

Green Chemistry and Sustainable Technology

Marcel Schlaf  
Z. Conrad Zhang *Editors*

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# Reaction Pathways and Mechanisms in Thermocatalytic Biomass Conversion II

Homogeneously Catalyzed  
Transformations, Acrylics from Biomass,  
Theoretical Aspects, Lignin Valorization  
and Pyrolysis Pathways

 Springer

# Green Chemistry and Sustainable Technology

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Editors

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Acrylics from Biomass, Theoretical Aspects,  
Lignin Valorization and Pyrolysis Pathways

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# Preface

Short carbon chain molecules ( $C_2$ – $C_9$ ) obtained either directly from sugars, the hydrolysis of starch, or preferably by the controlled breakup of lignocellulosic biomass into soluble components are the only conceivable sustainable source of carbon on the planet that could ultimately replace the fossil hydrocarbons that currently form the base of the chemical industry and hence our technological civilization at large. In particular, the production of polymer components and polymers that are chemically or at least functionally equivalent to those derived from the refining of crude oil would offer ecologic and environmental as well as economic advantages.

The use of sugars, starch, and ultimately lignocellulosic biomass, i.e., forestry (e.g., wood and bark chips, etc.) and agricultural (e.g., straws, husks, stovers, etc.) residues, as a renewable carbon resource will, however, require careful life-cycle analyses of the processes involved. This in turn is critically dependent on a deep and detailed understanding of the mass and energy flows in these processes and hence their mechanisms at the molecular level. Almost “by definition” these processes will have to be catalytic in nature to be ecologically sustainable and economically viable.

The development of new catalysts and catalytic processes that are specifically designed for and adapted to the unique properties of the biomass-derived carbon substrates poses a unique challenge. Due to the abundance of oxygen-containing functional groups, the pentose and hexose sugars and their furanic condensates obtainable from (hemi-)cellulose as well as the phenol propanoid units of lignin are characterized by a high polarity and reactivity that is very different – one could say almost opposite – to that of the traditionally employed alkane and arene sources available from refined crude oil. The fundamental study of the reaction cascades and mechanisms involved in the transformation of oxygenated biomass to value-added chemicals is the first step to meet this challenge.

Focusing on the use of thermochemical and acid-/base- or metal-catalyzed processes only, the two volumes of this book attempt to give an overview of and insights into the specific aspects of this challenge as perceived and formulated by expert contributors research-active in this field.

Volume I is comprised of chapters that address the nanoscale structure of lignocellulose, the application of acid-base reactions and catalysts to the depolymerization of cellulose, the use of heterogeneous hydrogenation catalysts for its direct conversion to polyols, as well as chapters that explore pathways for the metal-catalyzed dehydration and oxidation of sugars and sugar alcohols to furans and carboxylic acids, respectively.

The chapters of Volume II cover the hydrodeoxygenation of sugar-derived substrates by homogenous catalysts systems; the valorization of carboxylic acids, notably lactic acid and its derivatives; a theoretical approach to the elucidation of the conversion pathways of sugars and sugars condensates and their decomposition to humins; as well as mechanistic and practical aspects of the conversion and pyrolysis of lignin to functionalized monocyclic aromatics and the pyrolysis of biomass to synthesis gas.

We hope that the insights provided by the different and varied perspectives offered here will convince the readers that a switch to renewable biomass as a key carbon source for the chemical industry will be feasible and does indeed offer a way forward to a more sustainable future.

Guelph, Canada  
Dalian, China

Marcel Schlaf  
Z. Conrad Zhang

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# Chapter 1

## Deoxydehydration (DODH) of Biomass-Derived Molecules

Shuo Liu, Jing Yi, and Mahdi M. Abu-Omar

**Abstract** Deoxygenation of vicinal diols and polyols, common moieties in biomass-derived molecules, represents an important chemical pathway for making chemicals from renewable biomass resources. Catalytic deoxydehydration (DODH) is a promising deoxygenation reaction that removes two adjacent hydroxyl (–OH) groups from vicinal diols in one step to generate alkenes. Since the first catalytic DODH with  $\text{Cp}^*\text{Re}(\text{O})_3$  report by Cook and Andrews in 1996, a number of metal complexes based on rhenium, ruthenium, vanadium, and molybdenum have been investigated. High-valent oxorhenium complexes are among the most efficient catalysts for DODH reactions and have been studied using various reductants including organic phosphines, molecular hydrogen ( $\text{H}_2$ ), sulfite, and alcohols. These complexes exhibit intriguing oxophilic performance, which facilitates selective C–O bond cleavage of polyols. A flurry of investigations have appeared in the literature over the past few years on the scope and mechanism of the DODH reaction in the context of biomass conversion and sustainable chemistry. In this chapter, we briefly review the development of DODH reactions with a focus on homogenous Re-catalyzed transformations. Several heterogeneous and other metal catalysts are included for comparison.

**Keywords** Biomass • Deoxygenation • Deoxydehydration • Sustainable chemistry • Polyols • Rhenium • Alkenes

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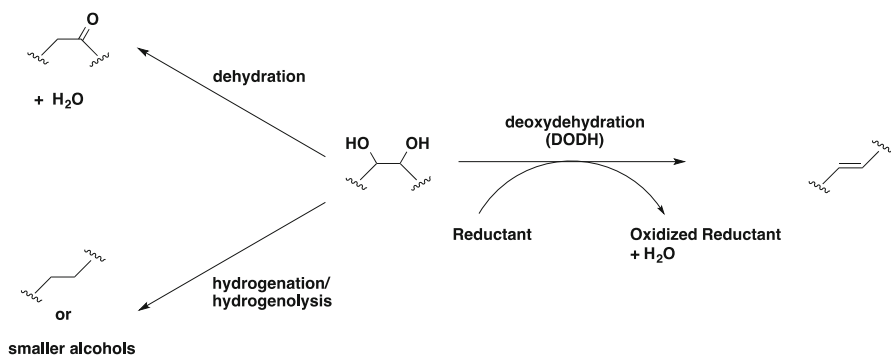
## 1.1 Introduction

Biomass-derived molecules can be used as a sustainable platform feedstock to produce high-value chemicals (HVCs) and biofuels [1–6]. Since carbohydrates, the major component of biomass, contain one oxygen atom per carbon, deoxygenation of carbohydrates and their derivatives such as sugar alcohols (polyols) represents a major path forward for making renewable compounds that can potentially replace petroleum-based chemicals. Current deoxygenation methods include high-temperature pyrolysis [7–9], acid-catalyzed dehydration [10–13], hydrogenolysis reactions [14, 15], and deoxydehydration (DODH) reactions (Fig. 1.1). This chapter focuses on deoxydehydration (DODH), which removes two adjacent hydroxyl (–OH) groups from vicinal diols in one step and represents an efficient approach to making olefins from renewable feedstock [16, 17].

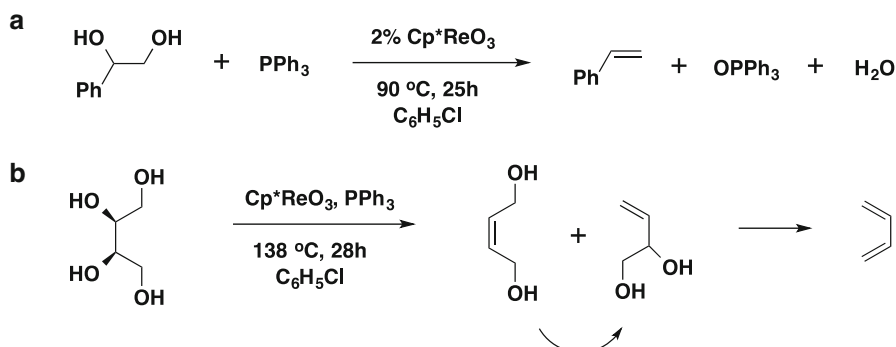
## 1.2 DODH of Diols and Polyols Catalyzed by Rhenium Complexes

### 1.2.1 High-Valent Oxorhenium and Rhenium Carbonyl Catalysts

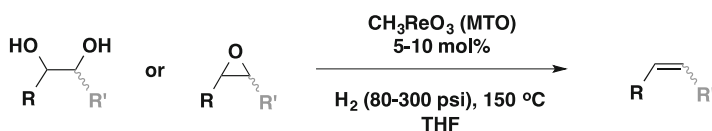
In a typical DODH reaction, the substrate (vicinal diol or polyol) is reduced to produce an alkene or allylic alcohol, while a reducing agent is oxidized via oxygen atom transfer (OAT). Rhenium complexes are among the most efficient and well-studied catalysts. Cook and Andrews reported in 1996 the first catalytic DODH of aromatic diols catalyzed by  $\text{Cp}^*\text{ReO}_3$ , employing stoichiometric amount of  $\text{PPh}_3$  as the reducing agent (Fig. 1.2a) [18]. The conversion was quite low; nevertheless, the addition of Brønsted acid enhanced the rate of reaction significantly. In the presence of *p*-toluenesulfonic acid ( $\text{TsOH}$ ), glycerol was reduced to allylic alcohol using



**Fig. 1.1** General strategies for deoxygenation of biomass-derived sugar alcohols (polyols)



**Fig. 1.2** DODH reactions of aromatic diol (**a**) and erythritol (**b**) catalyzed by  $\text{Cp}^*\text{ReO}_3$  employing  $\text{PPh}_3$  as a reductant



**Fig. 1.3** DODH/deoxygenation of diols and epoxides by MTO using  $\text{H}_2$

$\text{Cp}^*\text{ReO}_3$ ,  $\text{PPh}_3$ , and chlorobenzene in biphasic medium at 125 °C. When unprotected tetritol was used as substrate in this system, the main product was the fully deoxygenated butadiene (80 % yield), with the rest as 3-butene-1,2-diol and cis-2-butene-1,4-diol in an 85:15 ratio (Fig. 1.2b). The cis-2-butene-1,4-diol isomerized to 3-butene-1,2 diol under the catalysis conditions. Previously, the Gable [19–25] and Herrmann groups [26, 27] independently synthesized and characterized a number of oxorhenium(V) diolate complexes, investigated alkene extrusion from rhenium diolate complexes, and shed light on the mechanistic pathway of these reactions. The mechanism of the DODH reaction of diols by oxorhenium was suggested to proceed through three steps: (1) reduction of  $\text{Cp}^*\text{ReO}_3$  by phosphine to generate  $\text{Cp}^*\text{ReO}_2$ , (2) diol condensation with  $\text{Cp}^*\text{ReO}_2$  to generate  $\text{Re(V)}$ -diolate intermediate and water, and (3) extrusion of alkene from the  $\text{Re(V)}$ -diolate to regenerate  $\text{Cp}^*\text{ReO}_3$  and complete the catalytic cycle.

In 2009 the Abu-Omar group reported on methyltrioxorhenium (MTO)-catalyzed DODH/deoxygenation of vicinal diols and epoxides to alkenes and alkanes with the more practical reductant  $\text{H}_2$  (Fig. 1.3) [28]. Under lower  $\text{H}_2$  pressure, the products were dominated by alkenes, whereas under higher pressure, by the alkane. This indicated an extension of the DODH reaction to generate saturated products. Several biomass-derived substrates were also tested in the system. 1,4-anhydroerythritol, formed by acid-catalyzed ring closure of erythritol, yielded 25 % 2,5-dihydrofuran and 5 % tetrahydrofuran. However, erythritol gave significant charring. The authors also noted that only cis-cyclohexane diol gave the desired products, while trans-

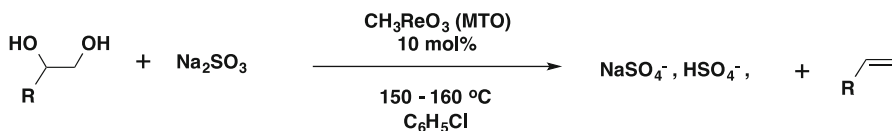


Fig. 1.4 DODH of diols by MTO using sulfite

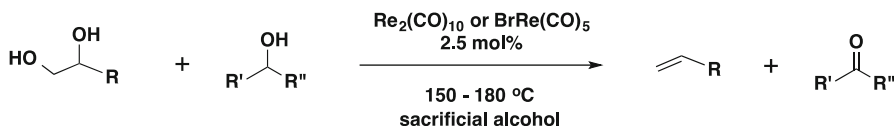


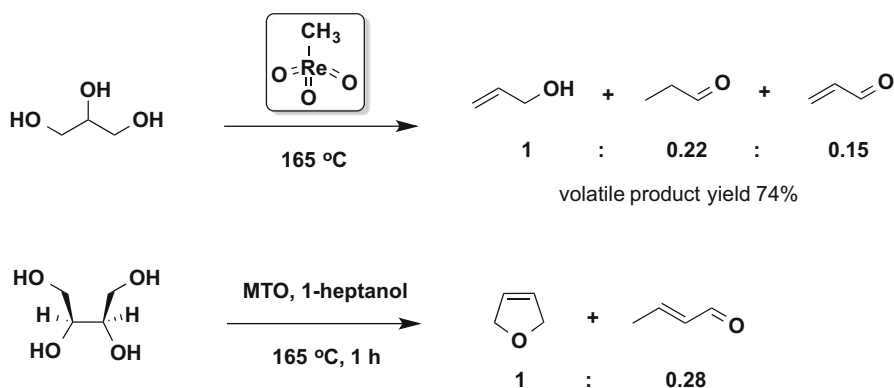
Fig. 1.5 DODH of diols by rhenium-carbonyl complexes in the presence of sacrificial alcohol

cyclohexane diol did not react, consistent with observations in other reports [18]. The specific stereoselectivity indicates the formation of a metal diolate intermediate, which would require *cis*-vicinal diols in the two adjacent hydroxyl groups.

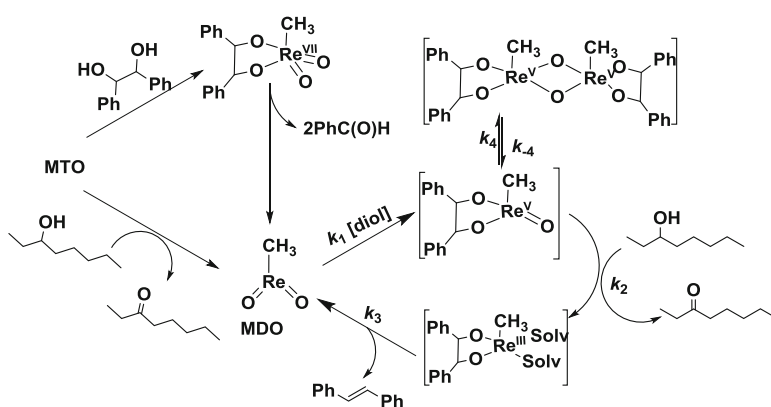
Soon afterwards, the Nicholas group reported MTO and perrhenate salts catalyzed DODH of diols using sulfite as the reductant (Fig. 1.4) [29, 30]. Both aromatic and aliphatic diols were converted to the corresponding alkenes with good to moderate yields, while the latter required longer reaction times. Addition of the crown ether 15-crown-5 as a phase transfer agent was found to significantly shorten the reaction time and increase conversions.  $[\text{NBu}_4][\text{ReO}_4]$  was a superior catalyst to MTO under these conditions in terms of conversion of erythritol. 1,3-butadiene (27 % yield), 2,5-dihydrofuran (6 % yield), and *cis*-2-butene-1,4-diol (3 % yield) were obtained using  $[\text{NBu}_4][\text{ReO}_4]$  as the catalyst, while substantial charring was observed for MTO.

The Bergman group employed rhenium carbonyl as the catalyst ( $\text{Re}_2(\text{CO})_{10}$  or  $\text{BrRe}(\text{CO})_5$ ) and a secondary alcohol as solvent and reductant (Fig. 1.5) [31]. In the presence of simple alcohols such as 3-octanol or 5-nonanol, both terminal and internal vicinal diols were deoxygenated to olefins with good yields, and a stoichiometric amount of the alcohol was oxidized to the corresponding ketone. In the presence of TsOH, erythritol could be converted to 2,5-dihydrofuran (62 % yield). Interestingly, the system required air and high temperature for activation, which indicated that the actual active catalyst is probably an oxidized rhenium species and shares a similar reaction mechanism with high-valent oxorhenium complexes.

Our group applied the MTO-catalyzed DODH reaction to glycerol, under either neat conditions or in the presence of a sacrificial alcohol (Fig. 1.6) [32]. The substrate, glycerol, participated in transfer hydrogenation and deoxygenation to form volatile products, for example, allyl alcohol, propanal, and acrolein, leaving the nonvolatile dihydroxyacetone (DHA) as by-product in the residual liquid reaction mixture. Under neat conditions, the glycerol itself can function as reductant. Utilization of  $\text{NH}_4\text{ReO}_4$  as the catalyst gave similar results to MTO, with allyl alcohol as the major product. The addition of acid ( $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$ ) increased the conversion rate and yield.



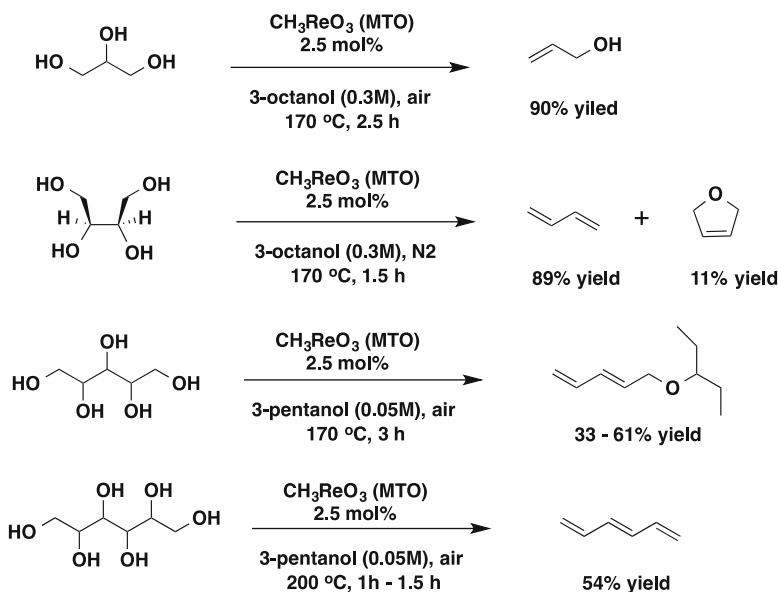
**Fig. 1.6** Rhenium-catalyzed DODH reactions of neat glycerol and erythritol



**Fig. 1.7** Mechanism of the major pathways for MTO-catalyzed DODH reaction of vicinal diols in the presence of sacrificial alcohol

We have also investigated the MTO-catalyzed DODH reaction with sacrificial alcohol as reductant and proposed a reaction mechanism based on detailed kinetics and spectroscopic studies [33]. The reaction kinetics were zero order in [diol] and half order in [MTO]. The different induction periods of MTO and MDO (methyldioxorhenium(V)) indicated that the active form of the catalyst was MDO, which was formed by reduction of MTO by alcohol or via a novel C-C bond cleavage of an MTO-diolate complex. The rate-determining step involved reaction with alcohol, and the majority of the MDO-diolate complex was present in dinuclear form, giving rise to the  $[\text{Re catalyst}]^{1/2}$  (half-order) dependence. Furthermore, the Re(V)-diolate did not extrude alkene at rates that are consistent with the catalytic rate unless a reductant was present. Thus we proposed a catalytic cycle in which MDO-diolate was reduced further by 3-octanol to a transient rhenium(III) diolate, which was responsible for alkene extrusion and regeneration of MDO (Fig. 1.7). It





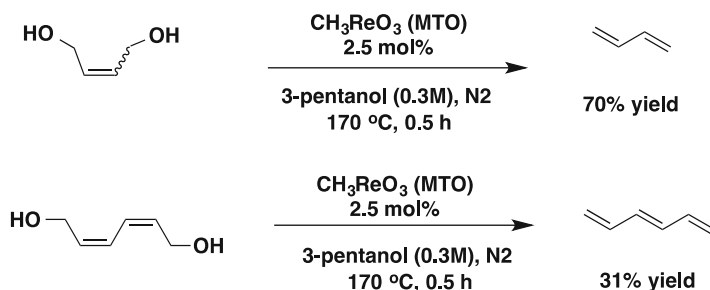
**Fig. 1.8** DODH reactions of  $\text{C}_3$ - $\text{C}_6$  sugar alcohols catalyzed by MTO

is worth noting that depending on the reducing agent, the rate-limiting step may shift under different conditions.

The reaction mechanism(s) of the MTO-catalyzed DODH of diols was also investigated by density functional theory (DFT) calculations [34, 35]. The DFT results supported the original reaction mechanism proposed by Gable and Cook, alkene extrusion from rhenium(V) diolate being the key rate-determining step.

The Toste group extended the reaction scope to larger sugar alcohols and sugars, demonstrating the general efficiency and high selectivity of DODH [36, 37].  $\text{C}_3$ - $\text{C}_6$  sugar alcohols can be readily obtained by pretreatment of naturally abundant sugars, such as hydrogenation, fermentation, and decarbonylation. These sugar alcohols were converted to the corresponding olefinic products with good yields using either secondary alcohols or primary alcohols (1-butanol) as reductants, albeit the former is more favorable than the latter (Fig. 1.8). The linear alkene products can be used as drop-in chemicals because they can serve as precursors for polymers and fuels that are already in use in the chemical industry. MTO displayed a higher activity than rhenium-carbonyl complexes previously reported by the Bergman group. When using a primary alcohol as the reducing agent, rhenium-carbonyl catalysts didn't generate any product, while high-valent oxorhenium complexes afforded alkene products with high yield and selectivity.

Following their initial work (Fig. 1.8), Toste and Shiramizu expanded the reaction to 1,4-DODH and 1,6-DODH via tandem [1, 3]-OH shift-DODH process [36]. This process merged different reaction intermediates into one product and thereby increased product selectivity, providing a new strategy for DODH reaction development for real biomass-derived sugar conversion (Fig. 1.9). The reaction was also



**Fig. 1.9** 1,4-DODH and 1,6-DODH reactions via tandem [1, 3]-OH shift-DODH process

applied to the conversion of sugar acids into unsaturated esters, employing  $\text{HReO}_4$  as both DODH catalyst and Brønsted acid. The DODH/acid dual-catalyst strategy was applied to produce plasticizer precursors from tartaric acid and erythritol.

### 1.2.2 Heterogeneous Rhenium Catalysts

There are few reports on heterogeneous DODH reactions. Jentoft and Nicholas reported on heterogeneous polyol-into-olefin DODH reactions catalyzed by carbon-supported perrhenate, employing both  $\text{H}_2$  and hydrogen-transfer reductants with moderate yield [38]. Interestingly, in 2011 the Schlaf group reported that stainless steel reactors could catalyze the deoxygenation of glycerol and levulinic acid in aqueous acidic medium [39]. Ferdi Schuth reported an iron oxide-catalyzed conversion of glycerol to allylic alcohol and proposed a mechanism through dehydration and consecutive hydrogen transfer [40]. Andreas Martin also reported glycerol deoxygenation reaction in the gas phase using a series of heteropolyacid catalysts [41].  $\text{Ir-ReOx/SiO}_2$  was also reported as the catalyst for the production of butanediol from erythritol via hydrogenolysis, by the Tomishige group [42]. More recently, Nicholas reported on deoxydehydration of glycols using heterogeneous elemental reductants such as zinc, iron, manganese, and carbon [43]. The molecular identity of the catalyst is more difficult to discern in these systems and the contribution from the metal surface in the reactor per Schlaf's study remains an open question. Nevertheless, these studies demonstrate the feasibility to translating the DODH reaction into a more practical process in which continuous fluidized bed reactors can be employed.

## 1.3 Other Transition Metal Catalysts for DODH

In addition to rhenium, other transition metal complexes based on vanadium [44], molybdenum [45, 46], and ruthenium [47, 48] have been used in DODH of vicinal diols. Nicholas reported a DODH reaction of diols to olefins catalyzed by

inexpensive metavanadate ( $\text{VO}_3^-$ ) and chelated dioxovanadium derivatives, with phosphine or sulfite as reductants [44]. Dioxomolybdenum(VI) complexes with acylpyrazolonate ligands were synthesized by the Pettinari group, and these complexes showed moderate activity toward diol DODH reactions with  $\text{PPh}_3$  as reductant [45]. The Frisrup group also reported another DODH reaction catalyzed by a series of Mo-oxo complexes under neat conditions [46]. In addition, Schlaf and Bullock have pioneered the use of organometallic ruthenium catalysts for the deoxygenation of alcohols [49, 50]. Two other Ru-catalyzed DODH reactions were reported by Srivastava and Nicholas, independently, using  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2$  or Ru(II)-sulfoxides as catalysts for hydrodeoxygenation (HDO) and hydrocracking of diols and epoxides [47, 48].

## 1.4 Conclusion

As one of the promising strategies to selective removal of oxygen atoms from biomass-derived molecules, DODH shows tremendous potential to producing important fine and commodity chemicals from renewable feedstock. Compared to conventional deoxygenation methods such as hydrogenation and hydrogenolysis, the advantages of DODH reaction are that the products are deoxygenated while remaining synthetically versatile through the retention of a double bond, making the most use of every atom in biomass. The successful development of stable and highly active homogenous and heterogeneous catalysts provides access to various synthetic procedures to produce specific molecules with tailored properties to be used as drop-in chemicals for making polymers and other useful products. However, many challenges remain in utilizing biomass-derived molecules and feedstock. Some of these challenges include the ability to use carbohydrates and polysaccharides directly and developing cost-effective, efficient, and active earth-abundant catalysts that can be employed under continuous reaction conditions with facile product/catalyst separation.

**Acknowledgment** Our research in deoxygenation of biomass-derived molecules has been support by the Department of Energy (DOE), Basic Energy Sciences (BES) grant no. DE-FG-02-06ER15794.

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