

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims the benefit of priority of United States provisional application Serial Number 60/419,390 filed October 17, 2002 which is incorporated herein by reference in its entirety. This application is related to United States Patent Application Serial Number 10/_____ filed October 17, 2002 entitled "METHOD OF RESTRICTED CARBON DIOXIDE PURIFICATION" which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

Carbon dioxide (CO₂) is used in a wide variety of industrial processes and products from the carbonation of beverages to the generation of semiconductors. Industrial applications for CO₂ include wafer cleaning, removal of residual photoresist, low K dielectric annealing and cleaning, use as laser gases, particle removal and plasma generation. The presence of contaminants in such ultrahigh purity applications can result in products that are unusable in the case of semiconductor applications or the damage of optics and lasers in other relevant applications. Various phases of CO₂, liquid, gas and supercritical, are used dependent upon the application.

Purification of CO₂ to a high level is difficult as CO₂ is inherently wet. Gases can be readily acquired that are $\geq 99.999\%$ pure (contaminants ≤ 10 parts per million, ppm; Ultra High Purity); however, there is a need to further purify gases to ≤ 5 parts per billion (ppb) contaminants to meet the current Semiconductor Industry Association guidelines. Future requirements will be for contaminants of ≤ 1 ppb, preferably ≤ 0.1 ppb. Contaminants of concern to the semiconductor industry include moisture, hydrocarbons, particulates and metals. Other contaminants include oxygen-, nitrogen-, sulphur- and phosphorus-containing compounds such as O₂, NO_x, SO_x, COS, and PO_x, wherein $x \leq 3$, and corresponding organoheteroatom derivatives wherein heteroatoms include, but are not limited to, oxygen, nitrogen, sulphur,

phosphate and silicon.

Purification of CO₂ to a high level is even more essential when it is used in the supercritical state. A supercritical fluid is a fluid which is in a state above its critical temperature and critical pressure where the gas and liquid phases resolve into a single medium, in which density can vary widely without a phase transition. This allows, for instance, for substances that normally act as solvents primarily for inorganic or polar substances to also become efficient solvents for organic or non-polar materials. The supercritical state of CO₂ can be reached under relatively moderate conditions at a critical point of 31.3°C, (88.3°F) and 74 barr (1070 psi).

Supercritical CO₂ is useful as a cleaning agent because it is able to enter small features on surfaces and porous interior surfaces to remove contaminants, etched photoresist and other undesirable materials from substrates. However, this property can also result in impregnation of wafers and other high purity substrates with contaminants present in the CO₂ stream. Additionally, the high pressure and temperature of the fluid can result in some contaminants becoming more nefarious. For example, water and oxygen in the context of supercritical CO₂ can become highly corrosive, whereby desired structural features on wafers are subject to degradation.

Equipment used in the semiconductor industry can also act as a source of contaminants. Stainless steel components can leach metals including iron, chromium and nickel as metal complexes or metal ions. Leached metals are volatile at low concentrations, ppb to parts per trillion (ppt), and are readily captured in the gas phase resulting in potential contamination of silicon wafers or other high purity products. Therefore, all equipment for use in the semiconductor manufacturing process must be thoroughly cleaned to remove potential surface contaminants.

Spiegelman et al (US Patent 6,361,696, incorporated herein by reference) teach the use of high silica zeolites for the continuous purification of CO₂ in a dual bed apparatus. Although the high silica zeolites are able to remove heavy hydrocarbons from CO₂ efficiently, removal of other contaminants is limited. Lansbarkis et al. (US Patent 6,511,528) teach the

use of a series of materials to remove a series of contaminants from CO₂ to all for its use in the semiconductor industry. The materials may be placed in a single or multiple containers. Either arrangement results in a complex system. If the materials are placed in a single container, the container must be discarded upon the breakdown of the least stable purification material. If multiple containers are used, complex replacement schedules must be followed to ensure the overall purity of the CO₂.

SUMMARY OF THE INVENTION

The invention pertains to a method for the purification of CO₂ to achieve sufficient purity for its use in the semiconductor industry. The method comprises contacting the CO₂ stream, gas, liquid or supercritical fluid, with a quantity of at least one mixed metal oxide wherein the mixed metal oxide comprises at least two oxidation states of one or more metals; or two metals with similar relatively high oxidation states with different chemical properties. The invention comprises the use of a single mixture of materials to achieve low levels of a number of contaminants. Decontamination of the CO₂ can take place in any of a number of purification apparatuses including both bed and canister apparatuses. The contaminants of primary concern are O₂, water, metals, sulfurous contaminants, especially COS, phosphorus containing contaminants, silicon containing contaminants, and non-methane hydrocarbons (NMHC). Contaminants of secondary concern are nitrogenous contaminants, especially NH₃ and NO_x, wherein $1 \leq x \leq 2$ and other inorganic compounds. Total contaminant levels are reduced to less than 100 ppb using the method of the invention.

The invention allows for removal of a broad range of contaminants from the CO₂. Oxidizable contaminants are absorbed on the high oxidation state portion of the material and reducible contaminants are adsorbed on the low oxidation state portion of the material. The selection and ratios of metals is dependent upon the source of CO₂ to be decontaminated in conjunction with the contaminants to be removed.

The invention further pertains to methods for the activation and

regeneration of the metal oxides to provide adsorbents with multiple oxidation states to allow for sequestration of a variety of contaminants. Activation and regeneration comprise exposure of the adsorbent to oxygen at a relatively high temperature for a period of time to nearly fully oxidize the metals. The adsorbents are then cooled and exposed to a reducing agent, such as 1-5% hydrogen (H_2) in an inert gas such as nitrogen (N_2) or argon (Ar) for a sufficient period of time to partially reduce the adsorbent. In addition to producing a mixed metal oxide, the activation and regeneration steps purge contaminants from the adsorbents. Exact methods for activation and regeneration depend on the type of beds, the adsorbents used and the major contaminants in the CO_2 .

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an O_2 removal test manifold.

FIG. 2 is a graph of the oxygen removal capacity of the Ni/NiO media of the invention.

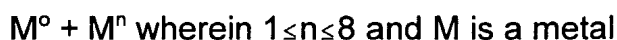
DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

The invention is a method for the production of highly purified CO_2 containing contaminants at less than 100 ppb, preferably less than 10 ppb, most preferably less than 1 ppb, for use in the semiconductor industry. Contaminants of primary concern are O_2 , water, metals, sulfurous contaminants, especially COS, phosphorus- and silicon-containing contaminants and non-methane hydrocarbons (NMHC). Contaminants of secondary concern are nitrogenous compounds, especially NH_3 and NO_x and other organic compounds.

Purification of CO_2 is exceptionally difficult as it typically reacts with most adsorbent materials (e.g., metal oxides) and render them inactive. In fact, CO_2 is commonly used to passivate highly active reduced metals prior to shipping for safety purposes. The instant invention overcomes the repressive nature of CO_2 with mixed-metal combinations where disparate chemical properties are exploited by proper choice of activation processes that are

further described below.

The invention comprises the use of at least one metal in multiple oxidation states as adsorbents. Multiple oxidation states are defined as:



The adsorbents combine properties of both high and low oxidation state metals. In the context of the instant invention a mixed metal oxide is defined as a composition containing at least one metal in multiple oxidation states or two or more metals with disparate chemical properties, such as electronegativities or coordination environments, in similar relatively high oxidation states. In the context of the instant invention, one of the components of the mixed metal oxide can be in the metallic state (e.g., Ni/NiO). A number of examples are presented that exemplify combinations of the mixed metal oxides of the instant invention. Although mechanisms of action are suggested for a number of materials, the invention is not bound by the proposed mechanisms and they are not limitations of the invention.

First, two or more metals in different oxidation states can be combined (e.g. Cu/ZnO, Fe/MnO_x). Second, two or more metals in similar oxidation states with sufficiently different properties can be combined (e.g. NiO/TiO_x, PdO/CeO_x). Third, a single metal which has oxidation states that vary throughout the metal can be used (e.g. Ni/NiO, V_yO_x wherein 1 ≤ y ≤ 5). The possible value of x varies depending on the compound and may or may not be a whole number. One skilled in the art would know the possible values for x in each case. Considerations for selecting the appropriate adsorbent or adsorbents are discussed below.

The materials of the instant invention are stable and their adsorption properties are not rendered ineffective by exposure to liquid and supercritical CO₂ which has substantial solvent properties. Additionally, standard purification conditions including pressures up to at least about 10,000 psi and temperatures up to at least about 60°C should not alter the stability or adsorption properties of the materials of the instant invention. The stability

of the materials is demonstrated by maintaining the desired level of decontamination of CO₂ for a time period of at least six months.

The materials of the instant invention may be prepared separately and mixed before loading into the purifier canister or bed. The materials can be an intimately co-mingled mixture prepared by impregnation, co-precipitation, sublimation or other relevant techniques. The materials may be supported on or mixed with an inorganic oxide including, but not limited to, silica, aluminum or zeolites for increased surface area, greater structural integrity, improved flow rate, or to accommodate other physical and mechanical considerations. Supports may also assist in the purification, especially in the removal of water. In a preferred embodiment, the adsorbent has a surface area of at least 50 m²/g, should be able to withstand the high pressure associated with all three fluid phases of CO₂ and should not become entrained in the fluid stream or introduce additional contaminants into the fluid stream. The surface area of the material should take into consideration both the interior and exterior surfaces that are characteristic of adsorbents that are typically highly porous. The use of co-mingled (i.e. intimately mixed) adsorbents allows for the removal of a variety of contaminants in a single step rather than having to perform multiple steps of decontamination through different beds or containers.

A variety of purification apparatuses are known including, but not limited to canister and multiple and single bed apparatuses. In a preferred embodiment, the method of the invention is carried out using a dual bed apparatus. Purification comprises contacting the adsorbent material with the CO₂ stream for sufficient time to allow decontamination to the desired level. Decontamination considerations such as time, pressure, flow rate and temperature may be readily determined by those skilled in the art and are typically considered on a case by case basis for each adsorbent.

Decontamination of CO₂ is alternated with regeneration of the adsorbent material. This cycle is preferably repeated multiple times to minimize the unit cost of CO₂ purification. Frequency and duration of regeneration of the adsorbent material varies depending on the size of the

adsorbent surface area, the level of contamination of the gas source and a number of other factors well known to those skilled in the art. Regeneration involves oxidation to prepare the material for adsorption of sulfurous and other contaminants and reduction to prepare the material for oxygen adsorption. The exact process of regeneration is dependent upon the adsorbents used and the contaminants that were removed from the CO₂. Such considerations are discussed below.

Activation and regeneration of adsorbents to obtain a mixed oxidation state is an important aspect of the instant invention. Regeneration rather than replacement of the adsorbents decreases cost and facilitates the use of the method of the invention. As combinations of metals and metallic states are selected to have various decontamination properties, they are also selected to have different activation/regeneration properties to allow for all of the contaminants to be purged from the adsorbent using heat or cooling in combination with oxygen, followed by reduction under specific conditions to allow only a portion of the adsorbent to undergo reduction.

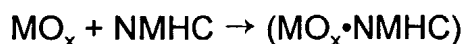
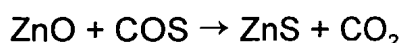
An example of an activation/regeneration protocol is to first contact the material with an oxidant regeneration gas (e.g. O₂, air, O₂/CO₂ mixture, O₂/inert gas mixture) for a sufficient time and a sufficient temperature to effect removal of all oxidizable contaminants. This oxidative step is performed at a relatively high temperature, about 300-550°C, preferably about 400°C for about 12-24 hours. After oxidation, the adsorbent is cooled to about 100-250°C and exposed to a reducing gas containing about 1-5% H₂ in an inert gas such as N₂ or Ar or an H₂/CO₂ mixture for sufficient time, typically about 12-24 hours, to result in a partial reduction of the material such that a mixed oxidation state is obtained. In a preferred embodiment, the regeneration and purge gases are both CO₂ based, i.e. O₂/CO₂ mixture for oxidation and H₂/CO₂ mixture for reduction.

The adsorbents and processes of the instant invention can effectively reduce the level of contaminants in CO₂. While we do not wish to be bound by any particular theory of chemical mechanism underlying the process of the invention, we believe that the following reactions are significant in the

process.

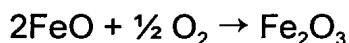
In a first embodiment of the instant invention, the adsorbent may contain two or more metals present in different oxidation states. Cu/ZnO and Fe/MnO_x are exemplary of such a combination. Preferred materials are those in which the higher oxidation-state portion of the material is reactive towards certain contaminants (e.g. by removing COS in a metathesis reaction that generates CO₂), while the lower oxidation-state portion of the material is reactive towards certain other contaminants (e.g. by absorbing oxygen, hydrogen, or carbon monoxide). Although such reactions are known to occur in the presence of inert gas, the reactions are surprising in the presence of CO₂. Particularly advantageous materials are those in which oxygen readily binds to an oxygen deficient portion of the material (e.g. for kinetic reasons), then diffuses into a co-mingled portion of the material which preferentially binds oxygen (e.g. for thermodynamic reasons). The ratios of the adsorbents to each other can be widely varied depending on the contaminants to be removed as well as other parameters known to those skilled in the art.

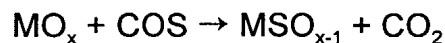
Cu/ZnO is known to exist as a combination of metallic copper and zinc oxide with Cu present in a substantially reduced state. The material may be supported on an inorganic oxide such as aluminum oxide as described above. ZnO is stable fully oxidized Zn^{II} and metal oxides adsorb NMHCs. Reactions can proceed as follows during the CO₂ purification method:



Thus, NMHCs are removed from the CO₂ stream. Cu/ZnO has been demonstrated to remove O₂, SO₂, COS, toluene and water from CO₂.

Similar reactions are possible using Fe/MnO_x, a material which has the properties of a substantially metallic iron mixed with iron and manganese oxides in widely varying oxidation states. Oxygen-deficient Fe reacts with O₂ and Fe and manganese oxides remove sulfur containing contaminants from the CO₂ stream.

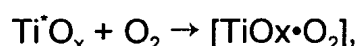
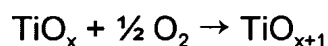




The combination of Fe/MnO is ideal for the removal of non-methane hydrocarbons (NMHC) and is particularly suited for the migration of chemisorbed oxygen and sulfur from Fe into bulk Mn oxide. MnO₂/Fe has been demonstrated to remove COS from both liquid and gas CO₂.

In a second embodiment of the invention, the adsorbent may contain two or more metals present in similar relatively high oxidation states for the corresponding metals, but in which the two metals vary considerably in chemical properties. NiO/TiO_x and PdO/CeO_x are exemplary of such combinations. The aforementioned adsorption properties are still relevant to this material, wherein two portions of the material have different, complementary adsorption properties (e.g., different coordination environments). Coordination environments are the electronic environments about a metal that yields preferences in coordination number and ligand type. Rather than the different adsorption tasks being accomplished by similar metals with an oxidation state differential, different portions of the material are in similar relatively high oxidation states. The different adsorption properties come from the presence of vastly different metals. An example is a mixture of a late transition metal oxide with an early transition metal oxide. As in the previous case, especially advantageous materials are those that undergo a degree of self-regeneration by diffusion of contaminants adsorbed in one portion of the material into another portion of the material. Again, although such reactions are known to occur in the presence of inert gas, the reactions are surprising in the presence of CO₂. The ratios of the adsorbents to each other can be widely varied depending on the contaminants to be removed as well as other parameters known to those skilled in the art.

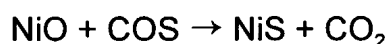
TiO_x may have oxygen vacancies or be able to adsorb oxygen on exposed metallic active sites. Reactions can proceed as follows during the CO₂ purification method:



wherein * indicates the Ti is in a metal complex. This form may involve

bridging dioxygen acting as a ligand rather than undergoing a redox reaction on a partially reduced titania surface.

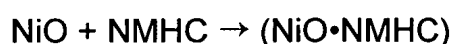
NiO also may be completely or partially reduced to Ni⁰, in which case redox chemistry may take place involving the Ni-containing portions of the material. Additionally, the NiO may participate in sulfur scavenging as shown in the following reactions:



Nickel sulfides/oxides are known to undergo further disproportionation reactions such as the reaction shown below:



which may generate additional reduced nickel active sites.



The various oxidation states of the oxygen-deficient oxides of CeO_x are well-known and their reactivity is believed to be similar to TiO_x and TiO₂ as shown above. The behaviors of Pd and PdO are well known on ceria and they display reactivity towards various contaminants in a manner similar to Ni which is in the same periodic group. The combinations of materials in this example function similarly to those of the previous example by providing different reactivities resulting in different adsorption and regeneration properties. Ni/NiO has been demonstrated to remove a wide variety of contaminants from CO₂ including water, O₂, metals including nickel, aluminum, iron, chromium, zinc and magnesium; sulfur-containing compounds, and a number NMHCs both large and small.

In a third embodiment of the invention, the adsorbent may contain a single metal oxide in which the metal oxidation state varies throughout the metal. V_yO_x exists in a number of oxidation states and is exemplary of such a metal. The aforementioned adsorption properties are still relevant to this material, wherein two portions of the material have different, complimentary adsorption properties (i.e. different oxidation states). The same metal present in different oxidation states within the material accomplishes the different adsorption tasks. For example, a low oxidation state portion of the material may adsorb oxygen, while a higher oxidation state portion may preferentially

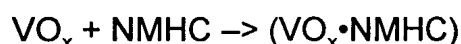
adsorb NMHCs or sulfurous contaminants.

Vanadia based materials in which vanadium is present in several incremental oxidation states are known. For example:



Vanadium sulfides, analogous to the vanadium oxides, are also possible.

The electropositive surface of vanadia is similar to titania, but with different oxidation characteristics, allowing the reaction:



for the adsorption of NMHCs.

The level of oxidation of vanadium can be controlled during the regeneration process of the invention.

Iron is known to have a number of oxidation states from zero to +4 and may exist in a number of oxidation states similar to vanadium. Fe_xO_y has been shown to remove a number of contaminants including toluene, H_2S , COS, benzene, acetaldehyde and water.

All references set forth herein are incorporated by reference in their entirety. All percentages are by weight unless otherwise provided. Parts of contaminants that are parts by volume.

EXAMPLE

A test purifier was filled with a adsorption media containing a including a pre-oxidized mixture of Ni/NiO, approximately 60% by weight on an a silica support, exposed to air for several days. The purifier was activated for 29 hours at ambient temperature using a 5% H_2 /95% Ar purge gas at 1 standard liter/ minute (slm) at 0 pounds / square inch gauge (psig). Afterwards, the purifier was purged with gaseous CO_2 purified with an Aeronex SS-500-KF-A-4R purifier. The temperature was monitored to indicate when each media was finished reacting with the CO_2 .

FIG. 1 represents the experimental setup. Mass flow controllers (MFCs) were used to maintain the flow rates of the 944ppm O_2 standard and the purified nitrogen (N_2) to attain a challenge gas containing 15ppm of O_2 . A

backpressure regulator was used to vent and maintain the pressure during purging of the test manifold. A Nanotrace Oxygen Analyzer (Delta-F) was used to measure the O₂ concentration. The lower detection limit of the oxygen analyzer is 0.2ppb ± 0.5ppb. The second purified N₂ line was used to purge the instrument. A rotameter was used to maintain the pressure of the gas flowing to the oxygen analyzer. The purifier was subjected to a challenge gas comprising 1 ppm of O₂ at 3 slm under 30 psig at ambient temperature. The oxygen level in the gas exiting the purifier was analyzed and the oxygen removal capacity for the media was determined as shown in FIG. 2. The capacity was shown to be between 8.10 and 8.76 liters of oxygen per liter of media (L/L) before 1 ppb breakthrough and over 11 L/L before 10 ppb breakthrough.

Although an exemplary embodiment of the invention has been described above by way of example only, it will be understood by those skilled in the field that modifications may be made to the disclosed embodiment without departing from the scope of the invention, which is defined by the appended claims.

WE CLAIM:

CLAIMS

1. A method of removing contaminants from a stream of carbon dioxide (CO₂), comprising:

contacting a stream of CO₂ with a quantity of a mixture that includes at least one mixed metal oxide for a period of time to reduce the contaminant content of the stream, wherein the mixed metal oxide is selected from the group consisting of iron (Fe) and manganese oxide (MnO_x); nickel oxide (NiO) and titanium oxide (TiO_x); palladium oxide (PdO_x) and cerium oxide (CeO_x); vanadium oxides (VO_x); nickel (Ni) and nickel oxide (NiO); and iron oxides (Fe_xO_y).

2. The method of claim 1, wherein the contaminant content is reduced to not more than 100 parts per billion (ppb).

3. The method of claim 2, wherein the contaminant content is reduced to not more than 10 ppb.

4. The method of claim 3, wherein the contaminant content is reduced to not more than 1 ppb.

5. A method of removing contaminants from a stream of carbon dioxide (CO₂), comprising:

Contacting a stream of CO₂, with a quantity of a mixture that includes at least one mixed metal oxide for a period of time to reduce the contaminant content of the stream to not more than 10 ppb, wherein said one mixed metal oxide comprises oxides of a metal having at least two different oxidation states, two or more metals present in different oxidation states; or two or more metals having different coordination numbers, ligand types, or both coordination numbers and ligand types.

6. The method of claim 5, wherein the contaminant content is reduced to not more than 1 ppb.

7. The method of claim 5, wherein said one mixed metal oxide comprises oxides of a metal having at least two different oxidation states, the metal being selected

from the group consisting of nickel, vanadium and iron.

8. The method of claim 5, wherein said one mixed metal oxide comprises two or more metals present in different oxidation states, the metal being selected from the group consisting of iron and manganese.

9. The method of claim 5, wherein said one mixed metal oxide comprises two or more metals having different coordination numbers, ligand types, or both coordination numbers and ligand types, the metals being selected from the group consisting of nickel, titanium, palladium and cerium.

10. The method of claim 5, wherein the mixed metal oxide is selected from the group consisting of copper (Cu) and zinc oxide (ZnO); iron (Fe) and manganese oxide (MnO_x); nickel oxide (NiO) and titanium oxide (TiO_x); palladium oxide (PdO_x) and cerium oxide (CeO_x); vanadium oxide (VO_x); nickel (Ni) and nickel oxide (NiO); and iron oxides (Fe_xO_y).

11. A method for activation and regeneration of mixed metal oxide adsorbents for the purification of carbon dioxide (CO_2) comprising:

heating the adsorbent to a first temperature to release contaminants adsorbed thereto;

exposing the heated adsorbent to an oxidizing agent to oxidize the adsorbent;

cooling the adsorbent to a second temperature; and

exposing the cooled adsorbent to a reducing agent to produce a mixed metal oxide.

12. The method of claim 11, wherein the first temperature is between 300°C to 550°C.

13. The method of claim 12, wherein the first temperature is 400°C.

14. The method of claim 11, wherein the oxidizing agent comprises oxygen (O_2).

15. The method of claim 11, wherein the second temperature is between 100°C to 250°C.

16. The method of claim 11, wherein the reducing agent comprises a mixture of hydrogen (H₂) and an inert gas.

17. The method as in claim 16, wherein the hydrogen gas comprises between 1% to 5% of the mixture by volume.

18. The method of claim 16, wherein the inert gas is selected from the group consisting of nitrogen (N₂) and argon and combinations thereof.

19. The method of claim 9, wherein the absorbent before the contaminants adsorbed thereto comprises a mixture that includes at least one mixed metal oxide, the mixed metal oxide being selected from the group consisting of copper (Cu) and zinc oxide (ZnO); iron (Fe) and manganese oxide (MnO_x); nickel oxide (NiO) and titanium oxide (TiO_x); palladium oxide (PdO_x) and cerium oxide (CeO_x); vanadium oxides (VO_x); nickel (Ni) and nickel oxide (NiO) and iron oxides (Fe_xO_y).

20. The method of claim 9, wherein the absorbent before the contaminants adsorbed thereto comprises a mixture that includes at least one mixed metal oxide, the mixed metal oxide being selected from the group consisting of iron (Fe) and manganese oxide (MnO_x); nickel oxide (NiO) and titanium oxide (TiO_x); palladium oxide (PdO_x) and cerium oxide (CeO_x); vanadium oxides (VO_x); nickel (Ni) and nickel oxide (NiO) and iron oxides (Fe_xO_y).

21. The method of claim 9, wherein the absorbent before the contaminants adsorbed thereto comprises a mixture that includes at least one mixed metal oxide, wherein said one mixed metal oxide comprises oxides of a metal having at least two different oxidation states, the metal being selected from the group consisting of nickel, vanadium and iron; two or more metals present in different oxidation states, the metals being selected from the group consisting of iron and manganese; or two or more metals having different coordination numbers, ligand types, or both coordination numbers and ligand types, the metals being selected from the group consisting of nickel, titanium, palladium and cerium,

22. A method for continuous purification of carbon dioxide (CO₂), comprising:
purification of CO₂ by the method of claim 1 and 5 in a first bed of a dual bed purifier apparatus;
regeneration of an adsorbent in a second bed of the dual bed purifier apparatus by the method of claim 8, during the coincident purification of the CO₂ in the previous step;
followed by purification of CO₂ by the method of any of claims 1 and 5 in the second bed after completion of regeneration of the adsorbent by the method of claim 11, coincident with the regeneration of the adsorbent of the first bed by the method of claim 11; and
repeating the steps for continuous purification.