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New solid oxo-rhenium and oxo-molybdenum catalysts for the deoxydehydration of glycols to olefins

Bryan E. Sharkey[a], Alana L. Denning[b], Friederike C. Jentoft[a], Raju Gangadhara[c], Tirupathi V. Gopaladasu[c], Kenneth M. Nicholas[c,*]

[a] Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA
[b] School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA
[c] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA

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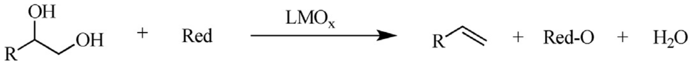
ABSTRACT

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.

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.



(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 [7–89]. Effective reductants include arylphosphines, H_2, SO_3^{2-}, and secondary alcohols. Reaction temperatures vary from about 90–185 °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

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* Corresponding author.
E-mail address: knicholas@ou.edu (K.M. Nicholas).

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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) δ6.8 (m, 2H), 6.6 (m, 1H), 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.

2.2.4. 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).

2.2.4.1. 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.

2.2.4.2. 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