹ Otherwise, cyclic alkanes would be primarily formed via HDO under relatively harsh reaction conditions.^{112,113}

It was shown that the synthesis of cyclopentanone could be achieved from furanic aldehydes (e.g., HMF) via 2,5-

Scheme 18. Formation of Possible Products during Self-Condensation of Acetone¹¹⁸Scheme 19. Reaction Pathways for the Conversion of Acetone to C₆₊ Ketones and Aromatics¹²²Scheme 20. Schematic Route To Synthesize C₁₂ Oxygenates with MIBK and H₂ over Dual-Bed Catalytic Systems¹²³

hexanedione as a key intermediate.^{114,115} Employing aldol adduct products derived from HMF and 2-ketones directly as the source of 2,5-hexanedione derivatives, Li et al. developed a novel cascade catalytic process comprising CaO-promoted solvent-free condensation of HMF with 2-ketone followed by Au/TiO₂-catalyzed aqueous phase hydrogenation to give triketone, which by solvent-free intramolecular aldol condensation and HDO mediated by a dual-bed catalyst system consisting of Pd-MgAl-HT and Ni-SiO₂, finally producing branched cycloalkanes in jet fuel range (Scheme 17).¹¹⁶ This class of cycloalkanes was confirmed to have low freezing points (ranging from −49 to −23 °C) and high densities (ca. 0.81 g/mL).

2.2. Carboxide Self-Condensation. As discussed above, cross-aldol condensation of biofuranic aldehydes with ketones to di- and trimeric adducts can be achieved over acidic and/or basic catalysts. In this catalytic process, the self-condensation of ketones (e.g., acetone) might occur to a small extent as one of the major side reactions, although it is not thermodynamically favored.¹¹⁷ Manríquez et al. demonstrated that HT-like materials (e.g., MgZnAlO_x, MgFeAlO_x, MgCuAlO_x, and

MgNiAlO_x) could transform acetone into isophorone (up to ca. 76% selectivity) and phorone (up to ca. 21%) at 300 °C through cascade reactions as presented in Scheme 18: (1) self-condensation of acetone to diacetone alcohol, (2) then dehydration to mesityl oxide, and (3) finally mesityl oxide reacted with acetone followed by dehydration of formed product to yield phorone and further ring-closing to isophorone.¹¹⁸ The solid catalysts with bigger pore diameters and larger surface areas were found to preferentially form isophorone rather than phorone. Moreover, enhancing the basicity of metal oxides improved the selectivity toward these two trimers.¹¹⁹ Over a dual-bed catalytic system with a base-metal containing bifunctionalized catalyst Pd/MgAl-HT, C₆–C₁₅ branched alkanes with 80% carbon yield was directly obtained from acetone self-condensation and succedent HDO,¹²⁰ indicating the feasibility of producing drop-in fuels using only acetone as substrate.

In an alternative approach, the combination of acid with metal species has also been explored for the synthesis of long-chain compounds from acetone. Typically, the in situ selective hydrogenation of C=C bond of the dimeric adduct (i.e.,

mesityl oxide) to methyl isobutyl ketone (MIBK) over metal particles (e.g., Pt) was necessary to alleviate the thermodynamical constraint of the initial self-condensation of acetone catalyzed by acid.¹²¹ Meanwhile, a low partial pressure of H₂ seemed to be necessary to avoid the competitive hydrogenation of the C=O bond in the product. Over a mixed catalyst system consisting of Amberlyst-15 and Ni/SiO₂-Al₂O₃, poly aldol adducts, including C₉ and C₁₂ ketones, were also formed in significant proportion with trace amounts of aromatic compounds (Scheme 19), apart from the formation of the dimeric adduct (MIBK, C₆ ketone).¹²² A very good total yield of C₆-C₁₂ ketones (84%) was obtained at 120 °C at 1.7 MPa 6 vol % H₂/Ar after 24 h. When replacing the Ni catalyst with Pd/C or Ru/C the C₉ yield decreased, but selectivity increased toward MIBK under identical conditions.

Sheng et al. reported that the self-condensation of MIBK could further convert it to either dodecanol or 2,4,8-trimethylnonane in high selectivity when changing the catalyst system to a two-bed continuous flow reactor (Scheme 20).¹²³ In the first catalyst bed, Pd/MgAl-HT catalyzed the condensation of MIBK (ca. 91% conversion; flow rate: 0.05 mL/min) to C₁₂ oxygenates (i.e., 2,6,8-trimethyl-4-nonanone and 2,6,8-trimethyl-4-nonanol) with a total carbon yield of 72% at 250 °C at 0.6 MPa H₂. Quite low yields of methyl-isobutyl carbinol (MIBC) was detected in the reaction mixture, ascribing to much higher selectivity of Pd (especially loaded on the basic support) toward the hydrogenation of C=C than that of C=O.¹²⁴ In the second bed, dodecanol or 2,4,8-trimethylnonane was efficiently produced over 5 wt % Ru/C at 100 °C or 5 wt % Cu/SiO₂ at 280 °C, both at 0.6 MPa H₂ with a flow rate of 150 mL/min, and total carbon yields of ca. 70% was attained in both cases.

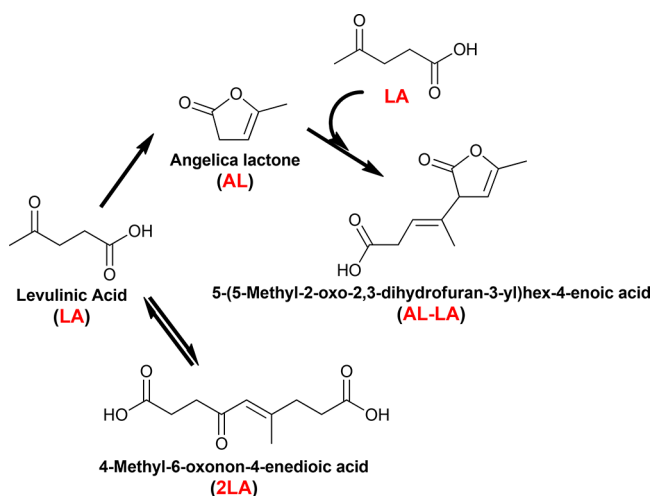
The cross-condensation of other methyl ketones including methyl ketone esters (e.g., 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, and ethyl pyruvate) to di- and trimeric adducts could also be performed over base and/or acid catalysts.^{125–127} Notably, MgZr-catalyzed conversion of levulinic acid (LA) in water gave two different aldol adducts with the same carbon number of 10 (i.e., 2LA and AL-LA; Scheme 21).¹²⁸ Two molecules of LA condensed with each other to directly afford 2LA, while AL-LA formed from one molecule of

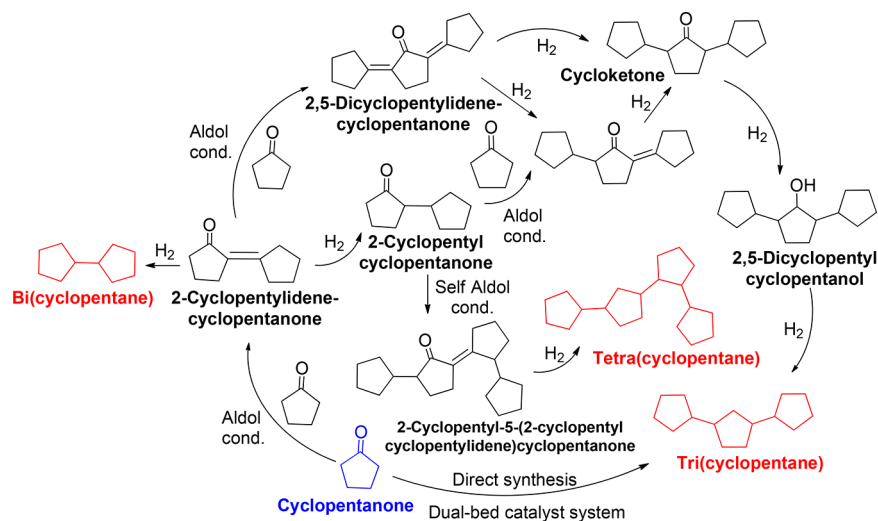
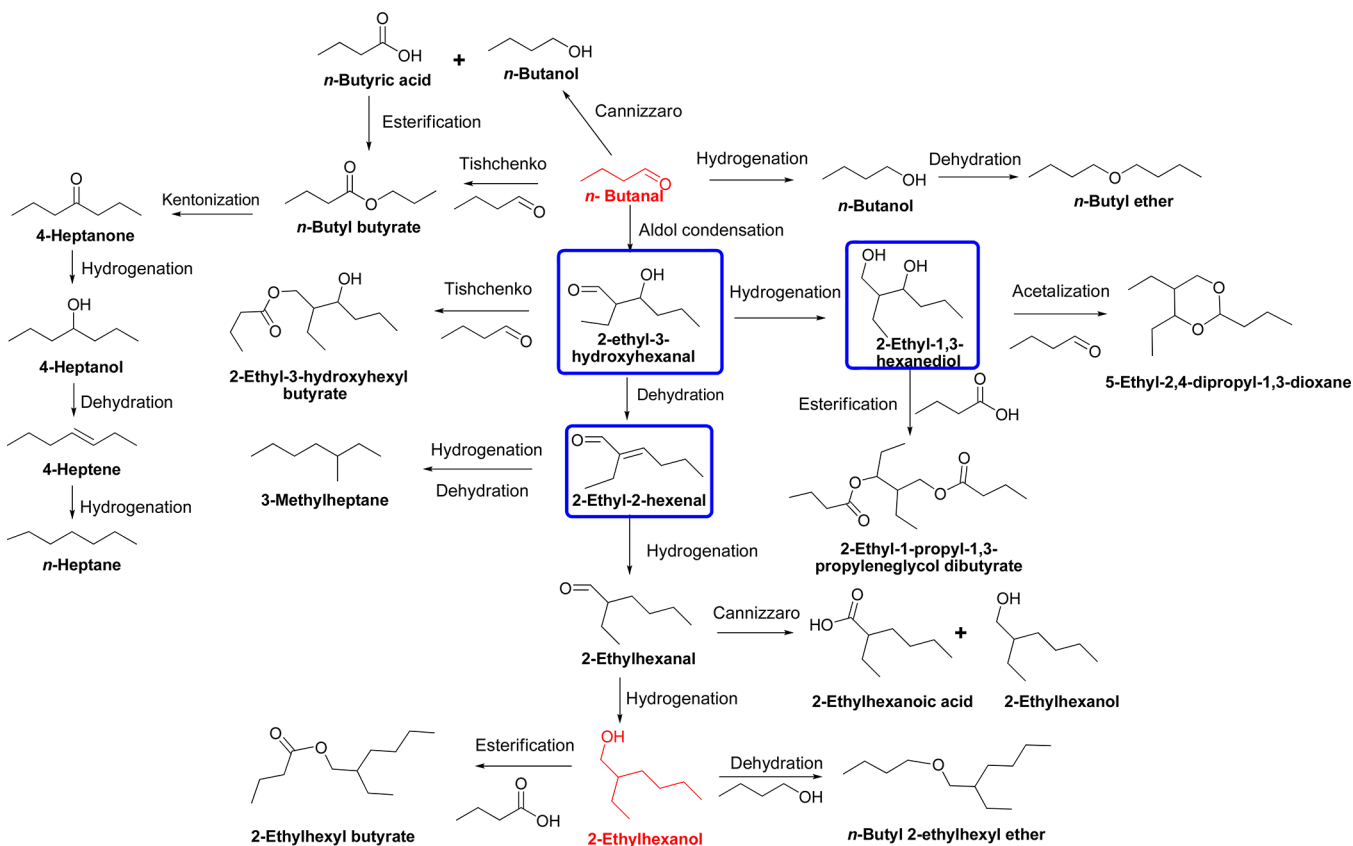
LA reacting with equivalent amount α -angelica lactone (AL) in situ byproduct formed by intramolecular cyclization of LA. Under the chosen reaction conditions of 50 °C and 0.1 MPa H₂ for 24 h, LA-LA was found with higher selectivity (ca. 90%) at 30% LA conversion over MgZr.¹²⁸ The retro-aldolization of adducts occurred after long reaction time or at high temperature, which might reduce LA conversion as well as aldol-adduct yield. Additionally, the carbon-chain length of carboxylic acids could be further increased by ketonization processes.¹²⁹

Apart from branched alkanes, the synthesis of high-density cycloalkanes has also been achieved from biomass-derived cyclic ketones (e.g., cyclopentanone that is an important component in bio-oil and can also be synthesized via hydrogenation of FUR) via direct aldol condensation,¹³⁰ or methyl ketones (e.g., 2-butanone, 2-pentanone, and 2-hexanone) with a carbon number of ≥ 4 through aldol condensation and Michael addition.¹³¹ However, the control of product distribution is quite challenging as the reaction proceeds through complicated pathways. Over the past several years, Zhang and co-workers made a great deal of effort on the selective transformation of cyclopentanone into mono- or poly condensed product (Scheme 22).^{132–136} Under solvent-free conditions, MgAl-HT with balanced acid–base sites (molar ratio of 1:0.55, 0.59 mmol/g in total) was able to transform cyclopentanone to 2-cyclopentylidene-cyclopentanone (C₁₀ adduct, Scheme 22) with a maximum yield of 86% at 150 °C after 8 h, followed by HDO to give the bicyclic C₁₀ hydrocarbon (up to 80% overall yield) having a high-density of 0.866 g/mL.¹³² MgO-ZrO₂ with medium-strong basicity seemed to facilitate the formation of C₁₀ adduct (ca. 85% yield) with 88% cyclopentanone conversion at 130 °C after 4.5 h.¹³³ In addition, the accessibility or shape-selectivity might have contributed to the pronounced selectivity toward C₁₀ adduct.¹³⁴ On the other hand, tri- or tetra(cyclopentane) in yields >80% was accomplished by partial hydrogenation of C=C bond of intermediates or by removal of in situ generated water by further aldol condensation (Scheme 22).^{135,136} The promotional effect of the selective hydrogenation of C=C bond of 2-cyclopentylidenecyclopentanone might be due to the formation of more reactive 2-cyclopentyl-1-cyclopentanone for the trimerization to yield cycloketone (Scheme 22),¹³⁵ while the removal of water could not only facilitate the formation of the tetramer 2-cyclopentyl-5-(2-cyclopentylcyclopentylidene) cyclopentanone from the point view of reaction equilibrium but also suppress the occurrence of retro-aldol condensation.¹³⁶

With respect to bioaldehydes (e.g., acetaldehyde, propanal, and *n*-butanal) containing α -H, di-, or poly aldol self-condensation was most likely to take place over an acid catalyst, and the selective hydrogenation of in situ generated C=C bonds, or even the rest of C=O groups with metal particles, could be achieved in the presence of H₂ atmosphere.^{137,138} Taking the catalytic conversion of *n*-butanal as an example, the product distribution varied with the reaction parameters (Scheme 23).^{139–141} In this integration reaction system, *n*-butanal mainly underwent aldol condensation to 2-ethyl-3-hydroxyhexanal in the presence of acidic catalyst, followed by dehydration to give 2-ethyl-2-hexenal (Scheme 23).¹⁴¹ In parallel, *n*-butanal was partially hydrogenated to *n*-butanol over metal species, which could be further dehydrated intermolecularly to yield *n*-butyl ether. Also, *n*-butanal might transform into *n*-butyric acid and *n*-butanol via Cannizzaro reaction. Butyl butyrate could be obtained by either

Scheme 21. Primary Products Observed in Self-Condensation of Levulinic Acid (LA) Catalyzed by Mixed Oxides¹²⁸

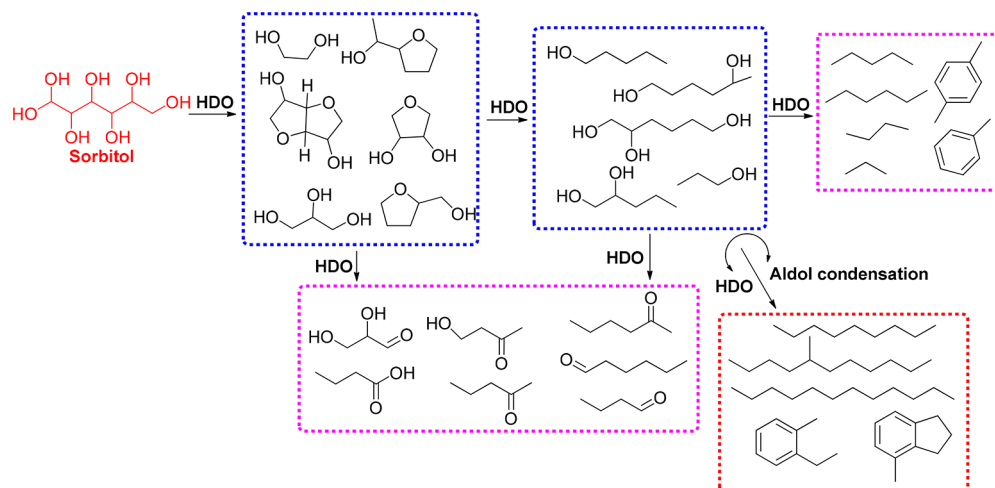
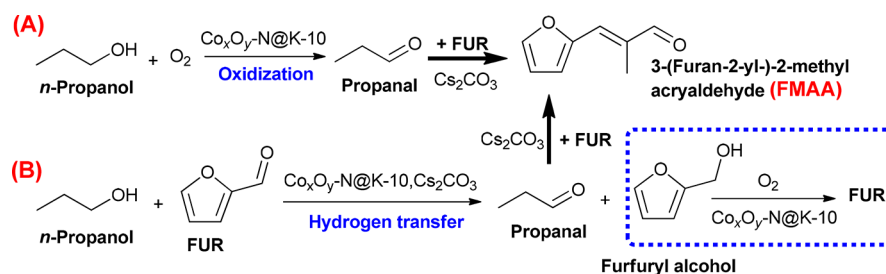


Scheme 22. Reaction Route to the Synthesis of High-Density Cycloalkanes Using Cyclopentanone^{132–136}Scheme 23. Reaction Pathways for Upgrading *n*-Butanal via Cascade Reactions¹⁴¹

esterification of *n*-butanol with *n*-butyric acid, or Tishchenko self-esterification of *n*-butanal. In addition, other byproducts such as 4-heptanone, 4-heptanol, *n*-heptane, 2-ethyl-3-hydroxyhexyl butyrate, dibutyrate, 2-ethylhexanol, 3-methylheptane, 2-ethyl-3-hydroxyhexanal, 5-ethyl-2,4-dipropyl-1,3-dioxane, 2-ethyl-1,3-hexanediol, 2-ethyl-1-propyl-1,3-propyleneglycol, 2-ethylhexanoic acid, 2-ethylhexyl butyrate, and *n*-butyl 2-ethylhexyl ether were also formed via the reactions like ketonization, hydrogenation, dehydration, and esterification.

In order to investigate the possibility in control of the selectivity toward products, the synthesis of 2-ethyl-2-hexenal

from *n*-butanal with different catalysts was conducted. 2-Ethyl-2-hexenal (up to 87.8% selectivity) was observed to be produced via self-condensation of *n*-butanal (89.7% conversion) in the presence of sulfonic acid-functionalized ionic liquids (SFILs) at 120 °C after 6 h, implying that *n*-butanal conversion positively correlated with the acid strength of the catalyst.¹³⁹ Under vapor-phase conditions, Sun et al. demonstrated the synthesis of 2-ethyl-2-hexenal (72.2% selectivity) from *n*-butanal (72.1% conversion) with Ag-modified TiO₂ at 220 °C with a H₂ flow rate of 20 cm³/min.¹⁴⁰ The use of H₂ carrier gas herein together with the loaded Ag inhibited the

Scheme 24. Possible Reaction Pathway for Upgrading Sorbitol to Hydrocarbons¹⁴³Scheme 25. Possible Reaction Routes for the Oxidative Condensation of FUR with *n*-Propanol to FMAA: (A) with or (B) without O₂¹⁴⁶

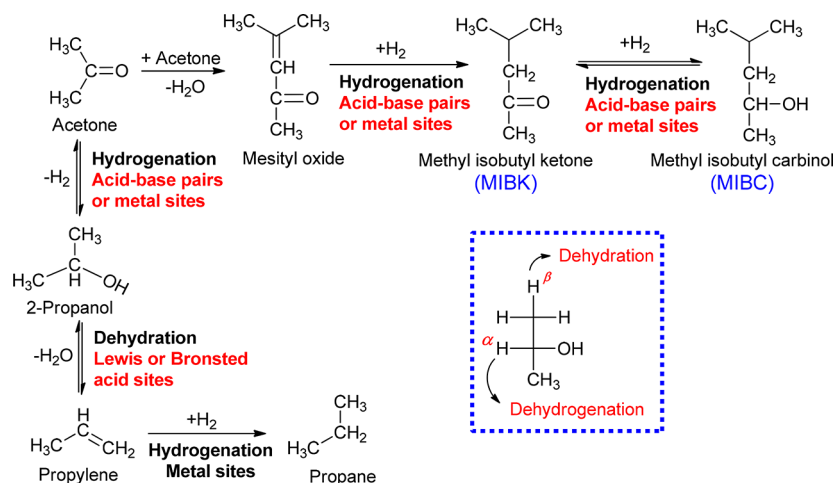
accumulation of carbon onto the surface of TiO₂ by preventing dehydrogenation. On the other hand, Ni- and Ce-incorporated Al₂O₃ (10% Ni loading) selectively converted *n*-butanal to 2-ethylhexanol with a high yield of 66.9% and 18.9% *n*-butanol, whereas no 2-ethyl-2-hexenal was formed at 170 °C and 4.0 MPa after 8 h (Scheme 23).¹⁴¹ The resulting higher yield of 2-ethylhexanol compared to *n*-butanol was attributed to the promotional effect of doped Ce species on enhancing the competitiveness of aldol condensation versus hydrogenation of *n*-butanal. However, it still cannot be ruled out that other side reactions such as Cannizzaro, esterification, Tishchenko, ketonization, and acetalization might have occurred (Scheme 23).¹⁴¹ The major drawback of the Ni/Ce–Al₂O₃ catalyst was its instability after the first use, resulting in drastically lower yield of 2-ethylhexanol from 66.9 to 2.3% under optimized reaction conditions. Instead, 2-ethylhexanal (57.6% yield) and 2-ethyl-2-hexenal (12.9% yield) were found to be the dominant product due to catalyst deactivation by covering Ni species with γ -AlO(OH) generated from γ -Al₂O₃ hydration.¹⁴¹

2.3. Oxidative-Aldol Condensation Reactions. Typically, the direct HDO of biomass-derived oxygenates or alcohols (e.g., sorbitol) could significantly reduce their oxygen contents, producing hydrocarbons with carbon numbers of 1–6 via repeated cycles of reforming, dehydration, and hydrogenation.¹⁴² In order to produce high-energy-density hydrocarbons from sorbitol, Weng et al. reported a one-pot, two-step cascade process including carbon-chain extension and HDO over a bifunctional catalyst Ni@H-ZSM-5/silica-gel (Scheme 24).¹⁴³ Gratifyingly, a high gasoline (C₅–C₁₂) yield of 46.9% composed of 45.5% of C₇–C₁₂ hydrocarbons was obtained in a fixed bed reactor at 300 °C and 4 MPa H₂. In addition, the

reaction conditions of sorbitol-to-gasoline conversion were slightly milder than compared to those of the traditional process for transforming methanol to gasoline (350–500 °C). The resulting superior activity of the bifunctional catalyst could be ascribed to the introduction of mesoporous silica-gel into Ni/H-ZSM-5, facilitating the oxidative condensation process to extend the length of carbon-chain.¹⁴³ However, sorbitol has a higher market value than alkanes and the catalytic process for upgrading sorbitol to alkanes is energy-consuming, which seems to be not promising and economic for practical production.

In the oxidative condensation process, the selective oxidation of an alcohol to carboxide was a prerequisite reaction step before proceeding to aldol condensation.^{144,145} In connection with this, Yu et al. found that Co_xO_y-N@K-10 in combination with a base additive Cs₂CO₃ exhibited good synergistic effect on the synthesis of 3-(furan-2-yl)-2-methylacrylaldehyde (FMAA; 92.8% selectivity) from FUR (75.1% conversion) and *n*-propanol at 140 °C and 0.3 MPa O₂ after 4 h (Scheme 25).¹⁴⁶ It was proposed that the dominant reaction pathway was the formation of propanal via in situ partial oxidation of *n*-propanol with O₂ and then rapid condensation with FUR to FMAA (Scheme 25A). Concurrently, propanal together with furfuryl alcohol could be formed through a process of hydrogen transfer between *n*-propanol and FUR over base, while Co_xO_y-N@K-10 could reoxidize the in situ generated furfuryl alcohol back to FUR (Scheme 25B). As a result, FMAA would also be formed via the subsequent aldol condensation over Cs₂CO₃.

In the absence of O₂ or other oxidant, the in situ formation of acetone from 2-propanol occurred over bifunctional Cu-containing mixed oxides CuM_I(M_{II})O_x (e.g., CuMg₁₀Al₇O_x) at

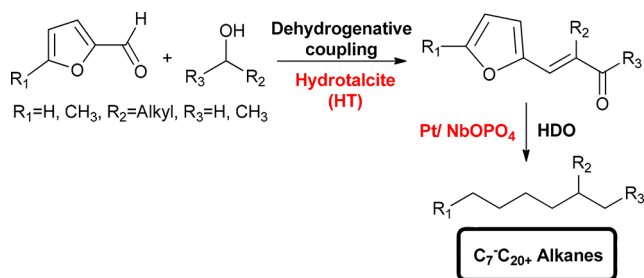
Scheme 26. Reaction Pathway for the Conversion of 2-Propanol to MIBK over Bifunctional CuM_I(M_{II})O_x Catalysts¹⁴⁷

200 °C by stripping H₂ and acetone from the reaction mixture.¹⁴⁷ During this catalytic process, 2-propanol was converted to acetone over the bifunctional catalyst (up to 99.6% selectivity), which would in situ proceed by aldol condensation to further give methyl isobutyl ketone (MIBK) with a maximum yield of 25%. It was postulated that conversion of 2-propanol to acetone through dehydrogenation, or the dehydration product propylene, was closely dependent on the dehydrogenating-dehydrating capability of the respective catalyst (Scheme 26).¹⁴⁷ Especially, the catalysts composed of Cu particles and moderate basic sites provided by oxides showed a high selectivity toward MIBK, as the rate-limiting step of aldol condensation needed a balanced distribution of medium-strength Brønsted base and weak Lewis acid sites.¹⁴⁷ Otherwise, the combination of copper with strong Brønsted acid sites could essentially promote 2-propanol conversion to propane via propylene.

Likewise, a variety of primary and secondary bioalcohols directly reacted with furanic aldehydes to produce C₇–C₁₉ adducts (up to 99% yield) via a cascade hydrogen transfer-aldol condensation pathway in the presence of commercially available HT at 150 °C after 20 h. The corresponding hydrocarbons (75–78% overall yield) were further obtained by subsequent HDO over 2 wt % Pt/NbOPO₄ (0.5 mol %) at 250 °C and 3.5 MPa for 4 h (Scheme 27).¹⁴⁸ Importantly, greenhouse gas net emissions could be reduced by 53–79% using this catalytic system, as compared with petroleum-derived fuels.¹⁴⁸ Moreover, other alcohols (e.g., ethanol and *n*-butanol) could also be transformed to a mixture of di-, tri-, and tetrameric counterparts

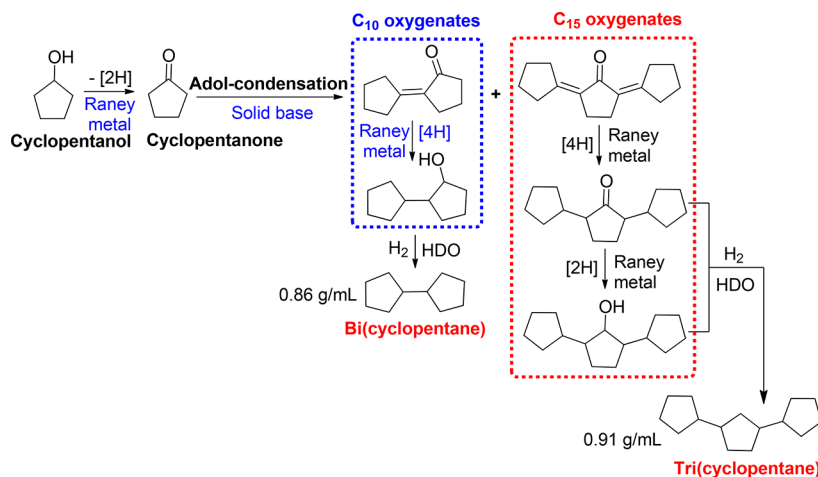
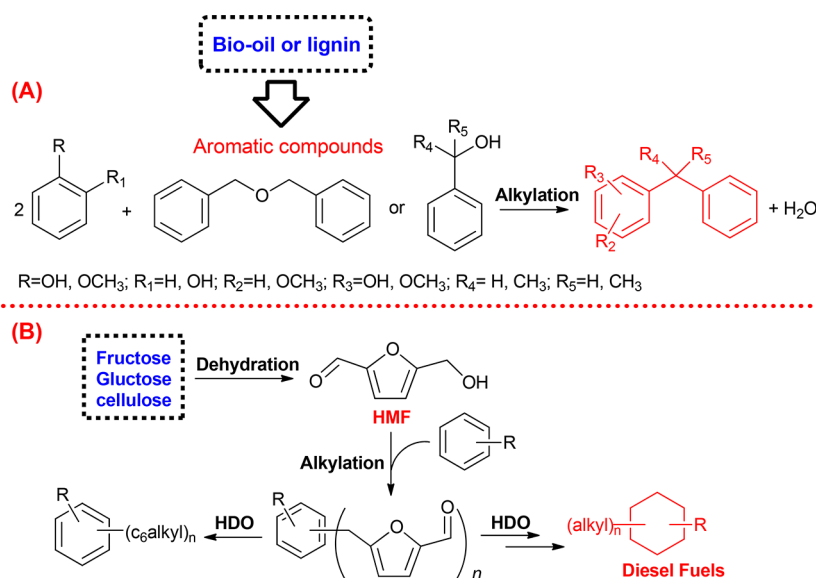
via Guerbet reaction,^{149,150} which could also undergo dehydrogenative condensation reactions with carboxides to give the corresponding adducts with increased carbon numbers suitable for producing diesel-range compounds.¹⁵¹

For either self-coupling of alcohols or α -alkylation of carboxides with alcohols, a borrowing-hydrogen pathway was undergone through the formation of ketones or aldehydes from dehydrogenation of alcohols, followed by aldol condensation to give α,β -unsaturated carbonyl compounds which could be finally hydrogenated by in situ formed metal–H species.¹⁵² In recent years, much attention has been focused on the production of high density aviation fuels from bioderived alcohols that are widely available. For example, Sheng et al. reported that Raney Ni in combination with MgAl-HT was able to sequentially catalyze the Guerbet reaction of cyclopentanol followed by HDO under solvent-free conditions (Scheme 28).¹⁵³ A high carbon yield of C₁₀ and C₁₅ oxygenates (96.7%) was obtained at 170 °C after 8 h, and the resulting alkanes bi(cyclopentane) and tri(cyclopentane), having high density of 0.86 and 0.91 g/mL, respectively, with a total yield of 95.6% after HDO reaction over 35 wt % Ni/SiO₂ prepared by deposition-precipitation method at 230 °C at 6.0 MPa H₂.¹⁵³ In addition to the sole alcohol, a mixture of 2-propanol, *n*-butanol and ethanol could also be transformed into C₈–C₁₉ long-chain ketones/alcohols with high selectivity (>90%) in water with a single catalyst (i.e., Pd on N-doped carbon) at 160 °C for 16 h.¹⁵⁴ The stability of Pd nanoparticles immobilized on the N-doped carbon was high enough to retain good activity (decreased by 10% with respect to the activity of fresh catalyst) after five consecutive cycles.

Scheme 27. Catalytic Upgradation of Furanic Aldehydes into Long-Chain Hydrocarbons via Cascade Hydrogen Transfer-Aldol Condensation and HDO¹⁴⁸

3. HYDROALKYLATION/ALKYLATION

Hydroalkylation/alkylation is one of the best approaches to increase the carbon-chain length of biobased oxygenates under mild conditions and has accordingly attracted wide-ranged attention lately for producing biofuels with improved energy content. The α -alkylation of biobased 2-ketone (e.g., acetone) with primary alcohol (e.g., ethanol and *n*-butanol) to long-chain oxygenates can be achieved via a hydrogen-borrowing methodology using noble metal nanoparticles together with base catalysts.^{155–157} In an improved manner, the use of acid as catalyst facilitated direct alkylation of aromatic compounds with C₂–C₄ light olefins derived from bio-oil or lignin, followed by HDO over Pd/AC to give high-density biofuels (C₈–C₁₅

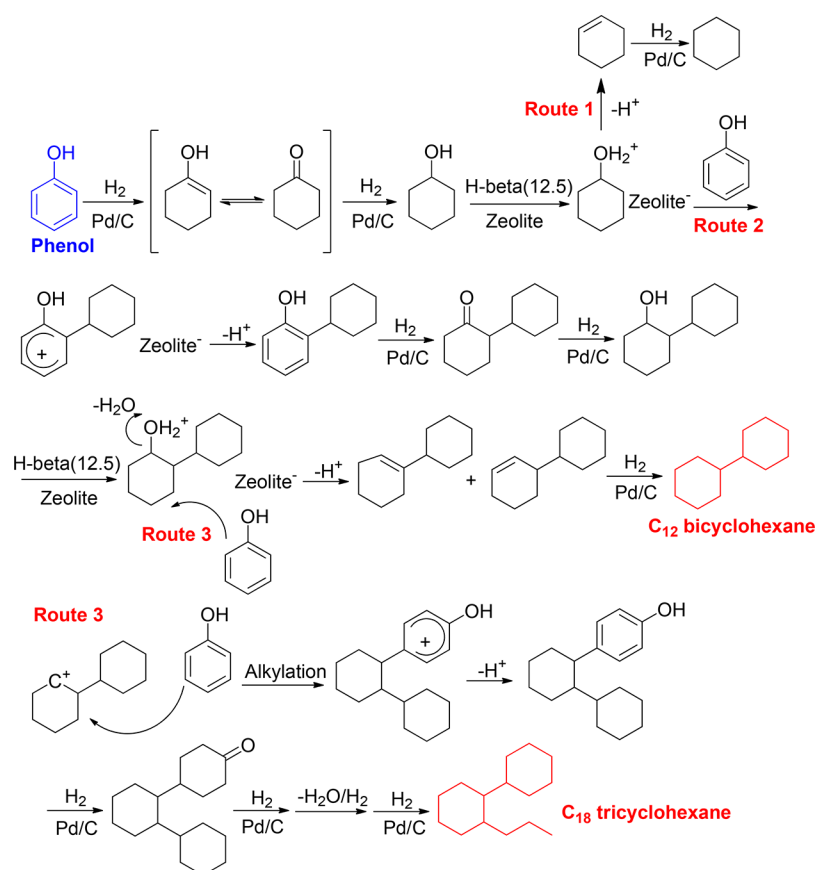
Scheme 28. Reaction Network for the Synthesis of Bi- and Tri(cyclopentane) using Cyclopentanol¹⁵³Scheme 29. Reaction Pathways for the Synthesis of Long-Chain Aromatics and Cyclic Alkanes via Alkylation-Involved Cascade Reactions^{160,161}

cycloparaffins).^{158,159} For instance, Friedel–Craft alkylation of benzene and derivatives (e.g., alkyl benzenes) with alcohols or alkenes (e.g., HMF) could take place over Brønsted and/or Lewis acids (e.g., zeolites and FeCl_3), as shown in Scheme 29.^{160,161} The stability of HMF as well as its solubility in aromatic solvents was improved by removing the reactive hydroxyl group, which significantly inhibited undesirable cross-polymerization reactions to exclusively yield monoalkylated products (95%) at 80 °C after 20 h.¹⁶⁰ The substrate scope also extended to other carbohydrates, including fructose, glucose and cellulose in a biphasic system composed of aqueous HCl and organic alkylating agent (e.g., mesitylene), affording moderate to good yields (37–72%) of HMF-derived alkylated products (e.g., mesitylmethylfurfural) at low temperatures of 100–120 °C. To a small extent, ethers might have formed in situ from dehydration of alcohols under acidic condition,¹⁶² which further reacted with aromatics,¹⁶³ thus maintaining the high selectivity toward monoalkylated products.

However, it was mandatory to conduct hydroalkylation of phenol and its derivatives that can be obtained from lignin using pyrolysis or hydrolysis techniques to realize the carbon–

carbon coupling reaction for the production of long-chain alkanes after HDO.¹⁶⁴ Zhao et al. illustrated that the proper balance of both metal (Pd) for partial hydrogenation of phenol and acid (zeolites) for succedent dehydration/alkylation of phenol with cyclohexanol or cyclohexene were essential to produce dimers (C_{12}) and trimers (C_{18}) of the reacting substrates (Scheme 30).¹⁶⁴ During the catalytic process catalyzed by Pd/C and H-beta(12.5), hydrogenation and alkylation were two parallel reactions while the dominant reaction pathway proved to be kinetically tailored by adjusting the phenol/Pd molar ratio. It was found that the selectivity toward alkylation markedly increased from 2 to 85% at quantitative phenol conversion with the increase of phenol/Pd molar ratio from 564 to 4508 at 160 °C under 5 MPa H_2 .¹⁶⁴ Notably, a very poor yield of alkylation products (2.1%) was obtained from phenol, which on the other hand, was directly hydrogenated/dehydrated to cyclohexane (>90% yield) when the phenol/Pd ratio was less than 564. In addition, Brønsted acid sites in the large pores of zeolites (e.g., H-beta(12.5)) were highly available to phenol and cyclohexanol, which were critical

Scheme 30. Possible Reaction Pathway for Producing C₁₂ and C₁₈ Bi- And Tricyclohexanes from C₆ Phenol Catalyzed by Pd/C and H-beta(12.5)¹⁶⁴



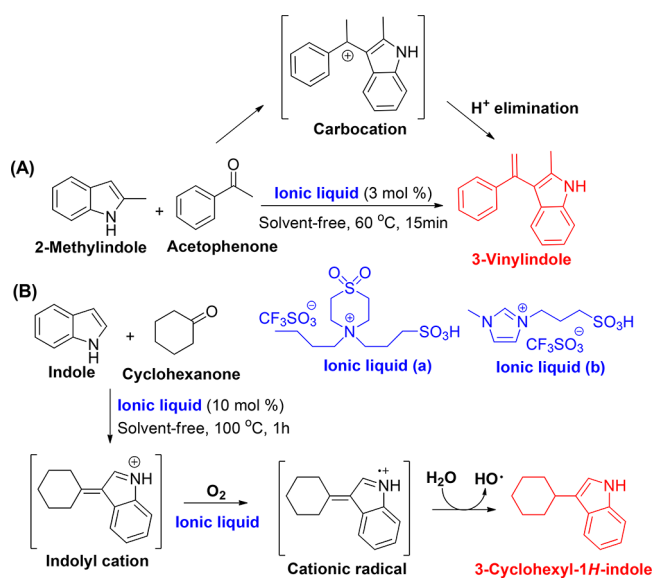
for the high selectivity (up to ca. 77%) toward C₁₈-cycloalkanes via hydroalkylation-HDO in water.¹⁶⁴

In a subsequent study, Zhao et al. found that an optimal H⁺/Pd ratio of 21 was appropriate to balance the competitive reaction between phenol hydrogenation to cyclohexanol over Pd/C and phenol alkylation with cyclohexanol or cyclohexene in situ generated from cyclohexanol dehydration over H-beta(12.5), thus ultimately producing bicyclohexane and tricyclohexane with enhanced selectivity.¹⁶⁵ Compared to H-beta(12.5), La-beta in combination with Pd/C was demonstrated to be more selective for hydroalkylation, probably due to the superior activity of La³⁺ cations in alkylation versus dehydration which was predominantly catalyzed by Brønsted acid sites. Interestingly, the introduction of metal particles into zeolites could alleviate the deactivation of acidic sites in the reaction mixture.¹⁶⁶ Although the acidity of H-mordenite(10) was higher than that of H-Y(30), the former with 1D-pore structure displayed lower activity than 3D-pore zeolites (e.g., H-Y) in the formation of alkylation compounds. These results clearly demonstrated that it was crucial to employ a bifunctional system with accessible and balanced acid/metal sites for simultaneously conducting hydrogenation and alkylation.

C₃-Cycloalkylated indoles appear in various pharmaceutically relevant compounds and natural products, and have typically been synthesized via a two-step approach involving condensation of indoles with cyclic ketones and subsequent reduction.¹⁶⁷ To simplify the synthetic procedure, one-pot reductive alkylation of indole with cyclic alkenes or cycloalkyl alcohols was developed over expensive metal-based catalysts via a hydrogen-borrowing process.^{168,169} Particularly, Han and Wu

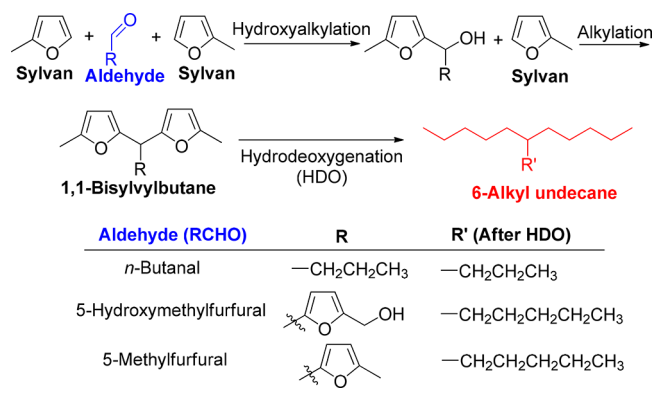
illustrated that trifluoromethanesulfonic acid (TfOH) with 2-methoxyacetophenone as initiator could directly convert indole with unactivated secondary alcohols to give C₃-cycloalkylindoles (up to 94% yield) at 100 °C after 1–12 h.¹⁷⁰ In a metal- and solvent-free system, Taheri et al. demonstrated that SO₃H-functionalized ionic liquids showed higher activity in the direct dehydrative coupling of 2-methylindole with acetophenone via a carbocation intermediate (Scheme 31A) to yield the corresponding 3-vinylindole (95%) at 60 °C after 15 min, as compared to TfOH (45%) and *para*-toluenesulfonic acid (TsOH; 37%).¹⁷¹ On the other hand, the reaction pathway was also proposed to proceed via an oligomer indole radical cation as key intermediate under acidic conditions when a cyclic ketone (e.g., cyclohexanone) instead of acetophenone was used to react with indole (Scheme 31B), and the in situ generated water molecules seemed to play a critical role in facilitation of the reductive coupling reaction.¹⁷²

Typically, the reactivity of heterocyclic compounds with acidophobic nature is less susceptible toward the formation of C–C bonds with high selectivity, and other parameters such as substrate, alkylating agent and acidic catalyst directly affected the product distribution.¹⁷³ By using 2-methylfuran (Sylvan) derived from FUR as substrate, the catalytic trimerization of Sylvan to 5,5-bis(5-methyl-2-furyl)pentan-2-one (ca. 86.8% selectivity) took place under acidic and aqueous conditions through hydrolysis of the furan ring to 4-oxopentanal and subsequent ring electrophilic aromatic substitutions, wherein the initial hydrolysis to open the furan-ring was the rate-determining step for the trimerization (Scheme 32).¹⁷⁴ On the other hand, catalytic tetramerization of Sylvan to 2,4,4-tris(5-

Scheme 31. (Reductive) Friedel–Craft Alkylation of Indoles with Ketones^{171,172}

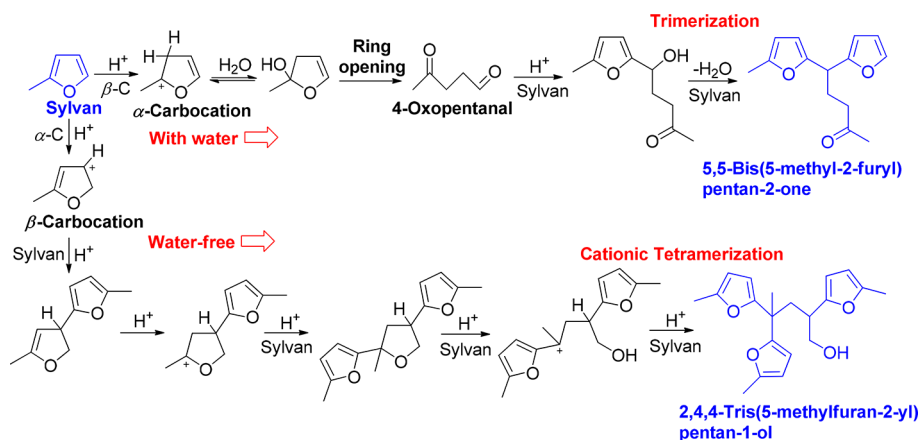
methylfuran-2-yl)pentan-1-ol (ca. 87.5% selectivity) was preferred in the presence of an acid without adding water at 85 °C for 3 h (Scheme 32).¹⁷⁵ It was proposed that α - and β -carbocations formed during Sylvan protonation could result in the selective trimerization and tetramerization, respectively.¹⁷⁵ Specifically, β -carbocations were formed at a much higher concentration than α -carbocations in the absence of water, which was thus more favorable for the cationic tetramerization (Scheme 32). In contrast, only the α -carbocation species were active and able to undergo the opening of furan-ring in the aqueous acidic system to form a trimer (Scheme 32).¹⁷⁵

Hydroalkylation and alkylation of Sylvan with other types of bioaldehydes (e.g., formaldehyde, *n*-butanal, FUR, HMF, and 5-methylfurfural) were performed by using either liquid or solid acids (Scheme 33).^{176–180} Sylvan reacted with *n*-butanal in a molar ratio of 2:1 and afforded 1,1-bisylvylbutane with 91% selectivity (85% conversion) in the presence of strong acid TsOH (2.5 wt %) at 60 °C after 16 h, and the selectivity was further increased to 95% (93% conversion) by adding a small excess of Sylvan (3.5:1).¹⁸¹ In these catalytic processes, 5,5-bis(5-methyl-2-furyl)pentan-2-one was obtained by trimerization of Sylvan as impurity (ca. 2% yield), but the product

Scheme 33. Synthesis of 1,1-Bisylvylbutane from Sylvan and an Aldehyde via Hydroalkylation/Alkylation, Coupled with Subsequent HDO to 6-Alkyl Undecade¹⁷⁶

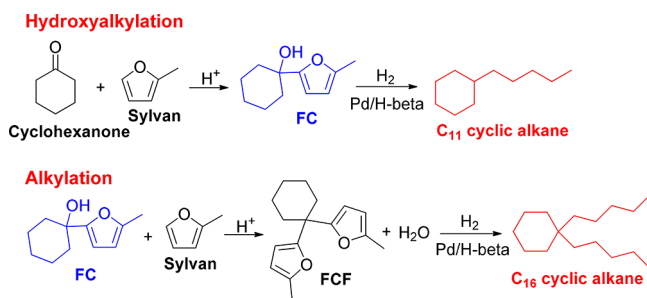
purification by distillation was demonstrated to be unnecessary as the crude mixture could directly undergo HDO.¹⁸² With respect to the solid catalysts, their enhanced hydrophobicity could reduce the retention of the products to prevent the furan ring opening during hydrogenation, unless otherwise HDO might take place.¹⁸³ In addition, the solid acid with increased surface area and acidity favored the hydroalkylation/alkylation, while the metal particles having smaller size and pore diameter were helpful for hydrogenation that was the main pathway for the C—O cleavage reaction, thus facilitating the HDO process.¹⁸⁴ In addition, strong acid was demonstrated to show higher activity than weak acid for the ring-opening reaction, but having higher acid strength along with excess of strong acid sites resulted in side reactions such as hydrocracking and hydroisomerization.¹⁸⁴ With balanced acid and metal sites, a number of bifunctional heterogeneous catalysts (e.g., Pt/MCM-41 and Pd/NbOPO₄) were demonstrated to be capable of efficiently producing drop-in fuels (long-chain hydrocarbons) via one-pot cascade hydroalkylation/alkylation and HDO reactions.^{185,186}

Ketone compounds (e.g., acetone) are generally less active compared to aldehydes in hydroalkylation/alkylation, which can be rationalized by the electronic and steric hindrance of alkyl groups of ketones.¹⁸⁷ The hydroxyl group present in the ketone (e.g., hydroxyacetone) was found to have an additional electron-withdrawing effect, which could assist the hydroalkylation/alkylation of ketone with Sylvan and make

Scheme 32. Tri- and Tetramerization of Sylvan with or without Water^{174,175}

subsequent HDO reactions smooth.¹⁸⁸ During the HDO process, the solid support possessing high acidity played a promotional effect in the steps of dehydration and furan-ring opening,¹⁸⁹ while the in situ formed water might decrease the catalyst acidity and induce side reactions.¹⁹⁰ The increase in hydrophobicity of solid acids was an effective way to avoid the adverse effect of water by suppressing the acid leveling effect and Sylvan self-trimerization.¹⁹⁰ In addition, the distribution of products derived from hydroxyalkylation/alkylation of Sylvan with lignin-derived cyclohexanone could be controlled by adjusting the strength of solid acids. For example, strong acidic Nafion-212 ($H_0 = -12$) catalyzed the reaction between Sylvan and cyclohexanone to give FCF in a high yield of 89.1% at 60 °C after 6 h, while relatively weak Amberlyst-15 ($H_0 = -3$) changed the product distribution to FC (76.0% yield) after 2 h (Scheme 34). Upon HDO with 5 wt % Pd/H-beta(12.5), FC

Scheme 34. Reaction Pathways for the Synthesis of FC and FCF from Cyclohexanone, Followed by HDO to C₁₁ and C₁₆ Cyclic Alkanes¹⁹¹



and FCF were transformed into C₁₁ and C₁₆ cyclic alkanes with a density of 0.804 and 0.825 g/mL, respectively.¹⁹¹ Similarly, some carbonyl derivatives such as angelica lactone and mesityloxide could also react with Sylvan via alkylation over super acid Nafion-212 followed by HDO to produce either linear or cyclic alkanes in jet fuel range.^{192,193} Most recently, Saha et al. conducted a series of studies on the hydroalkylation/alkylation over graphene oxide possessing Brønsted acidic oxygen functional groups and HDO with the catalytic system containing acid-metal dual sites (e.g., Ir-ReO_x/SiO₂ and supported Pd coupled with Lewis acidic Hf species) to produce jet-fuel-range alkanes with high efficiency (up to 99% yield), which further confirmed the positive role of acidic species with suitable strength in both reaction processes.^{194–196}

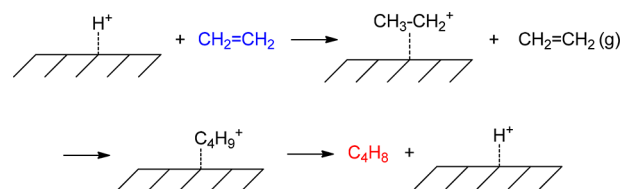
4. OLIGOMERIZATION

Generally, oligomerization reaction is used for the conversion of either pure or mixed monomers (e.g., alkenes and polyols) into oligomers. In petroleum refineries, olefin oligomerization processes are typically utilized to transform light olefins in cracked, or even tail gas, into liquid fuels.¹⁹⁷ Likewise, zeolites and acidic ion-exchange resins were reported to be highly efficient for the oligomerization of C₂–C₆ olefins (e.g., ethylene, butene, and hexene) able to be produced from biomass by various routes such as cracking and catalytic pyrolysis for producing high quality diesel fuels.^{198–201} In the case of medium-pore zeolite-mediated (e.g., H-ZSM-5) catalytic system at 200 °C, the density of Brønsted acid sites was found to be determinant for propene oligomerization, while additional mesoporosity was crucial for 1-pentene oligomerization.²⁰² With respect to the ion-exchange resins,

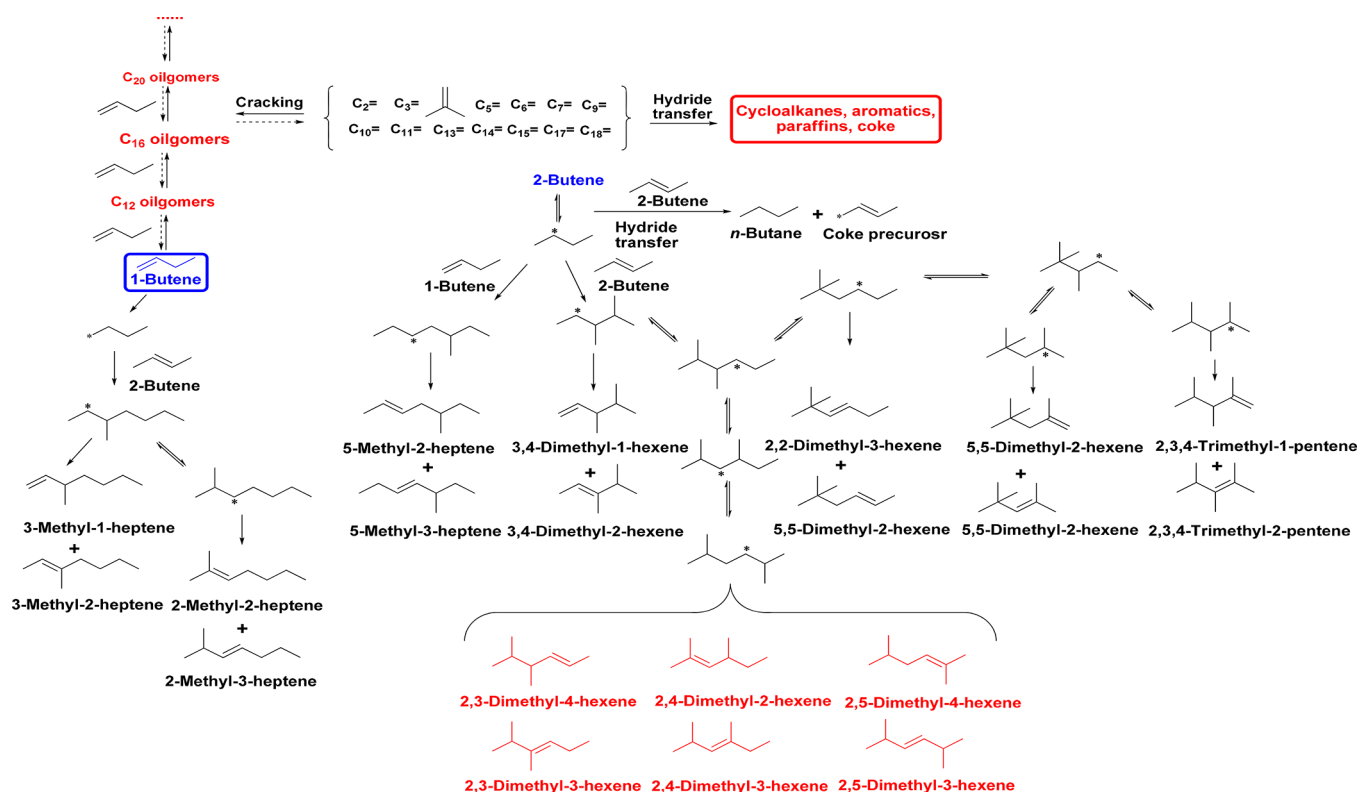
the relatively suitable reaction temperature was 120–130 °C, and the olefin conversion was simultaneously affected by the feedstock composition.²⁰³ More interestingly, 1-butyl-3-methylimidazolium chloroaluminate ionic liquid ([BMIM]Al₂Cl₇) was able to promote the oligomerization of gaseous C₂–C₄ olefins to desired C₈–C₁₅ iso-paraffins (80.6% selectivity) at room temperature, while other side reactions (e.g., hydrogen transfer, isomerization, and hydrogenation) might have taken place to a small degree.²⁰⁴ By using Brønsted–Lewis acidic ionic liquids [e.g., (3-sulfonic acid)-propyltriethylammonium chlorozincate] as catalysts, the alkylation of isobutane with isobutene, or of *n*-butane with butenes formed from γ -valerolactone (GVL) by decarboxylation, gave C₈-alkylates in near quantitative yields via a hydride transfer process.^{205–207} The protonation and adsorption of olefin, taking isobutene as example, were demonstrated to occur on the Brønsted and Lewis acid sites, respectively.²⁰⁵ Accordingly, a carbocation from isobutene was formed on the Brønsted acidic site to initiate the alkylation reaction with the adsorbed isobutene on Lewis acid site to give a more stable tertiary carbocation, which could either react with isobutene to yield the oligomerization product or directly remove a proton to give the dimerization product.²⁰⁵ Notably, the pronounced catalytic performance in dimerization indicated a synergetic effect of Brønsted and Lewis acid sites in ionic liquids, also implying that high-quality gasoline can be produced from biomass derivatives without performing HDO.²⁰⁵

4.1. Zeolites-Mediated Catalytic System. To thoroughly investigate the structure–activity relationship during oligomerization, pure olefins were generally employed as substrates. Catalytic oligomerization of ethylene to C₃ and C₄ olefins with H-ZSM-5 zeolites was achieved via Eley–Rideal mechanism (Scheme 35), but the hydrogen transfer process was limited

Scheme 35. Catalytic Oligomerization of Ethylene to C₃ and C₄ Olefins through Eley–Rideal Mechanism²⁰⁸



and might follow the Langmuir–Hinshelwood mechanism.²⁰⁸ It was found that ethylene conversion (up to 80%) was linearly correlated with the acid density of the respective zeolite, and the hydrogen transfer reaction was prone to occur as the acid density exceeded 0.14 mmol/g, thus lowering the yields of olefins.²⁰⁸ In addition, increasing the mesoporosity of Theta-1 zeolites by desilication led to increase of catalyst lifetime and initial activity with linear or monomethyl-branched oligomers as dominant products, suggesting the role of preserved density of Brønsted acid site and micropore volume.²⁰⁹ Rather than with high concentration of Brønsted acid sites (1.50 vs 2.20 arb. unit), dealuminated H–Y zeolite (steamed at 600 °C) was found to have increased Lewis acid sites (3.22 vs 1.63 arb. unit) compared to the pristine H–Y(1.4) zeolite.²¹⁰ Even though the resulting catalyst possessed decreased crystallinity and porosity, relatively higher selectivity toward trimers (52.4%) and tetramers (31.7%) were attained compared to the pristine zeolite at analogous isobutene conversion (98.4%) at 70 °C, clearly indicating the predominant role of Lewis acidity in the

Scheme 36. Main Reaction Pathways for Oligomerization of 1-Butene²¹⁴

enhancement of the catalyst efficiency. Importantly, the deactivated zeolites could be regenerated by simple calcination in air.²¹⁰

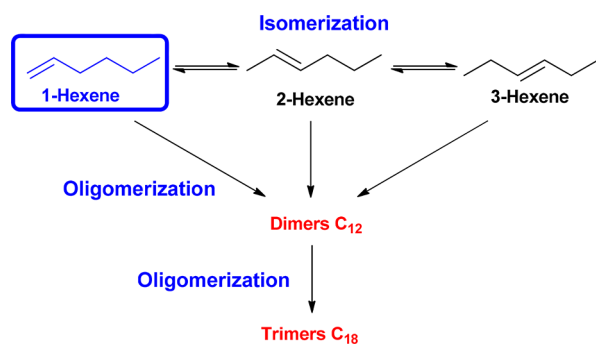
In the process of butene oligomerization, the activity of H-MFI(30) zeolites proved to be governed by the acidic sites on the external surface and subsurface of polycrystals.²¹¹ The formation rate of oligomers from 1-butene on H-beta(17) was most likely controlled by oligomer diffusion out of the zeolite pores, and the relatively slower diffusion was favorable for producing larger oligomers.²¹² Titration of external acid sites with n -octyltrichlorosilane further ensured that the formation rate of oligomers was not greatly affected by the reaction taking place on the external surface of the zeolite crystallites. Significant improvement on the selectivity of C_{8+} hydrocarbons (ca. 86 wt %) from 1-butene was observed with H-ZSM-5 when increasing the reaction temperature from 150 to 200 °C and partial pressure from 12.5 to 50 kPa over H-ZSM-5, showing that tuning of reaction conditions could greatly improve the efficiency on the production of long-chain hydrocarbons.²¹³ Generally, the major reaction pathways for 1-butene oligomerization involved a number of acid-catalyzed reactions, including oligomerization, (skeletal) isomerization, hydrogen transfer, cracking, and alkylation (Scheme 36).²¹⁴ For both C_4 and C_8 olefins, the double bond isomerization reactions could rapidly reach equilibrium at any temperature studied (100–250 °C).²¹⁴ High selectivities toward oligomerization products, following the Schulz–Flory chain growth distribution, were attained at low temperatures of ≤ 200 °C, while olefins might undergo cracking and hydride transfer reactions at temperatures > 200 °C. Apart from the rapid double bond isomerization, the type of zeolite framework was recently demonstrated to affect the product distribution, wherein zeolites composed of 10-membered (MFI) or 12-membered rings

(FAU and BEA) gave both dimerization and cracking products, whereas 8-membered zeolites MOR and FER were favored for cracking (complete conversion of C_{10} olefins) and dimerization (with rare cracking products), respectively.²¹⁵

4.2. Ion-Exchange Resins-Mediated Catalytic System.

Even though zeolites exhibited a promising activity toward oligomerization, the major drawback was deactivation of zeolites by blocking of microporous channel with bulky products. In order to overcome this, commercial macroreticular ion-exchange resins were employed as candidates for the oligomerization of olefins.²¹⁶ At a relatively low temperature (70 °C), the dimerization and trimerization of isoamylene mixture predominantly took place over Amberlyst-15, Amberlyst-16, Amberlyst-35, Amberlyst-36, Amberlyst-46, Amberlyst-48, and Amberlyst-70. Whereas increased reaction temperature (110 °C) resulted in high selectivity to dimerization the cracking and trimerization products diminished over the ion-exchange resins with more external active sites, suggesting that trimerization and cracking might have predominantly occurred inside the macroreticular resins.²¹⁶ The oversulfonated resins (e.g., Amberlyst-35 and Amberlyst-48) with high acidity and high cross-linking degree showed superior activity to the others. In contrast, a poor initial reactivity was observed over Amberlyst-16 and Amberlyst-36 bearing a more random structure of polymeric matrix.²¹⁶

In the case of 1-hexene oligomerization catalyzed by macroporous ion-exchange resins, Cadenas et al. demonstrated that the oversulfonated resins with sufficient acid strength were able to catalyze 1-hexene oligomerization and double-bond isomerization (Scheme 37), but skeletal isomerization, disproportionation, and cracking reactions were prohibited.²¹⁷ Likewise, resins with medium-high cross-linking degree (e.g., Amberlyst-48 and Amberlyst-35) were favorable for the

Scheme 37. Possible Reaction Pathway for Oligomerization of 1-Hexene²¹⁷

dimerization of 1-hexene with 40–56% selectivity and complete conversion at 100 °C after 6 h. With the increase of reaction temperature (≥ 110 °C), the selectivity toward dimers and trimers increased, whereas double-bond isomerization decreased.²¹⁷

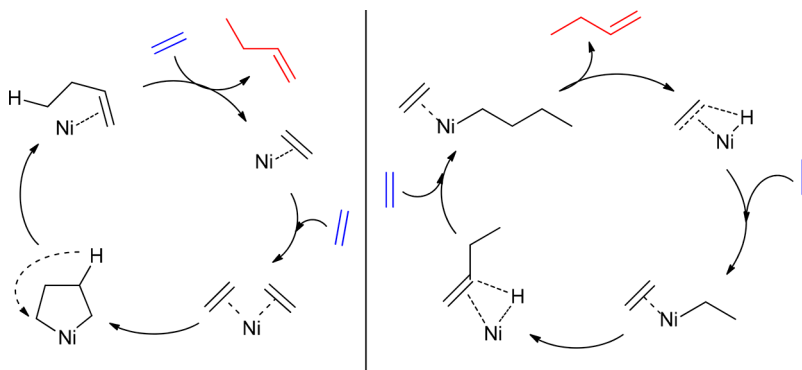
Interestingly, Amberlyst-70 pretreated with a ketone (e.g., 5-nonanone) demonstrated to improve the rate of 1-octene oligomerization, which could be due to the interaction between 5-nonanone and the surface of Amberlyst-70 to vary the polarity of the matrix, thus reducing transport limitations for alkene oligomerization.²¹⁸ In contrast, the physicochemical changes on the catalyst surface acidity and/or porosity and the oxygenated compounds like 5-nonanone had no influence on the oligomerization rate.²¹⁹ However, alcohols (e.g., 5-nonanol) in the feed might undergo dehydration to form water, thus inhibiting the rate of alkene oligomerization to some degree. In fact, an increase in the oligomerization rate was observed in the presence of small amounts of nonanol, which could be ascribed to the increased surface area of Amberlyst-70 generated by swelling in this polar media.²¹⁹

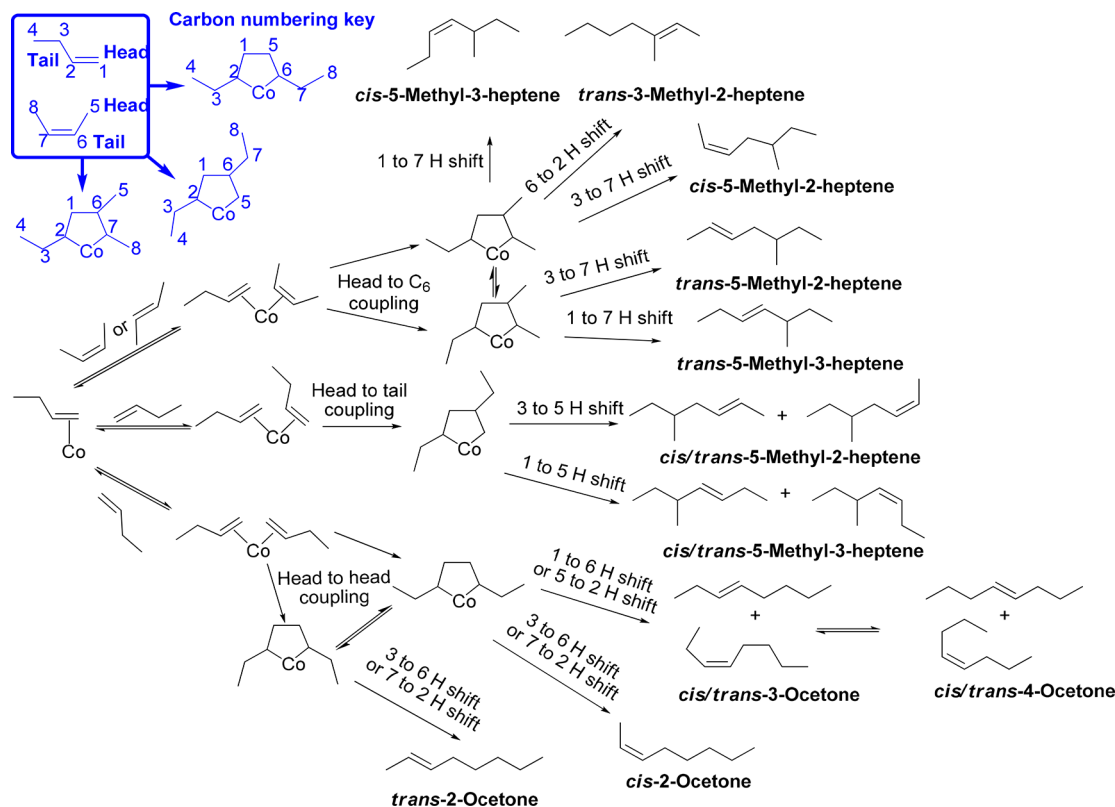
4.3. Solid Phosphoric Acid (SPA)-Mediated Catalytic System. In comparison with zeolites (e.g., MTW-C8), solid phosphoric acid (SPA) normally resulted in much less branched olefins (especially quaternary carbons), as evidenced from NMR studies.²²⁰ Interestingly, the reduction of benzene was observed by alkylation (>80% benzene conversion) at 160–180 °C, but no significant influence on the oligomerization of olefins (e.g., propene) was found with the same SPA catalyst.²²¹ However, SPA catalyst would lose its mechanical strength in the presence of water to produce free phosphoric acids by hydrolysis, which reflected on the catalytic activity. In this scenario, SPA with a relative content of 49% SiP_2O_7 and

51% $\text{Si}_5\text{O}(\text{PO}_4)_6$ was found to exhibit a better crushing strength and superior catalytic performance in the conversion of propene (above 99%) as well as improved lifetime (nearly 70 h).²²²

4.4. Metal Species-Mediated Catalytic System. Besides solid Brønsted acids discussed in Section 2.3.1–2.3.3, heterogenized metal ions could also be used as efficient catalysts for alkene oligomerization. For example, nickel- β -diimine complexes immobilized onto SiO_2 by using a sol–gel method in combination with ethylaluminum sesquichloride showed an outstanding performance in ethylene oligomerization, giving quantitative yield of C_4 fraction with a high selectivity (up to 91%) toward 1-butene at 10 °C at 1.5 MPa pressure after 0.5 h.²²³ Two reaction mechanisms for Ni-mediated ethene dimerization were proposed (Scheme 38): (1) The Cossee–Arlman mechanism was based on metal–alkyl species generated from a cocatalyst (e.g., alkylaluminum); (2) For the metallacycle mechanism, C–C coupling occurred by oxidative addition to form the metallacyclopentane species.²²⁴ On the basis of density functional theory (DFT) calculations, the Cossee–Arlman mechanism proposed that Ni^+ , Ni^{2+} , and Ni^0 were to be active sites in Ni-containing zeolites.²²⁴ By conducting operando electron paramagnetic resonance (EPR) and in situ X-ray absorption spectroscopy studies at 80 °C, the presence of single $\text{Ni}^+/\text{Ni}^{2+}$ were unambiguously identified as active species for the dimerization of butenes to C_8 target products.²²⁵ The active $\text{Ni}^+/\text{Ni}^{2+}$ redox couples agglomerated to inactive Ni^0 particles at ≤ 0.2 MPa reaction pressure but could be stabilized at elevated pressure.²²⁵

By deposition of NiSO_4 onto H-ZSM-5(25), the resulting Ni/H-ZSM-5 catalyst was found to increase the strength and number of Lewis and Brønsted acid sites, as compared with the pristine H-ZSM-5.²²⁶ Importantly, the catalytic activity seemed to be closely related to the $\text{Ni}^{2+}/\text{acid}$ sites ratio, and 2.21 wt % Ni/H-ZSM-5 exhibited relatively higher catalytic performance toward propene oligomerization (ca. 70% propene conversion) with diesel selectivity of around 80% at 270 °C under 4 MPa during 72 h time-on-stream. Likewise, the introduction of NiSO_4 onto $\gamma\text{-Al}_2\text{O}_3$ also exhibited a high selectivity toward dimer proceeding via surface rearrangement, but no significant deactivation during isobutene oligomerization was found.²²⁷ Typically, when increasing the reaction temperature, the propylene conversion ascended over Ni/support (e.g., Ni/beta, Ni/USY and Ni/Zn-MCM-41) with high stability, and the charge of the framework heteroatom in the support matching with that of the exchanged ion could possible reduce the undesired products.²²⁸ Nickel(II)-based metal–organic frame-

Scheme 38. Dimerization of Ethene on Ni Sites via Metallacycle (Left) and Cossee–Arlman Mechanism (Right)²²⁴

Scheme 39. Possible Reaction Pathway for 1-Butene Coupling on Cobalt Oxide²³³

works were illustrated to have comparable activity as Ni^{2+} -exchanged aluminosilicates in propene oligomerization at 180 °C but maintained high selectivity to linear oligomers (especially dimers), further indicating the significant role of the matching charges between support atoms and metal ions in improving selectivity to target products.²²⁹ In addition, 2 wt % Ni/SiO_2 completely converted acetylene at 140 °C with 75% H_2 (relative to acetylene) after 5 h, forming predominantly linear C_4 and C_5 products ($1 > \text{cis-2} > \text{trans-2}$) and branched, even carbon-numbered alkenes 3-fold higher than odd carbon-numbered alkenes.²³⁰ Interestingly, Ni/SiO_2 catalyst could be reused with no observable deactivation under the standard reaction conditions (i.e., 140 °C, 5 h, and 25% acetylene relative to H_2). However, increasing reaction temperature and acetylene concentration led to a rapid catalyst deactivation.²³⁰

A bifunctional catalyst with a high ratio of Lewis/Bronsted acid sites (0.34) prepared by loading Al^{3+} species into H-USY(30) zeolite via physical mixing was found to be a stable catalyst for isobutene conversion (up to 99.2%) with high selectivity to trimers (47.9%) and tetramers (31.1%) at 70 °C at 1.5 MPa pressure.²³¹ In contrast, the pristine H-USY(30) zeolite with a Lewis/Bronsted acid sites ratio of 0.31 was favorable for the production of dimers (59.6% selectivity) at 85.3% isobutene conversion. Moreover, the AlCl_3 -loaded USY zeolite gave 70% isobutene conversion with 40% trimers selectivity when used for 120 h time-on-stream, and the activity of the catalyst was regenerated by simple calcination at 400 °C for 6 h in air.²³¹ Similarly, supported bimetallic catalysts (i.e., AlCl_3 and TiCl_4) were also efficient for the oligomerization of 1-decene at 80 °C in a fixed-bed reactor, and a high yield of 90.8% poly- α -olefin was obtained over the coal-derived activated carbon-supported AlCl_3 - TiCl_4 catalyst with the highest chlorine content of 14.2%.²³² Catalyst deactivation

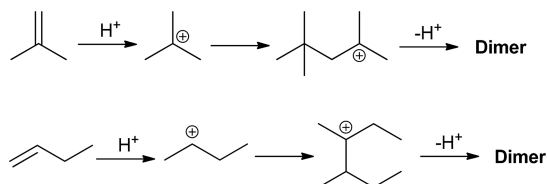
was however observed during reaction due to leaching of active species and blocking of pore structure by oligomers. Alternatively, $\gamma\text{-Al}_2\text{O}_3$ -supported AlCl_3 - TiCl_4 catalyst was found to show relatively higher stability, which could be further enhanced by thermal treatment but might result in reduced initial activity.²³²

In a continuous flow reactor, carbon-supported cobalt oxide catalysts were demonstrated to be highly selective (70–85%) for producing linear octenes from the oligomerization of 1-butene at 80 °C.²³³ The reaction pathways were proposed to involve a head-to-head coupling of two 1-butene molecules to yield internal linear octenes; otherwise, methyl-heptenes would be formed via head-to-tail coupling of two 1-butene molecules or a coupling between 1-butene and 2-butene generated from isomerization of 1-butene (Scheme 39). Moreover, the activated catalyst contained both Co_3O_4 and CoO species, and its activity increased with an increase of Co_3O_4 content.²³³ Besides linear alkanes, bicycloalkanes were also reported to form from C_5 – C_8 cycloolefins through a two-step process involving dimerization catalyzed by a Fe^{3+} salt (e.g., FeCl_3 and FeBr_3) and hydrogenation over Pd/C .²³⁴

4.5. Other Catalytic Systems. In comparison to typical solid acids, including H-beta, SiO_2 - Al_2O_3 and $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ was found to show preferential activity in the oligomerization of isobutene in a mixture of isobutene and 1-butene with a molar ratio of 1:1.²³⁵ Notably, the catalyst with a lower $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ loading of 10 wt % exhibited a superior selectivity (ca. 95%) for isobutene oligomerization at 120 °C, whereas the conversion of linear butenes increased by loading to 60 wt % $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. It could be speculated that secondary carbenium cations, formed in the oligomerization of linear butenes, were energetically unfavorable compared to tertiary carbenium cations for isobutene oligomerization proceeding via

the addition of H^+ to isobutene (Scheme 40), thus requiring strong and more acid sites for the oligomerization of linear

Scheme 40. Isobutene Oligomerization via the Addition of H^+ to Isobutene²³⁵



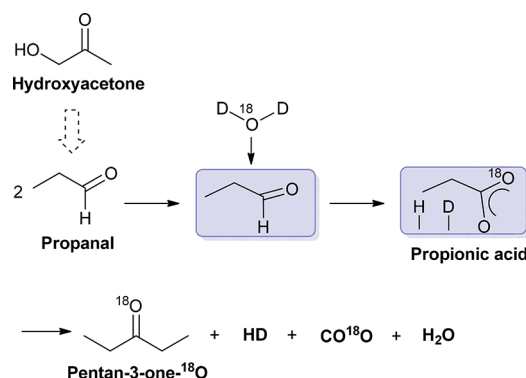
butenes.²³⁵ In addition, isobutene seemed to be more prone for adsorption on the acid sites compared to the linear butene in the reaction mixture, which might partially facilitate the oligomerization of isobutene.

A combination of ethylene oligomerization over 1.9 wt % Ni- AlSBA-15 at 200 °C and 1.0 MPa pressure with subsequent co-oligomerization over 5 wt % Amberlyst-35 at 100 °C under 3.0 MPa N_2 for 24 h, yielded greater than 98% C_{5+} liquid oligomers constituting 42% C_{10+} olefins attained from ethylene with 99% conversion.²³⁶ The higher density and strength of Brønsted acid sites in the catalyst might have determined the pronounced selectivity toward the C_{5+} oligomers in the gasoline-range with higher octane number.²³⁷ By choosing appropriate acidic catalysts, oligomerization and isomerization of dicyclopentadiene^{238,239} or pinene,^{240,241} di/trimerization of angelica lactone,^{242–244} and even cascade dehydration-dimerization of alcohols (e.g., 1-arylethanol, *tert*-butyl alcohol and glycerol)^{245,246} could take place with moderate to good selectivity, offering promising catalytic strategies for producing high-energy-density fuels from biomass-derived compounds.

5. KETONIZATION

It is known that ketonization of two carboxylic acids typically results in the formation of a ketone, CO_2 , and H_2O , but it has regained renewed interest in upgrading of biomass-derived oxygenates (e.g., acetone production from acetic acid) in the past decade.²⁴⁷ Organic acids such as acetic acid, propionic acid, butyric acid, pentanoic acid, and hexanoic acid are typically found in pyrolysis bio-oil solutions,²⁴⁸ which can be also selectively synthesized by anaerobic and aerobic oxidation of biomass derivatives.²⁴⁹ The ketonization approach is considered an important protocol to reduce the O/C content of biofuels, in which the role of oxide surface and supported metal are generally taken into account.²⁵⁰ The weak base catalyst CeO_2 was found to be one of several efficient metal oxides for upgrading the acid-rich phase of bio-oil via ketonization, and most acetic acid was converted to acetone.²⁵¹ The water and phenol components in bio-oil did not hamper the reaction, but FUR significantly deactivated the CeO_2 catalyst by deposition on its surface to cover active sites, which needed to be removed before further transformation.²⁵¹ Interestingly, the constituent of hydroxyacetone (acetol) was highly reactive over the CeZrO_x mixed oxide, which could be initially converted to pyruvaldehyde and 1,2-propylene glycol via transfer hydrogenation, and subsequently to produce ketones in the C_3 – C_6 range without influencing the ketonization activity of acetic acid.²⁵² The ketonization of hydroxyacetone was proposed to proceed via propanal for the in situ formation of propionic acid, as evidently illustrated by the incorporation of isotopically labeled water (Scheme 41).²⁵³ The key-step was identified to be

Scheme 41. Proposed Mechanism for the Formation of Bound Propionic Acid from Propanal on the Surface of Metal Oxide²⁵³

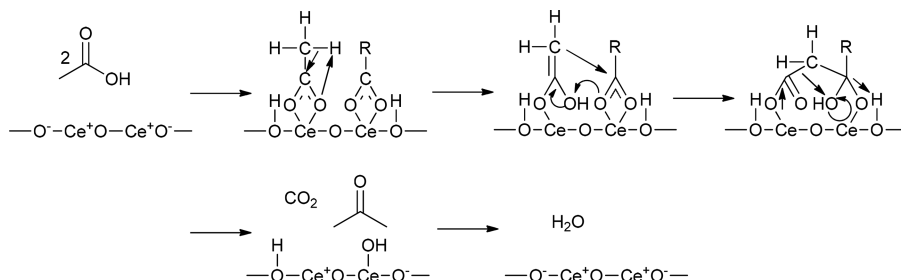
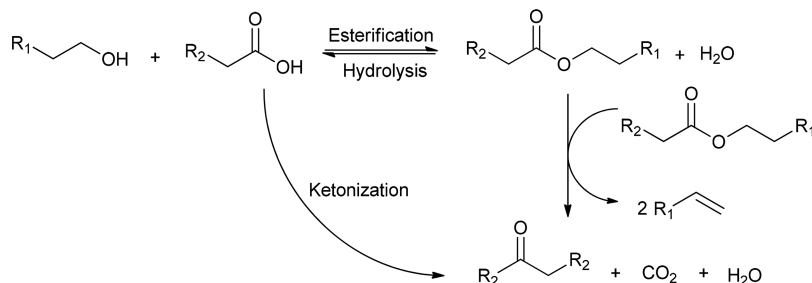


the adsorption of the aldehyde onto the metal oxide surface, followed by transferring a hydride species to the surface.²⁵⁴ Similarly, selective ketonization of *n*-butanol to dipropyl ketone or heptanone-4 could also be achieved over LaMn oxides via butyraldehyde as the key intermediate.^{255–257}

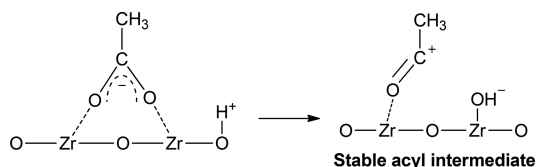
Typically, two separate pathways for either bulk or surface ketonization reactions were proposed in order to explain the interaction between metal oxides (e.g., CeO_2) and organic acids (e.g., acetic acid) or esters.^{258–260} On the contrary, Snell and Shanks illustrated that the formation of cerium acetate, either on the surface or throughout the bulk, followed by pyrolytic decomposition of cerium acetate, could explain the ketonization of acetic acid in a single reaction sequence (Scheme 42).²⁶¹ In other words, cerium acetate was a necessary intermediate species in either the bulk or surface-promoted cases, and the formation and decomposition of cerium acetate were highly dependent on the reaction temperature as follows; no break of Ce-O bonds by acetic acid at <150 °C, cerium acetate formed and was stable at 150–300 °C, and cerium acetate formed but rapidly decomposed at >300 °C.²⁶¹ Maximum catalytic activity was observed as the formation and subsequent decomposition of metal carboxylate were appropriately balanced, but no direct correlation was established between prereaction surface areas or the oxide reducibility with the ketonization activity at high or low temperatures.²⁶² Besides the lattice energy of the oxide, the calcination temperature was found to control the crystallinity of CeO_2 , and relatively higher ketonization rate was achieved with the increase of calcination temperature from 450 to 900 °C.²⁶³

When alcohols were present in the reaction mixture, the esterification of carboxylic acids was unavoidable with ceria-zirconia (CeO_2 – ZrO_2).²⁶⁴ It was found that the direct ketonization of esters (e.g., 1-pentylhexanoate) was much slower than that of carboxylic acids (e.g., pentanoic acid) and would take place once the acids were largely converted.²⁶⁴ Alternatively, the prehydrolysis with water followed by ketonization could promote the direct conversion of esters to the corresponding ketones (Scheme 43).²⁶⁵ In addition, anhydrides (e.g., hexanoic anhydride) were possibly formed from carboxylic acids (e.g., hexanoic acid) by the loss of a water molecule, which could be further converted to ketones (e.g., 6-undecanone) via decarboxylation.²⁶⁶ However, it cannot be exclusively concluded that the two-step mechanism proceeded through anhydrides for the ketonization of carboxylic acids.

The ketonization rate of pentanoic acid to 5-nonanone was proposed on the basis of the role of Lewis acidity generated by reducing the catalyst surface, which was responsible for

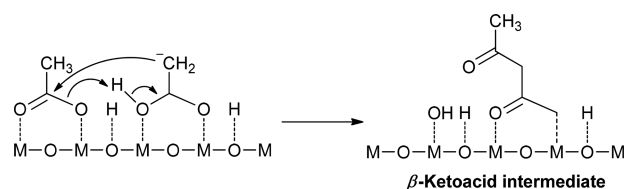
Scheme 42. Plausible Ketonization Reaction Sequence for the Synthesis of Acetone from Acetic Acid²⁶¹Scheme 43. Reaction Scheme for Ketonization of Carboxylic Acids/Esters²⁶⁵

significantly lowering the conversion of pentanoic acid over the $\text{CeO}_2\text{--ZrO}_2$ catalyst under N_2 compared with that under H_2 .²⁶⁷ Compared to MgO and MnO_x , ZrO_2 was demonstrated to have higher stability and activity in ketonization of pentanoic acid and hexanoic acid followed by subsequent HDO to afford corresponding fully deoxygenated hydrocarbons with very good yields (ca. 85%).^{268–270} The prereduction of Zr^{4+} to Zr^{3+} species was shown to have the overall effect to decrease the reaction barriers by generating a stable acyl intermediate (Scheme 44), thus facilitating the ketonization reaction.²⁷¹ In a

Scheme 44. Schematic Representation for the Formation of a Stable Acyl Intermediate²⁷¹

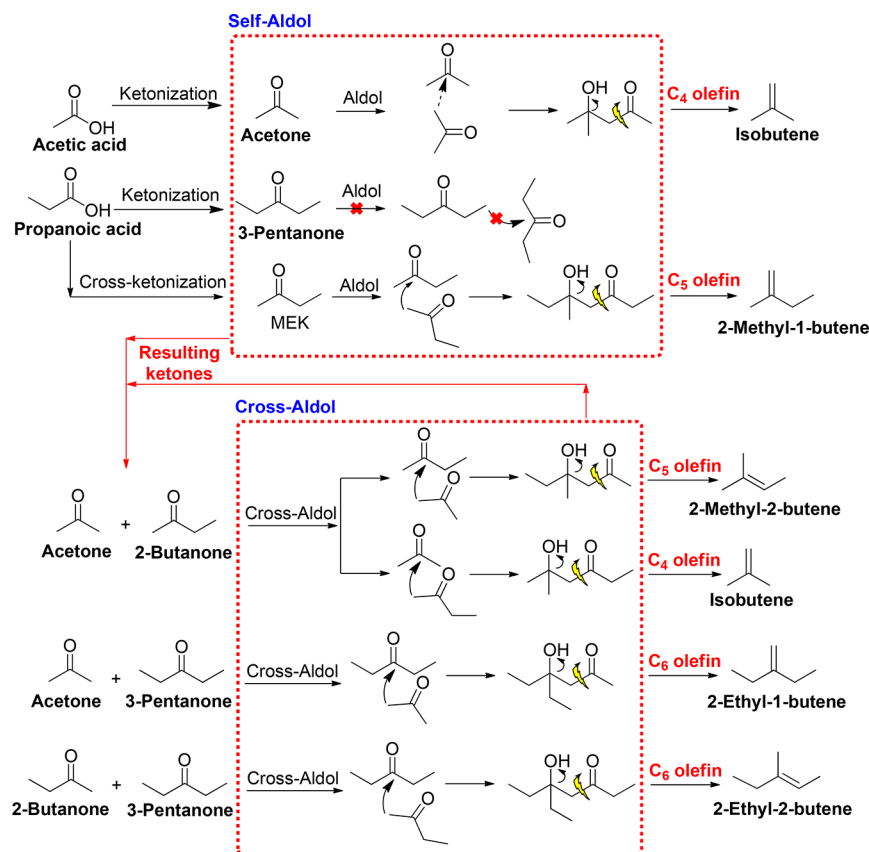
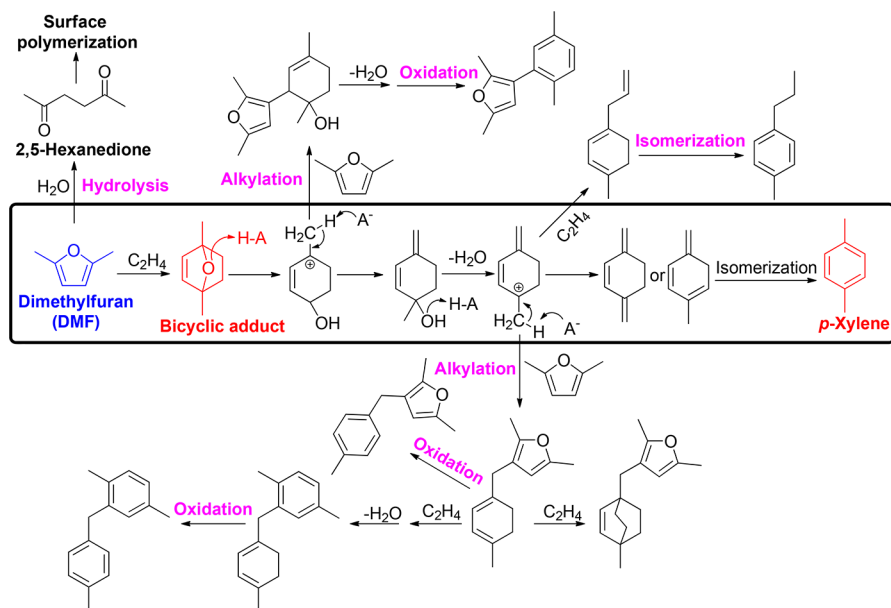
kinetic study, the interaction between the acyl group of acetic acid and a second acid was proposed to be the rate-determining step at 270–330 °C, and near quantitative selectivity toward the ketonization reaction to give acetone was observed.²⁷²

In aqueous-phase ketonization of acetic acid to acetone over TiO_2 -based catalysts at 180 °C for 5 h, Pham et al. demonstrated that the in situ prereduction of 5 wt % $\text{Ru/TiO}_2/\text{C}$ exhibited relatively higher activity (54.2% conversion) at 250 °C under 2.8 MPa H_2 after 3 h than prereduced 5 wt % Ru/C (1.3%), 5 wt % Ru/TiO_2 (32.9%), TiO_2/C (15.9%), and TiO_2 (1.5%), as well as unreduced TiO_2 (1.5%) and 5 wt % $\text{Ru/TiO}_2/\text{C}$ (1.2%).²⁷³ It could be surmised that the presence of Ru on TiO_2 might facilitate the formation of Ti^{3+} from Ti^{4+} species, thus favoring the ketonization reaction in water. A β -ketoacid intermediate was most likely to be formed in a bimolecular pathway over Ru/TiO_2 (Scheme 45), as substantiated on the basis of the reaction order (>1.5) with respect to acetic acid.²⁷⁴ Moreover, the hydrophobicity of the carbon

Scheme 45. Schematic for the Formation of a β -Ketoacid Intermediate²⁷⁴

support in $\text{Ru/TiO}_2/\text{C}$ was presumed to retard the inhibiting effect of water for the Ti^{3+} -mediated reactions.²⁷³ In the absence of a carbon support, partially hydrophobic 5 wt % Ru-TiO_2 rutile with a high contact angle of $\geq 90^\circ$ exhibited enhanced catalytic activity (TOF: 0.23 s^{-1}) in the liquid-phase ketonization of acetic acid at 220 °C, compared to hydrophilic Ru/TiO_2 anatase (0.13 s^{-1}) and amphiphilic Ru/TiO_2 rutile (0.15 s^{-1}).²⁷⁵ Interestingly, Ru-TiO_2 rutile was highly stable and prone to recycling for at least three cycles with conversion remaining unaltered, but with slightly decreased reaction rate from 483 to $450 \mu\text{mol g}^{-1} \text{ s}^{-1}$.

Similar to simple carboxylic acids and esters, the long-chain palm oil underwent ketonization to give heavy ketones (palmitone and stearone) with a yield of 68.9% at quantitative conversion over a basic catalyst $\text{MgO--Al}_2\text{O}_3$ at 420 °C.²⁷⁶ On the contrary, the Lewis acidic alumina (strong) and Na-faujasite zeolite (weak) favored the decarboxylation of carboxylic acids or esters (e.g., acetic acid and ethyl acetate) to produce the corresponding hydrocarbons containing a significant amount of olefins (56.1–60.4% yields), whereas Brønsted acidic H-ZSM-5 led to additional cracking and selectivity producing paraffins with smaller amount of aromatics.²⁷⁶ Interestingly, when using levulinic acid (LA) as substrate and a Red Mud bauxite mining waste catalyst, both direct ketonization and cascade dehydration-ketonization took place to yield C_9 ketones or a blend of C_9 alkenes and alkanes (up to 76% yield) at 365 °C at 5.5 MPa H_2 after 8 h.²⁷⁷ Likewise, cascade ketonic decarboxylation, reduction (via dehydrogenation-hydrogen transfer) and dehydration over TiO_2 might occur to produce olefins with $2n+1$

Scheme 46. Reaction Pathways of Acetic/Propanoic Acids to C₄–C₆ Olefins²⁷⁹Scheme 47. Detailed Reaction Network of DMF and Ethylene^{284,286}

carbon atoms instead of ketones at high temperatures (e.g., 400 °C) in a single pot.²⁷⁸ In the absence of noble metals, Baylon et al. showed that Zn_xZr_yO_z with only Lewis acid–base sites could directly produce C₃–C₆ olefins (up to 60 mol % yield) from the mixture of acetic acid and propanoic acid at 415 °C by cofeeding of H₂ via sequential (cross-)ketonization, (cross-)aldolization, and self-deoxygenation reactions (Scheme 46).²⁷⁹ This protocol apparently offers a quite sustainable way for the

direct production of long-chain olefins from biobased carboxylic acids.

6. DIELS–ALDER

Typically, the addition of unsaturated oxygenates via Diels–Alder reaction shows extensive application in the synthesis of pharmaceutical and polymer molecules.²⁸⁰ In virtue of the carbon-chain increasing strategy, the Diels–Alder reaction has

also recently been widely explored as a key step for producing high-density fuels.²⁸¹ Hence, lately much attention has been directed toward producing *p*-xylene, a precursor for terephthalic acid that can be used as monomer for polyester and polyethylene terephthalate plastics, from biomass-derived dimethylfuran (DMF) and ethylene via Diels–Alder coupled with dehydration reactions.^{282,283} This two-step reaction proceeds via a rate-determining bicyclic adduct (1,4-dimethyl-7-oxabicyclo[2,2,1]hept-2-ene) prior to Brønsted acid-catalyzed dehydration to *p*-xylene (Scheme 47).²⁸⁴ A high selectivity toward *p*-xylene (75%) with 95% DMF conversion with H–Y(30) was obtained at 300 °C under 6.2 MPa ethylene.²⁸⁵ However, a number of side-reactions occurred, mainly including hydrolysis of DMF to 2,5-hexanedione and succeeding polymerization, as well as *p*-xylene alkylation and oxidation (Scheme 47), which were demonstrated to be formed from DMF hydrolysis and electrophilic reactions of cationic intermediates catalyzed by acid.²⁸⁶ However, the selectivity of the desired product *p*-xylene can be enhanced by removing water from the mixture and by tuning the zeolite acidity.

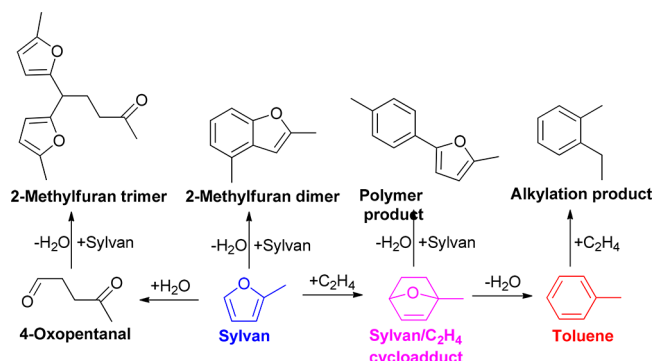
Over silica–alumina aerogel catalysts, a maximum selectivity to *p*-xylene (ca. 70%) at 90% DMF conversion was obtained at 250 °C at 3.0 MPa ethylene. Both conversion and selectivity were found to be proportional to the content of Brønsted acid sites and the use of polar solvent (e.g., 1,4-dioxane) could greatly increase the production rate of *p*-xylene.²⁸⁷ On the contrary, the total Brønsted acidity of the H-beta(12.5) zeolite was reported to not correlate with the reaction rate and catalytic activity.²⁸⁸ It seemed that the cycloaddition reaction barrier was not decreased by H⁺, substantiated by the results obtained from the comparable reaction activity between H-beta(12.5)²⁸⁸ and WO_x–ZrO₂.²⁸⁹ In this regard, Williams et al. clearly illustrated that the microporous structure of zeolites was most likely to control side-reactions like furan dimerization and hydrolysis.²⁹⁰ The overall reaction was demonstrated to be limited by either the dehydration rate of the Diels–Alder cycloadduct at a low concentration of Brønsted acid site ([H⁺] < 2.0 mM) or the Diels–Alder cycloaddition rate at [H⁺] > 2.0 mM. In addition, at high reaction temperature, low DMF concentration and high ethylene pressure contributed to the optimal *p*-xylene selectivity with maximum reaction rate.²⁹⁰ Likewise, computational study indicated that the yields of byproducts (e.g., 2,5-hexanedione) could be minimized by reaching high conversions of DMF.²⁹¹ Notably, the presence of 2,5-hexanedione and its high coverage onto the surface of zeolites (e.g., H–Y(2.6) and H-beta(12.5)) was the dominant factor inhibiting the isomerization of *p*-xylene.²⁹²

In comparison to H-beta(12.5), the Lewis acidic Zr-beta moderately promoted the Diels–Alder cycloaddition to yield more oxanorbornene from DMF and ethylene but was less efficient for succedent dehydration, thus giving a low yield of *p*-xylene of 10–20%.²⁹³ Moreover, the Zr-beta zeolite was more stable and highly recyclable due to its weak acidity that probably suppressed side reactions, especially the hydrolysis of DMF to 2,5-hexanedione and subsequent polymerization. By using either liquid Brønsted (haloacetic acids) or Lewis (rare-earth metal triflates) acids for the production of renewable aromatics, Song et al. found that the same type of acidic catalysts showed a similar apparent activity energy value (8.4 and 13.0 kcal mol^{−1} for Brønsted and Lewis acid, respectively).²⁹⁴ However, the rare-earth metal triflates showed a distinct higher TOF value (4.13 h^{−1}) than haloacetic acids (0.45 h^{−1}) under identical conditions, and a maximum *p*-xylene

yield of 70% was obtained over Sc(OTf)₃ bearing relatively higher Lewis acidity at 200 °C after 48 h. Besides the positive role of Lewis acidity, the confinement and charge transfer in zeolites were also elucidated to play a significant role in the catalytic process.²⁹⁵ Based on these viewpoints, a bifunctional catalyst appeared to have the potential to improve the rates of both Diels–Alder (by Lewis acid sites) and dehydration (by Brønsted acid sites).²⁹⁶

When 2-methylfuran (Sylvan) instead of DMF was used as substrate, the H-beta(12.5) zeolite was also able to catalyze the tandem Diels–Alder cycloaddition with ethylene and dehydration to produce toluene at 250 °C with a maximum selectivity of 46% at quantitative conversion of Sylvan.²⁹⁷ This could be attributed to the consumption of Sylvan by Brønsted acid-catalyzed side reactions such as the di/trimerization of Sylvan, and alkylation and incomplete dehydration of the Diels–Alder cycloadduct (Scheme 48).²⁹⁷ In contrast, Lewis

Scheme 48. Possible Side Reactions Involved in the Synthesis of Toluene from Sylvan and Ethylene²⁹⁷

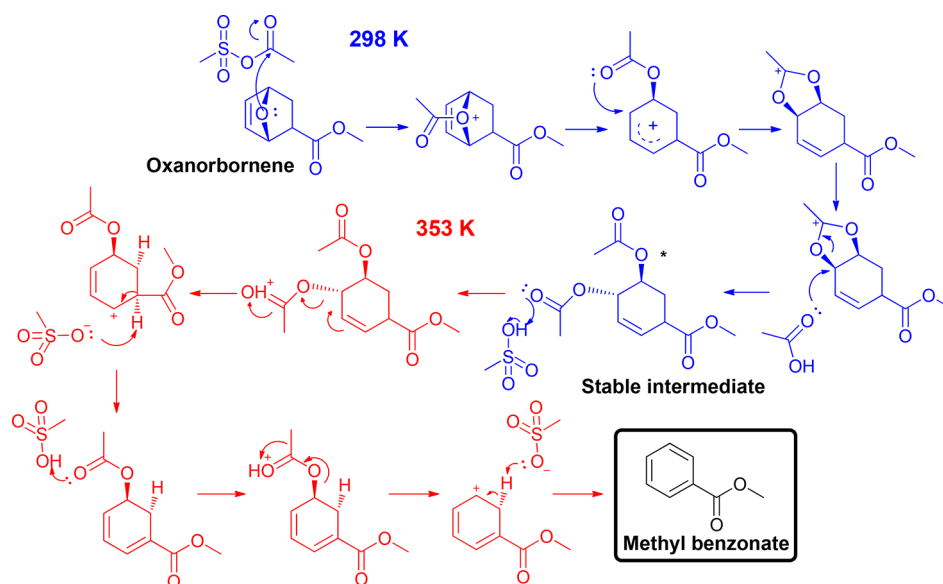


acid could accelerate the cycloaddition reaction but retard the side reactions, especially oligomerization.²⁹⁸ For example, AlCl₃ possessing stronger Lewis acidity than other studied metal chlorides (e.g., ZnCl₂, MgCl₂, NiCl₂, CrCl₃, and SnCl₄) was found to afford a good yield of toluene (ca. 70%) from Sylvan and ethylene at 250 °C after 24 h.²⁹⁸ In addition, a high regioselectivity toward *p*-xylene could be realized (up to 96%) from Sylvan and propylene by narrowing the zeolite (ZSM-5) pore openings to provide more space confinement.²⁹⁹

In the presence of pressurized ethylene other furanic compounds, including furan, FUR, furfuryl alcohol, HMF, 5-methyl-2-furoate and 2-ethyl-5-methylfuran were also reported to proceed via the same reaction pathway over zeolites (e.g., H-ZSM-5, H-beta, Sn-beta, and Zr-beta) to give corresponding aromatics with moderate-to-good yields.^{300–303} The introduction of electron-withdrawing groups into the dienophile (e.g., acrolein, maleic anhydride, methyl acrylate) was favorable for the Diels–Alder cycloadduct with furanic compounds,^{304–307} but the drawbacks such as the retro-Diels–Alder reaction of the endo adduct,³⁰⁸ furan ring-opening by hydrolysis,³⁰⁹ and furan self-condensation at high temperatures (>400 °C)^{310,311} were still unavoidable.

Recently, some efforts were made to avoid undergoing retro-Diels–Alder reaction, thus facilitating the dehydration of adducts (oxanorbornenes) to aromatic products at low temperatures (<100 °C). For example, the addition of methanesulfonic acid and acetic anhydride into the mixture containing oxanorbornene after Diels–Alder reaction of furan and methyl acrylate could form a stable intermediate (*) at 25

Scheme 49. Possible Reaction Mechanism for Dehydration of Unstable Oxanorbornene to Aromatic Product (e.g., Methyl Benzonate) in the Presence of Methanesulfonic Acid and Acetic Anhydride³¹²



°C after 2 h, and the subsequent dehydration at 80 °C for 4 h shifted the reaction to completion with up to 96% yield of methyl benzonate (Scheme 49).³¹² Similarly, phthalic anhydride was also produced from furan and maleic anhydride, and the resulting selectivity (80%) was much higher than with neat methanesulfonic acid (11% selectivity),³¹³ further indicating the significance of the oxanorbornene ring-opening on the acceleration of the reaction increasing the aromatic yield.

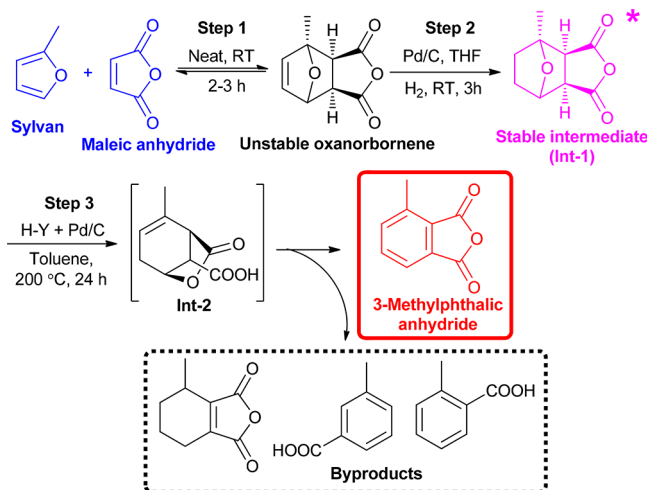
When a solid acid (e.g., H–Y zeolite) was combined with Pd/C, a three-step process comprising neat Diels–Alder reaction at room temperature, hydrogenation of the Diels–Alder adduct at room temperature, and the succeeding dehydrogenation coupled with dehydration at 200 °C was demonstrated to be efficient for producing phthalic anhydrides (>80% overall yields) from 2-methylfuran (Sylvan) and maleic anhydride (Scheme 50).^{314–316} The formation of a stable

intermediate (Int-1) via hydrogenation was the key step for enhancing the yield of aromatic products, and some minor byproducts were derived from the intermediate (Int-2) by either decarboxylation or transfer hydrogenation. Apart from improving catalytic activity, attention was also directed toward strengthening the renewability by using more abundant and upstream bioproducts. For example, olefins formed in situ from biomass-derived muconic acid or diacetone alcohol could be used as both diene and dienophile for producing aromatics and cycloalkanes with good yields (ca. 80%).^{317,318} On the other hand, ethanol or methanol was able to enhance aromatic production as dienophile precursor, indicating a significant synergistic effect between the alcohol and furanic compounds.^{319,320}

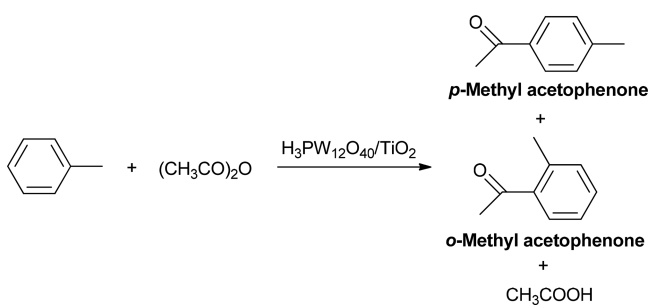
7. OTHER C–C COUPLING REACTIONS

7.1. Acylation. Typically, catalytic Friedel–Crafts acylation of aromatics with acid anhydrides or chlorides with Lewis acids (e.g., metal halides and zeolites) is an important approach to produce arylketones that are applied in pharmaceutical, agrochemical, and fragrance industries.^{321–323} Also, the acylation of renewable furans enabled control of the fluid surface, thus forming micelles in water with high capability.³²⁴ The selection of an appropriate type of acidic catalysts was likely to control the product distribution. For instance, Brønsted acid sites on H₃PW₁₂O₄₀/TiO₂ were favorable for the formation of *p*-methyl acetophenone (up to ca. 89% selectivity) from toluene and acetic anhydride at 130 °C after 5 h, while the generated weaker Lewis acid sites were facile to afford *o*-methyl acetophenone with a maximum selectivity of ca. 23% (Scheme 51).³²⁵ By employing a strong acid (e.g., H₂SO₄) as catalyst, the acetylation of acetic anhydride with the –OH species of sugar cane bagasse and Jatropha curcas cake to biocrude (mainly composed of glucopiranoside pentaacetate, glucopiranoside tetraacetate, lyxofuranoside tetraacetate, arabinoside 2,3,4,5-tetraacetate, 3,4-di-*O*-acetyl-arabinal, saccharose octaacetate, and triacetin) was also achieved under microwave radiation.³²⁶

Scheme 50. Three-Step Strategy Including Diels–Alder Addition, Hydrogenation, and Aromatization To Produce 3-Methylphthalic Anhydride and Some Minor Byproducts^{314–316}



Scheme 51. Acylation of Toluene with Acetic Anhydride To Produce *o*-/*p*-Methyl Acetophenone³²⁵

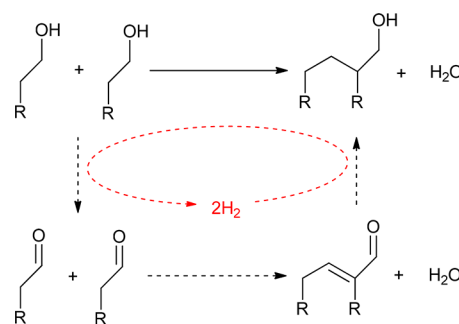


In the acylation of Sylvan with acetic anhydride to 2-acetyl-5-methylfuran, the synergistic effect of both Brønsted ($-\text{OH}$) and Lewis (unsaturated Al) acid sites in $\text{AlF}_{3-x}(\text{OH})_x$ possibly contributed to its pronounced performance (ca. 48% yield) under mild conditions (50°C , atmospheric pressure), as shown in Scheme 52.³²⁷ The use of strong polar solvent (e.g., nitromethane) could facilitate product desorption, thus improving the catalytic activity up to 100% selectivity with 92.6% yield.³²⁸ However, pore blockage and adsorption of byproducts on acid sites of H-beta(27) zeolite were generally unavoidable, accounting for its deactivation. Interestingly, the surface capping with tetraethoxysilane onto the catalyst surface of H-beta(27) led to enhanced stability and recyclability without a significant loss of catalytic activity.³²⁹ Apart from acetic anhydride, the direct carbon–carbon coupling of biofuranic compounds (e.g., Sylvan) with carboxylic acid (e.g., acetic acid and fatty acid) to acylated products could also be achieved over zeolitic catalysts (e.g., H-ZSM-5 and H-beta) at relatively high reaction temperatures ($>200^\circ\text{C}$),^{324,330,331} which was also able to integrate with further upgrading processes like Diels–Alder cycloaddition and dehydration to expand opportunities for the synthesis of biobased aromatic compounds.³⁰³

7.2. Ethanol Coupling (Guerbet) to Long-Chain Alcohols. Fermentable conversion of biomass derivatives to

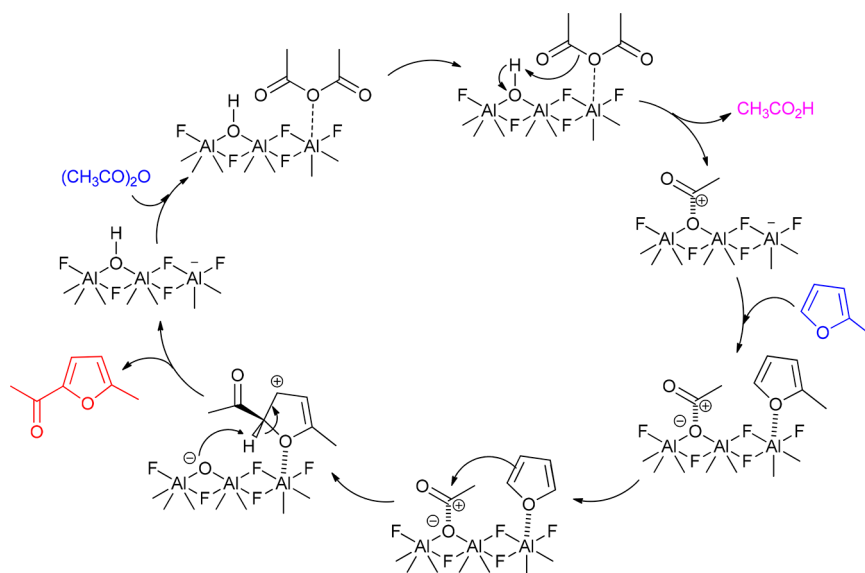
bioethanol is a commercial success reaching >30 billion gallons in 2017.³³² In the past decades, extensive investigations have been made on further transformation of ethanol into biofuels and valuable chemicals such as biodiesel,³³³ acetaldehyde,³³⁴ butyraldehyde,³³⁵ ethyl acetate,³³⁶ acetone,^{337,338} propene,³³⁹ 1,3-butadiene,^{340–343} and long-chain alcohols.^{344,345} In particular, the synthesis of butanols from ethanol has gained a great deal of attention, due to its wide applications as organic solvent, gasoline additive, plasticizer, and chemical intermediate.³⁴⁶ The coupling of alcohols was generally implemented via the Guerbet condensation reaction, wherein a primary or secondary alcohol was condensed with the same alcohol (self-condensation) or another alcohol (cross-condensation) involving a key “borrowed hydrogen” process, thus leading to a heavier alcohol (Scheme 53).³⁴⁷

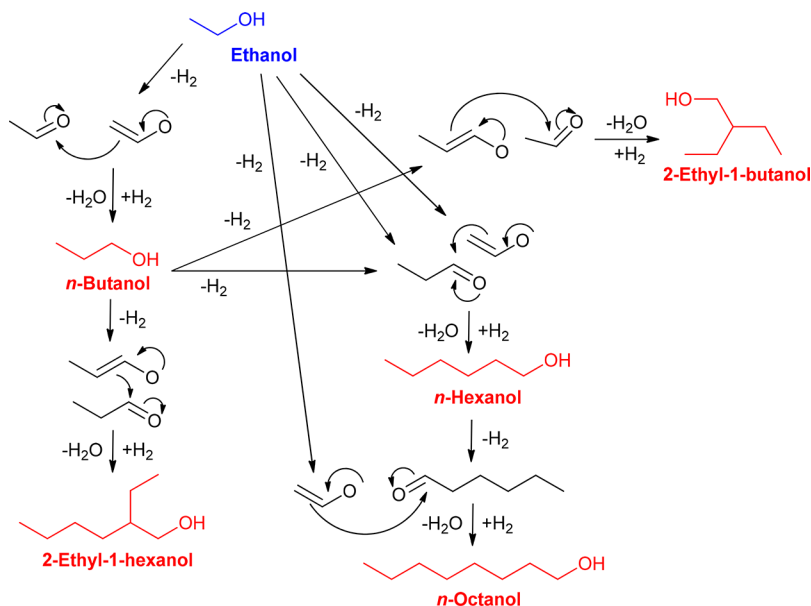
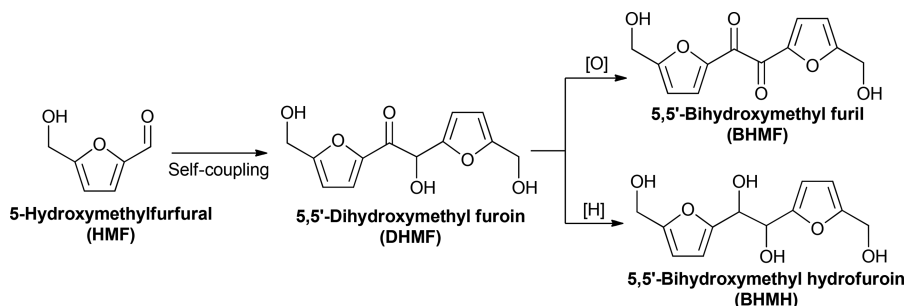
Scheme 53. Representative Pathway for the Guerbet Reaction of Primary Alcohols³⁴⁷



To fulfill the Guerbet condensation with high efficiency, used catalyst was reported to possess balanced acidic/basic and dehydrogenation/hydrogenation functions that could activate the reaction and suppress the formation of byproducts.³⁴⁸ In this regard, ruthenium nitrogen-containing complexes,^{349–352} iridium complex coupled with bulky Ni- or Cu-hydroxides,³⁵³ Co powder/ NaHCO_3 ,³⁵⁴ Cu/ CeO_2 ,^{355,356} hydroxyapatite,^{357–359} MgAlO_x ,^{360,361} and modified metal oxides^{362–366}

Scheme 52. Possible Mechanism for the Acylation of Sylvan with Acetic Anhydride to 2-Acetyl-5-methylfuran over $\text{AlF}_{3-x}(\text{OH})_x$ Bearing Brønsted ($-\text{OH}$) and Lewis (Unsaturated Al) Acid Sites³²⁷



Scheme 54. Schematic Network for the Ethanol Guerbet Reaction System^{367–369}Scheme 55. Synthesis of Biobased Difuranic Polyol Monomers (e.g., BHMF and BHMH) from HMF^{377,378}

were demonstrated to be highly efficient for the production of *n*-butanol (up to >99% selectivity) from ethanol at 230–400 °C. Besides *n*-butanol, ethanol might be further converted to C₆ (*n*-hexanol and 2-ethyl-1-butanol) and C₈ (*n*-octanol and 2-ethyl-1-hexanol) alcohols in as high as >30% yields (Scheme 54)^{367–369} and even give C₈₊ alcohols.³⁷⁰ In addition, the synthesis of secondary alcohols with increased carbon-chain could also be achieved from cross-coupling of different simple alcohols via the Guerbet condensation reaction.^{371–376}

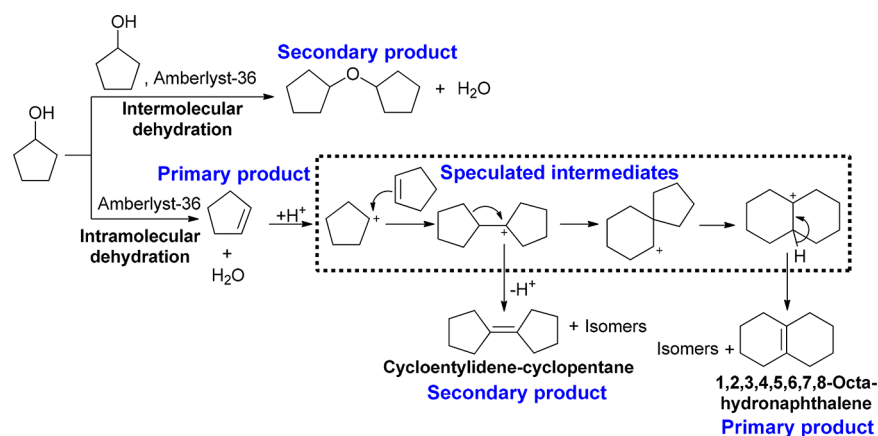
7.3. Self- and Cross-Coupling of Furanic Aldehydes. 5,5'-Dihydroxymethyl furoin (DHMF), 5,5'-bihydroxymethyl furil (BHMF), and 5,5'-bihydroxymethyl hydrofuroin (BHMH) have been developed as HMF-derived monomers for producing polymeric materials (Scheme 55), just as 2,5-furandicarboxylic acid and 2,5-bis(hydroxymethyl)furan.^{377,378} Donnelly et al. showed that benzaldehyde lyase was active for the self-carboligation of HMF to DHMF (28–42% yield) at room temperature after 18 h, and BHMF (22–45% yield) was also formed via spontaneous oxidation.³⁷⁹ On the other hand, Huang et al. illustrated that BHMH (>90% selectivity) was synthesized from HMF (>90% conversion) via reductive self-coupling with metal powders (e.g., Al, Mg, or Zn) and 10% NaOH at room temperature after 6 h, and long-chain alkane (C₁₂) was obtained via subsequent dehydration/hydrogenation in water at 300 °C under 4.0 MPa H₂ after 3 h catalyzed by a metal catalyst (e.g., Pt/C or Pd/C) and a solid acid (e.g., NbOPO₄, TaOPO₄ or ZnCl₂).^{380–382} By using either

homogeneous or immobilized N-heterocyclic carbenes (NHCs) as catalysts, Liu and Chen with co-workers conducted a series of studies on the self- and cross-coupling of HMF and FUR for the synthesis of C₁₀–C₁₂ furoins (>90% yields).^{383–387} This simple, metal-free in-air oxidation reaction process is highly promising for practical applications.

7.4. Other Relevant Catalytic Processes. To endow more sustainable and practical catalytic transformation processes, some bulky biomass derivatives were directly utilized as substrates for the production of long-chain compounds via a variety of integrated reactions in sequence. For instance, the cross-metathesis of eugenol with acrylates and the self-metathesis of methyl vinyl glycolate or α -methylene- γ -butyrolactone was achieved over Ru-based catalysts,^{388,389} and subsequent polycondensation afforded polyfunctional alkenes and polyesters with good yields (up to 100%).^{390–393} From the direct reaction of hexose (or pentose) sugar with β -diketone, 3-ethylnonane (or 3-ethyloctane), and 6-ethylnonyl acetate (or 6-ethyloctyl acetate) was formed in a total yield of >80% via a one-pot, two-step process involving aldol condensation over Fe(OTf)₃ in refluxing water for 24 h and hydrogenation catalyzed by Pd/C coupled with La(OTf)₃ in acetic acid at 200 °C under 1.4 MPa H₂ for 14 h.³⁹⁴

Due to the presence of multifunctional groups in bulky biomass derivatives, the involved reactions in a single catalytic process were typically variable with limited selectivity toward specific products. Under thermal reaction conditions over

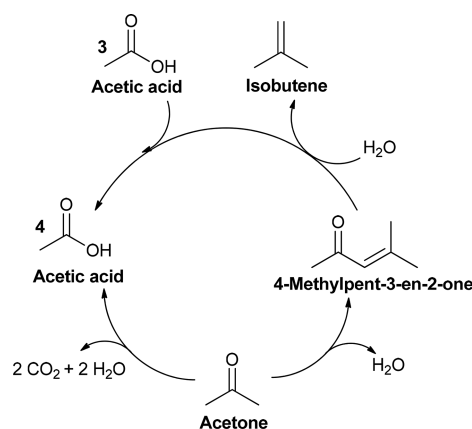
Scheme 56. Cascade Dehydration, Oligomerization, and Rearrangement of Cyclopentanol to 1,2,3,4,5,6,7,8-Octahydronaphthalene over Amberlyst-36^{397,398}



PtRe/C at 230 °C, aqueous solutions of sugars and polyols could be converted to hydrophobic monofunctional hydrocarbons, primarily containing ketones, alcohols, heterocycles, and organic acids, which spontaneously separated from the reaction system as an organic phase.³⁹⁵ However, further reactions such as aldol condensation, Michael addition and hydrogenation were required for producing long-chain alkane fuels.³⁹⁶ Moreover, some unavoidable byproducts might have formed in significant amounts in the catalytic transformation of biobased alcohols. In this context (as discussed above), cyclopentanol was able to be produced by the selective hydrogenation of FUR,³⁹⁷ which could be further selectively converted to bi- and tri(cyclopentane) via cascade partial oxidation, Aldol condensation, and HDO (Scheme 22). On the other hand, 1,2,3,4,5,6,7,8-octahydronaphthalene (56.1% yield) was obtained in the presence of Amberlyst-36 at 120 °C after 8 h from the oligomerization and rearrangement of cyclopentene (93.8% conversion) in situ formed by intramolecular dehydration of cyclopentanol, together with cyclopentyl ether as secondary product by intermolecular dehydration (Scheme 56).³⁹⁷ In turn, a diol 3-methyl-1,3-butanediol (70% yield) could be produced via Prins condensation and hydrolysis of isobutene and formaldehyde over Pr/CeO₂ at 135 °C after 3 h,³⁹⁸ showing the possibility in the interconversion between alcohols and alkenes.

In the catalytic process of ketonization, the formation of ketone and CO₂ was two dominant products. By integration of catalytic ketonization with subsequent aldol condensation and C–C hydrolytic bond cleavage reactions, it was found that acetic acid could be further transformed into isobutene (Scheme 57), and a maximum isobutene yield (ca. 50%) was attained over Zn₂Zr₈O₂ with a balanced concentration of acid and base sites (1:3.65 molar ratio) at 450 °C after 4 h.³⁹⁹ Meanwhile, the capture of CO₂ via chemical transformations could be a potential promising approach to synthesize long-chain compounds. For example, the reduction of CO₂ would lead to form CH₄⁴⁰⁰ or acetic acid,^{401,402} carboxylation of *p*-hydroxybenzoic acid to phthalic acid,⁴⁰³ and reactions with polyols or amines to cyclic carbonates^{404,405} or methylamines,⁴⁰⁶ respectively. In addition, participation of bio-products, such as 2-ketones, aromatics, and furans, in conventional and commercial organic syntheses involving C–C bond formation might offer another sustainable route for biomass valorization.^{407–410}

Scheme 57. Possible Catalytic Cycle for the Conversion of Acetic Acid to Isobutene³⁹⁹



8. SUMMARY AND OUTLOOK

A number of C–C coupling reaction pathways, such as aldol condensation, alkylation, Diels–Alder, ketonization and oligomerization, which have been widely explored as efficient approaches for increasing the length of carbon chains to afford either value-added chemicals or high-quality fuels via HDO reactions, are in detail reviewed. Surveyed and discussed are also the correlation of bi- and multifunctionality (e.g., acidic, basic, and metallic sites) and fine morphological structure (e.g., porosity, accessibility, and stability) of solid catalytic materials and catalytic performance. Also, delineated is appropriate control of reaction parameters (e.g., pressure, solvent, temperature, and reactor type) that can contribute to pronounced selectivity toward desired products with acceptable carbon balance. Overall, those catalytic strategies in combination with integrated reaction processes show promising application to be a potential alternative for producing biofuels in gasoline and diesel range.

In parallel, a series of cascade reactions involving C–O bond formation over acidic catalysts to form relatively stable products with increased carbon-chains are summarized in this review; this approach offer another feasible strategy to produce energy-intensive fuels and chemicals from biomass. The type of aqueous-phase catalytic systems mainly include: (1) Etherification with or without being integrated with upstream reactions (e.g., hydrolysis and dehydration) to produce alkyl

glycosides/xylosides,^{411–417} furanic ethers (e.g., 2,5-bis-alkoxymethylfuran and 5-alkoxymethylfurfural),^{418–425} and long alkyl chain ethers (e.g., ethylene glycol, 1,2-propylene glycol, and glycerol-based ethers);^{426–430} (2) Esterification/acetylation of in situ formed biobased organic acids (e.g., levulinic acid and free fatty acid) with C₁–C₄ mono- and poly hydroxyl alcohols (methanol, ethanol, and glycerol) to yield biodiesel or long-chain esters;^{431–440} (3) Acetalation of bioaldehydes or ketones with alcohols to yield fuel additives;^{441–445} and (4) Oligomerization of poly hydroxyl alcohols to make bio-surfactants, hydrotropes, or polyesters.^{446–449} On the other hand, the construction of other C–X bonds (X = N and S) for the production of amines/amides and sulfides from bioproducts has also been recently realized as important transformations in biomass valorization,^{450–462} implying that the integration of C–X bond-forming processes with other reactions expand the transformation pathways thus diversifying the biorefinery products.

To establish well-defined and robust catalytic systems associated with appropriate functionality and relevant auxiliaries, several points should be further taken into account for the carbon-increasing strategies coupled with HDO processes for primarily producing energy-intensive fuels and chemicals:

- (1) HDO is one of the indispensable routes to reduce the oxygen content of biobased oxygenates, while the C–C cleavage or dissociation unavoidably takes place, shortening the carbon-chain of hydrocarbons.^{463,464} Depending strongly on the reactivity of substrates under optimized reaction conditions, the active metal and acid strength of the respective solid catalysts should be accordingly designed to suppress side reactions like cracking.
- (2) Both linear and cyclic hydrocarbons may undergo rearrangement or isomerization during catalytic processes,^{465,466} which typically does not affect the number of carbon atoms but possibly results in undesired side reactions. Besides screening suitable functional catalysts,⁴⁶⁷ finding mild reaction conditions to accelerate the target products selectivity while diminishing undesired products are preferable.
- (3) Simultaneous upgrading of multiple substrates via the same (or different) type of reactions avoiding adverse effects between each other has been attempted with some achievements,^{468,469} and this approach seems to be more promising for catalytic transformation of complicated biomass components.
- (4) The development of catalytic materials functionalized with variable active species favorable for specific carbon-increasing routes is highly required for achieving high efficiency, while the chemical/thermal stability of the used solid catalysts should be enhanced by having well-organized structure such as yolk– or core–shell and N-stabilized metal particles by using facile preparation methods.
- (5) The scope of carbon-increasing routes can be further extended by referring to the methodology of organic synthesis. In this regard, the type of products and catalytic systems will be variable with more research openings.
- (6) An extensive range of biomass-derived molecules have been used for the production of high-quality biofuels, while most of the rest bioderivatives are still unexplored

possibly because of the limitation of current techniques. Future studies can be conducted to develop more efficient approaches to further extend the pool of platform compounds capable of producing fuel candidates.

- (7) Harsh reaction conditions like high temperature and gas pressure with relatively low product selectivity are typically encountered when H₂ is used as hydrogen-donor. Although some novel catalytic systems or processes by coaddition of Lewis acid as catalyst have been demonstrated to be efficient for the increase of product efficiency under relatively mild conditions, the exploration of active hydrogen-donors may provide potential possibilities in the further acceleration of catalytic performance.

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Notes

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