Appendix A. Catalog of Useful Chemical Transformations

A.1 Background

Contaminated starting materials often cause the syntheses of complex materials to contain undesired side products or to fail entirely. Thus high quality and purity starting materials are a must. There are many books and collections available on the purification of basic chemicals, but the time and uncertainty involved in purifying a contaminated material often makes it more expedient to buy a new bottle of the needed chemical.

As such, this appendix focuses on materials that are either not available commercially, or are expensive enough that recovery of usable chemical from contaminated stores is desirable. Many of the syntheses and purifications described here are based on well-known methods. All of these syntheses were performed by the author, and he hopes that current and future members of the laboratory will find the procedures documented here to be useful in their own work.

A.2 Rhenium and Its Oxides

A.2.1 Background

Rhenium was the last non-radioactive element to be discovered, and its chemistry is quite complex. In addition, it is rather expensive, roughly $100 per gram in 2009. Only the pure metal is stable in air for months, but ReO_2 and ReO_3 can be worked with on the benchtop as they decompose slowly (~weeks) in air. The other oxides are exceptionally deliquescent, and must be worked with inside a glovebox and stored under vacuum. Additionally, the reduced oxides disproportionate at relatively low temperatures via the reactions,

$$Re_3O_{10} \xrightarrow{ca\,200°C} Re_2O_7 + ReO_3$$

$$3\ ReO_3 \xrightarrow{ca\,370°C} Re_2O_7 + ReO_2$$

$$7\ ReO_2 \xrightarrow{ca\,750–900°C} 3Re + 2Re_2O_7$$

and Re_2O_7 sublimes above 250 °C (boils at 350 °C). This relative instability of rhenium oxides complicates the synthesis of both the binary oxides and more complex materials. The

disproportionation of ReO_3 can be suppressed by the application of ~65 kbar of pressure (see **Figure A.2-2**). Presumably the decomposition of ReO_2 and Re_3O_{10} can be stabilized in a similar manner.

The author was able to synthesize four oxides: ReO_2 (including ReO_{2+x}), ReO_3, Re_3O_{10}, and Re_2O_7. The oxides Re_2O_8, Re_2O_5, Re_2O_3, ReO, and Re_2O have been reported, but their existence is doubtful. The oxygen contents of these phases were inferred solely based on the starting compositions, not a valid approach given the instability of the starting oxides. Based on the reported colors, synthesis techniques and patterns, the author believes that green "Re_2O_8" is $H_2Re_2O_8 = Re_2O_7 \cdot H_2O$, that deep blue "$Re_2O_5$" is Re_3O_{10}, and that monoclinic "Re_2O_3", "ReO", and "Re_2O" are ReO_{2+x}.

A.2.2 Preparation of Re metal

$$HReO_{4(s)} \xrightarrow{H2O} HReO_{4(aq)}$$

$$HReO_{4(aq)} + NH_4OH_{(aq)} \longrightarrow NH_4ReO_{4(aq)} \xrightarrow{evaporate,chill} NH_4ReO_{4(s)}$$

$$NH_4ReO_{4(s)} \xrightarrow{800°C,\ flowing\ NH3} Re_{(s)} + \text{gases}$$

Rhenium metal is easily prepared via the decomposition of ammonium rhenate under flowing ammonia, although 5% H_2/Ar probably also works, but the author did not test it. Ammonium rhenate is prepared by dissolving $HReO_{4(s)}$ in ~ 50 *mL* Millipore water per gram of solid in an Erlenmeyer flask. The resulting solution is highly acidic and colored blue-green due to the formation of the perrhenic acid. Ammonium hydroxide is then *slowly* added with stirring until the color disappears and pH ~ 9. The open flask is then heated with stirring in an oil bath at 90-98 C until the volume of the solution is reduced to 2-5 *mL* per gram of $HReO_4$. The flask is then stoppered and removed from the bath. If the liquid is sufficiently reduced, small colorless/white crystals of $NH_4ReO_{4(s)}$ will form as the solution returns to room temperature. Place the stoppered flask in a refrigerator at 4 °C overnight to complete precipitation. Remove the excess water by filtering with a Buchner funnel to dryness. Place the crystals in an alumina boat in a tube furnace under a fast (3-5 bubbles/sec) flow of ammonia, and heat at 60 °C/hr to 800 C. Leave at 800 °C

for 2 hr to complete the decomposition to rhenium metal, and then turn off the furnace and cool under flowing gas. If desired, the resulting coarse metal powder can be pulverized under liquid nitrogen to yield a fine gray powder. Performing the decomposition at lower temperatures (ca. 300 °C) is reported to produce rhenium nitride, ReN_x, x ~ 0.34.

A.2.3 Preparation of ReO_3

$$ReO_x \xrightarrow{220-260°C,\ flowing O2} ReO_{3(impure)} + HReO_4$$

$$ReO_{3(impure)} \xrightarrow{washwater} ReO_{3(pure)} + HReO_{4(aq)}$$

Rhenium metal or any lower oxide ReO_x (x < 3) is placed in an alumina boat in a quartz sleeve (as shown in **Figure A.2-1**) in a tube furnace under flowing oxygen gas (3-5 bubbles/sec) and heated for 2 hr at 220-260 °C. The powder is allowed to cool to room temperature under flowing gas and then removed and ground up. This heating and grinding process is repeated until a bright red-magenta powder with no lower oxides or Re metal is obtained. The exact temperature depends on the furnace used and the author recommends starting at 220 °C, and going up in steps of 10 °C until a significant change in the pattern is noted between heatings.

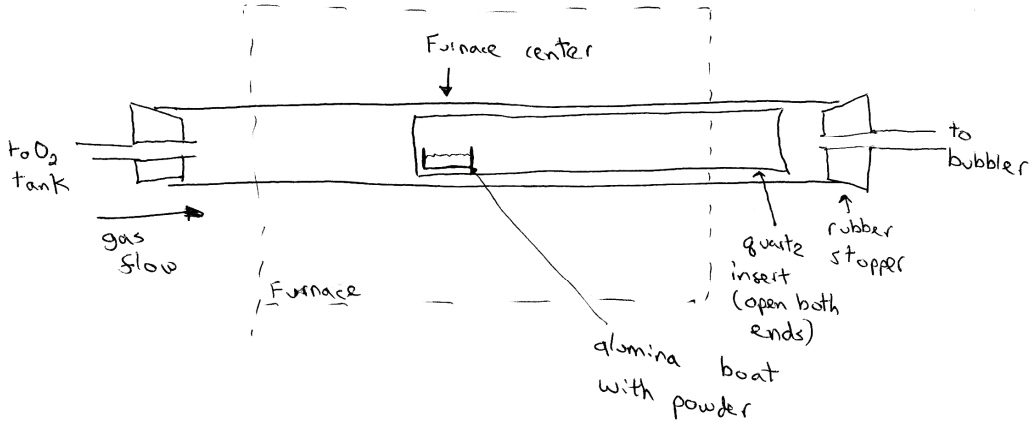

Figure A.2-1 Schematic of the setup to make ReO_3.

The short heating times and multiple grindings are absolutely essential for a high yield. Typical yield is 90-95%, with Re_2O_7 as the principal impurity, although unless special steps are taken to dry the oxygen gas and all delivery components (quartz tube, gas lines, etc), the impurity is actually $HReO_4$. Residual $HReO_4$ is present in the magenta powder, even if not observed in the x-ray, and can be removed from the otherwise pure product by washing with Millipore water using a

Buchner funnel. The $HReO_4$ that condenses on the quartz sleeve can also be dissolved in water. If desired, the aqueous $HReO_4$ from these rinses can be converted to Re metal (see A.2.2).

ReO_3 does not form any hydrates. Fresh ReO_3 is very bright red-magenta, but the color slowly darkens toward magenta-black when left exposed to air for extended periods (weeks), presumably due to the formation of $Re_3O_{10}{\cdot}xH_2O$ on the surface of the particles. It can be cleaned by the same procedure as the one used to initially prepare it, but the yield is slightly lower. Alternately, it can be purified by vapor transport using I_2, ~ 70 mg, with ~2 g of ReO_3 in a 5/8" OD quartz tube at 350 °C (hot) and 300 °C (cold).

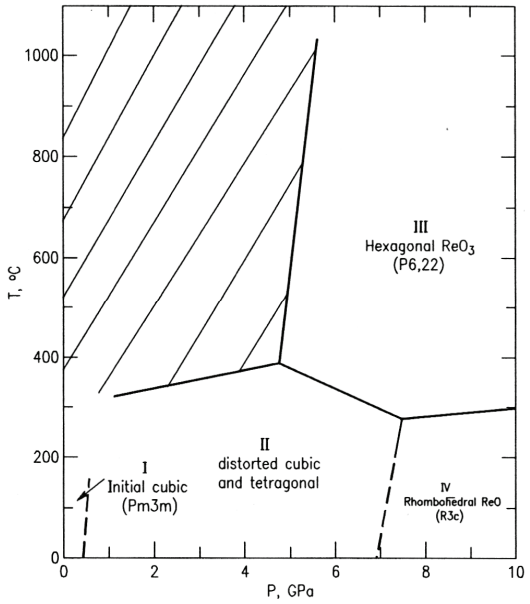

Figure A.2-2 Approximate phase diagram of ReO_3 under pressure. The shaded region is where disproportionation occurs.

The as-formed ReO_3 is cubic, but different crystal forms are reported to be prepared under pressure, including the suppression of disproportionation.

A.2.4 Preparation of ReO_2 (and ReO_{2+x})

$$(1\text{-}x)Re + (2+x)ReO_3 \xrightarrow{300\text{–}350^\circ C,\ sealed\ quartz\ tube} 3ReO_{(2+x)}$$

or

$$3ReO_3 \xrightarrow{425/120^\circ C,\ sealed\ quartz\ tube} ReO_2 + Re_2O_7$$

The first method converts all the Re to ReO_2, but is a difficult synthesis. Stoichiometric quantities of Re powder and ReO_3 are mixed gently in a mortar and pestle and pressed into a pellet. The pellet is sealed in a quartz tube under vacuum and heated at 300 °C for one week. The pellet is removed, reground and repressed, sealed in a quartz tube under vacuum. For stoichiometric ReO_2, the tube is heated from 300 °C to 350 °C at 1 °C/hr, held at 350 °C for 1-2 days, and then removed. The pellet is phase-pure ReO_2. For ReO_{2+x}, the tube is heated at 200 °C for 2-5 days and then quenched. The result is phase-pure ReO_{2+x}. It is essential that the starting ReO_3 be fresh (bright magenta), and that the quartz tubes be heated in a drying oven before use, and then dried again once attached to the vacuum line. The second method is much easier, a controlled disproportionation of rhenium (VI) oxide. See A.2.6 for details.

Stoichiometric ReO_2 is orthorhombic, and ReO_{2+x} is monoclinic. Both are black solids that decompose in air both by hydrating and oxidizing. Usually the rate is slow (days), but with high relative humidity, the powders hydrate rapidly (minutes). The hydrates are black but are much “stickier” than the freshly made powders. Once hydrated or oxidized, the powders cannot be directly restored to ReO_2, but must first be converted to ReO_3 (see A.2.3).

A.2.5 Preparation of Re_3O_{10}

$$HReO_{4(s)} \xrightarrow{ca120°C,continuousvacuum} Re_3O_{10} + Re_2O_7 + gases$$

The author was never able to clean Re_3O_{10} of all impurities, but this procedure produced a powder that was 90+% pure. A ~200 mg quantity of “dry” perrhenic acid (see A.2.7) is placed in a quartz tube that was previously dried in an oven. The quartz tube is connected vertically to a vacuum system and evacuated. The end of the tube containing the powder is then gently warmed to c.a. 120 °C using a sand bath, and the decomposition is allowed to proceed to completion, ~ 2 hours.

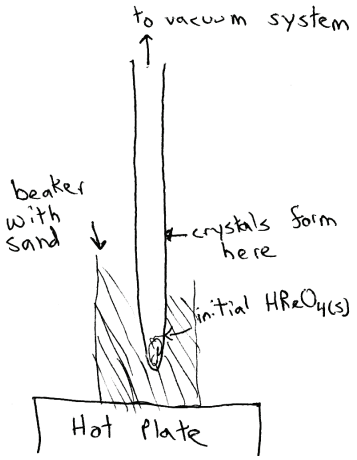

Figure A.2-3 Schematic of the apparatus used to make Re_3O_{10}.

The result is Re_3O_{10} powder at the bottom of the tube, with yellow-green crystals above the heated area. The tube should then be sealed off and opened inside the glovebox due to the air sensitive nature of both Re_3O_{10} and the yellow-green crystals ($Re_2O_7 \cdot xH_2O$). Yield is generally poor, but the yellow-green crystals can be reused in repeating the process.

Re_3O_{10} is a deep blue color, but it rapidly hydrates (seconds) in air to form a black compound. The Re_3O_{10} produced in this way is initially amorphous, but after a week at room temperature, was crystalline enough to obtain an x-ray pattern. This is similar to what is reported to happen when Re_3O_{10} is prepared by arc melting.

A.2.6 Preparation of Re_2O_7

$$3ReO_3 \xrightarrow{425/120°C,\ sealed\ quartz\ tube} ReO_2 + Re_2O_7$$

Roughly one gram of ReO_3 is placed in a quartz tube (1/2" O.D.) and sealed under vacuum, with a tube length of 6-7". The tube is then placed horizontally in a small tube furnace such that the end containing ReO_3 is in the hot zone and the other end protrudes from the edge of the furnace. The furnace is heated to 425 °C and left overnight. The furnace is then turned off and the tube allowed to cool. The result is black ReO_2 powder in the hot end and yellow crystals of Re_2O_7 in the cold end. The tube should be opened inside a glovebox due to the air sensitive nature of Re_2O_7. It is essential that the starting ReO_3 be fresh (bright magenta), and that the quartz tubes be heated in a drying oven before use, and then dried again once attached to the vacuum line.

Failure to do so will result in the production of hydrated Re_2O_7 ($HReO_4$), rather than the desired anhydrous product.

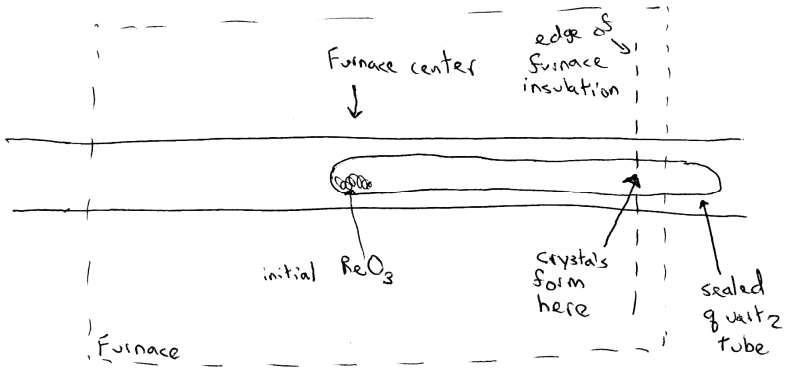

Figure A.2-4 Schematic of the apparatus used to make Re_2O_7.

Re_2O_7 is a bright yellow solid that is extremely deliquescent, and should be stored under vacuum and handled in a glovebox. Once hydrated, it is green in color, with formula $Re_2O_7 \cdot H_2O$ = $2HReO_4$. The author observed that Re_2O_7 hydrated inside a glovebox in a matter of hours.

A.2.7 Preparation of $HReO_{4(s)}$

$$Re_2O_{7(s)} \xrightarrow{\text{limitedH2O}} HReO_{4(s)}$$

Re_2O_7 is placed in an alumina boat and exposed to a limited amount of moisture by flowing argon gas (stock, not grade dry) over the powder in a tube furnace (at room temperature). The color will change from yellow to green, at which point the gas flow can be stopped and the pure $HReO_{4(s)}$ removed.

$HReO_{4(s)}$ is blue-green, and hydrates in minutes in air to form an aqueous solution of perrhenic acid. It is recommended that it be stored in a glovebox or under vacuum if not immediately needed.

A.3 Rhodium and Its Oxides

A.3.1 Background

Rhodium is the most expensive naturally occurring element, and, at ~$600 per gram in 2009, is more expensive than the synthetically prepared radioisotopes technetium and promethium. The

pure metal is stable in air but both oxides, Rh_2O_3 and RhO_2, hydrate when stored in air for prolonged periods.

The author was able to synthesize Rh metal, as well as both known oxides, Rh_2O_3 and RhO_2.

A.3.2 Preparation of Rh Metal

$$RhO_x \xrightarrow{5\%H2/Ar,800°C} Rh$$

Rhodium metal can be prepared directly via the reduction of the oxide at 800 °C, when heated overnight. The result is a coarse powder than can be pulverized under liquid nitrogen to a fine gray powder.

Rh metal is stable in air, and can be stored without any special precautions.

A.3.3 Preparation of Rh_2O_3

$$Rh \xrightarrow{air,600°C} Rh_2O_3$$

or

$$RhO_2 \xrightarrow{air,600°C} Rh_2O_3$$

Heating either Rh or RhO_2 in air at 600 °C overnight converts the powder to Rh_2O_3.

Rh_2O_3 is a dark gray powder that slowly hydrates in air (weeks), and should be stored in a dessicator. The hydrate is black.

A.3.4 Preparation of RhO_2

$$RhO_x \xrightarrow{O2,500°C} RhO_2$$

Heating Rh or Rh_2O_3 under flowing oxygen (3-5 bubbles/sec) at 500 °C produces RhO_2. The conversion is rather slow, requiring multiple grindings and overnight heatings to achieve purity. It is critical to allow the material to cool to room temperature under flowing O_2, as it decomposes to Rh_2O_3 if removed above ~120 °C.

RhO_2 is a very dark gray (almost black) powder that slowly decomposes to Rh_2O_3 and hydrates in air. It should be stored in a dessicator and checked (and repurified if necessary) before use.

A.4 Rare earth oxides, oxychlorides, nitrides, and phosphides

A.4.1 Background

The stable rare earth (Ln = La-Lu,Y) metal oxides in air are generally Ln_2O_3, except for Ln = Ce (CeO_2), Pr (Pr_6O_{11}), and Tb (Tb_4O_7). Stock bottles that have been stored in air for extended periods are generally contaminated with the hydroxide and should be checked and purified before use.

A.4.2 Preparation of Ln_2O_3 (or CeO_2, Pr_6O_{11}, Tb_4O_7)

$$Ln \xrightarrow{air,900°C} Ln_2O_3 \text{ (or } CeO_2, Pr_6O_{11}, Tb_4O_7)$$

or

$$Ln(OH)_3 \xrightarrow{air,900°C} Ln_2O_3 \text{ (or } CeO_2, Pr_6O_{11}, Tb_4O_7)$$

Heating either the rare earth metal powder or the hydroxide in air at 900 °C overnight is sufficient to produce the pure oxide. If a metal chunk is used, it should be ground after the first overnight heating and fired a second time to produce a powder that is pure oxide.

All slowly hydrate in air to form the corresponding $Ln(OH)_3$ hydroxide, and they should be checked and purified before use. They can be stored in a dessicator indefinitely.

A.4.3 Preparation of LnOCl

$$Ln_2O_3 \text{ (or } CeO_2, Pr_6O_{11}, Tb_4O_7) + 2NH_4Cl \xrightarrow{air,300°C,500°C,800°C} 2LnOCl$$

and

$$(1\text{-}x)Ln_2O_3 + 2x\ ACO_3 + 2NH_4Cl \xrightarrow{air,300°C,500°C} 2Ln_{1-x}A_xO_{1-x/2}Cl + \text{gases (A = Mg,Ca,Sr,Ba)}$$

A stoichiometric mixture of the rare earth oxide and ammonium chloride is ground together in a mortar and pestle and pressed into a pellet. The pellet is then heated in air at 300 °C for 2-4 hrs, then the temperature is increased to 500 °C. After another 2-4 hrs the temperature is increased to 800 °C and the sample heated for a final 2-4 hours. The furnace is then cooled and phase pure

LnOCl is obtained. Excess heating should be avoided as the oxychloride slowly (days) converts back to the oxide at the elevated temperatures. There is evidence that LnOCl is dopable with a small fraction (~10%) of an alkaline earth element to form oxygen-deficient $Ln_{1-x}A_xO_{1-x/2}Cl$. It can be prepared by mixing stoichiometric quantities, as shown in the equation above.

The oxychlorides decompose slowly in the presence of moisture and should be stored in a dessicator.

A.4.4 Preparation of LnN

$$Ln \xrightarrow{air-free,water-free NH_3, 900^\circ C} LnN$$

Roughly one gram of rare earth metal (as powder or chunk) is placed in an alumina boat in a tube furnace under flowing NH_3 (3-5 bubbles/sec). The furnace is heated to 900 °C overnight, and then cooled with the gas flowing. The sample is removed, ground, and heated a second time under the same conditions; note that this intermediate grinding should be done in a glovebox, as the nitride is extremely moisture sensitive. To minimize oxide contamination of the final product, clean metal must be used. The ammonia must also be purified before being passed over the rare earth, by running through columns of calcium oxide and 3 Å molecular sieves, and then passing over Mg, Al, and Zr powders. It is important that CaO and not $Ca(OH)_2$ be used, and that the molecular sieves have been activated by heating at 300 °C overnight prior to packing in the column. The Mg, Al, and Zr powders can be oxide-contaminated, but should contain sufficient unreacted metal to effectively getter the ammonia stream. The Mg and Al powders should be placed far enough away from the center of the furnace that the temperature does not exceed ~500 °C to prevent volatilization. The ammonia stream was clean enough if the Zr powder after the reaction is predominately the golden ZrN, not ZrO_2.

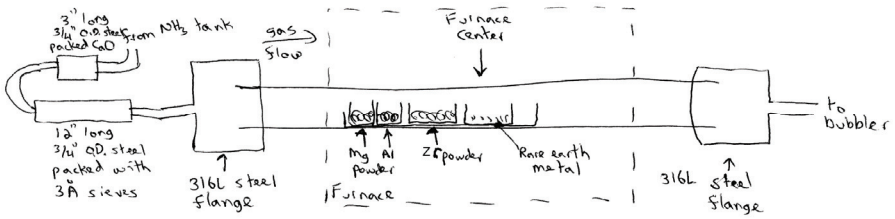

Figure A.4-1 Schematic of the apparatus to make clean LnN.

LnN are extremely moisture sensitive and should be worked with and stored in a glovebox, although limited exposure to air during the winter months is usually ok. Once contaminated, there is no easy way to purify the material. The formed powders are usually dark brown to black due to a small number of anion vacancies.

A.4.5 Preparation of Binary Phosphides

$$M_{(s,powder)} + P_{(red)} \xrightarrow{400-800°C,30°C/hr} MP_{(s)} \text{ (M = Mn,Fe,Co,Ni)}$$

The binary phosphides of first row transition metals can be prepared directly from the elements in sealed quartz tubes. Care must be taken to ensure that both the metal powder used and phosphorus are clean (see A.4.6). If metal chunk is used, this procedure is not appropriate as it results in an unacceptably high phosphorus vapor pressure, which *will* cause explosions and fires. Instead, a long quartz tube should be used, with the metal chunk placed at one end (hot, 800 °C), and the red phosphorus at the other (cold, 350 °C).

A.4.6 Purification of Phosphorus

$$\text{P(red, impure)} \xrightarrow{water,90°C,20\,\text{min}} \xrightarrow{filter,dry\,120°C} \text{P(red,pure)}$$

$$\text{P(red)} \xrightarrow{400°C(hot)/50°C(cold),sealed\,quartz} \text{P(white)}$$

Red phosphorus is the most appropriate source of phosphorus for the preparation of phosphides as white phosphorus is highly unstable and spontaneously ignites in air. However, red phosphorus slowly oxidizes and hydrates in air. It can be purified by a two-step process. First, ~15 g of phosphorus is added to ~150 mL of deionized H_2O, placed on a hot-plate, and simmered with stirring at 90 °C for 20 minutes. The slurry is then filtered in a Buchner funnel and dried in a drying oven at 120 °C. Pure red phosphorus is a bright red free-flowing powder that is not sticky.

If desired, white phosphorus can be prepared by heating red phosphorus in a sealed quartz ampoule in a temperature gradient from 400 °C (hot end) and 50 °C (cold end).

A.5 Purification of Other Reagents

A.5.1 Purification of Other Reagents

Table A.5-1 Purification of miscellaneous reagents.

Material	Problem	Purification
CaO	hydrates	heat 1200 °C, 12 hr, air
IrO_2	hydrates	heat 500 °C, overnight, air
Li_2CO_3	hydrates	heat 120 °C, overnight (drying oven)
Mn_2O_3	stable	heat MnO_2 or MnO, 900 °C, 12 hr, air
MnO	oxidizes	heat MnO_2 or Mn_2O_3, 1000 °C, 12 hr, 5% H_2/Ar
MoO_2	oxidizes	heat MoO_2/MoO_3, 500 °C, 5% H_2/Ar until reduced
Na_2CO_3	hydrates	heat 120 °C, overnight (drying oven)
NbO_2	oxidizes	heat 900-1000 °C, 12 hr, 5% H_2/Ar
PdO_2	hydrates	heat 500 °C, overnight, oxygen
PtO_2	hydrates	heat 500 °C, overnight, oxygen
RuO_2	hydrates	heat 700 °C, 4 hr, air
V_2O_3	oxidizes	heat 800 °C, overnight, 5% H_2/Ar
ZnS	oxidizes	heat 400 °C, 16 hr, Ar bubbled through CS_2