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Heterogeneous Catalysis

A Reusable Unsupported Rhenium Nanocrystalline Catalyst for Acceptorless Dehydrogenation of Alcohols through γ-C–H Activation**

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Abstract: *Rhenium nanocrystalline particles (Re NPs), of 2 nm size, were prepared from NH_4ReO_4 under mild conditions in neat alcohol. The unsupported Re NPs convert secondary and benzylic alcohols to ketones and aldehydes, respectively, through catalytic acceptorless dehydrogenation (AD). The oxidant- and acceptor-free neat dehydrogenation of alcohols to obtain dihydrogen gas is a green and atom-economical process for making carbonyl compounds. Secondary aliphatic alcohols give quantitative conversion and yield. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Re K-edge X-ray absorption near-edge structure (XANES), and X-ray absorption fine structure (EXAFS) data confirmed the characterization of the Re NPs as metallic rhenium with surface oxidation to rhenium(IV) oxide (ReO_2). Isotope labeling experiments revealed a novel γ-CH activation mechanism for AD of alcohols.*

Catalytic acceptorless dehydrogenation (AD) reactions of alcohols, which generate dihydrogen and a more reactive functional group (carbonyl), are attracting significant research attention.[1] They eliminate production of organic and inorganic waste side products and the only by-product, hydrogen, is useful as a source of green energy. Until now, chemists have focused on AD using homogeneous catalysts; however, most homogeneous catalysts require an acid or base additive, extensive synthesis of ligands, and are difficult to separate and recycle.[1–6] Heterogeneous catalysts[7–14] for AD reactions are also highly dependent on the support acting as a base or acid. Our work and that of others on deoxydehydration (DODH) of biomass-derived polyols illustrate the use of discrete oxorhenium complexes as homogeneous catalysts.[15–21] While there are many examples of homogeneous rhenium deoxygenation catalysts, a limited number of rhenium nanoparticle catalysts have been reported.[22–26] Herein, we report on rhenium nanocrystalline particles (Re NPs), of 2 nm size, that catalyze AD of alcohols through a novel γ-CH activation mechanism.

Re NPs of 2 nm size without any support (Figure 1a) were prepared from NH_4ReO_4 under mild conditions (180 °C, without the need to protect from air) in neat 3-octanol. Figure 1b shows a HRTEM image of a Re nanocrystal aligned to the [0001] zone axis. An interplanar spacing of 2.39 Å, which belongs to {1−100} crystallographic planes in a hexagonal structure, is measured based on the HRTEM image as well as the fast Fourier transform (FFT) pattern (inset of Figure 1b). Both TEM and powder XRD (Figure S7 in the Supporting Information) are consistent with hexagonal Re crystals ($P6_3/mmc$) for the structure of Re NPs. Approximately 200 Re atoms make up the nanoclusters (2 nm). The surface or outside Re atoms are irregular in shape because they are susceptible to oxidation upon exposure to air to give rhenium(IV) oxide.

In alcohol solution and under reflux, catalytic AD reactions with Re NPs can be conducted without the need for protection from the ambient atmosphere (air). The addition of ten equivalents of mercury metal relative to Re does not poison the catalyst. However, isolated Re NPs contain surface Re atoms that are oxidized to $Re^{IV}O_2$, as evident by X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). According to the Re K-

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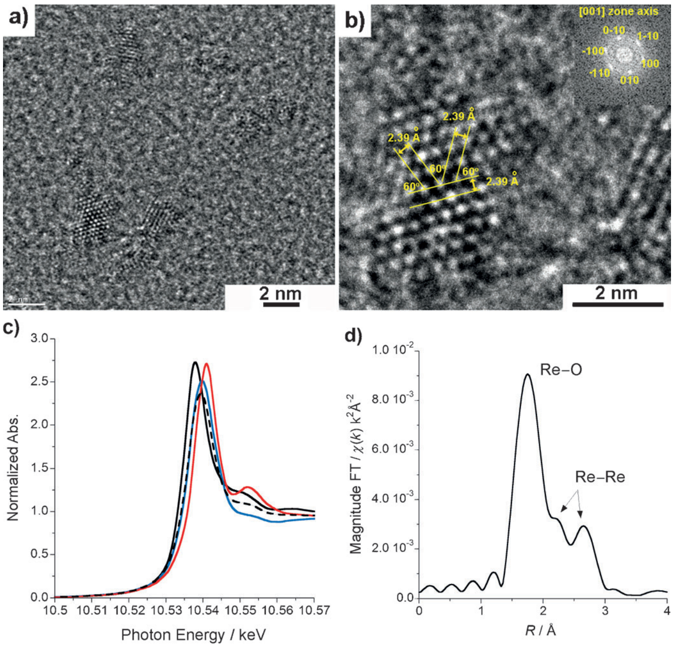


Figure 1. Identification of Re NPs. a) TEM image of Re NPs diluted in acetone and evaporated over Cu grids without interference of other supports. b) HRTEM image of hexagonal Re NPs, revealing the {1−100} crystallographic planes with a *d* spacing of 2.39 Å. The inset in (b) shows the FFT pattern of a single Re nanoparticle. c) Re L_3 XANES (10.50 to 10.57 keV) for Re^0 (black ——), ReO_2 (blue ——), and NH_4ReO_4 (red ——) references, and the Re NP sample (black – – –). d) EXAFS Fourier transforms of Re NPs ($\Delta k = 2.7$ to 10.4 A^{-1}).

edge X-ray absorption near-edge structure (XANES) in Figure 1c, the K-edge energy of the Re NPs is similar to that of ReO_2. However, the shape is slightly different, thus illustrating additional types of Re. A fit of the XANES shows 45% of the sample being ReO_2 and 55% rhenium(0). This result is also consistent with Fourier transforms (FT) of k^2-weighted extended X-ray absorption fine structure (EXAFS) data in Figure 1d and Table S1 in the Supporting Information. EXAFS indicates besides Re−O bonds (2.05 Å) metallic Re−Re bonds (2.70 Å). Assuming that the oxidation takes place at the surface of the Re NPs, the Re−O bond in the nanoparticles (2.05 Å) is longer than that in bulk ReO_2 (1.98 Å).[27] The fraction of oxidized Re in the nanoparticles can be estimated from the number of Re−O bonds, which are 6 in bulk ReO_2 and 2.8 in Re NPs. Thus the percentage of ReO_2 in Re NPs is 2.8/6 = 0.47 (i.e. 47%). In summary, Re NPs are approximately 2 nm in size composed of a rhenium(0) core with surface $Re^{IV}O_2$. Since many metallic nanoparticles are susceptible to oxidation,[28] it is not surprising that our Re NPs show oxidation of surface Re atoms to rhenium(IV) oxide.

X-ray photoelectron spectroscopy (XPS) provided further characterization of the surface atoms in Re NPs. Two samples were compared, Re NPs open to air and Re NPs transferred in a glovebox under Ar atmosphere. Figure S3 compares Re NPs transferred under Ar with Re polycrystalline foil as a reference. The curve fitting analysis shows the Re NPs exhibit a Re $4f_{7/2}$ peak at 40.8 eV, which is 0.5 eV higher than that observed for Re foil (Figure S3). This difference is attributed to the particle size effect. In comparison, the Re NPs that have been exposed to air do not show a Re $4f_{7/2}$ peak at 40.8 eV and only rhenium(IV) oxide is observed on the surface (Figure S4). In summary, Re NPs can be made by a solution method in alcohol at 180 °C. The surface atoms are easily oxidized to $Re^{IV}O_2$.

Since the Re NPs are prepared in neat 3-octanol solution starting from rhenium(VII), the alcohol must be sufficiently reducing. Indeed under acidic and neutral conditions reduction of rhenium oxides to the metal is exergonic [$ReO_4^-/Re = 0.375$ and $ReO_2/Re = 0.276$ V versus the normal hydrogen electrode (NHE)]. Because of their small size, the Re NPs disperse evenly in 3-octanol and do not aggregate, thereby making their separation by filtration difficult. Therefore, the Re NPs are isolated by evaporation of the 3-octanone product under vacuum. Remarkably, the recovered Re NP catalyst can be recycled several times without major loss in activity and selectivity (Table 1). FTIR spectra of the recycled Re NP catalyst (Figure S12) do not show Re=O stretching frequencies in the characteristic region for Re=O multiple bonds 800–1000 cm^{-1}.

Table 1: Dehydrogenation of 3-octanol over recycled Re NP catalyst.[a]

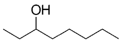
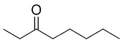
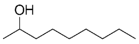
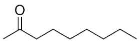
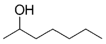
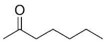
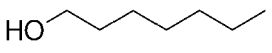
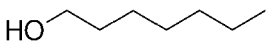
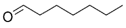
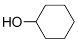
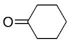
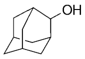
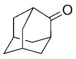
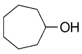
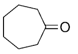
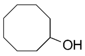
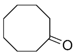
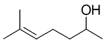
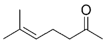
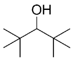
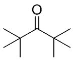
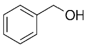
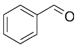
Reuse	1st	2nd	3rd	4th	5th	6th	7th	8th
Conv. [%][b]	100	100	97	96	90	83	82	79

[a] Reaction conditions: NH_4ReO_4 (0.3 mmol) and 3-octanol (15 mmol) were mixed and refluxed at 180 °C for 10 h, followed by vacuum distillation of 3-octanone and drying of Re NPs for the next catalytic cycle. [b] Conversions are based on ^1H NMR spectroscopy.

The effect of temperature on the conversion rate for dehydrogenation of 3-octanol into 3-octanone is shown in Figure S11a. Temperatures of 180 °C or higher give maximum conversion rate while retaining product selectivity for 3-octanone. Testing of several precursors for preparing the Re NP catalyst showed NH_4ReO_4 to be the best precursor (Figure S11b). Although MTO (CH_3ReO_3, methyltrioxorhenium) also gave a high conversion rate, its slightly lower selectivity (83% 3-octanone) is due to the known activity of homogeneous MTO for alcohol dehydration. The major by-product with MTO is 3-octene (17%). Similar behavior was observed for $(Ph_3SiO)ReO_3$ as a precatalyst, which also gave dehydration by-product. However, the conversion rate when starting with $(Ph_3SiO)ReO_3$ was also significantly lower (28% in 10 h). Other rhenium oxides such as Re_2O_7 and ReO_3 are suitable precursors for making the Re NP catalyst but at a lower efficacy than NH_4ReO_4 or MTO. NH_4ReO_4 appears to be the best starting precatalyst to produce Re NPs, which is consistent with a previous report.[26]

Dehydrogenation of various alcohols was investigated and the results are summarized in Table 2. Secondary aliphatic alcohols (Table 2, entries 1–3) all afforded quantitative conversion (100%) and high selectivity (>99%). Primary alcohols such as 1-heptanol (Table 2, entry 4a) did not convert to aliphatic aldehydes. Using 2-heptanol as an additive (1:1 molar ratio to 1-heptanol, entry 4b) also gave low conversion (5%) of 1-heptanal and even low conversion (35%) of 2-

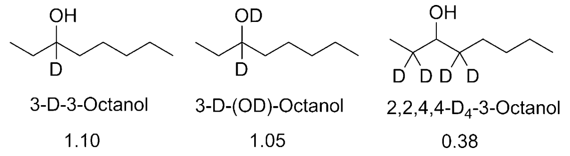
Table 2: Dehydrogenation of alcohols by Re NPs.[a]

Entry	Substrate	Additives	Product[b]	Conv. [%][c]	Sel. [%][c,d]
1		–		100	> 99
2		–		100	> 99
3 a		–		100	> 99
3 b		1-heptanal[e]		33	33
4 a		–	–	0	0
4 b		2-heptanol[e]		5	5
5		C_6Me_6[f]		45	44 (42)
6		C_6Me_6[f]		40	40 (39)
7		–		100	99
8		–		100	99
9		–		100	80[g] (78)
10		–		25	2[h]
11		C_6Me_6[f]		100	61[i] (55)

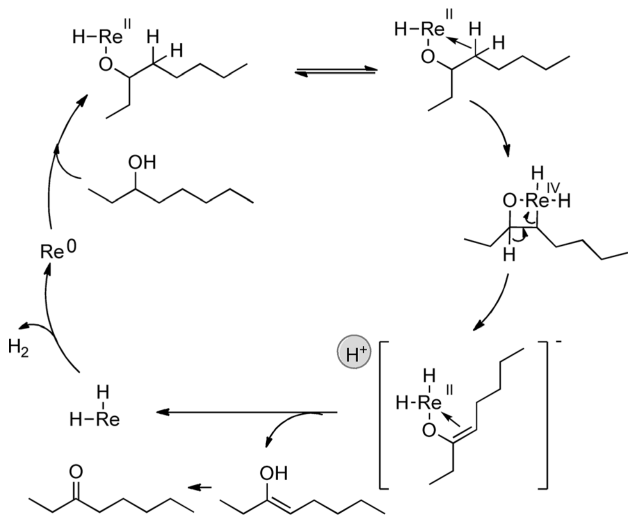
[a] Reaction conditions: NH_4ReO_4 (0.1 mmol) and alcohol (5 mmol) were mixed and refluxed at 180 °C for 10 h. [b] Confirmed by GC, GC–MS, and NMR (the Supporting Information). [c] Based on GC. [d] The values in brackets correspond to those after isolation by silica column chromatography. [e] Additive and substrate molar ratio is 1:1. [f] Additive and substrate molar ratio is 2:1. [g] Side products: 6-methyl-2-heptanone (15 %) and 6-methylhept-6-en-2-one (5 %). [h] Major product is 2,2,4-trimethylhex-3-ene (22 %). [i] Protected under Ar, reaction time is 3 h, and the yield of toluene is 38 %.

heptanol to 2-heptanone. This result indicates that primary alcohols and aldehydes act as inhibitors of the dehydrogenation reaction. Indeed mixing 1-heptanal and 2-heptanol in a 1:1 molar ratio (Table 2, entry 3b), gave low conversion (33 %) to 2-heptanone. Dehydrogenation of cyclohexanol (Table 2, entry 5) gave lower conversion (45 %) than other C7- or C8-cyclo-alcohols (entries 7 and 8, 100 %). The reason might be due to the difference in the C−H bond strength between these molecules. Dilution of cyclohexanol with hexamethylbenzene as a solvent reduced the aldol side product. While hexamethylbenzene is a solid at room temperature, it is a liquid at the reaction temperature of 180 °C. Upon completion of the reaction and cooling, the mixture was dissolved in CH_2Cl_2 for GC and GC–MS analyses, then concentrated and run through a silica column to separate cyclohexanone and recycle hexamethylbenzene. Dehydrogenation of the unconjugated alkene alcohol 6-methyl-5-hepten-2-ol (Table 2, entry 9) gave 100 % conversion and moderate selectivity for 6-methyl-5-hepten-2-one. Other side products included 6-methyl-2-heptanone and 6-methylhept-6-en-2-one. Conjugated systems like benzyl alcohol (entry 11) must be proceeding through a different pathway/mechanism because the reaction is not strictly AD. The reaction of the Re NP catalyst with benzyl alcohol produces only approximately 20 % H_2 and a large amount of toluene (38 %) from complete deoxygenation of the alcohol.

The Re NPs quantitatively convert secondary aliphatic alcohols to ketones through catalytic acceptorless dehydrogenation (AD). To explore the mechanism of Re NP catalyzed AD reactions of alcohols, we used deuterated 3-octanol substrates (Scheme 1). Deuteration of the alcohol hydrogen atom (-OH versus -OD) did not result in a kinetic isotope effect (KIE). Surprisingly, deuteration of the β-CH also did not result in a KIE. However, when γ-CH was replaced with γ-CD, an inverse KIE of 0.38 was observed (Scheme 1). This result indicates that the γ-CH is involved, and since the KIE is < 1.0, it must be resulting from a combination of a prior equilibrium and a kinetic C–H cleavage step. Therefore, we hypothesize that an alkane complex with γ-CH is formed with rhenium NPs followed by C–H activation (Scheme 2). This mechanistic proposal is corroborated by the observation of C-H/D scrambling in the 3-octanone product as well as a previously suggested agostic interaction in heterogeneous rhenium catalysts.[22] Further support for C–H scrambling and involvement of the γ-CH was obtained by detecting HD and D_2 products by mass spectrometry [see residual gas analysis (RGA) in the Supporting Information]. In Scheme 2, a Re^0 is used to represent the active atoms on the Re nanocluster. The generated proton (in gray circle) during the course of the reaction is most likely accommodated on an oxo-Re site or picked up by rhenium hydride to release dihydrogen.



Scheme 1. Deuterated alcohol substrates for KIE experiments. Reaction conditions: NH_4ReO_4 (0.2 mmol) and alcohol or deuterated alcohol (20 mmol) were mixed and refluxed at 180 °C for 180 min. Results are based on ^1H and/or ^2D NMR as the average of two runs.



Scheme 2. Proposed acceptorless dehydrogenation (AD) of 3-octanol through γ-CH activation.

Additionally the γ-abstraction mechanism was tested with 2,2,4,4-tetramethyl-3-pentanol, which has no γ-CH (entry 10 in Table 2). The conversion was low with the corresponding ketone product as the minor product (2%), and the major product 2,2,4-trimethylhex-3-ene (22%), which must be resulting from a sigmatropic methyl shift in association with alcohol dehydration.

In conclusion, unsupported crystalline Re NPs (ca. 2 nm) were generated under very mild conditions (180°C and neat 3-octanol). The resulting Re NPs are easily oxidized to ReO_2 on the surface while maintaining some metallic rhenium(0) in the core. The Re NPs are excellent and selective catalysts for AD reactions of different alcohols. The dehydrogenation mechanism is quite novel involving γ-CH bond activation. Further investigation of the Re NPs to broader green chemistry applications are under way.

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