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(54) **RECOVERY OF RHENIUM FROM A SPENT CATALYST VIA SUBLIMATION**

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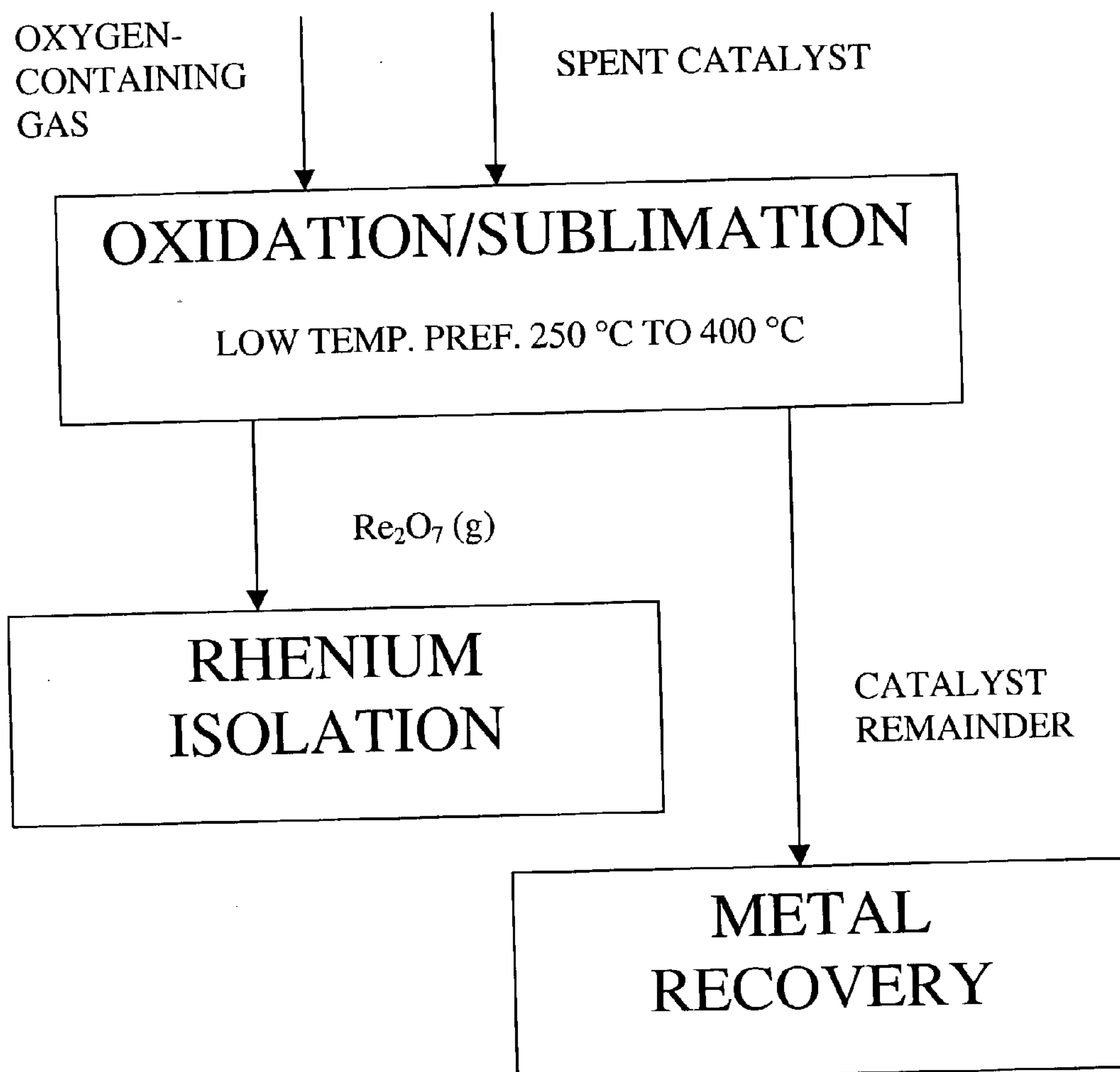
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(57) **ABSTRACT**

This invention provides a method for recovering rhenium oxide from a material containing rhenium by itself or rhenium in combination with some other element, such as an element catalytically active for a catalytic process, such as hydrogenation, oxidation, reforming, and hydrocracking. The method includes conversion of rhenium to a sublimable oxide via oxidation, heating in an oxidizing atmosphere to sublime the oxide as a volatized oxide, and then isolation of rhenium from the volatized oxide.



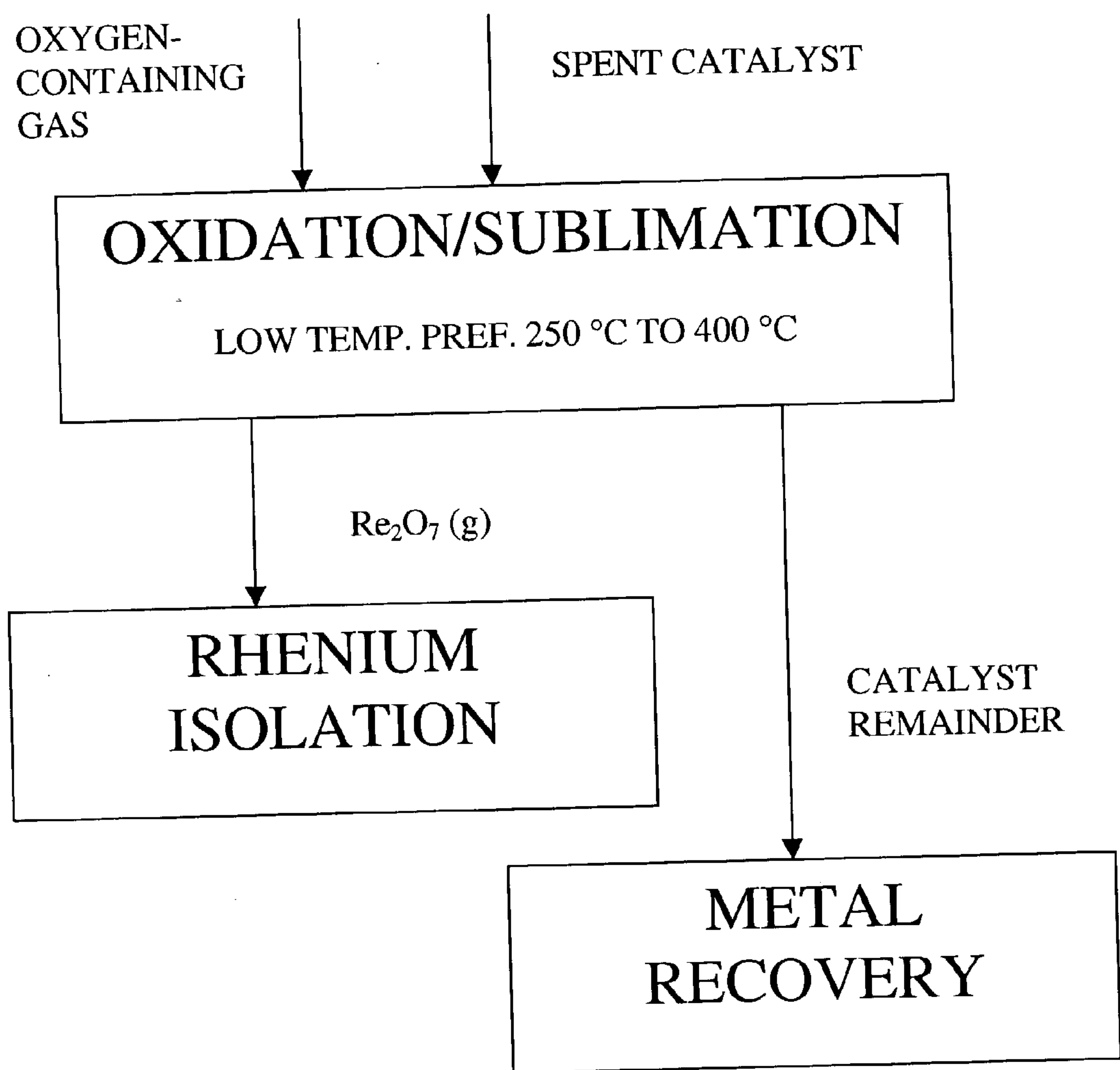


FIG. 1

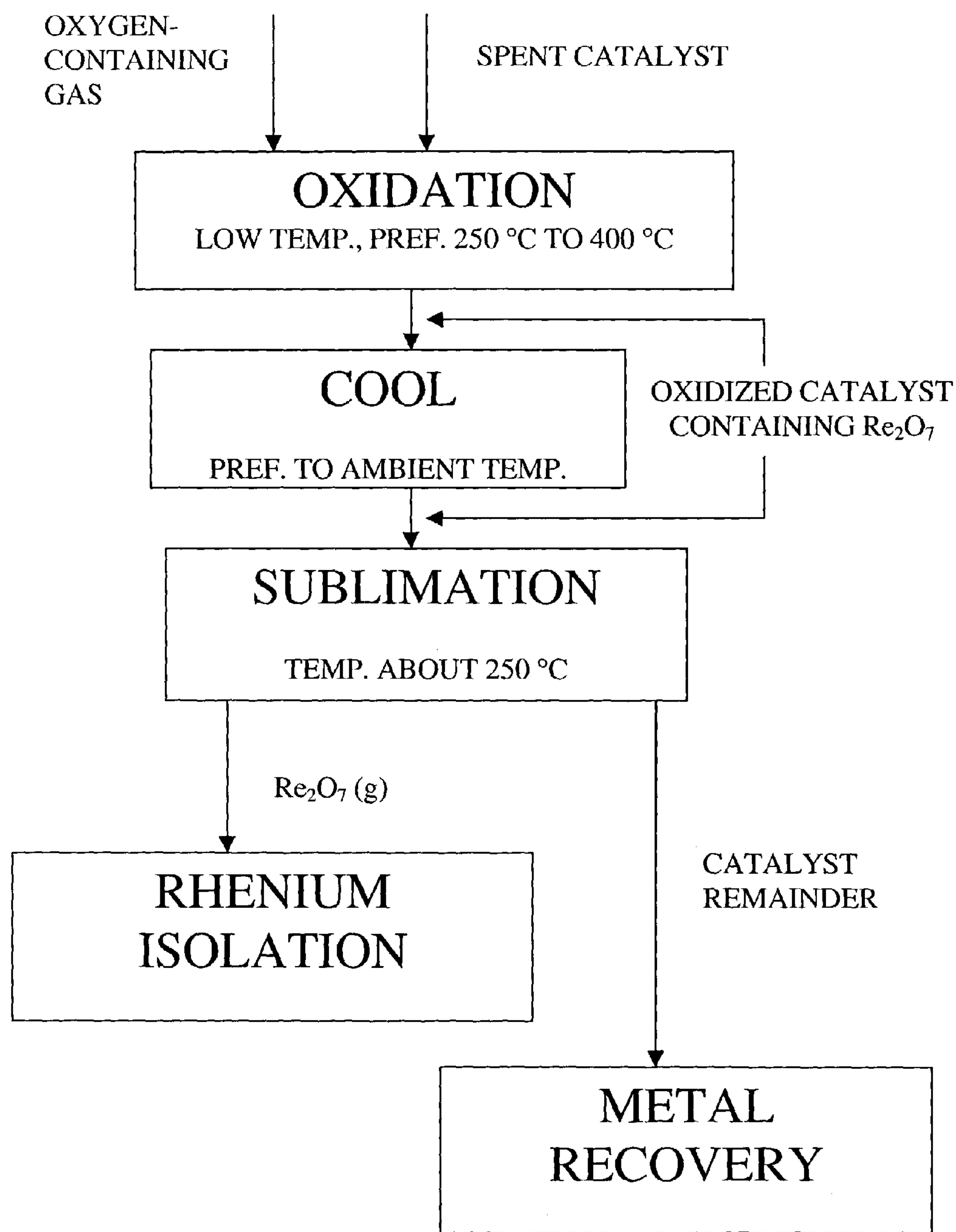


FIG. 2



## RECOVERY OF RHENIUM FROM A SPENT CATALYST VIA SUBLIMATION

### RELATED APPLICATIONS

**[0001]** The present application claims the benefit of 35 U.S.C. 111(b) provisional application Serial No. 60/344,950 filed Dec. 21, 2001, and entitled Recovery of Rhenium From A Spent Catalyst Via Sublimation.

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

**[0002]** Not Applicable.

### FIELD OF THE INVENTION

**[0003]** The present invention generally relates to a process for the recovery of rhenium from a spent catalyst. Still more particularly, this invention relates to a method that includes heating the catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of the rhenium as a volatilized oxide.

### BACKGROUND OF THE INVENTION

**[0004]** Catalysts for use in facilitating chemical reactions often contain precious metal components which aid in the function of the catalyst. For example, rhenium is a relatively scarce and expensive material, typically recovered from ores, which has however found utility in certain catalysts. The most common catalytic use of rhenium is in improved platinum-based reforming catalysts for the production of high-octane hydrocarbons for low-lead, lead-free gasoline. Rhenium also is known to improve hydrogenation catalysts. In particular, rhenium has been used as a promoter for cobalt-based catalysts in the Fischer-Tropsch reaction for the production of multi-carbon molecules, such as hydrocarbons, from methane. In this connection, reference is made to U.S. Pat. No. 4,801,573 and International Publications WO 98/47618 and WO 98/47620, each hereby incorporated herein by reference. Further, rhenium is known as a component in some oxidation catalysts. For example, U.S. Pat. Nos. 4,042,533, 6,008,389, and 5,720,901, each hereby incorporated herein by reference, illustrate the role of rhenium in oxidation of unsaturated aliphatic aldehydes, preparation of epoxides, and partial oxidation of a hydrocarbon feedstock to produce carbon monoxide and hydrogen (synthesis gas), respectively. Still further, rhenium is known as a component in some hydrocracking catalysts, as disclosed in, for example, U.S. Pat. Nos. 5,494,569 and 6,235,670, each hereby incorporated herein by reference.

**[0005]** In the life of a catalyst, the catalyst may lose some or all of its activity. A catalyst may deactivate through the accumulation of a layer of carbon deposits, or coke. Coke accumulation typically occurs throughout the catalyst pore systems and physically blocks access to active sites. Further, metal agglomeration may occur, which can severely reduce catalyst activity. Still further, poisons (e.g., lead, arsenic, sulfur) may permanently deactivate the catalyst.

**[0006]** Cycles of reaction and regeneration may occur for many years. The catalyst may be regenerated in situ or removed for ex situ regeneration. In one strategy, a fixed bed or slurry bed reactor unit and a regenerator unit are paired in tandem, for simultaneous operation. After the catalyst is regenerated ex situ it is commonly loaded back to the same

or another unit. This procedure has the advantage of reducing down time of the reactor. Alternatively, a catalyst may continuously recirculate between an entrained bed reactor and a regenerator. Cost savings over fresh catalyst vary widely, but using regenerated catalyst can save 50-80% of the new catalyst cost.

**[0007]** A catalyst that has been through cycles of use and regeneration may, with time, lose the ability to be regenerated to an adequate level of activity, becoming a spent catalyst. This loss of regenerability may be due to incompleteness of the regeneration. For example, in an oxidative regeneration of a coked catalyst, sulfur in the coke is typically not removed to as low a level as coke is removed during regeneration. Further, sulfates associated with alumina supports are typically not removed, nor are metal poisons. Permanent loss of acceptable activity may also occur through sintering or other structural changes.

**[0008]** Often a spent catalyst is discarded. However, a spent catalyst, if discarded, represents a loss of precious material. Further, use of landfills for such disposal is problematic. For example, landfills have decreased in number by 75% in the past 20 years, a trend that is expected to continue. Further, environmental liability can reach unacceptable levels if the landfill releases toxins to the environment. Still further, the environmental protection agency (EPA) "Land Ban" imposes restrictions on disposal.

**[0009]** Thus it is desirable to have a method for reclamation of catalyst materials. Reclamation is the process of recovering and recycling a material. For a precious-metal-containing catalyst, reclamation is particularly desirable for economic reasons. For example, a single drum of spent catalyst may contain thousands of dollars worth of valuable metals, such as platinum, palladium, iridium, ruthenium, and rhenium.

**[0010]** In particular, it is desirable to have a method for reclamation of precious metal from a spent catalyst. The costs of an entire catalytic process could be reduced appreciably by recovery of the precious metal, such as rhenium, from spent catalysts and subsequent recycling of the metal.

**[0011]** Methods that have been used to recover rhenium from rhenium-bearing sources have varied, depending in part on the nature and identity of other substances admixed with the rhenium. It is well known from the art of chemical analysis of materials, such as elemental analysis, that techniques for isolation, separation, and recovery of elements tend to vary in method or implementation with the composition of the material.

**[0012]** Methods of rhenium recovery that have been applied to ores that are the typical natural source of rhenium, such as molybdenite, conventionally have involved oxidative roasting of the ore and recovery of rhenium from the roaster gases by methods such as wet scrubbing. In this connection, reference is made to U.S. Pat. Nos. 2,414,965, 2,809,092, 3,739,549, and 3,798,306, each hereby incorporated herein by reference.

**[0013]** Alternatively, solution-based methods have been used for the recovery of rhenium from spent platinum-rhenium catalysts. In this connection, reference is made to U.S. Pat. Nos. 3,672,874, 3,855,385, and 3,932,579, hereby incorporated herein by reference. These methods usually involve complete dissolution of the various rhenium-bearing



source materials, such as using an acid, followed by the use of an anion exchange resin or another chemical separation method to isolate the rhenium. A disadvantage of complete dissolution is the necessity for typically complex separation of the rhenium from the solution. Further, the solvent used for dissolution tends to vary with the material, as does the method of separation.

[0014] In one method for selective dissolution of rhenium from a spent platinum-rhenium catalyst, the rhenium is selectively dissolved from the catalyst through use of a slight alkali solution, such as  $\text{NaHCO}_3$ . See, for example, T. N. Angelidis et al., in: "Selective Rhenium Recovery from Spent Reforming Catalysts," *Ind. Eng. Chem. Res.* 1999, 38, 1830-1836). This method has the disadvantage that it relies on the insolubility of the catalytic metal, in particular platinum, in the weak alkali solution. Catalytic materials that are insoluble in weak alkali solutions include for, example Al, Cd, and Zn. A survey of the solubilities of metals from *Lange's Handbook of Chemistry*, J. A. Dean, McGraw-Hill Handbooks, 15<sup>th</sup> edition (1998), Table 3.2, Page 3.14, hereby incorporated by herein reference, lists reference acid or weak acid solutions for dissolution.

[0015] Notwithstanding the above teachings, there remains a need for a selective and economical method for recovering rhenium from a spent catalyst.

#### SUMMARY OF THE INVENTION

[0016] A method is provided for recovering a metal from a metal-containing source. The metal-containing source may contain the metal present in mixed oxidation states, that is, different metal atoms in the source may have different oxidation states. The metal-containing source is preferably a spent catalyst. The present method has the advantage that selective recovery of the metal may be achieved.

[0017] The metal preferably has a desirable oxidation state that is the oxidation state of that elemental metal when present in a sublimable compound of the metal. The sublimable compound is preferably a sublimable oxide. The sublimable compound preferably sublimates to form a volatilized compound. The volatilized compound is preferably one from which the elemental metal may be recovered.

[0018] According to a method of recovering a metal from a metal-containing source, the metal-containing source is oxidized to form the metal in the desirable oxidation state. The metal in the desirable oxidation state is preferably recovered by heating the source to obtain the sublimable compound. The sublimable compound may be further treated for recovery of the metal.

[0019] In accordance with a preferred embodiment of the present invention, a method for recovering rhenium from a spent catalyst containing rhenium includes heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of the rhenium as a volatilized oxide. The spent catalyst may contain the rhenium, by itself or in combination with at least one other metal.

[0020] In accordance with another preferred embodiment of the present invention, a method for recovering rhenium and a second metal from a spent catalyst that contains rhenium and the second metal includes heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of the rhenium as a volatilized oxide

and to form a catalyst remainder, and removing at least a portion of the second metal from the catalyst remainder.

[0021] In accordance with still another preferred embodiment of the present invention, a method for reclaiming rhenium from a spent catalyst includes heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of rhenium as a volatilized oxide, isolating the rhenium from the volatilized oxide, and incorporating the isolated metal in a fresh catalyst.

[0022] In any one of the above-described embodiments, a catalyst, including a spent catalyst or a fresh catalyst, may be any suitable catalyst using rhenium, including but not limited to a catalyst selected from among hydrogenation catalysts, oxidation catalysts, reforming catalysts, and hydrocracking catalysts.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0023] For a more detailed description of the preferred embodiment of the present invention, reference will now be made to the accompanying drawings, wherein:

[0024] **FIG. 1** is a schematic flow chart illustrating a method of rhenium recovery, according to an embodiment of the present invention; and

[0025] **FIG. 2** is a schematic flow chart illustrating an alternate method of rhenium recovery, according to an alternate embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### [0026] Rhenium Recovery

[0027] Referring initially to **FIG. 1**, according to a preferred embodiment of the present invention, a method for separating rhenium from a spent catalyst includes oxidation of the spent catalyst. The rhenium is preferably oxidized to form a sublimable oxide, in particular rhenium heptoxide. More preferably, at least 60% of the elemental rhenium is present as rhenium heptoxide in the oxidized catalyst. A sublimable oxide is a compound that, when present in a solid state, undergoes a transition to a gaseous state upon heating. The standard sublimation temperature of a compound is conventionally given as the sublimation temperature for standard (i.e. atmospheric) pressure. For example, the standard sublimation temperature of rhenium heptoxide is 250° C. An advantage of a sublimable oxide is that it may be readily isolated and separated from other solid compounds in a source by heating the source at a temperature effective to sublime the sublimable oxide as a volatilized oxide. Volatilized oxide denotes herein the sublimable oxide in a gaseous state.

[0028] Oxidation is conventionally any process that increases the proportion of oxygen or acid-forming radical in a compound. An element in a compound typically has a formal oxidation state (herein termed oxidation state) that is increased upon oxidation and decreased upon reduction. Reduction is conventionally any process that decreases the proportion of oxygen or acid-forming or radical in a compound.

[0029] Referring still to **FIG. 1**, the spent catalyst may include rhenium compounds of various oxidation states, such as fully reduced metallic rhenium, Re(III) (i.e. rhenium



with a formal oxidation state of 3), Re(IV) (i.e. rhenium with a formal oxidation state of 4), Re(VI) (i.e. rhenium with a formal oxidation state of 6), Re(VII) (i.e. rhenium with a formal oxidation state of 7), and combinations thereof. Exemplary rhenium oxides having at least one of these oxidation states are indicated in Table 1. Rhenium sesquioxide is unstable and thus would tend not to be present in a spent catalyst. The spent catalyst preferably contains rhenium in the form of at least one rhenium oxide compound. The spent catalyst preferably contains any one or combination of rhenium dioxide,  $\text{ReO}_2$ , rhenium trioxide,  $\text{ReO}_3$ , and rhenium heptoxide,  $\text{Re}_2\text{O}_7$ . Alternately, the rhenium in the spent catalyst may be present in coordinated complexes, including their oxides, with other elements, such as another catalyst metal. Further, when the catalyst includes a support, the rhenium may be found in coordinated complexes, such as oxides, with an element included in a support. For example, for a cobalt-rhenium catalyst supported on alumina, the rhenium may be present in a rhenium oxide, a metal-rhenium oxide (i.e. a composition containing cobalt, rhenium, and oxygen), an aluminum-rhenium oxide, or an aluminum-cobalt-rhenium oxide (i.e. a composition containing alumina, cobalt, rhenium, and oxygen). It will be understood that cobalt is exemplary of a catalytically active metal and aluminum is exemplary of a support element. The various percentages of rhenium compounds having various oxidation states in a spent catalyst may depend on the length of time the catalyst has been in use, as well as whether the catalyst has been exposed to air.

TABLE 1

Rhenium Oxide	Chemical Formula	Re Oxidation State
Rhenium Heptoxide	$\text{Re}_2\text{O}_7$	7
Rhenium Trioxide	$\text{Re}_2\text{O}_3$	6
Rhenium Peroxide	$\text{Re}_2\text{O}_6$	6
Rhenium Dioxide	$\text{ReO}_2$	4
Rhenium Sesquioxide	$\text{Re}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	3

[0030] It will be appreciated that the various percentages of rhenium compounds in a spent catalyst typically differ from those in a fresh or regenerated catalyst. The rhenium in a fresh catalyst or regenerated catalyst mostly exists in the 0 (metallic) oxidation state, due to reduction of the catalyst to make it active. In contrast, the rhenium in a spent catalyst has a range of rhenium oxidation states due to the oxidation of metallic rhenium during its use. Further, there is typically not much rhenium in a spent catalyst in the +7 oxidation state, due in part to the availability of other oxides and to the reaction conditions. Thus, a spent catalyst typically contains a greater proportion of rhenium selected from among Re(IV) and Re(VI) than a fresh or regenerated catalyst.

[0031] Referring still to FIG. 1, the oxidation is preferably carried out by contacting the spent catalyst with an oxygen-containing gas under conditions effective to oxidize at least a portion of the rhenium in the spent catalyst. The oxygen-containing gas may be chosen from among air, oxygen gas, oxygen-helium mixtures and the like. Oxidation is preferably achieved by heating the spent catalyst in an oxidizing atmosphere. The oxidizing atmosphere preferably contains the oxygen-containing gas. The oxidation conditions preferably include a temperature greater than the sublimation temperature of rhenium heptoxide. The oxidation conditions preferably include a pressure approximately equal to atmo-

spheric pressure. At atmospheric pressure the sublimation temperature of rhenium heptoxide is 250° C. Thus, when the spent catalyst is heated under conditions of atmospheric pressure, the conditions preferably further include a temperature of at least about 250° C. Heating above the sublimation temperature of a sublimable oxide such as rhenium heptoxide preferably effects sublimation of at least a portion of the rhenium as a volatilized oxide during oxidation. Thus, oxidation and sublimation may occur together as one step.

[0032] Further, when the spent catalyst further contains at least one other metal, recoverable from the solid catalyst remainder, the conditions for oxidizing the spent catalyst by heating the spent catalyst in an oxidizing atmosphere preferably include a temperature less than any transformation temperature of the other metal. Heating under conditions that include a temperature below the lowest transformation temperature of the other metal preferably suppresses transformations of compounds of the other metal contained in the spent catalyst and thus suppresses conversion of the other metal to forms that may be difficult to recover or that may interfere with the process of recovery of rhenium from the spent catalyst. It is preferred that the other metal remains intact in the spent catalyst during the oxidation. In some embodiments, the other metal is any metal catalytically active for a catalytic process benefiting from a rhenium-bearing catalyst. Thus, in such embodiments, the other metal may be a metal catalytically active for hydrogenation, oxidation, reforming, hydrocracking, and the like. A catalytically active metal is one known to be active in suitably activated or regenerated catalyst and may be present either in an active or an inactive state in a spent catalyst.

[0033] Still further, the conditions for oxidizing a spent catalyst by heating the spent catalyst in an oxidizing atmosphere preferably include a temperature less than the decomposition temperature of a decomposable rhenium oxide. At atmospheric pressure, rhenium trioxide decomposes at 400° C. Thus, when the spent catalyst is heated under conditions of atmospheric pressure, the conditions preferably further include a temperature less than about 400° C. Heating under conditions that include a temperature below the decomposition temperature of a decomposable oxide of rhenium, such as rhenium trioxide, preferably suppresses decomposition of rhenium-bearing species contained in the spent catalyst and thus suppresses conversion of rhenium to forms that are not available to be oxidized to a sublimable oxide.

[0034] Still further, the above considerations for the temperature are preferably combined, such that a method for separating rhenium from a spent catalyst includes heating the spent catalyst in an oxidizing atmosphere under conditions that include a temperature greater than the sublimation temperature of rhenium heptoxide and less than the decomposition temperature of rhenium trioxide, more preferably a temperature between about 250° C. and about 400° C.

[0035] Referring to FIG. 2, in an alternate embodiment, an oxidized catalyst is cooled to ambient temperature. After cooling the oxidized catalyst, a method of recovering rhenium includes heating the oxidized catalyst under conditions effective to sublime a rhenium oxide and produce a gaseous stream containing a vaporized rhenium oxide, preferably rhenium heptoxide. The sublimation conditions preferably further include a pressure approximately equal to atmospheric pressure. Thus, the sublimation conditions prefer-



ably include a temperature of at least about 250° C. Temperature-programmed reduction indicates that reduction of  $\text{Re}_2\text{O}_7$  occurs at 280-350° C. Thus, it is preferred that the atmospheric pressure conditions of heating to effect sublimation be maintained preferably below about 280° C. Reheating the catalyst to effect sublimation has the advantage of increasing recovery of rhenium from the catalyst.

[0036] Referring to **FIGS. 1 and 2**, a catalyst solid remainder includes the remains of the catalyst solid after oxidation and sublimation, whether occurring together or separately. The catalyst solid remainder preferably includes less than 70%, more preferably less than 50%, and most preferably less than 20% of the elemental rhenium content of the spent catalyst. Thus, a method of separating rhenium from a spent catalyst preferably includes recovering at least 25% of the rhenium, more preferably at least 50%, and most preferably at least 80%.

[0037] Referring to **FIGS. 1 and 2**, according to a preferred embodiment, a method of recovering rhenium from a spent catalyst includes isolating rhenium from the volatilized oxide. Isolating rhenium from the volatilized oxide preferably includes wet scrubbing of a gaseous stream containing vaporized rhenium, preferably rhenium heptoxide. The wet scrubbing preferably proceeds according to conventional methods, such as disclosed in U.S. Pat. Nos. 2,414,965 and 2,809,092, which are incorporated herein by reference. The scrubbing may be performed in conventional scrubbing and/or absorption equipment, such as venturi scrubbers, cyclonic scrubbers, packed towers, other gas cleaning equipment, and the like. Rhenium heptoxide ( $\text{Re}_2\text{O}_7$ ) is soluble in water and forms perrhenic acid when it goes into solution. The scrubbing produces a rhenium-bearing aqueous solution containing rhenium and other soluble and suspension products. The resulting rhenium-bearing aqueous solution may be concentrated, which then allows the rhenium content to be separated by conventional methods such as ion exchange and precipitation. In ion exchange, a portion of the rhenium-bearing aqueous solution is passed through an ion exchange column to obtain a column eluent and rhenium is then precipitated from a portion of the eluent. In some embodiments, at least 25% of the rhenium is separated.

[0038] Referring to **FIGS. 1 and 2**, according to a preferred embodiment, the present method of separating rhenium from a spent catalyst preferably additionally includes recovery of other catalytic metals, such as cobalt, from a catalyst solid remainder. The method of recovering the other metal(s) may depend on the structural form of the spent catalyst. For example, for a supported cobalt-rhenium catalyst, the cobalt is preferably recovered by a method that includes conventional acid extraction or other methods known to those skilled in the art. In acid extraction, the catalyst remainder is dissolved in an acid solution and cobalt is then extracted from the acid solution. However, it will be understood that, according to other embodiments contemplated herein, a catalyst solid remainder may be discarded. In some embodiments, at least 80% of the cobalt is recovered.

[0039] Heating preferably occurs in any conventional heating zone suitable for subliming rhenium heptoxide from a spent catalyst. The spent catalyst is preferably maintained in the heating zone for a sufficient period of time to effect maximum conversion of different oxides of rhenium to

rhenium heptoxide. Any of a number of heating techniques and equipment in practice may be used and they can operate under static or flowing conditions. Selection of suitable techniques and equipment for heating are within the skill of one of ordinary skill in the art.

[0040] Cooling preferably occurs in any conventional cooling zone suitable for condensing the vapors of rhenium heptoxide. The rhenium heptoxide is preferably maintained in the cooling zone for sufficient period to effect the condensation of vapors. The rhenium heptoxide preferably collects in the cooling zone (which acts as a condenser). Any of a number of cooling techniques and equipment in practice may be used and they can operate under static or flowing conditions. Selection of suitable techniques and equipment for heating are within the skill of one of ordinary skill in the art.

[0041] Catalyst

[0042] It will be understood that the selection of a catalyst or catalyst system requires many technical and economic considerations. The process of selecting a precious metal catalyst can be broken down into components. Key catalyst properties include high activity, high selectivity, high recycle capability and filterability. Catalyst performance is determined mainly by the precious metal component. A metal is chosen for a catalyst based both on its ability to activate a desired reaction and its inability to promote an unwanted reaction.

[0043] A rhenium-bearing catalyst according to the preferred embodiments of the present invention may include any suitable support material. Preferably, the support is a catalyst support. The catalyst support may be any of a variety of materials on which a catalytically active material may be coated. The catalyst support preferably allows for a high degree of metal dispersion. The choice of support is largely determined by the nature of the reaction system. The support catalyst is preferably stable under reaction and regeneration conditions. Further, it preferably does not adversely react with solvent, reactants, or reaction products. Suitable supports include activated carbon, alumina, silica, silica-alumina, carbon black,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CaCO}_3$ , and  $\text{BaSO}_4$ . Preferably, the catalytically active material is supported on carbon, alumina, zirconia, titania or silica.

[0044] It will be understood that alternative choices of support may be made without departing from the preferred embodiments of the present invention by one of ordinary skill in the art. A support preferably favorably influences any of the catalyst activity, selectivity, recycling, refining, material handling reproducibility and the like. Properties of a support include surface area, pore volume, pore size distribution, particle size distribution, attrition resistance, acidity, basicity, impurity levels, and the ability to promote metal-support interactions. Metal dispersion increases with support surface area. Support porosity influences metal dispersion and distribution, metal sintering resistance, and intraparticle diffusion of reactants, products and poisons. Smaller support particle size increases catalytic activity but decreases filterability. The support preferably has desirable mechanical properties, attrition resistance and hardness. For example, an attrition resistant support allows for multiple catalyst recycling and rapid filtration. Further, support impurities preferably are inert. Alternatively, the support may contain additives that enhance catalyst selectivity.



[0045] In rhenium-bearing catalyst according to the preferred embodiments of the present invention, the rhenium may have catalytic activity. Alternatively, the rhenium may be present in combination with a second metal that is a catalytically active metal for any suitable reaction.

[0046] Thus, a rhenium-bearing catalyst according to the preferred embodiments of the present invention may further include any suitable catalytically active metal. Exemplary catalytically active metals for hydrogenation are the metals of Groups 8, 9, and 10, combinations thereof, and the like. For hydrogenation of carbon monoxide, also known as the Fischer-Tropsch reaction, preferred metals are iron, nickel, and cobalt, and combinations thereof. Exemplary catalytically active metals for oxidation include noble metals (also termed precious metals), such as ruthenium, rhodium, palladium, osmium, iridium, platinum, rhenium, gold, and silver, combinations thereof, and the like. Further exemplary catalytically active metals for oxidation include, the elements of molybdenum, vanadium, and tungsten in combination. A molybdenum, vanadium, tungsten catalysts may further include one or more of manganese, iron, copper, tin, aluminum, cobalt, nickel, phosphorous, zinc, bismuth, silver, cadmium, niobium, arsenic, chromium, the alkali and the alkaline earth elements. Exemplary catalytically active metals for reforming include platinum, and the like. Exemplary catalytically active metals for hydrocracking include platinum, palladium, tungsten, nickel, combinations thereof, and the like. Thus, a rhenium-bearing spent catalyst may further contain any one or more of the above-listed catalytically active metals.

[0047] An advantage of the process of the present invention is that, when the catalytically active metal does not have a sublimable oxide, the catalytically active metal remains in a spent catalyst remainder upon heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of the rhenium as a volatilized oxide. For example, none of the non-rhenium noble metals has a sublimable oxide.

[0048] The recovered rhenium is preferably recycled for use in a fresh catalyst. The catalysts of the present invention may be prepared by any of the methods known to those skilled in the art. By way of illustration and not limitation, such methods include loading a catalyst metal, in the form of a catalytic component or precursor thereof onto a support. Catalytic components include catalytically active metals and promoters. According to the function of the catalyst, rhenium may be either a catalytically active metal or a promoter. Methods of loading a support with a catalyst metal include impregnating the catalyst metal onto a support, extruding one or more catalyst metals together with support material to prepare catalyst extrudates, and/or precipitating the catalyst metal onto a support. Accordingly, the supported catalysts of the present invention may be used in the form of powders, particles, pellets, monoliths, honeycombs, packed beds, foams, and aerogels.

[0049] The most preferred method of preparation may vary among those skilled in the art, depending for example on the desired catalyst particle size. Those skilled in the art are able to select the most suitable method for a given set of requirements.

[0050] One method of preparing a supported metal catalyst is by incipient wetness impregnation of the support with

an aqueous solution of a soluble metal salt such as nitrate, acetate, acetylacetonate or the like. Another method of preparing a supported metal catalyst is by a melt impregnation technique, which involves preparing the supported metal catalyst from a molten metal salt.

[0051] Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following embodiments are to be construed as illustrative, and not as constraining the scope of the present invention in any way whatsoever.

What is claimed is:

1. A method for recovering rhenium from a spent catalyst comprising rhenium, the method comprising:

heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of the rhenium as a volatilized oxide.

2. The method according to claim 1 wherein the atmosphere is at standard pressure and the temperature is between about 250° C. and about 400° C.

3. The method according to claim 1 further comprising:

scrubbing the volatilized oxide with an aqueous medium to form a rhenium-bearing aqueous solution.

4. The method according to claim 3 further comprising:

separating rhenium from the aqueous solution so as to form a rhenium-bearing solid.

5. The method according to claim 1 wherein the portion comprises at least 25% of the rhenium.

6. The method according to claim 1 wherein the spent catalyst further comprises a second metal.

7. A method for recovering rhenium and a second metal from a spent catalyst comprising rhenium and the second metal, the method comprising:

(a) heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of the rhenium as a volatilized oxide and to form a catalyst remainder; and

(b) removing at least a portion of the second metal from the catalyst remainder.

8. The method according to claim 7 wherein the atmosphere is at standard pressure and the temperature is between about 250° C. and about 400° C.

9. The method according to claim 7 further comprising:

(c) scrubbing the volatilized oxide with an aqueous medium to form an aqueous rhenium-bearing solution.

10. The method according to claim 9 further comprising:

(d) separating rhenium from the aqueous solution so as to form a rhenium-bearing solid.

11. The method according to claim 7 wherein the portion of the rhenium comprises at least 25% of the rhenium.

12. The method according to claim 7 wherein step (b) comprises:

(b1) dissolving the catalyst remainder in an acid solution; and

(b2) extracting the second metal from the acid solution.

13. The method according to claim 12 wherein the portion of the second metal comprises at least 50% of the second metal.



**14.** The method according to claim 7 wherein the second metal is a metal catalytically active for a catalytic process selected from among hydrogenation, oxidation, reforming, and hydrocracking.

**15.** A method for reclaiming rhenium from a spent catalyst, comprising:

- (a) heating the spent catalyst in an oxidizing atmosphere at a temperature effective to sublime a portion of rhenium as a volatilized oxide;
- (b) isolating the rhenium from the volatilized oxide; and
- (c) incorporating the isolated metal in a fresh catalyst.

**16.** The method according to claim 15 wherein the atmosphere is at standard pressure and the temperature is between about 250° C. and about 400° C.

**17.** The method according to claim 15 further comprising:

- (d) scrubbing the volatilized oxide with an aqueous medium to form a rhenium-bearing aqueous solution.

**18.** The method according to claim 17 further comprising:

- (e) separating rhenium from the aqueous solution so as to form a rhenium-bearing solid.

**19.** The method according to claim 15 wherein the portion of rhenium comprises at least 25% of the rhenium.

**20.** The method according to claim 15 wherein step (c) comprises loading a catalyst support with the reclaimed rhenium.

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