New Solid Oxo-Rhenium and Oxo-Molybdenum Catalysts for the Deoxydehydration of Glycols to Olefins

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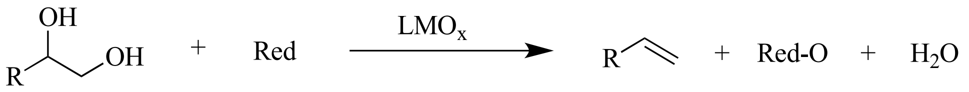
ABSTRACT

Several new solid oxo-rhenium and oxo-molybdenum catalysts were tested for the deoxydehydration (DODH) of 1,2-diols to terminal olefins employing aromatic solvents and reaction temperatures of 150-200 °C. A catecholato oxo-rhenium catalyst tethered to silica was prepared and found to have comparably high DODH activity to its soluble analog with triphenylphosphine as the reductant. Catalyst re-use and leach-test experiments show significant leaching into the liquid phase. Silica, ceria and, for the first time, alumina and iron oxide were tested as supports for perrhenate, with ceria producing the least active material in 1,2-decane diol DODH. Decene yields obtained with ReO_x/SiO_2, ReO_x/Fe_2O_3, ReO_x/Al_2O_3 were highest when triphenylphosphine was the reductant and reached 70–78% (at 90–100% conversion) at 150 °C. These three catalysts were also effective with gaseous reductants H_2 or CO. Leaching of rhenium species occurred for all supports and was most pronounced for SiO_2. New solid oxo-molybdenum catalysts were synthesized. At 200 °C, decene yields observed using MoO_x/Fe_2O_3, MoO_x/SiO_2, MoO_x/Al_2O_3, MoO_x/TiO_2 and MoO_x/ZrO_2 were comparable and did not exceed 20%. There were homogeneous contributions through leached molybdenum species.

Keywords: deoxydehydration, rhenium, molybdenum, oxide supports, leaching, α-olefins, carbon monoxide, hydrogen, triphenylphosphine

1. Introduction

The realization that fossil fuel sources are finite and the observation of rising atmospheric CO_2 levels have sparked a major research effort into the use of renewable biomass as a feedstock for chemicals and fuels. Various routes towards this goal are explored, with the first step typically being the conversion of lignocellulosic biomass into a gas or a liquid. Hydrolysis of biomass produces sugars, which can be hydrogenated to sugar alcohols. The obtained polyols can be further processed via fermentation or chemical conversion. An attractive catalytic upgrading step for vicinal diols is deoxydehydration (DODH), that is, the simultaneous removal of one oxygen atom and a molecule of water (Eq. 1) [1]. The product is an olefin and thus a versatile chemical intermediate. A stoichiometric reductant is needed, the oxidation of which makes the reaction thermodynamically feasible.



(eq. 1)

Homogeneous catalysts for DODH have been known for nearly two decades [2,3] and have been tested for various diols, mostly in organic media. The first catalysts discovered were rhenium compounds such as Cp^*ReO_3 [2], $MeReO_3$ [4], $ZReO_{3,4}$ [5,6], $Re_2(CO)_{10}$ [3] and NH_4ReO_4 [7-9]. Effective reductants include arylphosphines, H_2, SO_3^{2-}, and secondary alcohols. Reaction temperatures vary from about 90 to 185 °C [1], depending on catalyst and reductant. Suitable complexes of other transition metals that are less expensive than rhenium have also been identified. Oxo-vanadium complexes of the type $Z^+LVO_2^-$ including tetrabutylammoniumdioxovanadium(v)dipicolinate and a recently discovered complex $[Bu_4N]^+(Salhyd)VO_2^-$ were shown to be active for DODH at temperatures of 150-170 °C [10,11]. Carbon monoxide proved to be an effective reductant in conjunction with the latter vanadium complexes [11]. Dissolved ammonium heptamolybdate was also reported to catalyze DODH, with the diol itself as reductant at reaction temperatures of 195–220 °C [12] or with isopropanol as reductant at 240-250 °C [13].

The prospective benefits of heterogeneously catalyzed DODH for large scale processing recently led to the development of the first solid DODH catalyst. The carbon-supported perrhenate catalyst [14] proved active for conversion of a variety of diols to olefins, and operated with the reductants triphenylphosphine (PPh_3), H_2, and secondary alcohols. While the catalysis was predominantly heterogeneous, rhenium was found to be leaching from the carbon support and was contributing to the catalytic turnover. Sandbrink et al. [15] tested a series of oxide-supported oxorhenium catalysts for the conversion of 1,2-hexanediol and some triols with 3-octanol as a reductant and compared them to ReO_x/C. Among ReO_x/TiO_2, ReO_x/ZrO_2, and ReO_x/SiO_2, the most stable catalyst could be produced by pre-reducing ReO_x/TiO_2. More recently, Ota et al. [16,17] presented a palladium-doped ReO_x/CeO_2 catalyst. The noble metal activates H_2 and promotes the reduction of the catalyst, which was active for DODH with H_2 as the reductant, but the product olefin was hydrogenated. Tasawa et al. [18] replaced the palladium by gold and the obtained Au-ReO_x/CeO_2 proved to be an excellent and thus far most active known catalyst for DODH. Moreover, the catalyst could be reused several times in glycerol DODH with 1,4-dioxane as the solvent without significant alteration of performance. Recently, the first supported molybdenum catalyst MoO_x/TiO_2 was reported [19].

Two issues are noted for the solid ReO_x DODH catalysts: the high price of rhenium and in most applications, some leaching of the active rhenium species. The goal of this work was to test new strategies to immobilize rhenium and to explore the capability of other transition metals to catalyze DODH. The first strategy was to ligate rhenium and tether the complex to a support. The second strategy was to use a variety of oxide supports with different polarity and acid base properties to support oxo-rhenium species, while using various preparation methods to deposit the oxo-rhenium species. The third part of the paper is dedicated to solid catalysts on the basis of other transition metals; both bulk and supported oxo-transition metal species are employed. Catalysts are tested using 1,2-diols and a variety of reactants including gas phase reductants CO and H_2.

2. Experimental Section

2.1. General

Chemicals were used as obtained commercially without further purification. Unless otherwise noted, reaction solvents (benzene, toluene, CH_2Cl_2) were ACS grade and used as received. Commercial carboxy-functionalized silica (1.2 mmol/g) was stored in a desiccator over $CaCl_2$. NMR spectra were collected on 300 MHz or 400 MHz Varian instruments and the NMR data were processed using Spin Works. Gas chromatography was conducted using a ramped thermal program on a 3% SE-54 packed column with FID detector.

2.2. *Catalyst Preparation*

*2.2.1. Synthesis of soluble (catecholato)oxorhenium complex **1***

To a suspension of 3-hydroxytyramine hydrochloride 0.19 g (1.0 mmol) in 15 mL of toluene, $[ReCl_3(O)(PPh_3)_2]$ (0.83 g, 1.0 mmol) was added and Et_3N (0.45 mL, 3.3 mmol) added, followed by anhydrous DMSO (425 µl, 6.0 mmol). The reaction mixture was heated under reflux for 8 h during which time the color changed from green to dark blue to black. After cooling the reaction mixture the solid was filtered, washed with dichloromethane and dried and characterized by ^1H NMR and IR spectroscopy. H-NMR (CD_2Cl_2) δ 6.8 (m, 2H), 6.6 (m, 1 H), 3.1 (t, 2H), 2.8 (t, 2H). IR (KBr, cm^{-1}) 3000-3500 (br), 1597, 1533, 1431, 1252, 1207, 1016, 933, 813, 654.

*2.2.2. Synthesis of silica supported catechol ligand **2***

To a suspension of carboxy-silica gel (0.5 g, 0.6 mmol) in CH_2Cl_2 (100 ml) was added PyBOP (0.978 g, 1.86 mmol). After that 3-hydroxytyramine hydrochloride (0.587 g, 3.00 mmol) and EtN^iPr_2 (1.20 g, 9.28 mmol) were slowly added. The mixture was stirred for 72 h at room temperature. The mixture was then filtered and the solid was washed with three portions of water, methanol and dichloromethane. The solid was dried in vacuum to obtain the silica supported catechol ligand **2**.

*2.2.3. Synthesis of heterogeneous (catecholato)oxorhenium complex **3***

To a suspension of silica functionalized catechol ligand (0.238 g, 1.00 mmol) in 15 ml of toluene, $[ReCl_3(O)(PPh_3)_2]$ (0.833 g, 1.00 mmol) was added, followed by anhydrous DMSO (425 µl, 6.0 mmol). The reaction mixture was heated under reflux for 8 h during which time the color changed from green to dark blue and to black. After cooling, the solid was recovered by filtration, washed with dichloromethane and then vacuum dried to obtain 0.451 g of **4**. IR (KBr, cm^{-1}) 3000-3500 (br), 1603, 1502, 1284, 1196, 1116, 1016, 933, 875, 816.

2.2.3. Preparation of oxide-supported oxorhenium and oxomolybdenum catalysts

The following oxides were used as supports: SiO_2 (Aerosil 150 Evonik), γ-Al_2O_3 (Alfa Aesar), hydrous zirconia XZO880/01 (MEL Chemicals), pure anatase TiO_2 (Alfa Aesar, 99.6 %), a mixed anatase and rutile TiO_2 (P25, Evonik), and α-Fe_2O_3 (US Research Nanomaterials). ZrO_2 was produced by calcining the hydrous zirconia at a temperature of 550 °C for 2 h. Ceria was prepared by precipitation from a solution of cerium (III) nitrate hexahydrate (Aldrich Chem. Co., 99.99 % trace metals basis) through addition of sodium hydroxide. The precipitate was vacuum-filtered, washed, dried at 110 °C and then calcined for 2 h at 300 °C.

Three different methods were used to support oxo-rhenium and oxo-molybdenum species: diffusion impregnation, incipient wetness impregnation, and equilibrium adsorption. The metal concentrations, volumes and support amounts were chosen such that the metal concentration in the final catalyst would fall into one of two ranges, 3.3-4.3 wt% or 9-10 wt% metal (rhenium or molybdenum).

2.2.3.1. Diffusion impregnation (DI). A measured amount of catalyst support was added to a round-bottomed flask with a stir bar and a solution of a precursor. To produce supported oxo-rhenium catalysts, supports were immersed into a solution of ammonium perrhenate (Alfa Aesar or Aldrich, 99 %). After evaporation of the solvent, the materials were dried at 100-110 °C and then calcined or treated under N_2 at 400-420 °C. To produce silica or titania-supported oxo-molybdenum catalysts, 500 mg of silica (Aerosil) or titania (anatase, Alfa-Aesar) was added to 200 mL of a 1 mM solution of ammonium heptamolybdate tetrahydrate. The silica sample was stirred overnight and the water was removed by rotary evaporation at a temperature of 80 °C over a period of 2 h. The titania sample was stirred for 5 h and was dried by rotary evaporation at 60 °C for 3 h. Both samples were calcined at 500 °C for 2 h in air.

2.2.3.2. Incipient wetness impregnation (IW). Supports were dried for 24 h at 110 °C. Eighty-five mg of ammonium perrhenate was dissolved in a minimal volume of water (~1-2 mL). The dry support was ground in a mortar while the ammonium perrhenate solution was slowly added. If the mixture became too pasty, it was intermittently dried in an oven, and the process was continued until all perrhenate was added. The loaded support was dried overnight at 110 °C, then calcined at 420 °C for 4 h. The calculated rhenium content after calcination was approximately 4.3 wt% (expressed as Re metal). Carbon-supported perrhenate was prepared as described in Ref. [14].

Supported oxo-molybdenum catalysts were prepared using an analogous procedure. Supports were pre-dried in a muffle furnace at 115 °C. Two hundred milligrams of ammonium heptamolybdate tetrahydrate was dissolved in 1 mL of DI water and then slowly added to 1000 mg of dried support under vigorous grinding. The obtained paste was dried in a muffle furnace at a temperature of 115 °C for 12 h, and then calcined under 0.5 scfm dry air flow at 550°C for 2 hours.

2.2.3.3. Equilibrium Adsorption (EA). Equilibrium adsorption largely followed the procedure by Mensch et al. [20]. One point two grams of γ-alumina (Alfa-Aesar) were dried at 180 °C overnight and added hot to a 50 mL solution of 10 mM ammonium heptamolybdate tetrahydrate and stirred for 1 h. The alumina remained immersed for two weeks, and was stirred periodically. The sample was centrifuged, the supernatant was removed and the sample was dried at 120 °C overnight in vacuum. Elemental analysis by optical emission spectroscopy completed by Galbraith Laboratories gave a molybdenum content of 3.31 wt% (specified as metal).

2.3. Solid Catalyst Characterization

2.3.1. Surface area determination. The surface areas of most supports were specified by the manufacturer and, in case of very wide ranges, were verified by analyzing N_2 adsorption isotherms using BET theory. Samples were outgassed at 200 °C for 6 hours and a 40-point isotherm was recorded with a Quantachrome Autosorb-IQ.

2.3.2. Diffuse reflectance UV-vis spectroscopy. Diffuse reflectance UV-vis spectra in the wavelength range from 200 to 1500 nm were obtained using a Perkin Elmer Lambda 950 spectrophotometer with a Harrick Praying Mantis accessory. Fluorilon^{TM} (Avian Technologies) was used as a white standard with 100% reflectance.

2.4. Catalytic Testing

2.4.1. General procedure for the (catecholato)oxorhenium complex-catalyzed deoxydehydration of glycols. The glycol (1.00 mmol), rhenium catalyst (5 mol %), reductant (1.5 mmol) and naphthalene (0.47 mmol, internal reference) were mixed with 5.0 mL of reagent grade benzene in a 15 mL thick-walled glass tube fitted with a Teflon® screw-cap/plunger (Ace Glass) and a spin bar was added. The reaction mixture was heated at 150 - 170 ºC while stirred in a preheated silicone oil bath for the indicated time period. After cooling the mixture to room temperature a 300 μL aliquot of the reaction mixture was removed and added to 300 μL $CDCl_3$ and 5.0 μL of DMSO as internal standard for NMR analysis. The olefin products were identified and quantified by comparison of their NMR spectra with authentic samples or published data.

2.4.2. General procedure for the oxide-supported oxo-rhenium and oxo-molybdenum catalyzed deoxydehydration of glycols. Reaction stock solutions were prepared using benzene (to be comparable with prior reports [14]) or toluene (to avoid toxic benzene and to not exceed the vessel pressure limit at high reaction temperatures) as the solvent and 0.2 M concentration of 1,2-decanediol and a 0.1 M concentration of internal standard. In reactions where triphenylphosphine (PPh_3) was the reductant, it was used in slight excess (0.23 M). The rhenium or molybdenum catalysts were added to achieve a nominal rhenium or molybdenum concentration of 0.01 M, corresponding to a reactant-to-catalyst ratio of 20:1.

In reactions using triphenylphosphine as a reductant, the reaction was carried out in a 15 mL thick-walled glass tube fitted with a Teflon screw-cap/plunger (Ace Glass) and a spin bar was added. The reaction vessel was heated in a silicon oil bath and reported temperatures are those of the oil bath. Reactions with gas phase reductants were carried out in a stainless steel Parr reactor pressurized at 200 psig with H_2 or CO.

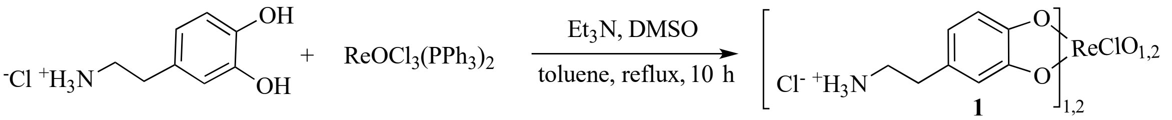
2.4.3. Leach testing of catalysts. To test for leaching, the reaction mixtures were filtered, either hot, using a dip tube and a Swagelok 2 µm inline filter, or cold, by centrifuging for 15 minutes. Fresh reactant and reductant were added to the filtrate and the cumulative yield after an additional 24 h (oxo-rhenium) or 6 h (oxo-molybdenum) of reaction was determined. To test their reusability, catalysts were separated from the reaction mixture by centrifugation or settling, removal of reaction solution, catalyst washing several times with benzene or toluene, optional drying at room temperature (oxo-molybdenum catalysts) and recharging with reactants.

3. Results and Discussion

3.1. Tethered Catecholato-Oxo-Rhenium Complexes

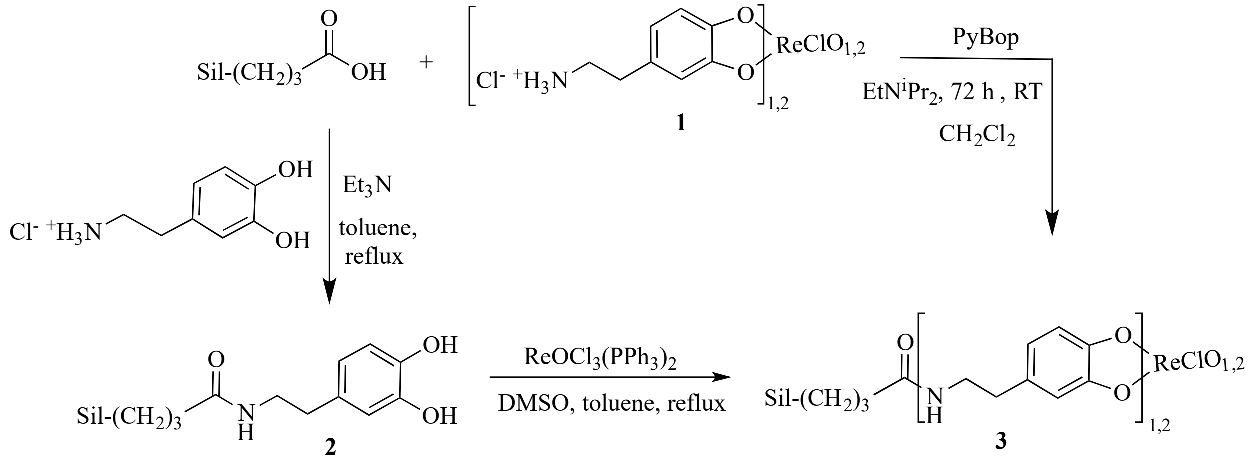
3.1.1. Preparation of Tethered Catecholato-Oxo-Rhenium Complexes

We sought robust, ligated oxo-rhenium species that could be produced in both soluble and supported forms with a common active site structure for comparative DODH reactivity studies. We selected as a dual function ligand the natural amino-catechol derivative, dopamine, which possesses the strongly ligating bidentate catechol moiety and the reactive amino group for tethering to carboxy-functionalized silica. Using a procedure similar to that reported for the preparation of a polystyrene-grafted dopamine-ReO_x species [21], dopamine hydrochloride and $Re^{V}OCl_3(PPh_3)_2$ (1:1) were combined with Me_2SO and Et_3N to afford a black solid **1** (eq. 2). The ^{1}H-NMR spectrum of **1** showed only sharp signals derived from the dopamine fragment, while its IR spectrum showed diagnostic bands at 933 cm^{-1} (Re=O) and 3000-3500 cm^{-1} (-OH or $-NH_2$). Unfortunately, the exact structure and composition of **1** remains uncertain as it had no ESI-MS signal and quantitative elemental analysis results were ambiguous. Based on oxidation state and coordination number considerations together with the spectroscopic data and the structure of other Re-catecholate complexes [22,23] we formulate **1** as $(\text{dopamine})_{1,2}ReO_{1,2}Cl$.



(eq. 2)

The preparation of a catechelato oxo-rhenium complex tethered to silica was pursued by two routes as shown in Scheme 1. In route A, the catecholato ligand was attached to the rhenium first, and the complex was then attached to functionalized silica; in route B, the ligand was fist attached to the silica and then the complex was formed. Route A from **1** to **3** gave a blackish material whose IR spectrum supported the presence of the amide linkage (1602 cm^{-1}) and a Re-oxo unit (933 cm^{-1}), and thus is formulated as shown. A material with the same appearance and IR spectrum was also obtained by reacting the dopamine-derivatized silica **2** with $ReOCl_3(PPh_3)_2$.

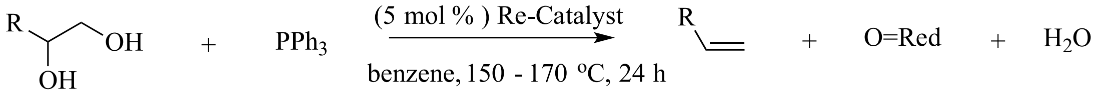


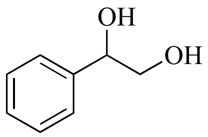
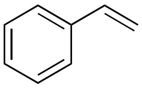
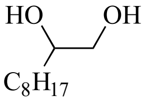
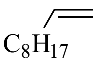
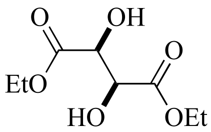
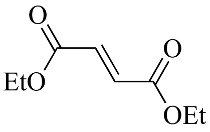
Scheme 1. Preparation of heterogeneous (catecholato)oxo-rhenium complex

3.1.2. Catalytic Testing of the Catecholato-rhenium Materials

An initial screening of the DODH catalytic activity of the soluble complex **1** with styrene glycol and different potential reductants, that is, CO, H_2, Na_2SO_3, benzyl alcohol and PPh_3, under typical conditions (150 °C, 24 h) was conducted. This survey revealed that PPh_3 was uniquely effective with the catalyst **1**, giving styrene in 61% yield (Table 1, Entry 1). Under the same conditions the corresponding silica-supported catalyst **3** with styrene diol/PPh_3 afforded a virtually identical yield of 62%. A comparative study of the catalytic efficiencies of the soluble and supported catalysts with two other representative substrates was conducted; the results are summarized in Table 1. The typically less reactive diols, 1,2-decanediol and diethyl tartrate, were each efficiently converted to the corresponding olefins in excellent yield at a higher reaction temperature. Once again, there was no appreciable difference in catalytic efficiency between the soluble and supported catalysts (Entries 3-6). The efficiencies and qualitative reaction rates for the present catalysts with PPh_3 as reductant are comparable to those found with Cp*ReO_3-based catalysts (Cp*=substituted cyclopentadienyl) [2,24].

Table 1. (Dopamine)oxorhenium-catalyzed DODH with triphenylphosphine as reductant



Entry	Substrate	Catalyst	Temp °C	Conv. (%)	Product	Yield (%)[b]
1		**1**	150 °C	100		61
2		**3**		100		62
3		**1**	170 °C	90		89
4		**3**		90		89, 98[e]
5		**1**	170 °C	100		94
6		**3**		100		94, 92[c], 83[d]

[a]Reaction conditions: 150-170 °C (oil bath) with 1.0 mmol glycol, 1.5 mmol reductant and 5 mol% of catalyst in 5 mL of benzene in a sealed thickwalled glass reactor tube. [b]Conversion and yield determined by gas chromatography with naphthalene as the internal standard. [c]1.1 mmol of reductant used. [d]after 5th cycle. [e]catalyst hot filtration leach study

Catalyst reusability and leaching are two important practical issues for supported and heterogeneous catalysts. To test for reusability of the supported catalyst **3**, a sequence of five cycles of reaction (170 °C, 24 h) - catalyst recovery (at rt) - reagent recharge was conducted with diethyl tartrate as the substrate. The fumarate yield was 83% after the fifth cycle, only a small decrease of yield (see Table 1), which may be largely attributable to catalyst loss during recovery. To address the issue of leaching and the related matter of whether the active Re-DODH catalyst species from **3** is truly heterogeneous, a reaction mixture from decanediol/PPh_3/**3** was hot filtered (>100 °C) after 24 h to remove the solid catalyst, the filtrate was re-charged with reagents and then tested for DODH activity. In this case (in the absence of **3**) a quantitative yield of 1-decene was still obtained. This observation suggests that a soluble ReO_x species is released from the silica support under operating reaction conditions and is largely responsible for the catalysis. A release could conceivably result from either a glycol–catechol ligand exchange on rhenium or reversible amide hydrolysis and condensation. The recycle results indicate that the catalytically active soluble species is apparently re-adsorbed at room temperature, which was also observed for ReO_x/C [14]. This positive feature would enable batch-type DODH processes to be operated with minimal catalyst leaching using the supported catalyst **3**.

3.2. Oxide-Supported Oxo-Rhenium Catalysts

3.2.1. Preparation of Oxide-Supported Oxo-Rhenium Catalysts

Oxides were selected for their documented suitability as supports for oxo-rhenium species or their surface properties. Silica and alumina were chosen as supports because they are proven components in rhenium-containing metathesis catalysts [25]. The reducible oxides Fe_2O_3, and CeO_2 were chosen because integrating an oxygen of the perrhenate ion into an oxygen vacancy of the support might produce a more tightly bound active species.

The catalysts were prepared by diffusion impregnation (DI), incipient wetness impregnation (IW), or by equilibrium adsorption (EA), as labeled in the tables. The first two methods offer excellent control of the concentration of active species, whereas equilibrium adsorption limits the loading to strongly anchored species, thus possibly restricting leaching.

3.2.2. Catalytic performance of oxide-supported oxo-rhenium catalysts

Test reactants were 1,2-decanediol and in some cases the more reactive styrene diol, which is however more prone to form side products. Three different reductants were used to test the catalytic activity: PPh_3, H_2, and CO. Both H_2 and CO are attractive reagents because of their economic availability in large quantity and the formation of innocuous and easily separable co-products (H_2O and CO_2), and at least H_2 has a record of reduction activity with oxo-metal complexes [26-28]. The survey of catalytic activity and efficiency results is summarized in Table 2. Triphenylphosphine was generally the most effective, with highest conversions and highest yields. Because PPh_3 is basic, metal-coordinating and highly soluble, we speculate that it may suppress side reactions catalyzed by Lewis or Brønsted acid sites on the support [29] and also enables more efficient reduction of intermediate oxo-metal species [2,30,31]. Hydrogen was less effective than PPh_3, and so was CO. Still, the data allow the conclusion that CO, which has only been used for DODH with soluble vanadium catalysts [11], is a viable reductant. Remarkably, DODH of 1,2-decanediol with CO as a reductant and ReO_x/Al_2O_3 could be achieved at a temperature as low as 100 °C.

Table 2. Performance of supported oxo-rhenium catalysts in 1,2-decane diol conversion to 1-decene

Catalyst	*Reducing Agent*	*Conv. (%)*[b]	*Yield (%)*[b]	*Moles decene per mol rhenium*
ReO_x/C – DI	PPh_3, 1.15 mmol	100	82	23
ReO_x/Al_2O_3–IW	PPh_3, 1.15 mmol	100	78	22
ReO_x/Al_2O_3– IW	CO, 200 psi	33	7	2
ReO_x/Al_2O_3– IW	H_2, 200 psi	31	7	2
ReO_x/SiO_2– IW	PPh_3, 1.15 mmol	100	78	22
ReO_x/SiO_2– IW	CO, 200 psi	100	28	8
ReO_x/SiO_2– IW	H_2, 200 psi	73	6	2
ReO_x/CeO_2– IW	PPh_3, 1.15 mmol	17	5	1
ReO_x/CeO_2– IW	CO, 200 psi	12	0	0
ReO_x/CeO_2– IW	H_2, 200 psi	36	7	2
ReO_x/Fe_2O_3– DI[a]	PPh_3, 1.5 mmol	92	70	9
ReO_x/Fe_2O_3– DI[a]	CO, 400 psi	85	33	4
ReO_x/Fe_2O_3 – DI[a]	H_2, 200 psi	62	23	3
ReO_x/Fe_2O_3 – IW	PPh_3, 1.15 mmol	100	56	16

[a] 80 µmol ReO_x, all other experiments 35 µmol ReO_x; [b] after 24 h of reaction at 150 °C

The data in Table 2 show that the supported oxo-rhenium catalysts can be grouped into two categories according to their performance for the DODH of 1,2-decane diol. High conversions and high yields were obtained with the ReO_x/C benchmark catalyst from Ref. [14] and with ReO_x/SiO_2, ReO_x/Al_2O_3, and ReO_x/Fe_2O_3. The highest conversions were observed using silica, with moderate 1-decene yields unless PPh_3 was the reductant. ReO_x/Al_2O_3 and ReO_x/Fe_2O_3 were overall the most efficient catalysts for DODH with the three tested reductants. ReO_x supported on CeO_2 was found to not be very active and perhaps not even catalytic as the low number of moles of decene per rhenium indicates. This observation is consistent with reports on ReO_x/CeO_2 catalyst that show that, at least with H_2 as a reductant, a noble metal promoter is needed [17,18].

The difference between diol conversion and olefin yield was appreciable in many cases. Previous preparative-scale investigations with ReO_x/C as the catalyst [14] showed that diol oxidation and condensation products such as the 2-alkanone, cyclic ethers and acetals are major side products that can reach more than 20% yield. Here, tests with some of the bare supports showed that interaction with the oxide support can account for disappearance of the diol up to a level of 15-26% (TiO_2, Fe_2O_3 at 150 °C) of the starting concentration. While this effect would become negligible at higher reactant-to-catalyst weight ratios, it contributes significantly at this scale. The highest yields were generally achieved with PPh_3 as the reductant, suggesting that rapid reduction of the active species and perhaps also blockage of acid sites on the support enhance selectivity.

To detect possible leaching of the active species into the liquid phase, filtrates of the reaction mixture were combined with fresh reactant and PPh_3 reductant, and the cumulative yield was determined. While the difference between cumulative and initial yield was close to the uncertainty of the measurement for some catalysts, cumulative yields were consistently higher than initial yields, suggesting a general tendency to leach. The results shown in Figure 1 indicate that leaching was severe with ReO_x/SiO_2 and appreciable for ReO_x/Fe_2O_3, whereas the additional yields for ReO_x/Al_2O_3 and ReO_x/CeO_2 were rather small. Generally, the color of the filtrates ranged from dark yellow or orange (SiO_2 support) to nearly colorless (CeO_2), consistent with the trend in filtrate activity from leached rhenium species. In all of the cases, the filtrate activity was significantly lower than the initial yield obtained with the solid catalyst, although the most effective reductant, PPh_3, was used for filtrate testing. Hence, this data suggest the majority of the product yield is from heterogeneous catalysis, except for ReO_x/SiO_2.

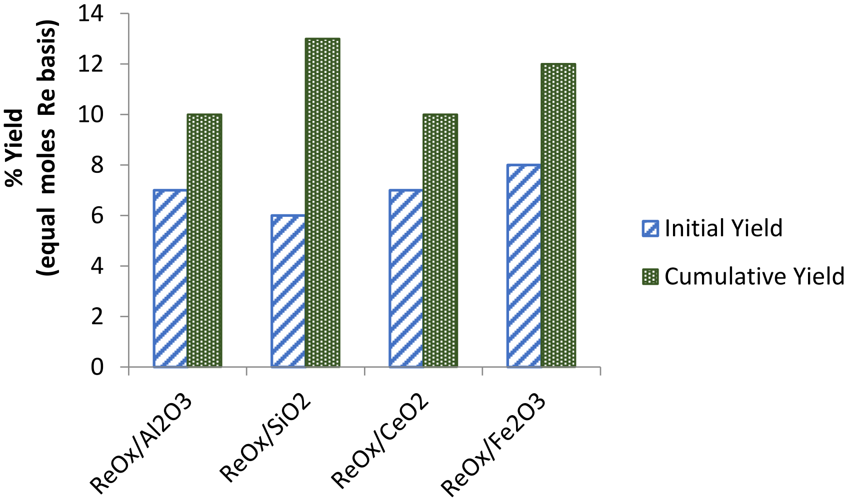


Figure 1. Leaching tests. Initial 1-decene yields using solid catalyst for 24 h reaction at a reaction temperature of 150 °C with 200 psi H_2; and cumulative yields using the filtrate recharged with 1.0 mmol glycol and 1.5 mmol PPh_3 for an additional 24 h at 150 °C. The yield of ReO_x/Fe_2O_3 was scaled to account for the higher Re content in the reaction mixture.

The reusability of the catalyst producing the highest olefin yields, ReO_x/Fe_2O_3, was investigated. Consistent with the observed rhenium leaching, a steady decline in activity was observed during reuse of the recovered catalyst material in 1,2-decanediol DODH (Figure 2). Other mechanisms of deactivation such as site-poisoning, however, cannot be excluded. Similar observations were made with styrene diol as the reactant: a yield of 36% was achieved after 24 h with the fresh catalyst and PPh_3, whereas 36 h were necessary to reach the same yield when the catalyst was used a third time.

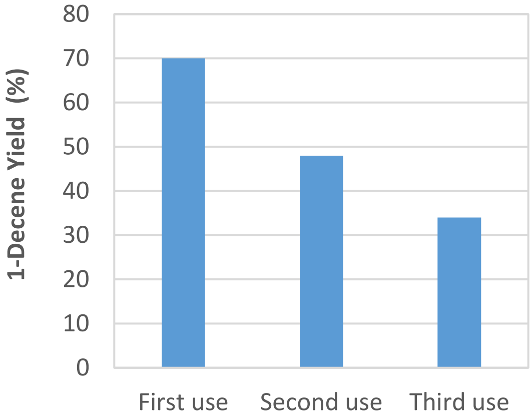


Figure 2. Reusability of ReO_x/Fe_2O_3 in 1,2-decane diol DODH with PPh_3 as the reductant; yield after 24 h reaction at a temperature of 150 °C.

The performance of ReO_x/Fe_2O_3 was further investigated. Styrene diol was also found to be converted to styrene in modest yield with both H_2 and Na_2SO_3 as reductants (benzene, 150 °C), giving 17% and 15% styrene yield, respectively; the latter result is surprising given the expected insolubility of both reductant and catalyst in this solvent.

3.3. Other Transition Metal Catalysts, Including Oxide-Supported Oxo-Molybdenum Catalysts

Due to the rarity and value of rhenium, leaching and catalyst stability are of paramount concern. Another strategy that was pursued was supporting less expensive metals that are reported to be DODH active or have a chemistry that is promising. Based on investigations of homogeneous catalysis, both vanadium and molybdenum are candidates. Vanadium is the more active of the two but requires a very specific ligand environment [11], whereas molybdenum is less active but can be used in the form of commercially available heptamolybdate [12]. To explore whether solid molybdenum catalysts would be viable, oxide-supported molybdenum-based catalysts analogous to the oxide-supported rhenium catalysts were prepared and tested. The criteria for selection of additional transition metals as catalyst candidates were derived from the postulated mechanism, which involves an oxidation state change by two with the formation of a metalloglycolate and elimination of the olefin by retrocyclization [5]. The elements chosen were known to form glycolates like molybdenum [32] and vanadium [33], or at least known to have the ability to bear two oxo ligands, thus allowing for reduction and bidentate coordination of the diol. The choices were tungsten [34] and chromium, and oxo species of these transition metals were deposited on the selected oxide supports.

The following materials did not exhibit significant DODH activity with 1,2-decane diol as the reactant: WO_3, Cr/SiO_2, VO_x/TiO_2, VO_x/CeO_2; in a few cases, reactant conversion was high but no olefin product was formed. Only molybdenum-containing materials were found to exhibit significant activity.

3.3.1. Catalytically active oxide-supported oxo-molybdenum species

The results obtained with bulk and supported MoO_x species are summarized in Table 3. Given appropriate conditions and reaction times, all materials produced some 1-decene from 1,2 decanediol, excluding MoO_3, a commercially acquired oxide with presumably very low surface area. Below 200 °C, no appreciable amounts of 1-decene formed within 24 h. The behavior of the solids is consistent with that of homogeneous catalysts, which were reported to be active at 195 °C [12]. A possible reason for the inactivity at lower temperatures is the higher resistance of supported Mo(VI) towards reduction relative to supported Re(VII) [35,'36]. Likely, the higher reaction temperature is the reason for the lack in selectivity of supported MoO_x species. The side products presumably were higher molecular weight compounds such as condensation and oligomerization products, as they did not appear in the standard chromatograms. Molybdenum, especially MoO_3, is known to be a catalyst for the dehydration of alcohols [37].

The first series of supported oxo-molybdenum species (Entries 1-5 in Table 3) produced a maximum of 2 moles of 1-decene per mole molybdenum within the observation span. Given the uncertainty of the measurement, catalytic turnover could not be demonstrated for these materials. These samples contained only 3.3 to 4.3 wt% molybdenum, and the next series (Entries 8-12) was prepared with a higher molybdenum content of 9 to 10 wt% by the incipient wetness method and included supports that were successfully used for oxo-rhenium species. These materials clearly acted as catalysts at 3-4 moles of decene produced per mole of molybdenum, and they were selected for further investigation. The highest turnover number, 8, was observed for ammonium heptamolybdate, which dissolves well enough in benzene for the catalysis to be considered homogeneous.

At complete diol conversion, the selectivity of the homogeneous ammonium heptamolybdate is 42%, while the supported catalysts have selectivities between 14-18%. This discrepancy could originate from the supports, which may adsorb the diol on their surfaces or may even catalyze side reactions, thus reducing the diol concentration in solution. Up to 41% diol conversion was observed in control reactions using only the oxide support (Al_2O_3, 190 °C), while no side products were detected by GC analysis. These results imply that adsorption and side reactions on the support can partly but not entirely account for the difference between diol conversion and decene yield.

Table 3. Performance of oxo-molybdenum catalysts in 1,2-decane diol conversion to 1-decene

Entry	***Catalyst***	***Reducing Agent***	***1,2-Decanediol Conv. (%)***[d]	***1-Decene Yield (%)***[d]	***Moles decene per mole molybdenum***
1	MoO_x/SiO_2 - DI[a]	H_2, 200 psi	100	17	< 1
2	MoO_x/Al_2O_3– EA[b]	PPh_3, 1.15 mmol	80	12	2
3	MoO_x/Al_2O_3 – EA[b]	CO, 150 psi	51	8	2
4	MoO_x/Al_2O_3 – EA[b]	H_2, 200 psi	64	10	2
5	MoO_x/TiO_2 – DI[a]	H_2, 200 psi	100	10	< 1
6	MoO_3 bulk	H_2, 200 psi	100	14	-
7	Ammonium Heptamolybdate [c]	PPh_3, 1.15 mmol	100	42	8.0
8	$MoO_x/\alpha\text{-}Fe_2O_3$-IW [c]	PPh_3, 1.15 mmol	89	16	3.4
9	MoO_x/TiO_2-IW [c]	PPh_3, 1.15 mmol	100	17	3.3
10	MoO_x/Al_2O_3-IW [c]	PPh_3, 1.15 mmol	100	17	3.5
11	MoO_x/SiO_2-IW [c]	PPh_3, 1.15 mmol	79	15	4.1
12	MoO_x/ZrO_2-IW [c]	PPh_3, 1.15 mmol	100	14	3.7

[a] 297 µM MoOx; [b] 52 µmol MoO_x; [c] 35 µM MoOx; [d] after 24 h reaction at 200°C

3.3.2. Molybdenum Catalyst Characterization

Characterization data for the oxo-molybdenum catalysts are summarized in Table 4. Since the surface areas of the oxide supports – Fe_2O_3, TiO_2, Al_2O_3, SiO_2, and ZrO_2 – varied greatly, the similar molybdenum contents implied a wide range of theoretical surface coverages. The surface coverage was calculated using an approximation of the molybdenum site density on these oxides at monolayer coverage from Ref. [38]. The estimated surface coverages for the Al_2O_3, SiO_2, and ZrO_2 supports were near the monolayer, whereas much higher coverages resulted for Fe_2O_3 and TiO_2.

Table 4. Oxide-supported Molybdenum Catalyst Characterization

Catalyst	*Molybdenum content (Weight %)*	*BET Support Surface Area ($m^2\,g^{-1}$)*	*BET Catalyst Surface Area ($m^2\,g^{-1}$)*	*Surface Coverage (%)*
$MoO_x/\alpha\text{-}Fe_2O_3$	9.1	24	29.9	530
MoO_x/TiO_2	9.3	53.2	49.8	245
MoO_x/Al_2O_3	8.8	151.6	143.2	82
MoO_x/SiO_2	10.1	150[a]		94
MoO_x/ZrO_2	9.0	99.5	81.8	127

[a] manufacturer's information

To assess the degree of oligomerization of molybdate, which can undergo polycondensation reactions, UV-vis diffuse reflectance spectra were recorded of these catalysts, see Figure 3. Unfortunately, the TiO_2 and Fe_2O_3 support absorption obscured the molybdate bands for the respective catalysts, whereas the absorption of Al_2O_3, SiO_2, and ZrO_2 did not interfere. The onset of the charge transfer band shifts towards the visible range as the degree of oligomerization increases [39]. It can be seen that the MoO_x/SiO_2 catalyst spectrum has a very similar onset of absorption as the heptamolybdate precursor. Both the MoO_x/Al_2O_3 and the MoO_x/ZrO_2 catalysts have a more UV-shifted band, indicating a lower degree of oligomerization.

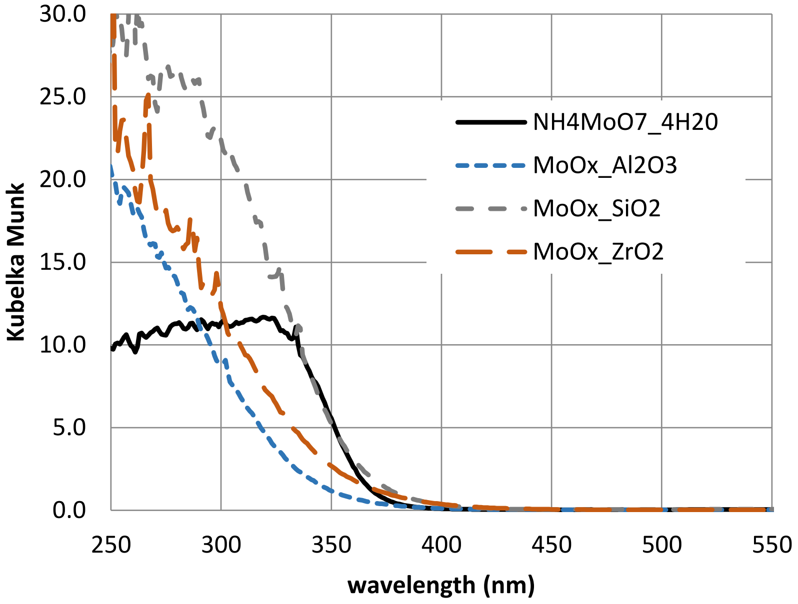


Figure 3. Diffuse reflectance UV-vis spectra of oxo-molybdenum catalysts

In aqueous solutions, molybdates are known to be present as mixtures of monomeric and oligomeric species, with the position of the equilibria and composition depending on concentration, temperature, and pH [40]. Molybdates have a tendency to condense to higher oligomers at decreasing pH, whereas under neutral/basic conditions the monomolybdate form would be favored. While heptamolybdate is the precursor, at least partial dissociation is expected in the solutions used for catalyst preparation. According to the literature, the point of zero charge of the support is crucial for the structure that is ultimately formed [39], and the results here are in agreement with this concept and the associated trends. Heptamolybdate is present on the surface of silica even at or below monolayer coverage, monomolybdate dominates on alumina, and a mixture of monomeric and oligomeric species is present on zirconia. In the absence of meaningful spectra, hepta- and octamolybdate species are inferred on TiO_2 and Fe_2O_3 because the coverage significantly exceeds a monolayer.

3.3.3. Comparison of oxo-molybdenum catalysts- activity, longevity and leaching

A series of experiments was conducted with a short reaction time to keep the conversion low. At this lower conversion, the decene yield was roughly stoichiometric as compared to the molybdenum content of the supported catalysts. The conversion of 1,2-decanediol was 36% or less, Table 5, and these initial rates were used to estimate turnover frequencies. These approximate TOFs indicate that all supported catalysts have similar activities per site whereas the homogeneous ammonium heptamolybdate catalyst is comparatively more active. The turnover frequencies determined for the molybdenum catalysts are much lower than those observed for rhenium catalysts. For example, a TOF of 9.6x10^{-5} s^{-1} was measured for MoO_x/Fe_2O_3-IW at 200 °C, whereas a TOF of 1.5x10^{-3} s^{-1} was measured for ReO_x/Fe_2O_3-IW at 165 °C. This difference indicates that at least one of the steps in the catalytic cycle is energetically more demanding for molybdenum sites than for rhenium sites. Temperature-programmed reduction in H_2 suggests that the reduction step may be a critical barrier for molybdenum catalysts. Reduction of perrhenate can commence at temperatures below 200 °C [35], whereas significantly higher temperatures are needed for molybdate reduction [41]. This principal difference in reducibility seems to hold also for PPh_3 as the reductant. Another trend is that oxometallates of both rhenium and molybdenum become more easily reducible with increasing degree of oligomerization [35,42]. The higher activity of samples with higher molybdenum content (entries 8-12 in Table 3), which generally promotes oligomerization of molybdate [39], is explainable by this trend.

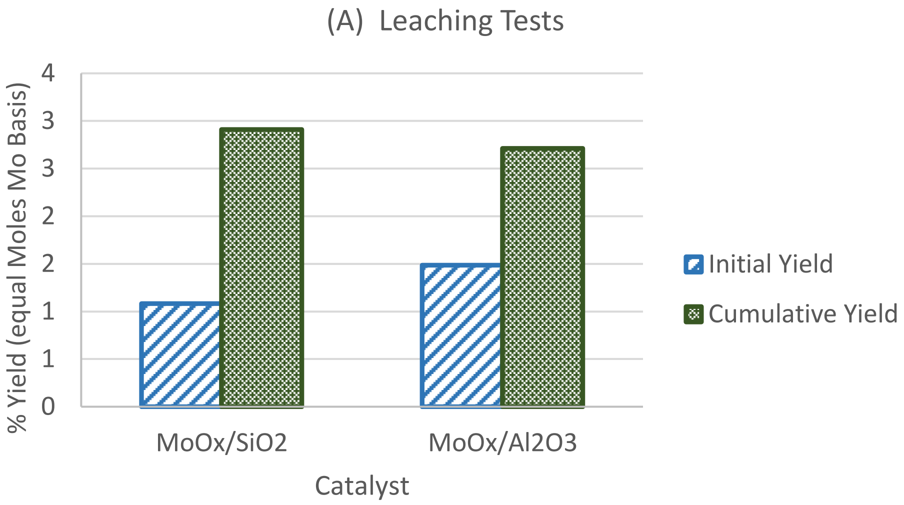
Table 5. Turnover frequencies for oxo-molybdenum catalysts

Catalyst	*TOF (mol decene)(mol Mo)$^{-1}$(s)$^{-1}$*	*Diol Conversion (%)^{a}*	*Decene Yield (%)^{a}*	*Selectivity (%)*
Ammonium Heptamolybdate	1.6E-04	36	12	33
MoO_x/α-Fe_2O_3-IW	9.6E-05	15	6	40
$MoO_x/TiO_{2\text{-IW}}$	1.2E-04	27	6	23
MoO_x/Al_2O_3-IW	1.1E-04	33	6	19
MoO_x/SiO_2-IW	1.2E-04	27	6	24
MoO_x/ZrO_2-IW	9.0E-05	28	6	21

[a] 50 µmol Mo; after 3 h at 200 °C

Comparison of the data in Table 3 and Table 5 also shows that the selectivities are slightly higher at low conversions, which suggests that some pathways leading to side products are secondary reactions of the product olefin.

MoO_x/SiO_2 and MoO_x/Al_2O_3 were chosen for stability tests because the UV-vis spectra indicated that they may contain the most different forms of molybdenum species. On alumina, molybdate and tungstate were found to adsorb more strongly than perrhenate and could not be rinsed off with water [43], raising hope that leaching may be less pronounced. Supernatants were tested in a second reaction to determine whether there are leached active molybdenum species present in the reaction solution. The total decene yield from both reactions is reported in Figure 4 as cumulative yield. Supernatant activity was seen for both MoO_x/SiO_2 and MoO_x/Al_2O_3 indicating that there were leached active species for these catalysts. The recovered solids were reused and as can be seen, the activity of these materials declined with each use, interestingly more so for the alumina support. Further improvement of these catalysts is thus needed.



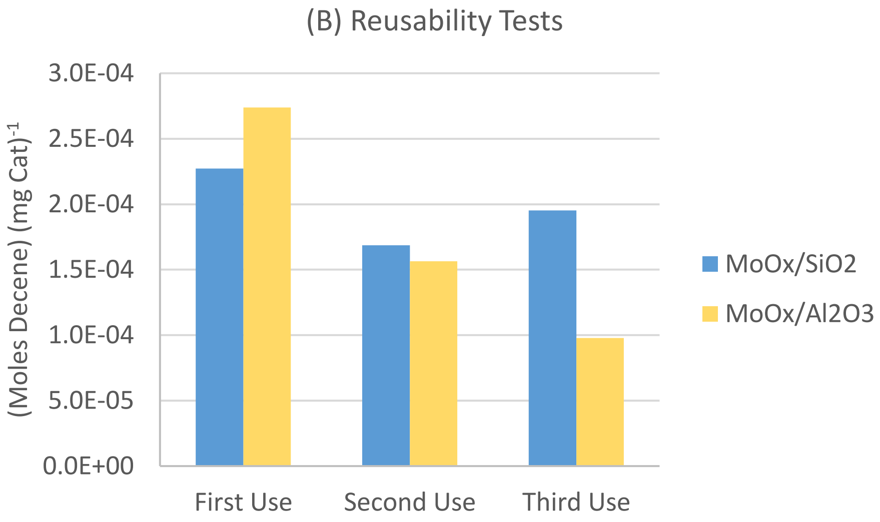


Figure 4. Leaching and reusability tests for supported MoO_x. (A) Initial and cumulative yields for MoO_x/SiO_2 and MoO_x/Al_2O_3 - cumulative yield shows additional conversion during subsequent reaction using supernatant from the initial run after hot filtration. (B) Reusability - moles decene referenced to milligrams solid employed. All reactions conducted at 200 °C for 3 h in toluene with 1,2-decanediol and triphenylphosphine as reactants.

4. Conclusions

Three new solid oxo-rhenium catalysts were discovered, namely catecholato-oxo-rhenium tethered to silica, ReO_x/Al_2O_3 and ReO_x/Fe_2O_3, that are capable of converting 1,2-diols into terminal olefins at a temperature of 150 °C. Oxo-molybdenum species were deposited on a variety of supports, and all obtained materials were active for DODH, with the best catalysts characterized by a high degree of molybdate oligomerization. MoO_x catalysts required higher temperatures than ReO_x catalysts and, as a result, were less selective. Catalysts were most effective with PPh_3 as reductant, but also operated with gaseous CO or H_2. The difference between rhenium and molybdenum, the influence of the degree of oligomerization of the oxometallate, and the effect of the reductant consistently point towards the reduction as the critical step in the DODH cycle.

The strategies to complex rhenium as catecholate or to use polar oxides instead of carbon as supports to curb leaching brought improvement in this respect, but not a satisfactory solution. There is an obvious influence of the support on leaching; for example, in comparison with ReO_x/SiO_2 and previously reported ReO_x/C, ReO_x/Fe_2O_3 was more stable. Still, all materials lost activity upon reuse through leaching of active species. As in previous investigations [14], it was observed that leached rhenium specie are apparently re-deposited upon cooling the reaction mixture, opening up avenues for improving catalyst recovery.

5. Acknowledgements

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