A review of thermal homogeneous catalytic deoxygenation reactions for valuable products

Zhaoni Kong, Liang He, Yuzheng Shi, Qingqing Guan, Ping Ning

Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China
Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming, 650500, China

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ABSTRACT

To remove high oxygen content is important to make high quality oil and valuable products. In this paper, the research on homogeneous catalytic deoxygenation reactions, including decarboxylation (DCX)/decarbonylation (DCN), hydrodeoxygenation (HDO) is reviewed. Based on DCX/DCN, the classic radical reactions such as the Barton decarboxylation, Henkel, Hunsdiecker and Kochi reactions were introduced, the practice and overall performance are also discussed. In addition, the different reaction pathways and mechanisms were demonstrated and the key chemical processes have been selected from the literature as examples to elaborate the critical emphasis on the mechanistic understanding. The applications of the catalytic deoxygenation reactions for high-value products have also been highlighted. Overall, this review provides insight discussions on the DO issues and progresses in homogeneous catalytic aspects.

1. Introduction

Biomass derived products have been considered to be renewable and environmental friendly (Saidur et al., 2011). In recent decades, there has been increased interest and demand for bio-mass products from bio-crude. The bio-crude quality depends not only on the characteristics of raw materials but also the technical processes such as biomass fast pyrolysis and hydrothermal liquefaction (Liu et al., 2010; Savage et al., 2010; Yang et al., 2015). In general, bio-crude has high amounts of oxygen and acidic groups, which is unsuitable for direct use (Mortensen et al., 2011; Saber et al., 2016). Therefore, it is necessary to include a catalytic refining stage to improve the quality for high-value bio-mass products.

A catalytic refinery based on thermochemistry is a typical technology for the deoxygenation (DO) and cracking processes. For conventional crude, the cracking process is used to produce light hydrocarbon species. However, for those products derived from biomass (where the oxygen content may be over 10 wt.%), DO becomes the most important process in the upgrading of bio-crude (Bu et al., 2012; Kenar et al., 2017). Currently, decarboxylation (DCX), decarbonylation (DCN) and hydrodeoxygenation (HDO) reactions can be performed for the DO process.

In recent years, the processes of catalytic DO reactions have been intensively investigated (Robinson et al., 2016). They can include either homogeneous or heterogeneous complexes. As each of these has its advantages and disadvantages, the processes must be balanced accordingly. Compared with the heterogeneous catalytic process, homogeneous catalysis has the advantages of greater activity and greater selectivity, since the reactive sites among the ancillary ligands can achieve far better performances than heterogeneous catalytic processes, e.g., using enzymes (Trost, 2010). Additionally, the high water/liquid phase content of bio-crude could allow homogeneous catalysts to achieve rapid and selective DO reactions under the mild conditions (Dawes et al., 2015).

There are several general reviews relevant to bio-crude refining. Zacher et al. at Pacific Northwest National Laboratory reviewed the hydrodeoxygenation (HDO) of bio-oil, in which it focused on process integration as well as physical and chemical modification (Zacher et al., 2014). Several other reviews also give introductions on bio-crude refining (Peterson et al., 2008; Helwani et al., 2009; Demirbas, 2011; Mortensen et al., 2011; Chang et al., 2012; Elliott, 2015; Yuan et al., 2016; Pattanaik and Misra, 2017). However, there are few literature studies reporting about homogeneous catalytic DO. The purpose of this review is to fill this gap by providing an in depth insight into the homogeneous catalytic
Deoxygenation reactions for the production of high-value bio-mass products, including DCX/DCN and HDO.

2. Decarboxylation (DCX)/decarbonylation (DCN)

DCX/DCN is an effective way to remove -COOH and release CO₂ or CO to produce n-alkanes with and without H₂. In the HDO method, the oxygen atom is removed or partially removed by introducing hydrogen (H₂) to form n-alkanes or synthesize products in the presence of a catalyst (Kubickova and Kubicka, 2010). However, a DCX/DCN process using a catalyst to produce n-alkanes requires much less or even no H₂, making the process simpler and more economical.

2.1. Classic radical reactions

Classic radical reactions of DCX/DCN are the Barton decarboxylation reaction, Henkel reaction, and Hunsdiecker, Kochi reaction and so on, which are all types of free radical oxidative reactions.

In the Barton decarboxylation, -COOH is removed to form a Barton ester (by heating with radical initiator) producing a small amount of H₂, as shown in Figure 1 (Barton et al., 1979, 2015; Gutekunst and Baran, 2011). The Barton reaction provides a possible route for decarboxylation, however the derivatives can still be formed due to radical-substitution reactions (Barton and Beaton, 1960; Ishmuratov et al., 2005; Petrović and Ceković, 2010). For instance, when the thermal DCX/DCN of O-acetylpodocarpic acid and N-hydroxypyridine-2-thione, a high yield of alkene was obtained by heating (Cochrane et al., 1989). Although some reductive decarboxylation and decarboxylative oxygenation applications have been used for conversion of acids (Saraiva et al., 2009; Wim et al., 2011), Barton decarboxylation has mostly been applied in the organic synthesis (Sugimoto et al., 2009; Wim et al., 2011).

The Henkel process, also known as the Raecke process (Brolley et al., 1955), is widely used for converting the aromatic carboxylates into symmetrical aromatic dicarboxylates via thermal rearrangement with alkali metals. As shown in Figure 2, the process requires not only alkali salts as a catalyst but also a high temperature (e.g., 350–500 °C) and should be operated in inert conditions (Kucera and Jancar, 1998). Some results have shown that potassium salts are effective for the production of terephthalic acid (Ogata et al., 1957; Jiang et al., 2008; Wang et al., 2013). Zuo et al. (2010) found that the inert pure nitrogen atmosphere can be replaced by CO₂, which can enhance the radical oxidation and can lead to a high yield of toluene and p-toluic acid (over 90%) in the liquid-phase oxidation system (Xiao et al., 2010). Some studies have further applied supercritical CO₂ for higher purity and a more active DCX/DCN process (Pérez et al., 2011).

A similar Henkel route was also reported for producing furan and 2,5-furandicarboxylic acid (2,5-FDCA) (Pan et al., 2013), in which the conversion rate can reach up to 61% and the selectivity for 2,5-FDCA about 86% by ZnCl₂ catalysis at 250 °C and a duration of 180 min. Other studies have also used this Henkel reaction to produce 2,5-furandicarboxylic acid with metal salts as the catalysts (e.g., potassium permanganate or gold nanoparticles), the results showed up to 99 mol% selectivity at 130 °C in water with air as an oxidant can be achieved. The Henkel route was also considered as an important process for bio-products such as furfural and 2,5-FDCA (Colonna et al., 2011).

It was reported that the Hunsdiecker reaction could be carried out for DCX/DCN with silver salts and organic halides (Hunsdiecker and Hunsdiecker, 1942; Borodine, 2010). Figure 3 shows the Hunsdiecker reaction mechanism in the presence of silver salts and organic halides to generate the radical intermediates. In a typical process, the Ag⁺ will be replaced by Br, which can create the diradical intermediate 3. After the rapid DCX/DCN, n-alkanes and CO₂ will be produced with some undesired organic halides (Johnson and Ingham, 1956).

Kochi et al. (Kochi et al., 1967; Anderson and Kochi, 1970) further discovered that Ag(I)-catalyzed oxidative decarboxylation could remove COOH group(s) by using Cu²⁺ and sodium peroxydisulfate, which was widely applied to DCX/DCN of fatty acids. Fatty acids are the components derived from natural plant and algae oils, which are typically stearic acid (C₁₈H₃₆O₂), palmitic acid (C₁₆H₃₂O₂) and unsaturated fatty acids such as oleic acid (C₁₈H₃₄O₂), linoleic acid (C₁₈H₃₂O₂) and lignocellulosic, cellulosic and semicellulosic acid. Figure 4 shows the proposed mechanism in which Ag(I) complexes are converted to Ag(II) by persulfate oxidation and the Ag(II) subsequently oxidizes CO₂ into the acyloxy radical. The acyloxy radical is unstable, and breaks down to release CO₂ and form an alkyl radical. By getting H from the solvent or chain, the alkyl radical is converted into alkane or alkene products. Additionally, Ag(II) accepts e⁻ from H and is reduced to Ag(I). The catalytic copper (II) can produce alkenes by the oxidative elimination.
The silver/copper decarboxylation/decarbonylation requires the stoichiometric peroxydisulfate or sulfate. To produce an alkane, a hydrogen donor solvent is needed. DCX/DCN by Ag(I)-catalyzed oxidation can be used in the decarboxylation of several saturated or unsaturated fatty acids. At 78°C for 20 min, a 24% yield of 8(Z)-heptadecene with 79% purity was obtained from oleic acid. With the addition of Cu²⁺, (Z)-heptadeca-1,8-diene was found to be the major byproduct (Dawes et al., 2015). Additionally, silver/copper DCX/DCN was used for decarboxylating ortho-anisic acid to anisole (98 mol%), cinnamic acid to styrene (75%) and hydroxymethylfurfural to caprolactone (Buntara et al., 2011). Recently, Weng et al. (2017) reported the DCX/DCN of cross-link polyacrylic acid (PAA) and hydrophilic polymers, in which the cross-linking reaction was readily achieved with only 0.03 wt% AgNO₃ and a small amount of persulfates in mild conditions (a room temperature in air). The results show promise in the use of oxidative decarboxylation to prepare hydrogels of copolymers and interpenetrating polymer network (IPN).

Unproductive reactions tend to occur as a result of the radical reactions, leading to disproportionation and rearrangement of the byproducts. Ag₂O generation has been observed at temperatures above 200°C, and can be further reduced to metallic silver. The results of two studies (Lee et al., 2002; Koen Binnemans et al., 2004) showed that intermediate silver carboxylates present as dimeric (RCO₂)₂Ag₂ ring structures tended to generate Ag metal, CO₂, and organic products at ~300°C.

An insight view on the decarboxylation and simultaneous reduction was provided by Hatamura et al. (2015). The molecular structures of Ag(I) β-ketocarboxylates are shown in Figure 5. According to the DFT
structures and the experimental results, Ag(I) β-ketocarboxylates can be classified into either type 1, type 2 or type 3. These indicate that the coordination of C=O to Ag is unstable, which leads to e− transfer during decomposition to produce (Ag2)þ. The intermediates 2 and 3a make the e− transfer. After e− transfer, the keto radical, CO2 and Ag can be produced from bond-cleavages. Thus, Ag(I) is the key to the radical oxidation for DCX/DCN of fatty acids.

2.2. Organometallic precursor catalysts

The organometallic precursor catalysts, i.e., noble metal based catalysts (such as Rh-, Ir-, Pd-, Ru-) and transition metal based catalysts (such as FeCl2/KI, or FeI2/KI, Cu-), have been applied for the catalytic decarboxylation, which could offer an alternative way to the DCX/DCN approaches. Table 1 summaries the results from the DCX/DCN of fatty acids by the organometallic precursor catalysts such as Rh-, Ir-, Pd-, Ru-, Fe- and Cu-based catalysts. The results indicate that the use of Rh- and Ir-provides the best alkene selectivity in the reaction.

RhCl3 serves as one of the best organometallic precursor catalysts. Rhodium trichloride (RhCl3) and triphenylphosphine can efficiently catalyze the DCX/DCN of stearic acid to alkanes, such as 2-heptadecene, 3-heptadecene and 1-heptadecene (Foglia and Barr, 1976), as shown in Table 1. The proposed mechanism is shown in Figure 6. There are four kinds of Rh complexes during the DCX/DCN of stearic anhydride, i.e., chlorocarbonyl [bis-triphenylphosphine] Rhodium(I) (type 2), six coordinate acyl-metal (type 3), five coordinate acyl (type 4), and six coordinate alkyl rhodium metal (type 5). After Type 2, Type 3 takes place, and then Type 4 is initiated by the elimination of triphenylphosphine or CO, which later converts into Type 5 generating an acid, 1-heptadecene and Type 2 for recycle. The RhCl3 can also be used in the Cativa™ Process for the manufacture of acetic acid (Kozub et al., 2000), and the reaction might also be useful for the production of benzoic acid derivatives (Jing et al., 2013).

IrCl(CO)(PPh3)2, i.e., Vaska’s complex, can be used as a catalyst for DCX/DCN of fatty acids to alkenes in the presence of KI, the alkene yield can reach to 97% (Maetani et al., 2011). Iridium catalysis has also been used in the Cativa™ process (Sunley and Watson, 2000), Figure 7 shows the proposed mechanism. In a typical process, the acyl Ir (type A) could be produced by the condensation of the C(O)-O bond from Ac2O and carboxylic acids. Type A then generates the alkyl Ir by DCX/DCN, Type B. The Ir hydride complex C may be produced by the elimination of β-Hydride from Type B, which forms the Ir(I) complex. Additionally, Type C produces alkenes and the alkyl Ir, Type D. It should be noted that Type C might lead to different pathways, forming both n-C15H30 and n-C14H28.

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### Table 1. Comparison of DCX/DCN of fatty acids.

| Catalyst          | Fatty acid        | Catalyst loadings | Time (h) | Temp (°C) | Yield alkene | Reference                  |
|-------------------|-------------------|-------------------|----------|-----------|--------------|----------------------------|
| RhCl3             | stearic acid      | 1% (mol/mol)      | 1        | 280       | 90%          | Foglia and Barr (1976)     |
| IrCl(CO)(PPh3)2   | stearic acid      | 2% (mol/mol)      | 5        | 200 (KI, Ac2O) | 97%          | Maetani et al. (2011)     |
| PdCl2             | stearic acid      | 2% (mol/mol)      | 3        | 280       | 15%          | Nötke et al. (2010)       |
| PdCl2(PPh3)2      | nonanoic acid     | 0.01 mol%         | 0.5      | 230       | 68%          | Liu et al. (2014)         |
| Ru3(CO)12[Ru(CO)2(EtCO2)]n | 10-undecenoic acid | 0.87 wt%         | 4        | 250       | ~60%         | Muench et al. (2016)      |
| FeCl2             | aliphatic carboxylic acids | 10 mol% | 3        | 250       | 79%          | Maetani et al. (2012)     |
| Cu(OAc)2          | vinylic carboxylic acids | 2 mol% | 12      | 110       | 45%          | Cui et al. (2012)         |
Palladium-based catalysts, such as PdCl$_2$, PdBr$_2$, Pd(OAc)$_2$, (dba)$_2$Pd, Pd(PPh$_3$)$_4$ and PdCl$_2$(PPh$_3$)$_2$ also show high activity during decarboxylation. The DCX/DCN of aliphatic carboxylic acids into olefins can occur with palladium-based catalysts. The Pd-precursor at 110 °C can be used to effectively eliminate decarbonylation and β-hydride. PdBr$_2$ has proved to be more active than PdCl$_2$, since 60–75% yield can be achieved with Pd(PPh$_3$)$_4$ (0.01 mol%) for the DCX/DCN of carboxylic or dicarboxylic acids at about 190 °C (Notre et al., 2010). For myristic acid, a 91% yield was observed with PdCl$_2$, Ph$_3$P and Pivalic Anhydride, and 55% of 1,9-decadiene and 65% of 11-dodecadiene were obtained from the diacids. Notre et al. also reported that about 96% 1-heptadecene yield was achieved at 18 h and 110 °C with additive trialkylamines for the DCX/DCN of aliphatic carboxylic acids. Liu et al. (2014) reported that the decarbonylative dehydration using a low catalyst loading (PdCl$_2$(PPh$_3$)$_2$) under relatively mild and solvent-free conditions can achieve a 90% yield by the addition of isophthalic acid with 0.1% Pd catalyst under specific conditions (132 °C for 2 h in 1 atm of N$_2$–CO). Additionally, direct DCX/DCN of benzoic acids was observed by Congyang et al. (2009). A Pd-catalyst was used in the Heck coupling system (Fu et al., 2016).

Figure 6. Decarbonylation of stearic acid by Rh- complexes.

Figure 7. Decarbonylation reaction mechanism of Ir-complex.
There are four main reactions in the catalyzed carbynylation mechanism, oxidative addition, coordination, insertion of carbon monoxide (transmetalation), and reductive elimination (Beller and Wu, 2013). A similar Pd-catalyzed decarboxylationative cross-coupling mechanism for the decarbonylation of fatty acids was reported, in which the decarbonylation proceeds via the formation of an anhydride, coordinated to the palladium atom to produce an alkene, as shown in Figure 8.

Recently, \([\text{Ru(CO)}_2(\text{EtCO}_2)]\_n\), an isomerization-decarboxylation catalyst precursor complex, has also been studied. It isomerizes the substrate and then facilitates the decarboxylation without additional co-reagents (Muench et al., 2016; Yang et al., 2016). For 9-cis-octadecenoic acid, the conversion to alkene can be carried out without pre-catalysis at 250 °C and 24 h, while a 36% yield of alkene conversion with 0.10 wt % Ru\_8(CO\_12 was found. A 60% yield of 10-undecenoic acid was achieved under the conditions of 0.89 wt % Ru\_3(CO\_12 at 250 °C and 4 h duration (Muench et al., 2016). Moser et al. (2016) further reported that 77.6% heptadecene and 18.0% heptadecane was obtained by Ru-catalyzed DCX/DCN of fatty acids. There were also other reactions such as the decarboxylation, dehydrogenation, isomerization, hydrogenation, and cyclization/aromatization took place, which made a mixture of predominantly alkenes (Knothe et al., 2017). Doll et al. (2017) calculated and fitted the activation energy of the oleic acid decarboxylation reaction, which was 249 kJ mol\(^{-1}\) (Knothe et al., 2017).

Some transition metal based homogeneous catalysts were proved to be highly active. Iron-based catalysts have been found to be effective catalysts for the DCX/DCN processes. Iron-catalyzed DCX/DCN reactions of fatty acids to \(\alpha\)-olefins (Maetani et al., 2012). The reaction was accelerated by the addition of KI and \(\text{Ac}_2\text{O}\), decarbonylation of stearic acid produced a 79% yield of heptadecenes. \(\text{FeI}_2\) serves a similar function to \(\text{FeCl}_2/\text{KI}\), and \(\text{FeI} (\text{CO})_2\text{Cp}\), can generate a 40% yield in the presence of KI. The proposed mechanism for this is shown in Figure 9. In the first step, acid anhydrides are produced from carboxylic acid and \(\text{Ac}_2\text{O}\) by \(\text{FeCl}_3\), proceeding to iron-carbonyl \(\text{B. KI or Phosphide}\) reacts with CO and 1 to form the active catalytic species A. The DCX/DCN of B then produces the alkyl iron C, which eliminates \(\beta\)-hydroxide into \(\alpha\)-olefins and iron hydride D. D then releases acyl iron A, and hence the cycle is completed. It was also found that D may generate by-products, isomerization olefins.

Additionally, copper-catalyzed decarboxylative alkylamination has also been reported (Cui et al., 2012). The pathways lead to the formation of alcohols, esters, and hydrocarbons to make (E)-alkenes. The results indicated Cu\(^{\text{II}}\) was more active than CuBr\(_2\), CuBr and Cu(OAc)\(_2\)-H\(_2\)O, and the 62% product yield was achieved with 1 mol% Cu. Copper-catalyzed protodecarboxylation of aromatic carboxylic acids was investigated using DFT calculations, as shown in Figure 10. The results indicate that the type [((phen)Cu)]\(^{+}\) is an important precursor for a successful decarboxylation. The calculations showed the species [((phen)Cu)]\(^{+}\) would be formed by coordinating anions or carboxylate ions to Cu(II) via a phenyl anion intermediate. The [((phen)Cu)]\(^{+}\) would be rapidly transmitted, leading to the DCX/DCN or the reactivity of the benzoic acids. Thus, the π-system affects the DCX/DCN.

3. Homogeneous Hydrodeoxygenation (HDO)

Hydrodeoxygenation (HDO) is a process to use hydrogen or hydrogen resources to remove O atoms from compounds. Organometallics are commonly considered as catalysts for the homogeneous catalysis process. However, according to recent reports, the homogeneous Lewis acids have higher activities for the HDO process (see Table 2).

Parks and Piens (1996) have reported firstly that the trispentafluorophenylborane (\(\text{B(C}_6\text{F}_5)_3\)), a homogeneous Lewis acid, can be used for a HDO with a reductant such as silane. These results indicate that Lewis acid complexes such as \(\text{B(C}_6\text{F}_5)_3\) can be used for HDO of carbonyl by reaction with silane, as shown in Figure 11. \(\text{B(C}_6\text{F}_5)_3\) was applied to catalyze HDO of fatty acids and biomass derivatives for alkanes and alkenes (Li et al., 2015). The results showed that the reaction can take place even at room temperature with the reducing agent poly(-methylhydrosiloxane) (PMHS). Dichloromethane and cyclohexane serve as effective solvents. The catalyst system can also be applied to HDO of ketones, aldehydes, ethers, esters, carboxylic acids (Gevorgyan et al., 2001; Chandrasekhar et al., 2002; Nimmagadda and Mcrae, 2006) and even lignin model compounds with Et\(_3\)SiH as the reducing agent (Elias...
and Thibault, 2013). So far, this is the only metal-free method reported for catalyzing the HDO of fatty acids and biomass derivatives to alkanes and alkenes.

Organometallics are effective catalysts for HDO. Some Organometallics have been applied for the catalytic decarboxylation of levulinic acid. The HDO process requires that the homogeneous catalysts must be very stable in water- and acid-media.

The complex ruthenium(II) appears to be water and acid-stable. The complex \([\text{(4-Ph-terpy)} \text{Ru-(H}_2\text{O)}_3\text{]}\text{(OTf)}_2\) (terpy = 2,2',6',2'-terpyridine), and its iridium analogue \([\text{(4-Ph-terpy)} \text{Ir(OTf)}_3\] are active for the HDO of 2,5-hexanediol and 2,5-dimethylfuran. Those complexes have higher oxidation states (+3) than that of the metal–ligand bonds. During the catalytic process, the isoelectronic relationship (RuII/d6 \(\rightarrow\) IrIII/d6) can be altered slightly to complete the cycle (Sullivan et al., 2014). The complexes \([\text{Ru(2,2'-dipicolylamine)(OH}_2\text{]}_2\text{(OTf)}_2\] and \([\text{Ru(6,6'-bis(a-aminomethyl)-2,2'-bipyridine)(OH}_2\text{]}_2\text{(OTf)}_2\] were also found to be active. For the HDO of 2,5-hexanediol, a 94% yield of 2,5-hexanediol or 55% yield of 2,5-dimethyltetrahydrofuran was obtained at 150 °C with H₃PO₄ in H₂O. Also, about 55% 2,5-hexanediol and 23% 2,5-dimethyltetrahydrofuran were converted from 2,5-dimethylfuran at 175 °C.

![Figure 9. Decarbonylation reaction by Fe-based homogeneous catalysts.](image)

![Figure 10. Copper-catalyzed decarboxylative alkenylation.](image)

| Table 2. The HDO by homogeneous catalysts. |
| --- |
| Catalyst | Feedstocks | Catalyst loadings | Time (h) | Temp (°C) | Yield Hydrocarbons | References |
| B(C₆F₅)₃ | tristearin | 5 mol% | 6 | Room Temp | 95% | Li et al. (2015) |
| Cp*Ru(CO)₂Cl₂ | glycol | 10% (mol/mol) | 8 | 170 | 70% | Sullivan et al. (2014) |
| \([\text{(4'-Ph-terpy)} \text{Ru(2,5-Hexanediol)(OTf)}_2\] | 2,5-Hexanediol | 1 mmol/L = 0.1 mol % | 16 | 200 | 96% | Stanowski et al. (2012) |
| \([\text{Pd(2py)Cl)}_2\] | Benzaldehyde | 5% (mol/mol) | 4 | 100 | 90% | Delucia et al. (2018) |
| Ni(COD)₂ | allyl aryl ethers | 20% (mol/mol) | 16 | 80 | 98% | Sergeev et al. (2011) |
| b-diketiminato magnesium | isocyanates | 10 mol% | 1.5 | 60 | 76% | Yang et al. (2017) |
[Cp*Ru(CO)2]2 (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, i.e., η5-C5Me5) has been developed as stable organometallic catalyst. At reaction conditions of 170 °C, 4 atm of H2, 70% hexane was obtained from 1,2-hexanediol (Stanowski et al., 2012). Similar to Decarboxylation/decarbonylation, [Cp*Ru(CO)2]2 serves as precatalyst in these reactions. In addition to the hydride intermediates Cp*Ru(CO)2H (Andrews and Klaeren, 1989) or [Cp*Ru(μ-H4)RuCp*] (Cheng and Bullock, 2002), some alternative redox olefin complexes (Saidi et al., 2010) and reduced-carbon aldehyde complexes (Andrews and Gould, 1991) have also been developed (Clarke et al., 2007). In the typical process, as shown in Figure 12, the hydrodehydroxylation, deoxygenation, and hydrocracking reactions are the main pathways.

The Ru-complex can also be used to upgrade the real bio-oil. Mahfud et al. reported the use of RuCl2(PPh3)3 to upgrade the water-soluble fraction of pyrolysis oil, and 1,2-ethanediol was found to be main product (Mahfud et al., 2007). Huang et al. (2010) also used the Ru-complex for HDO of bio-oil fraction, and observed a dramatic improvement of bio-oil quality. Use of the Ru-complex can significantly promote bio-oil quality, although specific fractions of bio-oil are improved more than others. Additionally, Busetto et al. (2011) achieved the reduction of bio-oil in pyrolysis of white poplar. Thus, there is potential for the application of ruthenium(II) complexes for upgrading the real bio-oil even in mild conditions.

Pd-based organometallics offer the highest selectivity. Wang et al. (2017) reported the HDO of phenols with an ArOSO2F intermediates Pd(OAc)2 complex. In the system, SO2F2 was observed to produce aryl fluorosulfates which then underwent Pd(cat.)/Et3N/HCO2H mediated hydrogenation to the arene products (Wei et al., 2004; Zhu et al., 2015; Chen et al., 2016). When DMSO was used under optimal conditions, a 99% yield was achieved. A possible mechanism (Peter et al., 2010) is shown in Figure 13. In the first step, phenol 1 reacts with SO2F2 to form intermediate 2, then intermediate 2 forms ArLnPdOSO2F II by Pd(0) catalysis. The intermediate III is subsequently generated from the reaction of FSO2OCH3 with HCOO(-), releasing CO2 to produce intermediate IV. Lastly, arene 3 can be produced from intermediate IV, releasing the Pd(0) complex. [Pd(tpy)(Cl)2][Ni(tpy)][PF6]2 has been also observed to be active in the hydrodeoxygenation of model lignin monomers (Delucia et al., 2018). The Pd-tpy catalyst exhibited excellent selectivity during hydrodeoxygenation towards benzyl alcohol, C6H5CHO and (C6H5)2CO. An almost complete conversion of benzyl alcohol to the desired toluene could be achieved at 100 °C and 20 bar H2.

Some transition metals can also be used in the organometallic complexes. Ni-SiPr system (Sergeev and Hartwig, 2011) is an effective approach, in which the complexes from Ni(COD)2 (COD, 1,5-cyclooctadiene) and PCy3 (Cy, cyclohexyl) may have good selectivity on the HDO of Aryl Ethers. Additionally, the nickel carbene complex can convert aromatic C-O bonds into arenes and alcohols at 80–120 °C. Some forms of nickel complexes use N-heterocyclic carbene (NHCs) as active sites, which can achieve 85% yields of toluene and o-cresol. The Ni-SiPr system (Dankwardt, 2004; Guan et al., 2008; Mamoru et al., 2008) provides a new approach for the HDO of aromatic C-O compounds.

Recently, homogeneous magnesium catalysts have been studied for use in HDO reactions (Arrowsmith et al., 2011; Mukherjee et al., 2014; Lampland et al., 2015). Yang et al. (2017) used a b-diketiminato magnesium catalyst for the HDO of isocyanate at 60 °C over 1.5 h, and a 76% conversion rate was achieved. They postulated a generic mechanism for the HDO of phenols with an ArOSO2F intermediates Pd(OAc)2 complex. In the system, SO2F2 was observed to produce aryl fluorosulfates which then underwent Pd(cat.)/Et3N/HCO2H mediated hydrogenation to the arene products (Wei et al., 2004; Zhu et al., 2015; Chen et al., 2016). When DMSO was used under optimal conditions, a 99% yield was achieved. A possible mechanism (Peter et al., 2010) is shown in Figure 13. In the first step, phenol 1 reacts with SO2F2 to form intermediate 2, then intermediate 2 forms ArLnPdOSO2F II by Pd(0) catalysis. The intermediate III is subsequently generated from the reaction of FSO2OCH3 with HCOO(-), releasing CO2 to produce intermediate IV. Lastly, arene 3 can be produced from intermediate IV, releasing the Pd(0) complex. [Pd(tpy)(Cl)2][Ni(tpy)][PF6]2 has been also observed to be active in the hydrodeoxygenation of model lignin monomers (Delucia et al., 2018). The Pd-tpy catalyst exhibited excellent selectivity during hydrodeoxygenation towards benzyl alcohol, C6H5CHO and (C6H5)2CO. An almost complete conversion of benzyl alcohol to the desired toluene could be achieved at 100 °C and 20 bar H2.

Some transition metals can also be used in the organometallic complexes. Ni-SiPr system (Sergeev and Hartwig, 2011) is an effective approach, in which the complexes from Ni(COD)2 (COD, 1,5-cyclooctadiene) and PCy3 (Cy, cyclohexyl) may have good selectivity on the HDO of Aryl Ethers. Additionally, the nickel carbene complex can convert aromatic C-O bonds into arenes and alcohols at 80–120 °C. Some forms of nickel complexes use N-heterocyclic carbene (NHCs) as active sites, which can achieve 85% yields of toluene and o-cresol. The Ni-SiPr system (Dankwardt, 2004; Guan et al., 2008; Mamoru et al., 2008) provides a new approach for the HDO of aromatic C-O compounds.

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HDO with b-diketiminato magnesium catalysis (Figure 14). In this pathway, the magnesium hydride first generates formamidate and borate intermediates. The borate intermediate then reacts with the Lewis acid HBpin and the boron is transferred to the magnesium hydride. Additionally, other compounds will be consumed by the B–H/Mg–O complex, producing R(pinB)NCH2-OBpin, which releases species 6 and 4 for the catalytic cycle.

All in all, some single-site homogeneous catalytic systems are able to provide selective HDO reactions, which shows promise for finding new ways of forming valuable products under mild conditions. It should, however, be noted that recovery of the homogeneous catalyst is still difficult. Some new recycling methods for environmental-friendly or cost-effective processing are encouraging, but need to be further explored to overcome these difficulties.

4. Conclusions and prospective

Significant progress has been made in recent years regarding the methods, materials, and mechanistic study of homogeneous catalytic deoxygenation reactions for high-value products. Due to the difference between bio-crude and conventional crudes, the homogeneous catalysis of DCX/DCN and HDO have provided a new direction. Classic radical reactions of DCX/DCN such as Barton decarboxylation, the Henkel reaction, and the Hunsdiecker and Kochi reaction proceed via free radicals, which have lower selectivities. Organometallic precursor catalysts and organometallic complexes such as trispentafluorophenylborane (B(C6F5)3), [Cp*Ru(CO)2]2, [Pd(tpy)Cl]Cl, Ni(COD)2 and B–H/Mg–O complexes can achieve high DO activity and selectivity at mild conditions, which can improve crude bio-oil quality significantly.

Currently, the most common experimental processes are still set at batch scale. The scale-up process is likely to drastically alter the kinetics and mass transfer, meaning that the efficiencies and selectivities of products observed at batch scales may no longer be relevant. To overcome this limitation, the use such as external stimuli should be investigated in specific processes for kinetic control. Additionally, the problem of catalyst recovery also needs further investigation before these processes can be practical.

Declarations

Author contribution statement

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Additional information

No additional information is available for this paper.
