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Transition Metal-Catalyzed Deoxydehydration: Missing Pieces of the Puzzle

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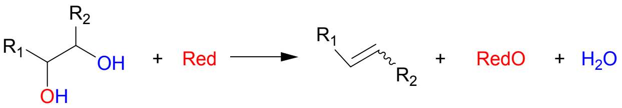
Abstract

Deoxydehydration (DODH) is a transformation that converts a vicinal diol into an olefin with the help of a sacrificial reductant. The reaction has drawn interest in the past 25 years for its potential to upgrade polyols from biomass to chemicals or fuels. This minireview is organized in 7 sections, and, while providing a comprehensive survey of the literature in tabular form, focuses on aspects that are not extensively discussed in prior reviews. The first three brief sections consist of an introduction to DODH, followed by an overview of present research thrusts and a listing of prior reviews and the patent literature. The fourth section addresses reaction thermodynamics. The fifth section provides a survey of catalysts investigated for DODH, most of which are rhenium, molybdenum, and vanadium compounds. These catalysts have been used in heterogeneous and homogenous catalysis alike. The catalyst compositions are discussed including the effect of counterions that are not part of the active metal moiety. The sixth section reviews rate laws that have been formulated and the steps identified as rate controlling, which are mostly olefin extrusion or catalyst reduction. In this context, the somewhat mysterious trends among alcohol reductants are inspected. It emerges that the DODH field would benefit from benchmark reactions that will quantitatively connect the collected catalytic data. The seventh section considers phase chemistry, separations, and energy input.

1. Introduction

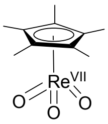
Deoxydehydration is a reaction that converts a vicinal diol into an olefin, as illustrated in Scheme 1. The term deoxydehydration (DODH) captures the fate of the atoms in the two removed OH groups; DODH is characterized by the abstraction of an oxygen with the help of reductant and the simultaneous formation of a molecule of water. The reductant, while needed in stoichiometric quantities, is flexible within certain boundaries.



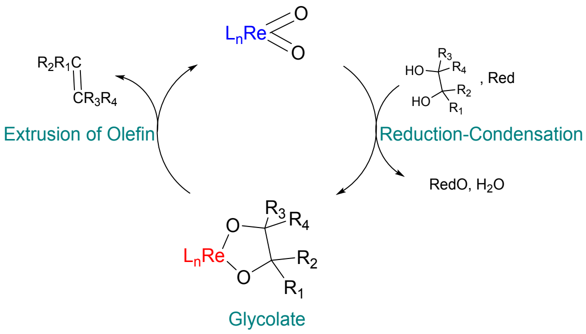
Scheme 1: Deoxydehydration of a vicinal diol to an olefin, using an oxygen-abstracting reductant.

Formally, the transformation is a removal of two OH groups or a didehydroxylation. Early reports of this type of overall transformation, that is, from diol to olefin, date back more than a century, when Sabatier and Gaudion[1] reported allyl alcohol as one of the products from conversion of glycerol on copper. Over the past century, various attempts have been made to achieve such transformations. The historic development of DODH, including a discussion of related catalytic and non-catalytic chemistries, some of which are named transformations, was recently laid out by Tshibalonza and Monbaliu.[2]

Two factors promoted a recent heightened interest in this chemistry. First, Cook and Andrews[3] introduced the *catalytic* deoxydehydration of diols and polyols to alkenes and allylic alcohols. The authors used a rhenium complex, (η^5-pentamethylcyclopentadienyl)trioxidorhenium, $Re(C_5Me_5)O_3$, as catalyst (Scheme 2). The stoichiometric reductant was triphenylphosphane (PPh_3, former name triphenylphosphine). It is worth noting that there was significant prior work by other groups on the relevant individual steps of the reaction, however, without closing a catalytic cycle. Gable and coworkers investigated the association of rhenium complexes with diols to give rhenium diolates (also referred to as rhenium glycolates)[4] and the extrusion of alkenes from such complexes.[5–7] They had also published on the reverse reaction, the transformation of alkenes to diols.[8,9] Gable and Ross[10] expressly attribute the catalytic transformation to Cook and Andrews. The simplified catalytic cycle in Scheme 3 shows how combining catalyst, diol, and reductant ultimately produces a diolate with the metal in an oxidation state that is lower by 2. The catalyst is recovered by olefin extrusion.

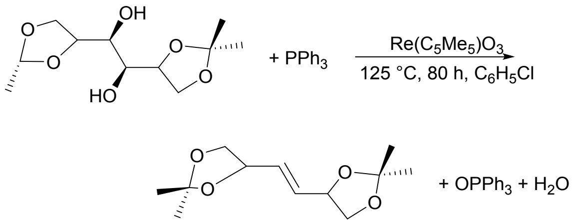


Scheme 2: (η^5-Pentamethylcyclopentadienyl)trioxidorhenium used by Cook and Andrews[3] as catalyst for deoxydehydration.



Scheme 3: Simplified deoxydehydration catalytic cycle with rhenium complex. Steps leading to glycolate formation are lumped for simplicity. Olefin extrusion leads to reoxidation of the catalyst, which changes its valence by +/-2 in the cycle.

Cook and Andrews found the reaction to be stereospecific, that is, 1,2:5,6-diisopropylidene-D-mannitol gave the corresponding *trans*-alkene (Scheme 4). The reaction may also be deemed regioselective, as the double bond appears between the carbon atoms that initially bear the two hydroxy groups.



Scheme 4: DODH of 1,2:5,6-diisopropylidene-D-mannitol to *trans*-olefin using $Re(C_5Me_5)O_3$ as catalyst, triphenylphosphane as reductant, and chlorobenzene as solvent. As reported by Cook and Andrews.[3]

The second factor promoting interest in DODH has been an enhanced need for sustainable production of fuels and chemicals, which triggered research on biomass use and conversion. Glycerol (propane-1,2,3-triol) became available in large quantities as a byproduct of biodiesel, a first-generation biofuel; and routes were sought to convert glycerol to chemicals, for example to allyl alcohol (prop-2-ene-ol).[11,12] More recently, motivation for DODH stems from the attempt to use the carbohydrate fraction of lignocellulosic biomass, which poses the challenge to transform the large number of OH groups present in sugars and sugar alcohols into other functionalities.

As a result of the power of DODH to deoxygenate polyols, the number of publications on DODH has been rapidly increasing in the past decade. We start this mini-review with a brief survey of the three main components in catalytic DODH – the catalyst, the substrate, and the reductant –, followed by a guide to previous reviews and the patent literature. We then present a catalyst survey and focus the subsequent discussion on selected aspects of DODH not extensively addressed in prior reviews.

2. Brief Survey of Main Research Thrusts

2.1 Development of new catalysts

The efforts to develop new catalysts include expansion of the family of rhenium complexes. Because the extrusion of an olefin from a diolate leads to oxidation of the metal with an increase of valence by two and formation of a dioxido complex (Scheme 3), many compounds used as starters of the catalytic cycle are characterized by the dioxido structural motif. Common commercially available materials with this motif include perrhenate ReO_4^- as salt or acid and methyltrioxidorhenium $ReCH_3O_3$.

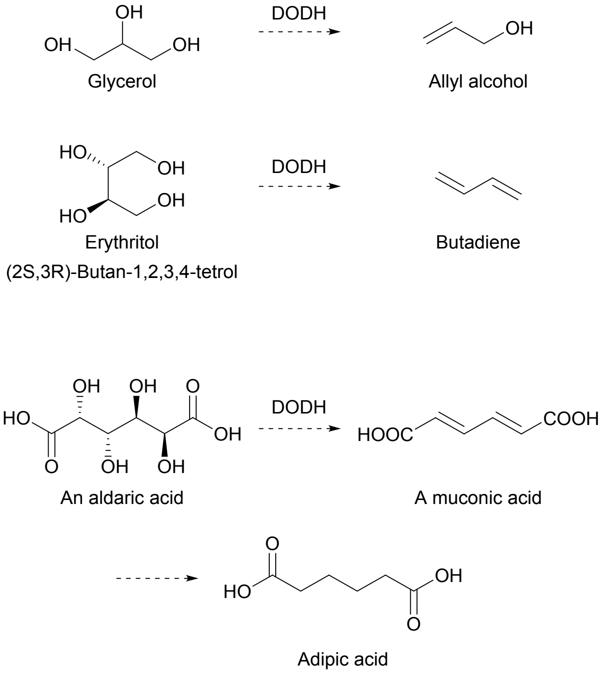
Given the rarity and resulting high price of rhenium, alternatives are being sought. Some successes were achieved using complexes of molybdenum or vanadium, including molybdates and vanadates in analogy to using perrhenate.

Another significant area is the development of solid catalysts for DODH for both liquid and vapor phase application. The most common approach has been to support coordination compounds of rhenium, molybdenum, or vanadium with known DODH activity on typical solid catalyst supports, such as activated carbon,[13] silica, metal oxides,[14] or zeolites.[15] Bulk solid catalysts have also been reported.[16] In liquid-phase applications, leaching of the active component to various extents has emerged as an issue, and the leached species have been found to be active.[13,17] Interestingly, some literature indicates that the soluble coordination compounds used for homogeneous catalysis may not be the active species; rather, solids formed from these compounds during an induction period may be the active species.[18] Consequently, the shares of heterogeneous and homogeneous contributions to the overall conversion may vary and be difficult to determine.[17]

Finally, bifunctional catalysts have been introduced for use with reductants that will otherwise not readily engage in the DODH cycle. Specifically, noble metals have been used in conjunction with molecular hydrogen H_2 as a reductant;[19–23] however, care must be taken not to hydrogenate the olefinic product (unless that is desired).

2.2 Expansion of substrate scope

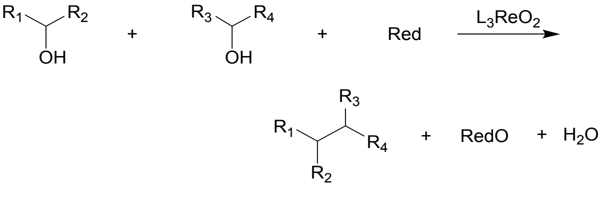
A wide array of substrates has been tested for DODH, and they can be loosely grouped into several overlapping categories by the motivation to investigate them. The transformations of some substrates are of interest because of potential commercial application, that is, the substrate is readily available or expected to become so, for example from biomass, and an interesting target product can be obtained. Examples are given in Scheme 5. In addition to glycerol as starting compound for allyl alcohol, tetritols such as erythritol are interesting for manufacture of butadiene, and C6 aldaric acids (which are dicarboxylic acids obtainable through aldose sugar oxidation) can serve as precursors of muconic acids, which in turn are precursors for adipic acid and, ultimately, nylon.



Scheme 5: Three examples of possible application of DODH to produce commercially interesting compounds from glycerol, erythritol, or aldaric acids.

Another group of substrates are model diols that are used to demonstrate the substrate scope and functional group tolerance of DODH, for example alkane diols, styrenediol (1-phenyl-1,2-ethanediol), sugars, and sugar acids and their esters. Several diols have been chosen to demonstrate characteristics of the DODH mechanism, specifically stereospecificity. These include diols with chiral carbons and cyclic diols, which have reduced flexibility regarding the relative orientation of the vicinal OH groups depending on ring size. A few diols are simply practical for laboratory DODH tests because of their solubility or volatility, and the volatility of the product. These properties facilitate conducting the DODH either in the liquid or in the vapor phase and make recovery and detection of the product convenient. For example, 2,3-butanediol has been used for vapor-phase catalysis,[24] whereas longer 1,2-alkane diols between C6 to C14 are commonly used as test reactants in liquid-phase DODH catalysis.

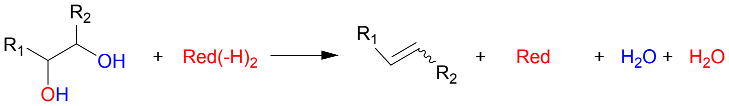
It is also possible to use DODH as an intermolecular reaction between two alcohols instead of an intramolecular transformation of a vicinal diol.[25,26] In the reductive coupling, a single bond results, as illustrated in Scheme 6.



Scheme 6: Reductive coupling of two alcohols via DODH

2.3 Exploration of feasible reductants

DODH requires a stoichiometric amount of reductant for the deoxygenation. The reductant oxidation significantly contributes to thermodynamic feasibility of DODH, and the reductant must be able to engage with a species in the catalytic cycle. Many reductants have been successfully employed, with most of them falling into one of two categories. As shown in from Scheme 1, oxygen may be abstracted by the reductant, and the first reported catalytic DODH relied on a reductant of this category, triphenylphosphane. Alternatively, the reductant may transfer hydrogen to produce a second molecule of water, as illustrated in Scheme 7. The diol substrates as alcohols are able to transfer hydrogen and belong to this category, that is the substrate can (and may to a significant extent) act as a reductant. Therefore, DODH can be and has been conducted without addition of an external reductant,[27] although yields are then limited to 50%.

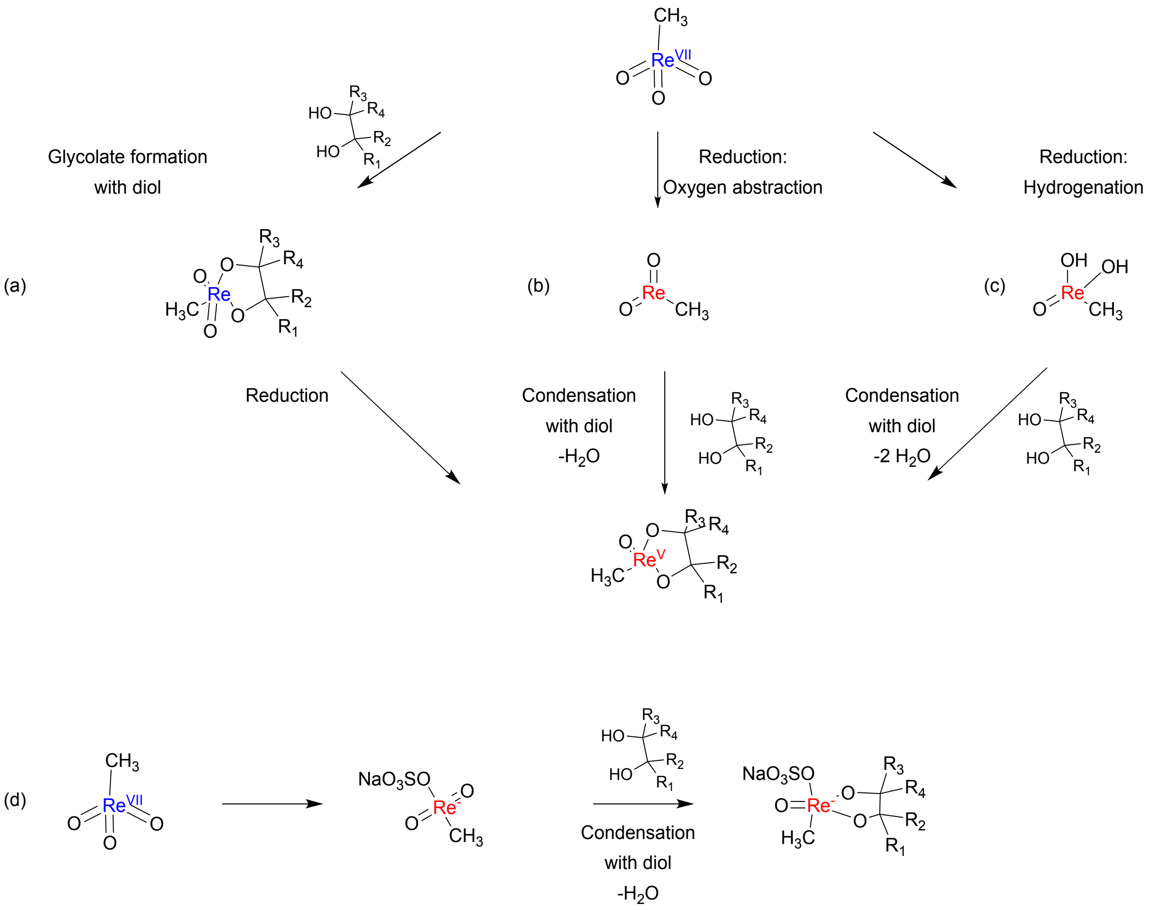


Scheme 7: Deoxydehydration of a vicinal diol to an olefin, using a hydrogen-transferring reductant.

Target properties of reductants, beyond effectivity, are sustainable sourcing and recyclability, large scale availability, cost, and separability from the reaction mixture. For oxygen-abstracting reductants, a number of inorganic compounds have shown potential, foremost sulfite,[28] as have several elements including zinc and manganese.[29] These reductants also give solid or easily precipitable oxidation products. Attempts have been made to use the industrially available molecules or carbon monoxide[30,31] or dihydrogen,[32] where the former is transformed to easily separable CO_2. To promote the activation of H_2, noble metals have been added,[33] as mentioned above. Among the hydrogen-transferring molecules, secondary alcohols[34] and hydroaromatic compounds are the most commonly targeted organic molecules and are mainly used in the liquid phase or even as solvent (in particular alcohols).

2.4 Clarification of the DODH mechanism

The steps of the catalytic cycle are principally similar for the three reported metals, rhenium, molybdenum and vanadium.[35,36] While there is consensus that the product-forming step of deoxydehydration is extrusion of the olefin from a glycolate with increase of the metal oxidation state by +2 as shown in Scheme 3,[35] the steps leading to this intermediate are under debate and may depend on the nature of reductant and catalyst. The possibilities are distinguished by the sequence of reduction and diol complexation,[37] as shown in Scheme 8 . One option is the redox-neutral condensation of the diol with the oxido metal complex to a diolate (glycolate) and subsequent reduction of the complex by removal of one oxido ligand (Scheme 8a). Another option is the reduction of the oxido metal complex and subsequent condensation with the diol (Scheme 8b). The product of the initial reduction can vary. In the simplest case, an oxido ligand is removed. In a variant, two oxido ligands may be turned into hydroxido ligands with subsequent elimination of two molecules of water during the condensation step (Scheme 8c).[38] Finally, one oxido ligand can be converted into an oxo bridge, for example to sulfur from sulfite and simultaneously, a negative charge is imparted on the rhenium. In this mechanism, the nascent sulfate remains coordinated past the extrusion and is released in a final step with recovery of the catalyst (Scheme 8d).[39] Along with the sequence, the oxidation state of the metal is debated. For example, it has been proposed that rhenium cycles between the oxidation states +VII/+V,[37] +VI/+IV,[19] or +V/+III.[40]



Scheme 8: Sequence variations of reduction and glycolate formation with diol and variations of reduced species for methyltrioxidorhenium catalyst: a) Glycolate formation precedes reduction; b) reduction by oxygen abstraction precedes gycolate formation; c) reduction by hydrogenation precedes gycolate formation and d) reduction by sulfite precedes glycolate formation and sulfite remains coordinated until after olefin extrusion. The cycle is closed by the olefin extrusion in Scheme 3.

3. Reviews and Patent Literature

3.1 Prior reviews and perspectives

Somewhat surprisingly for such a young field, yet illustrating its growth and reflecting the perceived potential of DODH, a number of review articles on DODH or incorporating DODH have appeared in rapid succession. These reviews and perspectives have emphasized different aspects. Metzger[41] started in 2013 with a highlight on the potential of DODH as powerful reaction for employing carbohydrates as a renewable resource. In a similar vein, Boucher-Jacobs and Nicholas[42] cited sustainability as motivation for DODH in their review. The authors addressed both uncatalyzed DODH and DODH catalyzed by oxido metal compounds, and they included an overview of reductants and mechanistic aspects. Raju et al.[43] focused on rhenium catalysts and reviewed dehydration as well as DODH. Dethlefsen and Fristrup[44] gave a short overview of rhenium complexes as DODH catalysts with substrates and reductants. In 2017, Petersen and Fristrup[36] provided insights on non-rhenium DODH catalysts and the variations in mechanism depending on the catalyst. In 2019, DeNike and Kilyanek[45] gave a mechanistic overview on homogeneously catalyzed DODH using the nature of the reductant as guiding principle, whereas Donnelly et al.[46] reviewed the progress in DODH of diols and polyols during the preceding 5 years. The most recent addition is a tutorial review on DODH by Tshibalonza and Monbaliu[2] that was published in 2020. This review includes E-factor[47] calculations for several biomass-relevant transformations.

The application of compounds as DODH catalysts has also found entry in materials-centered reviews. In a broader context, Harms et al.[35] discussed oxygen transfer of organorhenium dioxides including DODH. Sousa and Fernandes[48] chose deoxygenation reactions for their review, while including both oxido-molybdenum and oxido-rhenium complexes as catalysts. Tomishige et al.[49] published a short review on rhenium-mediated catalysis in biomass conversion to chemicals.

Finally, recent reviews of bio-refining have incorporated DODH. Dutta chose DODH as one reaction in a Highlights article;[50] Mika et al.[51] included DODH in a discussion of the role of water in biomass conversion, and Palkovits[52] presented it as a young deoxygenation method in an article on concepts and challenges in biomass conversion. DODH has been reviewed in conjunction with several platform molecules: Wozniak et al.[53] listed DODH as one method to convert 5-hydroxymethylfurfural, Khalil et al.[54] integrated DODH into an article on muconic acid as a platform molecule, Tamura et al.[55] briefly mentions DODH in a perspective on exploiting the asymmetric carbons in sugars, and Nakagawa et al.[56] dedicated a section to DODH in a mini-review on erythritol. Suárez-Pantiga and Sanz[57] included DODH into a review on deoxygenation reactions catalyzed by dioxidomolybdenum complexes. Muzyka and Monbaliu[55] wrote a perspective on upgrading vicinal diols, in which they provide short overviews of catalyzed and uncatalyzed DODH.

3.2 Patent literature

The numbers of patents and patent applications that expressly reserve DODH and related chemistries is limited. Bergman et al. filed a method for polyol conversion to olefins with carboxylic acid addition, whereby one example was glycerol conversion to allyl alcohol with formic acid as a reducing agent, without requiring catalyst.[58] A number of patents and applications focus on materials. Dethlefsen and Fristrup[59–62] claimed molybdenum and vanadium catalysts for biomass functionalization and deoxygenation. Rhenium catalysts for DODH and recovery of rhenium catalysts are central to documents submitted by Kon et al.[63] and Jeong et al.,[64] respectively. Catalysts containing a noble metal have been patented for H_2-driven DODH.[65] Another set of patents and applications focuses on methods for the manufacture of specific compounds or compound groups. These target products are allyl alcohol or allylic compounds,[66–71] acrylate esters,[72] muconic acid or muconate,[73–75] or adipic acid.[76–78] A large number of claims were made by Toste et al.,[79] who disclosed methods for deoxygenation of sugars using H_2 as reducing agent.

4. Reaction Thermodynamics

4.1 Example thermodynamics – substrate perspective

To analyze the thermodynamics of deoxydehydration, one can subdivide the reaction as presented in Scheme 1 and Scheme 2 into three thermodynamic contributions, namely the transformation of the substrate, the elimination of a molecule of water, and the oxidation of the reductant with optional formation of a second molecule of water. The Gibbs energies of formation $\Delta_f G$ of example diols and olefins are given in Table 1; for simplicity, pure compounds are considered. The transition from diol to olefin is afflicted with a significant step up in Gibbs energy of formation, implying a large endergonic contribution to the overall DODH reaction ($\Delta\Delta_f G_{PR}$). While the elimination of water, a small stable molecule, alleviates this issue ($\Delta\Delta_f G_{PWR} < \Delta\Delta_f G_{PR}$), there is still considerable burden on the reductant to provide a thermodynamic driving force for the reaction to proceed. This contribution must be exergonic with $|\Delta\Delta_f G_{RED}| >> 150$ kJ/ mol to make the reaction feasible. As a consequence, the reductant must be strong and easily accept oxygen, or a transfer reagent must be used that places the removed oxygen into another small and stable molecule, such as water or carbon dioxide.

Table 1: Differences between Gibbs energies of formation of typical DODH products and reactants[a]

Entry	Reactant			Product			Difference Product(s) – Reactant	
	Name	State	$\Delta_f G$ kJ/mol	Name	State	$\Delta_f G$ kJ/mol	$\Delta\Delta_f G_{PR}$ kJ/mol	$\Delta\Delta_f G_{PWR}$ incl. H_2O (L,G) kJ/mol
1	Glycerol	L	-428	Allyl alcohol	G	-49	379	153
2	1,2-Hexanediol	G	-259	1-Hexene	G	118	377	151

[a]Data from AspenPLUS; temperature 100 °C; pressure 1 atm

4.2 Reductants

4.2.1 Reductant transformation and thermodynamics

The thermodynamic reduction power of various reductants is given in Table 2 ($\Delta\Delta_f G_{RED}$). The reductants can generally be classified into oxygen-abstracting agents (Entries 1 and 9-15), whereby oxygen from the diol is ultimately transferred to the reductant, and hydrogen-transfer agents (Entries 2-

8) that provide hydrogen to eliminate water as a small, thermodynamically favored molecule. Such hydrogen transfer agents may be hydroaromatics or alcohols. Comparison of the last columns of Table 1 and of Table 2 demonstrates that a significant number of viable reductants exist for DODH.

4.2.2 Discussion of reductants

Reductant will be discussed in order of appearance in Table 2, which is first organic and then inorganic reductants. The "reductant"-free scenario, in which the diol itself serves as reductant, will be discussed with alcohol reductants. Triphenylphosphane was used in the first catalytic DODH and remains a commonly used strong reductant (Entry 1 in Table 2) for liquid-phase reactions in a laboratory setting. It is an oxygen-abstracting reductant (Scheme 9 a) and is transformed to triphenylphosphane oxide. Variants are tri-*n*-butylphosphane and triethoxyphosphane.[80] Another strong organic reductant is formic acid (Entry 2), which is used both in catalyzed[12] and uncatalyzed DODH.[81–84] As a variant, trimethylformate[85] or triethylorthoformate has been used.[82]

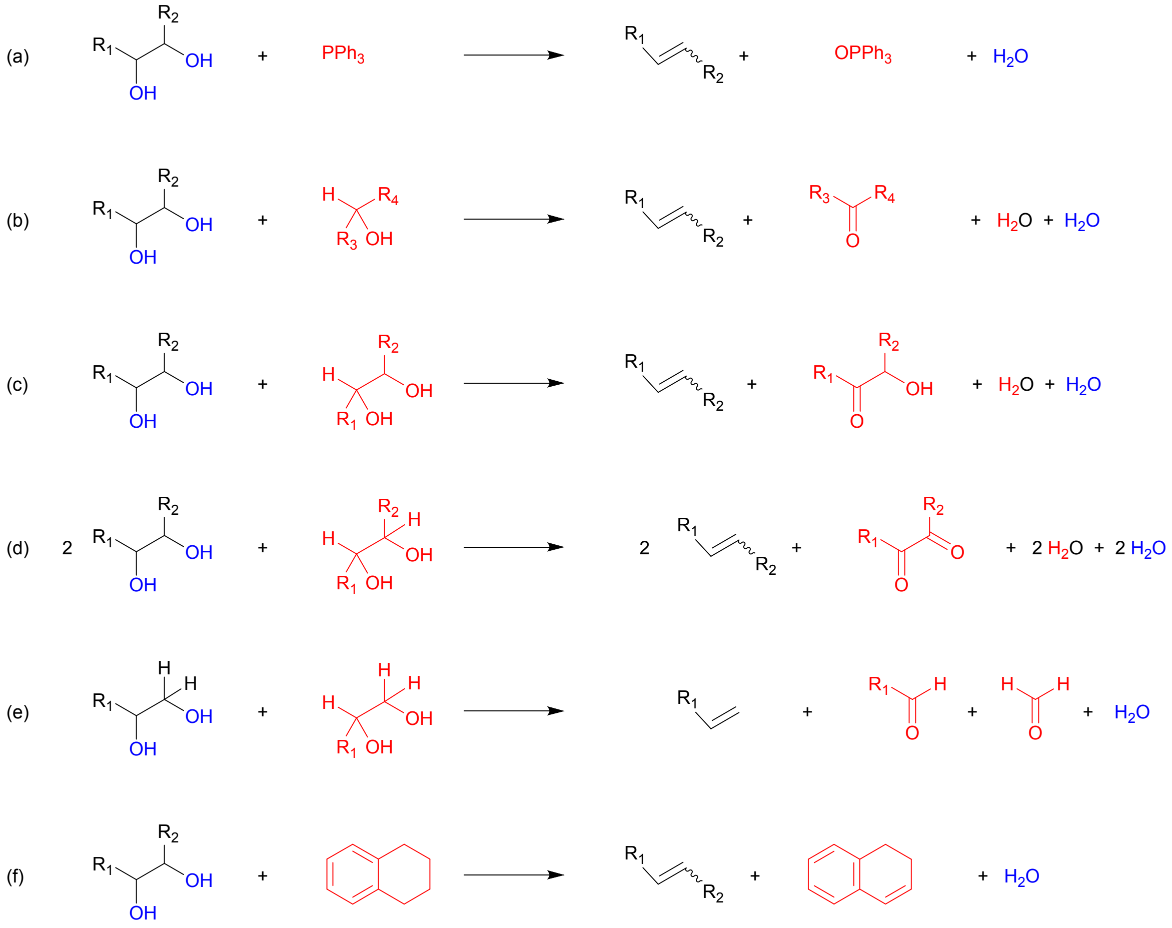
Table 2: Gibbs Energy contribution to DODH from reductant and optionally formed water[a]

Entry	Reductant			Oxidized Reductant			Water (L,G)	Difference
	Name	State	Δ_fG kJ/mol	Name	State	Δ_fG kJ/mol	Δ_fG kJ/mol	$\Delta\Delta_fG_{RED}$ kJ/mol
1	PPh_3	L	259	$OPPh_3$	S	-89		-348
2	Formic acid	L,G	-345	CO_2	G	-395	-226	-276
3	1-Butanol	L	-122	Butanal	L	-91	-226	-194
4	1-Hexanol	L	-96	Hexanal	L	-66	-226	-196
5	2-Hexanol	L	-110	2-Hexanone	L	-96	-226	-212
6	Cyclohexanol	L	-72	Cyclohexanone	L	-63	-226	-217
7	1,2,3,4-Tetrahydronaphthalene	L	191	1,2-Dihydronaphthalene	L	244	-226	-173
8	1,2-Dihydronaphthalene	L	244	Naphthalene	L	230	-226	-240
9	CO	G	-144	CO_2	G	-395		-251
10	SO_2	G	-301	SO_3	G	-365		-64
11	H_2	G	-0.25	H_2O	L,G	-226		-226
12	C	S	0	CO	G	-137		-137
13	Zn	S	0	ZnO	S	-314		-314
14	Mn	S	0	MnO	S	-364		-364
15	Na_2SO_3	S		Na_2SO_4	S			-258

[a]Entries 1-11, data at a temperature of 100 °C and a pressure of 1 atm from ASPENPlus; Entries 12-13, 298 K from Ref. [86], Entry 14, from Ref. [87], and Entry 15, from Ref. [88]

Primary and secondary alcohols can serve as reductants and will be oxidized to aldehydes and ketones, respectively. Looking at alcohols as reductants in general (Entries 3-6 in Table 2), the corresponding carbonyl compounds have a Gibbs energy of formation that is slightly lower than that of the alcohols – after all, the difference is only H_2, an element. Instead, the main exergonicity of alcohol-driven DODH is provided by the formation of water as a byproduct, that is, the alcohol serves as H-transfer agent (Scheme 9b).[71,75] The variations among these reductants in terms of thermodynamic driving force in Table 2 are less than 25 kJ/mol, since the main contribution comes from water. However, the formation of an aldehyde is less favorable than that of a ketone, giving a thermodynamic edge to secondary alcohols (while tertiary alcohols are unsuitable for lack of an alpha hydrogen).

Some of the alcohols are viewed as sustainable reductants, since they can be made from biomass, for example 1-butanol.[89,90] Alcohols may simultaneously serve as reductant and as solvent.



Scheme 9: Possibilities for reductants to effect DODH. (a) Oxygen-abstracting triphenylphosphane; (b) Hydrogen transfer with alcohol; (c) and (d) diol serving as hydrogen transfer agent; (e) oxidative cleavage of diol, also referred to as deformylation; (f) hydroaromatics as hydrogen transfer agent; first of two possible transfers for tetrahydronaphthalene.

The diol substrates may serve as reductants, which may be considered as a special case of alcoholic reductant. An “external”, that is, a deliberately added reductant, is not necessary, and DODH without external reductant has been practiced.[27,91,92] The ability of diols to serve as reductants implies that to demonstrate efficacy of external reductants, they must lead to more than 50% yield, or olefin must be produced in excess of diol oxidation product, or a control experiment without external reductant shows an insignificant contribution of the diol as reductant. The nature of the diol oxidation product may vary, which makes closing a balance by quantifying this byproduct difficult. One possibility is the formation of the corresponding hydroxyketone (Scheme 9c); for example, for glycerol, dihydroxyacetone was detected.[92] When using an internal diol, namely octane-4,5-diol, Arceo et al.[91] temporarily observed the formation of octane-4,5-dione, but the vicinal diketone was not stable under reaction conditions and could not be fully traced (Scheme 9d). A third possibility is deformylation, that is, a cleavage of the diol into a shorter aldehyde and formaldehyde (Scheme 9e).

Similar thermodynamic considerations as those for alcohols apply for hydroaromatics as H-transfer agents. Molecules tested include dihydroanthracene,[93] indoline,[80,93] and tetrahydronaphthalene, which could provide 2 equivalents of H_2 (Table 2, Entries 7&8, Scheme 9f).

Of the gaseous reductants (Entries 9-11), carbon monoxide and H_2 are attractive because of their industrial availability. However, they may require elevated pressures or a second catalyst to be effective, or both. For example, CO was used at 13.8 bar with rhenium catalysts[30] and at 20 bar with vanadium catalysts.[31] Dihydrogen was successfully used at 1 to 14 bar with rhenium catalysts,[13,94] whereas it was not very effective with vanadium catalysts.[95] The activation of H_2 can be facilitated through addition of a metal catalyst.[19,33] The availability of atomic hydrogen can lead to hydrogenation of the olefinic product to a saturated compound,[94] which may in some cases be desired.[33] The problem of product double bond hydrogenation can be controlled by using a mild hydrogenation catalyst such as gold.[21]

Many solid inorganic reductants (Entries 12-15) provide enough thermodynamic driving force. The poor solubility of these reductants in organic solvents can be an issue, whereas the formation of a solid byproduct through oxidation of the reductant is advantageous for separation. Sodium sulfite is an effective reductant for DODH, and crown ethers have been added to aid with the solubilization of Na_2SO_3.[28,37] Examples for solid reductants that are oxidized to solids are Zn, Fe and Mn, which have been shown to be feasible.[29,80] Weaker reductants such as carbon, which is oxidized to CO (rather than CO_2),[29] may face thermodynamically limited yields (Entry 12 in Table 2).

4.2.3 Summary reductants

In general, with strong reductants, olefin yield in DODH is not likely to be thermodynamically limited, even if actual values in the reaction mixture may deviate from the estimates in Table 1 and Table 2. For some constellations, continuous removal of components from the reaction environment is possible (see Section 7.2), which could be used to shift equilibria. Related to reductants, several reasons may be cited for incomplete yields. There can be side reactions of the reductant, which is often applied in excess to compensate for such losses or to serve as a solvent. These side reactions include overreduction of the catalyst or the olefinic product. Another reason is the inadvertent action of the diol substrate as reductant.

Selection of a reductant may be dictated by substrate phase chemistry and solubilities, or by economic and sustainability considerations concerning both the production of the reductant and the fate of the oxidized version of the reductant. Selecting the best reductant merely upon its action in the transformation is complicated. In published mechanisms for transition metal-catalyzed DODH, the reductant interacts with an oxido group at the metal center or the metal center itself, and hence the suitability of the reductant depends on the nature of the metal complex that serves as catalyst. Moreover, mechanistic detail is lacking. As discussed in Section 0, the sequence of reduction and glycolate formation is debated, and consequently, the target species to be reduced could be the pristine catalyst or the diolate complex.

5. Catalysts for Deoxydehydration

5.1 Role of catalysts in DODH and reported catalytic materials

DODH can be performed without a metal-containing catalyst, and such efforts are continuing.[12,82,96,97] Other than enhancing the rate of conversion, a catalyst may also enhance selectivity towards the olefin, make more efficient use of a reductant, and induce stereoselectivity or stereospecificity. Since there are two molecules, the substrate and the reductant, one can envision that two catalytic functions may be advantageous.

The rate enhancement is obvious for most tested catalysts, and the reported olefins yields in control experiments under the same conditions without catalysts are low. Conversions are not always reported, and, hence, the selectivity enhancement is more difficult to assess. Common side reactions of DODH related to the diol are dehydration to ketones or aldehydes (via enols), ether formation, oxidative cleavage (to aldehydes or ketones), and secondary reactions such as acetalization (with aldehydes formed from the diol or an alcohol reductant) to give dioxolanes. Secondary reactions of olefinic products are also possible, such as oligomerization or polymerization, or just rearrangement, for example from terminal to internal double bonds.

The development of supported catalysts implies that side reactions on the support surface can become an issue. For example, acid or base sites on high-surface-area supports can lead to double bond shift – thus potentially converting a valuable terminal into an internal olefin-, dehydration, or etherification. The supports may also simply serve as adsorption sites for substrate, reductant, or products, which would be noticeable in a batch process with small reactant-to-catalyst ratios.

DODH was also found to be stereospecific in the absence of a metal catalyst, however, the pathway to stereospecifity is not clear. Ando et al.[85] investigated the stereospecificity for various substrates with trimethylorthoformate as a reductant and concluded that it is not a "simple thermal reaction". Rather, they found the nature of the solvent to be important and formulated a pathway with a reactive role for the "solvent" acetanhydride.

As mentioned in Section 2.1, DODH catalysts have been developed on the basis of rhenium, molybdenum, or vanadium. There have been isolated attempts to use other transition metals such as tungsten or manganese. Supported catalysts have been developed using classical supports, including carbon, SiO_2, TiO_2, and CeO_2.

Some researchers have added a secondary catalyst to activate the dihydrogen and facilitate its action as a reductant. These secondary catalysts are transition metals from Group VIII and coinage metals that are known to activate H_2.

5.2 Guide to DODH catalysis literature and catalyst tables

5.2.1 Classification of catalysts

In this section, we present a summary of the investigated catalysts, substrates, and reductants in tabular form. The primary guiding principle is catalyst material, the secondary guiding principle is chronology. One may be tempted to organize by heterogeneous and by homogeneous catalysis, but this distinction is often difficult in DODH. On one hand, solids may precipitate from soluble catalysts or compounds may not dissolve entirely; on the other hand, some of the intended solid catalysts were found to leach. We thus distinguish pure catalysts, consisting of the active component only, from supported catalysts. Table 3, Table 4, and Table 5 list investigations on pure catalysts; Table 6 and Table 7 summarize supported catalysts. Conversions and yields are included if the product distribution favors one or two products and mostly identical parameters make meaningful comparisons possible. Experimental and computational investigations are equivalently included in these tables. In the next section, the emerging picture is discussed, and areas of incomplete understanding are highlighted.

5.2.2 Catalysts only consisting of active component – soluble and bulk

Table 3: Rhenium catalysts with [Conversion of substrate in %, yield product in %], for #-marked catalyst, substrate, product, reductant, temperature in list

Reference	Compounds[a]	Substrate→Product	Reductant(s)	Temperature (°C)	Remarks
Cook and Andrews, 1996[3]	$Re(C_5Me_5)O_3$	Phenyl-1,2-ethanediol→Styrene [100,100] Glycerol→Allyl alcohol [66,67] Erythritol→Butadiene [-,37] 3-Butene-1,2-diol→Butadiene 1,2:5,6-Diisopropylidene-D-mannitol→ *trans*-3,4-didehydro-3,4-dideoxy-1,2:5,6-di-O-isopropylidene-D-threo-hexitol [56,48] Xylitol→ 2,4-Pentadiene-1-ol	PPh_3	90-135	• First catalyzed DODH • Stereospecific • Deactivation by "Re(III) formation"
Ziegler et al., 2009[32]	$ReCH_3O_3$	1,2-Hexanediol→ 1-Hexene [-,18] *cis*-1,2-Cyclohexanediol→Cyclohexene [-,60] *trans*-1,2-Cyclohexanediol→no alkene 1,4-Anhydroerythritol→Furan [-,25]	H_2 (80 to 300 psi)	150	• Variable amounts of saturated product formed depending on conditions
Arceo et al., 2010[91]	$^{\#}Re_2(CO)_{10}$ $ReCp^*(CO)_3$ $ReBr(CO)_5$	(4*S**,4*S**)-Octane-4,5-diol→3-Octene 1,2-Tetradecanediol→1-Decene [100,83] (3*R**,4*R**)-decane-3,4-diol→3-Decene [100,82] *cis*-1,2-Cyclohexanediol→Cyclohexene [100,70] *trans*-1,2-Cyclohexanediol→no alkene Erythritol→2,5-Dihydrofuran [-,62]	Diol itself 2-Octanol #3-Octanol 5-Nonanol	155-180	• $ReCp^*(CO)_3$ no activity • Others no activity in N_2, activity under aerobic conditions • Positive effect of acid addition associated with facilitated olefin extrusion by protonation of a rhenium diolate intermediate
Vkuturi et al., 2010[37]	$^{\#}ReCH_3O_3$ $NaReO_4$	1-Phenyl-1,2-ethanediol→Styrene [100,59] 1,2-Octanediol→1-Octene [75,60] *cis*-1,2-Cyclohexanediol→Cyclohexene [95,25]	Na_2SO_3	150	• Performance of "sparingly soluble" $NaReO_4$ improved by addition of 10 mol% 15-crown-5 and even further by addition of dehydrating agent Na_2SO_4
Ahmad et al., 2011[28]	$ReCH_3O_3$ $NaReO_4$ NH_4ReO_4 $^{\#}Bu_4NReO_4$ Re_2O_7	1-Phenyl-1,2-ethanediol→Styrene [100,71] 1,2-Octanediol→1-Octene [100,68] 1,2-Decanediol→1-Decene [100,70] 1,2-Tetradecanediol→1-Tetradecane [100,89] *cis*-1,2-Cyclohexanediol→Cyclohexene [-,18] *trans*-1,2-Cyclohexanediol→no appreciable conversion (+)-diethyl L-tartrate→diethylfumarate [16,10]	Na_2SO_3	150	• Highest yields of styrene or *n*-alkene 60 to 89 % with $ReCH_3O_3$ and Bu_4NReO_4 • Basic N- and P-ligands retard DODH

	$^{\#}Bu_4NReO_4$ $ReCH_3O_3$	1-Phenyl-1,2-ethanediol→Styrene	Na_2SO_3 [100,71] $(NH_4)_2SO_3$ [100,49] $NaHSO_3$ [95,5] Tri-*o*-tolylphosphane [100,70] 2-Butanol [0,0] 2,4-Dimethyl-3-pentanol [100,55] $PhSCH_3$ [100,8]	160	• $PhSCH_3$ 52% styrene yield in combination with $ReCH_3O_3$ • $(NH_4)_2SO_3$ and $NaHSO_3$ faster reaction with lower yields, ascribed to acid-catalyzed etherification and dehydration side reactions
J. Yi et al., 2012[92]	$ReCH_3O_3$ [100,27] $NaReO_4$ [9,2] $KReO_4$ [27,9] NH_4ReO_4 [100,13]	Glycerol→Allyl alcohol	Glycerol (thus limiting allyl alcohol yield to a maximum of 50%)	165	• Addition of chlorides NaCl, KCl, HCl, NH_4Cl; results suggest "need for a proton or activating cation"
	$ReCH_3O_3$	Glycerol→Allyl alcohol	1-Heptanol [100,50] 3-Octanol [100,48] Cyclohexanol [100,50] 1,3-Propanediol [30,9] 1,2-Propanediol [100,55]	165	• Products from alcohol reductants (alkenes and ketones) are quantified • NH_4ReO_4 performs better than $ReCH_3O_3$ with 3-octanol as reductant at 72% allylic alcohol yield
		meso-Erythritol→2,5-Dihydrofuran [-,45] *meso*-Threitol *trans*-1,2-Cyclohexanediol→not converted *cis*-1,2-Cyclohexanediol	Polyol itself $^{\#}$1-Heptanol	165	• Transformation is stereospecific
		Glycerol-$(OD)_3$ d_5-Glycerol-$(OH)_3$	Glycerol	165	• Kinetic isotope effect only for d_5-glycerol-$(OH)_3$
Shiramizu and Toste, 2012[98]	$ReCH_3O_3$ [100,70] $Re_2(CO)_{10}$ [0,0] $ReO(PPh_3)_2Cl_3$ [54,20] NH_4ReO_4 [62,25] $ReIO_2(PPh_3)_2$ [100,68] $HReO_4$ [100,66]	1,4-Anhydroerythritol→2,5-Dihydrofuran	1-Butanol	170	• $ReCH_3O_3$ most effective catalyst with different reductants
	$ReCH_3O_3$	1,4-Anhydroerythritol→2,5-Dihydrofuran	1-Propanol [-,28] 1-Butanol [100,70] 3-Pentanol [100,95] 3-Octanol [100,92]	170	• Ethanol, 2-propanol, and 2-butanol not effective [0,0]
			1-Pentanol [100,51]] Isopentanol [100,61] 2-Methyl-1-butanol [100,57]	155	• Secondary alcohols better than primary

			2,2-Dimethyl-1-propanol [89,42] 3-Pentanol [100,91] 2-Pentanol [100,78] 3-Methyl-2-butanol 85,62] 2,4-Dimethyl-3-pentanol [100,>99] 3-Octanol [100,97] Benzhydrol [56,39]		
		Glycerol→Allyl alcohol [-,90] Erythritol→Butadiene [-,90] DL-Threitol→Butadiene [-,81] D-Erythrose→Furan [-60] L-Threose→Furan [-,47] Pentoses	3-Octanol	155-170	• Low yields for pentoses
		C5 and C6 Sugar alcohols Inositols (Hexahydroxycyclohexanes) Hexoses	3-Pentanol	155-200	
Shiramizu and Toste, 2013[99]	$^{\#}ReCH_3O_3$ $HReO_4$	*cis*-Butene-1,4-diol→Butadiene [-,70] *trans*-Butene-1,4-diol→Butadiene [-,70] *cis,cis*-Muconic alcohol→Hexatriene [-,31] Cyclic diols Mucic acid/derivatives Gluconic acid D-erythronolactone→γ-crotonolactone D(+)-Ribono-1,4-lactone L-(+)-Tartaric acid + Erythritol	$^{\#}$3-Pentanol (±)2-Methyl-1-butanol	155-170	• Initial internal DODH of polyols does not prevent complete DODH: 1,4 and 1,6 unsaturated diols are converted • Acid $HReO_4$ mediates [1,3] OH shifts
S. Liu et al., 2013[40]	$ReCH_3O_3$	*trans*-1,2-Cyclooctanediol→no reaction *cis*-1,2-Cyclooctanediol→Cyclooctene [100,64] (*R,R*)-(+)-Hydrobenzoin→*trans*-Stilbene [100,80] (*S,S*)-(+)-Hydrobenzoin→*trans*-Stilbene [100,80] *meso*-Hydrobenzoin→*cis*-Stilbene [100,40] 1,2-Decanediol→1-Decene [100,67] 1-Phenyl-1,2-ethanediol→ Styrene [100,60] *meso*-Erythritol→2,5-Dihydrofuran [100,40]	1-Heptanol $^{\#}$3-Octanol Cyclooctanol 2-Nonanol 5-Nonanol Benzyl alcohol 1-Phenylethanol Diphenylmethanol (*R,R*)-(+)-Hydrobenzoin	140-170	• Primary alcohols not effective • Re nanoparticles recovered, found to be less active than supernatant • Zero-order kinetics in [hydrobenzoin] and half-order in [Re] • Re(V)/Re(III) cycle proposed
	$ReCH_3O_2(PPh_3)_2$ $ReCH_3O_2(Pcy_3)_2$	Hydrobenzoin→Stilbene	3-Octanol	140	• No induction period, zero order in reactant

S. Raju et al., 2013[100]	1,2,4-tri(*tert*-butyl)cyclopentadienyl trioxidorhenium	1,2-Octanediol→1-Octene	PPh_3 [99,94] Pcy_3 [5,5] $P(C_6F_5)_3$ [7,3] $P(nBu)_3$ [<1,trace] Na_2SO_3 [3,trace] H_2 3-Pentanol [9,9] 1,2-Octanediol [16,7]	110-180 $^{\#}$135	• Optimal temperature with 1,2-octanediol and PPh_3 is 135 °C • Isomerization to 2-octenes at higher temperatures • Best solvent chlorobenzene • PPh_3 most effective reductant • Octane produced with H_2
		1,2-Octanediol→1-Octene [>99,94] 1,2-Decanediol→1-Decene [>99,90] 1,2-Dodecanediol→1-Dodecene [86,94] *cis*-Cyclohexanediol→Cyclohexene [21,10] *trans*-Cyclohexanediol→Cyclohexene [12,trace] Phenyl-1,2-ethanediol→Styrene [>99,99] (*R*,*R*)-1,2-Diphenyl-1,2-ethanediol→*trans*-Stilbene [>99,>99] (*R*,*S*)-1,2-Diphenyl-1,2-ethanediol→*cis*-Stilbene [>99,89] 1,4-Anhydroerythritol→2,5-Dihydrofuran [>99,49] *syn*-4,5-Octanediol→*trans*-4-octene [29,17] Glycerol→Allyl alcohol Erythritol→1,3-Butadiene	$^{\#}PPh_3$ 3-Octanol	135-180 $^{\#}$135	• Allyl alcohol yield from glycerol 91% under optimized conditions • Max. butadiene yield 30% with PPh_3, 67% with 3-octanol
P. Liu and Nicholas, 2013[39]	$ReCH_3O_3$	Ethylene glycol →Ethene	Na_2SO_3	25	• DFT calculations suggest fragmentation of the Re(V)−glycolate to olefin turnover-limiting • Last step is dissociation of $NaSO_4^-$ from catalyst to regenerate $ReCH_3O_3$
Boucher-Jacobs and Nicholas, 2013[101]	$ReCH_3O_3$ $^{\#}NH_4ReO_4$	1,2-Octanediol→1-Octene [-,50] Glycerol→Allyl alcohol [-,23] Glycerol 3-allyl ether→Diallyl ether [-,83] 3-Octadecyl glycerol ether (Batyl alcohol)→1-(2-Propen-1-yloxy)octadecane [-,83] 1-Monostearin→Allylstearate [-,80-90] Diethyl tartrate→Diethyl fumarate [-,95]	$^{\#}$Benzyl alcohol 4-Z-$ArCH_2OH$ with Z=NMe_2, OMe, Cl 3-Octanol	140-170	For glycerol and $ReCH_3O_3$, allyl alcohol yields of 70 and 47% with 3-octanol and benzyl alcohol as reductant, respectively
S. Qu et	$ReCH_3O_3$	1,4-Anhydroerythritol→2,5-Dihydrofuran	3-Octanol	25	• DFT investigation of

al., 2013[38]					mechanism, new proposed Re(V) intermediate with two hydroxido ligands
McClain and Nicholas, 2014[29]	$^{\#}NH_4ReO_4$ $[(Py)_4ReO_2]Cl$ $[(Py)_4ReO_2]PF_6$	$^{\#}$1,2-Decanediol→1-Decene 1-Phenyl-1,2-ethanediol→Styrene Diethyl tartrate→Diethyl fumarate 3-Octadecyl glycerol ether (Batyl alcohol)→1-(2-Propen-1-yloxy)octadecane	Zn [≥99,68] Fe [≥99,68] Mn [≥99,64] C [≥99,69]	150	• Elemental reductants
Davis and Srivastava, 2014[102]	$^{\#}ReCH_3O_3$ $Re_2(CO)_{10}$	1-Phenyl-1,2-ethanediol→Styrene [-,97] 1,2-Hexanediol→1-Hexene [-,10] 1,2-Tetradecanediol→1-Decene [-,50] *cis*-1,2-Cyclohexanediol→Cyclohexene [-,15]	$^{\#}$5-Nonanol 3-Octanol 1-Butanol	90-200	• Only traces of product with $Re_2(CO)_{10}$ • Yield styrene depends on solvent and reductant with benzene>toluene>THF and 5-nonanol>3-octano>1-butanol
Canale et al., 2014[103]	$ReCH_3O_3$ [-,25] NH_4ReO_4 [-,5] $ReCp^*O_3$ [-,21] ReO_3 [-,30] $Re_2(CO)_{10}$ [-,variable because of catalyst sublimation]	Glycerol→Allyl alcohol	Glycerol $^{\#}H_2$	130-170 $^{\#}$170	• Comparison of air and H_2 atmosphere • Solvent comparison
X. Li et al., 2014[104]	$^{\#}ReCH_3O_3$ Re_2O_7	Mucic acid→Mucic acid 3-pentyl ester and diester [-,99] Mucic acid/esters	1-Butanol $^{\#}$3-Pentanol 3-Octanol	120	• Includes DFT investigation of mechanism • Hydrogenation to adipic acid and ester demonstrated
Boucher-Jacobs and Nicholas, 2015[93]	$^{\#}NH_4ReO_4$ $ReCH_3O_3$	$^{\#}$Diethyl tartrate→Diethyl fumarate 1,2-Octanediol	Tetrahydronaphthalene [-,92] 1-Hydroxyindan [-,70] 9,10-Dihydroanthracene [-,25] Indoline [-,99] 1,3-Cyclohexadiene Acenaphthene [,-90] Fluorene [-,82]	150	• Indoline also outdoes 2-butanol (glycerol substrate) and 3-pentanol (diethyl tartrate substrate) • Cycloadditions of fumarate product with cyclohexadiene and anthracene
	NH_4ReO_4 $^{\#}ReCH_3O_3$	1,2-Octanediol→1-Octene Diprophylline→7-Allyl-1,3-dimethylxanthine [-,99] Glycerol→Allyl alcohol [-,80] 3-Octadecyl glycerol ether (Batyl alcohol)→1-(2-Propen-1-yloxy)octadecane [-,78]	Indoline	150-170	• Esters of the DODH products are formed from the three carboxylic acids in 1-butanol solvent

		1-Monostearin→Allylstearate [-,80] Erythritol→Butadiene [-,43] Xylitol→2,4-Pentadien-1-ol [-,56] Glyceric acid Tartaric acid Mucic acid			
S. Raju et al., 2015[105]	1,2,4-tri(tert-butyl)cyclopentadienyl-based trioxorhenium	Ethylene glycol→Ethene	PPh_3	25-120	• Spectroscopic investigation of intermediates
Dethlefsen and Fristrup, 2015[106]	$ReCH_3O_3$	1,2-Tetradecanediol	3-Octanol	140-185	• TOF 30 or 41 h^{-1} at a temperature of 174 or 183 °C, respectively • Rate-limiting step octanol oxidation • Reduction of catalyst before condensation with diol
S. Raju et al., 2016[107]	ReCp'O_3 with Cp'= 1,2,4-tri-tert-butylcyclopentadienyl [100,94] 1,3-di-tert-butylcyclopentadienyl [100,96] 1,2,3-triisopropylcyclopentadienyl [100,94] pentamethylcyclopentadienyl [100,84] ethyltetramethylcylcopentadienyl [100,72]] 1,2,3-trimethyl-4,5,6,7-tetrahydroindenyl [100,96] tetramethylcyclopentadienyl [100,96]	1,2-Octanediol→1-Octene	PPh_3	$^{\#}$135 180	• In N_2 atmosphere
X. Li and Y. Zhang, 2016[108]	$ReCH_3O_3$ modified with pyridine ligands: pyridine [90,76] 2-bromopyridine [100,69] 2,2'-bipyridine [30,26]	L-(+)-Tartaric acid→Maleic acid$^{\#}$ Mucic acid	3-Pentanol	120	• Py ligands increase selectivity to free acids (as opposed to 3-pentylesters)
	Re_2O_7 [100,73] NH_4ReO_4 [100,96] $AgReO_4$ [99,78] $KReO_4$ [20,17] $CsReO_4$ [38,35] $(n\text{-}C_4H_9)_4NReO_4$ [30,27]	L-(+)-Tartaric acid→Maleic acid	3-Pentanol	120	• Re_2O_7 and $AgReO_4$ highly active but not as selective to free acid as NH_4ReO_4
H. Zhang et al., 2016[109]	NH_4ReO_4 [100,82] Re_2O_7 [100,39] NH_4ReO_4 [100,82] $AgReO_4$ [100,43] $KReO_4$ [no reaction]	Mucic acid→Muconic acid	3-Pentanol in flowing N_2	120	• With $ReCH_3O_3$, only pentyl esters of muconic acid are produced

	CsReO$_4$ [no reaction] (n-C$_4$H$_9$)$_4$NReO$_4$ [no reaction]				
Kasner et al., 2016[25]	ReIO$_2$(PPh$_3$)$_2$	Benzhydrol→Tetraphenylethane [-,90] Fluoren-9-ol→9,9'-Bifluorenene [-,91] Cinnamyl alcohol→Diphenyl-1,5-hexadienes [>95,-] Benzylalcohol→Diphenylbutane [98,13]	PPh$_3$	150	• Coupling of benzylic alcohols, allylic alcohols, α-keto alcohols, including cross coupling • Deoxygenation and other side reactions occurred
Sandbrink et al., 2016[14]	HReO$_4$ [68,63] NH$_4$ReO$_4$ [29,27]	1,2-Hexanediol→1-Hexene	3-Octanol	170	• HReO$_4$ "homogeneous benchmark"
D. Wu et al., 2016[110]	ReCH$_3$O$_3$	3-Butene-1,2-diol *cis*-2-Butene-1,4-diol *trans*-2-Butene-1,4-diol 1,6-Butandienediols 1,8-Octatrienediol	1-Butanol	25	• DFT investigation • Methyloxodihydroxyrhenium(V) catalyzes allylic alcohol isomerization
Morris et al., 2017[111]	Pyridinium salts of perrhenate NH$_4$ReO$_4$ Primary, secondary, tertiary and quaternary ammonium salts of perrhenate	1-Phenyl-1,2-ethanediol→Styrene	PPh$_3$	80	• Lowest yields with NH$_4$ReO$_4$ and quaternary alkylammonium perrhenates
	2,6-Dimethylpyridinium perrhenate	1-Phenyl-1,2-ethanediol→Styrene	PPh$_3$ [>99,-]] H$_2$ (1 bar) [10,-] CO (1 bar) [40,-] 1-Phenyl ethanol [19,-] 1,2,3,4-C$_{10}$H$_{12}$ [15,-]	$^{\#}$80 40-90	• PPh$_3$ most effective reductant in chloroform solvent, however low conversions in pyridine or acetonitrile
	2,6-Dimethylpyridinium perrhenate	1-Phenyl-1,2-ethanediol→Styrene [>99,>99] 1-(4-Methoxyphenyl)→4-Methoxystyrene [80,50] 1-(4-Bromophenyl)-1,2-ethanediol →4-Bromostyrene [>99,>99] 1-(4-Nitrophenyl)→4-Nitrostyrene [55,22] 1-(2-Naphthyl)-1,2-ethanediol→2-Vinylnaphthalene [>99,>99] *meso*-Hydrobenzoin→Stilbene [-,98] (+)-Diisopropyl L-tartrate→Diisopropylfumarate [>99,>99] 1,4-Anhydroerythritol→2,5-Dihydrofuran [77,51] 1,2-Hexanediol→1-Hexene [41,28] Glycerol→Allyl alcohol [-,21]	PPh$_3$	90-140	• Some conversions not measurable for lacking solubility or miscibility of substrate with CHCl$_3$ solvent

Gossett and Srivastava, 2017[112]	NH_4ReO_4	1-Phenyl-1,2-ethanediol→Styrene [-,84] 1,2-Tetradecanediol→1-Tetradecene [-,99] 1,2-Hexanediol→1-Hexene [-,9] Batyl alcohol→1-(2-Propen-1-yloxy)octadecane [-,73] 3-Phenoxy-1,2-propanediol→Allyl phenyl ether [-,90] (+)-Diethyl tartrate→Diethylfumarate [-,57] (*R*,*R*)-(+)-Hydrobenzoin→Stilbene [-,60]	2,4-Dimethyl-3-pentanol	140-165	• Optimal solvent was toluene
Larson et al., 2017[94]	$ReCH_3O_3$	D-Glucaric acid, 6,3-lactone, 1-ethylester→$C_8H_{10}O_5$	3-Octanol Ethanol H_2 H_2 with Pd catalyst	150	
Shakeri et al., 2017[113]	ReO_4^-	1-Phenyl-1,2-ethanediol	PPh_3		• DFT study of mechanism including solvent influence (chlorobenzene)
N. Shin et al., 2017[114]	$^{\#}ReCH_3O_3$ Re_2O_7 NH_4ReO_4 (with and without acid co-catalyst)	Galactaric acid→1,6-Dialkyl 2,4-hexadienedioates with alkyl depending on the alcohol used as reductant and solvent	Methanol [-,0] Ethanol [-,0] Isopropanol [0,0] 1-Butanol [,72] 3-Pentanol [-,29] Cyclohexanol [-,11] 1-Heptanol [-,84]	120 to 200 or mixture bubble point	• 1-Butanol deemed best solvent for process (also considering separations); diesters of muconic acid obtained • Ionic liquid layer used for separations
J. Li et al., 2018[115]	1,3-di-*tert*-Butylcyclopentadienyl trioxorhenium ($ReCp^{tt}O_3$)	1,2-Octanediol→1-Octene [>99,93] 1,4-Anhydroerythritol→2,5-Dihydrofuran [>99,83] 1-Phenyl-1,2-ethanediol→Styrene [>99,76] (*R*,*R*)-1,2-Diphenyl-1,2-ethanediol→Stilbene [>99,95] Glycerol→Allyl alcohol [>99,99] Erythritol→Butadiene [93,69] DL-Threitol→Butadiene [93,71] Xylitol D-Arabinitol Adonitol Mucic acid D-Glucose D-Galactose D-Mannose	PPh_3 Na_2SO_3 C H_2 (40 bar) $^{\#}$3-Octanol 3-Pentanol 2,4-Dimethyl-3-pentanol 1-Butanol Isobutanol	120-170 $^{\#}$135	• Only PPh_3 and sec. alcohols effective for olefin formation • Turn-over number up to 900 per Re in glycerol DODH • Some ligand dissociation observed • C5 sugar alcohols give DODH product ethers with alcohol reductants • Mucic acid gives muconic acid alkyl esters with alcohol reductant

Wozniak et al., 2018[116]	$ReCH_3O_3$ [>99,96] Re_2O_7 [>99,98] NH_4ReO_4 [>70,67] $Re_2(CO)_{10}$ [>-,-] 2,6-Lutidium perrhenate [85,84]	1,2,6-Hexanetriol→5-Hexen-1-ol	$^{\#}PPh_3$ 3-Pentanol 3-Octanol NaH_2PO_2 Zn Na_2SO_3 HCO_2NH_4 H_2 CO	165	• PPh_3, secondary alcohols, Zn, H_2, effective reductants • High yields with Re_2O_7 without external reductant and under aerobic conditions
	Re_2O_7	1,2,5-Pentanetriol→5-Hexen-2-ol [20,10] 1,2,4-Butanetriol→3-Buten-1-ol [98,97] 1,2,3-Butanetriol→3-Buten-2-ol [83,42] 1,2,5-Pentanetriol→4-Penten-1-ol [97,91] 1,2,8-Octanetriol→7-Octen-1-ol [>99,98] 1,2,10-Decanetriol→9-Decen-1-ol [>99,99]	PPh_3	165	•
Boucher-Jacobs et al., 2018[26]	$ReIO_2(PPh_3)_2$	Benzylic and Allylic alcohols	PPh_3		• DFT investigation into mechanism of reductive coupling of alcohols
R. Lu et al., 2018[117]	Re_2O_7 $HReO_4$ NH_4ReO_4 $ReCH_3O_3$	Erythritol	*n*-Butanol iso-Butanol *n*-Pentanol 2-Methyl-1-butanol 2-Ethylhexanol 2-Propylheptanol	170/120	• Tandem DODH and Diels Alder with fumaric acid • Re_2O_7 highest yield of cycloadduct • Cycloadduct yields for various alcohols in narrow range
Sharkey et al., 2018[31]	(Catechelato)oxidorhenium complex	1-Phenyl-1,2-ethanediol→Styrene [100,61] 1,2-Decanediol→1-Decene [90,89] Diethyl tartrate→Diethylfumarate [100,94]	PPh_3	150-170	•
Jefferson and Srivastava, 2019[118]	NH_4ReO_4 [-,67] Re_2O_7 [-,49] $Re_2(CO)_{10}$ [-,9] $ReCH_3O_3$ [-,99]	1-Phenyl-1,2-ethanediol→Styrene	Indoline	190	• Toluene best solvent with CH_3ReO_3, followed by THF, dichloroethane, indoline, benzene
	$ReCH_3O_3$	1-Phenyl-1,2-ethanediol→Styrene [-,99] Tetradecanediol→1-Tetradene [-,63] *cis*- ,2-Cyclohexanediol→Cyclohexene [-,9] *trans*-1,2-Cyclohexanediol [no reaction] 3-Phenoxy-1,2-propanediol→Allyl phenyl ether [-,73] Batylalcohol→1-(2-Propen-1-yloxy)octadecane	Indoline	150-190	

		[-,48] Diprophylline→N-Allyl-purine [,70] Mucic acid (+Butenol-1)→ 2,4-Hexadienedioic acid, dibutyl ester, (*E*,*E*)- [-,36] (+)Diethyl tartrate→Diethyl fumarate [,-58] (*R*,*R*)-(+)-Hydrobenzoin→Stilbene [-,80] Inositol→Phenol, Benzene [-,20]			
Lupacchini et al., 2019[18]	$ReCH_3O_3$ [-,87] ReO_3 [-,91] NH_4ReO_4 [-,7] $ReCl_5$ [-,38] Re_2O_7 [-,68] $Re(C_5Me_5)O_3$ [-,15] ReI_3 [-,60] $Re_2(CO)_{10}$ [-,0] $ReCl_3O(PPh_3)_2$ [-,81] $ReCl_3O[OPPh_3][S(CH_3)_2]$ [-,80] $ReIO_2(PPh_3)_2$ [-,84]	Glycerol→Allyl alcohol	Glycerol in air or H_2 $^{\#}$2,4-Dimethyl-3-pentanol in air or $^{\#}H_2$	140	• Comparison of air and H_2 atmosphere $Re_2(CO)_{12}$ inactive • Highest yields of about 90% for $ReCH_3O_3$, ReO_3, $ReIO_2(PPh_3)_2$ with 2,4-dimethyl-3-pentanol and H_2 • Active species "solid in appearance"
J.H. Jang et al., 2019[119]	ReO_2 nanoparticles	Glycerol→Allyl alcohol[89,76] 1,2-Hexanediol→1-Hexene [91,80] *meso*-Erythritol→Butadiene [100,34] *cis*-But-2-ene-1,4-diol→Butadiene [97,41]	1-Octanol $^{\#}$3-Octanol 1,2-Propanediol 1,3-Propanediol Glycerols	170	• Primary alcohols and polyols not as effective as 3-octanol • Hot filtration test showing no leaching; particles recyclable
Shakeri et al., 2019[120]	$NaReO_4$ [88,33] $KReO_4$ [41,23] NH_4ReO_4 [100,36] Bu_4NReO_4 [100,73] (2-ppyH)[ReO_4] with 2-ppyH$^+$=2-phenylpyridinium cation [100,76]	1-Phenyl-1,2-ethanediol→Styrene	PPh_3	150	• Experiments plus DFT study of mechanism • K, Na negative effect because of interaction with oxido-ligand
J. Lin et al., 2019[121]	$ReCH_3O_3$	D-Glucaric acid-1,4-lactone	Butanol	120	• 50% combined yield of five-membered ring lactone with one OH group and dibutyl hexa-2,4-dienedioate
Sharkey and Jentoft, 2019[17]	$ReCH_3O_3$	Decanediol	PPh_3	150	• TOF of 24 h^{-1}
J.H. Jang and Abu-Omar,	ReO_2 nanoparticles	Tartaric acid	2-Propanol	170–250	• Succinic acid and maleic acid are investigated for transfer hydrogenation

2020[122]					
Scioli et al., 2020[123]	$ReCH_3O_3$ [-,66] ReO_3 [-,5] Re_2O_7 [-,46] NH_4ReO_4 [-,2]	1,2-Propanediol→Propene	1,2-Propanediol #2,4-Dimethyl-3-pentanol	140-170 #150	• Not clearly demonstratable if homogeneous or heterogenous catalysis
J. Li et al., 2020[124]	(NNO)Re(I)tricarbonyl complexes with NNO=2-(((2-dimethylamino)ethyl)(methyl)amino)methyl)-phenol and different substituents on the phenyl ring including 4-methoxy 4-nitro #2,4-di-tert.-butyl 2,4-dichloro	1,2-Octanediol→1-Octene [-,92] 1,2-Dodecanediol→1-Decene [-,93] 1-Phenyl-1,2-ethanediol→Styrene [-,83] Glycerol→Allyl Alcohol [-,97] 1,4-Anhydroerythritol→2,5-Dihydrofuran Erythritol→Butadiene [-,78] DL-Threitol→Butadiene [-,64] L-(+)-Tartaric acid→Fumaric acid and fumarates [-,81] Mucic acid→Muconates [-,46] Erythritol D-Glucose D-Galactose D-Mannose	#3-Octanol 2-Octanol 1-Butanol 2-Butanol 3-Pentanol 2,4-Dimethyl-3-pentanol	180	• 2,4-Di-tert.-butyl-substituted phenolato complex best catalyst • 2-Octanol and 3-octanol by far best reductants with this complex, 1-octene yields around 90% • Complexes are air-stable at room temperature
J. Li et al., 2020[125]	*cis*-[(*S,S*-BPBP)ReO_2]PF_6 with *S,S*-BPBP = (2*S*,2'*S*)-1,1'-bis(pyridine-2-ylmethyl)-2,2'-bipyrrolidine) [27,27] *cis*-[(BPMEN)ReO_2]PF_6 with BPMEN = (N^1,N^2-dimethyl-N^1,N^2-bis(pyridine-2-ylmethyl)ethane-1,2-diamine) [34,34] *cis*-[(BmdmPMEN)ReO_2]PF_6 with BmdmPMEN = (N^1,N^2-bis((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)-N^1,N^2-dimethyl ethane-1,2-diamine) [41,41] $ReIO_2(PPh_3)_2$ [16,14] *trans*-[(Py_4)ReO_2]PF_6 [>99,>99]	#1,2-Octanediol→1-Octene Erythritol→Butadiene 1-Phenyl-1,2-ethanediol→Styrene 1,4-Anhydroerythritol→2,5-Dihydrofuran Glycerol→Allyl Alcohol L-(+)-Tartaric acid→Fumaric acid and fumarates Mucic acid→Muconates	#PPh_3 3-Pentanol	135-180 #180	• ReO_2^+ with N_2Py_2 ligands are precursors only and are converted into active species upon reaction with water • Yields for all other substrates with *trans*-[(Py_4)ReO_2]PF_6 between 65 and 99%
Hočevar et al., 2021[126]	$ReCH_3O_3$, with Pd/C or Pt/C as secondary catalysts $HReO_4$ $KReO_4$	Aldaric acids	None (N_2) H_2 (0.5 – 1 MPa)	100-140	• Secondary catalyst and H_2 promote adipates over muconates
Feilner et al., 2021[127]	Bu_4NReO_4 H_4NReO_4	Step in pimarane synthesis	Na_2SO_3 Indoline		• Traces of product only

[a]cy=cyclohexyl, X=2,6-lutidinium, Cp*=pentamethylcyclopentenyl.

Table 4: Molybdenum catalysts with [conversion of substrate in %, yield product in %], for #-marked catalyst, substrate, product, reductant, temperature in list

Reference	Compounds[a]	Substrate(s)	Reductant(s)	Temperature range (°C)	Yields / Remarks
J. Yi et al., 2012[92]	$(NH_4)_2MoO_4$	Glycerol	Glycerol	165	• No yield
Hills et al., 2013[128]	$Mo(O)_2(Q^R)_2$ with HQ = 3-methyl-1-phenyl-4-alkylcarbonyl-5-pyrazolone; R = cyclohexyl [60,10] R=hexyl [90,13]	#1-Phenylethane-1,2-diol→Styrene Cyclooctane-1,2-diol	PPh_3	110	• Alkene yields occasionally exceeding $OPPh_3$ • MoO_3 and ammonium heptamolybdate low solubility in toluene
Dethlefsen et al. 2014[129]	$Mo(bipy)(CH_3)_2O_2$	1,2-Tetradecanediol	3-Octanol [-,37] PPh_3 [-,57] 1-Decanol [-,29] Benzyl alcohol [-,8] 1,2-Tetradecanediol [,40-50]	195-220	• Diol itself more effective reductant than others
	$Mo(bipy)Cl_2O_2$ [-,13] $Mo(bipy)(CH_3)_2O_2$ [-,19] $(NH_4)_6Mo_7O_{24}$[-,16] Na_2MoO_4 [-,9]	1,2-Hexanediol→1-Hexene	1,2-Hexanediol		• 2-Hexanone and 1,2-epoxyhexane side products
	$Mo(CO)_6$ [-,40] $Mo(bipy)(CO)_4$ [-,43] $Mo(bipy)O_2Cl_2$ [-,38] $Mo(bipy)O_2Br_2$ [-,27] $Mo(bipy)(CH_3)_2O_2$ [-,40] $(NH_4)_6Mo_7O_{24}*4H_2O$ [-,43] $H_3PMo_{12}O_{40}$ [-,37] Na_2MoO_4 [-,0]	1,2-Tetradecanediol→1-Decene	1,2-Tetradecanediol		• $Mo(bipy)Br_2O_2$ and $Mo(bipy)Cl_2O_2$ not completely soluble • Na_2MoO_4 “practically insoluble”
Beckerle et al., 2016[130]	Di(oxo){1,4-dithiabutanediyl-2,2’-bis(phenolato)}molybdenum [21,3] Di(oxo){1,4-dithiabutanediyl-2,2’-bis(4,6-di-tert-butylphenolato)}molybdenum [41,<1] Di(oxo){1,4-dithiabutandiyl-2,2’-bis(4,6-dichloro-phenolato)}molybdenum [35,3] Di(oxo){1,5-dithiapentanediyl-2,2’-bis(4,6-di-tertbutylphenolato)}molybdenum [74,37] Di(oxo){1,4-diazabutanediyl-N,N’-dimethyl-2,2’-bis(4,6-di-	Anhydroerythritol→2,5-Dihydrofuran	3-Octanol	160-200 #200	• Complexes are considered catalyst precursors • Microwave irradiation tested

	tertbutylphenolato)}molybdenum [25,5]				
Sandbrink et al., 2017[131]	No catalyst [9,0] $Mo(CO)_6$ [36,21] $MoCl_3$ [75,22] MoO_2Cl_2 [60,28] $Na_2MoO_4 \cdot 2H_2O$ [9,0] Na_2MoO_4 [11,1] $(NH_4)_2MoO_4$ [55,27] MoO_3 [91,29] $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [83,38]	1,4-Anhydroerythritol→2,5-Dihydrofuran	3-Octanol	200	• Ketal formation significant side reaction
Shin et al., 2017[114]	MoO_3 (with acid co-catalyst)	Galactaric acid	1-Butanol	Mixture bubble point	• No reaction
Stalpaert and De Vos, 2018[132]	Mo complexes with β-diketoneligands, e.g. #$MoO_2(acac)_2$ with 2,2,6,6-tetramethylheptane-3,5-dione	1,2-Hexanediol→1-Hexene [-,93] Cyclohexanediol→Cyclohexene [-,59] 1-Phenyl-1,2-ethanediol→Styrene [-,51] Erythritol→Butadiene [-,3] Diethyl tartrate→Diethyl fumarate [-,92] Anhydroerythritol→2,5-Dihydrofuran	#PPh_3 2-Octanol Na_2SO_3 CO H_2	150-200	• Significant increase in yield with dione addition • Hypothesis is that dione stabilizes complex and inhibits molybdenum oligomerization
Navarro and John, 2019[133]	Ammonium heptamolybdate	Alkanediols #1-Phenyl-1,2-ethanediol→Styrene (+)-Diethyl L-tartrate	PPh_3 [-,31] Na_2SO_3 [-,18] 3-Octanol [-,2] Fe filings [-,23] KI [-,24] $NaHSO_3$ [-,10]	#170 170-220	• Yields up to 23% with Na_2SO_3
		1,2-Octanediol→1-Octene [-,13] 1,2-Decanediol→1-Decene [-,21] Diethyl tartrate→Diethyl fumarate [-,20]	Na_2SO_3	170 #190	• Ester hydrolysis is a side reaction for diethyl tartrate
Jiang et al., 2019[134]	Mo(0) $Mo(Oac)_4$ MoO_2 MoS_2 $MoCl_5$ H_2MoO_4 $(NH_4)_6Mo_7O_{24}$ $MoO_2(acac)_2$ Dioxido-8-quinolinol molybdenum complex	Tartaric acid→Dibutyl fumarate	1-Butanol	160	• Dioxido-8-quinolinol molybdenum complex best of catalysts tested, up to 83% dibutyl fumarate yield • $MoO_2(acac)_2$ over 20% yield, all others belower yields • Low yields with MoO_3 and H_2MoO_4 "probably due to the low solubility of these bulk solid catalysts"

Tran and Kilyanek, 2019[135]	Molybdenum dioxo-complex with dianionic pincer ligand: #(ONO)MoO$_2$(OPPh$_3$) (ONO)MoO$_2$ with ONO=2,2'-(2,6-Pyridinediyl)bis[4,6-bis-(1,1dimethylethyl) phenolato	1,2-Octanediol→1-Octene [-,59] 1-Phenyl-1,2-ethanediol→Styrene [-,39] (*R*,*R*)-(+)-Hydrobenzoin→Stilbene [-,62] (*L*)-(+)-Diethyltartrate→Diethyl fumarate [-,18]	#PPh$_3$ Na$_2$SO$_3$ Zn C 2-Propanol 3-Octanol	150–190	• Complexes sensitive to water • For hydrobenzoin, mechanism involves formation of two aldehydes from diol
		1-Phenyl-1,2-ethanediol→Styrene [-,39]	Na$_2$SO$_3$ [-,29] Zn [-,36] C [-,37] 2-Propanol [-,10] 3-Octanol [-,10]	150	
Siu et al., 2020[136]	Dioxidomolybdenum complexes with amine bisphenolate ligands #with ligand = Phenol, 2,2'-[[(phenylmethyl)imino]bis(methylene)]bis[6-(1,1-dimethylethyl)-4-methyl- (9CI, ACI)	1-Phenyl-1,2-ethanediol→Styrene	PPh$_3$ [-,34] 3-Octanol [-,5]] Na$_2$SO$_3$ [-,37] Zn granules [-,31] Carbon [-,31]	150 #170	• Significant amounts of benzaldehyde formed from 1-phenyl-1,2-ethanediol and hydrobenzoin • Stilbene predominantly *trans* • Different solvents tested
		1,2-Decanediol→1-Decene [-,5] 1,2-Cyclohexanediol→Cyclohexene [-,3] Diethyl tartrate→Diethyl fumarate [-,18] (*R*,*R*)-(+)-Hydrobenzoin→Stilbenes [-,47] meso-Hydrobenzoin→Stilbenes	PPh$_3$	#170 220	
J. Li et al. 2020[80]	$[MoCp^*O_2]_2O$ [>99,55] $[MoCp^{tt}O_2]_2O$ [>99,55] *n*Bu$_4$[MoCp*O$_3$] [>99,38] Mo(Me$_3$tacn)O$_3$ [38,9] MoO$_2$(acac)$_2$ [>99,47] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ [87,38]	1,2-Octanediol→1-Octene	#PPh$_3$ P*n*Bu$_3$ P(OEt)$_3$ Indoline Na$_2$SO$_3$ 3-Octanol Zn 1,2-Octanediol	170-225 #200	• $[MoCp^*O_2]_2O$ used to test different solvents and reductants; halobenzenes and PPh$_3$ best performance
	$[MoCp^*O_2]_2O$	*cis*-1,2-Cyclohexanediol→Cyclohexene *cis*-1,2-Cyclooctanediol→Cyclooctene 1,2-Hexanediol →1-Hexene [>99,22] 1,2-Decanediol →1-Decene [>99,56] 1,2-Dodecanediol →1-Dodecane [>99,51] 1-Phenyl-1,2-ethanediol→Styrene [>99,47]	PPh$_3$	-	• Solubility issues with glycerol in anisole solvent

		1,4-Anhydroerythrito →2,5-Dihydrofuran [-,5] Glycerol→Allyl alcohol [-,0]			
Jiang et al., 2021[137]	MoO_3 [42,7] $(NH_4)_6Mo_7O_{24}$ [67,7] $MoO_2(acac)_2$ [>99,6] Mo-Phen [65,8] Mo-Bipy [88,8] Mo-Salen [>99,14] Mo-8-HQ [>99,48]	Anisic alcohol→4,4'-dimethoxybibenzyl	PPh_3	160–240 $^{\#}$220	• Coupling of alcohols by DODH • Significant amount of 4-methylanisol formed

[a] Bipy= 2,2'-bipyridyl, Cp*=pentamethylcyclopentadienyl, Cptt=1,3-di-terttbutylcyclopentadienyl, acac=acetylacetonate, Me_3tacn =1,4,7-trimethyl-1,4,7-triazacyclononane, Phen=1,10-phenanthroline, Salen=tetradentate Schiff base, 8-HQ=8-hydroxyquinoline.

Table 5: Vanadium and other catalysts with [conversion of substrate in %, yield product in %], for #-marked catalyst, substrate, product, reductant, temperature in list

Year and Reference	Compounds[a]	Substrate(s)	Reductant(s)	Temperature (°C)	Remarks
Chapman and Nicholas, 2013[95]	$NaVO_3$ [40,36] NH_4VO_3 [60,43] *n*-Bu_4NVO_3 [40,33] $NaV(acac)_2O_2$ [5,trace] [*n*-Bu_4N]$V(CA)_2O_2$[5,3] [*n*-Bu_4N]V(dipic)O_2 [100,87] $V(HC(Pz)_3)O_2BF_4$ $[VO_2TPA]PF_6$	Octane diol Tetradecanediol $^{\#}$1-Phenyl-1,2-ethanediol→Styrene	$^{\#}Na_2SO_3$ PPh_3 H_2 2,4-Dimethyl-3-pentanol	150-170	• Best performance by [*n*-Bu_4N] V(dipic)O_2 with olefin yields up to 97% • Mechanism with the dipic complex studied by DFT by Galindo,[138] Jiang et al.[139] and by de Vicente Poutás et al.,[140] all in 2016
	[*n*-Bu_4N]V(dipic)O_2	1-Phenyl-1,2-ethanediol→Styrene [99,87] 1,2-Octanediol→1-Octene [95,87] 1,2-Hexanediol→1-Hexene [99,85] *cis*-1,2-Cyclohexanediol→Cyclohexene [25,15] Diethyl tartrate→Diethyl fumarate [90,85] 2,3-Dimethylbutane-2,3-diol (Pinacol) →2,3-Dimethyl-2-butene [90,85]	PPh_3		
Geary et al., 2014[141]	[*n*-Bu_4N]V(dipic)O_2	Diol-diene cycloadducts	Na_2SO_3	180	• Application of DODH for an aromatization step in a synthesis
Gopaladasu and Nicholas, 2016[30]	$Z^+LVO_2^-$ with Z=Bu_4N; L = 2,6-pyridine dicarboxylate	1-Phenyl-1,2-ethanediol→Styrene	$^{\#}Na_2SO_3$ PPh_3	160	• Yields up to 48% with salicylaldehyde hydrazide complex

	[100,95] Z=Bu$_4$N; L = 8-hydroxyquinoline (2L) [100,7] Z=Ph$_4$P; L= triazene-hydroxylamine derivative [100,24] Z=Bu$_4$N and L = salicylaldehyde hydrazide [100,27]		H$_2$ (20 atm) CO (20 atm) Benzyl alcohol Zn		and CO • Complex with 8-hydroxyquinoline ligands not very effective (yields < 10%)
Kasner et al., 2016[25]	Bu$_4$N[(salicyl-2-thiophenyl-hydrazide)VO$_2$]$_{40}$	Diphenylmethanol →Tetraphenylethane [-,>75]	CO (10 atm)	180	• Coupling of alcohols
N. Shin et al., 2017[114]	WO$_3$ (with acid co-catalyst)	Galactaric acid	1-Butanol	Mixture bubble point	• Trace of butyl ester of muconic acid
Petersen et al., 2018[27]	NH$_4$VO$_3$ [-,22] NaVO$_3$ [-,14] V$_2$O$_4$ [-,6] V$_2$O$_5$ [-,22] V(acac)$_3^-$ [-,21] VO(acac)$_2^-$ [-,20]	Glycerol→Allyl alcohol	Glycerol	275	• “lower solubility of NaVO$_3$ in glycerol than that of NH$_4$VO$_3$ accounts for the different reactivity”, V$_2$O$_4$ remains “black powder”, V$_2$O$_5$ dissolves • Various salts tested as additives
R. Lu et al., 2018[117]	NaVO$_3$ WO$_3$	Erythritol→Butadiene	*n*-Butanol	170/120	• No DODH activity
Steffensmeier et al., 2018[142]	tridentate-L(V)O$_x$ compounds: Bu$_4$N[(pyridine-2,6-dicarboxylate)VO$_2$] Bu$_4$N[(pyridine-2,6-dithiocarboxylate)VO$_2$] $^{\#}$Bu$_4$N[(salimin)VO$_2$] SaliminV(O)$_2$OMe	Benzyl alcohol→Diphenylethane [63,32] Benzhydrol→1,1,2,2-Tetraphenylethane [100,100] 1-Phenylethanol→2,3-Diphenylbutane [95,98] Allyl alcohol→Diallyl [4,3] α-Cyclopropylbenzyl alcohol→Dihydronaphthalenes [100,84]	Alcohol itself	150	• Unactivated primary and secondary alcohols largely unreactive • Other alcohols were tested, often giving specific side reactions
Steffensmeier et al., 2019[143]	[(Salimin)VO$_2$]$^-$ Bu$_4$N [(Y-salimin)VO$_2$] with Y=NO$_2$, OMe or H	4-X-Bn-OH with X=OMe, Me, Cl, CN Ph$_2$CHOH, Ph$_2$CDOH	Alcohol itself	150	• Investigation of mechanism
Griffin and Schafer, 2020[144]	Tris(pyridonate)vanadium(III) complex	Benzylic alcohols	Benzylic alcohols	140	• Coupling of alcohols • V(IV)/V(III) cycle proposed

[a]acac = acetylacetonate; CA = cinnamate, TPA = tris(2-pyridylmethyl)amine, dipic = 2,6-pyridinedicarboxylate; HC(Pz)$_3$ = tris(pyrazol-1-yl)methane.

5.2.3 Supported catalysts

Table 6: Supported rhenium catalysts with [conversion of substrate in %, yield product in %], for #-marked catalyst, substrate, product, reductant, temperature in list

Reference	Compounds tested[a]	Substrate(s)	Reductant(s)	Temperature (°C)	Remarks
Denning et al., 2013[13]	ReO_x/C, from NH_4ReO_4 precursor	Tetradecanediol→1-Tetradecene [-,42] 1-Phenyl, 1,2-ethanediol→Styrene [-,39] (+)-Diethyl tartrate→Diethyl fumarate [-,95]	Diisopropyl carbinol Benzyl alcohol Tetrahydronaphthalene #H_2 (0.7–1.4 MPa)	150–175 #150	• First supported DODH catalyst
Sandbrink et al., 2016[14]	NH_4ReO_4/C NH_4ReO_4/TiO_2 NH_4ReO_4/ZrO_2 NH_4ReO_4/SiO_2 ReO_x/C #ReO_x/TiO_2 ReO_x/ZrO_2 ReO_x/SiO_2	1,2-Hexanediol→1-Hexene [-,46] Glycerol→Allyl alcohol [-,48] 1,2,4-Butanetriol→3-Buten-1-ol [-,27] 1,2,6-Hexanetriol→5-Hexen-1-ol [-,38]	3-Octanol	170	• Yields up to 60% • Productivities up to 0.13 mol g_{metal}^{-1} h^{-1} • Best recycling stability: ReO_x/TiO_2 • Oxidation state of Re by X-ray absorption finds mixture of Re(VII), Re(IV), and Re(0)
N. Ota et al., 2015[83]	#ReO_x–Pd/CeO_2 ReO_x–Pd/SiO_2 ReO_x–Pd/C ReO_x–Pd/AC ReO_x–Pd/Al_2O_3 ReO_x–Pd/ZrO_2 ReO_x–Pd/TiO_2 ReO_x–Pd/MgO ReO_x–Pd/CaO ReO_x–Pd/La_2O_3 ReO_x–Pd/Y_2O_3 ReO_x/CeO_2	1,4-Anhydroerythritol→Tetrahydrofuran [99,99] Glycerol→1-Propanol [>99,87] Erythritol→Butanediols [98,91] Xylitol→Pentanemono-ols [>99,98] Sorbitol Xylitol→Hexanediols [>99,85]	H_2	130-170 #170	• Hydrodeoxygenation resulting in saturated products, see also Tamura et al., 2018[145] • With ReO_x–Pd/CeO_2 and 1,4-anhydroerythritol: Turnover frequency 300 h^{-1} Turnover number 10 000
N. Ota et al., 2016[19]	ReO_x–Pd/CeO_2	Alkane diols, vicinal or not vicinal *cis* and *trans* 1,2-cyclopentanediols *cis* and *trans* 1,2-cyclohexanediols	H_2 (8 MPa)	140	• Hydrodeoxygenation resulting in saturated products • Extensive catalyst characterization and detection of oxidation states Re(IV) and Re(VI) in cycle
Tazawa et al., 2016[20]	ReO_x-$Ru_{0.3}$/CeO_2 ReO_x-$Rh_{0.3}$/CeO_2 ReO_x-$Pd_{0.3}$/CeO_2 ReO_x-$Pt_{0.3}$/CeO_2	Glycerol→Allyl alcohol [>99,90] Erythritol→Butadiene [97,81] 1,2,4-Butanetriol→3-Buten-1-ol [80,64] 1,4-Anhydroerythritol→2,5-Dihydrofuran	H_2 (8 MPa)	170	• Glycerol to allyl alcohol, TON 300

	ReO_x-$Ir_{0.3}/CeO_2$ ReO_x-$Ag_{0.3}/CeO_2$ $^{\#}ReO_x$-$Au_{0.3}/CeO_2$ ReO_x/CeO_2	[93,80] *cis*-1,2-Cyclohexanediol→Cyclohexene [91,86]			
X. Li and Y. Zhang, 2016[108]	$ReCH_3O_3$/PVP $^{\#}HReO_4$/P-Bn $HReO_4$/PMF	L-(+)-Tartaric acid→Maleic acid [100,94]	3-Pentanol (in flowing N_2)	120	• First polymer-supported DODH catalysts • 48% $HReO_4$/P-Bn best activity and selectivity, 90% yield of free maleic acid • 51% Re lost over 5 uses • Leached species less active than immobilized species
Y. Kon et al., 2017[63]	ReO_x/Al_2O_3 [>99,77] ReO_x/SiO_2 [61,41] ReO_x/TiO_2 [>99,82]	Glycerol→Allyl alcohol	2-Hexanol	148	• Variation of Re content, Yields > 90% for 10 wt% ReO_x/Al_2O_3
	ReO_x/Al_2O_3		1-Butanol [99,48] 2-Butanol [51,40] 1-Hexanol [>99,73] 2-Hexanol [>99,91] 3-Hexanol [>99,85] Cyclohexanol [52,30] 1-Octanol [93,45] 3-Octanol [93,84] Benzyl alcohol [85,8] 1-Phenyl ethanol [83,0]	170 (bath)	
Sharkey et al., 2018[31]	SiO_2-tethered catecholato-oxido-rhenium complex	1-Phenyl-1,2-ethanediol→Styrene [100,62] 1,2-Decanediol→1-Decene [90,89] Diethyl tartrate→Diethylfumarate [100,94]	$^{\#}PPh_3$	150-170	• Decene yields with ReO_x/SiO_2, ReO_x/Fe_2O_3, ReO_x/Al_2O_3 and PPh_3 70 –78%; catalysts also effective with H_2 or CO • Re leaching for all supports, most pronounced for SiO_2
	ReO_x/C [100,82] ReO_x/Al_2O_3 [100,78] ReO_x/SiO_2 [100,78] ReO_x/CeO_2 [17,5] ReO_x/Fe_2O_3 [100,56]	1,2-Decanediol→1-Decene	$^{\#}PPh_3$ H_2 CO	150	• Different synthesis methods tested, incipient wetness and deposition impregnation • Leaching of rhenium observed
Y. Xi et al., 2018[146]	ReO_x–Pd/CeO_2	1,4-Anhydroerythritol	H_2	140	• Computational investigation of mechanism • Pd dissociates H_2 which spills over on CeO_2

					• Re(VII) more active then Re(VI)
Nakagawa et al., 2018[21]	#ReO_x-Au/CeO_2 ReO_x-Pd/CeO2 And physical mixtures of ReO_x/CeO_2 and Au/CeO_2 or Pd/CeO_2	1,2-Octanediol→1-Octene [42,32] *cis*-1,2-Cyclohexanediol→Cyclohexene [91,86] *trans*-1,2-Cyclohexanediol→Cyclohexene [9,7]	H_2	140-170 #170	• Au promotes reduction of Re species
MacQueen et al., 2019[147]	ReO_x–Pd/CeO_2	1,4-Anhydroerythritol→Tetrahydrofuran [99.9,99.7] Xylitol→1,2-Dideoxypentitol and 1,2,5-Pentanetriol	H_2 (40 to 80 bar)	100–180	• Gives saturated products • ^{18}O Exchange on catalyst in Ref. [148]
Sharkey et al., 2019[17]	ReO_x/TiO_2 ReO_x/ZrO_2 ReO_x/SiO_2 ReO_x/Fe_2O_3 ReO_x/Al_2O_3	1,2-Hexanediol→1-Hexene 1,2-Decanediol→1-Decene	PPh_3	150	• Promotion of leaching through complexation with diol • Redeposition of leached species upon full conversion of diol
T. Wang et al., 2019[149]	ReO_x/CeO_2 ReO_x/Al_2O_3 ReO_x/SiO_2 ReO_x//ZrO_2 ReO_x/TiO_2 ReO_x/C	1,4-Anhydroerythritol	H_2	140	• Ultimate product is 1,4-butanediol, DODH only one step • Mixtures of two catalysts are investigated • Different types of carbons used as supports
J. Lin et al., 2019[121]	ReO_x/ZrO_2 [-,93] ReO_x/TiO_2 [-,77] ReO_x/SiO_2 [-,71] ReO_x/Al_2O_3 [-,44] ReO_x/MgO [-,15]	D-Glucaric acid-1,4-lactone→five-membered ring lactone with one OH group and dibutyl hexa-2,4-dienedioate	Butanol (N_2 flow)	120	• Yields represent the sum of the two products
T. Wang et al., 2020[150]	ReO_x/WO_3-ZrO_2 ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 ReO_x/CeO_2 + ReO_x/WO_3-ZrO_2	1,4-Anhydroerythritol	H_2 (8 MPa)	140	• Focus is on catalysts for conversion of 2,5-dihydrofuran to 1,4-butanediol; DODH only a preceding step
J. Cao et al., 2019[151]	ReO_x-Au/CeO_2	Methyl α-D-mannopyranoside→ Methyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside [99,90] Methyl β-D-galactopyranoside→ β-D-*erythro*-Hex-3-enopyranoside, methyl 3,4-dideoxy- [>99,87] Methyl β-L-arabinopyranoside→ (2*S*,3*R*)-3,6-Dihydro-2-methoxy-2*H*-pyran-3-ol [97,90] Methyl α-L-rhamnopyranoside→ (2*S*,3*R*,6*R*)-3,6-	H_2	140	• Synthesis of unsaturated sugars

		Dihydro-6-methoxy-2-methyl-2*H*-pyran-3-ol [93,78] Methyl α-L-fucopyranoside→ (2*R*,3*S*,6*S*)-3,6-Dihydro-2-methoxy-6-methyl-2*H*-pyran-3-ol [67,61] Methyl α-D-glucopyranoside→ [<1,0]			
J. Cao et al., 2020[152]	ReO_x–Pd/CeO_2	Methylglycosides	H_2	130-150	• DODH combined with hydrogenation, gives dideoxy sugars • Investigation of mechanism
Y. Xi et al., 2020[153]	ReO_x/TiO_2(101)	1,4-Anhydroerythritol→2,5-Dihydrofuran	H_2	140, 200	• Computational investigation • First O–H bond cleavage of 1,4-anhydroerythritol rate-determining step
Hočevar et al., 2021[126]	ReO_x/C ReO_x/SiO_2 ReO_x/Al_2O_3 Second catalyst Pd/C or Pt/C	Aldaric acids	No external red. MeOH H_2	100-175	• Negligible yields with ReO_x/SiO_2 and ReO_x/Al_2O_3 • Muconates at low, adipates at high temperature
J.H. Jang et al., 2021[154]	ReO_x/C Pt-ReO_x/C	#Mucic acid→Dialkylmuconate Diisopropyl L-(+)-tartarate	Methanol [88,53] Ethanol [94,62] Isopropanol [94,71] 3-Pentanol [83,72]	#170 170-230	• Alkyl esters formed with reducant alcohols • With Pt, hydrodeoxygenation to saturated product, adipic acid
Meiners et al., 2021[15]	NH_4ReO_4 supported on zeolites H-β, H-ZSM-5 and H-Y	1,2-Hexanediol→1-Hexene	3-Octanol	170	• Productivities up to 0.24 mol 1-hexene $g_{Re}^{-1}\cdot h^{-1}$
W. Deng et al., 2021[155]	ReO_x/activated carbon	Potassium glucarate	H_2 (2 MPa)	110	• DODH as one step in route from glucose to adipic acid
Albarracin-Suazo et al., 2022[156]	ReO_x-Pd/TiO_2	1,4-Anhydroerythritol→Tetrahydrofuran [26,10]	H_2 (52 bar)	140	
Yamaguchi et al., 2022[23]	ReO_x-Ag/CeO_2 [100,86]] ReO_x-Au/CeO_2 [94,37] ReO_x-Ir/CeO_2 [88,11]	Erythritol→Butadiene	H_2 (8 MPa)	140	Catalyst with metals Cu,Pd,Ru,Ni or without metal or without ReOx yields <2%
	ReO_x-Ag/CeO_2	Glycerol→Allyl alcohol [93,92 1,2-Hexanediol→1-Hexene [95,94] 1,4-Anhydroerthrito→2,5-Dihydrofuran [98,88] *cis*-1,2-Cyclohexanediol→Cyclohexene [100,88] *trans*-1,2-Cyclohexanediol→Cyclohexene [<1,trace] Methyl α-L-fucopyranoside→ (2R,3S,6S)-3,6-Dihydro-2-methoxy-6-methyl-2H-pyran-3-ol	H_2		

		[94,91] Methyl β-D-ribofuranoside→ D-*glycero*-pent-2-enofuranoside, methyl 2,3-dideoxy- [99,88]			

[a] PVP=poly(4-vinylpyridine), P-Bn=poly-benzylamine, PMF=poly(melamine-formaldehyde)

Table 7: Other supported catalysts with [conversion of substrate in %, yield product in %], for #-marked catalyst, substrate, product, reductant, temperature in list

Reference	Compounds[a]	Substrate(s)	Reductant(s)	Temperature (°C)	Remarks
Kwok et al., 2017[24]	VO_x/SiO_2	2,3-Butanediol	2,3-Butanediol	250-500	• Monovanadate, oligovanadate, V_2O_5 present depending on V loading • Gas phase process
Sandbrink et al., 2017[131]	$Na_2MoO_4 \cdot 2H_2O/TiO_2$ [27,1] MoO_x/TiO2 (Na_2MoO_4·precursor) [39,5] $(NH_4)_6Mo_7O_{24} \cdot 4H_2O/TiO_2$ [100,48] MoO_x/TiO_2 [$(NH_4)_6Mo_7O_{24}$ precursor] [94,55] in situ mixture $Na_2MoO_4+TiO_2$ in situ mixture $(NH_4)_6Mo_7O_{24} \cdot 4H_2O+TiO_2$	1,4-Anhydroerythritol→2,5-Dihydrofuran	3-Octanol	200	• Yields up to 76% with “in situ mixture $(NH_4)_6Mo_7O_{24} \cdot 4H_2O+TiO_2$” catalyst
Sharkey et al., 2018[31]	$MoO_x/\alpha\text{-}Fe_2O_3$ [89,16] MoO_x/TiO_2 [100,17] MoO_x/Al_2O_3 [100,17] MoO_x/SiO_2 [79,15] MoO_x/ZrO_2 [100,14] Ammonium heptamolybdate {100,42] MoO_3	1,2-Decanediol→1-Decene	#PPh_3 H_2 (200 psi) CO (150 psi)	200	• Significant catalytic conversion only with PPh_3 • Mo leaching reported
J. Lin et al., 2019[121]	VO_x/ZrO_2 [-,0] MoO_x/ZrO_2 [-,9.7] WO_x/ZrO_2 [-,2.9]	D-Glucaric acid-1,4-lactone→five-membered ring lactone with one OH group and dibutyl hexa-2,4-dienedioate	Butanol	120	• Yields represent the sum of the two products
Y. Xi et al., 2020[153]	MoO_x/TiO_2(101)	1,4-Anhydroerythritol→2,5-Dihydrofuran	H_2	140, 200	• Computational investigation • Dihydrofuran extrusion rate-determining step
J. Cao et al., 2020[152]	$VO_x\text{-}Pd/CeO_2$ $CrO_x\text{-}Pd/CeO_2$ $MnO_x\text{-}Pd/CeO_2$ $NbO_x\text{-}Pd/CeO_2$ $MoO_x\text{-}Pd/CeO_2$ $WO_x\text{-}Pd/CeO_2$	Methyl α-D-mannopyranoside	7.7 MPa H_2	140	• DODH combined with hydrogenation, gives mixture of DODH product and dideoxy sugars

Albarracin-Suazo et al., 2022[156]	MoO_x-Pd/TiO_2 [29,28] MoO_x-Pt/TiO_2 [28,23] MoO_x-Rh/TiO_2 [29,13] WO_x-Pd/TiO_2 MoO_x-Pd/ZrO_2 MoO_x-Pd/SiO_2 MoO_x-Pd/Al_2O_3 MoO_x/TiO_2	$^{\#}$1,4-Anhydroerythritol→Tetrahydrofuran Erythritol→1,2-Butanediol Glycerol→1-Propanol	H_2 (21-72 bar)	120-160 $^{\#}$140	• DODH followed by hydrogenation to saturated product
Hacatrjan et al., 2022[22]	MoO_x-Au/TiO_2	1,4-Anhydroerythritol→2,5-Dihydrohydrofuran [79,71]	H_2	190	• Anatase, rutile and mixed supports • Variation of synthesis method

5.3 Trends and questions emerging from DODH catalyst survey

5.3.1 Catalyst compositions and syntheses

The comparison between rhenium and other catalysts is somewhat confounded by the uneven amount of data available. However, all compounds that are active without further oxidation are at least dioxido species. Further, it does emerge that high yields are obtained with a wider variety of rhenium compounds whereas only specific molybdenum or vanadium complexes excel. This result could mean that, as is expressly mentioned in some articles,[91,125] some rhenium compounds are only precursors and the active species form during the reaction. These active species could then be more similar than thought irrespective of the starting rhenium complex. More knowledge about the active rhenium species is needed to clarify this question. Another explanation is that the higher reaction temperatures that are generally applied with molybdenum and vanadium complexes promote more side reactions and are inherently prohibitive of high yields. To date, no other metals have delivered DODH yield levels similar to those obtainable with the three named metals.

Many "classical" supports, that is, oxides and carbon, have been tested in combination with rhenium, molybdenum, or vanadium as active component. The interaction between support and active component can be weak, and leaching is a reported issue. There is only partial agreement in the literature as to which supports produce the most active and the most stable catalysts. For example, ReO_x/TiO_2,[14] ReO_x/CeO_2[33] and ReO_x/ZrO_2[121] have each been identified as the best among a series of catalysts. Some reports conclude that ReO_x/TiO_2 is the most stable catalyst, whereas others find this combination to leach rhenium.[17] It has become evident that there are additional circumstances such as substrate and solvent that may contribute to leaching.[17] Moreover, rhenium loading and the method of preparation of the catalyst can be factors, and these results are not necessarily contradictory.

The field of supported catalysts has room for exploration of other support materials, for example investigations of zeolites started only recently,[15] and research on non-oxidic materials is limited to carbon and a few polymers. Common precursors are ammonium metalates such as ammonium perrhenate, which are applied to the support in aqueous phase. Consequently, other precursors and syntheses have yet to be explored systematically.

The addition of a secondary catalyst to activate the reductant has been successfully implemented but is presently limited to the addition of noble metals for activation of H_2.

Most of the comparisons of catalysts are on a yield basis at this point, and there are relatively few published initial rates, which would be best for catalyst assessment in batch reactions.[157] Given the multitude of components and conditions, and the absence of a community-accepted benchmark, it is difficult to even compare yields between different papers. This issue is further discussion in Section 6.

5.3.2 Counter ion effects

A significant fraction of the known DODH catalysts are anionic complexes of the active metals rhenium, molybdenum, or vanadium. As a result, a counter ion, an inorganic or organic cation, is automatically added to the reaction mixture. Not only is it evident that these counter ions influence the measured yields for rhenium, molybdenum, and vanadium catalysts (see Table 8 for a compilation of examples), but there are subtle effects on the selectivity. For example, Ahmad et al.[28] pointed out that $nBuNReO_4$ is more selective whereas NH_4ReO_4 is more active. Several proposals have been made regarding the action of the counter ions. The proposed explanations for the role of the counter ions include differences in solubility depending on the nature of the cation, an acid function of counterions with protons, and coordination of counter ions with oxido ligands of the metal catalyst. Both experiments and DFT have been applied to elucidate the role of the counter ion.

Table 8: Illustration of counter ion effect

Catalyst	Substrate (Difference in conditions)	Yield target olefin	Reference
$NaReO_4$	Glycerol (18 h reaction)	6	Yi et al.[92]
NH_4ReO_4	Glycerol (1 h reaction)	80	
Na_2MoO_4	1,4-Anhydroerythritol	1	Sandbrink et al.[131]
$(NH_4)_2MoO_4$		27	
$NaVO_3$	1-Phenyl-1,2-ethanediol	33	Chapman and Nicholas[95]
NH_4VO_3		43	

The low solubility of sodium salts has been pointed out on several occasions, sometimes in direct comparison with ammonium salts. Vkuturi et al.[37] noted that $NaReO_4$ is "sparingly soluble" (in chlorobenzene in that case) and were able to improve the yield by adding a crown ether to promote solubilization. Morris et al.[111] investigated a series of ammonium and pyridinium salts and found differences in catalytic performance depending on the cation. DFT studies revealed a role of the cations only in a pathway not integral to the catalytic cycle, and the authors concluded that variations in solubility were responsible for the experimental observations. Dethlefsen et al.[129] ascribed the inactivity of Na_2MoO_4 to its insolubility (in dodecane in the investigated case). Petersen et al.[27] related the lower activity of $NaVO_3$ to its lower solubility in the reaction medium in comparison to that of NH_4VO_3.

Yi et al.[92] deliberately added chlorides with alkali, ammonium, or protons as the cations. In the DODH of glycerol with $ReCH_3O_3$ as the catalyst, the amount of volatile products was not affected by addition of NaCl, whereas addition of HCl or NH_4Cl enhanced the rate. The use of $NaReO_4$ as the catalyst with NH_4Cl gave a similar result as the use of NH_4ReO_4. The authors came to the preliminary conclusion that acidic protons released from HCl or ammonium or another type of cation must activate the perrhenate.

Shakeri et al.[120] addressed the role of the counter ion by experiment and theory. They tested perrhenates with 5 different cations in the DODH of 1-phenyl-1,2-ethanediol with PPh_3 as reductant in chlorobenzene, and their results agreed with the findings of Ahmad et al.[28] in that nBu_4NReO_4 is more selective while NH_4ReO_4 is more active. In a set of experiments exploring various parameters, styrene yields almost did not vary with the choice of reductant, PPh_3 or Na_2SO_3. The yields did vary with the nature of the cation; further, yields were much higher for reaction in chlorobenzene than for reaction in methanol. In the ensuing DFT calculations, the interactions between cations and species in the cycle in each step were considered. Mostly, the cations interacted with oxygens in the structures. The authors found that $n\mathrm{Bu_4N^+}$ and 2-phenylpyridinium decrease barriers, whereas Na^+ and K^+ increase barriers. Ammonium was found to be of little effect. These results corresponded to the experimental findings.

Obviously, these effects are not mutually exclusive, and in some settings, all three could apply. This area of DODH would benefit from further detailed research.

6. Deoxydehydration Kinetics and Mechanism

6.1 Rate laws for deoxydehydration

Several groups have attempted to measure the kinetics of DODH and establish rate laws. The findings for rhenium catalysts are discussed in the following.

Cook and Andrews[3] evaluated $Re(C_5Me_5)O_3$-catalyzed DODH with PPh_3 as the reductant. They found the 1-phenyl-1,2-ethanediol DODH rate comparable with known rates of styrene extrusion from diolates. Consequently, they viewed the alkene extrusion step as rate-determining.

The group of Abu-Omar has made significant efforts to elucidate the kinetics of rhenium-catalyzed DODH.[40,92,119] Yi et al.[92] measured the rates of glycerol DODH with methyltrioxidorhenium as catalyst and glycerol as reductant. The experimentally observed kinetics were a rate of allyl alcohol formation that was first order in glycerol and first order in methyltrioxidorhenium. The author proposed an underlying, more elaborate rate law that would show second order dependence in glycerol at lower glycerol concentrations but would transition to the experimental observations at higher glycerol concentrations. There was no kinetic isotope effect (KIE) for glycerol-$(OD)_3$, whereas a KIE of 2.4 was determined for d5-glycerol-$(OH)_3$, indicating a C-H/D bond in glycerol is involved in the rate-determining step. Liu et al.[40] investigated the kinetics of (*R*,*R*)-(+)-hydrobenzoin DODH with methyltrioxidorhenium as catalyst and 3-octanol as reductant. The authors found a half-order dependence on rhenium and concluded that a dinuclear rhenium complex is the active species. The reaction was zero order in the diol, and showed a KIE of 1.4 for use of a deuterated 3-octanol, which prompted the authors to propose that reduction of Re(V)diolate to a Re(III)diolate species is the rate-determining step in the cycle. Jang et al.[119] formulated a rate law for glycerol conversion on ReO_x nanoparticles. Based on rate dependencies and kinetic isotope effects – no KIE for glycerol-$(OD)_3$ or 3-(OD)-octanol but a KIE of 4.2 for 3-d-3-octanol, they postulated first order kinetics in glycerol, total rhenium, and 3-octanol.

Dethlefsen and Fristrup[106] monitored the conversion of 1,2-tetradecanediol with methyltrioxidorhenium as the catalyst and 3-octanol as the reductant by in situ liquid-phase IR spectroscopy. They found the DODH reaction to be zero order in the diol, first order in catalyst, and first order in alcohol. This information, in combination with a KIE of 2.1 for $C_5H_{11}CH(OH)C_2H_5$ vs. $C_5H_{11}CD(OH)C_2H_5$, let them conclude that oxidation of the alcohol (that is, reduction of the rhenium) is rate determining.

Raju et al.[107] found apparent first order in 1,2-octanediol for its DODH with PPh_3 as reductant and several Re Cp'O_x complexes at the catalysts, where Cp' stands for differently substituted cyclopentadienyl ligands. From this result, it was inferred that octene extrusion is rate determining.

Ota et al.[19] and Cao et al.[152] determined reaction orders for the DODH of 1,4-anhydroerythritol (including hydrogenation) and methylglycosides on ReO_x-Pd/CeO_2 and found zero order in the substrates and zero order in the reductant, H_2. They concluded that the diols interact strongly with the rhenium site and that alkene elimination is rate determining. When palladium was replaced by gold, the order in H_2 increased, depending on H_2 pressure and synthetic method of gold addition,[21] consistent with the more sluggish activation of H_2 by gold relative to palladium. Xi et al.[146] conducted a computational investigation into the DODH of 1,4-anhydroerythritol on ReO_x/CeO_2 and ReO_x-Pd/CeO_2. In the absence of abundant hydrogen atoms, the authors found the reduction of ReO_x to be rate controlling. They found an order of zero in H_2 and an order of 1 or 0.5 order in 1,4-anhydroerythritol in the absence or presence of palladium, respectively. For the same reaction on ReO_x/6H–TiO_2, Xi et al.[153] found an order in H_2 of zero and in substrate of 1. The cleavage of the first O-H bond of 1,4-anhydroerythritol was identified as rate controlling.

Two different boundary scenarios emerge from these works. 1) The alkene extrusion step, which is also the catalyst reoxidation step, is rate determining – this scenario is favored if the reduction step is rendered facile through use of a strong reductant such as PPh_3 or through the presence of a noble metal that dissociates H_2, or if the alkene extrusion is not favorable. 2) The reduction of the catalyst is the rate-limiting step. This scenario is favored when the catalyst is difficult to reduce or an alcohol is used as reductant, and from isotope experiments, the hydrogen abstraction from the α-carbon of the alcohol is crucial. For assessing catalysts, it may be desirable to evaluate these two properties of a catalyst separately by switching the rate-determining step. If feasible, a potent reductant would allow evaluation of the extrusion step 1) and a readily extruded product would allow evaluation of the reduction step 2). For designing catalysts or co-catalysts, both properties must be optimized.

6.2 Supporting and exclusive insights from computational chemistry

6.2.1 Molecular catalysts

A significant number of publications on molecular DODH catalysis include computational chemistry, often to explain feasibility of proposed mechanisms or rationalize experimental results. A few purely computational investigations exist. Molecular rhenium, molybdenum, and vanadium catalysts have all been subject to these computational efforts and are discussed in this order.

One direction for application of computational methods has been the determination of stability and properties of rhenium-containing species involved in DODH chemistry, and this information has been used for various purposes. To compare catalysts, Ahmad et al.[28] calculated the exothermicity of glycolate formation with ethylene glycol, which they found to be higher for $ReCH_3O_3$ than for ReO_4^-, in line with the observed higher reactivity of the metalorganic compound. Lupacchini et al.[18] sought to assess the viability of species formed by side reactions in $ReCH_3O_3$-catalyzed glycerol DODH. Experimentally, a precipitate was observed, and calculations confirmed the stability of various Re(VII) to Re(V) dimers, in part with coordinated molecules of 2-propanol. Raju et al.[105] computed stable configurations and spectra of a model for DODH catalysts, a cyclopentenyl ReO_x complex and its dimer. Dethlefsen and Fristrup[106] calculated the stability and vibrational spectra of species considered in the $ReCH_3O_3$-catalyzed DODH promoted by secondary alcohols and used this information to interpret spectroscopic data.

As a further step in most publications, building on information regarding stable species, free energy profiles for reaction pathways have been computed and rate-limiting steps have been extracted. Liu and Nicholas[39] calculated the lowest energy pathway for sulfite-mediated DODH, which involved the attachment of $NaSO_3^-$ species on $ReCH_3O_3$ to give a lower energy complex, followed by ethylene glycol coordination, several intramolecular steps, and turnover-limiting fragmentation of the Re−glycolate. Dethlefsen and Fristrup[106] formulated reaction kinetics for the $ReCH_3O_3$-catalyzed DODH promoted by secondary alcohols and concluded that a reversibly formed Re(VII) glycolate slows the desired DODH. Lupacchini et al.[18] reported on $ReCH_3O_3$-catalyzed glycerol DODH, and their calculations suggested that initial methane release and reduction of Re(VII) to Re(V) present high barriers of 154 and 168 kJ/mol, respectively. Qu et al.[38] investigated the sequence of reduction and glycolate formation for the 3-octanol-driven $ReCH_3O_3$-catalyzed DODH of 1,4-anhydroerythritol. The authors found both pathways to be energetically challenging with overall barriers of 189 kJ/mol (reduction first) and 222 kJ/mol (glycolate formation first) and proposed a third pathway involving formation of a dihydroxidomethyloxidorhenium complex. The reduction step to give this species at a cumulative barrier of 164 kJ/mol accounted for the highest barrier in the proposed DODH mechanism; and primary alcohols resulted in an increase of this barrier. Li et al.[104] applied 1-butanol as a reductant to methyltrioxidorhenium and compared the formation of methyldioxidorhenium with that of dihydroxidomethyloxidorhenium. They found the hydroxido complex to be thermodynamically favored by 48 kJ/mol, and the overall energy barrier for its formation to be only 166 kJ/mol vs 199 for methyldioxidorhenium. Further confirmation for this intermediate came from Wu et al.,[110] who investigated the DODH of diols with differently spaced OH groups with $ReCH_3O_3$ as catalyst and 1-butanol as reductant and also found formation of a $ReCH_3O(OH)_2$ complex to be the first step.

These reports make $ReCH_3O_3$ the molecular DODH catalyst that is most frequently investigated by computational methods. Even though the catalyst is the same, the effect of reductant and possibly of substrate is strong enough to alter the nature of the intermediates and the rate-determining step. In all these reports, the B3LYP functional was used. Qu et al.[38] cross-checked energetics using other levels of DFT. Various solvents were considered in these computations, *viz*., ethanol,[106] propanol,[18] 1-butanol,[104,110] chloroform,[38] and benzene.[39] Solvents were treated by using implicit solvation models; mostly variants of the polarizable continuum model (PCM), such as integral equation formalism PCM (IEFPCM),[18,104,110] SMD-PCM,[38] or the conductor-like PCM (CPCM).[39]

Focusing on a different catalyst, Morris et al.[111] addressed the question of the sequence of reduction and condensation for the combination pyridinium perrhenate, styrene diol, and triphenyl phosphane. Computationally, using B3LYP and the SMD continuum solvation model to include the chloroform solvent, they found a preference for reduction occurring first, prior to condensation. Shakeri et al.[113] also considered perrhenate ReO_4^- as the catalyst, with styrene diol as the reactant and triphenylphosphane as the reductant. Using the M06 functional and the PCM for methanol or chlorobenzene, they found the condensation–reduction sequence to have the lower overall activation barrier (216 kJ/mol in chlorobenzene) in comparison to variants of the reduction–condensation sequence. The energetically most demanding steps were associated with the reduction. Further expanding on their work, Shakeri et al.[120] addressed the role of the counter ion and found tetrabutylammonium and phenylpyridinium to lower activation barriers, whereas sodium and potassium increased activation barriers through strong interaction with the oxido ligands of perrhenate.

DODH catalysis by molybdenum compounds was computationally investigated by Fristrup and coworkers.[34,158,159] One molecule of MoO_3 or MoO_2Cl_2 served as the model, methanol as the solvent, and B3LYP and an implicit solvation model as the methods. In Lupp et al.,[158] Fristrup's group computed the free energy profile for alkene extrusion from a monodiolate and from a bisdiolate complex formed from MoO_3 and 1,2-propanediol and found the activation energies to be similar; however, the monodiolate starting complex was 170 kJ/mol lower in energy. They also excluded a molybdenum oxetane intermediate for the extrusion step and investigated the effect of temperature on the entire cycle with propanediol as substrate and as reductant. Finally, they evaluated the DODH of pinacol with MoO_2Cl_2 as the catalyst. Dethlefsen et al.[34] compared the free energies for the reduction of molybdenum(VI) to molybdenum(IV) starting from MoO_3 and found that 1,2-propanediol and isopropylalcohol were more effective if the diolate had already formed, whereas H_2 was best added simultaneously to two oxido ligands. In the free-energy diagram for the DODH of 1,4-anhydroerythritol at 298 K, the isopropyl alcohol oxidation was identified as most demanding individual step with a barrier of 101 kJ/mol. Larsen et al.[159] focused on the free energy profiles for the reduction of MoO_3 and $MoO_2(OH)_2$ by 2-propanol in methanol and found reduction of the dehydrated form to be more favorable.

Galindo[138] was the first to computationally investigate the reduction−condensation sequence for vanadium-catalyzed DODH. The $[VO_2(dipic)]^-$ complex reported earlier by Chapman and Nicholas[95] was the catalyst, ethylene glycol the substrate, and PPh_3 the reductant. The B3LYP functional was employed, and benzene was incorporated via the CPCM model. Energy profiles for both possibilities were evaluated by three different criteria, which were found to be equal or in favor of reduction preceding condensation; these criteria were highest barrier, highest transition state relative energy, and maximum free energy difference between intermediates. Vicente Poutás et al.[140] focused on the same complex, $[VO_2(dipic)]^-$, and solvent benzene (treated via IEFPCM), but with a different functional B3PW91, and a small system size, which was accomplished by using ethylene glycol as substrate and trimethylphosphane as reductant. The calculations confirmed that the sequence starts with reduction. In addition, the authors proposed that the alkene extrusion involves homolytic C-O bond cleavage and generates a diradical metallacycle as intermediate. Jiang et al.[139] arrived at a contrasting result for the same complex. The model reaction was the DODH of 1,2-propanediol, and M06 and M06-L methods with the SMD solvation model for benzene were used. Reduction of the V(V) complex by triphenylphosphane or secondary alcohol was excluded as the first step. The proposed cycle involved several spin crossovers and consisted of diolate formation, reduction by triphenylphosphane, formation of a metallacycle and cleavage. Aksanoglu et al.[160] revisited $[VO_2(dipic)]^-$-catalyzed DODH. At the M06-L/SDD/6-311+G**/SMD level, they found the barrier for reaction initiation by diolate formation to be 96 kJ/mol lower than that for initiation by reduction. The authors further reported a stepwise mechanism for the DODH of cyclic *trans*-diols, to explain the experimentally observed feasibility and rationalize the positive effect of light.

Further computational work on vanadium concerns the $(salimin)VO_2^-$ complex and coupling of alcohols. Steffensmeier et al.[142,143] reported energy profiles for coupling of benzhydrol, obtained using B3LYP and the SMD model for benzene.

In summary, for some catalyst–substrate–reductant combinations, free energy profiles have been reported and employed to demonstrate feasibility of proposed mechanisms and to identify the most favorable pathway. However, the number of computationally investigated combinations is small relative to the vast array of experimental data. On the other hand, some species inferred from computations lack experimental verification. Broader studies, with systematic variations of molecular properties, would allow for a better comparison and understanding of trends.

6.2.2 Deoxydehydration on solid surfaces – insights from density functional theory

In contrast to the investigations of molecular DODH catalysts, which operate with well-defined starting compounds, investigations of supported DODH catalysts offer additional degree of complexity. The structure of the initial surface species is not generally known, and neither is the nature of the active site. Indeed, the models used to understand DODH catalysis by solid rhenium compounds vary significantly, depending on experimental observations, as detailed in the following paragraphs. At present, the number of supports included in these computational efforts is very limited.

In two papers led by Ota, Tomishige's group reported a Pd/ReO_x/CeO_2 catalyst in 2015,[33] and they applied DFT[19] to unravel active species and mechanism. The functional used was PW91, and the authors pointed out the trends towards about 30% lower activation barriers in comparison to other functionals. The CeO_2 (111) surface was modeled with a $Ce_{70}O_{140}$ cluster. The authors identified monomeric $Re^{IV}O_2$ and $Re^{VI}O_3$ moieties as active species in the cycle, while dimeric species were deemed to be likely inactive. The highest barrier was 153 kJ/mol for the extrusion of 2,5-dihydrofuran in the H_2-driven DODH of 1,4-anhydroerythritol. In a subsequent paper, Cao et al.[152] used periodic DFT with the PBE functional and a model of a fully hydroxylated ceria surface to reflect the reducing conditions, except for the binding site of ReO_x. The activation energies for DODH of two different methyl glycosides were calculated and compared with those obtained for $ReCH_3O_3$. Hosaka et al.[161] revisited the 1,4-anhydroerythritol DODH and found a mechanism involving an oxygen vacancy in the ceria to be favorable over a completely H-covered CeO_2 surface. The authors reported ReO_2(VII) as the most stable surface species on the fully hydroxylated CeO_2 surface, while emphasizing that +IV and +VI are the oxidation states of rhenium during the cycle.

In a series of papers, Heyden and coworkers[146] investigated DODH catalysts comprised of supported moieties by periodic DFT using the Perdew-Burke-Ernzerhof (PBE) functional. The first target was the Pd/ReO_x/CeO_2 catalyst, motivated by the work of Tomishige's group.[19,33] In Xi et al.,[146] they conducted an investigation into stable $ReO_x(OH_y)$ species on CeO_2 and found ReO to be the most stable species at a temperature of 413 K, and H_2 and H_2O partial pressures of 80 bar and 0.08 bar, with a rhenium oxidation state of +VI in the absence of Pd and of + VII in the presence of Pd in close proximity. Breaking of the C-O bond and release of 2,5-dihydrofuran was found to be rate controlling. In subsequent work, Xi et al.[153] switched to an anatase TiO_2 (101) support and included MoO_x species. Bidentate dioxido rhenium and bidentate monooxido molybdenum on hydroxylated surfaces were found to be the most stable species under reaction conditions. The rate-controlling steps depended on the catalyst and were the first OH bond cleavage of anhydroerythritol for rhenium and the extrusion of dihydrofuran for molybdenum. Finally, Xi and Heyden[162] proposed, based on calculations, that late transition metal dimers and trimers on a MoS_2 support should be promising DODH catalysts.

Some other investigations considered macroscopic rhenium species without support, based on experimental observations, in contrast to the supported molecular species considered by Tomishige and Heyden. Deng et al.[155] found large ReO_x particles on an activated carbon support by microscopy and, therefore, chose a $Re_{10}O_{30}$ cluster cut from a ReO_3 crystal to produce ReO_3 surfaces. Results obtained with the aid of the BP86 functional suggested cooperative action of neighboring Re sites during DODH, and the authors proposed a binuclear Re-O-Re site. Hocevar et al.[126] identified a pre-reduced Re/C catalyst as the most active state and, consequently, used a Re(0001) model to investigate the DODH of aldaric acids with methanol as reductant. The revised PBE functional was employed in these calculations.

As with the molecular catalysts, the chemical variety of catalysts is not yet captured in the associated computational literature. It is obvious that the combination of a reducible support and a reducible catalyst presents a challenge for identifying the active site configurations under reaction conditions. Characterization of the active species is compulsory for cross-validation.

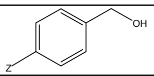
6.3 Alcohol reductants

6.3.1 Effectiveness of alcohols as DODH reductants depending on molecular weight and constitution

Alcohols present a class of important reductants for DODH and often serve as both, reductant and solvent. They can be involved in the rate-determining step, as emerged in Section 6.1, and deserve a more detailed inspection. However, comparison of the suitability of various alcohols for DODH is hampered by several circumstances. Often the reductant choice is viewed as part of an optimization process, and the information is relegated to the electronic supplementary documentation and not readily apparent in the indexing terms. Also, the reaction times may not be the same in a set of experiments, for focus on yield optimization or other reasons. Given that the diol itself can serve as reductant, a control experiment is necessary to extricate the contribution of the added alcohol reductant. The internal temperature of the reaction mixture is not always measured; rather bath temperatures are given which can be misleading if the mixture is not under autogenous pressure. The focus in this section is on rhenium catalysts, for which more data are available than for other transition-metal catalysts. We highlight where the literature agrees and where it digresses and cite the arguments that have been made to explain the differences between alcohols. The section starts with benzylic alcohols and continues with alkanols in order of decreasing molecular weight.

Benzylic alcohols were found to be principally effective reductants, albeit with often moderate yields, for example diphenylmethanol gave 39% yield in 1,4-anhydroerythritol DODH with methyltrioxidorhenium whereas 3-octanol gave 97%.[86] Boucher-Jacobs and Nicholas[101] used a series of para-substituted benzyl alcohols to investigate electronic effects. For the DODH of (+)-diethyl tartrate with NH_4ReO_4 as the catalyst, they obtained the results in Table 9 and concluded that the best reductant properties are found among the "neutral to moderately electron-rich alcohols". In combination with a supported catalyst, ReO_x/Al_2O_3, benzyl alcohol and 1-phenylethanol were ineffective for glycerol DODH at conversions over 80% but yields lower than 10%.[163]

Table 9: Electronic effects with 4-ZPhCH$_2$OH as reductants[101]

Substituent in 4-position (Z) 	Diethyl fumarate yield	Remarks

NMe_2	0	Diethyltartrate largely unreacted
OCH_3	90	
H	95	
Cl	73	Formation of 22% 4-ClPh-acetal

Results for heavier alkanols are largely but not entirely consistent. Arceo et al.[91] used $Re_2(CO)_{10}$ as catalyst precursor (under aerobic conditions) and compared three high-boiling alcohols for 1,2-tetradecanediol conversion at a reaction temperature of 170-180 °C. When all diol was consumed, the yields with 5-nonanol or 3-octanol were over 80%, whereas 2-octanol gave a slightly lower yield of 74%. The authors determined that 1 to 1.5 equivalents of the corresponding ketone were formed from these alcohols, indicating in part an excellent balance of product formation and reductant consumption. Of these alcohols, 3-octanol has frequently been used by other authors, and its superiority or at least equivalency as a reductant in comparison to other alcohols has been confirmed. Examples of the good performance of 3-octanol are the glycerol DODH with $ReCp^{tt}O_3$,[115] $ReCH_3O_3$,[92] ReO_x/Al_2O_3[63], and ReO_x nanoparticles.[119] Li et al.[115] however found 3-octanol to be inferior to PPh_3 for 1-phenyl-1,2-ethanediol DODH, with a yield of only 76 % vs 90% at complete conversion. The authors surmised that ketal formation from diol and 3-octanone could be the reason. Ketal formation consumes unreacted diol, and, if irreversible, limits the amount of diol that can react via DODH and hence the alkene yield. Ketals have been detected during $ReCp^{tt}O_3$-catalyzed DODH with 1-butanol or isobutanol as reductant,[115] and also with molybdenum-based catalysts.[80,130,131] In a comparison of secondary octanols, 2-octanol and 3-octanol were nearly equal with close to 90% yield, whereas 4-octanol was much worse with only 20% yield in the DODH of 1,2-octanediol with an N,N,O-coordinated rhenium tricarbonyl complex.[124] Only Li et al.,[104] who converted mucic acid using methyltrioxidorhenium, found a shorter alcohol, 3-pentanol, to excel more than 3-octanol, which they presumed resulted from the lower polarity of the octanol. 1-Octanol was consistently found to be inferior to secondary alcohols.[119,163]

Of the C6 and C7 alcohols, cyclohexanol performed always worse than the comparison alcohols, with 48 % yield vs. 50% for 1-heptanol in the glycerol DODH with methyltrioxidorhenium,[92] 30% vs. > 70% for acyclic hexanols in the glycerol DODH with ReO_x/Al_2O_3[163], and 19% vs. 84% for 1-heptanol in the galactaric acid DODH with methyltrioxidorhenium.[114] Among the acyclic hexanols, the order in yield was found to be 2-hexanol > 3-hexanol > 1-hexanol,[163] and the authors associated good performance with long chain secondary alcohols as opposed to primary or short chain alcohols. This observation is principally consistent with the above-described behavior of octanols, which were also more effective when secondary.

Li et al. found[115] 2,4-dimethyl-3-pentanol to neither undergo much dehydration nor to lead to ketals once oxidized; hence they chose it for glycerol DODH with $ReCp^{tt}O_3$ and obtained 99% yield. Shiramizu and Toste[98] obtained an equally high yield in 1,4-anhydroerythritol DODH with methyltrioxidorhenium as catalyst, and Ahmad and Nicholas[28] found it in the top group of various reductants for 1-phenyl-1,2-ethanediol DODH with Bu_4NReO_4. Accordingly, Li et al. were surprised to find 2,4-dimethyl-3-pentanol to be ineffective for DODH of 1,2-octanediol with tricarbonylrhenium 2,4-di-tert-butyl-6-(((2-(dimethylamino)ethyl)(methyl)amino)methyl)-phenolate.

The observations regarding C4 and C5 alcohols are puzzling in their spread. J. Li et al.[115] reported 1-butanol as inferior to isobutanol and 3-pentanol in glycerol DODH with $ReCp^{tt}O_3$ (11% yield vs 38 and 76%, respectively), whereas Shin et al.[114] reported 1-butanol as superior to 3-pentanol (72 vs 54% yield) in galactaric acid DODH, also with methyltrioxidorhenium as catalyst. Shiramizu and Toste[98] saw 0% yield with 2-butanol and 70% with 1-butanol in 1,4-anhydroerythritol DODH. For the same reaction, 3-pentanol produced a higher yield than 2-pentanol and 1-pentanol, respectively (91, 78, and 51 %). For branched pentanols, the sequence was 3-methyl-2-butanol ≈ 3-methyl-1-butanol > 2-methyl-1-butanol > 2,2-dimethyl-1-propanol. Interestingly, J. Li et al.[124] reported a lower octene yield in the presence of 1-butanol, 2-butanol, and 1-pentanol than in the control experiment with 1,2-octanediol as the reductant. Finally, X. Li et al.[104] saw a better yield from methyl trioxorhenium-catalyzed mucic acid conversion with 1-butanol than with 3-pentanol.

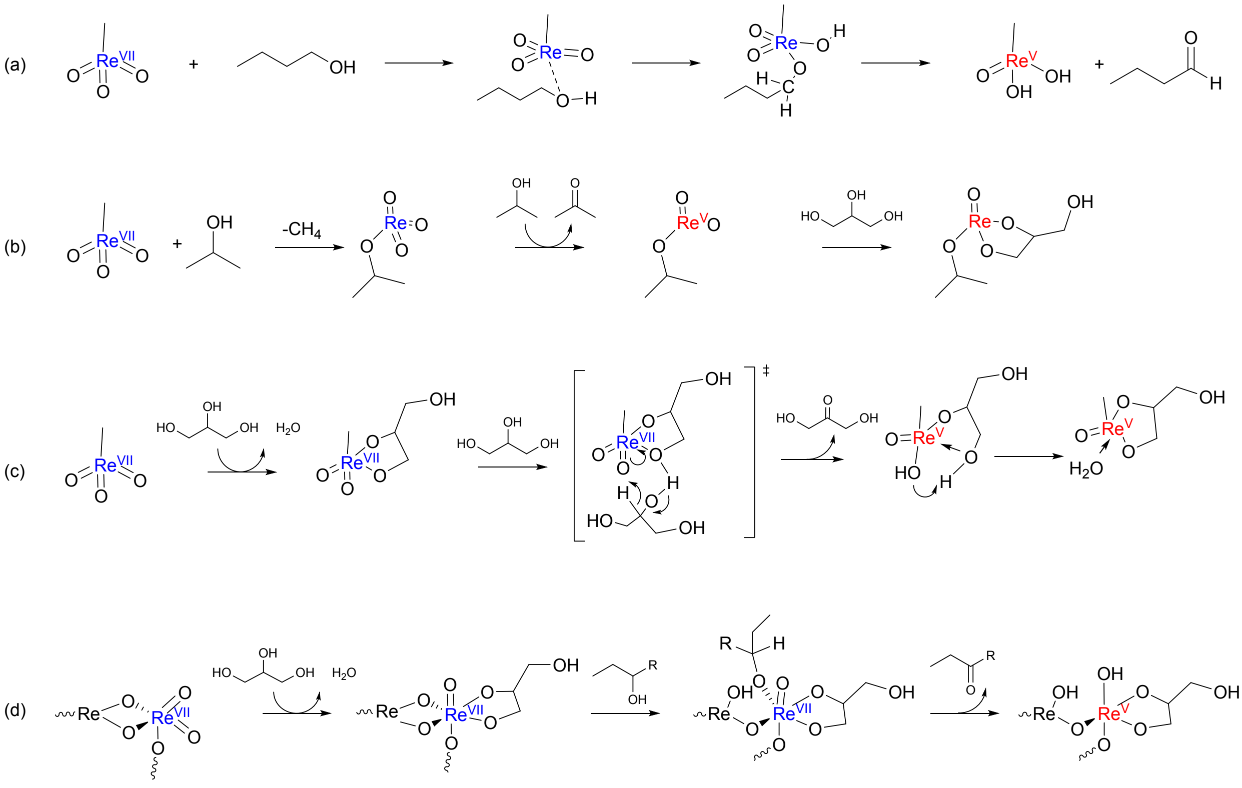
Diverse results have been obtained with short-chain alcohols (C1-C3). Shin et al.[114] used methanol and ethanol at their respective normal boiling points and did not obtain product. Even at a temperature of 170 °C, Shiramizu and Toste[98] did not observe product formation with ethanol as reductant. They thought the poor performance of small alcohols was due to the strong coordination of multiple alcohols to the rhenium center and excluded that an increased water content, resulting from the higher hydrophilicity of the short-chain alcohols, is responsible for the poorer performance. Larson et al.[94] however obtained 42% yield when converting D-glucarate-6,3-lactone using ethanol as reductant. Li et al.[104] found 2-propanol to be almost inactive, which they ascribed to the lower reaction temperature associated with the boiling point.

Overall, there is much consistency in the findings regarding heavier alcohols. The lack of clear trends among the short-chain alcohols will require collection of more data, with focused experiments that exclude effects such as different temperatures. It is noticeable though that success with short-chain alcohols is often achieved at higher reaction temperatures or with aldaric acids as substrates. The behavior of primary vs secondary alcohols is partially consistent with the literature. While secondary alcohols are generally considered to be the better hydrogen donors than primary alcohols, both are employed as hydrogen transfer agents in various applications.[164] The successes with both primary and secondary alcohols as reductants for DODH are thus no oddity. However, some extreme observations such as no yield at all will require further inspection.

6.3.2 Mechanism of alcohol action

To reconcile the seemingly contradictory findings regarding some alcohols, a look at the mechanism of catalyst reduction by alcohols may be instructive. There are two main distinctions between the published mechanisms, which are the sequence of reduction and diolate formation, and the interaction of the alcohol with either the rhenium directly or with its ligands only. Regarding the sequence, initial diolate formation implies a significantly higher coordination of the rhenium when the alcohol approaches since instead of removing an oxido ligand or forming two hydroxide ligands, an oxido ligand is replaced by the diolate (Scheme 8). It could be hypothesized that a more crowded rhenium environment makes it difficult for the alcohol to coordinate. In addition, it has been proposed that small alcohols crowd the rhenium center.

A mechanism first proposed by Qu et al.[38] on the basis of computational results for reduction of methyltrioxidorhenium involves an intermediate expansion of the rhenium coordination through addition of the alcohol to give an alkoxide (Scheme 10a). The authors compared ethanol and 3-octanol as representatives of primary and secondary alcohols and found slightly higher barriers for ethanol, by 6.7 and 4.4. kcal/mol. Zhang and co-workers[104,110] later investigated 1-butanol as reductant and confirmed this route, which produces a dihydroxidorhenium complex after completion of the reduction step.



Scheme 10: Possible mechanism for transfer hydrogenation by alcohol reductants. (a) Reduction of methyltrioxidorhenium through intermediate coordination of alcohol, precedes glycolate formation, which proceeds according to Scheme 8 c;[38,104,110] (b) initial methane formation from methyltrioxidorhenium and isopropanol, resulting in persistent isopropoxide, followed by reduction through second molecule of alcohol and glycolate formation;[18] (c) initial formation of glycolate followed by reduction through alcohol interaction with ligands;[92] (d) initial glycolate formation with ReO$_x$ nanoparticles followed by alcoholysis of Re-O-Re oxo bridge and release of carbonyl compound to give reduced rhenium complex.[119]

A completely different reaction initiation was proposed by Lupacchini et al.[18] for DODH with methyltrioxidorhenium as catalyst. The authors observed methane formation at the start of the reaction, and when deuterated 2,4-dimethyl-3-pentanol was used as the reductant, monodeuterated methane was obtained. The authors concluded that hydride is transferred from the alcohol, which afterwards is coordinated to the rhenium (Scheme 10b). A second molecule of alcohol effects the reduction to a Re(V) complex. The glycolate then forms afterwards and the Re(VII) complex is recovered by olefin extrusion, while one alkoxido ligand is present throughout the catalytic cycle.

For the same catalyst, methyltrioxidorhenium, the reverse sequence – diolate formation and then reduction – was also proposed on the basis kinetics including the use of deuterated glycerols. In the mechanism depicted by Yi et al.[92] (Scheme 10c) for glycerol DODH with glycerol as the reductant, the diolate is formed first, and the acidic proton from the alcohol is transferred to an oxygen of the diolate, while the hydride is transferred to an oxido group of the complex. After dihydroxyacetone leaves, a molecule of water is released and then the olefin is extruded. In this mechanism, the alcohol oxygen does not coordinate to the rhenium.

In the mechanism formulated by Jang et al.[119] for ReO_x nanoparticles, glycolate formation also precedes reduction. A Re-O-Re oxo bridge is opened by alcoholysis, and the oxygen of the alcohol coordinates to the rhenium of the diolate complex while the alcohol proton associates with the oxygen from the bridge and forms an OH group that is attached to the adjacent rhenium.

The partially inconsistent trends among alcohol behavior imply that further research is needed to clarify the action of alcohols. Assuming that the various mechanisms may all be valid, then the range of conditions under which each applies needs to be determined.

6.4 Quest for benchmark reactions

6.4.1 Catalyst performance markers

The wide variety of catalysts, substrates, reductants and, optionally, solvents, brings up the question about a suitable benchmark reaction that quantitatively connects all reported catalytic data. Thus, any new catalyst, substrate, or reductant would – chemical compatibility and solubility permitting – be tested in combination with two preset reaction partners. At present, it is difficult to find data sets that connect the published work, that is, reports on the performance of the same catalyst for the same reaction under comparable conditions, yet from different laboratories. In this section, we compare turnover frequencies and yields as far as available data permit. The scope is limited to rhenium.

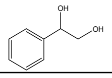
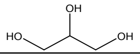
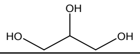
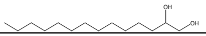
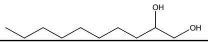
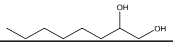
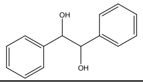
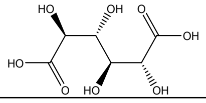
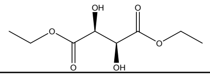
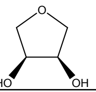
6.4.2 Reported turnover frequencies for rhenium catalysts

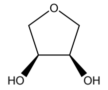
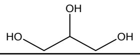
Table 10 summarizes turnover frequencies observed with rhenium catalysts. The values are either directly reported in the cited papers, or they were estimated from information in the papers, for example, from initial rates in graphs. Details on the estimates can be found in the supporting information. The turnover frequencies may be viewed in light of the possible rate-determining steps, and under consideration of the substrate and the respective alkene, the reductant, and the temperature.

The experimental turnover frequencies span three orders of magnitude, and for a family of compounds like the alkanediols and a limited range of temperatures, they are tightly clustered. The highest turnover frequencies are observed for the formation of stilbene (from hydrobenzoin), a highly conjugated product, and for the formation of a hydrogenated product, tetrahydrofuran (from 1,4-anhydroerythritol). At this point, one can only speculate regarding the reasons. The extrusion process may be facilitated if a highly conjugated system like that of stilbene is formed. In case of a fully hydrogenated product, such as tetrahydrofuran, there is no possibility for re-coordination of the olefinic product. The lowest experimental turnover frequency, notwithstanding a relatively high reaction temperature, is for glycerol with glycerol as reductant.

The number of reported turnover frequencies is relatively small given the vast number of catalysts, substrates, reductants, and solvents. More data points will be needed to extricate trends.

Table 10: Compilation of turnover frequencies for rhenium catalysts

Catalyst	Substrate	Reductant(s)	Temperature °C	Turnover frequency h^{-1}	Reference
$ReCp^{*}O_3$	1-Phenyl-1,2-ethanediol 	PPh_3	90	4.8	Cook and Andrews[3]
	Glycerol 	PPh_3	125	2.9[a]	
$ReCH_3O_3$	Glycerol 	Glycerol	165	2.0[a]	Yi et al.[92]
$ReCH_3O_3$	1,2-Tetradecanediol 	3-Octanol	175	48	Dethlefsen and Fristrup[106]
$ReCH_3O_3$	1,2-Decanediol 	PPh_3	150	24	Sharkey and Jentoft[17]
$ReCp^{ttt}O_3$[b]	1,2-Octanediol 	PPh_3	180	12.5[a]	Raju et al.[100]
$ReCH_3O_3$	Hydrobenzoin 	3-Octanol	140	233[a]	Liu et al.[40]
NH_4ReO_4	Mucic acid 	3-Pentanol	120	3.2[a]	Zhang et al.[109]
ReO_x/C	(+)-Diethyl L-tartrate 	H_2	150	6[a]	Denning et al.[13]
$ReO_x–Pd/CeO_2$	1,4-Anhydroerythritol 	H_2	170	300[c]	Ota et al. [33]
CM-	1,4-Anhydroerythritol	H_2	140	16	Xi et al.[146]

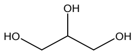
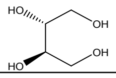
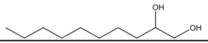
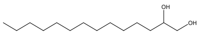
$ReO_x/CeO_2(111)$[d]					
CM-ReO-$Pd/CeO_2(111)$[d]			170	1512	
CM-ReO(2O)/6H–$TiO_2(101)$[d]			140	0.16	Xi et al.[153]
ReO_x-Au/CeO_2	Glycerol 	H_2	140	16	Cao et al.[151]

[a] TOF not expressly given, calculated/estimated from rates in text or graphs; [b] CP^{ttt}=1,2,4-tri(*tert*-butyl)cyclopentadienyl; [c] to saturated product; [d] *CM*=computational model

6.4.3 Reported yields for rhenium-catalyzed DODH

Obviously, yields have their limitations for comparison purposes, but are the most widely available quantitative performance measure of DODH catalysts. Prior comparisons of yields focus on the different chemistries catalyzed by the large variety of tested rhenium compounds[35,44] and do not include comparisons of duplicate experiments from different laboratories. In Table 11, yield data obtained with one of the most commonly used catalysts, methyltrioxidorhenium, are compiled. It is evident that there is always at least one parameter that differs between experiments conducted in different laboratories, which limits the comparability, and finding three different sources with at least similar conditions is a challenge.

Table 11: Comparison of yields obtained with methyltrioxidorhenium $ReCH_3O_3$ as catalyst

Substrate	Reductant(s)	Catalyst amount mol%	Conditions	Yield (Conversion) %	Reference
Glycerol (to allyl alcohol) 	Glycerol	2	Neat, 170 °C, 3 h, air Reactive distillation	15 (100)	Canale et al.[103]
		2	Neat, 165 °C, 1 h Reactive distillation	27 (100)	Yi et al.[92]
	3-Octanol	2	165 °C, 1 h Reactive distillation	48 (100)	Yi et al.[92]
		2.5	170 °C, 2.5. h, air Autogenous pressure	90	Shiramizu and Toste[98]
Erythritol (to butadiene) 	3-Octanol	2.5	170 °C, 2.5. h, air Autogenous pressure	89	Shiramizu and Toste[98]
		2	170 °C, 1 h Reactive distillation	1.5	Liu et al.[40]
1,2-Decanediol 	3-Octanol	2	170 °C, ~ 1 h	67	Liu et al.[40]
1,2-Tetradecanediol 	3-Octanol	2	175 °C, 1 h	85	Dethlefsen and Fristrup[106]
	3-Nonanol	10	150 °C, 95 h Benzene solvent	50	Davis and Srivastava[102]

6.4.4 Benchmark reaction catalysts, substrates, and reductants

It is evident from the published data, that there is no established benchmark reaction for DODH that would allow the test of a new catalyst, substrate or reductant. Benchmark ingredients should be commercially available and easy to handle, and we discuss some options below.

While soluble catalysts reduce the uncertainty that comes with counting active sites on supported catalysts, it still has to be ascertained that all rhenium participates. Complete dissolution must be confirmed, and induction periods associated with formation of the active sites need to be addressed in experiment and analysis. There are a significant number of rhenium compounds that demonstrate an induction period,[13] which has been attributed to the formation of active species.[40,103,107] Equally, deactivation, which can be hard to discern in batch experiments, can be a concern. A significant number of perrhenates are commercially available, but those with inorganic cations suffer from low solubility in organic solvents,[37] and the poor solubility of NH_4ReO_4 has been advertised for its recovery after reaction.[101] Likewise, ReO_3 has been reported to have poor solubility in 2-octanol and sulpholane.[103]

Lower valence rhenium complexes such as $Re_2(CO)_{10}$ and $ReBr(CO)_5$ are pre-catalysts only and need to be used in air to become active. Li et al.[124] mentioned that complexes of the type $ReCp'O_3$, with Cp' a substituted cyclopentadienyl ligand, have to be stored at low temperature or in N_2. Re_2O_7 has been reported to be hygroscopic and at risk to form $HReO_4$ with moisture.[104,165] This reaction and also the use of $HReO_4$ in the first place are problematic, because protons exert a promotional effect on DODH.[92] NH_4ReO_4 starts decomposing at about 200 °C.[166] Many rhenium compounds are volatile, including CH_3ReO_3, which some authors saw evaporate from solution when trying to dissolve the compound in dodecane by heating.[106]. Re_2O_7 has a sublimation temperature of 200 °C[167]. Canale et al.[103] reported that at a reaction temperature of 170 °C, $Re_2(CO)_{10}$ sublimes. Finally, the reduction of $ReCH_3O_3$ by PPh_3 is photosensitive,[106] and the reduction product, methyldioxidorhenium, can form oligomers.[40] These obstacles and the above-discussed counter ion effect (Section 5.3.2) make it rather difficult to select a rhenium benchmark catalyst. Knowledge is missing about solubility of many compounds in organic media and the nature of the dissolved species (e.g., does Re_2O_7 form mononuclear species and are they charged or not?). Considering the significant amount of data that has been accumulated for $ReCH_3O_3$ and NH_4ReO_4, they are possibly the best options, and two candidates will provide some redundancy and flexibility.

The substrate should produce an olefin not prone to secondary reactions and also not volatile, so as to facilitate quantitative analysis in the liquid phase. For example, glycerol to allyl alcohol and erythritol to butadiene are transformations with potential for applications, but the products are volatile and lack stability. Literature precedent shows that the products of glycerol or erythritol conversion are obtained by reactive distillation, but for a rate measurement, the temperature, which may change with the composition of the reaction mixture, would have to be carefully monitored. Longer alkanediols and hydrobenzoin may be interesting candidates instead.

To test a new catalyst, two types of reductants could be used. One reductant should be competent and ensure the catalyst can demonstrate its ability to extrude the olefin product; for example, atomic hydrogen or triphenylphosphane could be considered, whereby the latter is easier to administer and does not require a secondary catalyst for H_2 activation. A milder reductant, such as a secondary alcohol, would explore the reducibility and versatility of the catalyst. If liquid reductants are used, then boiling points higher or equal to the highest DODH reaction temperature would facilitate temperature control. For alcohols, C8 and higher would meet this criterion.

7. Process Aspects: Phase Chemistry, Separations, Reactor Choice and Energy Input

7.1 Phase chemistry and solvents

7.1.1 Phase chemistry

It is worthwhile to consider the complexity of the DODH process and in particular the phase chemistry. The number of ingredients in the reaction mixture varies between one and four or five. Occasionally, as a fifth component, substances such as crown ethers have been added to promote solubilization of alkali salts. The simplest possible scenario would consist of a single diol ingredient that serves as substrate, as reductant (by virtue of also being an alcohol), as solvent (in neat conditions), and is converted in the absence of a catalyst. The diol would undergo uncatalyzed disproportionation and dehydration as illustrated in Scheme 9.

The reaction may thus actively involve one, two, three or even four phases. Only a single liquid phase may be relevant if a soluble catalyst is used with a non-volatile substrate and reductant, and separation of the product phases does not occur. Phase separation in several liquid phases can occur, given that water is always a product while many of the solvents used are aprotic and non-polar. An additional phase is introduced if a solid catalyst is used. Also, substrate, reagents and products may be in different phases, for example, gaseous reductants such as CO or H_2 may be used in conjunction with a substrate present in the liquid phase. Equally, small olefinic products may evolve as gaseous species under reaction conditions.

The phase chemistry has been exploited for separations, by (i) using solid catalysts, (ii) using reductants that give a solid oxide, and (iii) by performing reactive distillations to remove a volatile product or oxidized reductant (see Section 7.2). What is not expressly investigated (although occasionally mentioned[91]) is the formation of several liquid phases during reaction and the resulting partitioning of substrate, reagents, reaction products, and catalysts that is likely to ensue. In addition, there are several articles ascribing the differences in activity among several catalysts to variations in the solubility, and others mentioning the formation of a solid catalyst during reaction. In other words, some catalysts may act both homogeneously and heterogeneously, and the observed activity is not easily relatable to a soluble or surface species, or the moles of catalyst present. The phase chemistry during DODH is thus an area that is not yet well addressed in the scientific literature.

7.1.2 Solvents and the effect of product water

DODH may be conducted in the absence of a solvent, that is, in the vapor phase,[24] in neat conditions in solution,[18,92] or in neat conditions in the melt.[29]

For the many diol substrates that are not very volatile, liquid phase processing is preferred over vapor phase processing. While not the primary topic of published papers, solvents are expressly addressed in some works (Table 12).[28] In addition to its key function of dissolving the reactants and, in homogeneous catalysis, dissolving the catalyst, the solvent should be inert and not be converted itself or poison the catalyst, and ideally, a sustainable choice. Combining these properties can be a challenge; for example finding inert solvents that provide solubility to compounds such as glycerol is a reported issue.[168]

Common solvents are aromatic compounds, including benzene, toluene, chlorobenzene, and anisole.[124] Another group are primary and secondary alcohols,[98,126] which are often selected to serve in two functions, as solvent and as reductant. In turn, when trying to determine the efficacy of a reductant in alcoholic solvent, the possible contribution of the alcohol as reductant needs to be determined or excluded.

Solvents capable of coordinating via free electron pairs on O or N atoms such as tetrahydrofuran,[3,112] N-methyl-2-pyrrolidinone,[3] acetonitrile,[37,111,112] methanol,[28] 2,2,2-trifluorethanol,[28] *tert*-butanol,[28] 1-methoxy-2-(2-methoxyethoxy)ethane (diglyme),[28] 1λ^6-thiolane-1,1-dione (tetramethylene sulfone, sulfolane),[28] formamide,[28] dimethyl formamide,[28] dimethylacetamide[28] and pyridine[111] are reportedly inferior to other solvents in conjunction with rhenium catalysts, presumably because of coordination to the rhenium. However, ethers such as dioxane, tetrahydrofuran, or dimethoxyethane are frequently used as solvents.[98,116]

Table 12: Investigations with comparison of a significant number of solvents

Reference	Catalyst	Substrate(s)	Solvents
Ahmad et al., 2011[28]	$ReCH_3O_3$, ReO_4^- (various counterions)	Alkanediols Styrene diol	Benzene, chlorobenzene, THF, acetonitrile, N-methyl-2-pyrrolidinone, MeOH, 2,2,2-trifluorethanol, tert-butanol, diglyme, tetramethylene sulfone (sulfolane), formamide, dimethyl formamide, dimethylacetamide
Raju et al., 2013[100]	1,2,4-tri(*tert*-butyl)cyclopentadienyl-trioxidorhenium	1,2-Octanediol	PhCl, toluene, benzene, THF, CH_3CN, pyridine
Canale et al., 2014[103]	$ReCH_3O_3$ ReO_3	Glycerol	Ethylene carbonate, dimethylpropylene urea (DMPU), sulpholane, 1-hexanol, DMP, 2-octanol, 1,3-propanediol, 2,4-dimethyl-3-pentanol, 1-phenyl-ethanol
Dethlefsen et al., 2015[34]	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	1,2-Decanediol	MeOH, EtOH, *n*PrOH, *i*PrOH, *t*BuOH, 3-pentanol, acetone, hexane, water
Ota et al., 2016[19]	ReO_x-Pd/CeO_2	Anhydroerythritol	1,4-Dioxane, 1,2-dimethoxyethane, dodecane, 1-pentanol, 3-pentanol, water
Gossett and Srivastava,	NH_4ReO_4	Styrene diol	Toluene, 1-butanol, benzene, THF, acetonitrile, 3-octanol, isopropanol

2017[112]			
Morris et al., 2017[111]	2,6-Dimethylpyridinium perrhenate	Styrene diol	C_6H_6, THF, CH_3CN, pyridine, $CHCl_3$
Li et al., 2020[80]	$[MoCp^*O_2]_2O$	1,2-Octanediol	PhCl, toluene, *m*-dichlorobenzene, *o*-dichlorobenzene, *p*-xylene, trichlorobenzene, tBuPh, anisole, mesitylene, sulfolane, trichlorobenzene
Jefferson and Srivastava, 2019[118]	$ReCH_3O_3$	1-Phenyl-1,2-ethanediol	Benzene, THF, acetonitrile, dichloroethane, indoline, isopropanol, toluene
Siu et al., 2020[136]	Dioxomolybdenum complexes with amine bisphenolate ligands	Styrene diol	Mesitylene, xylene, toluene, dimethylformamide, N,N'-dimethylpropyleneurea (DMPU), H_2O, 3-octanol, chlorobenzene

Water was found to be not suitable for use with rhenium catalysts,[19,152] which is significant since water is always a by-product of DODH. However, some DODH catalysts have been classified as being water tolerant, for example methyltrioxidorhenium.[92] The outcomes of efforts to remove product water are mixed. The addition of a dehydration agent, Na_2SO_4, resulted in an octene yield increase from 30% to 38% in $NaReO_4$-catalyzed 1,2-octanediol DODH with Na_2SO_3 as reducing agent.[37] Yi et al.[92] also observed a higher yield of volatile products in glycerol DODH after adding molecular sieve (4 Å). Gossett and Srivastava[112] saw differences in yields NH_4ReO_4-catalyzed DODH of 1-phenyl-1,2-ethanediol DODH with 2,4-dimethyl-3-pentanol as reductant depending on whether the solvents toluene or benzene were hydrated or anhydrous. Adding molecular sieve, however, did not affect the yields. Equally, Jefferson and Srivastava[118] did not detect an increase in yield when addition molecular sieve during the $ReCH_3O_3$-catalyzed 1-phenyl-1,2-ethanediol DODH with indoline as reductant. A computational investigation by Xi et al.[146] on ceria-supported rhenium species showed that in the presence of water, more ReO(OH) surface species formed and the number of active ReO species declined. Overall, the findings indicate that product water does affect the course of rhenium-catalyzed reactions and that mitigation is possible through removal of the water.

Ammonium heptamolybdate was also an ineffective catalyst in water as the solvent.[34] In contrast to rhenium catalysts, molybdenum catalysts do not seem to respond to attempts to capture the product water during catalysis. Hills et al.[128] tested different means of water removal during DODH with a dioxidomolybdenum(VI) complexes with acylpyrazolonate ligands. Neither the addition of Na_2SO_4, nor the addition of molecular sieve (4 Å), nor the use of a Dean-Stark apparatus improved the olefin yield. Molybdenum dioxido-complexes with dianionic ONO pincer ligands were found sensitive to water under catalytic conditions, as indicated by detection of free ligand.[135] Addition of molecular sieves, P_2O_5, or anhydrous $MgSO_4$ to the reaction mixture did not result in DODH product formation.

The role of two solvents, chlorobenzene and methanol, for the Gibbs energies along the perrhenate-catalyzed DODH trajectory was assessed by DFT calculations.[113] Activation energy barriers were also determined, and chlorobenzene was found to lower the barrier for triphenylphosphane attack on an oxido ligand of the rhenium diolate with styrene diol.

For solid-catalyzed DODH, the solvent should solubilize the reaction partners and not the catalyst. However, it has been demonstrated that the solvent can promote leaching of active species; solvents of higher polarity were found to increase leaching of rhenium species from inorganic supports.[17]

In conclusion, DODH is feasible in many solvents. Some are less suitable with rhenium catalysts because of coordination with the rhenium. Some information exists for molybdenum catalysts, while the same level of knowledge is absent for vanadium catalysts. Water is not a good solvent, which is an issue because it is a product of DODH. In general, the multicomponent mixtures imply that the optimum solvent depends on many factors.

7.2 Product separations

The methods used for separation of liquid mixtures containing catalyst, products, unconverted substrate, and oxidized reductant are reactive distillation and salting out.

Reactive distillation is a common DODH process intensification and has been applied with all types of catalyst. For example, Ahmad et al. [28] tested reactive distillation with methyltrioxidorhenium and several perrhenate compounds and various substrates. Yi et al.[92] removed the volatile products of glycerol DODH catalyzed by methyltrioxidorhenium by distillation. Dethlefsen et al.,[168] who used a variety of molybdenum compounds as catalysts, applied reactive distillation to the conversion of alkane diols. Equally, Petersen et al.[27] tested group V-VII transition metal compounds for glycerol DODH without external reductant in a reactive distillation setup. We note that reactive distillation may lead to partial separation only. For example, the volatile products of glycerol DODH, allyl alcohol and water, are not separated by these simple distillations; however, the advantages lie elsewhere. This method removes water from the reaction mixture, and water is potentially harmful to the catalyst (see Section 7.1). Moreover, Arceo et al.[12] found reactive distillation in protective N_2 atmosphere to be advantageous for the formic-acid mediated conversion of glycerol to allyl alcohol, and they emphasized the removal of the sensitive product.

Boucher-Jacobs and Nicholas[101] used polymeric benzylic alcohols as reductants, which are easily separable. These were, for example, poly(4-hydroxymethylsyrene) and [4-(hydroxymethyl)phenoxymethyl]polystyrene (Wang resin). Alternatively, the authors precipitated benzaldehyde through reversible formation of a bisulfite adduct by addition of aqueous $NaHSO_3$ to the reaction mixture.

Jia et al.[83] used a combination of precipitation, distillation, and salting out to recover allyl alcohol after reacting glycerol with formic acid in uncatalyzed DODH. The method was developed because of the close boiling points of formic acid, water, and allyl alcohol. Residual formic acid was precipitated as format using $Ca(OH)_2$, and water and allyl alcohol were removed by distillation and separated by addition of alkali salts. In contrast to the methods described above, this method was optimized and an allyl alcohol purity of >99.9% was reached.

Shin et al.[114] sought to transform galactaric acid, a biomass-derived feedstock, to muconate, which are precursors of adipic acid. The authors added an ionic liquid, which formed a separate layer containing methyltrioxidorhenium and an acid co-catalyst after the catalytic reaction, while the muconate product was in the alcoholic organic layer.

7.3 Reactor choice and energy input

7.3.1 Batch, semi-batch, or continuous flow operation DODH

Most liquid phase DODH reactions are conducted as batch reactions. Semi batch operation in the form of reactive distillation is also common, see Section 7.2. Continuous flow processes have been reported for vapor phase DODH with solid vanadium catalysts.[24] Li and Zhang performed the reaction between glycerol and formic acid as a continuous reactive distillation.[81] Tshibalonza et al. conducted uncatalyzed DODH of glycerol to allyl alcohol with formic acid or triethylorthoformate as reductant in a flow apparatus.[82] A similar approach was used for the conversion of erythritol to 3-butene-1,2-diol with triethylorthoformate as reductant.[96] In some of the reactions with triethylorthoformate as reductant, formic acid served as a catalyst.

7.3.2 Energy input to overcome activation barriers

To the best of our knowledge, DODH has been exclusively conducted as, at least in part, thermal catalysis, and no exclusive photo- or electrocatalysis has been reported thus far, that is, under conditions without thermally induced yields. We report here on a few observations related to energy input, but this aspect of DODH is obviously in its infancy.

Recently, Aksanoglu et al.[160] compared yields obtained in the dark and in the presence of visible light under exclusion of UV light by the use of borosilicate glass. They found a $[n\text{-}Bu_4N]V(dipic)O_2$ catalyst to give consistently higher olefin yields in the presence of light. The substrates were 1-phenyl-1,2-ethane diol and *cis* and *trans* 1,2-diols of cyclopentane and cyclohexane, respectively. The photosensitivity of the reduction of $ReCH_3O_3$ by PPh_3 was established,[106] but this behavior has not been exploited yet.

Steffensmeier et al.[143] used analytical electrochemistry and investigated the redox properties of a VO_2(salimin) species by cyclovoltammetry.

Regarding other means of energy addition such as microwaves, plasma, electrical fields, a microwave-assisted DODH was reported by Beckerle et al.[130] The authors used a Mo(VI)bis(phenolato)complex to convert anhydroerythritol to dihydrofuran with 3-octanol as the reductant and found that the reaction time could be shortened and the temperature could be lowered through use of microwaves.

8. Conclusions & Outlook

Deoxydehydration is a powerful reaction that can transform biomass-derived polyols to olefinic compounds in high yields and with regioselectivity and stereospecificity. In the past 25 years, numerous rhenium, molybdenum, and vanadium compounds have been found to catalyze DODH. Catalysts on the basis of other metals have yet to be developed, and the diversity of soluble catalysts is not yet reflected in the supported catalysts. Many compounds are soluble, but others are not while supported moieties can leach; therefore, the boundaries between homogeneous and heterogeneous catalysis can be challenging to identify.

A wide variety of suitable reductants for DODH have been identified. For the large group of alcohols, neither the mechanism of action nor the trends, in particular among short alcohols, nor primary vs secondary, are understood.

The rate-determining step in the catalytic cycle has been found to vary, and the most common options are the extrusion of the olefin or the reduction of the catalyst. The latter is often the case when alcohols are used as reductants. Computational efforts are complementing experimental findings regarding barriers and rate-determining steps but are comparatively few and can therefore not yet address the chemical variety of known catalysts.

Notwithstanding the wealth of existing data, the numerous possible combinations for the catalyst-substrate-reductant triangle have led to a lack of overlap among the published results. Benchmarking is needed to better connect reported results. A distinction of rates characteristic of the reduction step and rates characteristic of the extrusion step may be useful.

Several means of separations have been proposed for use with soluble catalysts, most prominently reactive distillations, which are however limited to distillable products. Solid catalysts thus far, are, like soluble catalysts, used in batch mode unless the reactant mixture is a vapor.

Deoxydehydration is, at present, a thermal catalysis, and the potential of other means of energy input is untapped.

9. Conflicts of interest

There are no conflicts to declare.

10. Acknowledgement

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