Deoxydehydration of Glycols Catalyzed by Carbon-Supported Perrhenate

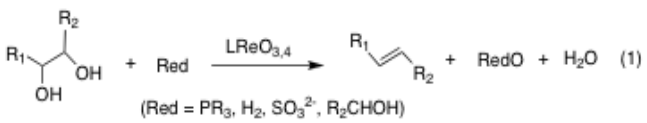
Alana L. Denning,[a] Huong Dang,[b] Zhimin Liu,[a] Kenneth M. Nicholas*[b] and Friederike C. Jentoft*[a]

[a] A. L. Denning, Dr. Z. Liu, and Prof. Dr. F. C. Jentoft
Chemical, Biological and Materials Engineering
University of Oklahoma
Norman, OK 73019, USA
Fax: (+1) 405 3255813
E-mail: fcjentoft@ou.edu
[b] H. Dang, Prof. Dr. K. M. Nicholas
Department of Chemistry and Biochemistry
University of Oklahoma
Norman, OK 73019, USA
Fax: (+1) 405 3256111
E-mail: knicholas@ou.edu

Introduction

A growing recognition that the earth's fossil-based, non-renewable resources are being depleted, causing increasing atmospheric carbon dioxide levels, has sparked interest in the development of new chemical processes for the conversion of renewable biomass into chemicals and fuels.[i] The high oxygen content of biomass feedstocks such as carbohydrates and triglycerides requires the development of selective oxygen-removal processes for the production of most chemicals and fuels. Traditionally, dehydration has been the primary focus of polyoxygenate conversion efforts.[1,ii] Reductive processes are also under investigation, and the partial hydrodeoxygenation (hydrogenolysis) of sugars and polyols has been achieved with variable selectivity and efficiency using heterogeneous[iii] or homogeneous[iv] transition metal catalysts.

A newer reaction involving the reductive conversion of glycols to olefins, termed deoxydehydration (DODH), has received increasing attention (eq. 1). The first catalytic DODH reaction was reported by Cook and Andrews, who employed arylphosphines (PR_3) as reductants and Cp^*ReO_3 as the catalyst.[v] Recently, a number of groups have expanded the range of effective reductants and rhenium catalysts for DODH to include the following combinations: $H_2/MeReO_3$,[vi] $Na_2SO_3/ZReO_{3,4}$[vii] and secondary alcohols/$Re_2(CO)_{10}$, $MeReO_3$, NH_4ReO_4.[viii] Mechanistic studies of the DODH reactions driven by phosphines with (*tris*-pyrazolylborate)ReO_3 catalysts[ix] and a recent computational study[x] suggest the operation of a catalytic cycle involving a deoxygenation–condensation (dehydration) sequence to produce a reduced metallo-*O,O*-glycolate, that undergoes fragmentation (retrocyclization) to produce the olefin.



All the effective DODH reactions reported to date have employed homogeneous (soluble) rhenium catalysts. The practical advantages of heterogeneous (solid) catalysts for large scale commercial processes motivated us to seek supported rhenium catalysts for DODH. We report herein our initial findings demonstrating the ability of a novel carbon-supported perrhenate catalyst to effect the DODH of glycols to olefins.

Results and Discussion

The catalyst was prepared by equilibrium adsorption of perrhenate onto activated carbon using aqueous NH_4ReO_4. The rhenium content was typically 3-4 mass% Re. Fig. 1 shows attenuated total reflectance (ATR) IR spectra of an as prepared ReO_x-C catalyst and reference samples. NH_4ReO_4 exhibits three vibrations at 3200, 1407 and 900 cm^{-1}. The band at 900 cm^{-1} is assigned to the Re–O stretching of the ReO_4^- ion;[xi] the bands at 3200 and 1407 cm^{-1} arise from the antisymmetric stretching and asymmetric bending of the NH_4^+ ion, respectively. In addition to bands characteristic of the activated carbon support, ReO_x-C shows an IR band at 900 cm^{-1}, consistent with the antisymmetric stretching of ReO_4^- ions. The bands at 3200 and 1407 cm^{-1} are absent in the IR spectrum of the ReO_x-C sample, suggesting that under the preparation conditions, the carbon support does not present suitable adsorption sites for NH_4^+.

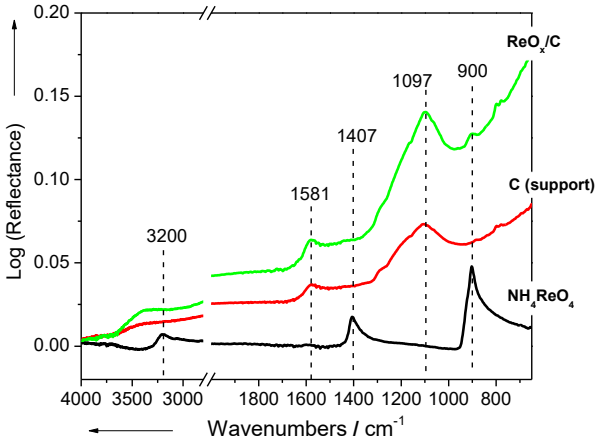


Figure 1. ATR-IR spectra of ReO_x-C, the carbon support, and solid NH_4ReO_4.

To confirm that the IR data are representative of all rhenium in the sample, X-ray absorption near edge structure (XANES) spectroscopy was used. Normalized Re L_3 edge XANES spectra of a fresh ReO_x-C catalyst and an NH_4ReO_4 reference (Fig. 2) show very similar positions and shapes, implying that the rhenium valence and local environment in these two materials are alike. First observations by high resolution electron microscopy indicate that the rhenium species are highly dispersed, consistent with perrhenate ions being the predominant species.

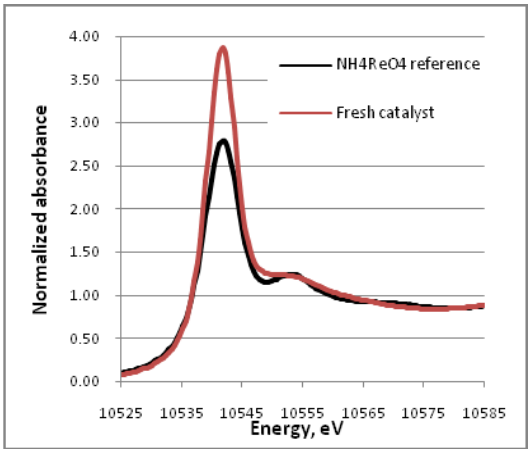
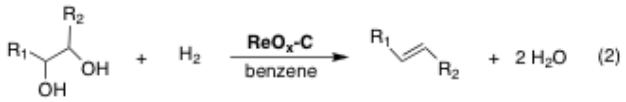
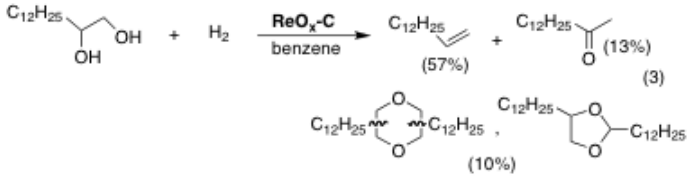


Figure 2. Re L3 edge XANES spectra of fresh ReO_x-C catalyst and NH_4ReO_4.

The ReO_x-C material was evaluated for catalytic activity with a representative set of glycols, models for biomass-derived carbohydrates and polyols, with H_2 as the reductant (eq. 2).



As summarized in Table 1, styrene glycol, 1,2-tetradecanediol and (+)-diethyl tartrate were each converted to the corresponding olefin in moderate to excellent yield. Little or none (<2%) of the respective alkane arising from over-reduction could be detected (at 150°C). A control reaction conducted under the same conditions with non-metallated activated carbon and 1,2-tetradecanediol showed no conversion of the glycol. As has been found for the homogeneous rhenium-catalyzed DODH reactions,[5-9] styrene diol (entry 1) is more reactive than the aliphatic glycols (entries 2-6). Small amounts of ethyl benzene, $PhCH_2CHO$, $PhCH_2CH_2OH$ and dimeric ethers were detected, probably arising from competing acid-catalyzed rearrangement, condensation and hydrogenolysis.[xii] With the slower reacting C_{14}-glycol (entries 2-4) it is noteworthy that the terminal olefin was produced regioselectively (>98 %), with no apparent isomerization. To assess the mass balance and to identify the non-olefinic products, a preparative scale (2 mmol) reaction of the C_{14}-glycol was conducted and the products were isolated by column chromatography (eq. 3).



In addition to 1,2-tetradecene (57% yield), 2-tetradecanone (13%), and a mixture of isomeric cyclic ethers and acetals (10 %) were identified with a total mass recovery of about 85%. The latter products likely arise by an acid-catalyzed pathway.[11] Initial tests of the effects of operating parameters on the conversion rate showed a significant retardation at lower H_2 pressure (Table 1, entry 6 vs. 5) and a substantial acceleration at higher temperature (entry 2 vs. 8).

TABLE 1. Deoxydehydration of glycols catalyzed by ReOx-c

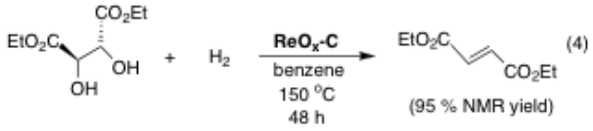
ENTRY	R_1	R_2	T (°C)	P (MPa)	Time (h)	OLEFIN YIELD (%)
1	Ph	H	150	1.4	24	39
2	$C_{12}H_{25}$	H	150	1.4	25	12
3					48	23
4					72	42
5	$C_{12}H_{25}$	H	175	1.4	72	30
6	$C_{12}H_{25}$	H	175	0.7	72	23
7	CO_2Et	CO_2Et[b]	150	1.4	48	95[c]
8	$C_{12}H_{25}$	H	175	1.4	24	36
9[d]	$C_{12}H_{25}$	H	175	1.4	24	23
10[e]	$C_{12}H_{25}$	H	175	1.4	24	20
11[f]	$C_{12}H_{25}$	H	175	1.4	24	10
12	$C_{12}H_{25}$	H	150	1.4	73	43(42)[g]
13	$C_{12}H_{25}$	H	150	1.4	73	31(30)[g]
14	$C_{12}H_{25}$	H	175	1.4	24	56(48)[h]

[a] a] yield determined by gc analysis with naphthalene as internal standard; [b] (+)-diethyl tartrate; [c] yield determined by ^{1}h-nmr integration with dimethylsulfoxide as internal standard; [d] recovered catalyst from run 8 recharged with reactants; [e] recovered catalyst from run 9 recharged with reactants; [f] recovered catalyst from run 10 recharged with reactants; [g] cumulative yield after charging filtrate with new reactant, yield in parentheses for preceding run with reo_x-c, room temperature filtration; [h] corresponding to [g] but with hot filtration.

The lifetime of the ReO_x-C catalyst was evaluated by determining the tetradecene yield in four consecutive reaction runs by recycling the recovered catalyst (ca. 90%) and recharging with fresh glycol, solvent and hydrogen (entries 8–11). A moderate loss in activity was detected over the four runs, suggesting that some catalyst deactivation or leaching into solvent had occurred. A key question is whether the active catalyst species is homogeneous (via leaching of rhenium into solvent*)* or heterogeneous. To address this point, three post-reaction mixtures from the C_{14}-glycol were filtered to remove the solid catalyst and the filtrates were tested for catalytic activity with additional glycol using the same conditions as in the preceding experiment with solid ReO_x-C (entries 12–14). If the filtration was carried out at room temperature, no appreciable increase in the olefin yield was detected (entries 12, 13). However, if the filtration was carried out while the reaction mixture was hot, further reaction was observed and the yield increased from 48 to 56% (entry 14). Thus, at high temperatures, some leaching occurs and the catalysis is partly performed by soluble rhenium species. However, the redeposition of soluble Re-species at room temperature allows the re-use of the recovered catalyst for batch applications. To exclude that the present reactions are entirely the result of homogeneous catalysis, yields obtained with the ReO_x-C catalyst were compared with those from reference compounds able to produce dissolved oxorhenium species. NH_4ReO_4 catalyzes the DODH reaction of tetradecanediol, but with lower yield than with ReO_x-C, likely as a result of its poor solubility in benzene. Re_2O_7 dissolved and showed high initial DODH rates, but deactivated fast. Overall tetradecene yields were much lower than with the heterogeneous catalyst (17–19% vs. 36% in entry 8). The observations of lower productivity with the oxorhenium reference compounds support the notion that a stabilized,

catalytically active perrhenate species exists on the carbon support. Interestingly, the solubility of both reference compounds was found to increase in the presence of diols, suggesting complexation of the rhenium by the diol.

The deoxydehydration of (+)-diethyl tartrate by ReO_x-C resulted in an efficient and very selective conversion to the *trans* olefin, diethyl fumarate, in excellent yield (>95%, eq. 4) with no detectable reduction or hydrolysis of the carboxyl groups. Diethyl fumarate is the expected product if the catalytic reaction proceeds via stereoselective *syn*-elimination of the vicinal hydroxyl groups, which can be realized through formation and concerted retrocyclization of a Re-*O,O*-glycolate intermediate, as has been proposed for the homogeneous rhenium-catalyzed DODH reaction.[5-10] Some caution must be applied with this result, as diethyl maleate (*cis*) was partially converted to diethyl fumarate under catalytic conditions (ReO_x-C, 1.4 MPa H_2, 150 °C, 24 h).



To gain first insight into the reaction kinetics, the DODH of diethyl tartrate was spectroscopically monitored in an autoclave with an ATR-IR probe integrated into the reactor wall. The specific IR bands of the reactant (diethyl tartrate) and product (diethyl fumarate) were used to calculate the respective liquid concentrations (see Supporting Information for reactor detail and calibration procedures). No other products except diethyl fumarate were observed by in-situ IR spectroscopy, consistent with the high selectivity observed by GC and NMR. Fig. 3 shows an excellent correlation between the conversion rate of the tartrate and the formation of fumarate.

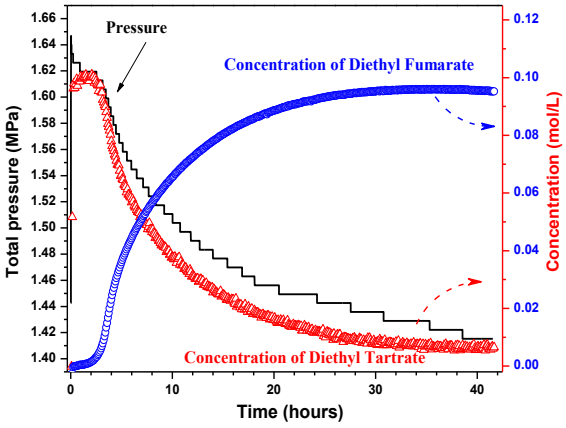
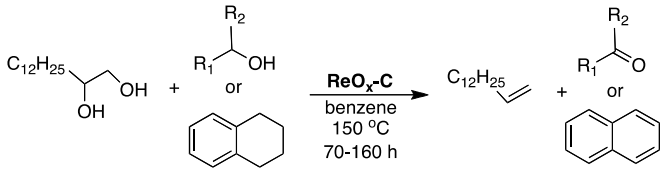


Figure 3. Concentrations of reactant and product as determined from in-situ ATR-IR spectra and pressure recorded during DODH of diethyl tartrate catalyzed by ReO_x-C at 150°C.

The change in total pressure, which can be largely ascribed to H_2 consumption under these conditions, follows the profile of the tartrate consumption, as would be expected from the reaction stoichiometry (eq. 4). A 2 h induction period was found when the ReO_x-C sample was pre-reduced for only 10 min prior to addition of diethyl tartrate, whereas the induction period was shorter when the catalyst was reduced for a longer time. These results indicate that the catalyst has first to be transformed into a reduced active state.

Finally, we have also assessed the ability of ReO_x-C to catalyze hydrogen-transfer DODH reactions of glycols. Heating a mixture of the C_{14}-glycol and diisopropyl carbinol with ReO_x-C (ca. 10 mol%; 150 °C, benzene) over a few days cleanly afforded 1,2-tetradecene (43% yield, 165 h, Fig. 4). With benzyl alcohol as the co-reactant under the same conditions, a faster reaction ensued with 52% of olefin being detected after 70 h, along with the co-product benzaldehyde. The H-donor tetrahydronaphthalene, which is abundant in petroleum, was also effective under the same conditions in the DODH reaction catalyzed by ReO_x-C, affording 40% of tetradecene (and naphthalene) after 161 h. In all cases, no alkane product was detected.



reductant	*olefin yield*
$R_1 = R_2 = CH(CH_3)_2$	43 %
R_1 = Ph, R_2 = H	52 %
hydronaphthalene	40 %

Figure 4. Equation and olefin yields for DODH using hydrogen-transfer reagents.

We have disclosed here the first polyol-to-olefin DODH reactions catalyzed by supported ReO_x, employing both H_2 and hydrogen-transfer reductants. It appears that DODH catalysis is effected by both soluble and surface-bound Re species. Efforts to expand the scope, improve the catalytic activity, selectivity and longevity, and to identify the active catalyst species are underway.

Experimental Section

The preparation of ReO_x-C was adopted from Choe et al.[xiii] with some modifications. Activated carbon (granular, Darco, 20–40 mesh) was dried at 150 °C. A 1 mM solution of NH_4ReO_4 (Alpha Aesar, 99+%) in water was used as prepared or adjusted to pH 3 by adding HCl. The hot, dry carbon was added and the resulting suspension was stirred for 5 h, with H_2 being bubbled through the liquid in some of the preparations. The solid matter was allowed to settle overnight, and the supernatant was removed using a cannula. The remaining damp solid was dried under a N_2 flow at 110 °C.

The rhenium content was determined by photometric analysis of the recovered solution. Quantitative analysis of the characteristic perrhenate absorption band at a wavelength of 227 nm gave the residual concentration, and the difference from the initial concentration was used to calculate the adsorbed amount; typical analyses gave 3-4 mass % Re. A ReO_x-C sample spot-checked by ICP-MS (Galbraith Laboratories) was found to contain 4.2 mass % Re (4.2 by photometric analysis).

In a typical reaction the glycol (1.0 mmol), and ReO_x-C (about 30 µmol) were combined with 5 mL benzene in a glass-lined stainless steel reactor, pressurized with H_2 up to a total pressure of 0.7–1.4 MPa and then heated to 150–175 °C for several hours. Samples withdrawn from the reactor were analyzed by GC (after addition of 0.5 mmol naphthalene as internal standard), GC–MS, and ^{1}H-NMR.

ATR spectra of solid samples were collected using a PIKE accessory with ZnSe crystal and a FTIR spectrometer. In situ ATR-IR spectra were recorded using a Mettler-Toledo ReactIR™ iC10 with a K4

conduit diamond integrated into the wall of a custom-design autoclave (see Supporting Information). The ReO_x-C sample was pretreated in benzene at 150 °C in 1.4 MPa H_2 prior to the addition of diethyl tartrate.

Acknowledgements

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