Fundamental Insights into Deactivation by Leaching During Rhenium-Catalyzed Deoxydehydration

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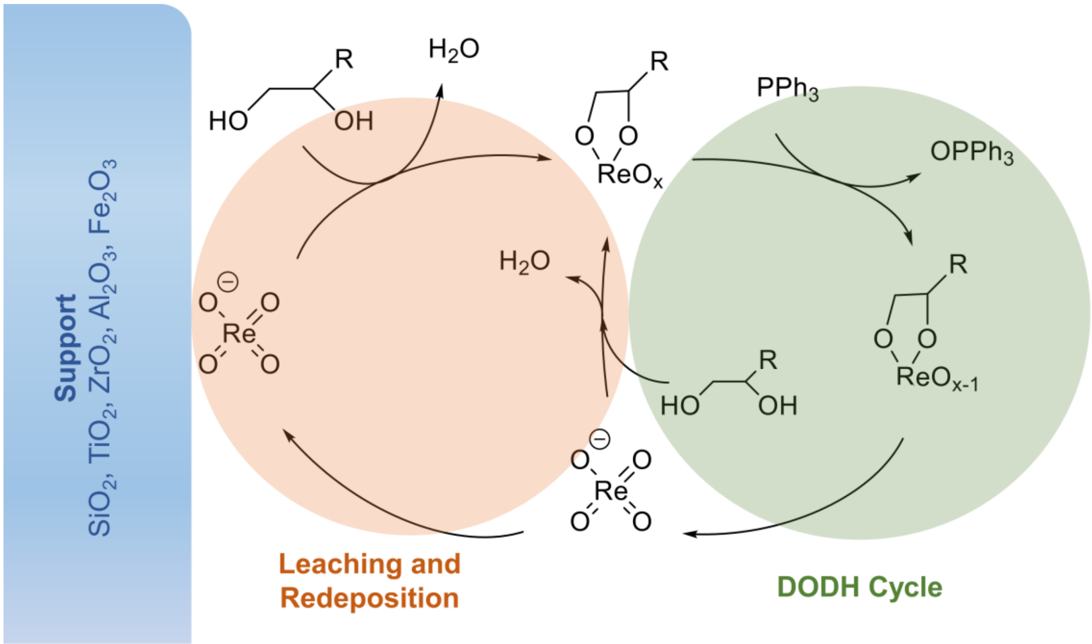
Graphical Abstract



Abstract

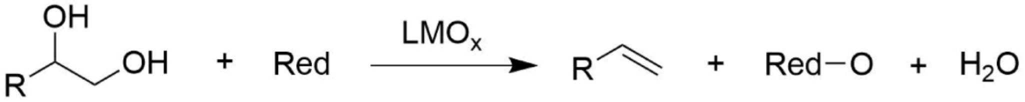
Deoxydehydration, a transformation that selectively converts diols into olefins in a single catalytic step, has great potential for biomass upgrading because it removes oxygen and the obtained double bond is useful for further functionalization. Recent efforts to produce heterogenized versions of known soluble oxido-rhenium catalysts have produced mixed results, with stability being a recurring issue. In the present work, the reasons for catalyst deactivation were systematically investigated by comparisons within a series of materials distinguished by the support. Catalysts were prepared by incipient wetness impregnation of ammonium perrhenate onto TiO_2 and ZrO_2 at 1, 2 or 4wt% rhenium, and SiO_2, Fe_2O_3, and Al_2O_3 at 4 wt% rhenium, with subsequent calcination. All catalysts were active in the conversion of 1,2-decanediol to 1-decene at a temperature of 150 °C, in toluene as the solvent at autogeneous pressure, and with triphenylphosphine as reductant. The rhenium-normalized 1-decene formation rates for TiO_2-and SiO_2-supported catalysts were comparable with that of a homogeneous methyltrioxorhenium catalyst with selectivities between 80 and 90%, whereas the other catalysts were significantly less active. High activity was correlated with rapid deactivation. It was found that rhenium leaching is the primary cause of deactivation and is induced via association of the catalyst with the diol to give a soluble glycolate complex. Homogeneous catalysis contributions were significant. In addition to choosing a suitable (*i.e.*, reducible or Lewis-acidic) support, leaching can be minimized through: an appropriately low rhenium loading that depends on the support; selecting a solvent that is less than ideal for the substrate; and by driving the reaction to 100% substrate conversion, which results in re-deposition of rhenium.

Keywords: sugars, deoxygenation, alpha-olefins, transition metal complex catalysis, immobilization

1. Introduction

The conversion of biomass to fuels and chemicals is an area of active research with the ultimate goal of transitioning from fossil feedstocks to renewable carbon sources. However, biomass processing is made difficult by the challenge of breaking down the complex lignocellulosic structure, and by the very high oxygen content of biomass, corresponding to a near 1:1 ratio of carbon and oxygen. The products of primary processing, that is the fluids obtained through biomass pyrolysis or hydrolysis, therefore must be upgraded by extensive deoxygenation.[1]

One potential biomass upgrading reaction of interest is deoxydehydration (DODH), which targets the vicinal OH groups characteristic of sugars and sugar alcohols. This transformation combines a deoxygenation using a sacrificial reductant and a dehydration into a single catalytic cycle, thus producing an alkene from a diol (Eq. 1).



(Eq. 1)

DODH was discovered by Cook and Andrews in 1996 who achieved over 90% selectivity to the alkene by using methyltrioxorhenium (L=CH_3, M=Re, x=3 in Eq. 1) as the active complex in a homogeneously catalyzed reaction with triphenylphosphine as reductant.[2] The portfolio of soluble catalysts for deoxydehydration has since been expanded, including improving activity by using bulky ligands on rhenium catalysts,[3] as well as identifying molybdenum,[4,5] and vanadium,[6,7] complexes capable of carrying out deoxydehydration. An array of reductants has been successfully employed, including triphenylphosphine, sulfite,[8,9] gaseous CO (and H_2,[10] elemental reductants,[11] hydroaromatic reductants,[12] and secondary alcohols.[13,14] Stoichiometric amounts of $OPPh_3$, sulfate, CO_2, water, aromatic compounds and ketones are formed accordingly.

The applicability of deoxydehydration was explored on a wide variety of polyol substrates. Cyclic diols were tested to see whether a particular orientation of the OH groups is needed; and cis-diols were generally found to be reactive, whereas steric constraints can apply to trans-cyclic diols such as 1,2-transcyclohexanediol.[15] For larger polyols, such as C4-C6 sugar derived polyols, there was the question of whether initial reaction of an interior pair of vicinal OH groups would inhibit complete conversion of the remaining, further spaced OH groups. However, Shiramizu and Toste demonstrated complete conversion of erythritol (a 1,2,3,4-tetrol) to butadiene and proposed a mechanism in which the rhenium catalyst also facilitates a hydroxyl and double bond shift.[15] There is agreement that the reaction has three fundamental steps, a reduction step in which the catalyst oxidation state decreases by 2, a condensation step in which the diol coordinates with the oxido-metal site to form a glycolate, and an elimination step in which the catalytic site is re-oxidized and the olefin is eliminated.[16] The sequence of the first two steps is not firmly established.

Due to the high cost and rarity of rhenium, there is significant interest in developing a stable solid catalyst for deoxydehydration. The principal strategy pursued towards this goal has been to heterogenize known active rhenium complexes. In 2013, Denning et al. reported a carbon-supported perrhenate catalyst that was active, selective and versatile with respect to substrate and reducing agent, but was also found to deactivate as a result of leaching.[17] Sandbrink et al. tested a variety of oxides as supports for oxido-rhenium and assessed the obtained catalysts with 1,2-hexanediol as reactant and 3-octanol as secondary alcohol reductant and solvent.[18] The authors found that they could produce a relatively stable ReO_x/TiO_2 catalyst when it was pre-reduced. Tomishige and coworkers tested a variety of ceria-supported oxido-rhenium catalysts with added noble metal promoters, including palladium, [19] platinum, [20] and gold. [21] The group developed a gold nanoparticle promoter that was capable of activating H_2 as reductant for deoxydehydration, while the resulting alkenes were not hydrogenated into less valuable alkanes. Leaching was reported to be insignificant. Li and Zhang sought to attach rhenium catalysts on polymer supports by various strategies that relied on amine-type ligands and ionic ammonium groups. However, these catalysts all demonstrated some leaching during DODH of diethyl tartrate with 3-pentanol as reductant and solvent.[22] Sharkey et al. tried using a catecholate ligand with a tether as an anchoring strategy, but rhenium was found to leach.[23]

In an approach to replace the expensive rhenium by alternative metals in supported deoxydehydration catalysts, Kwok et al. demonstrated the gas phase conversion of glycerol to allylic acid at 400 °C using a VO_x/SiO_2 catalyst.[24] Oxide-supported molybdenum catalysts were reported to be catalytic by Sandbrink et al.[25] and Sharkey et al.,[23] however, only with limited selectivity to the deoxydehydration product.

In the deoxydehydration literature, catalyst deactivation by leaching is of prime concern, since the typical substrates are molecules that require a solvent because their size and polarity make solid-gas phase reactions less feasible. In general, solid catalyst activity and stability in solution phase processing is of importance in relation to upgrading reactions for biomass-derived feedstock.[26] Moreover, leaching of active species from solid catalysts is a common phenomenon in liquid-phase processing and can be a key challenge to developing stable solid catalysts for conversion of non-volatile reactants. There are multiple examples of dissolution of supported noble metal species.[27,28] Leaching is not always easy to detect and requires a number of tests.[29-32]

Given the importance of leaching as an issue per se in catalytic processing,[33,34] and the fact that the extent of leaching in deoxydehydration varies significantly across the literature, the goal of this work is to explore the parameter space around rhenium leaching in liquid phase deoxydehydration reactions in order to better understand the leaching mechanism, and to develop strategies to prevent leaching. Supports, reactants, reductants and solvents are selected to ensure broad connection to prior work and are: various oxides; alkanediols; triphenylphosphine and secondary alcohols; toluene, dioxane and secondary alcohols.

2. Materials and Methods

2.1. Catalyst Synthesis

Methyltrioxorhenium (Strem, 98%) served as a soluble benchmark catalyst. Ammonium perrhenate (Sigma Aldrich, ≥99%) was used as the rhenium precursor. The oxidic supports tested were Aerosil 300 SiO_2 (Sigma Aldrich), P25 TiO_2 (Sigma Aldrich), γ-Al_2O_3 (Sigma Aldrich), α-Fe_2O_3 (US Nanomaterials, Inc.), and G2 hydrous zirconia (MEL Chemicals), as well as Darco Activated Carbon (Sigma Aldrich) for comparison to previous work. The hydrous zirconia was calcined prior to impregnation in a tube furnace under dry air flow for a duration of 5 h at a temperature of 550 °C to produce ZrO_2.

Catalysts were prepared by incipient wetness impregnation. The support was pre-dried in a muffle furnace at 115 °C for at least 8 h. Ammonium perrhenate was dissolved in an amount of deionized water corresponding to the pore volume of the pre-dried support (0.5-1.5 mL per 1000 mg of support). The concentration was chosen to produce a catalyst with a composition of 1, 2 or 4 weight % rhenium. In an agate mortar, ammonium perrhenate was added to the pre-dried support drop by drop, and solid and liquid were mixed thoroughly by pestle to produce a paste. The paste was dried in a muffle furnace at 115 °C for 8 to 12 h. The dried catalyst was then calcined in a tube furnace at a temperature of 420 °C for 4 h. A relatively mild temperature is required because Re_2O_7, if formed, would boil at 359 °C.

2.2. Catalytic Reactions and Solubility Experiments

Catalytic test reactions were carried out in a 15 mL glass pressure tube rated at 150 psig (Ace Glass) equipped with a Teflon coated stir bar. Since the reactions are conducted above the boiling point of the solvents at autogeneous pressure, care must be taken that the mixture´s vapor pressure does not exceed the rating of the vessel at the reaction temperature. The glass reactor was heated in a silicone oil bath with a magnetic stirrer (IKA hot plate). The reported temperature is from a K-type thermocouple that was placed into the glass reactor’s thermowell and read by a MicroDAQ thermometer. Post reaction, the reactor was cooled in a room temperature water bath. The catalyst and reaction solution were separated either at room temperature by centrifugation (10 min at 1500 rpm), or by hot filtration using a filter disk (porosity 10-20 µm). Since reactions were carried out at temperatures above the normal boiling point of the solvent, the filter disk was connected to the reactor top via a valve, such that immediate filtration at reaction temperature became possible.

For testing solubility effects and catalytic performance, a range of diol reactants, solvents, and reductants were employed. The diol reactants were 1,2-decanediol (Sigma Aldrich) and 1,2-hexanediol (Sigma Aldrich). Additional alcohols were 1-butanol (Acros 99%) and 1,4 butanediol (Sigma-Aldrich, 99+%). The solvents used were benzene (Sigma Aldrich, anhydrous), toluene (Sigma Aldrich, anhydrous), 1,4-dioxane (Sigma Aldrich, anhydrous), 3-octanol (Sigma Aldrich, 99%), 2-propanol (Sigma Aldrich, anhydrous 99.5%) or water. Triphenylphosphine (Sigma Aldrich) was the default reductant. Triphenylphosphine oxide (Sigma Aldrich) was used for calibration to quantify reductant oxidation. Some reactions were performed without a reductant, or with a secondary alcohol reductant, or with a secondary alcohol solvent. *n*-Hexadecane was added as an internal standard for GC-FID analysis.

The standard reaction volume was 5 mL containing 0.20 M of diol, 0.23 M of triphenylphosphine (*i.e.*, a slight excess of reductant), 0.10 M of *n*-hexadecane, and catalyst corresponding to an equivalent of 0.01 M of rhenium and a diol-to-rhenium molar ratio of 20:1.

2.3. Analysis

Support and catalyst surface areas were determined by N_2 adsorption and BET analysis using an Autosorb iQ2 (Quantachrome instruments). The catalysts were pre-treated in vacuum for 12 h at a temperature of 300 °C, isotherms were measured at 77 K.

The composition of the reaction mixture was quantitatively analyzed by using an Agilent 7890B GC with an Agilent HP-5 column (30 m, 0.320 mm diameter, 025 µm film) and flame ionization detection. Retention times and response factors were determined with the help of standards. Diol conversion was calculated from measured final concentration and the initial concentration of diol known from preparation of stock solution of solvent, diol, and internal standard. Yields are based on the initial diol concentration. Only the α-olefin was observed under the reported reaction conditions. Reductant consumption is based on the yield of triphenylphosphine oxide.

The amount of leached rhenium was quantified by ICP-MS. The ICP-MS samples were prepared by drying 0.1 mL of reaction supernatant to remove the solvent. The leftover solid was then digested in 5 mL of 5 wt % HNO_3 for 12 h at a temperature of 80 °C. Then a 0.2 mL aliquot of the digestion solution was filled up to 10 mL with additional 5 wt % HNO_3 for a total dilution factor of 2500x. The rhenium content of these solutions was measured by a Perkin Elmer NexION350D ICP-MS. A higher concentration standard solution was used to create 7 rhenium calibration standards between 0.1 and 500 ppb. The dilution factor was used to back-calculate the concentration of leached rhenium in the reaction solution.

Error bars indicate 3 experimental replicates from independent test reactions under the same conditions for both GC-FID and ICP-MS measurements; error is reported as the mean ± 1 standard deviation.

UV-visible transmission spectra of reaction supernatants were measured using a PerkinElmer Lambda 950 UV-vis-NIR spectrometer. The supernatant solution was diluted with excess solvent one in three parts by volume. The solutions were placed in 1 cm quartz cuvettes, and the pure solvent served as a reference. EPR spectra of reaction supernatants were collected at room temperature in 4 mm quartz EPR tubes (Wilmead-Glass) using a Bruker Elexsys E-500 EPR with ER 4105DR cavity.

3. Results

3.1. Catalyst Characterization

The texture of the original supports and the produced catalysts was characterized by N_2 physisorption. The BET surface areas and the catalyst loading can be found in Table 1. The loss of surface area through rhenium addition and calcination was marginal for TiO_2 and Fe_2O_3, appreciable ZrO_2 and Al_2O_3, and significant for SiO_2. Because of the spread of surface areas at nearly equal rhenium content, the rhenium surface density varied.

Table 1: Oxide-supported rhenium catalysts

Catalyst	**Rhenium Content (wt%)**	**Support BET Surface Area (m^2/g)**	**Catalyst BET Surface Area (m^2/g)**
ReO_x/TiO_2	4.09	53.2	51.5
ReO_x/ZrO_2	4.09	99.5	87.6
ReO_x/SiO_2	3.90	300[a]	204.0
ReO_x/Fe_2O_3	4.24	42.7	45.0
ReO_x/Al_2O_3	4.30	151.6	122.5

[a] Manufacturer's information

3.2. Catalytic and Solubility Experiments

All oxide-supported catalysts were screened for their activity in decanediol DODH. Homogeneous catalysis with methyltrioxorhenium and heterogeneous catalysis with previously reported ReO_x/C[17] were used for benchmarking. Since the catalysts differed significantly in their activity, an average rate of 1-decene formation was determined at comparable conversions (within ± 10%) to eliminate any reaction order-related rate effects. The most active supported catalysts, ReO_x/TiO_2 and ReO_x/SiO_2 were found to have turnover frequencies to 1-decene (mol decene per mol rhenium and hour) similar to homogeneous methyltrioxorhenium on a per rhenium basis, that is, 27.3 h^{-1} for ReO_x/TiO_2, 30.3^{-1} for ReO_x/SiO_2 as compared to 24.0 h^{-1} for methyltrioxorhenium. Re/C was also highly active as previously observed,[17] whereas all other oxide-supported catalysts were less active (Figure 1a). For a given catalyst, selectivity to the alkene product was largely invariant to diol conversion, between about 80-90% for ReO_x/TiO_2 and ReO_x/SiO_2. Consistently, the amount of triphenylphosphine oxide formed was proportional to the amount of decene with little deviation.

The solid catalysts were recovered and re-tested repeatedly with fresh reaction mixtures to monitor stability over multiple uses. The development of the DODH performance over five batch reactions is shown in Figure 1a, normalized to total catalyst mass, as the rhenium content becomes unknown after the first use. Because of the decreasing amount of catalyst in these experiments, the uncertainty in the rate increases during later uses.

The initially most active catalysts, ReO_x/SiO_2, ReO_x/TiO_2, and ReO_x/C, deactivated considerably even after a single use. In contrast, the initially less active catalysts, ReO_x/ZrO_2, ReO_x/Fe_2O_3, and ReO_x/Al_2O_3, were more stable. ReO_x/ZrO_2, ReO_x/Fe_2O_3 even consistently demonstrated a slightly higher activity in the second run in comparison to the first use. In order to investigate the cause for deactivation, the quantity of leached rhenium was determined by ICP-MS. The results in Figure 1b indicate a strong correlation between the leached rhenium and both the activity of the catalyst for a given run, and loss in activity observed in subsequent runs. The first correlation suggests that solubilized rhenium species contribute to the observed DODH activity.

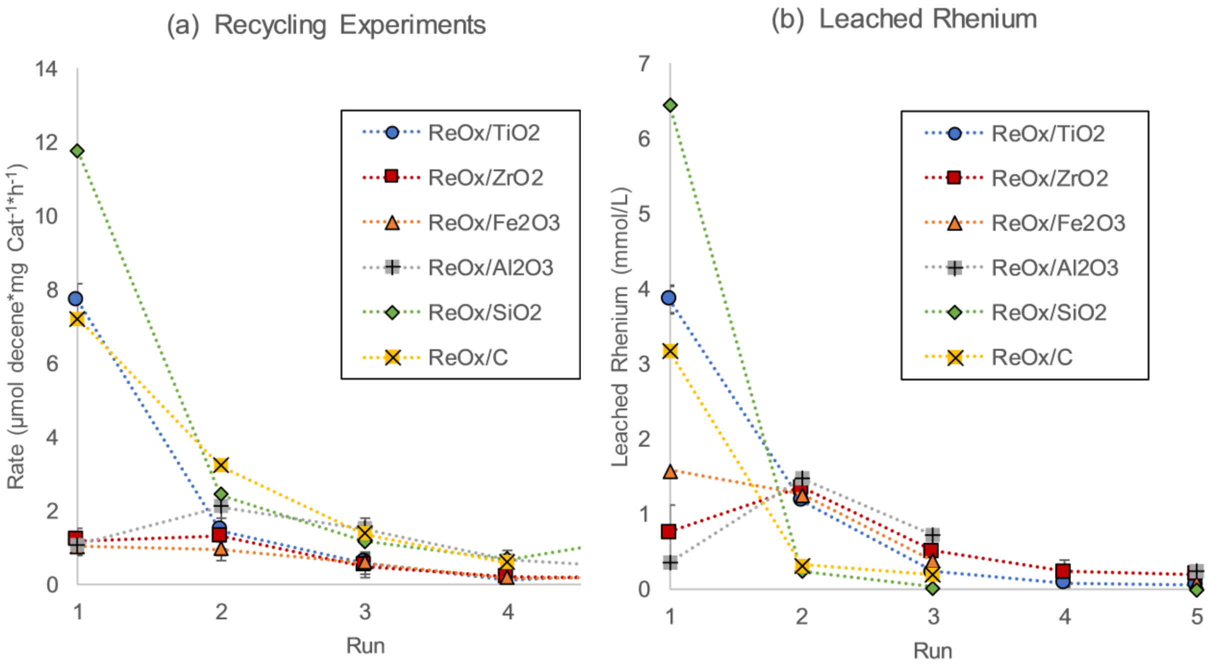


*Figure 1: (a) Catalysts activity over multiple uses, (b) Leached rhenium concentration as measured by ICP-MS over the 5 recycle runs of (a). **Reaction conditions:** Temp. 150 °C, time 15-40 min (40-60% diol conversion), solvent toluene, 0.2 M 1,2-decanediol, 0.23 M PPh_3, diol:Re=20.*

The amount of rhenium leached was measured for each of the repeat runs, and the cumulative amount of rhenium leached into the reaction solution by the supported catalysts was calculated. By normalizing the amount of rhenium lost to the total initial rhenium content on the catalyst from the incipient wetness impregnation, the fraction of rhenium lost by run was obtained, as seen in Figure 2. The ReO_x/SiO_2 catalyst, which deactivated most quickly, lost most of its rhenium to the reaction solution in the first run. The other catalysts leached more gradually, with ReO_x/TiO_2 losing about 80% of its rhenium content after 5 runs, while the other oxide-supported catalysts lost about 50% of their rhenium content after 5 runs.

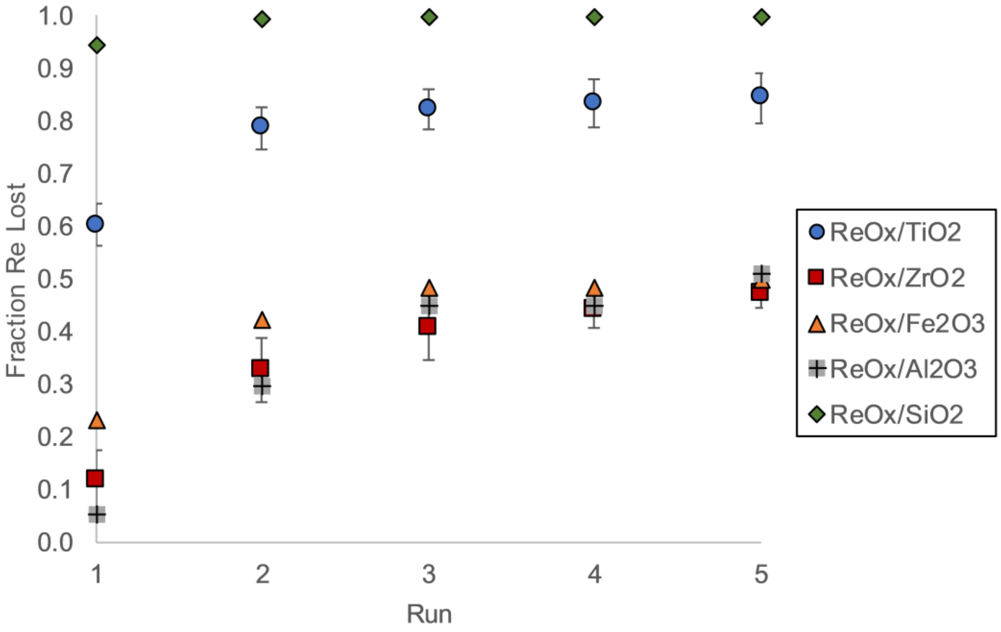


Figure 2: Fraction of rhenium leached over several recycle runs. ***Reaction conditions:*** *Temp. 150 °C, time 15-40 min (40-60% diol conversion), solvent toluene, 0.2 M 1,2-decanediol, 0.23 M* PPh_3*, diol:Re=20.*

These experiments would indicate that the solubilized rhenium species may be more active, but there seem to be firmly attached rhenium species on Al_2O_3, ZrO_2, Fe_2O_3, and to a less extent on TiO_2. For further investigations, we chose to focus on ReO_x/TiO_2 as an active but quickly deactivating catalyst, and ReO_x/ZrO_2 as a less active but more stable catalyst.

Hot filtration tests were performed for ReO_x/TiO_2 and ReO_x/ZrO_2 catalysts to investigate whether rhenium is redeposited on the support when the reaction mixture is cooled. Figure 3 shows the amount of leached rhenium measured by ICP-MS for three differently obtained reaction supernatants. In all cases, the catalytic reaction was started at a temperature of 150 °C for a duration designed to achieve an intermediate conversion, which depended on the catalyst. The reaction medium was then separated from the solid by hot filtration at the reaction temperature (150 °C) or at an intermediate temperature (100 °C). Alternatively, separation was accomplished by centrifugation at room temperature. It can be seen that the separation temperature did not have a significant effect on the amount of rhenium detected in the liquid, indicating that cooling the reaction mixture does not cause precipitation or redeposition of rhenium species. This result demonstrates that the solubility of the leached rhenium complexes is not a strong function of temperature, and measurements made after separation at ambient temperature properly represent the amount of rhenium leached under reaction conditions. Separations in this paper (including those conducted to generate Figures 1 & 2) were thus conducted at room temperature unless otherwise indicated, because of the difficulty of separating under autogeneous pressure and recovering the catalyst from the filter disk.

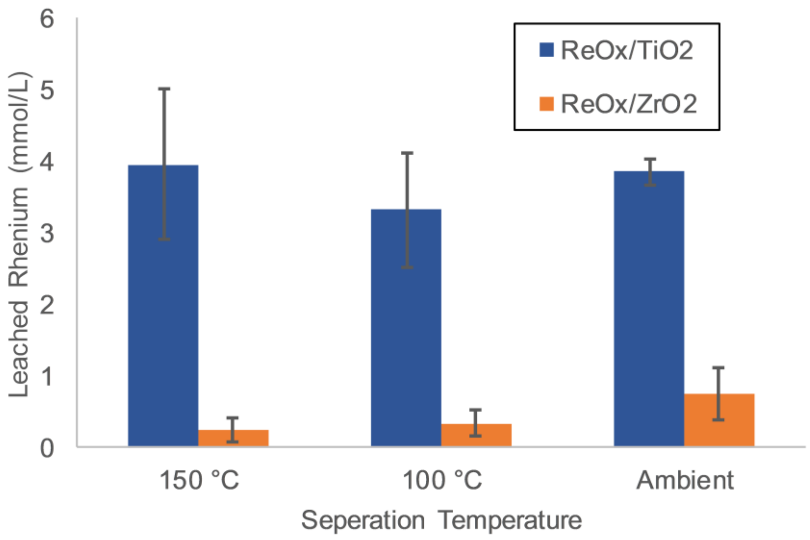


Figure 3: Leached rhenium vs catalyst separation temperature. ***Reaction conditions:*** *Temp. 150 °C, time 10 min* ReO_x/TiO_2*, 60 min* ReO_x/ZrO_2 *(40-60% diol conversion), solvent toluene, 0.2 M decanediol, 0.23 M* PPh_3*, diol:Re=20. Separation at 150 °C performed by filtration at set reaction time; separation at 100 °C performed by filtration after reaction at 150 °C and transfer to 80 °C oil bath to cool for 5 min; separation at ambient temperature performed by centrifugation after cooling in water bath.*

To test whether elevated temperatures are needed to solubilize rhenium in the first place, the amount of rhenium leached into an unheated reaction mixture was compared with that leached under reaction conditions. As seen in Figure 4, for ReO_x/TiO_2, the degree of leaching at room temperature was similar to that at reaction temperature. In contrast, ReO_x/ZrO_2 demonstrated almost no rhenium leaching at low temperature. These observations indicate different ReO_x-support interaction for these two catalysts. The interaction is weak between ReO_x and TiO_2, whereas it is strong between ReO_x and ZrO_2, requiring elevated temperatures to induce leaching.

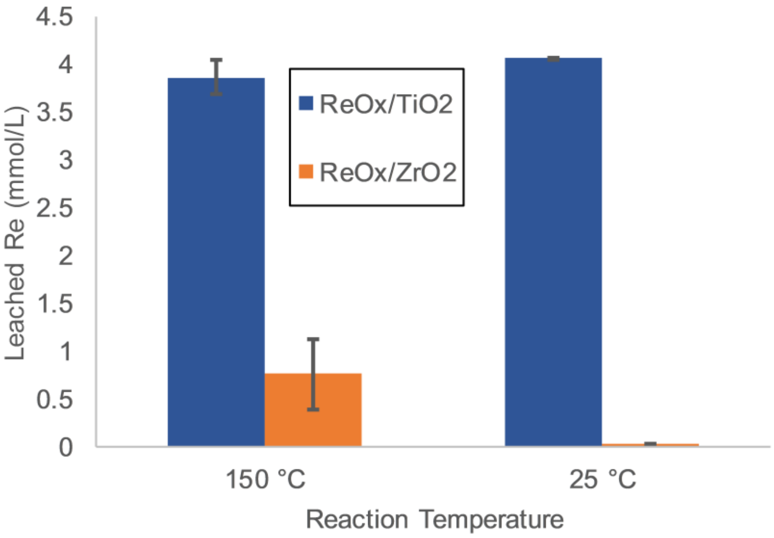


Figure 4: Reaction temperature vs. room temperature leaching. ***Reaction conditions:*** *Temp. 150 °C, time 15 min ReO_x/TiO_2, 60 min ReO_x/ZrO_2 (40-60% diol conversion), solvent toluene, 0.2 M 1,2-decanediol, 0.23 M PPh_3, diol:Re=20.*

To test the effect of loading, ReO_x/TiO_2 and ReO_x/ZrO_2 catalysts containing 1 and 2 wt % rhenium were prepared, and the rhenium leaching during reaction was compared with that of the 4 wt % rhenium catalysts (Figure 5). For both TiO_2 and ZrO_2 supported catalysts, the lower loadings resulted in significantly less leaching and a higher fraction of retained rhenium over several uses of the catalysts. However, the deoxydehydration rates per rhenium were not favorable, as seen in Table 2, suggesting that the more strongly bound rhenium species in the lower-loading catalysts tend to have lower activity for DODH and become largely inactive after several runs.

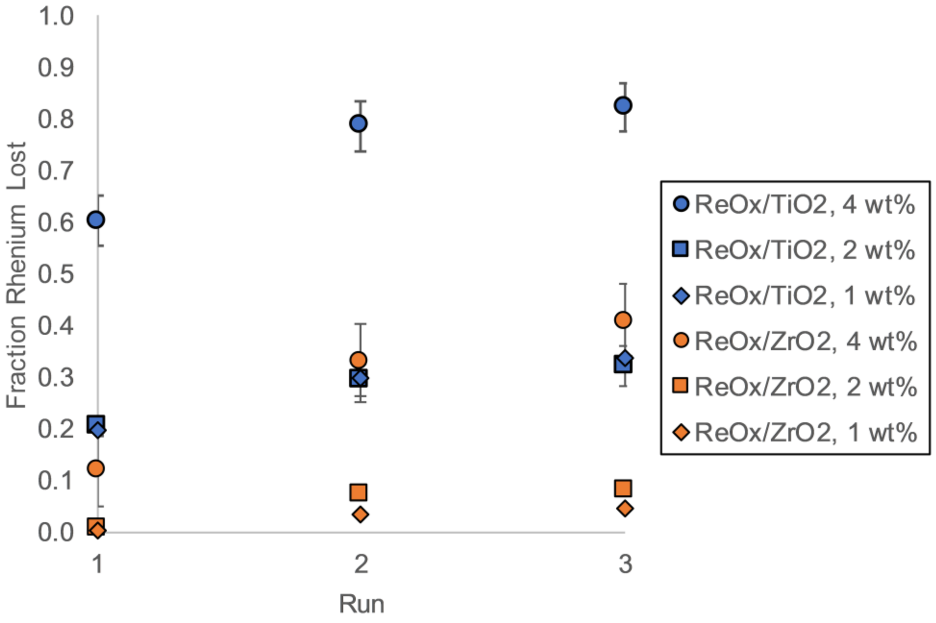


Figure 5: Fraction of rhenium leached over several recycle runs, effect of rhenium loading. ***Reaction conditions:*** *Temp. 150 °C, time 15-60 min, solvent toluene, 0.2 M diol, 0.23 M PPh_3, diol:Re=20.*

Table 2: Catalytic activity of titania- and zirconia-supported catalysts with various rhenium loadings

Catalysts		**Turnover frequency* (mol decene)(mol Re)$^{-1}$ h^{-1}**		
Composition	**Rhenium content (wt%)**	**Run 1**	**Run 2**	**Run 3**
ReO_x/TiO_2	3.87	36.3±1.6	16.4±8.4	12.0±4.6
ReO_x/TiO_2	1.86	17.8±2.5	4.2±0.6	0.0±0.0
ReO_x/TiO_2	0.97	10.6±2.7	4.4±0.4	0.7±1.3
ReO_x/ZrO_2	3.88	5.5±1.8	7.0±2.6	3.7±3.1
ReO_x/ZrO_2	1.88	0.2±0.4	2.3±0.1	0.5±0.4
ReO_x/ZrO_2	1.02	0.0±0.0	0.8±0.1	0.0±0.0

*****Reaction conditions:*** *Temp. 150 °C, time 15-60 min, solvent toluene, 0.2 M diol, 0.23 M PPh_3, diol:Re=20. Conversion < 25% for 1 and 2 wt% loadings. Max. conversion for 4 wt% was 40% (ReO_x/TiO_2). Turnover frequencies referenced to rhenium content corrected for leached fraction. Uncertainties are 1 standard deviation from 3 tests.*

A series of supernatant catalyzed reactions were performed to measure the catalytic activity of solubilized rhenium species and compare with that of solid catalysts. For a given catalyst, Figure 6 contains two data points (from two separate batch experiments), representing reaction progress with the solid catalyst present. Decene concentrations increased linearly with time, consistent with a constant rate of reaction and a zero-order reaction, which was also seen by Dethlefsen and Fristrup in a reaction kinetics investigation with homogeneous catalysts.[35] After the first reaction, the solid catalyst was removed, and only the reaction liquids were heated again to reaction temperature to monitor for additional conversion. Cumulative product formation is shown as a function of overall reaction time for these experiments, that is, the second set of data points (at longer time) for each catalyst represents the sum of initial and supernatant activity. It is expected that if there are no active solubilized species, the product yield should not further increase for the second reaction. Any increase in alkene yield indicates active solubilized species and generally contributions from homogeneous catalysis, which was evidently the case. To discriminate between heterogeneous and homogeneous catalysis contributions, cumulative product yields obtained with solid and supernatant need to be compared with that obtained with solids at the same overall reaction time. For both ReO_x/TiO_2 and ReO_x/ZrO_2 supernatants, the cumulative decene yield is below the linear trajectory seen for the solid catalysts, indicating a large portion of the catalytic activity comes from soluble species, but not all.

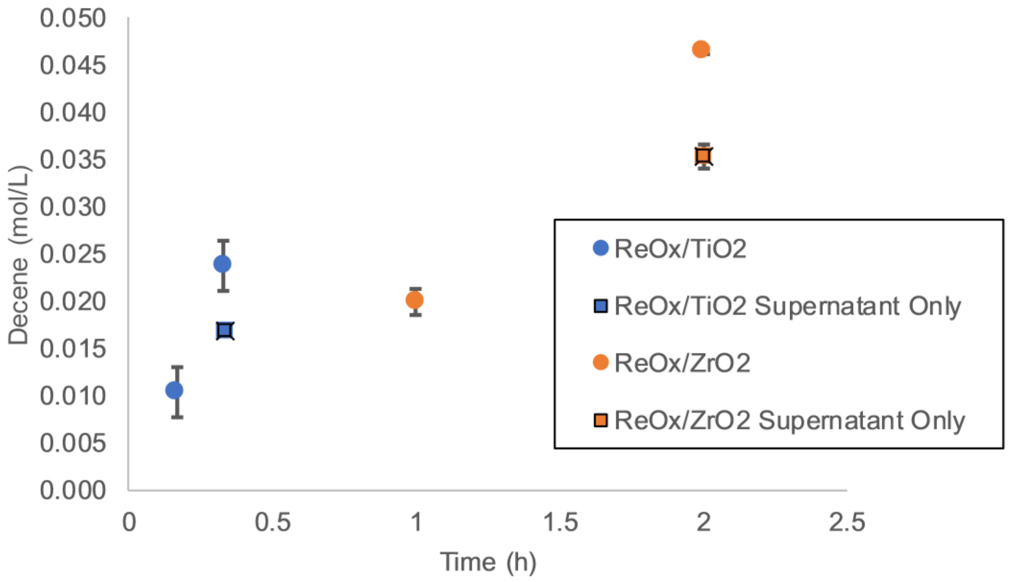


Figure 6: Hot filtration supernatant activity test. ***Solid catalyst reaction conditions:*** *Temp. 150 °C, time 15-60 min, solvent toluene, 0.2 M diol, 0.23 M PPh_3, diol:Re=40.* ***Supernatant reaction conditions:*** *Separated reaction filtrate from shorter reaction time was run for an additional 15 or 60 min at 150 °C without any solid catalyst. Lines are to guide the eye only.*

To further assess the relative contributions of homogeneous and heterogeneous catalysis, the rate of product formation during the reaction with the solid present was normalized in two different ways, while the supernatant rate was normalized to the amount of solubilized rhenium as determined by ICP-MS (Figure 7). If both rates are normalized to soluble rhenium, then a higher rate results for the initial run with solid present than for the supernatant, indicating that there is a heterogeneous catalysis contribution from supported rhenium in the solid. This contribution was significant only for the ReO_x/ZrO_2 catalyst. Comparison of the rate normalized to total supported rhenium in the first run with the rate per dissolved rhenium species in the supernatant run indicates a higher rate per rhenium in the supernatant, suggesting the dissolved species are more active on a per rhenium basis.

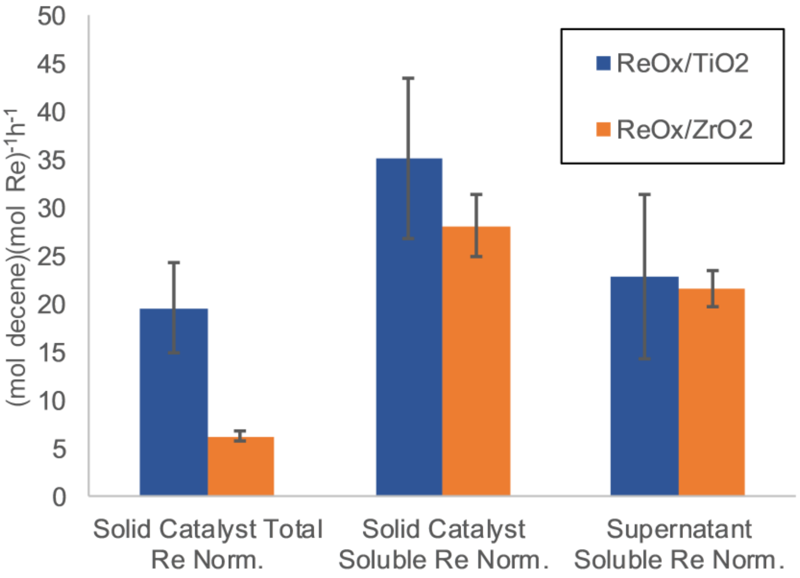
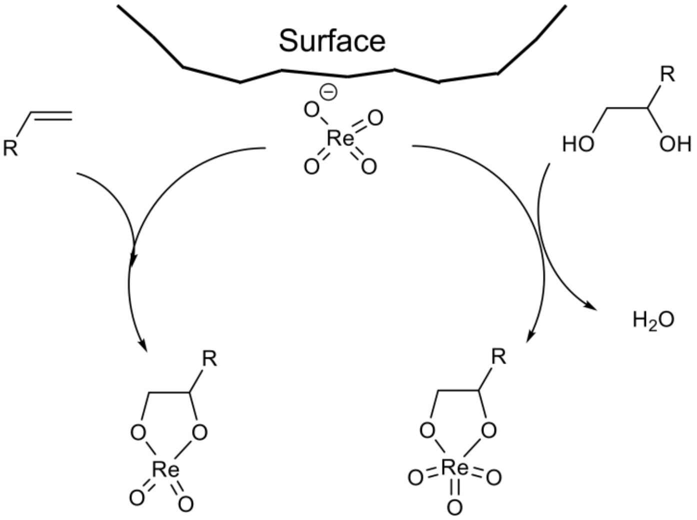


Figure 7: Solid vs supernatant reaction yield per total rhenium or solubilized rhenium measured via ICP-MS. ***Initial reaction conditions:*** *Temp. 150 °C, time 15-60 min, solvent toluene, 0.2 M diol, 0.23 M PPh_3, diol:Re=20.* ***Supernatant reaction conditions:*** *Separated reaction filtrate from the initial reaction was run for an additional 15 or 60 min at 150 °C without any solid catalyst. The activity is normalized to the solubilized rhenium as measured by ICP-MS.*

3.3. Solvent and Ligand Effect on Rhenium Leaching

The data in Figure 1 indicate a strong influence of the support on the propensity of rhenium to leach. However, a comparison with literature data suggests there might be additional factors affecting stability. Little to no leaching was reported by Sandbrink et al.,[18] whose most stable catalysts were a ReO_x/TiO_2 material and an even better, pre-reduced variant of this ReO_x/TiO_2 material. Tazawa et al.[21] found their $ReO_x/Au/CeO_2$ catalyst to lose only minor amounts of rhenium, corresponding to less than 0.25% of the loaded amount. Since the ReO_x/TiO_2 catalyst used in the present work is fundamentally similar to the non pre-reduced catalyst used by Sandbrink et al., the significant differences in leaching behavior require explanation. We hypothesized that in addition to the support, the solvent is likely to have an influence and, based on the proposed mechanism, also the reactant. If the species on the supported catalysts are similar to the perrhenate precursor, which was demonstrated for the carbon support,[17] then, as a charged inorganic moiety, they are not expected to be very soluble in the non-polar solvent toluene. During the catalytic cycle though, the rhenium complex receives new ligands. The proposed reaction mechanism for deoxydehydration involves a vicinal diol forming a glycolate with the active rhenium site followed by elimination of the alkene product. The glycolate intermediate would likely be far more soluble than the perrhenate alone, especially if the diol has a large non-polar region as with 1,2-decanediol, as illustrated in Scheme 1. The glycolate intermediates shown in the figure are based on published structures, for example, by Ahmad et al.[8] or by Shakeri et al.[36]



Scheme 1: Leaching hypothesis: Perrhenate (ReO_4^-) is not appreciably soluble in non-polar solvents, however diol and decene have surfactant-like properties when acting as a chelating ligand.

To test the theory of a chelating ligand inducing solubility of rhenium complexes, test reactions were performed to see which species present in the reaction might be capable of solubilizing rhenium, as seen in Figure 8. Negligible leaching is observed for the catalyst in the solvent alone, or in the presence of the triphenylphosphine reductant. The most severe leaching is seen when the diol is present in absence of any other reductant, with slightly less leaching in reaction conditions with both diol and triphenylphosphine in the medium. The 1-decene product also seemed to be capable of inducing rhenium dissolution, demonstrating that in addition to a soluble Re(VII) glycolate, there exists a soluble Re(V) glycolate. This behavior was observed for ReO_x/TiO_2, but not ReO_x/ZrO_2. The difference is likely due to a greater energetic barrier from stronger ReO_x-ZrO_2 interaction. Based on the results in Figure 8, it is evident that mainly the diol causes leaching, by coordinating with the rhenium.

To test whether the leaching effect observed when using a vicinal diol was caused merely by the presence of an alcohol group coordinating with the rhenium species, 1-butanol was tested as a primary monool, and 1,4-butanediol was tested as an α,ω-diol. These molecules were not measurably converted into any products at relevant reaction conditions and did not induce any significant rhenium leaching for either a titania- or a zirconia-supported catalyst. This result suggests that a vicinal diol is necessary to solubilize rhenium species, likely by dehydration to form a rhenium glycolate, as illustrated in Scheme 1. Interestingly, Shiramizu and Toste demonstrated that 2-butene-1,4-diol can be converted to butadiene using methyltrioxorhenium as catalyst and proposed an isomerization reaction to a vicinal diol followed by DODH.[15] Evidently, the double bond enables this rearrangement.

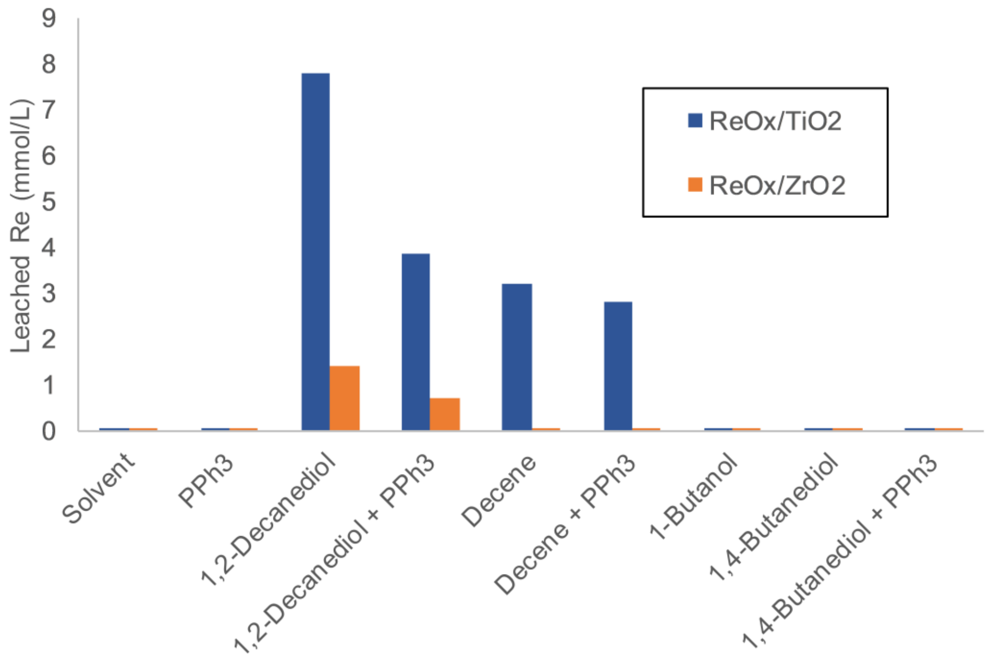


Figure 8: Ligand effect. ***Reaction Conditions:*** *Temp. 150 °C, time 15 min for ReO_x/TiO_2, 60 min for ReO_x/ZrO_2, solvent toluene, 0.2 M 1,2-decanediol, 1-butanol, or 1,4-butanediol if noted, 0.23 M PPh_3 if noted, 0.2 M 1-decene if noted, diol:Re=20.*

If the diol forming a glycolate complex with the rhenium is the primary cause of leaching, then it follows that the combination of diol and solvent may strongly control the degree of leaching. To further test this hypothesis, solvents with varying polarity were employed, which were toluene, 1,4-dioxane, 3-octanol, 2-propanol and water in order of increasing polarity. To ascertain the effects of the diol presence as such and of its hydrocarbon tail length, the options 1,2-decanediol, 1,2-hexanediol, and no diol were combined with the various solvents. The ReO_x/TiO_2 catalyst was chosen for this purpose, and it was principally active with all tested reactant, solvent and reductant combinations.

Figure 9 shows the amount of leached rhenium for the ReO_x/TiO_2 catalyst across the range of diols and solvents. In the no-diol condition, rhenium leaching was low for toluene, 1,4-dioxane, 3-octanol and 2-propanol though it did increase slightly with increasing solvent polarity. Rhenium leaching was significant when water was used, as expected for an inorganic, presumably ionic species. When diol was present, leaching was most prominent in the non-polar solvent and diminished as the solvent polarity increased, except for the case of water, when hexanediol acted as diluent. This effect was consistently more pronounced for 1,2-decanediol than for 1,2-hexanediol, showing the larger hydrocarbon tail exacerbates the diol-induced leaching.

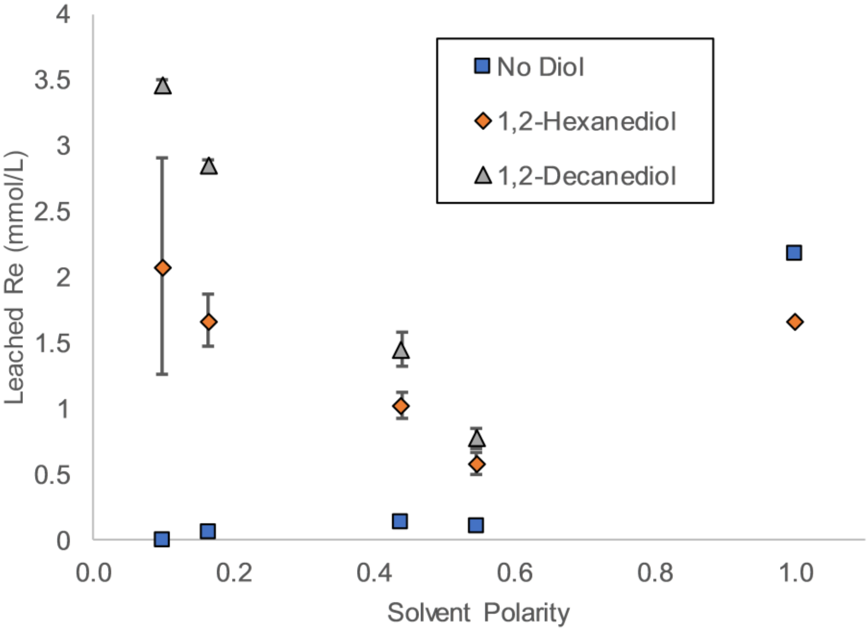


*Figure 9: Solvent effect. **Reaction Conditions:** Temp. 150 °C, time 15 min for ReO_x/TiO_2, solvents toluene, 1,4-dioxane, 3-octanol, 2-propanol, and water in order of increasing polarity,*[37] *0.2 M 1,2-decanediol or 1,2-hexanediol if noted, 0.23 M PPh_3 for toluene and 1,4-dioxane reactions, diol:Re=20.*

Since the diol induces rhenium solubility, we were curious whether driving the reaction to 100% diol conversion would cause rhenium species to redeposit, or whether they would persist as soluble species. To test this hypothesis, the ReO_x/ZrO_2 and ReO_x/TiO_2 catalysts were operated to final diol conversions of 40-60% or 100%. Figure 10a shows catalytic activity of the fresh and recycled catalysts after both complete and partial diol conversion. The recovered catalyst demonstrated significantly higher activity in the second use if the first reaction was stopped only after complete diol conversion. Even more striking is the analysis of leached rhenium observed by ICP-MS after the first use of the catalysts (Figure 10b); while significant amounts of leached rhenium were detected at incomplete conversion, the amount of solubilized rhenium was negligible at complete diol conversion. These measurements imply that rhenium is re-deposited onto the support or precipitated at complete diol conversion. Since the activity of the recovered catalyst does not correspond to that of the fresh catalyst even though there are almost no soluble rhenium species, additional deactivating processes must be inferred.

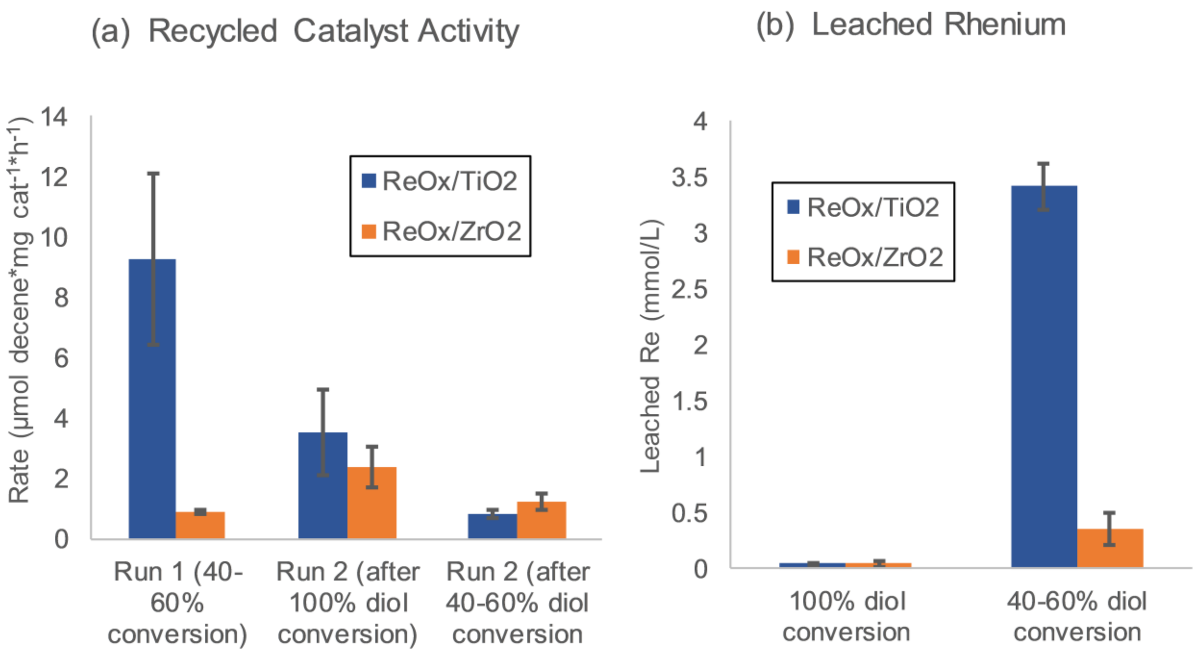
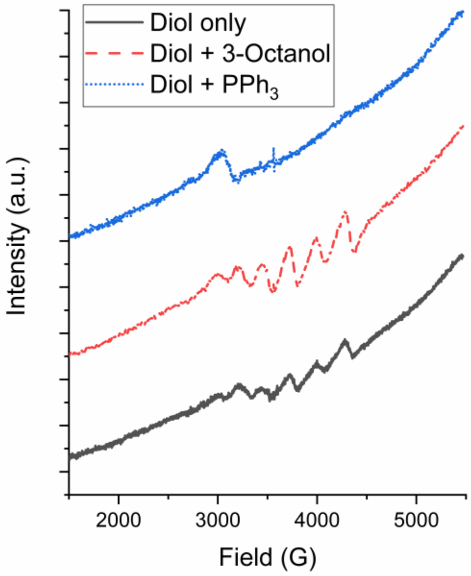


Figure 10: Diol conversion effect. ***Reaction Conditions:*** *Temp. 150 °C, time* ReO_x/TiO_2 *15 min incomplete and 60 min complete conversion,* ReO_x/ZrO_2 *1 h incomplete and 3 h complete conversion, solvent toluene, 0.2 M 1,2-decanediol, 0.23 M* PPh_3 *diol:Re=20. (a) Catalytic activity of the fresh catalyst and of the recycled catalyst after complete or incomplete diol conversion in the initial run. (b) Leached rhenium as measured by ICP-MS after either complete or incomplete diol conversion.*

To gain insight into the nature of the solubilized rhenium species, EPR and UV-vis spectra of the supernatants were recorded at room temperature within 5 days of generation, as color changes occurred both with temperature and also during long-term storage. EPR spectra (Figure 11a) indicate small concentrations of paramagnetic species. Spectra of solutions generated with diol only or diol and a secondary alcohol reductant showed a weak signal at g=1.910, with a hyperfine coupling (from I_{Re}=5/2) of a(Re) = 260 G = 232×10^{-4} cm^{-1}. These spectra are consistent with Re(VI), but the weak signal indicates a minority species given the concentrations measured by ICP and the typically excellent spectra obtainable with Re(VI) solutions. In presence of PPh_3, a signal with g = 2.263 is observed; chemically, Re(IV) is a likely species assuming further reduction. UV-vis spectra were characterized by a band at 493-499 nm for PPh_3-driven DODH of diols in various solvents (toluene, Figure 11b and dioxane, Figure 11c). Without PPh_3, a band at 400 nm was observed when the solvent was dioxane, suggesting a different predominant oxidation state and perhaps also coordination of dioxane. The region of perrhenate absorption (229 nm) was generally obscured by strong solvent absorption. The simplicity of the UV-vis spectra suggests there are very few different species; however, given the many options for the rhenium oxidation state and the significant wavelength shifts that occur for both charge transfer and d-d transitions with coordination and nature of the ligands, it was not possible to assign these transitions. The bands did disappear with complete conversion of the diol, confirming the diol as one of the ligands and consistent with reprecipitation of rhenium.



(a)

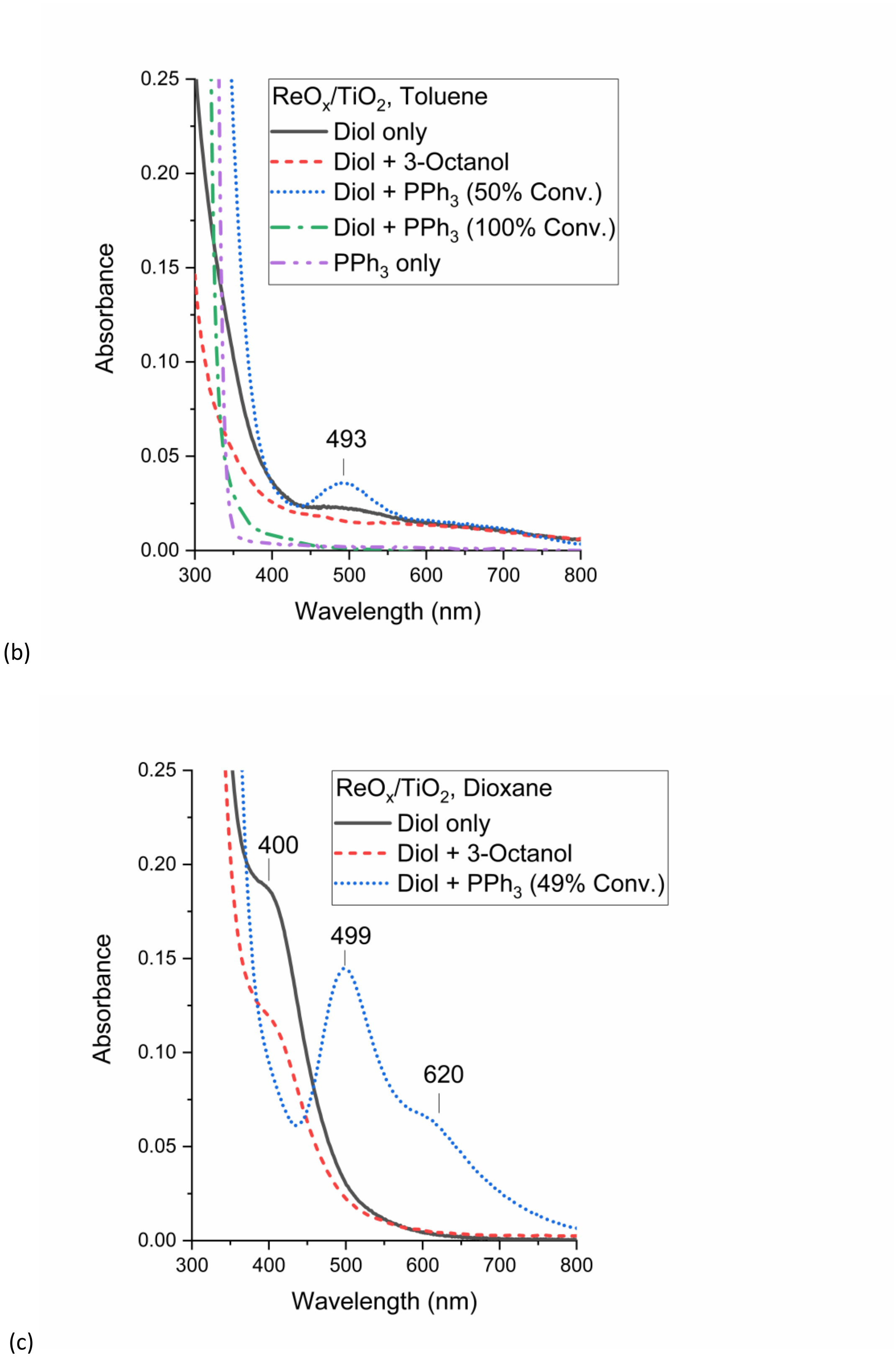


Figure 11: Reaction conditions: Temp. 150 °C, time 15 min, ReO_x/TiO_2 catalyst 4 wt% loading, 0.2 M diol (reported conversions relate to diol), 0.23 M PPh_3 or 3-octanol reductant as indicated,

diol:Re=20, solvent toluene or 1,4-dioxane. (a) EPR spectra of reaction supernatants, toluene solvent, 1,2-decanediol reactant with either no additional reductant, triphenylphosphine reductant, or 3-octanol reductant; (b) UV-vis spectra of reaction supernatants in toluene; and (c) UV-vis spectra of reaction supernatants in 1,4-dioxane.

4. Discussion

4.1. Catalyst Optimization by Activity and Stability

A strong role of the support for both ReO_x activity and stability emerges from the combined data of Denning et al.,[17] Ota et al.,[19] Sandbrink et al.,[18] and the present work. Ota et al. investigated catalysts consisting of a support, ReO_x as active component, and palladium as a promoter for DODH of 1,4 anhydroerythritol. Among a series of supports including carbon, SiO_2, TiO_2, ZrO_2, CeO_2, Al_2O_3, La_2O_3, Y_2O_3, MgO and CaO, the oxide CeO_2 was found to give the most active catalyst in the presence of palladium. Sandbrink et al. did not add a noble metal and reported an activity ranking for ReO_x/support in the order of carbon > SiO_2 > TiO_2 > ZrO_2, while finding the TiO_2-supported ReO_x material to be the most stable, particularly after a pre-reduction of the catalyst. The data in Figure 1a confirm the high activity of oxido-rhenium moieties supported on carbon, SiO_2, and TiO_2, but Figure 1b and Figure 7 suggest that much of the activity of these catalysts stems from leached species. The high supernatant activity (Figure 6) also demonstrates that the entire cycle can be homogeneous without temporary deposition, suggesting true homogeneous contributions and not a coupled homogeneous-heterogeneous cycle.

The support plays a primary role for the leach resistance of rhenium oxido complexes and sets the activation barrier for detachment. The mechanism of detachment depends on the bond to the support. A weakly, van der Waals-bound species may simply be solubilized. An option to release charged moieties is ion exchange, during which the rhenium complex is replaced by another ion with like charge. However, the reactants and reagents are expected to be neutral molecules, making this mechanism unlikely. Alternatively, ligand exchange may occur, and the support moiety that serves as a ligand in the complex is replaced by another ligand. Perrhenate behaves like other oxido anions with a single charge such as nitrate or perchlorate, and is expected to not have a strong affinity to most surfaces. The decisive role of the diol suggests that detachment is promoted by ligand addition or ligand exchange.

With respect to stability as measured by performance of the recycled solid, the successfully employed supports are reducible except for Al_2O_3, and the most easily reducible supports among those investigated, CeO_2 and TiO_2, give the highest activity. Sandbrink et al.[18] reported improved catalyst stability for ReO_x/TiO_2 if the catalyst was pre-reduced and ascribed this phenomenon to the lower solubility of rhenium complexes with lower oxidation states. In light of the aggregate results of several groups, stronger attachment of oxido-rhenium moieties on a reduced support is an alternative interpretation. In the experiments by Tomishige and coworkers,[19-21] CeO_2 may be easily reduced through spillover of hydrogen from the noble metals. The stability of the Al_2O_3-supported ReO_x catalyst may be understood on the basis of the findings of Zhang et al.[38] They report on supported oxido-rhenium metathesis catalysts and found the rhenium species to be interacting with silica via a single oxygen bridge, whereas with alumina, an additional interaction via a hydroxyl group was observed.[38] This increased rhenium-support interaction could be responsible for both the lower activity and the increased stability that is seen with ZrO_2, Al_2O_3, and Fe_2O_3 supports relative to SiO_2 and TiO_2 supports in Figure 1.

A second important factor is the loading of the rhenium. Figure 2 shows that the leached fraction depends on the support and that the amount leached decreases as the loading decreases with each recycling step. While the maximum loading could be explored by preparing catalysts with different loadings, it can be predicted by the cumulative leaching experiment in Figure 2. Since the initial rhenium loading was 4 wt%, the data suggest that SiO_2 is not a good support at any loading, TiO_2 should be limited to securely attaching around 1 wt%, and all others to about 2 wt% rhenium. The data in Figure 5, which compiles rhenium leached from catalysts with different loadings, are consistent with this prediction; zirconia retains rhenium better than titania, and the retained percentages approximately correspond to the anticipated values. The amounts may vary depending on support source, support pretreatment, and rhenium precursor. They are however far below monolayer coverages, which are estimated to be 8.0, 3.7, 8.2, and 3.3 wt% for Al_2O_3, TiO_2, ZrO_2 and SiO_2, respectively, on the basis of the surface areas of the catalysts in Table 1 and the densities calculated by Wachs.[39] Sandbrink et al.[18] applied between 3.5-5.5 wt% rhenium and found leaching (as measured by filtrate activity and rhenium concentration in solid) to occur only in the initial use of ReO_x/TiO_2 and to be insignificant afterwards. Even though CeO_2 was not tested here, the 1 wt% Re loading used by Tomishige and co-workers probably significantly lowered the risk of leaching.

Considering all reports on supported ReO_x catalysts and their suitability for DODH, the following conclusion can be drawn: If true heterogeneous catalysis is desired, then low rhenium loadings on supports such as ZrO_2, CeO_2, Al_2O_3 and Fe_2O_3, and on TiO_2 with suitable treatments are most promising. However, the data in Table 2 demonstrate that while lower loadings result in less leaching, the observed DODH rates per rhenium decline at the same time. There are two potential reasons for lower rates at low loadings, fewer homogeneous contributions and lower activity of more strongly bound surface species. Figure 6 indicates that homogeneous contributions dominate for high loadings, raising the general question about the contribution of heterogeneous DODH catalysis. The literature on supported catalysts is in favor of heterogeneous catalysis, and even some literature on soluble compounds suggests that a solid is the active species, resulting in an induction period.[40] However, other authors concluded that oligomerization of soluble catalyst leads to inactive species.[14,35]

4.2. Causes of leaching

The results in Figure 9 show that the pristine solid catalyst ReO_x/TiO_2 is reasonably stable in the reaction medium. It is the reaction of oxido-rhenium with diol that promotes leaching, which supports the hypothesis that a glycolate complex is the soluble species. The glycolate can be formed through condensation of oxido-rhenium species with a diol. Decene is also effective in solubilizing rhenium, presumably because a glycolate can be formed through addition of decene (Scheme 1), which is the reverse reaction of the third step of DODH, the alkene elimination. It is evident that steps of the catalytic cycle lead to formation of soluble species. At complete diol conversion, the amount of dissolved rhenium is negligible (Figure 10). This scenario is reminiscent of observations made with palladium catalysts for Heck and Suzuki couplings.[41-46] Dissolved palladium that forms during the course of the reaction serves as active species in these coupling reactions. The palladium is redeposited on the support at the end of the reaction; however, the high number of components in these reactions prevents the clear relationship between leaching and reactants or products that is seen in Figure 8 for rhenium-catalyzed DODH.

While the leached complexes could not be exactly identified, some knowledge could be gleaned from the assembled information. Since primary alcohols and α,ω-diols did not induce leaching, the complexes are likely to have diol-derived ligands. The complexes are not thermally or long-term stable, underlining the dynamics observed by others.[40] UV-vis spectra presented well-defined bands, suggesting well-defined species. EPR spectra suggest paramagnetic species such as Re(VI) and Re(IV) are a minority, consistent with the Re(VII)/Re(V)-based homogeneous catalysis cycle proposed by Ahmad et al.[8]

The association of catalyst with the reactant as primary cause of leaching presents challenges, both in detecting and in mitigating leaching, as discussed in the following.

4.3. Detecting leaching

The detection of leached species and homogeneous catalysis contributions requires accounting for a number of phenomena as illustrated by Sheldon et al.,[29] and, consequently, leach tests call for cautious experimenting[32] and may be augmented by application of scavengers, for example thiols in Heck and Suzuki couplings.[30] Mercury has been used as a poison for solid metals to demonstrate heterogeneous catalysis, but this test is also associated with difficulties.[47]

The most common recommendation is hot filtration[48] followed by testing of the filtrate for activity, which addresses the issue of redeposition of leached species onto the support upon cooling. For the rhenium species, the effect of the separation temperature is rather minor, as seen in Figure 3, indicating that at the test conditions, solubility of the leached rhenium species is not a limiting factor and saturation is not reached, or solubility is not strongly temperature dependent. The fact that the concentration of leached rhenium is the same at room temperature and at 150 °C for some catalysts (ReO_x/TiO_2) corroborates that the leached species are well soluble (Figure 4). In contrast, elevated temperatures were needed for other catalysts (ReO_x/ZrO_2) to overcome the detachment barrier and induce leaching in the first place.

In some cases, continued reaction of the catalyst with the substrate after separation has led to an inactive state of the catalyst and long induction periods in subsequent tests that can disguise supernatant activity.[29] Such a scenario can be avoided if the reaction is run to completion, that is, to 100% conversion, and for the test, more reactant is later added to the filtrate. This approach would fail here; if leaching is stimulated by the reactant, then it becomes undetectable at 100% conversion (Figure 10). In fact, at a reactant-to-catalyst ratio of 20 and an assumed diol-to-rhenium stoichiometry in the solubilized complexes of 1:1, conversions beyond 95% imply insufficient ligand availability. Soomro et al.[32] found a more complex relationship for Suzuki-Miyaura couplings, where in some cases the concentration of dissolved palladium passed through a maximum at 60% conversion even though the relative catalyst concentration was only 0.1 mol%. This observation and other data presented by the authors indicate that reagents and other additives also play a role for palladium solubilization. Their observations are not unique, for example, Sheldon saw chromium leaching from CrAPO-5 as a result of oxidation by a hydroperoxide which was added as a stoichiometric oxidant.[29] In contrast to these reports, the effect of conversion on leaching of rhenium from ReO_x/TiO_2 and ReO_x/ZrO_2 during DODH is absolutely clear (Figure 10), and the effect of PPh_3 is rather minor (Figure 8).

Sheldon et al.[29] also pointed out that recycled catalyst activity can be deceiving if the leached amount is very small but highly active. Indeed, upon second and further uses, which are representative of lower initial rhenium loadings, the activity of many solids remains more or less constant (Figure 1). In contrast the ICP analysis of the filtrate provides a sensitive measurement and thus an unambiguous account of trace amounts of leached rhenium (Figure 1, Figure 2).

4.4. Mitigating leaching through choice of reaction conditions

Ideally, the interaction between support and active moiety is so strong that leaching is kinetically hindered and prevented in the first place. If the activation barrier for detachment is high enough as appears to be the case for ReO_x/ZrO_2 (cf. Figure 3 and Figure 4), then lowering the reaction temperature should suppress leaching.

If detachment is principally possible, then the solubilities of all forms of the catalyst in the cycle, that is, in its original form and after association with a reactant or reagent in the solvent have a considerable influence. In the present case, minimizing solubility is challenging because of opposite trends. The pristine ReO_x/support catalyst, presumably containing an inorganic ion as active rhenium moiety, is not appreciably soluble in nonpolar organic solvents. In contrast, the glycolate complexes with their hydrophobic hydrocarbon tails are more soluble in nonpolar solvents than in polar solvents. As seen in the leaching map in Figure 9, the optimal solvent polarity for minimal leaching is the minimum resulting from combination of the solubility curves of the various catalyst forms. The optimal solvent is also a function of the reagent and of course must still be favorable for catalyst operation. A survey of recent DODH reports shows that Sandbrink et al.[18] converted hexanediol and octanediol and used 3-octanol as the solvent and reductant. Indeed, slightly more leaching was observed for octanediol than for hexanediol, as the leaching map in Figure 9 would have predicted. Tomishige and co-workers[19-21] combined 1,4-dioxane as the solvent with a variety of substrates and found little leaching with glycerol as the reactant,[21] suggesting that this combination works well together with the catalyst.

Solvents are typically chosen with the goal of dissolving reactants and products. For heterogenized catalysts such as those investigated here, the leach resistance becomes an additional criterion for selecting a solvent; namely, the solvent must be adapted to the reactant with the aim to lower the solubility of the catalyst-reactant complex.

An additional complication is the formation of water as a reaction product, which as per Figure 9 promotes rhenium leaching, at least of the oxido-anions used here. The fate of the water depends on the miscibility with the solvent. Solubility in toluene, which was used for most of the reactions, is low at 0.027 M,[49] and indeed a second phase forms if larger amounts of 0.5 M or more are added. This scenario could be problematic if the catalyst partitions to the aqueous fraction, while also implying ease of separation.

4.5. Release and Catch Catalysis

Since leaching is difficult to suppress entirely for rhenium-catalyzed DODH, an interesting alternative solution to this issue is a 'release and catch' catalytic scheme, where the active species becomes partially homogeneous during the reaction, but is then redeposited on the support, similar to what has been demonstrated for other liquid phase reactions such as the Suzuki couplings.[31] Figure 10 shows that dissolved rhenium species can be precipitated when the reaction is driven to complete diol conversion, which can additionally be promoted by excess reductant. Another possible benefit of excess reductant is that the reduced form of the catalyst is less likely to react with decene. However, the recycled catalysts do not reach the activity of the original catalyst, indicating that some rhenium is transformed into an inactive solid. The release and catch scheme thus has potential for small-scale applications that can be conducted in batch, but requires further optimization.

5. Conclusions

A series of oxide-supported ReO_x catalysts were tested for their performance in alkane diol deoxydehydration to the corresponding terminal alkenes. The materials fell into two groups; SiO_2 and TiO_2 supports produced highly active catalysts with a performance close to that of homogeneous benchmark catalysts while catalyst stability was low, whereas ZrO_2, Al_2O_3 and Fe_2O_3 produced less active although more stable catalysts with consistent results over multiple uses. The primary cause for deactivation of supported ReO_x catalysts during deoxydehydration was found to be leaching of active rhenium species. These less active catalysts lost less rhenium in the catalytic process, and possibly the stronger attachment to the support negatively altered the catalytic properties. Systematic tests indicated that leaching is induced by the formation of a glycolate complex through association of the diol with active rhenium surface moieties. Consequently, the extent of leaching depends on the diol–solvent combination and on the degree of conversion of the diol. Rhenium precipitates out of solution onto the support or as bulk solid upon completion of the reaction. The strong influence of reactant and diol implies that it cannot be claimed that a supported ReO_x catalyst is generally stable toward leaching; rather, the claim must include the particular catalytic transformation and the used reagents. It also follows that leach tests must be adapted to the situation; specifically, degree of conversion is a more important than separation temperature for deoxydehydration catalyzed by supported ReO_x.

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7. References

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(1) Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. Catalytic Conversion of Biomass to Biofuels Catalytic Conversion of Biomass to Biofuels. *Green Chem.* **2010,** *12*, 1493-1513.

(2) Cook, G. K.; Andrews, M. A.; Toward Nonoxidative Routes to Oxygenated Organics: Stereospecific Deoxygenation of Diols and Polyols to Alkenes and Allylic Alcohols Catalyzed by the Metal Oxo Complex (C_5Me_5)ReO_3. *J. Am. Chem. Soc.* **1996,** *118,* 9448.

(3) Raju, S.; Jastrzebski, J. T. B. H.; Lutz, M.; Witteman, L.; Klein Gebbink, R. J. M. Catalytic Deoxydehydration of Diols to Olefins by Using a Bulky Cyclopentadiene-Based Trioxorhenium Catalyst. *ChemSusChem* **2013,** *6,* 1673-1680.

(4) Dethlefsen, J. R.; Lupp, D.; Oh, B.; Fristrup, P. Molybdenum-Catalyzed Deoxydehydration of Vicinal Diols. *ChemSuschem* **2014,** *7,* 425-428.

(5) Dethlefsen, J. R.; Lupp, D.; Teshome, A.; Nielsen, L. B.; Fristrup, P. Molybdenum- Catalyzed Conversion of Diols and Biomass-Derived Polyols to Alkenes Using Isopropyl Alcohol as Reductant and Solvent. *ACS Catal.* **2015,** *5,* 3638-3647.

(6) Galindo, A. DFT Studies on the Mechanism of the Vanadium-Catalyzed Deoxydehydration of Diols. *Inorg. Chem.* **2016,** *55,* 2284-2289.

(7) Gopaladasu, T. V.; Nicholas, K. M. Carbon Monoxide (CO)- and Hydrogen-Driven, Vanadium-Catalyzed Deoxydehydration of Glycols. *ACS Catal.* **2016,** *6,* 1901-1904.

(8) Ahmad, I.; Chapman, G.; Nicholas, K. M. Rhenium-Catalyzed Deoxydehydration of Glycols by Sulfite. *Organometallics* **2011,** *30,* 2810-2818.

(9) Vkuturi, S.; Chapman, G.; Ahmad, I.; Nicholas, K. M. Sulfite-Driven, Oxorhenium-Catalyzed Deoxydehydration of Glycols. *Inorg. Chem.* **2010,** *49,* 4744-4746.

(10) Larson, R. T.; Samant, A.; Chen, J.; Lee, W.; Bohn, M. A.; Ohlmann, D. M Hydrogen Gas-Mediated Deoxydehydration/Hydrogenation of Sugar Acids: Catalytic Conversion of Glucarates to Adipates. *J. Am. Chem. Soc.* **2017,** *139,* 1401-1404.

(11) McClain II, J. M.; Nicholas, K. M. Elemental Reductants for the Deoxydehydration of Glycols. *ACS Catal.* **2014,** *4,* 2109-2112.

(12) Boucher-Jacobs, C.; Nicholas, K. M. Oxo-Rhenium-Catalyzed Deoxydehydration of Polyols with Hydroaromatic Reductants. *Organometallics* **2015,** *34,* 1985-1990.

(13) Boucher-Jacobs, C.; Nicholas, K. M. Catalytic Deoxydehydration of Glycols with Alcohol Reductants. *ChemSusChem* **2013,** *6,* 597-599.

(14) Liu, S.; Senocak, A.; Schmeltz, J. L.; Yang, L.; Wegenhart, B.; Yi, J.; Kenttämmaa, H. I.; Ison, E.; Abu-Omar, M. M. Mechanism of MTO-Catalyzed Deoxydehydration of Diols to Alkenes using Sacrificial Alcohols. *Organometallics* **2013,** *32,* 3210-3219.

(15) Shiramizu, M.; Toste, F. D. Expanding the Scope of Biomass-Derived Chemicals through Tandem Reactions Based on Oxorhenium-Catalyzed Deoxydehydration. *Angew. Chem. Int. Ed.* **2013,** *52,* 12905-12909.

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(16) Liu, P.; Nicholas, K. M. Mechanism of Sulfite-Driven, $MeReO_3$ -Catalyzed Deoxydehydration of Glycols. *Organometallics* **2013,** *32,* 1821-1831.

(17) Denning, A. L.; Dang, H.; Liu, Z.; Nicholas, K. M.; Jentoft, F. C. Deoxydehydration of Glycols Catalyzed by Carbon-Supported Perrhenate. *ChemCatChem* **2013,** *5,* 3567-3570.

(18)Sandbrink, L.; Klindtworth, E.; Islam, H.; Beale, A. M.; Palkovits, R. ReO_x/TiO_2: A Recyclable Solid Catalyst for Deoxydehydration. *ACS Catal.* **2015,** *6,* 677-680.

(19) Ota, N.; Tamura, M.; Nakagawa, T.; Okumura, K.; Tomishige, K. Hydrodeoxygenation of Vicinal OH Groups over Heterogeneous Rhenium Catalyst Promoted by Palladium and Ceria Support. *Angew. Chem. Int. Ed.* **2015,** *54,* 1897-1900.

(20) Liu, S.; Okuyama, Y.; Tamura, M.; Nakagawa, T.; Imai, A.; Tomishige, K. Catalytic Conversion of Sorbitol to Gasoline-Ranged Products without External Hydrogen over Pt-Modified $Ir\text{-}ReO_x/SiO_2$. *Catal. Today* **2015,** *269,* 122-131.

(21) Tazawa, S.; Ota, N.; Tamura, M.; Nakagawa, T.; Okumura, K.; Tomishige, K. Deoxydehydration with Molecular Hydrogen over Ceria-Supported Rhenium Catalyst with Gold-Promoter. *ACS Catal.* **2016,** *10,* 6393-6397.

(22) Li, X.; Zhang, Y. Highly Selective Deoxydehydration of Tartaric Acid over Supported and Unsupported Rhenium Catalysts with Modified Acidities. *ChemSusChem* **2016,** *9,* 2774-2778.

(23) Sharkey, B. E.; Denning, A. L.; Jentoft, F. C.; Gangadhara, R.; Gopaladasu, T. V.; Nicholas, K. M. New Solid Oxo-Rhenium and Oxo-Molybdenum Catalysts for the Deoxydehydration of Glycols to Olefins. *Catal. Today* **2018,** *310,* 86-93.

(24) Kwok, K. M.; Chen, L.; Choong, C. K. S.; Ong, D. S. W.; Ng, J. C. Q.; Gwie, C. G.; Borgna, A. Hydrogen-Free Gas-Phase Deoxydehydration of 2,3-Butanediol to Butene on Silica-Supported Vanadium Catalysts. *ChemCatChem* **2016,** *9,* 2443-2447.

(25) Sandbrink, L.; Beckerle, K.; Meiners, I.; Liffman, R.; Rahmini, K.; Okuda, J. Supported Molybdenum Catalysts for the Deoxydehydration of 1,4-Anhydroerythritol into 1,4-Dihydrofuran. *ChemSusChem* **2017,** *10,* 1-6.

(26) Sádaba, I.; López Granados, M.; Riisager, A.; Taarning, E. Deactivation of Solid Catalysts in Liquid Media: The Case of Leaching of Active Sites in Biomass Conversion Reactions. *Green Chem.* **2015,** *17,* 413.

(27) Hübner, S.; de Vries, J. G.; Farina, V. Why Does Industry Not Use Immobilized Transition Metal Complexes as Catalysts? *Adv. Synth. Catal.* **2016,** *358,* 3-25.

(28) Eremin, D. B.; Ananikov, V. P. Understanding Active Species in Catalytic Transformations: From Molecular Catalysis to Nanoparticles, Leaching, “Cocktails” of Catalysts and Dynamic Systems. *Coord. Chem. Rev.* **2017,** *346,* 2-19.

(29) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. Heterogeneous Catalysts for Liquid-Phase Oxidations: Philosophers’ Stones or Trojan Horses? *Acc. Chem. Res.* **1998,** *31,* 485-493.

(30) Richardson, J. M.; Jones, C. W. Strong Evidence of Solution-Phase Catalysis Associated with Palladium Leaching from Immobilized Thiols during Heck and Suzuki Coupling of Aryl Iodides, Bromides, and Chlorides. *J. Catal.* **2007,** *251,* 80-93.

(31) Köhler, K.; Heidenreich, R. G.; Soomro, S. S.; Pröckl, S. S. Supported Palladium Catalysts for Suzuki Reactions: Structure-Property Relationships, Optimized Reaction Protocol and Control of Palladium Leaching. *Adv. Synth. Catal.* **2008,** *350,* 2930-2936.

(32) Soomro, S. S.; Ansari, F. L.; Chatziapostolou, K.; Köhler, K. Palladium Leaching Dependent on Reaction Parameters in Suzuki–Miyaura Coupling Reactions Catalyzed by Palladium Supported on Alumina under Mild Reaction Conditions. *J. Catal.* **2010,** *273,* 138-146.

(33) Hammond, C. Intensification Studies of Heterogeneous Catlaysts: Probing and Overcoming Catalyst Deactivation during Liquid Phase Operation. *Green Chem.* **2017,** *19,* 2711-2728.

(34) Scott, S. L. A Matter of Life(time) and Death. *ACS Catal.* **2018,** *8,* 8597-8599.

(35) Dethlefsen, J. R.; Fristrup, P. In Situ Spectroscopic Investigation of the Rhenium-Catalyzed Deoxydehydration of Vicinal Diols. *ChemCatChem* **2015,** *7,* 1184-1196.

(36) Shakeri, J.; Hadadzadeh, H.; Farrokhpour, H.; Joshaghani, M.; Weil, M. Perrhenate-Catalyzed Deoxydehydration of a Vicinal Diol: A Comparative Density Functional Theory Study. *J. Phys. Chem. A.* **2017,** *121,* 8688-8696.

(37) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry 3rd Ed.*; Wiley-VCH Weinheim, Germany, 2003.

(38) Zhang, F.; Szeto, K. C.; Taoufik, M.; Delevoye, L.; Gauvin, R. M.; Scott, S. L. Enhanced Metathesis Activity and Stability of Methyltrioxorhenium on a Mostly Amorphous Alumina: Role of the Local Grafting Environment. *J. Am. Chem. Soc.* **2018,** *140,* 13854-13868.

(39) Wachs, I. E. Raman and IR Studies of Surface Metal Oxide Species on Oxide Supports: Supported Metal Oxide Catalysts. *Catal. Today* **1996,** *27,* 437-455.

(40) Lupacchini, M.; Mascitti, A.; Canale, V.; Tonucci, L.; Colacino, E.; Passacantando, M.; Marrone, A.; d'Alessandro, N. Deoxydehydration of Glycerol in Presence of Rhenium Compounds: Reactivity and Mechanistic Aspects. *Catal. Sci. Tech.* **2019,** *9,* 3036-3046.

(41) Zhao, F.; Shirai, M.; Arai, M. Palladium-Catalyzed Homogeneous and Heterogeneous Heck Reactions in NMP and Water-Mixed Solvents Using Organic, Inorganic and Mixed Bases. *J. Mol. Catal. A* **2000,** *154,* 39-44.

(42) Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J.; Köhler, K. Control of Pd Leaching in Heck Reactions of Bromoarenes Catalyzed by Pd Supported on Activated Carbon. *J. Mol. Catal. A* **2002,** *182,* 499-509.

(43) Köhler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, M. Highly Active Palladium/Activated Carbon Catalysts for Heck Reactions: Correlation of Activity, Catalyst Properties, and Pd Leaching. *Chem. Eur. J.* **2002,** *8,* 622-631.

(44) Pröckl, S. S.; Kleist, W.; Gruber, M. A.; Köhler, K. In Situ Generation of Highly Active Dissolved Palladium Species from Solid Catalysts—A Concept for the Activation of Aryl Chlorides in the Heck Reaction. *Angew. Chem. Int. Ed.* **2004,** *43,* 1881-1882.

(45) Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G. Pd Nanoclusters in C-C Coupling Reactions: Proof of Leaching. *Angew. Chem. Int. Ed.* **2006,** *45,* 2886-2890.

(46) Richardson, J. M.; Jones, C. W. Poly(4-Vinylpyridine) and Quadrapure TU as Selective Poisons for Soluble Catalytic Species in Palladium-Catalyzed Coupling Reactions – Application to Leaching from Polymer-Entrapped Palladium. *Adv. Synth. Catal.* **2006,** *348,* 1207-1216.

(47) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. On the Nature of the Active Species in Palladium Catalyzed Mizoroki–Heck and Suzuki–Miyaura Couplings – Homogeneous or Heterogeneous Catalysis, A Critical Review. *Adv. Synth. Catal.* **2006,** *348,* 609-679.

(48) Jones, C. W. On the Stability and Recyclability of Supported Metal–Ligand Complex Catalysts: Myths, Misconceptions and Critical Research Needs. *Topics Catal.* **2010,** *53,* 942-952.

(49) Kirchnerová, J.; Cave, G. C. B. The Solubility of Water in Low Dielectric Solvents. *Can. J. Chem.* **1976,** *54,* 3909-3916.